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APPENDIX

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Utility of deep sea CO_2 release experiments in understanding the biology of a high-CO_2 ocean: Effects of hypercapnia on deep sea meiofauna

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[1] Oceanic CO_2 levels are expected to rise during the next 2 centuries to levels not seen for 10–150 million years by the uptake of atmospheric CO_2 in surface waters or potentially through the disposal of waste CO_2 in the deep sea. Changes in ocean chemistry caused by CO_2 influx may have broad impacts on ocean ecosystems. Physiological processes animals use to cope with CO_2-related stress are known, but the range of sensitivities and effects of changes in ocean chemistry on most ocean life remain unclear. We evaluate the effectiveness of various designs for in situ CO_2 release experiments in producing stable perturbations in seawater chemistry over experimental seafloor plots, as is desirable for evaluating the CO_2 sensitivities of deep sea animals. We also discuss results from a subset of these experiments on the impacts of hypercapnia on deep sea meiofauna, in the context of experimental designs. Five experiments off central California show that pH perturbations were greatest for experiments using "point source" CO_2 pools surrounded by experimental plots. CO_2 enclosure experiments with experimental plots positioned within a circular arrangement of CO_2 pools had more moderate pH variation. The concentration of dissolution plumes from CO_2 pools were related to the speed and turbulence of near-bottom currents, which influence CO_2 dissolution and advection. Survival of meiofauna (nematodes, amoebae, euglenoid flagellates) was low after episodic severe hypercapnia but lower and variable where pH changes ranged from 0 to 0.2 pH units below normal.

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1. Introduction

[2] The chemistry of the world ocean is changing rapidly due to the influx of anthropogenic carbon dioxide from the atmosphere. This process will almost certainly intensify in the near future as CO_2 emissions increase, with potentially profound impacts on the structure and function of ocean ecosystems. Since the onset of the industrial revolution, the oceans have absorbed ~118 Pg of anthropogenic carbon, or roughly 48% of the total carbon emissions [*Sabine et al.*, 2004]. Present carbon emissions near 7 PgC yr^{-1} are expected to increase to 15 PgC yr^{-1} by 2050 [*Marland et al.*, 2001] (available at http://cdiac.esd.ornl.gov/trends/trends.htm) and potentially to over 20 PgC yr^{-1} by the end of this century [*Joos et al.*, 1999; *Legget et al.*, 1992]. Equilibration of ocean waters with the atmosphere has already acidified ocean surface waters by 0.1 pH units [*Haugan and Drange*, 1992] and ocean mixing, though slow, has allowed anthropogenic carbon to penetrate to 1000+ m over much of the ocean [*Sabine et al.*, 2004]. Continued acidification will reduce ocean pH by an additional 0.2 units by the end of this century [*Haugan and Drange*, 1992], and the accumulating atmospheric burden of carbon dioxide is expected to reach 1900 ppm during the next 200–300 years, leading to pH reduction of 0.7 units in ocean surface waters, levels nonexistent on Earth for over 300 million years [*Caldeira and Wickett*, 2003].

[3] The ecosystem consequences of elevated atmospheric CO_2 are large. The increase of 0.75°C in global temperature over the last century is considered by many scientists to have been driven by CO_2-related greenhouse warming, and is associated with broad changes in marine and terrestrial ecosystems [*Parmesan and Yohe*, 2003; *Root et al.*, 2003]. In addition to warming effects, acidification and the reduced carbonate saturation state of the oceans has now been implicated in reduced rates of calcification of many carbonate secreting marine taxa, ranging from microscopic plankton to coral reefs [*Feely et al.*, 2004].

[4] Efforts to stabilize atmospheric greenhouse gas levels or at least mitigate the effects of accelerating carbon dioxide emissions have led to several carbon management options including carbon sequestration in the terrestrial biosphere, the world ocean, and acceptable geological strata. Options

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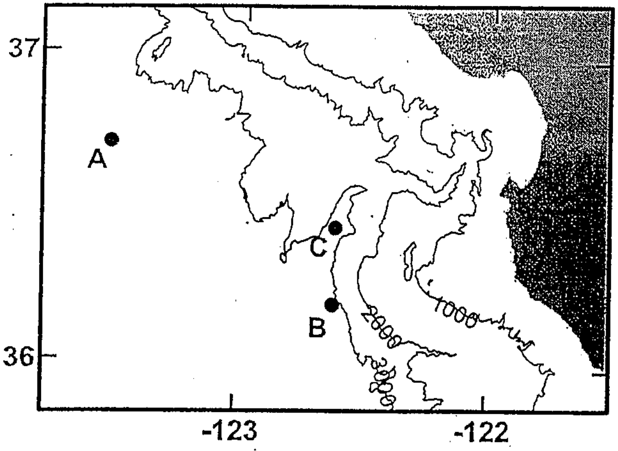

Figure 1. Map of sites for CO_2 release experiments off central California.

for ocean carbon storage have focused on direct deep sea CO_2 injection or indirect deep sea storage by enhancing the natural carbon flux to the deep sea via fertilization of ocean surface waters with micronutrients [*Martin*, 1990]. Although direct ocean sequestration of CO_2 was suggested 25 years ago [*Marchetti*, 1977], it has recently received more interest, due to greater awareness of climate trends and political attention to national energy policies [*Kerr*, 2001].

[5] Our understanding of the biological and ecological consequences of large changes in the carbonate chemistry of the oceans is poor, for both shallow and deep ocean ecosystems, and has received considerably less attention than terrestrial systems, where large-scale studies to measure the response of ecosystems to elevated CO_2 levels are ongoing [e.g., *McLeod and Long*, 1999] (available at http://cdiac.esd.ornl.gov). Recent sophisticated mesocosm studies of marine plankton communities [*Riebesell et al.*, 2000] and coral reef systems [*Langdon et al.*, 2003] have advanced our understanding of increased carbon dioxide levels on some surface ocean systems. However, a considerable increase in research is required to generate a comprehensive understanding of the response of marine organisms to changes in ocean chemistry caused by either the continuing invasion of carbon dioxide into surface waters or CO_2 sequestration in the deep sea. Experiments to examine the effects of hypercapnia on deep sea biota are an important step in advancing our understanding of the high-CO_2 ocean that is almost certain in Earth's future.

[6] We performed a series of deep sea CO_2 release experiments to investigate the effects of hypercapnia on deep sea biota, as might be expected to result from a direct ocean carbon sequestration program, by potential leakage into deep ocean water of CO_2 injected into geologic formations under the seabed, or eventually by the chronic elevation of seawater chemistry due to air-sea exchange and deep ocean mixing. Although seawater chemistry near CO_2 release sites of any large-scale CO_2 sequestration program will vary greatly depending on the rates and methods of release and the stirring and mixing rates of the near-bottom physical processes [*Shirayama*, 1998], long-term (i.e., centuries), large-scale (ocean basin) changes in total CO_2 and pH of the deep ocean will probably be less variable in space and time, with changes in ocean pH dependent upon CO_2 injection volumes and retention efficiency [*Harvey*, 2003]. Our CO_2 release experiments were intended to produce quasi-stable, month-long perturbations of the CO_2 content of waters overlying experimental plots on the seafloor through their exposure to the hypercapnic dissolution plume advected from adjacent seafloor pools of liquid CO_2. The severity of hypercapnia and pH disturbance was intended to approach values expected from either the regional effects of a direct deep sea CO_2 sequestration program or from the chronic acidification of the ocean by atmospheric CO_2 influx. In this paper we examine the efficacy of various experimental designs for CO_2 release experiments in providing stable perturbations to the CO_2 and pH content of seawater bathing experimental plots. In additional to our focus on the efficiency of these methods, we discuss a subset of the results from these experiments concerning the effects of hypercapnia on deep sea meiofauna.

2. Methods

2.1. Study Area

[7] CO_2 release experiments were conducted at three locations on the continental rise in 3250–3600 m depth off the coast of central California (Figure 1). The abyssal seafloor at sites A and B is flat and relatively featureless, covered with fine-grained clay-rich sediment with a high content of organic carbon (~3% dry wt). Bottom water at these sites is cold (1.5°–1.6°C), with oxygen levels of 120 μM, alkalinity of 2440 $\mu m\ kg^{-1}$, in situ pH of ~7.78 (SWS) and total CO_2 of 2350 $\mu m\ kg^{-1}$. Site C is located in the axis of lower Monterey Canyon, a large submarine canyon extending from the shore to >4000 m depth. This section of Monterey Canyon is wide (~2 km), and relatively flat, with fine-grained surficial sediments. Studies at all sites were at depths well below the intense oxygen minimum typical of eastern Pacific waters, where oxygen stress could compound the effects of hypercapnia alone on deep sea organisms [*Pörtner et al.*, 2005].

[8] Benthic and benthopelagic megafauna are common, but distributed sparsely at the study sites. The sediment-dwelling infauna at most sites was dominated by crustaceans, especially tube-dwelling ampeliscid amphipods, and polychaeta worms. Benthic meiofauna, the focus of this paper, were dominated by nematode worms, euglenoid flagellates, amoebae, ciliates, and allogromiid foraminifera.

2.2. Carbon Dioxide Release Experiments

[9] Several CO_2 release experiments were performed from 2001 to 2003 off central California at depths of 3100–3600 m (Table 1). The installation, sampling, and recovery of CO_2 experiments were performed using the ROV *Tiburon*, launched from the R/V *Western Flyer*, and operated by the Monterey Bay Aquarium Research Institute (MBARI). Details concerning the R/V *Tiburon* are available at http://www.mbari.org. A remotely operated vehicle (ROV)-mounted CO_2 release system developed by MBARI was used to dispense up to 40 L of liquid CO_2 per ROV dive. This system was nearly identical to the CO_2 release system described by *Brewer et al.* [1999], but had a capacity of 40 L. For each approximately month-long experiment,

Table 1. List of CO_2 Release Experiments

Experiment	Design	Site	Latitude, deg	Longitude, deg	Depth, m	Start Date	Duration, days
CO_2-1	point source	A	36.709	−123.523	3600	25 Jun 2001	36
CO_2-2	point source	B	36.200	−122.617	3310	25 Oct 2001	41
CO_2-3	point source	A	36.708	−123.531	3650	4 Apr 2002	27
CO_2-4	CO_2 enclosure	C	36.378	−122.676	3262	11 Nov 2002	29
CO_2-5	CO_2 enclosure	A	36.709	−123.523	3607	19 Aug 2003	31

we released liquid CO_2 into small "corrals" (sections of PVC pipe ~40–100 cm in diameter × 12–40 cm high) placed on the seafloor, creating small, contained pools of liquid CO_2 (Figure 2). Upon its release into corrals, liquid CO_2 dissolved slowly, producing a CO_2-rich, low-pH dissolution plume that was advected and dispersed downstream by near-bottom currents. The CO_2 dissolution plume becomes negatively buoyant as CO_2 hydration occurs [*Brewer et al.*, 2005], and thus, flows as a dense plume relative to seawater, interacting with the surficial sediments. Because of the difficulties of measuring seawater CO_2 in situ, we measured variation in pH caused by the CO_2 dissolution plume as a proxy for its CO_2 content. The intensity and variability of CO_2 dissolution plumes were measured just above the seafloor using pH electrodes installed on conductivity-temperature-depth (CTD) sensors.

[10] Depths greater than 3000 m were selected for CO_2 injection experiments for several reasons. Large-scale carbon sequestration by direct ocean injection will likely target abyssal depths due to the greater storage efficiency of CO_2 injections at these depths, compared to shallow injection scenarios [*Herzog et al.*, 2001]. Therefore research on the sensitivities of bathyal and abyssal deep sea biota to changes in seawater chemistry caused by CO_2 injection is required to assess the ecosystem consequences of any ocean carbon sequestration scenario. In addition, the phase stability characteristics of CO_2 are such that liquid CO_2 is positively buoyant to a depth of ~2600 m off central California. CO_2 released at 3200–3600 m has a density of 1.064–1.074 kg L^{-1} (E. Peltzer, unpublished data, 2004). Because CO_2 is denser than seawater at depths greater than 2600 m, we were able to release liquid CO_2 into PVC corrals placed on the seafloor. At shallower depths, the liquid CO_2 would float toward the surface and dissolve or undergo a phase change to a gaseous state (~340 m depth), making these experiments less tractable or impossible.

[11] The effect of hypercapnia on benthic meiofauna (flagellates, amoebae, nematodes) inhabiting the surficial (i.e., top 1 cm) sediments was examined in these experiments by assessing their survival (estimated from changes in abundance) in experimental plots near and distant from CO_2 pools, related to the severity of hypercapnia. Because meiofauna inhabit the sediment, the key measurements of interest are the pH and CO_2 content of pore fluids relative to ambient values. While limited pH profiles of the sediments were performed during one experiment [*Thistle et al.*, 2005], these measurements were only possible at the beginning or end of the experiments, and thus, could not track the temporal sequence of pore fluid perturbations by the dissolution plume. In view of this limitation, we assumed that pore fluids in top 1 cm of the sediment also became hypercapnic due to the CO_2 dissolution plume, as shown by [*Thistle et al.*, 2005]. It is expected that the temporal variability of hypercapnia observed in bottom water (see below) was smoothed somewhat in the upper sediment layer, but was representative of changes in the pH field measured ~3 cm above the seafloor.

[12] Five CO_2 release experiments with differing configurations of CO_2 pools and seafloor study plots were performed (Figure 3), among which the intensity and stability of hypercapnia were expected to vary (Table 1). These ranged from point source CO_2 designs, where pools of liquid CO_2 were surrounded by experimental plots containing organisms (Figures 3a and 3b), to layouts where plots were encircled by multiple CO_2 corrals (CO_2 enclosure designs (Figures 3c and 3d)). These latter designs, similar in configuration to terrestrial Free-Air CO_2 Enrichment (FACE) experimental designs [*Allen*, 1992a, 1992b; *Allen and Beladi*, 1990] were expected to produce the most stable pH and CO_2 perturbations.

2.3. Point Source CO_2 Pool Experiments

2.3.1. CO_2-1: Replicated Acute CO_2 Exposure Design

[13] This initial experiment to examine in situ the response of abyssal deep sea biota to hypercapnic conditions was designed as an ANOVA comparison of the survival of animals between replicated CO_2 and control treatments. Details of the experimental design and results concerning the impacts on benthic meiofauna are presented by *Barry et al.* [2004]. We provide a brief overview of that experiment here. Six small (48 cm diameter × 15 cm high) PVC corrals were placed on the seafloor (Figure 3a) at 3600 m depth at site A (Figure 1). Three of the six corrals were each filled with ~20 L of reagent-grade liquid CO_2 (Figures 2a and 2b) using the MBARI CO_2 delivery system, refilled after 14 days, and the experiment was terminated after a total of 36 days (Table 1).

[14] Seawater chemistry near these pools was measured using three CTDs equipped with pH sensors, positioned ~3 cm above the seafloor and near (<0.5 m) two of the CO_2-filled corrals (e.g., Figure 2a, upper left) and one of the control corrals. Current patterns at the site were measured with an upward-looking acoustic Doppler current profiler (ADCP) positioned 2 m above the seafloor on a small mooring located ~70 from the experimental pools.

[15] Tolerance to hypercapnia by sediment-dwelling meiofauna was examined by comparing the abundances of live meiofaunal taxa near CO_2 and control corrals, at the beginning of the study prior to dispensing liquid CO_2 and at the end of the experiment 36 days later (Table 1). Sediments were sampled from replicate sediment cores (MBARI tube cores: 7 cm diameters × 15–20 cm deep) collected adjacent to, i.e., <0.5 m from, CO_2 and control corrals.

[16] Meiofaunal abundance was quantified by extracting the top 1 cm of sediment from a subsample of each core

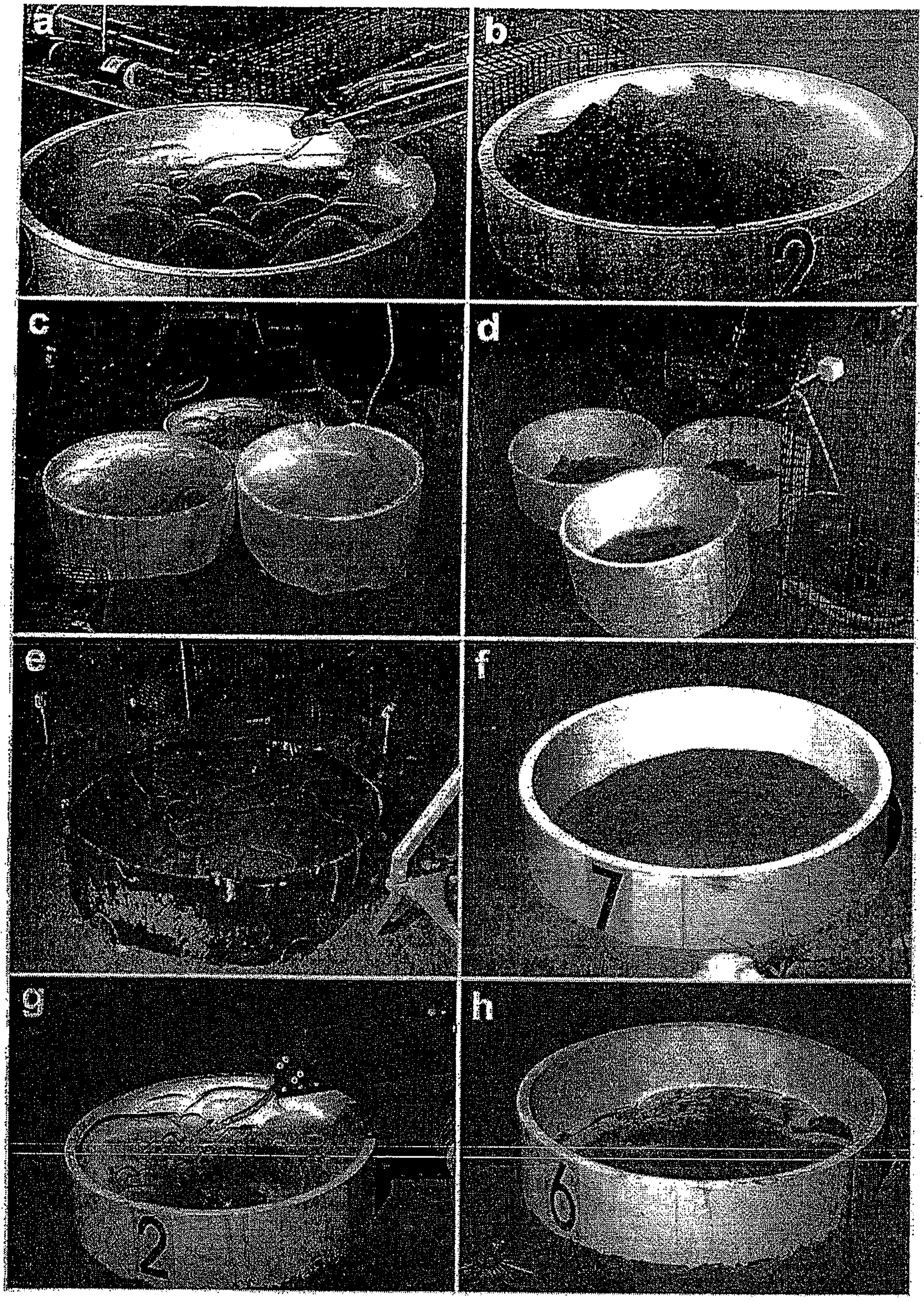

Figure 2. CO_2 corrals during CO_2 release experiments. (a) Initial filling of corral 2 during CO_2-1. Note pH sensor in upper left. (b) "Frost heave" of sediment in CO_2-1 corral 2 (Figure 2a) after 1 day, caused by interaction of CO_2 hydrate with sediment. (c) Full central CO_2 corrals (~100 L liquid CO_2) at beginning of CO_2-2. Macrourid fish is swimming above CO_2. (d) Central corrals after 49 days dissolution during CO_2-2. Note small amount of CO_2 hydrate in bottom and live abyssal zoarcid fish (*Pachycara* sp.) in cage at lower right. (e) Nearly 75% full CO_2 corral with liquid CO_2 and unknown amount of CO_2 hydrate at the end of CO_2-3. (f) Empty CO_2 corrals after 1 month at end of CO_2-4. (g) Full CO_2 corral at beginning of CO_2-5. (h) Partially full corral at end of experiment CO_2-5.

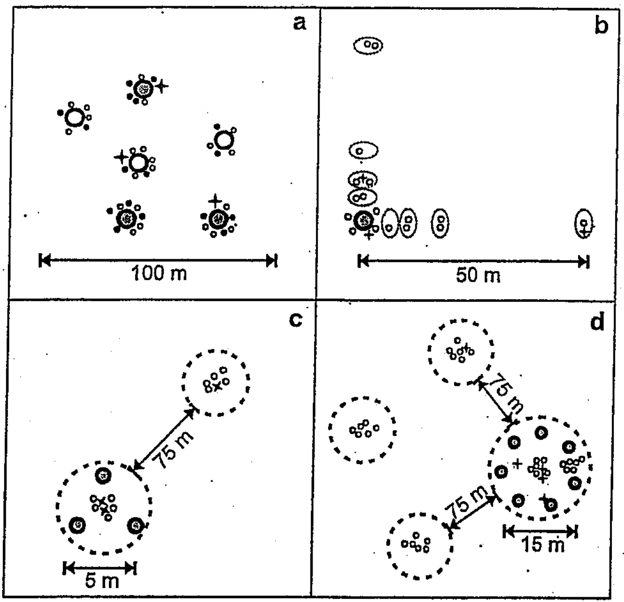

Figure 3. Experimental design of CO_2 release experiments. (top) Point source CO_2 release experiments. (bottom) CO_2-enclosure designs. (a) CO_2-1, with three randomly distributed CO_2 corrals with ~20 L of liquid CO_2 (large shaded circles) and three unfilled control corrals (open circles). Small circles indicate locations of sediment cores for collection of benthic meiofauna (black, samples prior to CO_2 release; white, samples at end of experiment). Star symbols indicate positions of pH sensors. (b) CO_2 pool layout used for release experiments CO_2-2 and CO_2-3. A single central CO_2 corral (~160 L), as used in CO_2-3, is shown. Triplicate smaller corrals (~100 L total) used in CO_2-2 not shown. Sediment samples were collected from distances of 1–50 m (indicated by dashed ellipses) from the CO_2 pool in two orthogonal directions. (c) Triangular CO_2 enclosure experiment CO_2-4 with three ~20 L CO_2 corrals. Dashed circles indicate general area of treatment (CO_2) and control samples. Control location was ~75 m from CO_2 pool area. (d) Circular CO_2 enclosure experiment CO_2-5. Symbols as above. Note the seven ~20 L CO_2 corrals.

using a 60 cc syringe with the Luer end removed. Subsamples were preserved immediately in a 2% glutaraldehyde solution in 0.1 M cacodylate buffered, filtered seawater. A Percoll density-gradient centrifugation technique was used to extract meiofauna from aliquots of the subsampled sediment. Counts and biovolume measurements of meiofauna stained with the fluorochrome DAPI were made using epifluorescence microscopy. Details of these techniques are presented by *Buck et al.* [2000]. Tissue condition (live/dead) was assessed for a subsample of nematodes collected. Individual nematodes stained with DAPI were inspected under epifluorescence microscopy for the presence (recently live) or absence (dead) of intact cell nuclei.

2.3.2. CO_2-2, CO_2-3: CO_2 Exposure Gradient Experiments

[17] We performed two CO_2 release experiments (CO_2-2, CO_2-3) using a regression design, by creating relatively large CO_2 pools in a single, central location, then characterizing the dissolution plume and assessing meiofauna' abundance at distances of 0.5–50 m in two direction (Figure 3b). Considering the acute CO_2 perturbations observed in close proximity to CO_2 pools (see results for CO_2-1 below), we expected more moderate pH changes (0.1–0.3 units) at distances of ~5–10 m from central CO_2 pools, due to diffusion and mixing of the dissolution plume.

[18] For CO_2-2 at site B (Figure 1, Table 1), we placed three PVC corrals (48 cm diameter × 40 cm high) in a tight group on the seafloor, filling them with ~100 L of liquid CO_2 (Figures 2c and 2d). Together, they formed a central point source for the hypercapnic dissolution plume. Seabird pH electrodes attached to Applied Microsystems Ltd (AML) CTDs were positioned distances of ~0.5, 5, and 50 m from the CO_2 pools to measure the magnitude of pH (thus CO_2) perturbations (Figure 3b). An acoustic Doppler current profiler (ADCP) meter mooring was deployed at the site as described for CO_2-1. The corrals were not refilled during the experiment, which was terminated after 41 days (Table 1). Sediment samples for meiofaunal analyses in each experiment were collected from 0.5, 2, 5, 10, and 50 m to the north and east of the central CO_2 pools at the end of the experiment.

[19] Release experiment CO_2-3 (site A (Figure 1)) had a similar design (Figure 3b), but used a 91 cm diameter × 30 cm high plastic corral, which was filled with ~75 L of liquid CO_2 at the beginning of the experiment (Figures 2e and 4b), leaving the corral approximately 35% full. Sensors were positioned from 0.5 to 50 m from the CO_2 source as in CO_2-2. Additional liquid CO_2 (80 L) was added to the corral after 13 days to bring it to ~75% full, and the experiment was terminated after 27 days (Table 1). Sediment samples were collected for meiofaunal analyses as in CO_2-2.

[20] We estimated the rate of survival for major meiofaunal taxa at the end of each experiment from changes in their biovolume along the exposure gradient, i.e., from 50 to

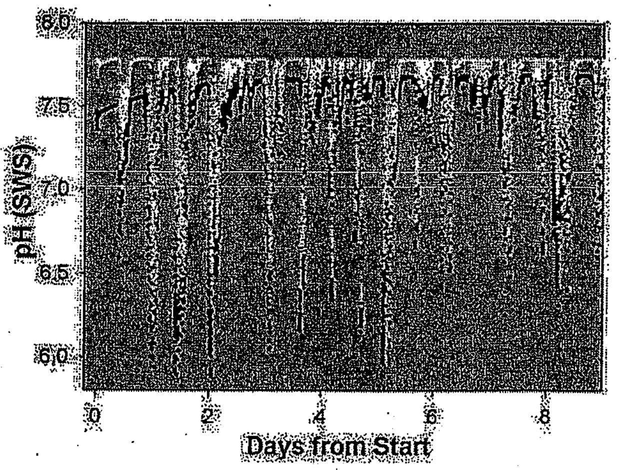

Figure 4. Adjustment of raw pH data. Raw data (black dots) were adjusted (white dots) to remove sensor drift, and the baseline pH was offset to match the ambient pH (7.78 SWS).

0.5 m from the CO_2. Mean meiofaunal biovolume 50 m from CO_2 pools was assumed to represent background (i.e., 100% survival) values, with lower biovolume nearer CO_2 pools reflecting reduced survival. A power function (biovolume = $a(\text{distance})^b$) was fit to the biovolume and distance data set for each meiofaunal taxon to characterize its "survival" versus distance relationship. Several interacting factors affect the dispersion of the dissolution plume and the taxon-specific responses of meiofaunal populations. Complex physical processes such as CO_2 hydration kinetics, dissolution plume density, diffusion, advection, and eddy turbulence will affect the intensity of hypercapnia and acidosis with distance from CO_2 pools. Changes in the biovolume of specific taxa during these experiments represent the integrated effects of individual and numerical population responses to hypercapnic stress. The power function is expected to represent a first-order approximation of the combined effects of physical and biological processes on the dispersal of the dissolution plume and the sensitivity and response of meiofaunal taxa.

2.4. CO_2 Enclosure Designs

2.4.1. CO_2-4: Triangular CO_2 Enclosure Design

[21] Release experiment CO_2-4 was performed using a CO_2 enclosure design in Monterey Canyon at site C (Figure 1, Table 1). Rather than a single-point CO_2 source surrounded by sensors and experimental plots, we designed a triangular CO_2 enclosure in which three CO_2-filled corrals (48 cm diameter × 15 cm high; ~20 L each) were positioned ~4 m apart at the apices of a roughly equilateral triangle (Figure 3c). Sensors were positioned near the center of the triangular CO_2 corral layout, and sediment samples for meiofaunal analyses were collected from the center of the triangle, and ~75 m from the CO_2 enclosure. An ADCP was moored nearby to measure the flow field, positioned ~16 m above the seafloor and in a downward looking configuration. Meiofauna were enumerated from the upper 1–5 cm of sediments sieved through a 63 μm filter [*Carman et al.*, 2004]. CO_2 was dispensed into all three CO_2 corrals, and the experiment was terminated after 29 days (Table 1).

2.4.2. CO_2-5: Circular CO_2 Enclosure

[22] A CO_2 release experiment performed during 2003 at site A (Figure 1) employed a circular layout of CO_2 corrals (Table 1, Figure 3d) that mimics the concept of terrestrial FACE experiments [*McLeod and Long*, 1999]. Perturbations to pH and CO_2 within the enclosure design were expected to be more stable than produced using point source designs. Seven CO_2 corrals (48 cm diameter × 15 cm high; ~20 L liquid CO_2 each (Figures 2g and 2h)) were positioned in a circle ~12–15 m in diameter. This size of the enclosure was selected using results of earlier experiments and targeting a ~0.2–0.3 unit pH reduction inside the circle.

[23] CTDs equipped with pH sensors were positioned near the margin of the circle adjacent to a CO_2 corral, ~1.5 m from the margin, and in the center of the circle, as well as in a control area ~75 m distant. Sensors were positioned from 3 to 50 cm above the seafloor.

[24] Sediment cores for meiofaunal studies were collected both before CO_2 injection and at the termination of the month-long experiment, from the center of the CO_2 enclosure, as well as from three nearby (~75 m distance) control areas. Meiofaunal abundances from this experiment are not yet available and will not be discussed further.

2.4.3. Current Measurements

[25] Near-bottom currents were measured during each CO_2 release experiment using an ADCP. The ADCP (RDI sentinel, 300 or 600 kHz) was generally mounted on a small mooring 2 m (CO_2-1, -2, -3), or 3 m (CO_2-5) above the seafloor, oriented upward. For CO_2-4, the ADCP was mounted 16 m above the seafloor, oriented downward. Time series data from a single measurement bin 8 m above the seafloor were used to characterize the flow patterns (mean speeds, progressive vector plots) and for spectral analyses (FFT; Matlab release 14, 2004). Vertical profiles of mean flow speed and eddy turbulence were calculated using all available ADCP data.

2.4.4. pH Measurements

[26] Seawater pH was measured using Seabird SBE 18 pH sensors attached to Seabird Model 19 plus or Applied Microsystems Ltd. CTDs. Sensors were mounted from 3 to 50 cm above the bottom, at varying distances from CO_2 pools, depending upon experimental layout. Data intervals varied among experiments from 1 to 6 min.

[27] Frequent failure or drift of deep-rated pH sensors complicated the interpretation of the pH field near CO_2 release experiments. Raw pH data were adjusted to remove sensor drift. Because we were interested primarily in excursions of pH from the average in situ values (assumed constant during each experiment), data from each pH sensor was adjusted such that its maximum values equaled the in situ bottom water pH for that location (normally near 7.78 SWS). Adjusted pH data were calculated as the in situ bottom water pH (7.78) minus the deviation for each measured pH datum from the local (within 12 hours) median or maximum pH (Figure 4).

[28] Spectral analyses of pH records were performed on adjusted data series following Fourier transformation (FFT; Matlab Release 14, 2004).

3. Results

3.1. Benthic Boundary Layer Currents

[29] The speed and direction of deep-sea currents during all CO_2 release experiments varied in time and among experiments, affecting both the rate of dissolution and advection of the dissolution plume from experimental CO_2 pools. Currents 8 m above the seabed were generally sluggish (mean speed ~3–6 cm/s) and oscillatory in speed and direction during all release experiments (Figure 5), and were dominated by tidal and, to a lesser degree, inertial motions. A summary of current data from 8 m above the seafloor, the depth nearest the seafloor where data are available from each experiment (no data are available from CO_2-3), is presented in Table 2.

[30] Although flow during all experiments was rotary to some degree, the key differences in flow among experiments related to the average speed and turbulence of flow near the bottom (Figure 6), which influence both the dissolution of liquid CO_2 and the dispersal and mixing of the plume. Highest mean absolute and net flow speeds were measured during CO_2-4 at site C where flow is constrained bathymetrically by the walls of Monterey Canyon (Table 2). Mean current speed was higher (5.7 cm s^{-1}) than measured

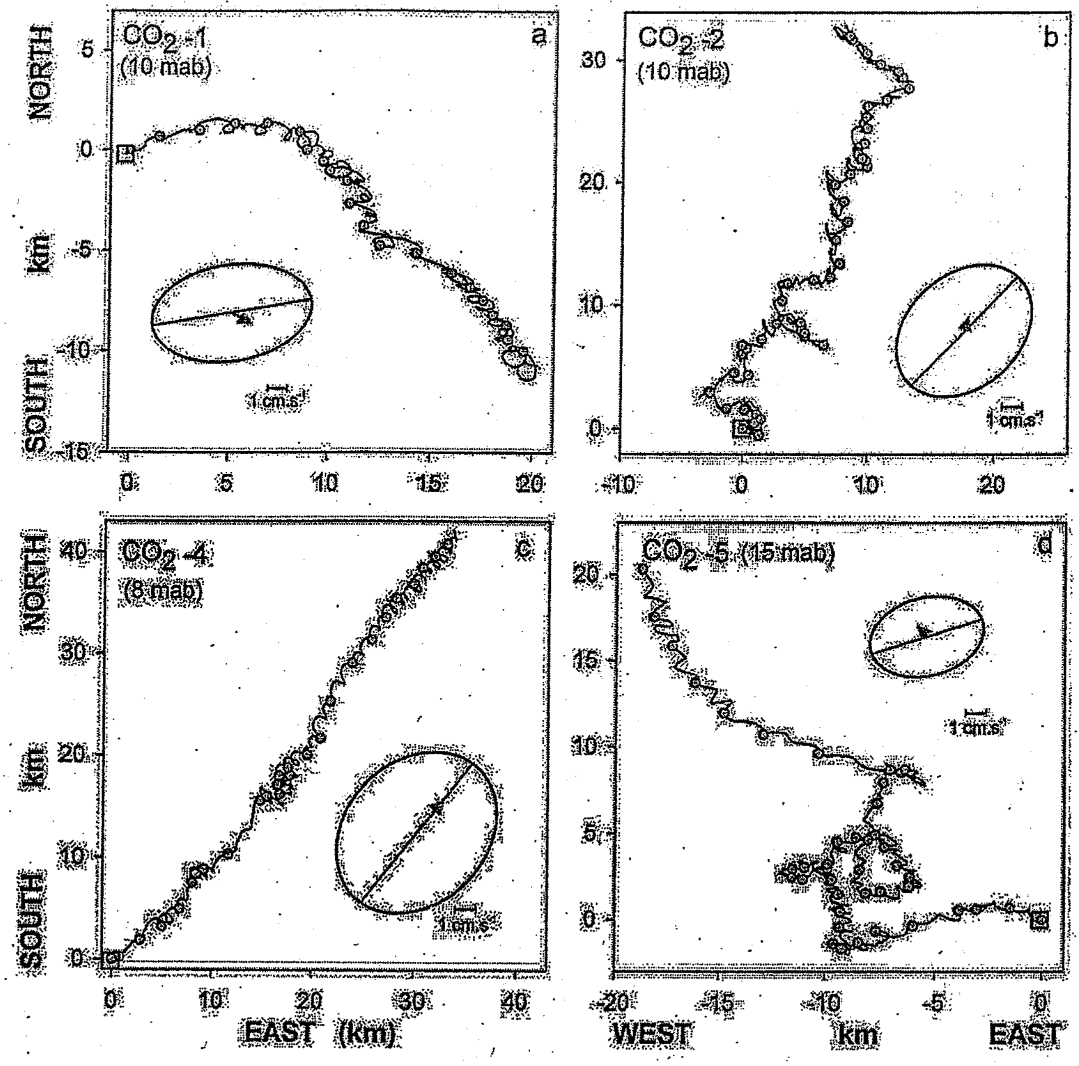

Figure 5. Progressive vectors plots for near-bottom currents measured during CO_2 release experiments. Small open box in each plot indicates starting location at beginning of experiment. A progressive vector indicating the directional flow sequence during each experiment is indicated by the black oscillating line. Start of each day marked by shaded circles. Principal axes of flow are indicated by an ellipse in each panel, in which major and minor axes represent one standard deviation of the mean current magnitude. Mean flow indicated by shaded arrow (same scale as principal axes ellipse). Height of the current measurements above the seafloor for each plot are indicated as meters above bottom (mab). (a) CO_2-1. (b) CO_2-2. (c) CO_2-4. (d) CO_2-5.

Table 2. Summary of Current Measurements and Estimates of Dissolution Rates for CO_2 Release Experiments[a]

Experiment	Interval, s	Data, hours	Magnitude Mean, cm s^{-1}	Net Flow, cm s^{-1}	Net Direction	K_{eddy}, $cm^2\ s^{-2}$	CO_2 Dissolution
CO_2-1	598	1198	4.3	1.22	119.4	11.06	rapid
CO_2-2	360	1166	4.4	0.81	29.3	11.81	rapid
CO_2-3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	slow
CO_2-4	300	667	5.7	2.29	36.7	17.17	rapid
CO_2-5	299	1016	2.9	0.77	312.2	5.36	slow

[a] Flow data calculated from a single acoustic Doppler current profiler 8 m above the seafloor for each experiment listed. No flow data were recovered for CO_2-3. Interval indicates the sampling interval (s) during each experiment. Magnitude represents the mean nondirectional current speed. Net flow is average net transport toward net direction. Eddy kinetic energy is calculated from u', v', and w'. Estimates of CO_2 dissolution rates are based on remotely operated vehicle observations of liquid CO_2 remaining in corrals at the end of each experiment.

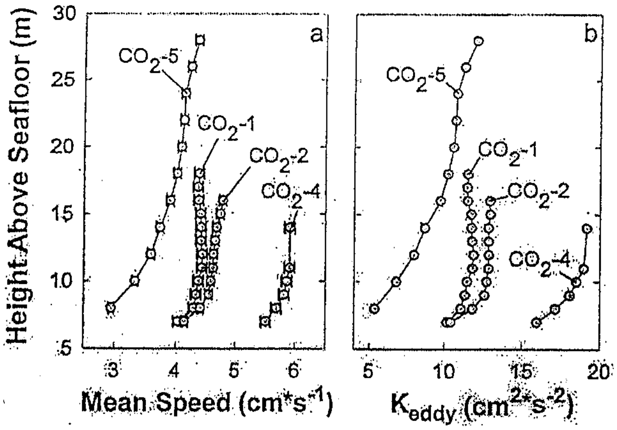

Figure 6. Mean current speed and eddy kinetic energy for CO_2 release experiments. (a) Vertical profiles of mean current nondirectional current speed (error bars represent 95% confidence limits) based on all available acoustic Doppler current profiler (ADCP) data from each experiment. (b) Vertical profiles of eddy kinetic energy, based on u', v', and w'. Note the large difference in mean speed between CO_2-5 and CO_2-4 for both mean speed and eddy kinetic energy. Note also the decreased energy nearer the seafloor.

at sites A or B, and net drift was aligned tightly with the major principal axis of flow (Table 2, Figure 5c) in the along-canyon axis. Flow was consistently in the up-canyon direction, a pattern which has been observed elsewhere along the axis of Monterey Canyon (J. P. Barry et al., unpublished data, 2004). Mean current speed, net transport and eddy kinetic energy were each roughly 2–3 times greater than measured at the noncanyon sites. The apparent rate of CO_2 dissolution during this experiment was rapid, based on the observation of completely empty corrals at the end of the 31 day experiment.

[31] In contrast to the relatively energetic currents during CO_2-4, flow at site A during CO_2-5 was the most sluggish observed in any experiment, and was associated with very slow rates of CO_2 dissolution (Figure 6). The mean speed (2.9 cm s^{-1}) and net drift (0.8 cm s^{-1}) measured during CO_2-5 were roughly half the speeds measured in Monterey Canyon during CO_2-4. Eddy kinetic energy (5.4 cm^2 s^{-2}), which probably plays the largest role in CO_2 dissolution from seafloor corrals, was only 31% of that observed during CO_2-4.

[32] Flow patterns during CO_2-1 and CO_2-2 were intermediate in energy between the high energy flow during CO_2-4 and very sluggish flow observed during CO_2-5. Mean absolute current speeds and eddy kinetic energy for CO_2-1 and CO_2-2 were both near 4.4 m s^{-1} and 2.3 cm^2 s^{-2}, respectively, though these were performed at two different sites. Even though net transport during CO_2-1 (1.2 cm s^{-1}) was much higher than during CO_2-1 (0.8 cm s^{-1}) the major and minor axes of flow were similar (ellipses in Figures 5a and 5d), leading to comparable levels of eddy turbulence near the seafloor. Site B is located along the base of the continental rise off central California, where flow during CO_2-2 (Figure 5b) may have followed the general path of bottom contours (Figure 1). No current data were recovered during CO_2-3 due to instrument failure.

[33] Spectral analyses of current time series showed that periodic flow at all sites was dominated by the semidiurnal lunar constituent M_2 (period ~12.4 h). The lunisolar diurnal (K_1 = 23.9 hours) and principal lunar diurnal (O_1 = 25.8 hours) constituents contained the greatest energy density for some components of flow. Spectra calculated from eastward flow for each experiment were nearly uniformly dominated by M_2 (Figure 7, right column). Spectra generated using northward, absolute magnitude, or flow heading yielded generally similar results, with some variation in the importance of M_2, K_1, O_1, and other constituents. Spectra based on current magnitude (Figure 7, left column), matched most closely the spectral patterns of pH records (see below).

3.2. CO_2 Dissolution and pH Variability

[34] Rates of CO_2 dissolution varied among experiments, based on qualitative observations of differences in the amount of liquid CO_2 remaining in CO_2 corrals at the end of each experiment (Figure 2), and appear to be related to the magnitude of eddy kinetic energy measured during each experiment (Table 2). High rates of dissolution were observed during CO_2-1, CO_2-2, and CO_2-4 (Figures 2c, 2d, and 2f). During CO_2-1, ~20 L of liquid CO_2 dissolved from each corral in only 2–3 weeks. In CO_2-2 (~100 L) and CO_2-4 (~20 L per corral), near-complete dissolution of injected CO_2 was observed after 41 and 29 days, respectively. Because only a small amount of hydrate (CO_2-2 (Figure 2d)) or no liquid CO_2 or hydrate (CO_2-4) was remaining at the end of these experiments, the majority of dissolution may have occurred prior to the end of the experiments.

[35] Eddy kinetic energy was high during all three of these experiments (Table 2). Dissolution rates during CO_2-3 were difficult to estimate, due to the refilling of the corral midway through the experiment, and the apparent formation of entrainment of water during CO_2 hydrate that appeared to have formed within the CO_2 pool. The corral was approximately 70% full at the end of the experiment (Figure 2e), reflecting either sluggish dissolution or significant hydrate formation (and seawater entrainment [*Brewer et al.*, 1999]), or both. Unfortunately, no flow data were recovered during CO_2-3. Dissolution during CO_2-5 was slow. Several CO_2 corrals used in CO_2-5 remained partially (1/8 to 1/2 full) of liquid CO_2 after 30 days, very likely related to the low mean current speeds and low turbulence measured at the site during this experiment.

[36] The magnitude and variability of pH perturbations varied among experiments, related to experimental design, distance from CO_2 pools (Figure 8), and current variability at each site. Shifts in pH caused by the CO_2 dissolution plume were highly variable and periodic during point source CO_2 experiments with centrally positioned CO_2 pools surrounded by study organisms and sensors (experiments CO_2-1, -2, -3).

[37] The greatest pH changes were measured during experiment CO_2-1, as reported by *Barry et al.* [2004]. Excursions of up to −1.7 pH units were measured within 1 m of the CO_2 pools during this experiment, related to the very near proximity of pH sensors to experimental CO_2

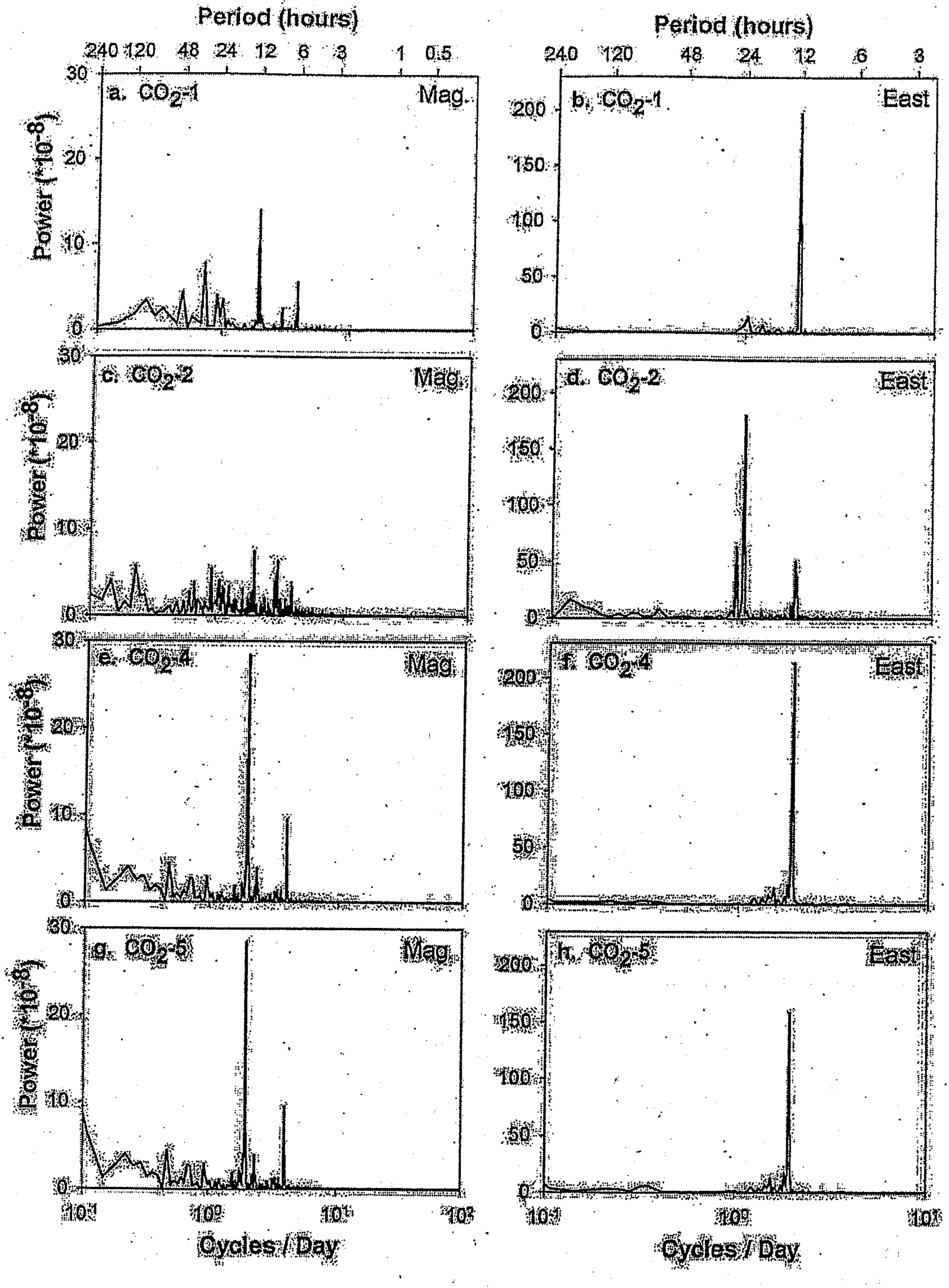

Figure 7. Spectral analyses of near-bottom currents during CO_2 release experiments. Left column includes spectra generated from time series of absolute current speed (Mag.). Right column displays spectra generated from time series of eastward current velocity (East). (a, b) CO_2-1, site A. (c, d) CO_2-2, site B. (e, f) CO_2-4, site C. (g, h) CO_2-5, site A. Note the strong periodicity at ~12.4 hours, representing the M_2 tide. Height above bottom for current measurements in each experiment is indicated in Figure 5.

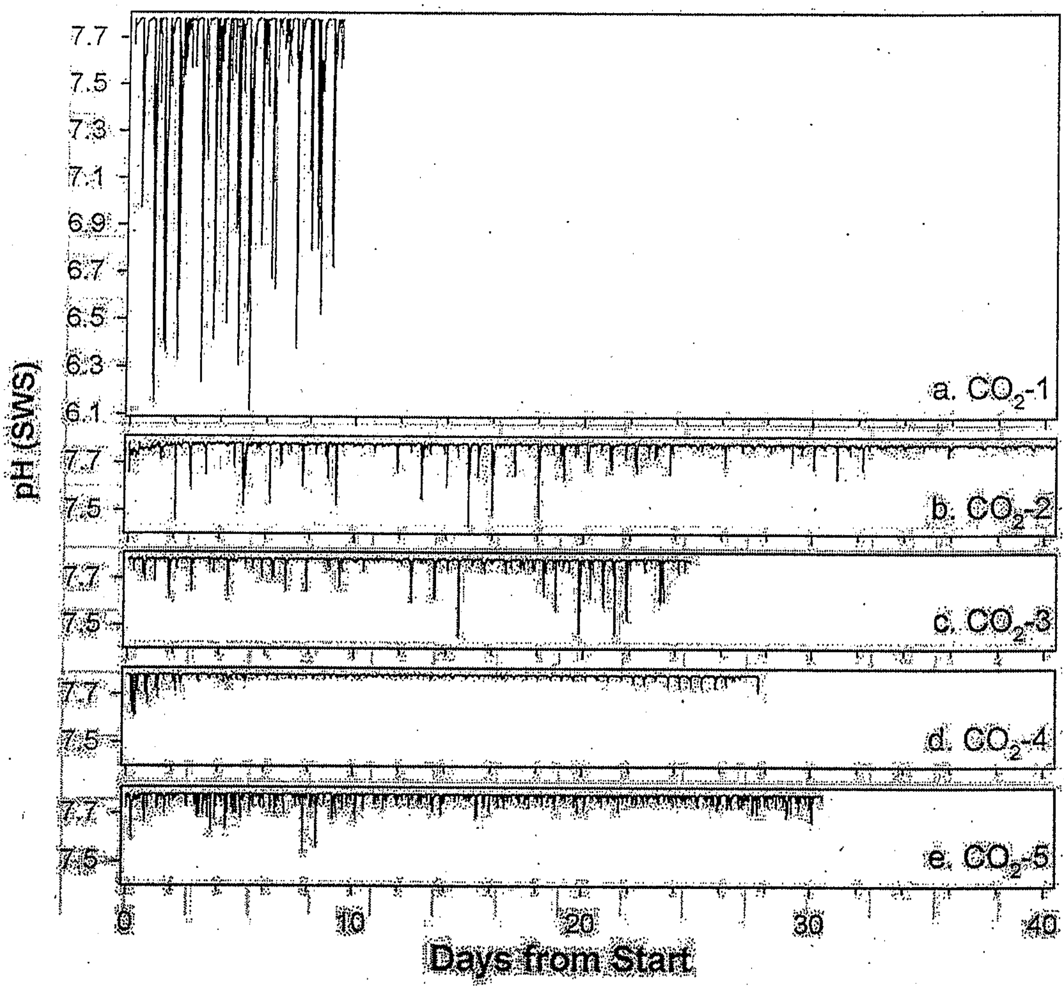

Figure 8. Time series of adjusted pH measurements during part of each CO_2 release experiment. (a) Release experiment CO_2-1 (distance between pH sensor and CO_2 pool = 0.5 m), (b) CO_2-2 (5 m), (c) CO_2-3 (5 m), (d) CO_2-4 (2.5 m), and (e) CO_2-5 (5 m). Height of sensors above seafloor was ~3 cm. Note the strong diurnal periodicity in Figures 8a–8c and higher-frequency variation in Figures 8d and 8e. pH adjustments were applied to all data (see text). The magnitude of pH perturbations during CO_2-4 are suspected to be erroneous. The length of all data records is near the total duration of each experiment, except for a (CO_2-1), in which this pH sensor failed after 9 days during the 36 day experiment.

pools (Figure 8a). Perturbations in pH were highly periodic, however, indicating that the variable speed and direction of near-bottom currents controlled the advection of the dissolution plume and bathed the seafloor (i.e., pH sensor) alternately with the CO_2 dissolution plume and ambient seawater (pH = 7.78 SWS). Owing to the rotary character of near-bottom currents dominated by the M_2 tides, large reductions in pH occurred nearly every 12.4 hours, followed by periods of normocapnia (pH = 7.78). Extreme excursions in pH (>0.5 units) were rare, and the average pH during the experiment was 7.64 (ΔpH = −0.14 units), with near-background values (7.78) through most of the experiment (Figure 9a). Unfortunately, only one of three pH sensors functioned reliably during the experiment, and this sensor also failed after ~10 days. In addition, though no pH data were collected near control corrals without CO_2, subsequent experiments indicated that pH perturbations near control corrals ~50 m away were nearly undetectable (i.e., ΔpH < 0.01 units).

[38] The central position of liquid CO_2 pools during experiments CO_2-2 and CO_2-3 produced a pattern of periodic pH variability similar to CO_2-1. Unfortunately, pH sensors very near (~0.5 m) CO_2 pools failed in both experiments, preventing comparison of pH changes for that distance with those measured during CO_2-1. Maximum pH excursions during CO_2-2 and -3 (approximately −0.3 units) were much smaller than measured during CO_2-1 (Figures 8b and 8c, Table 3), due to the greater distance (5 m) between sensors and CO_2 corrals and perhaps also to slightly lower rates of CO_2 dissolution. As in CO_2-1, the exposure of organisms and sensors to the dissolution plume around CO_2 corrals was brief and episodic, with hypercapnic events approximately every 12 hours in association with the clockwise rotation of the M_2 tide. Seawater with near

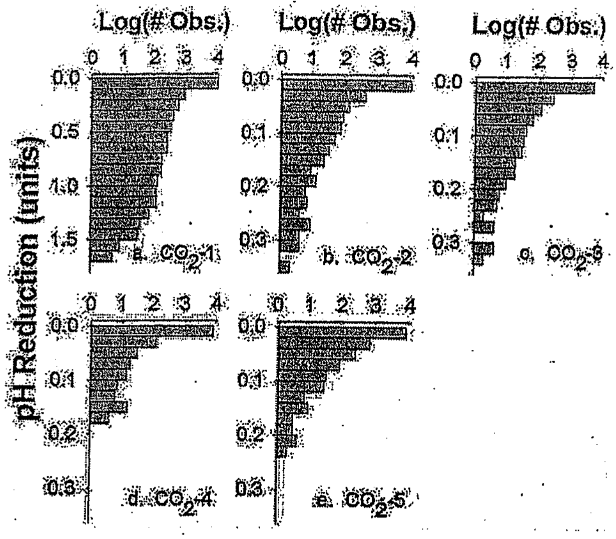

Figure 9. Frequencies of pH perturbations during CO_2 release experiments. Bars represent the number of observations during each experiment with shifts in pH of increasing magnitude (from a baseline of pH = 7.78 SWS). (a) CO_2-1. (b) CO_2-2. (c) CO_2-3. (d) CO_2-4. (e) CO_2-5. Note the log scale of frequencies and the overwhelming dominance of very mild or no pH reduction for all experiments.

normal pH ($\Delta pH < 0.05$ units) persisted more than 95% of the time, with excursions in pH > 0.1 units accounting for only ~2% of the pH measurements during these experiments (Figures 9b and 9c). The magnitude and temporal variability of pH reductions measured 5 m from CO_2 pools for CO_2-2 and CO_2-3 was quite similar for ~25 days, just prior to the end of CO_2-3. Because the corrals were not refilled during CO_2-2, it appears that dissolution diminished, as indicated by the reduced pH variability (and lessened hypercapnic stress) during the latter half of this experiment (Figure 8b).

[39] Spectral analyses of pH time series (Figures 10a–10c) and current measurements (Figures 7a–7c) made during point source CO_2 release experiments CO_2-1 to CO_2-3 confirmed the importance of oscillatory, near-bottom currents in the advection and dispersal of the CO_2 dissolution plume, and the very similar pattern of pH variability among these experiments. In addition to the M_2 tide, diurnal periodicity associated with the K_1 tide was evident in both the flow and pH variation at site B during CO_2-2. The M_4 tide (6.2 hours) was secondary in importance at site A for pH and bottom currents.

[40] CO_2 enclosure experiments CO_2-4 and CO_2-5, in which organisms and sensors were encircled by three or seven CO_2 corrals, respectively, were expected to produce somewhat more stable shifts in pH, as desired for investigations of the sensitivities of deep sea organisms to hypercapnia. Performance of pH sensors was poor during CO_2-4, and the adjustment required to remove drift was large, reducing our confidence in the magnitude, but perhaps not the periodicity, of pH changes in this experiment (Figure 8d). Exposure to the CO_2 dissolution plume from surrounding pools of liquid CO_2 was more frequent during these experiments due to the multiple CO_2 sources, but pH shifts were generally mild ($\Delta pH < 0.1$ units) and short lived (Figures 8d and 8e). Maximum pH reductions were near 0.2 units, and the average shift in pH during each experiment was only −0.008 units (Table 3). This low average pH shift is due to the high percentage of mild pH perturbations; more than 99 and 97% of all observations during experiments CO_2-4 and CO_2-5, respectively, showed pH changes of −0.05 units or less (Figures 8d and 8e).

[41] Even though the shifts in pH were small, experimental plots (i.e., animals, sensors) were exposed more frequently to the CO_2 plume during each of the CO_2 enclosure experiments than during point source CO_2 release experiments. The variance:mean ratio for pH measurement during CO_2 enclosure experiments (Table 3) was low, indicating a more stable pH field than was found for point source experiments. The greater frequency of hypercapnic events during CO_2 enclosure experiments is evident in Figures 8d and 8e, showing the time series of pH perturbations, and Figures 11d and 11e, characterizing pH variability in the lower 1 m of the water column during 10 days of each experiment. The less frequent and staccato character of pH events during earlier point source experiments is driven by the dominance of the M_2 barotropic tide on bottom currents. During CO_2 enclosure experiments, the frequent, though milder, perturbations indicate a partial decoupling of the pH field from the periodicity of bottom currents.

[42] Spectral analyses also indicated the higher frequency of hypercapnic events. Although the M_2 tide exerted strong dominance over pH variability within the triangular enclosure of CO_2 corrals during CO_2-4, variability was also observed on shorter frequencies not observed in near-bottom currents at the site (Figures 7e, 7f, 9d, and 10d). The persistent up-canyon flow within Monterey Canyon at site C may also have reduced both the residence time and recirculation of the dissolution plume within the experimental site. High-frequency variation in pH due to multiple CO_2 sources was most evident during CO_2-5. Spectral density is mixed among several nontidal frequencies in the center of the enclosure (Figure 9e), with the greatest energy at a period of 4.6 hours.

3.3. Biological Responses of Benthic Meiofauna to Hypercapnia

[43] The effects of exposure to the acute hypercapnia very near CO_2 corrals during the first CO_2 release experiment

Table 3. Summary of pH Perturbations During CO_2 Release Experiments[a]

	CO_2-1	CO_2-2	CO_2-3	CO_2-4	CO_2-5
Max	7.78	7.78	7.78	7.78	7.78
Min	6.12	7.44	7.45	7.61	7.54
Mean	7.64	7.77	7.77	7.78	7.77
SD	0.28	0.02	0.03	0.01	0.02
N	13,363	10,018	5921	7977	8790
			Deviations		
Max	−1.660	−0.342	−0.326	−0.166	−0.239
Mean	−0.142	−0.008	−0.008	−0.003	−0.008
SD	0.275	0.023	0.025	0.011	0.017
S^2: mean	0.533	0.066	0.078	0.040	0.036

[a] Deviations for pH measurements are shown in lower rows. The pattern of maximum perturbations is related principally to distance from CO_2 pools, rather than its design.

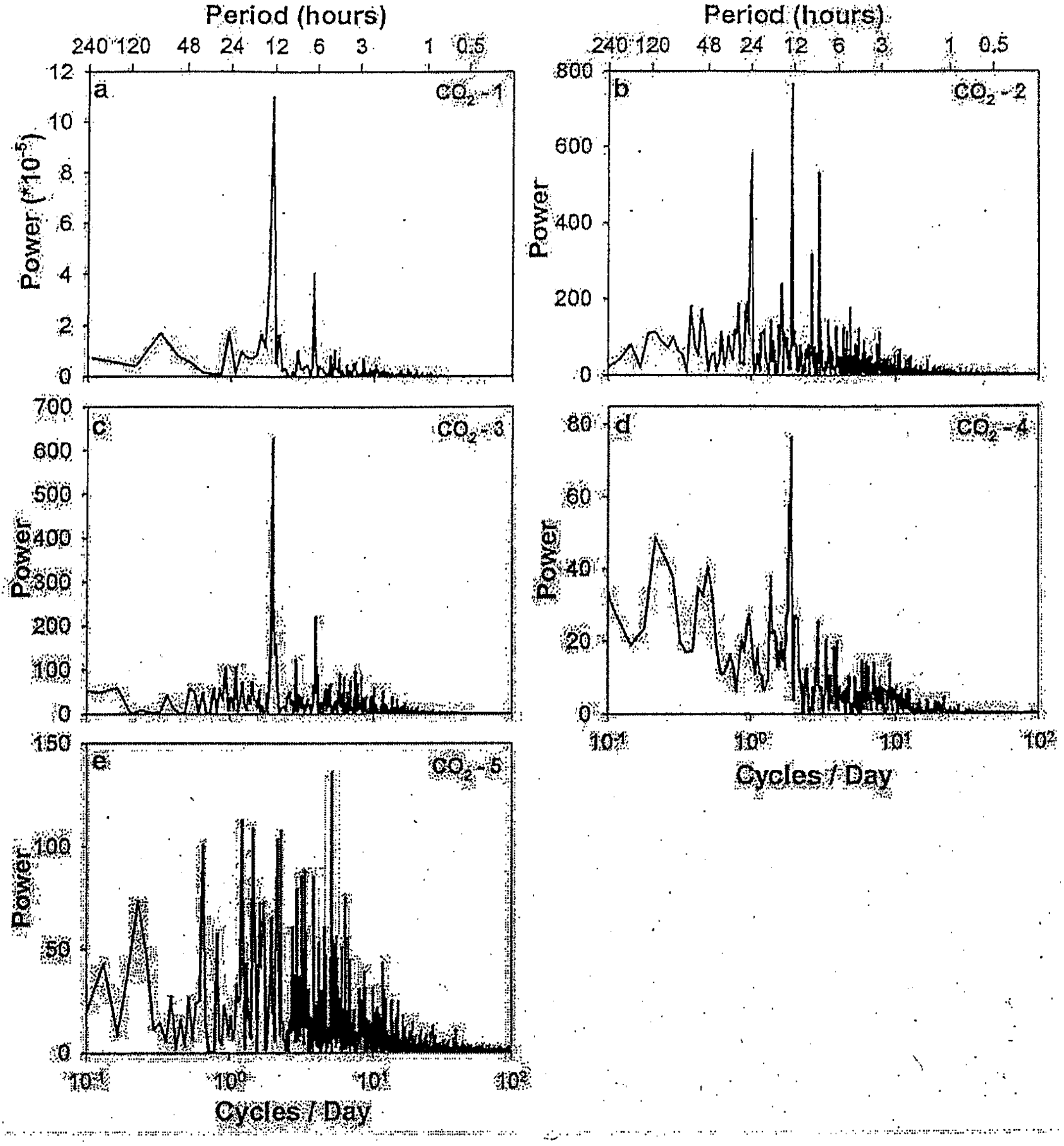

Figure 10. Power spectra for pH variability during CO_2 release experiments. (a) CO_2-1. (b) CO_2-2. (c) CO_2-3. (d) CO_2-4. (e) CO_2-5. Note differences in y axis scale among figures and the strong periodicity near 12.4 hours (M_2 tidal flow) for point source CO_2 experiments (Figures 10a–10c) and weaker, higher-frequency periodicity for CO_2 enclosure experiments (Figures 10d and 10e).

(CO_2-1) were severe, as reported by *Barry et al.* [2004]. All major meiofaunal taxa (nematodes, flagellates, amoebae) experienced high (>90%) mortality within 0.5 m of CO_2 pools after 30 days of exposure to episodic reductions in pH of up to −1.6 pH units. In contrast, mortality near control corrals was minor or undetectable.

[44] The effects of hypercapnia and acidosis on benthic meiofauna varied among regression design CO_2 release experiments (CO_2-2 and CO_2-3) that we examine in this paper. Although the pattern and intensity of pH variability was similar for these two experiments (Table 3), changes in meiofaunal abundance (i.e., survival rates) differed. Unlike the severe hypercapnia and high meiofaunal mortality observed during experiment CO_2-1, the abundance of nematodes, flagellates, and amoebae did not change with distance from the central CO_2 pools during experiment CO_2-2 after 41 days of episodic, moderate hypercapnia. During CO_2-3, nematodes did not vary in abundance with distance from the CO_2 pool, but flagellates and amoebae each decreased significantly ($p < 0.005$) closer to CO_2 pools by the end of the experiment. Survival nearest the CO_2 pool was only ~30%, but increased to 75% survival 10 m from the pool (Figures 12d and 12e).

4. Discussion

4.1. Efficacy of pH Perturbations During CO_2 Release Experiments

[45] A highly stable shift in seawater chemistry desirable for studies of tolerance to hypercapnia was not observed

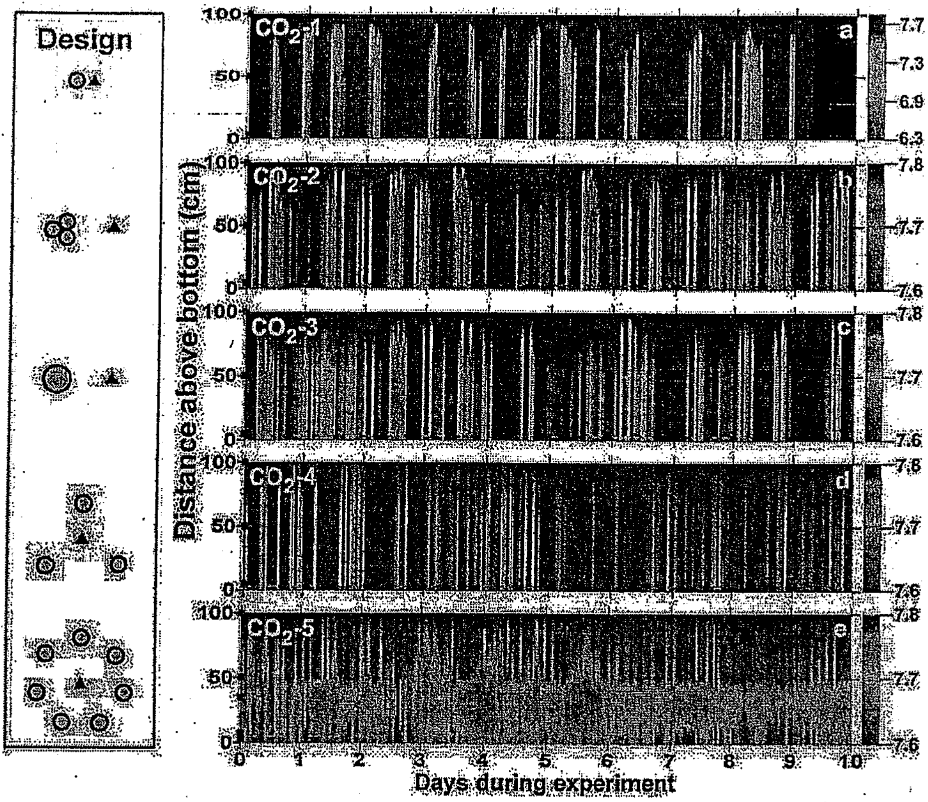

Figure 11. Time series of seawater pH to 1 m above the seafloor during CO_2 release experiments. (left) Layout of CO_2 pools (blue circles) and pH sensors (red triangles) during each experiment. (right) pH changes during 10 days of each CO_2 release experiment. Note scale difference between Figure 11a and Figures 11b–11e. Positions of pH sensors (red squares on left *y* axis) were ~3 cm above bottom for CO_2 release experiments 1–4 (Figures 11a–11d), for which pH at 50 cm above bottom was not measured (assumed to equal the pH at 5 cm). For CO_2 enclosure experiment CO_2-5 (Figure 11e), four pH sensors were located at 5 cm height, one at 35 cm, and one at 50 cm. Background pH (100 cm above seafloor) for all panels was assumed to be 7.78 (SWS). Note the roughly semidiurnal periodicity of pH perturbations for point source CO_2 release experiments with a central CO_2 pool (Figures 11a–11c) and high-frequency or more constant pH variability for CO_2 enclosure experiments (Figures 11d and 11e).

during any of the CO_2 release experiments. Instead, CO_2 concentrations (measured as pH) varied throughout all experiments, with the vast majority of observations near normal seawater pH. This high variability in CO_2 and pH stress impairs our ability to interpret the dose tolerance responses of animals to hypercapnia. It is not possible to partition the importance of episodic moderate hypercapnia or chronic mild hypercapnia during these experiments on animal survival. More useful experiments would provide relatively stable CO_2 perturbations within the range of variation expected in the future for surface or deep ocean [*Hoffert et al.*, 1979]. Enclosure designs used in this study, though not ideal, damped the high pH variation observed in point source experiments. Further studies to compare the impacts of episodic, severe hypercapnia with those arising from stable, but mild hypercapnia would improve our understanding of the dose tolerance patterns of deep sea animals. Information generated from such studies will serve as important inputs for models of ecosystem dynamics under various scenarios of future ocean chemistry.

[46] The interpretation of faunal responses to hypercapnia and acidosis was also complicated by the frequent failure, poor reliability, and considerable drift of pH sensors during these long-term, deep sea studies. The adjustment of raw pH data to fit both the expected background pH (7.78 SWS) and to remove the sometimes significant drift of each sensor may have eliminated some significant, though relatively small, pH perturbations. This pH adjustment method retains the larger spikes in pH variation very effectively, but sometimes removed small-scale variation in pH which might have represented real hypercapnic events. Development of more sophisticated sensors, including pH and CO_2 sensors for deep sea studies [*Someya et al.*, 2004], would catalyze progress in this area.

[47] Because we could not measure pore fluid pH throughout these experiments, we assumed that pH perturbations measured in the benthic boundary layer immediately above the seafloor would be correlated, or at least coupled, with pore fluid pH. Shipboard measurements of pore fluid pH reported by *Thistle et al.* [2005] for the upper sediment

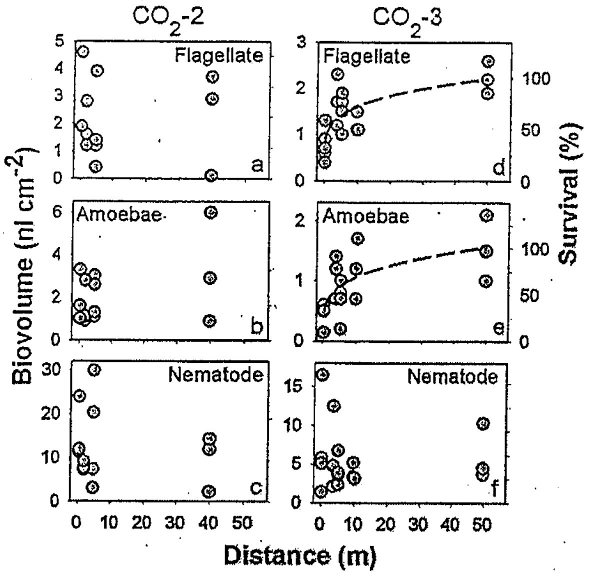

Figure 12. Variation in meiofaunal abundance at the end of CO_2 release experiments CO_2-2 and CO_2-3. (a, b, c) Results from CO_2-2, sampled 48 days after CO_2 release. (d, e, f) Results from CO_2-3, sampled 27 days after CO_2 release. Meiofaunal taxa are indicated in each panel. Abundance is measured as biovolume. Distance indicates distance from central CO_2 pools. Shaded dots indicate biovolume values for individual cores collected at the end of each experiment. Dashed black curves indicate statistically significant power functions ($y = ax^b$) for flagellates ($r^2 = 0.56$, $p < 0.0004$) and amoebae ($r^2 = 0.47$, $p < 0.0017$) in CO_2-3. Right axis indicates estimated survival, assuming that background biovolume values (i.e., 50 m from pool) represent zero CO_2-related mortality.

layer (top 8 mm) near the center of the triangular CO_2 enclosure during CO_2-4 showed pH reductions of ~0.6 pH units compared to control areas. Measurements with in situ sensors we deployed just above the seafloor indicated much milder pH perturbations, however the accuracy of these sensors were suspect during this experiment. Therefore although the scaling of interstitial pH with the pH of the overlying water remains unclear, it is certain that the two are coupled. Additional study is required to resolve this relationship.

[48] Rates of dissolution for liquid CO_2 and CO_2 hydrate are poorly constrained, and are affected by the presence of CO_2 hydrate and the flow speed or strength of turbulence eddies near the CO_2-seawater interface [*Fer and Haugan*, 2003; *Rehder et al.*, 2004; *Teng and Yamasaki*, 2000]. Slow rates of CO_2 dissolution estimated for experiments CO_2-3 and CO_2-5 were likely related to low turbulence during these experiments, but may have been influenced by several other factors, including mean currents, sedimentation on the liquid CO_2, formation of CO_2 hydrate, and the hydrodynamics of the CO_2 corral. The high aspect ratios (48 cm diameter × 40 cm high) and multiple corrals used during CO_2-2 (Figures 2c and 2d) may have enhanced turbulence over the corrals, thereby accelerating dissolution. In contrast, the larger (91 cm diameter × 30 cm high) CO_2 pool used in CO_2-3 may have impeded dissolution, particularly when partially full. Although the CO_2 surface in this large corral was near the top of the corral at the end of the experiment, seawater entrainment during hydrate formation [*Brewer et al.*, 1999] may have increased the volume of the liquid-hydrate pool. Nevertheless, CO_2 dissolution appears to have been slow for such a large volume to remain after 1 month, perhaps due to sluggish currents, and the insulating effects of a veneer of sediment that was deposited on the hydrate surface of the pool during the experiment (likely caused by the ROV).

[49] The effects of CO_2 dissolution and hydration on seawater salinity [*Brewer et al.*, 2005] suggest that salinity could be a useful proxy for pCO_2 or pH. *Brewer et al.* [2005] have shown that salinity initially drops during CO_2 dissolution, as liquid dilutes seawater, but finally rises to values greater than ambient values as CO_2 hydration reactions proceed to completion. Salinity varied considerably in each experiment, but its relationship to CO_2 chemistry could not be determined. CO_2 hydration proceeds considerably faster at depth than in surface waters, but there is insufficient time for hydration to equilibrate during the transit of the dissolution plume through our experimental plots. Because the system is in disequilibrium, the salinity data provide a complex view of CO_2 changes in the experiments. For this reason, we relied only on pH perturbations to estimate changes in CO_2 chemistry. Temperature variation was low (<0.2°) throughout each experiment and was not useful in estimating pH or CO_2 levels.

[50] Dominance of semidiurnal periodicity in pH during the point source CO_2 release experiments was not surprising, especially considering the magnitude of M_2 tides along central California (Figure 7) [*Beaulieu and Baldwin*, 1998; *Breaker and Broenkow*, 1994; *Filloux*, 1971]. Baroclinic M_2 tides, generated along the continental shelf break in Monterey Bay [*Rosenfeld*, 1990], may reflect seaward, increasing turbulence in offshore waters [*Lien and Gregg*, 2001], and could have contributed to the flow field measured in these experiments. Variation in the direction and speed of currents between experiments are likely caused by changes in the relative importance of factors contributing to abyssal current, including seasonal and interannual variability. *Beaulieu and Baldwin* [1998] noted large shifts in abyssal currents at station M in 4100 m depth off central California, attributing them to the "spring transition" characteristic of the west coast of North America. This seasonal shift caused by changes in the wind field at the surface has also been documented in the eastern North Atlantic [*Dickson et al.*, 1982], and may have affected flow at site A.

[51] The tight coupling between current variability in the benthic boundary layer and the periodicity in pH perturbations during each experiment suggests that boundary layer flows measured 5 or more m above the seafloor extend to very near the seabed. Our flow measurements were no closer than 5–6 m above the seabed, which is above the log-layer (the range of depths where current speeds decreases scales according to the log of distance above the seabed, due to the frictional effects of the bottom). The log-layer for the flows observed in this study is expected to be ~2–3 m at deep sea depths [*Gross et al.*, 1986].

Beaulieu and Baldwin [1998] estimated the boundary layer flow to the seabed from measurements of currents 2.5–600 m above the bottom at station M. Estimates of z_0 (flow at the seabed) for station M ranged from 0.11 to 0.91 cm s^{-1}, based on mean currents 2.5 m above the bottom of ~2–4 cm s^{-1}. Considering the similar mean flow speeds and bottom characteristics of station M to our study sites, flow at the seabed is likely to fall within the range estimated by *Beaulieu and Baldwin* [1998], and should vary roughly in proportion to the mean speed measured further above the bottom. Extrapolating the pattern of flow measured in the benthic boundary layer to the seabed during our experiments could explain the observed variation in apparent rates of CO_2 dissolution among experiments.

[52] The extent of pH variation in the triangular and circular CO_2 enclosure experiments was unexpected, however, even though the observed pH periodicity was generally higher in frequency than for point source CO_2 designs. The enclosure designs were expected to produce a more stable and more persistent pH perturbation within the enclosure, due to both the multiple CO_2 dissolution sources and some anticipated overlap in the dissolution plumes emanating from each pool. Although episodes of reasonably large pH perturbations (approximately −0.2 pH units) were observed in all experiments, they were generally short lived in all but CO_2-1, in which pH sensors were positioned very near the CO_2 pools. Terrestrial FACE CO_2 perturbation systems can also suffer from high pCO_2 variation (data available from http://cdiac.esd.ornl.gov/programs/FACE/face.html), but the active control of CO_2 injection for these systems provides much tighter control on mean and maximum changes in pCO_2 within enclosures.

4.2. Biological Sensitivity of Benthic Meiofauna

[53] Mortality associated with hypercapnia was detected in most CO_2 release experiments, even though perturbations in pH were generally short lived, and in some cases, mild. High rates of mortality observed after even short-term exposure to pH reductions >1 pH unit, as occurred during CO_2-1 [*Barry et al.*, 2004] are not surprising, since such large changes in pH exceed greatly the range of natural environmental variability. Variation in the pH of the aerobic surficial layer of deep sea sediments is generally much less than one unit, and most meiofaunal taxa studied here may not experience this entire range [*Giere*, 1993]. During CO_2-1, the close proximity of sediment samples to the CO_2 pools probably led to very high CO_2 perturbations in the upper sediment layer. Although we did not measure pH in sediments during CO_2-1, cores collected from within CO_2 corrals which had been covered with liquid CO_2 effervesced to a depth of nearly 10 cm down-core upon recovery to the surface. This indicates a deep penetration of liquid CO_2 within the sediment (e.g., Figure 2b). Even though we did not observe similar CO_2 outgassing in sediment cores analyzed for meiofauna, the surface sediments surrounding the CO_2 corrals were likely quite hypercapnic.

[54] Perturbations of pH measured in CO_2-2 and CO_2-3 were relatively mild, (−0.1 to −0.2 pH units) and infrequent (<2% of observations), but still led to upward of 30% mortality 5 m from CO_2 pools for flagellates and amoebae during CO_2-3 (Figures 12d and 12e). This mortality rate suggests that pH perturbations were either more severe in the sediment column than measured in the overlying water, or that these meiofaunal taxa are quite sensitive to relatively small and brief changes in pH. The contrasting results for the survival of flagellates and amoebae between CO_2-2 and CO_2-3 may be related to the longer duration of CO_2-2, its smaller CO_2 dose, and apparently diminished dissolution toward the end of the experiment. Approximately 100 L of liquid CO_2 were released in the central pools used for CO_2-2, for an experiment lasting 41 days. In contrast, ~150 L were injected into the CO_2 corral used for CO_2-3, (80 L after 17 days) during this much shorter experiment. Although much CO_2 remained at the end of CO_2-3, its pH record (Figure 8c) suggests that hypercapnic stress was as high as or higher than during CO_2-2. It is possible that meiofaunal survival was high during CO_2-2, as suggested by the abundance patterns detected at the end of the experiment, or that the local population had recovered to some extent, by either immigration and/or population turnover as hypercapnic stressed lessened after the first month. Deep sea ciliate and flagellate generation times are not well known, but probably range near days to weeks, considering the growth rates of several hours for shallow planktonic ciliates [*Hansen and Bjornsen*, 1997]. The sensitivities of benthic meiofauna to CO_2 elevation during the triangular CO_2 enclosure experiment (CO_2-4) were measured by *Carman et al.* [2004] and *Thistle et al.* [2005], who detected mortalities among meiofaunal harpacticoid copepods near 50% at the center of the triangular CO_2 enclosure. Although the abundances of harpacticoids and other meiofauna (nematodes, nauplii, kinorhynchs, polychaetes) were similar among control and hypercapnic samples, closer inspection of individuals from each indicated that ~50% of animals in hypercapnic samples were partially degraded, indicated death prior to collection by the ROV. Profiles of pH within the sediment column within the enclosure compared to those from a control site ~50 away indicated a pH reduction of nearly 0.6 pH units in the upper sediment column.

[55] Patterns of mortality for benthic meiofauna detected during these experiments are somewhat mixed, but in most experiments (all but CO_2-2) suggests that chronic acidosis and hypercapnia that may be typical in the future ocean could have large effects on benthic meiofaunal populations. Maximum perturbations in pH at a distance of ~5 m was generally in the range of −0.2 pH units in the overlying water, or perhaps greater in the pore fluid [*Thistle et al.*, 2005], but these hypercapnic events were short lived, and rare (pH was most often very near normocapnic). Even after exposure to infrequent, relatively mild hypercapnia in the overlying bottom water, meiofaunal mortality in two of three experiments (CO_2-3, -4) was near 30% or more. The impacts of chronic hypercapnia are expected to be more severe.

[56] The large variation in pH observed in the CO_2 release experiments limits our ability to determine key thresholds of hypercapnia that could trigger physiological stress or death for any of the animals studied. An understanding of the biological and ecological consequences of increased hypercapnia over shallow and deep waters of the world ocean will require knowledge of the physiological responses of organisms as a function of the severity and duration of hypercapnia. Thus thresholds (e.g., dose tolerance data) for individual survival, as well as information on

the effects of sublethal, but potentially energetically costly hypercapnic exposure, are most easily considered in terms of chronic, stable changes in pH by known intervals [*Auerbach et al.*, 1996]. A broad base of information concerning the dose tolerance responses of a phylogenetically and environmentally diverse set of animals, as well as the development of effective ecosystem models [*deYoung et al.*, 2004] may be important precursors to predicting ecosystem changes that may result from "business as usual" [*Legget et al.*, 1992] changes in ocean chemistry.

[57] Exposure to hypercapnic, acidic seawater, from either direct CO_2 injection or the long-term increase in deep sea CO_2 levels drawn from atmospheric CO_2 emissions pose physiological challenges for marine animals that have a scope of tolerance to such stresses defined by their evolutionary history of adaptation to environmental variability. Optimal metabolic performance for most animals requires tight control (or narrow uncontrolled variability) of internal pH, which influences a variety of cellular physiological functions [*Hochachka and Somero*, 2002]. Owing to the reduced environmental variability typical of deep sea environments [*Kennett and Ingram*, 1995], coupled with apparently strong selection for adaptations to minimize energy requirements in deep, typically food-poor ocean environments, deep sea animals often exhibit higher sensitivities to environmental variation than their shallow-water counterparts (or hydrothermal vent taxa), including variation in pH and CO_2 [*Seibel and Walsh*, 2003]. Thus while animals that typically experience large pH variation may have the physiological capacity to maintain internal acid/base balance even during severe hypercapnic events (e.g., hydrothermal vents animals [*Goffredi et al.*, 1998]), most deep sea animals may not survive even milder hypercapnia.

[58] Meiofauna, including those studied here, are expected to be equipped poorly to tolerate acidosis. Flagellates, amoebae, and nematodes are primitive groups that rely on diffusion through cell membranes for respiration. The absence of respiratory proteins in these groups may limit the potential impacts of hypercapnia on oxygen binding that can be acute in some more complex taxa [*Seibel and Walsh*, 2003], and tolerance to hypercapnia may be restricted by the inability of most taxa to maintain acid-base balance within normal levels. Diffusion of CO_2 through cell membranes will quickly equilibrate the CO_2 tensions and pH of intra and extracellular fluids with ambient seawater concentrations. Nematodes, with their thicker cuticle, may be buffered somewhat more effectively than flagellates and amoebae from brief pH events, but persistent changes in seawater chemistry will swamp the internal fluids of all of these taxa rather quickly. At present, the key cellular processes impacted by hypercapnia or acidosis for these taxa remain unknown.

4.3. Future Studies of the Impacts of Hypercapnia on Deep Sea Ecosystems

[59] In view of the nearly inevitable continuing rise in atmospheric CO_2, the world ocean is faced with a hypercapnic future that may rival levels unseen for upward of 100 million years, with potentially large changes in the ecosystem patterns and function of the oceans. Progress in understanding the consequences of elevated CO_2 levels on marine populations and communities depends on our ability to measure the response of organisms to changes in CO_2, pH and perhaps other factors. Although laboratory studies of physiological performance are possible for shallow water species, in situ studies are required for most deep sea species [*Shirayama*, 1998], at least for water depths exceeding ~1500 m, owing to their general intolerance of surface pressures. Capture of animals at depth, and return to the laboratory under in situ pressure and temperature is possible, and should supplement field studies. In many cases, however, field experiments that provide tight control over seawater chemistry can be used to measure at least the short-term response of various species to perturbations in CO_2 and pH. Our experimental approach provides some inference concerning the sensitivity of some deep sea species to hypercapnia, but do not determine the range of pH and CO_2 perturbations tolerable for survival (e.g., LD_{50}). Nor have deep sea experiments to date measured the sublethal consequences of hypercapnia that may have important negative consequences for populations. For example, *Kurihara et al.* [2004] used laboratory experiments to demonstrate that littoral sea urchins and copepods exposed to moderate hypercapnia experienced reduced rates of growth, developmental delays, and anomalies (sea urchins) and reduced reproductive success (fertilization: urchins, egg production and hatching: copepods). Likewise, *Auerbach et al.* [1996] and *Caulfield et al.* [1997] compiled data on the dose tolerance (survival rates) of a variety of shallow water marine organisms, providing the first overview of the general pattern of pH (and hypercapnia) stress tolerance of marine organisms. *Shirayama* [1998, p. 381] noted that deep sea species have "1) Low biological activities, 2) Long life span, 3) High sensitivity to the environmental disturbance, 4) High species diversity, and 5) Low density," suggesting that they are hypersensitive to environmental disturbance. *Seibel and Walsh* [2001] examined metabolic performance data for a variety of species inhabiting depths from 0 to ~1500 m, suggesting that deep water species are potentially orders of magnitude more sensitive to CO_2-related stresses than their shallow water counterparts. The role of the intense eastern Pacific oxygen minimum, which is confounded with depth in their data set, remains to be examined.

[60] Future in situ studies will require more sophisticated designs and perhaps significantly more complex subsea instrumentation to provide stable perturbations in CO_2 and pH levels that will allow researchers to examine the dose tolerance responses of deep sea taxa to changes in seawater chemistry caused by ocean carbon sequestration or long-term increases in CO_2. Several alternatives are possible, from in situ collections of deep sea organisms returned to surface laboratories under pressure for controlled physiological study, to deep sea mesocosms akin to those developed for CO_2 studies in terrestrial systems, or automated in situ chamber systems capable of small-scale metabolic studies. FACE experiments [*McLeod and Long*, 1999] are underway at dozens of sites across the globe to measure the response of terrestrial communities to elevated CO_2 levels. FACE studies regulate pCO_2 over replicated terrestrial plots, based on rapid air flow sensors and sophisticated upstream CO_2 injectors. Similar efforts, representing an advanced form of our CO_2 enclosure designs may be required for

ocean studies before either the determination of dose responses, or the effects of chronic, long-term hypercapnia on most marine species can be examined.

[61] While the application of FACE technology may be productive in understanding the impacts of increasing CO_2 levels in the oceans, the spatial and temporal scales, and focus on specific habitats relevant for ocean studies must be considered. Deep sea bathypelagic and sediment habitats, which dominate ocean ecosystems, may require vastly different applications of mesocosm-like technology. Unlike terrestrial systems, marine microbial processes often dominate carbon cycling in deep sea ecosystems. Thus the appropriate spatial scale of experimental enclosures may be quite small. Pelagic habitats also present complex technical challenges for controlled volume experiments. Automated small-scale in situ chamber systems capable of measuring metabolic responses of individual animals or sediment samples to hypercapnia may represent the most productive technological developments for studies of the biology of a high-CO_2 ocean.

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References

Allen, L. H., Jr. (1992a), Field techniques for exposure of plants and ecosystems to elevated CO_2 and other trace gases, *Crit. Rev. Plant Sci.*, *11*, 85–119.

Allen, L. H., Jr. (1992b), Free-Air CO_2 Enrichment field experiments: An historical overview, *Crit. Rev. Plant Sci.*, *11*, 121–134.

Allen, L. H., Jr., and S. E. Beladi (1990), Free-Air CO_2 Enrichment (FACE): Analysis of gaseous dispersion arrays for the study of rising atmospheric CO_2 effects on vegetation, in *Green Report Series, Response of Vegetation to Carbon Dioxide, Prog. Rep. 057*, U.S. Dep. of Energy Carbon Dioxide Res. Div., U.S. Dep. of Agric. Agric. Res. Serv., Washington, D. C.

Auerbach, D., J. Caulfield, H. Herzog, and E. Adams (1996), Environmental impacts of ocean disposal of CO_2, in *Ocean Storage of CO_2: Workshop 2, Environmental Impact*, edited by B. Omerod and M. Angel, pp. 41–56, Int. Energy Agency Greenhouse Gas Res. and Develop. Prog., Gloucestershire, U. K.

Barry, J. P., K. R. Buck, C. F. Lovera, L. Kuhnz, P. J. Whaling, E. T. Peltzer, P. Walz, and P. G. Brewer (2004), Effects of direct ocean CO_2 injection on deep-sea meiofauna, *J. Oceanogr.*, *60*, 759–766.

Beaulieu, S., and R. Baldwin (1998), Temporal variability in currents and the benthic boundary layer at an abyssal station off central California, *Deep Sea Res., Part II*, *45*, 587–615.

Breaker, L. C., and W. W. Broenkow (1994), The circulation of Monterey Bay and related processes, *Oceanogr. Mar. Biol.*, *32*, 1–64.

Brewer, P. G., G. Friederich, E. T. Peltzer, and F. M. Orr Jr. (1999), Direct experiments on the ocean disposal of fossil fuel CO_2, *Science*, *284*, 943–945.

Brewer, P. G., E. T. Peltzer, P. Walz, I. Aya, K. Yamane, R. Kokima, Y. Nakajima, N. Nakayama, P. Haugan, and T. Johannessen (2005), Deep ocean experiments with fossil fuel carbon dioxide: Creation and sensing of a controlled plume at 4 km depth, *J. Mar. Res.*, *63*, 9–33.

Buck, K. R., J. P. Barry, and A. G. B. Simpson (2000), Monterey Bay cold seep biota: Euglenozoa with chemoautotrophic bacterial epibionts, *Eur. J. Protistol.*, *35*, 117–126.

Caldeira, K., and M. E. Wickett (2003), Oceanography—Anthropogenic carbon and ocean pH, *Nature*, *425*, 365.

Carman, K. R., D. Thistle, J. W. Fleeger, and J. P. Barry (2004), The influence of introduced CO_2 on deep-sea metazoan meiofauna, *J. Oceanogr.*, *60*, 767–772.

Caulfield, J. A., D. I. Auerbach, E. Adams, and H. J. Herzog (1997), Near field impacts of reduced pH from ocean CO_2 disposal, *Energy Conver Manage.*, *38*, 343–348.

deYoung, B., M. Heath, F. Werner, F. Chai, B. Megrey, and P. Monfray (2004), Challenges of modeling ocean basin ecosystems, *Science*, *304*, 1463–1466.

Dickson, R. R., W. J. Gould, P. A. Gurbutt, and P. D. Killworth (1982), A seasonal signal in ocean currents to abyssal depths, *Nature*, *295*, 193–198.

Feely, R. A., C. L. Sabine, K. Lee, W. Berelson, J. Kleypas, V. J. Fabry, and F. J. Millero (2004), Impact of anthropogenic CO_2 on the CaCO3 system in the oceans, *Science*, *305*, 362–366.

Fer, I., and P. M. Haugan (2003), Dissolution from a liquid CO_2 lake disposed in the deep ocean, *Limnol. Oceanogr.*, *48*, 872–883.

Filloux, J. H. (1971), Deep-sea tide observations from the northeastern Pacific, *Deep Sea Res. Oceanogr. Abstr.*, *18*, 275–284.

Giere, O. (1993), *Meiobenthology: The Microscopic Fauna in Aquatic Sediments*, 328 pp., Springer, New York.

Goffredi, S. K., J. J. Childress, F. H. Lallier, and N. T. Desaulniers (1998), How to be perfect host: CO_2 and HS^- accumulation and H^+ elimination in the hydrothermal vent tube-worm Riftia pachyptila, in *Proceedings of the First International Symposium on Deep-Sea Hydrothermal Vent Biology*, vol. 39, pp. 297–300, Stat. Biol. de Roscoff, France.

Gross, T. F., A. J. I. Williams, and W. D. Grant (1986), Long term in situ calculations of kinetic energy and Reynolds stress in a deep-sea boundary layer, *J. Geophys. Res.*, *91*, 8461–8469.

Hansen, P. J., and P. K. Bjornsen (1997), Zooplankton grazing and growth: Scaling within the 2–2,000 μm body size range, *Limnol. Oceanogr.*, *42*, 687–704.

Harvey, L. D. D. (2003), Impact of deep-ocean carbon sequestration on atmospheric CO_2 and on surface-water chemistry, *Geophys. Res. Lett.*, *30*(5), 1237, doi:10.1029/2002GL016224.

Haugan, P. M., and H. Drange (1992), Sequestration of CO_2 in the deep ocean by shallow injection, *Nature*, *357*, 318–320.

Herzog, H., K. Caldeira, and E. Adams (2001), Carbon sequestration via direct injection, *Encycl. Ocean Sci.*, *1*, 408–414.

Hochachka, P. W., and G. N. Somero (2002), *Biochemical Adaptation*, 466 pp., Oxford Univ. Press, New York.

Hoffert, M. I., Y. C. Wey, A. J. Callegari, and W. S. Broecker (1979), Atmospheric response to deep-sea injections of fossil-fuel carbon dioxide, *Clim. Change*, *2*, 53–68.

Joos, F., G. K. Plattner, T. F. Stocker, O. Marchal, and A. Schmittner (1999), Global warming and marine carbon cycle feedbacks on future atmospheric CO_2, *Science*, *284*, 464–467.

Kennett, J. P., and B. L. Ingram (1995), A 20,000-year record of ocean circulation and climate change from the Santa Barbara Basin, *Nature*, *377*, 510–514.

Kerr, R. A. (2001), Bush backs spending for a "global problem," *Science*, *292*, 1978.

Kurihara, H., S. Shimode, and Y. Shirayama (2004), Effects of elevated concentration of CO_2 on the life histories of marine organisms, *J. Oceanogr.*, *60*, 743–750.

Langdon, C., W. S. Broecker, D. E. Hammond, E. Glenn, K. Fitzsimmons, S. G. Nelson, T.-H. Peng, I. Hajdas, and G. Bonani (2003), Effect of elevated CO_2 on the community metabolism of an experimental coral reef, *Global Biogeochem. Cycles*, *17*(1), 1011, doi:10.1029/2002GB001941.

Legget, J., W. J. Pepper, and R. J. Swart (1992), *Climate Change 1992: The Supplementary Report to the IPCC Scientific Assessment*, Cambridge Univ. Press, New York.

Lien, R.-C., and M. C. Gregg (2001), Observations of turbulence in a tidal beam and across a coastal ridge, *J. Geophys. Res.*, *106*, 4575–4591.

Marchetti, C. (1977), On geoengineering and the CO_2 problem, *Clim. Change*, *1*, 59–69.

Marland, G., T. A. Boden, and R. J. Andres (2001), Global, regional, and national CO_2 emissions, in *Trends: A Compendium of Data on Global Change*, pp. 59–69, Carbon Dioxide Inf. Anal. Cent. Oak Ridge Natl. Lab., Oak Ridge, Tenn.

Martin, J. H. (1990), Glacial-interglacial CO_2 change: The iron hypothesis, *Paleoceanography*, *5*, 1–13.

McLeod, A. R., and S. P. Long (1999), Free-Air Carbon Dioxide Enrichment (FACE) in global change research: A review, *Adv. Ecol. Res.*, *28*, 1–56.

Parmesan, C., and G. Yohe (2003), A globally coherent fingerprint of climate change impacts across natural systems, *Nature*, *421*, 37–42.

Pörtner, H. O., M. Langenbuch, and B. Michaelidis (2005), Synergistic effects of temperature extremes, hypoxia, and increases in CO_2 on marine animals: From Earth history to global change, *J. Geophys. Res.*, doi:10.1029/2004JC002561, in press.

Rehder, G., S. H. Kirby, W. B. Durham, L. A. Stern, E. T. Peltzer, J. Pinkston, and P. G. Brewer (2004), Dissolution rates of pure methane hydrate and carbon dioxide hydrate in under-saturated seawater at 1000 m depth, *Geochim. Cosmochim. Acta.*, *68*, 285–292.

Riebesell, U., I. Zondervan, B. Rost, P. D. Tortell, R. E. Zeebe, and F. M. M. Morel (2000), Reduced calcification of marine plankton in response to increased atmospheric CO_2, *Nature*, *407*, 364–367.

Root, T. L., J. T. Price, K. R. Hall, S. H. Schneider, C. Rosenzweig, and J. A. Pounds (2003), Fingerprints of global warming on wild animals and plants, *Nature*, *421*, 57–60.

Rosenfeld, L. K. (1990), Baroclinic semidiurnal tidal currents over the continental shelf off northern California, *J. Geophys. Res.*, *95*, 22,153–22,172.

Sabine, C. L., et al. (2004), The oceanic sink for anthropogenic CO_2, *Science*, *305*, 367–371.

Seibel, B. A., and P. J. Walsh (2001), Potential impacts of CO_2 injection on deep-sea biota, *Science*, *294*, 319–320.

Seibel, B., and P. Walsh (2003), Biological impacts of deep-sea carbon dioxide injection inferred from indices of physiological performance, *J. Exper. Biol.*, *206*, 641–650.

Shirayama, Y. (1998), Biodiversity and biological impact of ocean disposal of carbon dioxide, *Waste Manage.*, *17*, 381–384.

Someya, S., S. Bando, Y. Song, B. Chen, and M. Nishio (2004), Laser-dye imaging of the pH field in a laboratory experiment, *J. Oceanogr.*, *60*, 789–795.

Teng, H., and A. Yamasaki (2000), Dissolution of buoyant CO_2 drops in a counterflow water tunnel simulating the deep ocean waters, *Energy Convers. Manage.*, *4*, 929–937.

Thistle, D., K. R. Carman, L. Sedlacek, P. G. Brewer, J. W. Fleeger, and J. P. Barry (2005), Deep-ocean experimental tests of the sensitivity of sediment-dwelling animals to imposed CO_2 gradients, *Mar. Ecol. Prog. Ser.*, *289*, 1–4.

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Anthropogenic carbon and ocean pH

The coming centuries may see more ocean acidification than the past 300 million years.

Most carbon dioxide released into the atmosphere as a result of the burning of fossil fuels will eventually be absorbed by the ocean[1], with potentially adverse consequences for marine biota[2-4]. Here we quantify the changes in ocean pH that may result from this continued release of CO_2 and compare these with pH changes estimated from geological and historical records. We find that oceanic absorption of CO_2 from fossil fuels may result in larger pH changes over the next several centuries than any inferred from the geological record of the past 300 million years, with the possible exception of those resulting from rare, extreme events such as bolide impacts or catastrophic methane hydrate degassing.

When carbon dioxide dissolves in the ocean it lowers the pH, making the ocean more acidic. Owing to a paucity of relevant observations, we have a limited understanding of the effects of pH reduction on marine biota. Coral reefs[2], calcareous plankton[3] and other organisms whose skeletons or shells contain calcium carbonate may be particularly affected. Most biota reside near the surface, where the greatest pH change would be expected to occur, but deep-ocean biota may be more sensitive to pH changes[4].

To investigate the effects of CO_2 emissions on ocean pH, we forced the Lawrence Livermore National Laboratory ocean general-circulation model[5] (Fig. 1a) with the pressure of atmospheric CO_2 (pCO_2) observed from 1975 to 2000, and with CO_2 emissions from the Intergovernmental Panel on Climate Change's IS92a scenario[1] for 2000–2100. Beyond 2100, emissions follow a logistic function for the burning of the remaining fossil-fuel resources (assuming 5,270 gigatonnes of carbon (GtC) in 1750; refs 6, 7). Simulated atmospheric CO_2 exceeds 1,900 parts per million (p.p.m.) at around the year 2300. The maximum pH reduction at the ocean surface is 0.77; we estimate, using a geochemical model[8,9], that changes in temperature, weathering and sedimentation would reduce this maximum reduction by less than 10%.

A review[10] of estimates of palaeo-atmospheric CO_2 levels from geochemical models, palaeosols, algae and forams, plant stomata and boron isotopes concluded that there is no evidence that concentrations were ever more than 7,500 p.p.m. or less than 100 p.p.m. during the past 300 million years (Myr). Moreover, the highest concentrations inferred from the geological record were thought to have developed over many millions of years owing to slow processes involving tectonics and biological evolution.

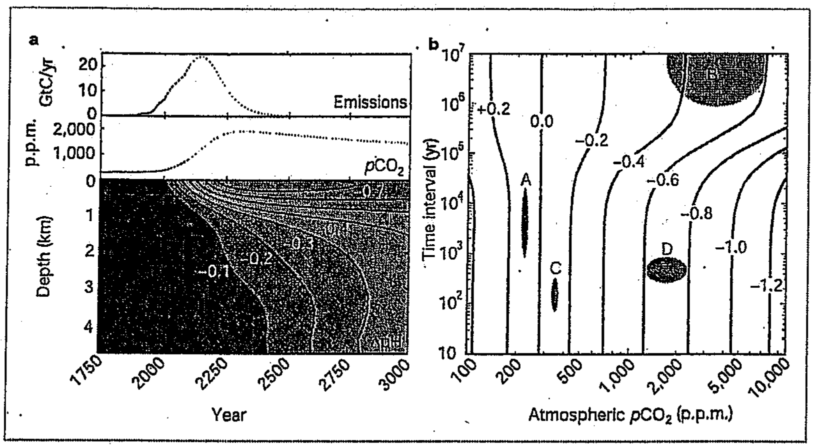

Figure 1 Atmospheric release of CO_2 from the burning of fossil fuels may give rise to a marked increase in ocean acidity. **a**, Atmospheric CO_2 emissions, historical atmospheric CO_2 levels and predicted CO_2 concentrations from this emissions scenario, together with changes in ocean pH based on horizontally averaged chemistry. **b**, Estimated maximum change in surface ocean pH as a function of final atmospheric CO_2 pressure, and the transition time over which this CO_2 pressure is linearly approached from 280 p.p.m. A, glacial–interglacial CO_2 changes[13]; B, slow changes over the past 300 Myr; C, historical changes[1] in ocean surface waters; D, unabated fossil-fuel burning over the next few centuries.

We estimated the effect of past changes in atmospheric CO_2 levels on ocean pH by using a four-box ocean/atmosphere model[8,9]. Modelled processes include weathering of carbonate and silicate minerals on land, production of shallow-water carbonate minerals, production and oxidation of biogenic organic carbon, production and dissolution of biogenic carbonate minerals in the ocean, air–sea gas exchange of carbon, and transport by advection, mixing and biological processes.

In a series of simulations, atmospheric pCO_2 was varied linearly from the pre-industrial value (about 280 p.p.m.) to stabilization values from 100–10,000 p.p.m. over time intervals of 10–10^7 yr. For each simulation, we recorded the maximum predicted perturbation in pH in the surface-ocean boxes (Fig. 1b). When a CO_2 change occurs over a short time interval (that is, less than about 10^4 yr), ocean pH is relatively sensitive to added CO_2. However, when a CO_2 change occurs over a long time interval (longer than about 10^5 yr), ocean chemistry is buffered by interactions with carbonate minerals, thereby reducing sensitivity to pH changes[11].

Based on the record[10] of atmospheric CO_2 levels over the past 300 Myr and our geochemical model[8,9], there is no evidence that ocean pH was more than 0.6 units lower than today. Our general circulation model results indicate that continued release of fossil-fuel CO_2 into the atmosphere could lead to a pH reduction of 0.7 units. We conclude that unabated CO_2 emissions over the coming centuries may produce changes in ocean pH that are greater than any experienced in the past 300 Myr, with the possible exception of those resulting from rare, catastrophic events in Earth's history[8,12].

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1. Houghton, J. T. *et al.* (eds) *Climate Change 2001: The Scientific Basis* (Contribution of Working Group I to the Third Assessment Report of the IPCC, Cambridge Univ. Press, Cambridge, 2001).
2. Kleypas, J. A. *et al. Science* 284, 118–120 (1999).
3. Riebesell, U. *et al. Nature* 407, 364–367 (2000).
4. Seibel, B. A. & Walsh, P. J. *Science* 294, 319–320 (2001).
5. Caldeira, K. & Duffy, P. B. *Science* 287, 620–622 (2000).
6. Metz, B., Davidson, O., Swart, R. & Pan, J. (eds) *Climate Change 2001: Mitigation* (Contribution of Working Group III to the Third Assessment Report of the IPCC, Cambridge Univ. Press, Cambridge, 2001).
7. Marland, G., Boden, T. A. & Andres, R. J. Global, regional, and national CO_2 emissions. *Trends: A Compendium of Data on Global Change* http://cdiac.esd.ornl.gov/trends/emis/tre_glob.htm (2002).
8. Caldeira, K. & Rampino, M. R. *Paleoceanography* 8, 515–525 (1993).
9. Caldeira, K. & Rau, G. H. *Geophys. Res. Lett.* 27, 225–228 (2000).
10. Crowley, T. J. & Berner, R. A. *Science* 292, 780–781 (2001).
11. Caldeira, K., Berner, R., Sundquist, E. T., Pearson, P. N. & Palmer, M. R. *Science* 286, 2043 (1999).
12. Beerling, D. J. & Berner, R. A. *Global Biogeochem. Cycles* 16, 101–113 (2002).
13. Sanyal, A., Hemming, N. G., Hanson, G. N. & Broecker, W. S. *Nature* 373, 234–236 (1995).

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CARBON DIOXIDE AND OUR OCEAN LEGACY

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Global warming is increasing ocean temperatures and raising sea levels. New scientific research shows that ***our oceans are beginning to face yet another threat due to global warming-related emissions – their basic chemistry is changing because of the uptake of carbon dioxide released by human activities.***

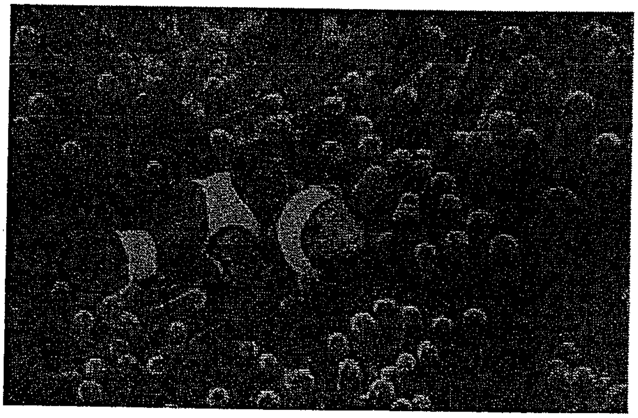
When carbon dioxide is absorbed by the oceans it reacts with seawater to form carbonic acid. Ocean acidification, as the phenomenon is called, over time will create major negative impacts on corals and other marine life, with anticipated adverse consequences for fishing, tourism, and related economies.

Ocean acidification and climate change are both effects of excessive carbon dumping into the atmosphere. While climate change encompasses the varied impacts resulting from the greenhouse effect, ocean acidification is a straightforward chemical response to carbon dioxide emissions, and is measured and predicted with a high degree of certainty.

Over the past 200 years the oceans have absorbed 525 billion tons of carbon dioxide from the atmosphere, or nearly half of the fossil fuel carbon emissions over this period. This natural process of absorption has benefited humankind by significantly reducing the greenhouse gas levels in the atmosphere and thus minimizing some impacts of global warming. However, the ocean's daily uptake of 22 million tons of carbon dioxide is starting to take its toll on the chemistry of seawater.

> *Ocean acidification and climate change are both effects of excessive carbon dumping into the atmosphere.*

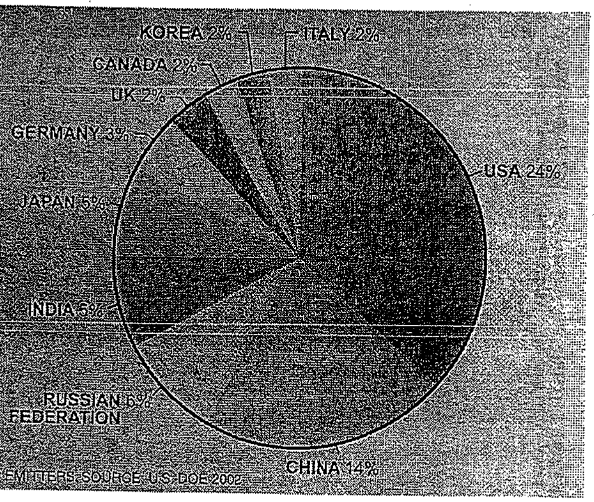
About the Authors
Drs. Richard Feely and Christopher Sabine are oceanographers at the Pacific Marine Environmental Laboratory of the National Oceanic and Atmospheric Administration, where they specialize in the ocean carbon cycle. Dr. Victoria Fabry is a biologist at the California State University San Marcos, with expertise in the effects of carbon dioxide on marine life.[1,2]



> *Ocean acidification is a straightforward consequence of increasing carbon dioxide emissions due to human activities, and is predicted with a high degree of certainty.*

Carbon Dioxide: Our Role

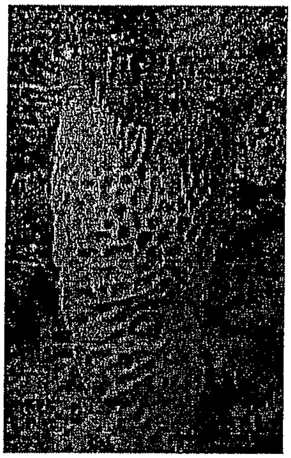
The United States is the single largest contributor to global warming, responsible for nearly one-quarter of all human-made emissions. Every day the average American adds about 118 pounds of carbon dioxide to the atmosphere, due largely to energy-consuming activities that burn fossil fuels. On a yearly basis, the average American produces 22 tons of carbon dioxide, more than six times as much as the average person living outside of the United States. Together, Americans produced 6.5 billion of the 27.7 billion tons of carbon dioxide generated in 2003, and these numbers are growing every year.



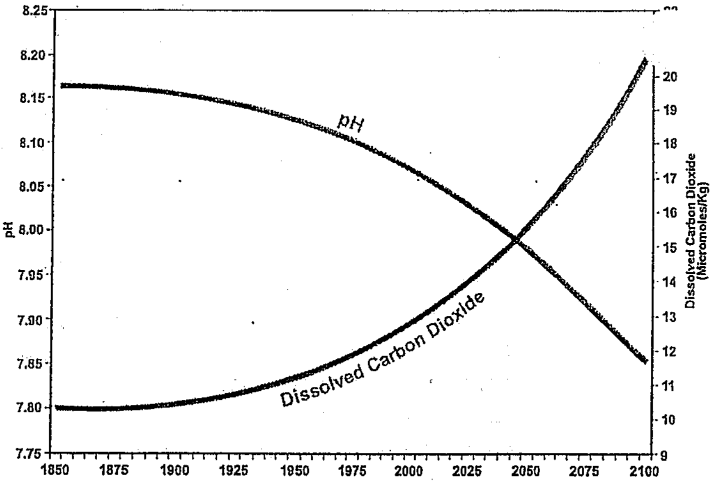
TOP 10 EMITTERS SOURCE: US DOE 2002

Changing Chemistry – Changing Oceans

Carbon dioxide does not sit idly in the oceans. Recent field and laboratory studies reveal that the chemical changes in seawater resulting from the absorption of carbon dioxide are lowering seawater pH. *(See box below.)* The pH decline then decreases the availability of chemical building blocks needed by organisms that produce shells and skeletons made of a mineral called calcium carbonate. Corals, as well as some free-floating plants and animals at the bottom of the food chain, have a more difficult time producing their shells, with potential consequences for other sea life that depend on the health and availability of these shelled organisms.



Historical & Projected pH & Dissolved CO_2



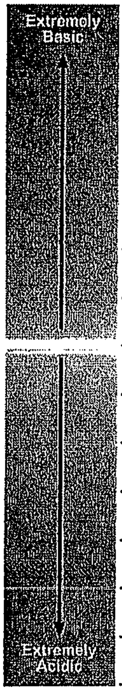
As the ocean concentration of carbon dioxide increases, so does acidity (causing pH to decline).

At present, ocean chemistry is changing at least 100 times more rapidly than it has changed during the 650,000 years preceding our industrial era. And, ***if current carbon dioxide emission trends continue, computer models show that the ocean will continue to undergo acidification, to an extent and at rates that have not occurred for tens of millions of years.***

Nearly all marine life forms that build calcium carbonate shells and skeletons studied by scientists thus far have shown deterioration due to increasing carbon dioxide levels in seawater, and the resulting decline in pH. In experiments, when dissolved carbon dioxide was increased to two times pre-industrial levels (i.e., before the 1850s), the shell and skeleton-building rate of organisms studied declined by as much as 50%.

For example, increasing ocean acidification has been shown to significantly reduce the ability of reef-building corals to produce their skeletons, affecting growth of individual corals and making

What is pH?

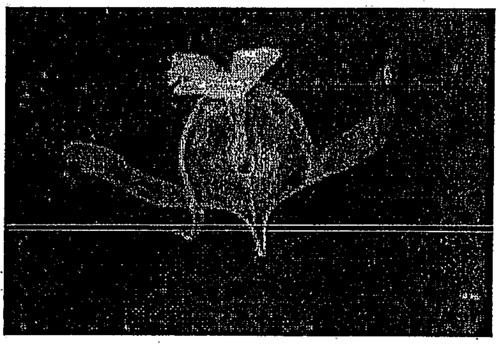


pH	
14	**Sodium Hydroxide**
13	**Oven Cleaner**
12	**Household Bleach**
11	**Household Ammonia**
10	**Milk of Magnesia**
9	**Baking Soda**
*8.16	**SEA WATER (Historical)**
7	**Pure Water, Blood**
6	**Milk**
5	**Black Coffee**
4	**Wine, Tomatoes**
3	**Beer, Vinegar**
2	**Lemon Juice**
1	**Hydrochloric Acid**
0	**Battery Acid**

pH is a measure of acidity. On the pH scale, 7.0 is neutral, with points higher on the scale being "basic" and points lower being "acidic."

The pH of our ocean surface waters has already fallen by about 0.1 units from about 8.16 to 8.05 since the beginning of the Industrial Revolution around 200 years ago,[4] and it may fall by as much as 0.4 units by 2100.[5]

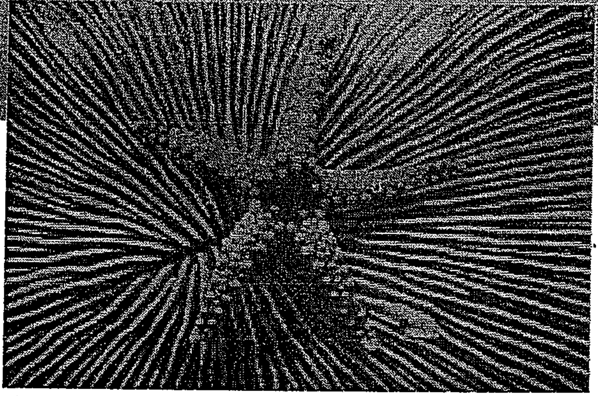
The oceans have not seen a change in pH this abrupt and large for at least 650,000 years, and many sea creatures require stable conditions to survive.



V. J. FABRY

Reefs at Risk

Healthy coral reefs are the foundation of many viable fisheries, as well as the source of jobs and businesses related to tourism and recreation. Approximately half of all federally managed fisheries depend on coral reefs and related habitats for a portion of their life cycles, and the National Marine Fisheries Service estimates the value of coral reefs to the U.S. fish stocks at over $100 million.[7] Local economies also receive billions of dollars from reef tourism. In the Florida Keys, for example, coral reefs generate more than $1.2 billion in tourism revenue annually. In Hawaii, reef-related tourism and fishing generate $360 million per year, and their overall worth has been estimated at close to $10 billion. Worldwide, coral reefs sustain a local tourism economy – including diving tours, recreational fishing trips, hotel and restaurant sales, and other related businesses – that makes up 10 percent of all jobs.[8] Plus, coral reefs provide vital protection to coastal areas that are vulnerable to storms and tidal surges.



At present, ocean chemistry is changing more rapidly than it has over the past 650,000 years.

the reef more vulnerable to erosion. ***By the middle of this century, coral reefs may well erode faster than they can be rebuilt.***[6] Lab results indicate that coral reefs cannot easily adapt to this changing seawater chemistry. While long-term consequences are unknown, this could affect the geographic range of corals and the life forms that depend on the reef habitat.

Cracks in the Food Chain

One type of free-swimming creature called a pteropod *(see photo below left)*, a small snail with a calcium carbonate shell, is eaten by animals ranging from tiny krill to giant whales. Pteropods can be an important food source for juvenile North Pacific salmon, and are also eaten by mackerel, herring, and cod.

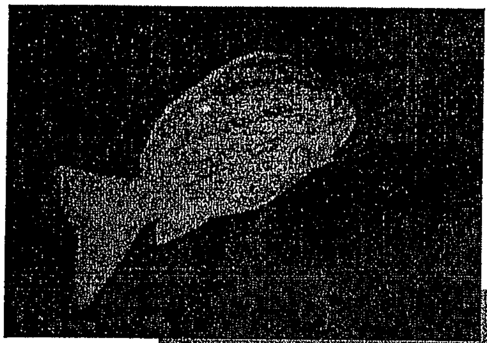
Scientists believe that under conditions of increased ocean acidification the weakened pteropod shells will compromise the health and success of these organisms, which could allow competing species to take over. This could mean ***substantial changes in the biodiversity of our oceans***, though more research is needed to identify large-scale ecosystem impacts. Other species – like snails, sea urchins, starfish, lobster, and bivalves such as oysters, clams, mussels, and scallops – also construct their shells or skeletons in the same way and could be jeopardized.

Furthermore, it is suspected that higher marine life forms, including even some fish, may be affected by declining pH through a process called ***acidosis***, or carbonic acid buildup in body fluids. Acidosis can lead to lowered immune response, metabolic decline, and reproductive or respiratory difficulties.[9] Combined with coral and other ecosystem impacts, acidosis could spell trouble for fishing and tourism-dependent economies and communities.

One region of special concern is the northern Pacific Ocean, including the Bering Sea between Alaska and Russia. The climate and ecosystem of the region have changed dramatically over the last 50 years, representing a transition from primarily cold and icy Arctic ecosystems earlier in the 20th century to warmer, sub-Arctic conditions today. Already vulnerable, the region – holding one-half of all U.S. fish and shellfish landings – is expected to be impacted most immediately by our changing ocean chemistry.

Fish – It's What's For Dinner

Any threat to marine ecosystems, such as ocean acidification, will reverberate through our economy and food supply. The United States is the third largest seafood consumer in the world. Americans ate a record of nearly 17 pounds of seafood per person in 2004, while total consumer spending for fish and shellfish topped $62 billion. In that year alone, coastal and marine commercial fishing generated $32 billion for the economy and employed over 67,000 people.[10]



Where Do We Go From Here?

The impacts of ocean acidification on shelled organisms and other animals could negatively affect marine food webs, and, when combined with other climatic changes, could substantially alter the number, variety, and health of ocean wildlife. As humans continue to send more and more carbon dioxide into the oceans, the impacts on marine ecosystems will be direct and profound.

Today's carbon dioxide emissions will continue to affect global ocean chemistry for many hundreds of years to come, but a significant effort to curb our emissions will help slow the rate of change, allowing ecosystems a better chance to adapt and decreasing our ultimate negative impact on the environment. While our understanding of how the web of sea life will respond to ocean acidification is still in its early stages, initial findings from studying ocean chemistry show cause for great concern. ***The message is clear: excessive carbon dioxide poses a threat to the health of our oceans.***

Summary Points

- Human activities are changing the ocean's chemistry at a significant rate.
- The pH changes are predicted with a high degree of certainty.
- These changes have a negative impact on corals and other sea life, especially at the base of the food chain, with potential adverse economic consequences.
- Curbing carbon dioxide emissions will help slow the rate of change, reduce the human impact on the environment, and allow ecosystems a better chance to adapt.

www.cleartheair.org

www.oceanlegacy.org

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ENDNOTES

1 Organizational affiliation is provided for reference only. The findings and conclusions in this science brief are those of the authors and do not necessarily represent the views of the National Oceanic and Atmospheric Administration or the California State University.

2 This brief is adapted largely from Feely et al. (2004), Sabine et al. (2004), and Orr et al. (2005). Feely, R.A., C.L. Sabine, K. Lee, W. Berelson, J. Kleypas, V.J. Fabry, and F.J. Millero (2004): Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. Science, 305(5682), 362-366.

Sabine, C.L., R.A. Feely, N. Gruber, R.M., Key, K. Lee, J.L. Bullister, R. Wanninkhof, C.S. Wong, D.W.R. Wallace, B. Tilbrook, F.J. Millero, T.H. Peng, A. Kozyr, T. Ono, and A.F. Rios (2004): The oceanic sink for anthropogenic CO_2. Science, 305(5682), 367-371.

Orr, James C., Victoria J. Fabry, Olivier Aumont, et al. (2005): Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature, 437, 681-686.

3 EIA, U.S. DOE (December 2005). Emissions of Greenhouse Gases in the United States 2004, Washington, D.C.

4 The Royal Society (2005). Ocean Acidification Due to Increasing Atmospheric Carbon Dioxide, The Clyvedon Press Ltd., Cardiff, UK.

5 IOCCP. Please see http://ioc.unesco.org/ioccp/HighCO2/HighCO2 world.htm.

6 Hood, Maria (October-November 2004). A carbon sink that can no longer cope? A World of Science, 2(4), 2-5.

7 NOAA Coral Reef Conservation Program. Please see http://www.coralreef.noaa.gov/outreach/protect supp_income.html.

8 *Ibid.*

9 Hood, Maria, *op. cit.* (2004).

10 NOAA Fisheries Office of Science and Technology. Please see http://www.st.nmfs.gov/st1/fus/fus04/index.html.

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April, 2006

Impact of Anthropogenic CO_2 on the $CaCO_3$ System in the Oceans

Richard A. Feely,[1,*] Christopher L. Sabine,[1] Kitack Lee,[2] Will Berelson,[3] Joanie Kleypas,[4] Victoria J. Fabry,[5] Frank J. Millero[6]

Rising atmospheric carbon dioxide (CO_2) concentrations over the past two centuries have led to greater CO_2 uptake by the oceans. This acidification process has changed the saturation state of the oceans with respect to calcium carbonate ($CaCO_3$) particles. Here we estimate the in situ $CaCO_3$ dissolution rates for the global oceans from total alkalinity and chlorofluorocarbon data, and we also discuss the future impacts of anthropogenic CO_2 on $CaCO_3$ shell–forming species. $CaCO_3$ dissolution rates, ranging from 0.003 to 1.2 micromoles per kilogram per year, are observed beginning near the aragonite saturation horizon. The total water column $CaCO_3$ dissolution rate for the global oceans is approximately 0.5 ± 0.2 petagrams of $CaCO_3$-C per year, which is approximately 45 to 65% of the export production of $CaCO_3$.

Atmospheric CO_2 concentrations oscillated between 200 and 280 parts per million (ppm) over the 400,000 years before the industrial period. Current atmospheric concentrations are now approaching 380 ppm as a result of the industrial and land use activities of humankind. In the past few decades, only half of the CO_2 released by human activity has remained in the atmosphere; of the remainder, about 30% has been taken up by the ocean and 20% by the terrestrial biosphere (*1*).

Most previous estimates of oceanic uptake of CO_2 were made using ocean circulation models calibrated with tracer observations. Recently, a large global data set of ocean tracer and carbon system observations has been acquired through the World Ocean Circulation Experiment/Joint Global Ocean Flux Study. These observations indicate a total ocean uptake of anthropogenic CO_2 of approximately 118 ± 19 Pg of C (1 Pg of C = 10^{15} g of C) between 1800 and 1994 (*1*).

Estimates of future atmospheric and oceanic CO_2 concentrations, based on the Intergovernmental Panel on Climate Change emission scenarios and general circulation models, suggest that by the end of the century CO_2 levels could be over 800 ppm (*2*). Corresponding models for the oceans indicate that surface-water dissolved inorganic carbon (DIC) could probably increase by more than 12%, and the carbonate ion concentration would decrease by almost 60% (*3*) (Fig. 1). The corresponding pH drop would be about 0.4 pH units in surface waters (*4*). Such dramatic changes of the CO_2 system in open-ocean surface waters have probably not occurred for more than 20 million years of Earth's history. If they do occur, they can potentially have significant impacts on the biological systems in the oceans in ways we are only beginning to understand (*5*). Thus, the delicate balance of marine planktonic species could undergo significant shifts in the future as humankind continues along the path of unintentional CO_2 sequestration in the surface oceans.

Concern about the long-term fate of anthropogenic CO_2 in the atmosphere and ocean has motivated scientists to examine the distributions of DIC and total alkalinity (TA) in the oceans. Processes that increase the TA in the upper ocean facilitate the uptake of anthropogenic CO_2 from the atmosphere. The dissolution of marine carbonates, including biogenic magnesian calcites (from coralline algae), aragonite (from corals and pteropods),

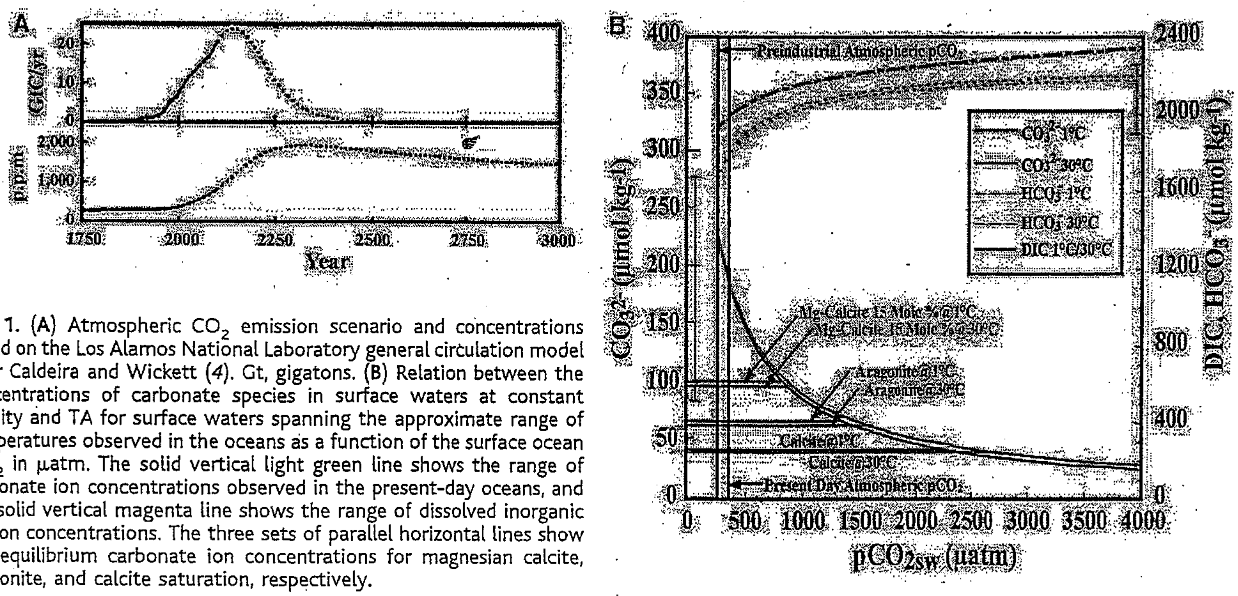

Fig. 1. (**A**) Atmospheric CO_2 emission scenario and concentrations based on the Los Alamos National Laboratory general circulation model after Caldeira and Wickett (*4*). Gt, gigatons. (**B**) Relation between the concentrations of carbonate species in surface waters at constant salinity and TA for surface waters spanning the approximate range of temperatures observed in the oceans as a function of the surface ocean pCO_2 in µatm. The solid vertical light green line shows the range of carbonate ion concentrations observed in the present-day oceans, and the solid vertical magenta line shows the range of dissolved inorganic carbon concentrations. The three sets of parallel horizontal lines show the equilibrium carbonate ion concentrations for magnesian calcite, aragonite, and calcite saturation, respectively.

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and calcite (from coccolithophorids and foraminifera) neutralizes anthropogenic CO_2 and adds to TA via the reaction

$$CO_2 + CaCO_3 + H_2O \leftrightarrow 2HCO_3^- + Ca^{2+} \quad (1)$$

The primary contributors to this reaction are the carbonate shells of marine plankton that are produced in the euphotic zone. Upon death, these carbonate tests fall through the water column and are either dissolved or deposited in shallow- or deep-sea sediments. As the oceans become enriched in anthropogenic CO_2, the locations and extent of dissolution will increase as a function of the decrease in the calcium carbonate ($CaCO_3$) saturation state. Until recently, it had been commonly thought that the dissolution of pelagic $CaCO_3$ particles primarily occurs at great depths below the calcite saturation depth (*6*). However, recent analyses of the global carbonate budget and carbonate data for the global oceans (*7–9*) have indicated that perhaps as much as 60 to 80% of the $CaCO_3$ that is exported out of the surface ocean dissolves in the upper 1000 m.

Calcite and aragonite saturation in the global oceans. The degree of saturation of seawater with respect to aragonite and calcite (Ωarg or Ωcal) is the ion product of the concentrations of calcium and carbonate ions, at the in situ temperature, salinity, and pressure, divided by the stoichiometric solubility product (K^*_{sp}) for those conditions

$$\Omega arg = [Ca^{2+}][CO_3^{2-}]/K^*_{sparg} \quad (2)$$

$$\Omega cal = [Ca^{2+}][CO_3^{2-}]/K^*_{spcal} \quad (3)$$

where the calcium concentration is estimated from the salinity, and the carbonate ion concentration is calculated from the DIC and TA data. Because the calcium- to-salinity ratio in seawater does not vary by more than 1.5%, variations in the ratio of $[CO_3^{2-}]$ to the stoichiometric solubility product primarily govern the degree of saturation of seawater with respect to aragonite and calcite (Fig. 2). There is pronounced shoaling of both the aragonite and calcite saturation horizons from the Atlantic through the Indian to the Pacific Oceans because of the higher DIC/TA ratios in the intermediate and deep waters of the Indian and Pacific relative to the Atlantic. This is due to the cumulative enrichment of DIC relative to TA resulting from respiration processes as ocean water circulates along the deep conveyor belt from the Atlantic to Indian and Pacific (*10, 11*). The intermediate waters of the North Pacific show evidence for undersaturation in the shallow waters from 200 to 1000 m, where they have also been affected by anthropogenic CO_2 (*12*). Surprisingly, portions of the northern Indian Ocean and southeastern Atlantic Ocean are also undersaturated with respect to aragonite at shallow depths, and this region also appears to increasing in areal extent as a consequence anthropogenic CO_2 accumulations (*13–15*). This can best be shown by plotting vertical sections of the present-day (solid line) and preindustrial (dashed line) saturation horizons superimposed on the anthropogenic CO_2 contours from data collected along the axis of the three basins (Fig. 3). The preindustrial levels are calculated by subtracting the anthropogenic CO_2 values from the total DIC. A comparison of the preindustrial and present-day saturation horizons reveals several distinct regions where the undersaturation zone has expanded. In regions between 20°N and 50°N in the North Atlantic Ocean, the aragonite saturation horizon for the preindustrial era is nearly the same as today (Fig. 3). In the eastern South and North Atlantic, however, the aragonite saturation horizon ha migrated upward by approximately 80 t 150 m between 50°S and 15°N. In the Indian Ocean, saturation depths have shoaled increasingly north of 30°S, so that aragonite saturation depths in the Arabian Sea and Bay of Bengal are now 100 to 200 m shallower than in preindustrial times. In the Pacific, the upward migration of the aragonite saturation horizon is between 30 and 80 m south of 38°S and between 30 and 100 m north of 3°N. The calcite saturation horizon has also shoaled by about 40 to 100 m north of 20°N in the North Pacific. Su shoaling is due to the effects of anthropogen CO_2 ventilation and biological respiration processes in the intermediate waters. This also implies that the dissolution of $CaCO_3$ particles will likely increase as the waters become increasingly undersaturated over time.

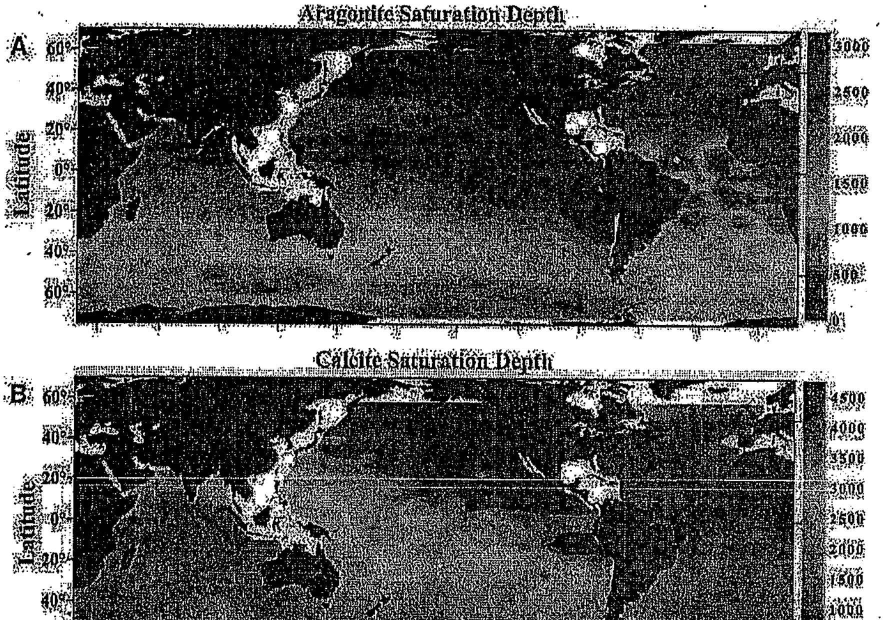

Fig. 2. Distribution of (A) aragonite and (B) calcite saturation depth (Ω = 1) in the global oceans. The pressure effect on the solubility is estimated from the equation of Mucci (*31*) that includes the adjustments to the constants recommended by Millero (*45*). The level at which aragonite and calcite are in thermodynamic equilibrium is known as the saturation depth. When the degree of saturation, Ω, is greater than 1, seawater is supersaturated with aragonite and calcite; conversely, seawater is undersaturated with respect to these minerals when Ω < 1. This depth is significantly shallower for aragonite than for calcite, because aragonite is more soluble in seawater than calcite.

$CaCO_3$ dissolution. The amount of CaCO dissolved in a subsurface water parcel ($\Delta CaCO_3$) is estimated from changes in TA by subtracting out the preformed TA concentration and correcting for the TA decrease resulting from the release of protons during the oxidation of organic matter (*12, 13*) according to the equation

$$\Delta CaCO_3(\mu mol\ kg^{-1}) = 0.5 \times (TA_{MEAS} - TA°) + 0.63(0.0941 \times AOU) \quad (4)$$

where TA_{MEAS} is the measured TA, TA° is the preformed TA, and AOU is apparent oxygen utilization. The second term on the right-hand side accounts for the decrease in TA resulting from the oxidation of organic matter by using AOU [O_2 (saturated values at a given temperature and salinity) – O_2 (measured)] and the N/O_2 ratio (= 0.094 ± 0.02) (*16*). A coefficient of 0.63 proposed by Kanamori and Ikegami (*17*) is used to account for TA contributions from the oxidation organic nitrogen, phosphorus, and sulfur. T

TA° is estimated for each ocean basin with a multiparameter linear regression model using conservative tracers, such as salinity and NO or PO, as independent variables. NO is defined as $NO = O_2 - R_{O_2/N} \times N$ (*16*); we used $R_{O_2/N} = -10.625$ (*16*). The standard error (1σ) of the estimated TA° is ~10 μmol kg^{-1}.

To estimate in situ $CaCO_3$ dissolution rates in waters where values of $\Delta CaCO_3$ are positive, we plotted $\Delta CaCO_3$ against water parcel ages derived from chlorofluorocarbon-11 (CFC-11) or CFC-12 for the upper ocean and from ^{14}C for deep waters where CFC-11 or CFC-12 is not detected (*18*). The highest $CaCO_3$ dissolution rates in the North Atlantic occur near or below the average aragonite saturation horizon at approximately 3500 m (Fig. 4). The change in depth where the maximum rate occurs is consistent with the corresponding changes in the aragonite 100% saturation horizon. In the South Atlantic, $CaCO_3$ dissolution rates reach a maximum (~0.55 μmol kg^{-1} year^{-1}) near 900 m, decreasing to less than half that below 1250 m. In the Indian Ocean, the highest $CaCO_3$ dissolution rates occur in shallow waters south of 20°S, with rates ranging from 0 to 1.2 μmol kg^{-1} year^{-1} occurring between 200 and 1400 m. North of 20°S, the $CaCO_3$ dissolution maximum corresponds to a depth of about 250 m. In the Pacific, the highest dissolution rates (up to ~1.2 μmol kg^{-1} year^{-1}) occur between 400 and 600 m, within the core of the North Pacific Intermediate Water. Significantly lower rates are observed below these depths. The large spatial differences in the patterns of the dissolution rates between the three major ocean basins appear to be related to the positions of the aragonite and calcite saturation horizons. The integrated carbonate dissolution rate for the three major ocean basins is estimated to be 0.5 ± 0.2 Pg of $CaCO_3$-C year^{-1}, or about 45 to 65% of the export flux of $CaCO_3$ in the global oceans.

Sediment trap fluxes. Sediment traps measure the rain of particulate matter through the water column. Traps located at different depths at the same location can be used to estimate the dissolution rate of $CaCO_3$ particles between those two depths. This approach has well-recognized caveats: It assumes that particles fall vertically between one trap and another, that both traps collect particles with equal efficiency, and that particles are not altered inside the trap collection cup. Traps deployed between 100 and 1000 m indicate dissolution rates (Table 1; 0.02 to 0.67 μmol kg^{-1} year^{-1}) that are comparable to the rates presented here. However, sediment traps at any depth, particularly those moored <1000 m below the ocean surface, can have high $CaCO_3$ flux losses and may be suspect because of over- and undertrapping artifacts caused by current turbulence or by the addition of heterotrophs swimming into the trap. Thus, there is a lower degree of confidence in this approach when shallow data are included. The deepwater sediment trap data, also presented in Table 1, are from sites in the equatorial and North Pacific Ocean and represent deployments of paired traps that collected particles for at least 200 days. Generally, traps in deeper water are considered more reliable in collecting vertical particle fluxes. In 9 of 10 data sets, there is evidence of carbonate dissolution occurring in the water column between 1000 and 4500 m in the Pacific Ocean. Dissolution rates in the deep water are low, ranging from 0.003 to 0.03 μmol kg^{-1} year^{-1}. These values are consistent with the estimates of carbonate dissolution in the deep Pacific (*12*) insofar as they do not exceed the water-mass tracer results; the water-mass tracer method allows for dissolution both in the water column and in surface sediments, whereas the trap data measures dissolution in the water column only. The very low particle dissolution rates in the deepwater column of the tropical and subtropical regions imply a greater role for sedimentary dissolution in these areas. In the northeastern subarctic Pacific, however, carbonate particle dissolution in the water column may contribute 20 to 80% of the total dissolution burden predicted by the water-mass approach. The highest rate determined by this trap summary is for a site in the northeastern North Pacific, which suggests that water column dissolution may be more important than sediment dissolution at higher latitudes.

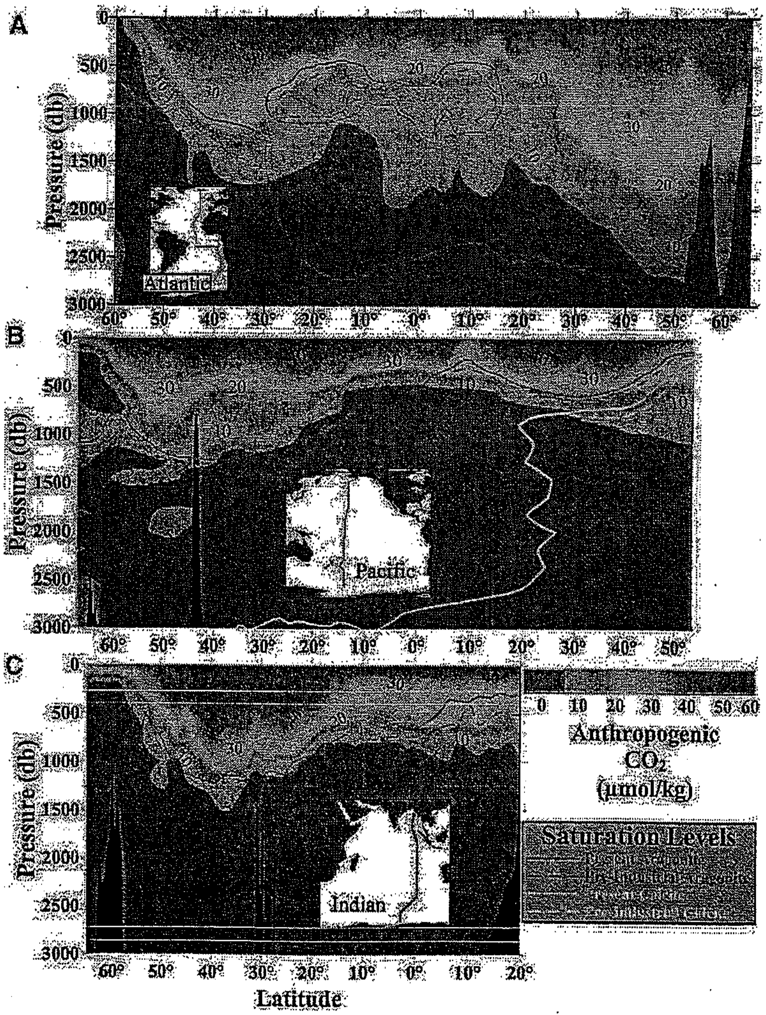

Fig. 3. Vertical distributions of anthropogenic CO_2 concentrations in μmol kg^{-1} and the supersaturation/undersaturation horizons for aragonite and calcite along north-south transects in the (A) Atlantic, (B) Pacific, and (C) Indian Oceans.

$CaCO_3$ budget of the global oceans. The major components of the $CaCO_3$ budget have recently been reassessed (*1*, *9*, *19*) and are summarized in Fig. 5. Global new production of $CaCO_3$ ranges from 0.8 to 1.4 Pg of $CaCO_3$-C year^{-1} (*19*, *20*), based on models or observations of seasonal changes in alkalinity in the euphotic zone. The most recent updates of globally averaged sediment trap data through 2000 m indicate a global average flux of about 0.4 Pg of $CaCO_3$–C year^{-1}, suggesting that anywhere from 50 to 71% of the $CaCO_3$ produced is dissolved in the upper water column (*19*). This is consistent with our estimates of the water column dissolution of $CaCO_3$, which show an average dissolution of approximately 0.5 Pg of $CaCO_3$-C year^{-1} globally. It is also consistent with the recent summary of the fluxes of foraminiferal $CaCO_3$ tests in the oceans, which indicates that approximately 65% of the tests are dissolved in the upper 1000 m of the water column (*21*). The present-day accumulation of $CaCO_3$ in marine sediments is about 0.1 to 0.14 Pg of $CaCO_3$–C year^{-1} along the continental margins or in the deep sea, and 0.13 to 0.17 Pg of $CaCO_3$–C year^{-1} in continental shelf sediments (*9*, *19*, *22*). Thus, of the total amount of $CaCO_3$ that is produced annually, no more than about 30% is buried in shallow and deep sediments. The rest is dissolved in the water column, at the sediment-seawater interface or in the upper portion of the sediment column. These new results, however, indicate that a very large fraction of this dissolution, up to 60% or more, occurs in the upper water column above 2000 m.

Future impacts. The long-term impacts of anthropogenic CO_2 on the saturation state of the oceans with respect to aragonite and calcite particles in the oceans have been discussed previously (*23*, *24*). In the cold high-latitude surface waters typical of the subarctic North Pacific, aragonite and calcite undersaturation will occur when partial pressure of CO_2 (pCO_2) values reach 1200 and 1900 μatm, respectively, and in warm tropical and subtropical waters when pCO_2 values reach 1700 and 2800 μatm, respectively (Fig. 1). These values are greater than what is normally observed in present-day surface waters (*25*), but if present trends in anthropogenic CO_2 continue for the next several hundred years, we can expect regions of aragonite undersaturation to develop in the northern subarctic surface waters, followed by calcite undersaturation. This would first occur in the winter, when pCO_2 values are highest because of cold temperatures and wind-driven mixing of subsurface waters into the mixed layer. From there, the progression of undersaturated regions would proceed toward the equator, although it is unlikely that the tropical and warmest subtropical surface waters will ever become undersaturated with respect to calcite, because model projections of CO_2 emissions predict an upper limit of atmospheric CO_2 of about 2000 μatm (*4*). Nevertheless, large-scale decreases in the aragonite and calcite saturation values over the global oceans can have profound impacts on calcification rates for many species of $CaCO_3$ shell–forming organisms.

Biological implications. Because the upper ocean is supersaturated with respect to all phases of $CaCO_3$, carbonate chemistry was not previously considered as a limiting factor in biogenic calcification. Recent field and laboratory studies (table S1), however, reveal that the degree of supersaturation has a profound effect on the calcification rates of individual species and communities in both planktonic and benthic habitats. With one exception (*26*), the calcification rate of all calcifying organisms investigated to date decreased in response to a decreased $CaCO_3$ saturation state, even when the carbonate saturation level was >1. This response holds across multiple taxa—from single-celled protists to reef-building corals—and across all $CaCO_3$ mineral phases. Differences in the response of calcifiers to decreasing carbonate ion concentrations may reflect differences in carbonate mineralogy; in environmental parameters such as temperature, light, and available nutrients (*27*, *28*); and in the mechanism of biomineralization (*29*, *30*).

Aragonite and magnesian calcite are at least 50% more soluble in seawater than calcite (*31*), suggesting that organisms that form these types of $CaCO_3$ may be particularly affected by increasing pCO_2. Coralline algae, a major source of biogenic magnesian calcite, show a strong calcification response to decreases in saturation state. The main aragonite producers are reef-building corals and planktonic pteropod and heteropod molluscs. Nearly all reef-building corals tested so show a marked decline in calcification un reduced [CO_3^{2-}] conditions (*27*, *32*, *33*), and one of us (V.F.) has observed shell dissolution in living *Clio pyramidata*, a pteropod in the subarctic North Pacific, as increasing respiratory CO_2 forced aragonite saturation to <1 (fig. S1). The effects of elevated CO_2 on other producers of aragonite and magnesian calcite, including calcareous green algae, echinoderms, bryozoans, and benthic foraminifera, are unknown. Although these labile carbonate producers are associated with benthic habitats, in the North Atlantic many of them are also found in the open ocean encrusting on *Sargassum* clumps (*34*–*36*).

Calcite is secreted by two important planktonic calcifiers—coccolithophores and fora-

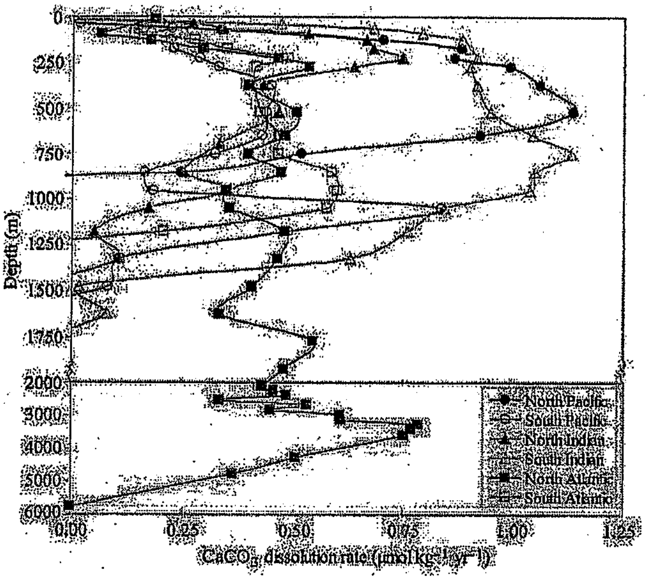

Fig. 4. In situ $CaCO_3$ dissolution rates plotted as a function of depth in the three major ocean basins.

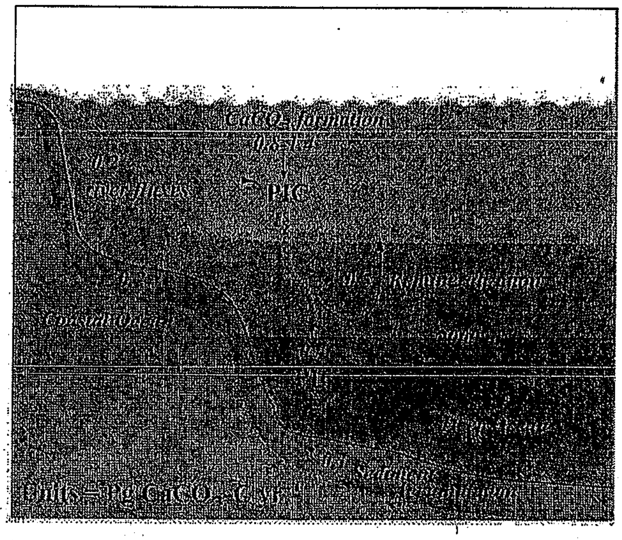

Fig. 5. Schematic diagram of the $CaCO_3$ budget for the global oceans. The values are in Pg of $CaCO_3$-C year^{-1}.

Table 1. Sediment trap particulate $CaCO_3$ dissolution fluxes in the Pacific Ocean. The difference between the mean carbonate flux in the upper trap and the lower trap defines the dissolution flux. In all but one of the deepwater cases, the $CaCO_3$ flux collected in the midwater trap is higher than the carbonate flux collected in the deepwater trap. The dissolution rates are derived from the differences in $CaCO_3$ sediment trap fluxes between the upper and lower sediment traps divided by the depth range between the traps.

Location	Trap depth range (m)	Dissolution rate (μmol kg^{-1} $year^{-1}$)	Reference
	Shallow sediment traps		
Northwestern Pacific	100–1000	0.12	(*46*)
Equatorial Pacific	105–320	0.67	(*47*)
Northwestern Pacific	500–1000	0.02	(*48*)
Northeastern Pacific	200–1000	0.10	(*49*)
	Deep sediment traps		
Northwestern Pacific	2000–4000	0.003–0.006	(*48*)
Equatorial Pacific	2300–3600	0.005–0.014	(*50*)
2°59.8′N 135°1.0′E	1592–3902	0.012	(*51*)
4°7.5′N 136°16.6′E	1769–4574	0.013	(*51*)
0°0.2′N 175°09.7′E	1357–4363	0.005	(*51*)
0°01′N 175°02′E	2200–4300	—	(*52*)
13°00′N 175°01′E	1500–5100	0.006	(*52*)
00°04′N 139°45′W	2284–3618	0.005–0.014	(*50*)
11°58′S 135°02′W	1292–3594	0.003	(*52*)
50°0′N 145°0′W	1000–3800	0.024	(*49*)

miniferans—and species in both groups appear to be sensitive to changes in seawater carbonate chemistry. The calcification rates of two bloom-forming coccolithophores, *Emiliania huxleyi* and *Gephyrocapsa oceanica*, decreased by 25 and 45%, respectively, when grown at pCO_2 concentrations that were three times the preindustrial values (*37*, *38*). Shell weights of similarly sized planktonic foraminiferans have also been shown to vary because of the effects of seawater carbonate chemistry on both biological calcification and dissolution (*39*, *40*). The available empirical evidence suggests that the relation between calcification and carbonate ion concentration in these coccolithophore and foraminiferan species is asymptotic, implying that reduction of the carbonate saturation state below a threshold value will lead to large decreases in calcification rates, even when saturation is >1.

At the global scale, calcium carbonate plays a dual role in regulating carbon sequestration by the oceans. First, an increase in $CaCO_3$ dissolution in the upper ocean will result in a more uniform alkalinity profile with depth. Presently, the TA of temperate surface waters is about 50 to 150 μmol kg^{-1} less than in the deep oceans because carbonate precipitation in the upper ocean removes alkalinity, whereas dissolution of calcium carbonate at depth increases alkalinity. Moreover, a decrease in carbonate precipitation in the upper ocean would increase the capacity of the oceans to take up CO_2 from the atmosphere. A complete shutdown of surface ocean calcification would decrease surface ocean pCO_2 by about 10 to 20 μatm (*41*). Second, a decrease in $CaCO_3$ production would affect the ratio of organic:inorganic carbon delivery to the deep sea. If the processes regulating the "rain" of organic carbon and inorganic carbon to deep-sea sediments are uncoupled, then a decrease in calcium carbonate production would lead to increased dissolution of calcium carbonate sediments, which would raise ocean pH and its capacity to store CO_2 (*42*). If the two processes are coupled, such as through the process of $CaCO_3$ ballasting of organic carbon (*43*), then reducing the carbonate production could result in shallower remineralization of organic carbon (*44*) and a diminished role of sediments in buffering increases in atmospheric CO_2. Clearly, more research on the mechanistic controls of these seemingly coupled processes is needed.

References and Notes

1. C. L. Sabine *et al.*, in *The Global Carbon Cycle: Integrating Humans, Climate, And The Natural World. SCOPE 62*, C. B. Field, M. R. Raupach Eds. (Island Press, Washington, DC, 2004), pp. 17–46.
2. C. Prentice *et al.*, in *Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, J. Houghton *et al.*, Eds. (Cambridge Univ. Press, New York, 2001), pp. 183–238.
3. P. G. Brewer, *Geophys. Res. Lett.* **24**, 1367 (1997).
4. K. Caldeira, M. E. Wickett, *Nature* **425**, 365 (2003).
5. B. A. Seibel, V. J. Fabry, in *Climate Change and Biodiversity: Synergistic Impacts*, L. Hannah, T. Lovejoy, Eds. (Conservation International, Washington, DC, 2003), pp. 59–67.
6. W. S. Broecker, in *The Fate of Fossil CO_2 in the Oceans*, N. R. Anderson, A. Malahoff, Eds. (Plenum, New York, 1977), pp. 207–212.
7. J. D. Milliman, *Global Biogeochem. Cycles* **7**, 927 (1993).
8. J. D. Milliman, A. W. Droxler, *Geol. Rundsch.* **85**, 496 (1996).
9. J. D. Milliman *et al.*, *Deep-Sea Res. Part I* **46**, 1653 (1999).
10. W. S. Broecker, T.-H. Peng, *Tracers in the Sea* (Lamont-Doherty Geological Observatory, Palisades, New York, 1982).
11. W. S. Broecker, in *Treatise on Geochemistry*, H. D. Holland, K. K. Turekian, Eds. (Elsevier, London, vol. 6, 2003), pp. 1–21.
12. R. A. Feely *et al.*, *Global Biogeochem. Cycles* **16**, 1144 (2002).
13. S. Chung *et al.*, *Global Biogeochem. Cycles* **17**, 1093 (2003).
14. S.-N. Chung *et al.*, *Limnol. Oceanogr.* **49**, 315 (2004).
15. C. L. Sabine, R. M. Key, R. A. Feely, D. Greeley, *Global Biogeochem. Cycles* **16**, 1067 (2002).
16. L. A. Anderson, J. L. Sarmiento, *Global Biogeochem. Cycles* **8**, 65 (1994).
17. S. Kanamori, H. Ikegami, *J. Oceanogr. Soc. Jpn.* **38**, 57 (1982).
18. The details of the methods for determining the $CaCO_3$ dissolution are given in the supporting online materials.
19. D. Iglesias-Rodriguez *et al.*, *Eos* **83**, 365 (2002).
20. K. Lee, *Limnol. Oceanogr.* **46**, 1287 (2001).
21. R. Schiebel, *Global Biogeochem. Cycles* **16**, 10.1029/2001GB001459 (2002).
22. N. R. Catubig *et al.*, *Paleoceanography* **13**, 298 (1998).
23. W. S. Broecker, T. Takahashi, H. J. Simpson, T.-H. Peng, *Science* **206**, 409 (1979).
24. J. A. Kleypas *et al.*, *Science* **284**, 118 (1999).
25. T. Takahashi *et al.*, *Deep-Sea Res. Part II* **49**, 1601 (2002).
26. S. Reynaud *et al.*, *Global Change Biol.* **9**, 1 (2003).
27. F. Marubini, H. Barnett, C. Langdon, M. J. Atkinson, *Mar. Ecol. Prog. Ser.* **220**, 153 (2001).
28. A. Sciandra *et al.*, *Mar. Ecol. Prog. Ser.* **261**, 111 (2003).
29. K. Simkiss, K. M. Wilbur, *Biomineralization* (Academic Press, New York, 1989).
30. H. A. Lowenstam, S. Weiner, *On Biomineralization* (Oxford Univ. Press, Oxford, 1989).
31. A. Mucci, *Am. J. Sci.* **238**, 780 (1983).
32. C. Langdon *et al.*, *Global Biogeochem. Cycles* **14**, 639 (2000).
33. F. Marubini, B. Thake, *Limnol. Oceanogr.* **44**, 716 (1999).
34. M. Spindler, *Neues Jahrb. Geol. Palaontol. Mh.* **9**, 659 (1980).
35. H. Pestana, *J. Sediment. Petrol.* **55**, 184 (1985).
36. V. J. Fabry, W. G. Deuser, *Deep-Sea Res. Part A* **38**, 713 (1991).
37. U. Riebesell *et al.*, *Nature* **407**, 364 (2000).
38. I. Zondervan, R. E. Zeebe, B. Rost, U. Riebesell, *Global Biogeochem. Cycles* **15**, 507 (2001).
39. H. J. Spero, J. Bijma, D. W. Lea, B. E. Bemis, *Nature* **390**, 497 (1997).
40. S. Barker, H. Elderfield, *Science* **297**, 833 (2002).
41. N. Gruber *et al.*, in *The Global Carbon Cycle: Integrating Humans, Climate, and The Natural World. SCOPE 62*, C. B. Field, M. R. Raupach, Eds. (Island Press, Washington, DC, 2004), pp. 45–76.
42. D. Archer, E. Maier-Reimer, *Nature* **367**, 260 (1994).
43. R. A. Armstrong, C. Lee, J. I. Hedges, S. Honjo, S. G. Wakeham, *Deep-Sea Res.* **49**, 219 (2002).
44. A. J. Ridgwell, *Geochem. Geophys. Geosyst.* **4**, 1051 (2003).
45. F. J. Millero, *Geochim. Cosmochim. Acta* **59**, 661 (1995).
46. P. R. Betzer *et al.*, *Science* **224**, 1074 (1984).
47. M. Rodier, R. LeBorgne, *Deep-Sea Res. Part II* **44**, 2085 (1997).
48. S. Tsunogai, S. Noriki, *Tellus Ser. B Chem. Phys. Meteorol.* **43**, 256 (1991).
49. C. S. Wong *et al.*, *Deep-Sea Res.* **46**, 2735 (1999).
50. S. Honjo, J. Dymond, R. Collier, S. Manganini, *Deep-Sea Res.* **42**, 831 (1995).
51. H. Kawahata, A. Suzuki, H. Ohta, *Deep-Sea Res.* **47**, 2061 (2000).
52. S. Noriki, K. Hamahara, K. Harada, *J. Oceanogr.* **55**, 693 (1999).

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SOM Text
Fig. S1
Table S1
References

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Effect of calcium carbonate saturation of seawater on coral calcification

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Abstract

The carbonate chemistry of seawater is usually not considered to be an important factor influencing calcium-carbonate-precipitation by corals because surface seawater is supersaturated with respect to aragonite. Recent reports, however, suggest that it could play a major role in the evolution and biogeography of recent corals. We investigated the calcification rates of five colonies of the zooxanthellate coral *Stylophora pistillata* in synthetic seawater using the alkalinity anomaly technique. Changes in aragonite saturation from 98% to 585% were obtained by manipulating the calcium concentration. The results show a nonlinear increase in calcification rate as a function of aragonite saturation level. Calcification increases nearly 3-fold when aragonite saturation increases from 98% to 390%, i.e., close to the typical present saturation state of tropical seawater. There is no further increase of calcification at saturation values above this threshold. Preliminary data suggest that another coral species, *Acropora* sp., displays a similar behaviour. These experimental results suggest: (1) that the rate of calcification does not change significantly within the range of saturation levels corresponding to the last glacial-interglacial cycle, and (2) that it may decrease significantly in the future as a result of the decrease in the saturation level due to anthropogenic release of CO_2 into the atmosphere. Experimental studies that control environmental conditions and seawater composition provide unique opportunities to unravel the response of corals to global environmental changes. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Scleractinan corals; calcification; carbonate chemistry; global change

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1. Introduction

Human activities increase the atmospheric CO_2 partial pressure (pCO_2), mostly through fossil fuel utilization, cement production and biomass burning. Approximately half of the released CO_2 remains in the atmosphere, presently increasing pCO_2 at a rate of 0.4% yr^{-1} (Houghton et al., 1996). The remaining CO_2 is stored in terrestrial biomass by photosynthetic CO_2 uptake and in the ocean through air–sea CO_2 exchange which tends to equilibrate pCO_2 across the air–sea interface. The amount of CO_2 stored in both sinks is not well known (Sarmiento, 1995) but it appears that the global ocean presently increases its storage of CO_2 by 1.7 ± 0.9 Pg C yr^{-1}

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(Keeling et al., 1996). CO_2 uptake by surface seawater increases the concentration of dissolved inorganic carbon and decreases pH. The saturation of seawater with respect to calcium carbonate (calcite and aragonite) is defined as the ratio of the ion activity product to the stoichiometric solubility product (Morse and Mackenzie, 1990).

If the saturation equals 100%, the solid and solution are in equilibrium; if it is lower than 100%, the solution is undersaturated and dissolution can occur; and if it is greater than 100%, the solution is supersaturated and precipitation can occur (Morse and Mackenzie, 1990). The aragonite saturation state decreases as a function of decreasing pH and it has been estimated that a doubling of the preindustrial pCO_2 could reduce tropical sea surface carbonate saturation levels to about two-thirds of present values (Smith and Buddemeier, 1992).

Seawater carbonate chemistry also displayed significant changes in the past. It is virtually certain that the oceanic surface waters have been supersaturated or saturated with respect to calcite and aragonite since early Precambrian time (Holland, 1984). However, evolution of calcifying organisms and the appearance of the various forms of calcium carbonate (calcite, aragonite, Mg–calcite) in the geologic record have been linked to the evolution of saturation levels in the oceanic geochemical system (Mackenzie and Agegian, 1989). In terms of more recent changes, the estimated decrease of surface water pH by 0.2 ± 0.1 units in the tropical Atlantic and Pacific Oceans between glacial age and the Holocene (Sanyal et al., 1995) has certainly affected the carbonate saturation level.

Such past, present and future changes in the seawater carbonate chemistry may have several implications for rates of photosynthetic CO_2 fixation (photosynthesis) and $CaCO_3$ precipitation (calcification) of marine organisms and ecosystems. CO_2 fertilization may increase productivity, as has been shown in most terrestrial plants and certain marine macrophytes (Bowes, 1993). It has also been repeatedly suggested during the past few years that carbonate saturation state may control calcification both at the ecosystem and organism scales because the rate of deposition of a mineral from solution is controlled, at the cellular level, by the degree of saturation in addition to solubility, nucleation and crystal growth (Mann, 1986). Broecker and Takahashi (1966) discussed the possibility of saturation control on the precipitation of calcium carbonate on the Bahama banks. Smith and Pesret (1974) investigated the community metabolism of the Fanning Island atoll lagoon and suggested that the carbonate mineral saturation state may influence the rate of $CaCO_3$ precipitation in calcifying ecosystems. This possibility has been discussed further (e.g., Smith and Buddemeier, 1992; Buddemeier, 1994; Buddemeier and Fautin, 1996a,b; Holligan and Robertson, 1996), although there remains a paucity of experimental data on coral reef organisms, and the most definitive experimental information has been obtained on marine calcareous algae (Mackenzie and Agegian, 1989; Gao et al., 1993a) and zoospores of freshwater algae (Hepperle and Krienitz, 1997). Additionally, some authors have assumed that community calcification in coral reefs is a linear function of aragonite saturation (Suzuki et al., 1995).

Smith and Buddemeier (1992) concluded that: "we clearly know very little about the links between atmospheric CO_2, marine benthic productivity, and marine calcification; and available information is partially contradictory. Growth-rate and metabolic experiments that carefully and explicitly define and control aqueous CO_2 chemistry are required...".

The objective of the present paper is to investigate the effect of calcium carbonate saturation state on the calcification rate of two reef-building corals maintained under controlled laboratory conditions. Since manipulation of saturation state by changing the inorganic carbon system equilibrium might have confounding effects on coral photosynthesis and its effect on calcification, the experiments controlled saturation state through the calcium concentration in artificial seawater.

2. Materials and methods

Branches were cut from six different parent colonies of the zooxanthellate scleractinian corals *Stylophora pistillata* (Esper, 1797) and one parent colony of *Acropora* sp. several months prior to the experiments, attached to nylon string and suspended in aquaria supplied with Mediterranean seawater (exchange rate: ca 2% h^{-1}). The healing process took

3–4 weeks, after which the specimens were completely surrounded by living tissue. Specimens were approximately rod-like in form, with dimensions in the range of 3–5 cm and skeletal weights in the range of 7.2–25.7 g. Culture conditions were: $S = 38.5$; temperature = 27 ± 0.5°C; aragonite saturation = ca. 360%, photosynthetic photon flux density = ca. 450 μmol m^{-2} s^{-1} (metal halide lamp, Philips HPIT 1000 W); photo-period = 12:12.

For an experimental run, five branches of *S. pistillata* (one from each parent colony) and one branch of *Acropora* sp. were transferred into individual 250-ml beakers and incubated for 2.5 h in synthetic seawater (SSW) of controlled aragonite saturation level, under environmental conditions otherwise similar to the culture conditions. Another branch of *S. pistillata*, sampled from a different parent colony, served as a control and was simultaneously incubated in Millipore (0.45 μm) filtered Mediterranean seawater at the same temperature and light conditions. The total experimental sequence consisted of five such runs, at aragonite saturation levels of 390, 98, 585, 293 and 195%, in the sequence indicated.

The incubation media were stirred continuously and a transparent plastic film was placed over each beaker in order to reduce evaporation. SSW was freshly prepared, a few hours prior to the experiments, as described by DOE (1994) but adapted to a salinity of 38.5 and an inorganic carbon content of 2.008 mmol kg^{-1}. The calcium concentration was set to 25, 50, 75, 100 or 150% the natural concentration (ca. 11.4 mmol kg^{-1}). SSW composition was determined as follows (Table 1): (1) the concentration of $CaCl_2$ was set according to the desired aragonite saturation level, (2) both Na_2CO_3 and HCl were added in order to obtain the desired values (i.e., close to Mediterranean levels) of dissolved inorganic carbon (DIC) and total alkalinity (TA) and (3) the NaCl concentration was then adjusted to respect the chlorinity (and the salinity).

All chemicals used were reagent grade (Merck). $CaCl_2$ and $MgCl_2$ were added volumetrically, using a Mettler DL 70 titrator, after accurate determination of densities and concentrations of stock solutions (Mohr titration). HCl (0.1 N) was also added volumetrically. TA was checked on freshly prepared SSW; experimental values were within 2 μeq kg^{-1} of the theoretical values. Preliminary experiments showed that the stability of a SSW saturated at 300% with respect to aragonite was longer than 24 h. Strontium concentration was measured using an ICP-MS; it was much lower in SSW than in Mediterranean seawater (0.9 vs. 105 μmol kg^{-1}).

Parameters of the inorganic carbon system were calculated using the CO_2 constants from Goyet and Poisson (1989), the CO_2 solubility coefficient from Weiss (1974) and the aragonite saturation constants from Morse et al. (1980). The pH electrode (Orion, 81-02) was calibrated daily using TRIS and AMP buffers (Dickson, 1993) and pH was expressed on the seawater scale (SWS).

Rates of calcification were estimated from the changes in total alkalinity (TA) during the course of

Table 1
Composition (mol kg^{-1}) of synthetic seawater (SSW) based on the recipe provided by DOE (1994) (SSD) and adapted for inorganic carbon

	SSD	SSW		Comment
		50% Ca	100% Ca	
NaCl	0.453893	0.463532	0.452136	$[NaCl]_{SSW} = [NaCl]_{SSD} + 2([CaCl_2]_{SSD} - [CaCl_2]_{SSW}) - [HCl]_{SSW}$
$CaCl_2$	0.011396	0.005698	0.011396	$[CaCl_2]_{SSW} = 0.01$ (%sat) $[CaCl_2]_{SSD}$
KCl	0.011231	0.011231	0.011231	
Na_2SO_4	0.031064	0.031064	0.031064	
$MgCl_2$	0.058113	0.058113	0.058113	
Na_2CO_3	0	0.002008	0.002008	$[Na_2CO_3]_{SSW} = DIC$
HCl	0	0.001757	0.001757	$[HCl]_{SSW} = 2DIC - TA$

DIC: dissolved inorganic carbon; TA: total alkalinity; %sat: aragonite saturation.
Salinity = 38.5, DIC = 2008 μmol kg^{-1}, TA = 2259 μeq kg^{-1}.

the incubation using the alkalinity anomaly technique (Smith and Key, 1975) and normalized with the protein content. TA was measured using a potentiometric titration as described by Gattuso et al. (1993). Upon completion of all experiments, proteins were solubilized in 1 N NaOH at 90°C for 30 min. Samples were allowed to cool, neutralized with 1 N HCl and the protein content was measured using the method given by Bradford (1976) against a series of bovine gamma globulin standards. The response curve of the rate of calcification vs. aragonite saturation was modelled using nonlinear regression techniques with the shareware package MacCurveFit 1.3. Statistical testing was performed with JMP 3.1.6 (SAS Institute, Cary, USA). Results are reported as mean ± standard error of the mean (SE). N is the sample size.

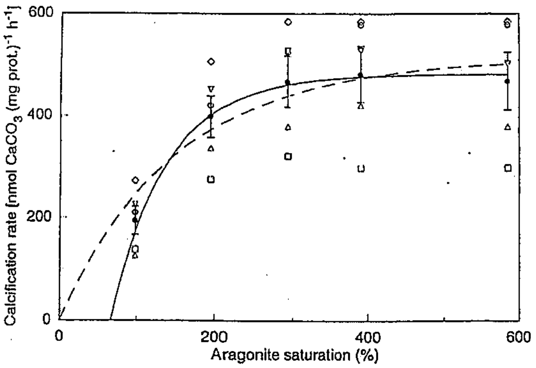

Fig. 1. Calcification rate of colonies of *S. pistillata* as a function of aragonite saturation (open symbols). Average calcification rates (●) are displayed ±1 standard error of the mean. The average relationships forced (dashed line) or not forced (continuous line) through the origin are shown. The corresponding curve fitting parameters are given in Table 3.

3. Results

Experimental results are summarized in Table 2. The calcification rate of the control colony of *S. pistillata* changed by only 13% (at most) during the course of the experiment [20 days; 784–882 nmol $CaCO_3$ (mg prot.)$^{-1}$ h^{-1}] and was, on average, 833 ± 18 nmol $CaCO_3$ (mg prot)$^{-1}$ h^{-1} ($N = 6$). The rate of calcification of *S. pistillata* and *Acropora* sp. ranged from 126 to 584 nmol $CaCO_3$ (mg prot)$^{-1}$ h^{-1} depending on the colony and the incubation medium. *Acropora* sp. and *S. pistillata* calcified at a similar rate (paired t-test; $P = 0.55$).

The rate of calcification of all colonies of *S. pistillata* increased as a function of increasing aragonite saturation and reached a saturation plateau at aragonite saturation ranging between 426% and 585% (Fig. 1). The relationship is well described by exponential functions, forced through the origin or not, with coefficients of determination higher than 0.92 (Table 3).

The control colony of *S. pistillata* incubated in Mediterranean seawater (aragonite saturation ≈ 360%) calcified at a significantly higher rate than the colonies incubated in artificial seawater with arago-

Table 2
Rate of calcification [nmd $CaCO_3$ (mg prot)$^{-1}$h^{-1}] of colonies of *S. pistillata* (five specimens from different parent colonies) and *Acropora* (one specimen) as a function of aragonite saturation

Species	Aragonite saturation (%)				
	98	195	293	390	585
S. pistillata					
Sp1	272.5	506.1	584.0	584.0	584.0
Sp2	210.2	420.5	525.6	578.2	578.2
Sp3	126.4	337.1	379.2	421.4	379.2
Sp4	226.1	452.2	527.5	527.5	502.4
Sp5	137.7	275.5	321.4	298.4	298.4
Mean ± SE	194.6 ± 25.2	398.3 ± 37.6	467.5 ± 45.5	481.9 ± 49.6	468.4 ± 51.4
Acropora sp.	214.3	500.1	535.8	428.7	428.7

SE: standard error of the mean.

Table 3
Nonlinear regression parameters of the relationship between the calcification rate and the aragonite saturation

Function	a	b	c	n	r^2
$y = a(1 - \exp(-x/b)) + c$					
Sp1	1323 ± 218	69 ± 8	-723 ± 223	5	0.997
Sp2	906 ± 90	115 ± 14	-312 ± 98	5	0.996
Sp3	1245 ± 573	64 ± 20	-846 ± 582	5	0.98
Sp4	1460 ± 589	61 ± 16	-938 ± 597	5	0.99
Sp5	1148 ± 858	51 ± 20	-842 ± 864	5	0.98
Average	1214 ± 92	72 ± 11	-732 ± 111	–	–
$y = a(1 - \exp(-x/b))$					
Sp1	619 ± 38	134 ± 27	–	5	0.96
Sp2	637 ± 49	190 ± 38	–	5	0.98
Sp3	432 ± 60	165 ± 65	–	5	0.92
Sp4	549 ± 46	135 ± 37	–	5	0.94
Sp5	321 ± 28	126 ± 38	–	5	0.92
Average	512 ± 59	150 ± 12	–	–	–

n = Number of samples; r = correlation coefficient; mean ± asymptotic standard error. The average values are shown as mean ± standard error of the mean.

nite saturation of 390% (833 ± 18 vs. 482 ± 50 nmol $CaCO_3$ (mg prot)$^{-1}$ h^{-1}; Welch ANOVA, $P = 0.002$), but the differences within experimental specimens were well within the range of natural variability in calcification rates (Buddemeier and Kinzie, 1976).

4. Discussion

Our results demonstrate that manipulating calcium carbonate saturation through changes in calcium concentration has a highly significant short-term effect on coral calcification. The work of Marubini and Atkinson (pers. comm.) and Langdon et al. (pers. comm.), which address similar issues by manipulation of carbonate concentration in natural seawater, arrived at essentially the same overall conclusion. For the experiments described here, the rate of calcification appears to increase exponentially as a function of increasing aragonite saturation state above the 100% saturation level, and reaches a plateau at saturation values greater than 300%.

Curve-fitting can provide useful descriptions of the data. The first relationship derived from the experimental data is a three-parameter saturated exponential function. Extrapolation of this relationship at saturation levels lower than those used in the present study indicates that calcification is 0 when aragonite saturation is 66%. Such extrapolation does not agree with the observation that some azooxanthellate scleractinians are known to calcify in deep-sea environments, and with the observations of Marubini and Atkinson (pers. comm.), who have shown that colonies of the coral *Porites compressa* calcify at saturation states < 50%. It is probable that the decrease of calcification in seawater undersaturated with respect to aragonite is not as dramatic. Fitting a two-parameter function to the data makes it possible to force the line to 0 (Fig. 1). The lack of experimental data at low saturation values prevents choice of one fitting function rather than the other. In the rest of the discussion we will use the three-parameter function as a predictive function for environments with saturation state > 100% since (1) it provides the best fit to the data, as shown by the high r^2 and (2) the response of calcification to saturation levels below 100% is relevant to overall understanding of the mechanisms of calcification control, but is not a major factor in the role of neritic carbonate production in global carbon cycle and its changes over time.

Other studies have previously shown that calcification changes as a function of calcium concentration in several taxonomic groups. For example, the rates of calcification and photosynthetic $^{14}CO_2$ fixation increase as a function of external Ca^{2+} concentration in cells harvested from the exponential growth phase of a high-calcifying strain of the coccolithophorid *Emiliania huxleyi* (Nimer et al., 1996). The rates of photosynthesis and calcification are closely coupled, and are saturated at 10 mM Ca^{2+} compared with the Ca^{2+} concentration of 8 mM in seawater. Lea et al. (1995) also suggested that the calcification rate of the foraminiferan *Orbulina universa* is proportional to the degree of carbonate saturation.

There is little direct information on the effect of the carbonate saturation state on coral calcification (Smith and Buddemeier, 1992). Several authors demonstrated, however, that the seawater calcium concentration has a significant effect on calcification (e.g., Yamazato, 1966 in Swart, 1979; Chalker, 1981; Krishnaveni et al., 1989; Ip and Krishnaveni, 1991; Tambutté et al., 1996). Most studies showed that the rate of calcification follows a saturation kinetics but the calcium concentration at which the saturated rate is reached encompasses a rather wide range: 10–25 mM Ca^{2+}. It is difficult to draw conclusions on the effect of saturation state from these studies because they did not control, measure, or report the parameters of the inorganic carbon system which prevents derivation of the aragonite saturation levels from calcium concentrations. An artificial seawater formula recently designed for chemical oceanography (DOE, 1994) was used in the present study. It permitted strict control of pH, dissolved inorganic carbon and total alkalinity of the incubation medium thereby avoiding any effect of parameters other than saturation state on the rate of calcification.

Our results are in agreement with those obtained on the calcareous alga *Porolithon gardineri* by Agegian (1985) (see also Mackenzie and Agegian, 1989). The linear growth rate of this species was measured under controlled environmental conditions in which the calcite saturation state was changed by manipulating the seawater pH. It displayed a twofold increase when the saturation state increased from 100 to 800%. There was, however, no evidence of a saturation kinetics as the increase appears to be linear over this range of calcite saturation.

Differences in the strontium concentration between normal and artificial seawater of similar aragonite saturation level, may explain that the rate of calcification was lower in the synthetic than in the Mediterranean seawater. Strontium is incorporated into the coral skeleton and its deposition is linear with respect to Sr^{2+} concentration (Ip and Krishnaveni, 1991). Additionally, Chalker (1976) and Ip and Krishnaveni (1991) have suggested that strontium can be a competitive inhibitor of calcification, although it has been suggested that Sr^{2+} and Ca^{2+} deposition appear to involve different biochemical pathways (Ip and Krishnaveni, 1991).

The effect of the seawater saturation state on calcification may explain the distribution of calcifying and noncalcifying Cnidaria (Buddemeier and Fautin, 1996a). Sea anemones are found at greater depth than are corals, which is consistent with the decrease of calcium carbonate saturation as a function of depth and the resulting solubility of $CaCO_3$ at depth (Buddemeier and Fautin, 1996b). Additionally, the latitudinal range of reef-building (zooxanthellate) corals is narrower than the distribution of either symbiotic sea anemones or non reef-building (azooxanthellate) corals, which implies that symbiotic calcification is latitudinally restricted whereas neither algal symbioses nor coral calcification are individually limited. Buddemeier and Fautin (1996a) acknowledged that temperature is an important factor controlling biogeography but made the points that saturation state may also be involved, and that the latitudinal distribution of saturation state is qualitatively similar to that of temperature. Kleypas (1997) has recently demonstrated that the latitudinal distribution of reefs can also be reproduced using light as a controlling variable. The results of the present study provide experimental support for the hypothesis that saturation state is important, as do the results of Atkinson and Marubini (pers. comm.), but it remains impossible at this stage to estimate the relative importance of temperature, saturation state, and light as controls on the distribution of corals.

The occurrence of coral reefs and the distribution of most reef-building (= hermatypic) corals are limited to the tropics and subtropics (Veron, 1995), and encrusting red algae are more heavily calcified in temperate than in cold water (see Lowenstam and Weiner, 1989) Such distribution is traditionally explained by temperature limitation at higher latitudes (Veron, 1995). An increase in the extent of biomineralization across a latitudinal temperature gradient has been observed in the scales and bones of marine fish (Moss, 1963). These differences were attributed to a decreased calcium concentration in the low-salinity Arctic waters. King and Schramm (1982) also suggested that the calcium ion concentration and not salinity per se affects calcification rates of the Baltic sea coralline alga *Phymatolithon calcareum*. Lastly, $CaCO_3$ precipitation over the Bahama Banks (the so-called 'whitings') is strongly correlated with the degree of supersaturation (Broecker and Takahashi, 1966). Opdyke and Wilkinson (1993) have correlated the accumulation of Holocene reefal carbonates with saturation state.

4.1. *Inferences on the effect of* $CaCo_3$ *saturation on calcification in the past*

The saturation of calcium carbonate in seawater is essentially controlled by the concentration of calcium and carbonate ions (neglecting the effect of changes in salinity and temperature at this stage). It is mostly dependent on CO_3^{2-} on short time scales as Ca^{2+} concentration is two orders of magnitude higher than CO_3^{2-} concentration. For time scales longer than a million years (i.e., longer than the residence time of calcium in the sea), shifts in both Ca^{2+} and in CO_3^{2-} ion concentrations need to be considered (Broecker and Peng, 1982).

There is some information suggesting that the calcium concentration has increased dramatically between 2 and 1 Ga (Kempe and Kazmierczak, 1994). It has been proposed that the onset of skeletal biomineralization at the Precambrian–Cambrian boundary was a detoxification response to an environmental calcium shock (Kazmierczak et al., 1985). Bengtson (1994) rejected that proposal because it appears to clash with evidence of substantial $CaCO_3$ precipitation in sedimentological records from the Middle Archean. Other studies have proposed that changes in $CaCO_3$ saturation had profound impacts on the biology of the early ocean. For example, it has been suggested that the decline of Proterozoic stromatolites could, in part, be related to a reduction in carbonate saturation through time (Grotzinger, 1994). According to Grotzinger (1994), the advent of calcification in the terminal Proterozoic and earliest Cambrian did not substantially change the calcium carbonate saturation state of seawater.

The more recent history of the calcium content of seawater shows that it has decreased during the last 20 million years, but that the carbonate content increased in similar proportions; the carbonate saturation was therefore roughly the same during the 5–20-million-year time period (Broecker and Peng, 1982; see also Lasaga, 1985). Note, however, that the magnitude of the recent changes in the calcium content are poorly known; Opdyke and Wilkinson (1988) suggested that it did not depart from the average value of the last 150 million years by more than 20%.

There is comparatively more information on the chemistry of tropical surface water during the last glacial–interglacial period than there is from the distant past. The atmospheric pCO_2 was approximately 80 μatm lower 18 kyr ago than during the preindustrial period (200 vs. 280 μatm). Since the ocean surface is, on the long term, essentially in equilibrium with the atmosphere, such a large-scale change in pCO_2 is likely to have had a profound effect on the seawater inorganic carbon system (Archer and Maier-Reimer, 1994). This was recently demonstrated using the isotopic composition of borates incorporated into foraminiferan shells as a proxy record of oceanic pH. Sanyal et al. (1995) estimated that the pH of tropical surface water was 0.2 ± 0.1 higher during the last glacial age than during the Holocene.

We estimate that aragonite saturation during the last glacial period, calculated using the estimated pCO_2 (200 μatm) and total alkalinity (2457 μeq kg^{-1}; Broecker and Peng, 1982), was 566% compared to 446% in the late 1800s (Table 4). This estimate of the seawater carbonate chemistry during the glacial time requires a difference in pH of 0.12 unit, which is consistent with the paleo-pH data proposed by Sanyal et al. (1995). The rate of calcification of *S. pistillata* is essentially constant for aragonite saturation states between 400% and 600% (Fig. 1). Our experimental data suggest therefore that

Table 4
Carbonate chemistry of tropical surface seawater in glacial and interglacial periods

	Glacial	Preindustrial	Present	Future 1 (×2 pCO_2)	Future 2 (pCO_2 = 1000)
pH (SWS)	8.29	8.17	8.08	7.93	7.71
TA (μeq kg^{-1})	**2457**	**2350**	**2350**	**2350**	**2350**
pCO_2 (μatm)	**200**	**280**	**360**	**560**	**1000**
Aragonite saturation (%)	566	446	387	293	192

Secondary parameters (standard fonts) were computed from primary parameters (in bold). The estimate of TA during the glacial time is from Broecker and Peng (1982). TA was held constant at its preindustrial value from the late 1800s onwards. Temperature and salinity were set at 25°C and 35, respectively.

the deposition of $CaCO_3$ by scleractinian corals may not have changed significantly in response to the decrease in aragonite saturation that occurred during the last 18 kyr. The decrease in tropical sea surface temperature by 3–6°C during the last glacial maximum is likely to have diminished $CaCO_3$ deposition.

4.2. Inferences on the effect of $CaCO_3$ saturation on calcification in the future

The present atmospheric pCO_2 is approximately 360 μatm and is increasing at a rate of 0.4% yr^{-1} due to the anthropogenic release of CO_2 (Houghton et al., 1996). The Intergovernmental Panel on Climate Change (IPCC) has made predictions of future atmospheric pCO_2 levels according to a number of scenarios (Houghton et al., 1996), most of which predict a doubling of preindustrial levels within the next century.

CO_2 equilibrates between the surface ocean and the atmosphere through air–sea exchange at the air–water interface. Our calculations predict that seawater pH will decrease from 8.08 at present to 7.93 and 7.71 for pCO_2s values of 560 (i.e., a doubling of the preindustrial value) and 1000 μatm (Table 4). These decreases will drive the aragonite saturation down from its present value (387%) to 293 and 192%, respectively. The relationship between the rate of calcification and aragonite saturation derived in the present paper suggests that calcification may not decrease significantly (461 vs. 476 nmol $CaCO_3$ (mg prot.)$^{-1}$ h^{-1}) at a saturation level corresponding to $pCO_2 = 560$ μatm. However, a significant decrease (14%) may be observed if pCO_2 reaches 1000 μatm (398 vs. 476 nmol $CaCO_3$ (mg prot.)$^{-1}$ h^{-1}). Langdon et al. (pers. comm.) observed much more important changes in Biosphere 2 by manipulating the aragonite saturation through the reef metabolism and additions of carbonate and bicarbonate. They suggest that calcification may decline by 10 and 75% at pCO_2s of, respectively, 560 and 1000 μatm.

It must be noted that additional weathering of terrestrial carbonates is likely to occur under elevated atmospheric pCO_2, thereby increasing Ca^{2+} delivery to the oceans and partly counteracting the decrease in aragonite saturation due to the decrease in pH (Holland, pers. comm. in Riding, 1996).

5. Conclusion

The aragonite saturation state has a significant short-term effect on the rate of calcification of the scleractinian coral *S. pistillata* between 98 and 585%. It is found: (1) that the rate of calcification does not change significantly over a range of saturation levels corresponding to the last glacial-interglacial cycle, and (2) that it may decrease significantly in the future as a result of global environmental changes. It is important to point out the limitations of this prediction. Firstly, the response of only two species was investigated. It can be argued that these species, especially, *S. pistillata*, are not major reef builders. However, results obtained by other groups (Langdon et al., pers. comm.; Marubini and Atkinson, pers. comm.) suggest that the response that we report is valid across a wide range of species, including the major reef building species *P. compressa*. Secondly, only the short-term effect has been investigated. Corals display quite impressive acclimation processes to changes in some environmental parameters (Brown, 1997) and many species have survived the major global environmental cycles of the Quaternary period (Veron, 1995). Thirdly, the saturation state was manipulated by altering the seawater calcium content and not pCO_2. The effect observed in the present study relates therefore to the aragonite saturation per se. It would be interesting to investigate the effect of increased pCO_2 which may also have an effect on photosynthesis of zooxanthellae, the microalgae living in symbiosis in the cells of most reef-building corals. Since photosynthesis has been suggested to stimulate coral calcification (Barnes and Chalker, 1990), an increase of zooxanthellar photosynthesis may counteract the decrease of calcification resulting from decreased aragonite saturation state. Increase of photosynthesis under high pCO_2 has been observed in macroalgae (e.g., Gao et al., 1993b) but the situation is not as clear in zooxanthellate corals. The rate of photosynthesis has never been investigated under elevated pCO_2 but indirect evidence indicates that increased pCO_2 resulting from a decrease in pH (pH_{SWS}: 8.22–7.70, derived empirically) in a closed system slightly inhibits the rate of photosynthesis of colonies of *Galaxea fascicularis* (Allemand, in press). There is clearly a need to pursue experimental studies using controlled environmental conditions and seawater composition to unravel the response of corals to global environmental changes.

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References

Agegian, C.R., 1985. The biogeochemical ecology of *Porolithon gardineri* (Foslie). University of Hawaii.

Allemand, D., in press. Mechanisms of carbon acquisition for endosymbiont photosynthesis in Anthozoa. Can. J. Bot.

Archer, D., Maier-Reimer, E., 1994. Effect of deep-sea sedimentary calcite preservation on atmospheric CO_2 concentration. Nature 367, 260–263.

Barnes, D.J., Chalker, B.E., 1990. Calcification and photosynthesis in reef-building corals and algae. In: Dubinsky, Z. (Ed.), Coral Reefs. Elsevier, Amsterdam, pp. 109–131.

Bengtson, S., 1994. The advent of animals skeletons. In: Bengtson, S. (Ed.), Early Life on Earth. Columbia Univ. Press, New York, pp. 412–425.

Bowes, G., 1993. Facing the inevitable—plants and increasing atmospheric CO_2. Annu. Rev. Plant Physiol. Plant Mol. Biol. 44, 309–332.

Bradford, M.M., 1976. A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein dye binding. Anal. Biochem. 72, 248–254.

Broecker, W.S., Peng, T.-H., 1982. Tracers in the sea. Lamont-Doherty Geological Observatory, Columbia University, Palisades, NY, 690 pp.

Broecker, W.S., Takahashi, T., 1966. Calcium carbonate precipitation on the Bahama Banks. J. Geophys. Res. 71, 1575–1602.

Brown, B.E., 1997. Adaptations of reef corals to physical environmental stress. Adv. Mar. Biol. 31, 221–299.

Buddemeier, R.W., 1994. Symbiosis, calcification, and environmental interactions. Bull. Inst. Océanogr., Monaco, no. spéc. 13, pp. 119–131.

Buddemeier, R.W., Fautin, D.G., 1996. Saturation state and the evolution and biogeography of symbiotic calcification. Bull. Inst. Océanogr., Monaco, no. spéc. 14, pp. 23–32.

Buddemeier, R.W., Fautin, D.G.,1996. Global CO_2 and evolution among the Scleractinia. Bull. Inst. Océanogr., Monaco, no spéc. 14, pp. 33–38.

Buddemeier, R.W., Kinzie III, R.A., 1976. Coral growth. Oceanogr. Mar. Biol. Annu. Rev. 14, 183–225.

Chalker, B.E., 1976. Calcium transport during skeletogenesis in hermatypic corals. Comp. Biochem. Physiol. A 54, 455–459.

Chalker, B.E., 1981. Skeletogenesis in scleractinian corals: the transport and deposition of strontium and calcium. In: Skoryna, S.C. (Ed.), Handbook of Stable Strontium. Plenum, New York, pp. 47–63.

Dickson, A.G., 1993. pH Buffers for sea water media based on the total hydrogen ion concentration scale. Deep-Sea Res. I 40, 107–118.

DOE, 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water, version 2,

Gao, K., Aruga, Y., Asada, K., Ishihara, T., Akano, T., Kiyohara, M., 1993a. Calcification in the articulated coralline alga *Corallina pilulifera*, with special reference to the effect of elevated CO_2 concentration. Mar. Biol. 117, 129–132.

Gao, K., Aruga, Y., Asada, K., Kiyohara, M., 1993b. Influence of enhanced CO_2 on growth and photosynthesis of the red algae *Gracilaria* sp. and *G. chilensis*. J. Appl. Phycol. 5, 563–571.

Gattuso, J.-P., Pichon, M., Delesalle, B., Frankignoulle, M., 1993. Community metabolism and air–sea CO_2 fluxes in a coral reef ecosystem (Moorea French Polynesia). Mar. Ecol. Prog. Ser. 96, 259–267.

Goyet, C., Poisson, A., 1989. New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. Deep-Sea Res. 36, 1635–1654.

Grotzinger, J.P., 1994. Trends in Precambrian carbonate sediments and their implication for understanding evolution. In: Bengtson, S. (Ed.), Early Life on Earth. Columbia Univ. Press, New York, pp. 245–258.

Hepperle, D., Krienitz, L., 1997. *Phacotus lenticularis* (Chlamydomonadales, Phacotaceae) zoospores require external supersaturation of calcium carbonate for calcification in culture. J. Phycol. 33, 415–424.

Holland, H.D., 1984. The Chemical Evolution of the Atmosphere and Oceans. Princeton Univ. Press, Princeton, 582 pp.

Holligan, P.M., Robertson, J.E., 1996. Significance of ocean carbonate budgets for the global carbon cycle. Global Change Biol. 2, 85–95.

Houghton, J.T., Meira filho, L.G., Callander, B.A., Harris, N., Kattenberg, A., Maskell, K., 1996. Climate Change 1995. The Science of Climate Change. Cambridge Univ. Press, Cambridge, 572 pp.

Ip, Y.K., Krishnaveni, P., 1991. Incorporation of strontium ($^{90}Sr^{2+}$)into the skeleton of the hermatypic coral *Galaxea fascicularis*. J. Exp. Zool. 258, 273–276.

Kazmierczak, H.J., Ittekot, V., Degens, E.T., 1985. Biocalcification through time: environmental challenge and cellular response. Paläontol. Z. 59, 15–33.

Keeling, R.F., Piper, S.C., Heimann, M., 1996. Global and hemispheric CO_2 sinks deduced from changes in atmospheric O_2 concentration. Nature 381, 218–221.

Kempe, S., Kazmierczak, J., 1994. The role of alkalinity in the evolution of ocean chemistry, organization of living systems, and biocalcification processes. Bull. Inst. Océanogr., Monaco, no. spéc. 13, pp. 61–117.

King, R.J., Schramm, W., 1982. Calcification in the maerl coralline alga *Phymatolithon calcareum*: effect of salinity and temperature. Mar. Biol. 70, 197–204.

Kleypas, J., 1997. Modelled estimates of global reef habitat and carbonate production since the last glacial maximum. Paleoceanography 12, 533–545.

Krishnaveni, P., Chou, L.M., Ip, Y.K., 1989. Deposition of calcium ($^{45}Ca^{2+}$) in the coral *Galaxea fascicularis*. Comp. Biochem. Physiol. A 94, 509–513.

Lasaga, A.C., 1985. An improved geochemical model of atmospheric CO_2 fluctuations over the past 100 million years. In: Sundquist, E.T., Broecker, W.S. (Eds.), The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present. American Geophysical Union, Washington, DC, pp. 397–411.

Lea, D.W., Martin, P.A., Chan, D.A., Spero, H.J., 1995. Calcium uptake and calcification rate in the planktonic foraminifer *Orbulina universa*. J. Foram. Res. 25, 14–23.

Lowenstam, H.A., Weiner, S., 1989. On Biomineralization. Oxford Univ. Press, New York, 324 pp.

Mackenzie, F.T., Agegian, C.R., 1989. Biomineralization and tentative links to plate tectonics. In: Crick, R.E. (Ed.), Origin, Evolution, and Modern Aspects of Biomineralization in Plants and Animals. Plenum, New York, pp. 11–27.

Mann, S., 1986. Biomineralization in lower plants and animals—chemical perspectives. In: Leadbeater, B.S.C., Riding, R. (Eds.), Biomineralization in Lower Plants and Animals. Clarendon, Oxford, pp. 39–54.

Moss, M.L., 1963. The biology of acellular Teleost bone. Ann. New York Acad. Sci. 109, 337–350.

Morse, J.W., Mackenzie, F.T., 1990. Geochemistry of Sedimentary Carbonates. Elsevier, Amsterdam, 707 pp.

Morse, J.W., Mucci, A., Millero, F.S., 1980. The solubility of calcite and aragonite in seawater of 35% salinity and atmospheric pressure. Geochim. Cosmochim. Acta 44, 85–94.

Nimer, N.A., Merrett, M.J., Brownlee, C., 1996. Inorganic carbon transport in relation to culture age and inorganic carbon concentration in a high-calcifying strain of *Emiliania huxleyi* (Prymnesiophyceae). J. Phycol. 32, 813–818.

Opdyke, B.N., Wilkinson, B.H., 1988. Surface area control of shallow cratonic to deep marine carbonate accumulation. Paleoceanography 3, 685–703.

Opdyke, B.N., Wilkinson, B.H., 1993. Carbonate mineral saturation state and cratonic limestone accumulation. Am. J. Sci. 293, 217–234.

Riding, R., 1996. Long-term change in marine $CaCO_3$ precipitation. Mém. Soc. Géol. Fr. 169, 157–166.

Sanyal, A., Hemming, N.G., Hanson, G., Broecker, W.S., 1995. Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. Nature 373, 234–236.

Sarmiento, J.L., 1995. Modelling the oceanic uptake of anthropogenic carbon. U.S. JGOFS Newsletter, pp. 4–6.

Smith, S.V., Buddemeier, R.W., 1992. Global change and coral reef ecosystems. Annu. Rev. Ecol. Syst. 23, 89–118.

Smith, S.V., Key, G.S., 1975. Carbon dioxide and metabolism in marine environments. Limnol. Oceanogr. 20, 493–495.

Smith, S.V., Pesret, F., 1974. Processes of carbon dioxide flux in the Fanning Island lagoon. Pac. Sci. 28, 225–245.

Suzuki, A., Nakamori, T., Kayanne, H., 1995. The mechanism of production enhancement in coral reef carbonate system: model and empirical results. Sedim. Geol. 99, 259–280.

Swart, P.K., 1979. The effect of seawater calcium concentrations on the growth and skeletal composition of a scleractinian coral *Acropora squamosa*. J. Sediment. Petrol. 49, 951–954.

Tambutté, E., Allemand, D., Mueller, E., Jaubert, J., 1996. A compartmental approach to the mechanism of calcification in hermatypic corals. J. Exp. Biol. 199, 1029–1041.

Veron, J.E.N., 1995. Corals in Space and Time. The Biogeography and Evolution of the Scleractinia. Cornell Univ. Press, Ithaca, 321 pp.

Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar. Chem. 2, 203–215.

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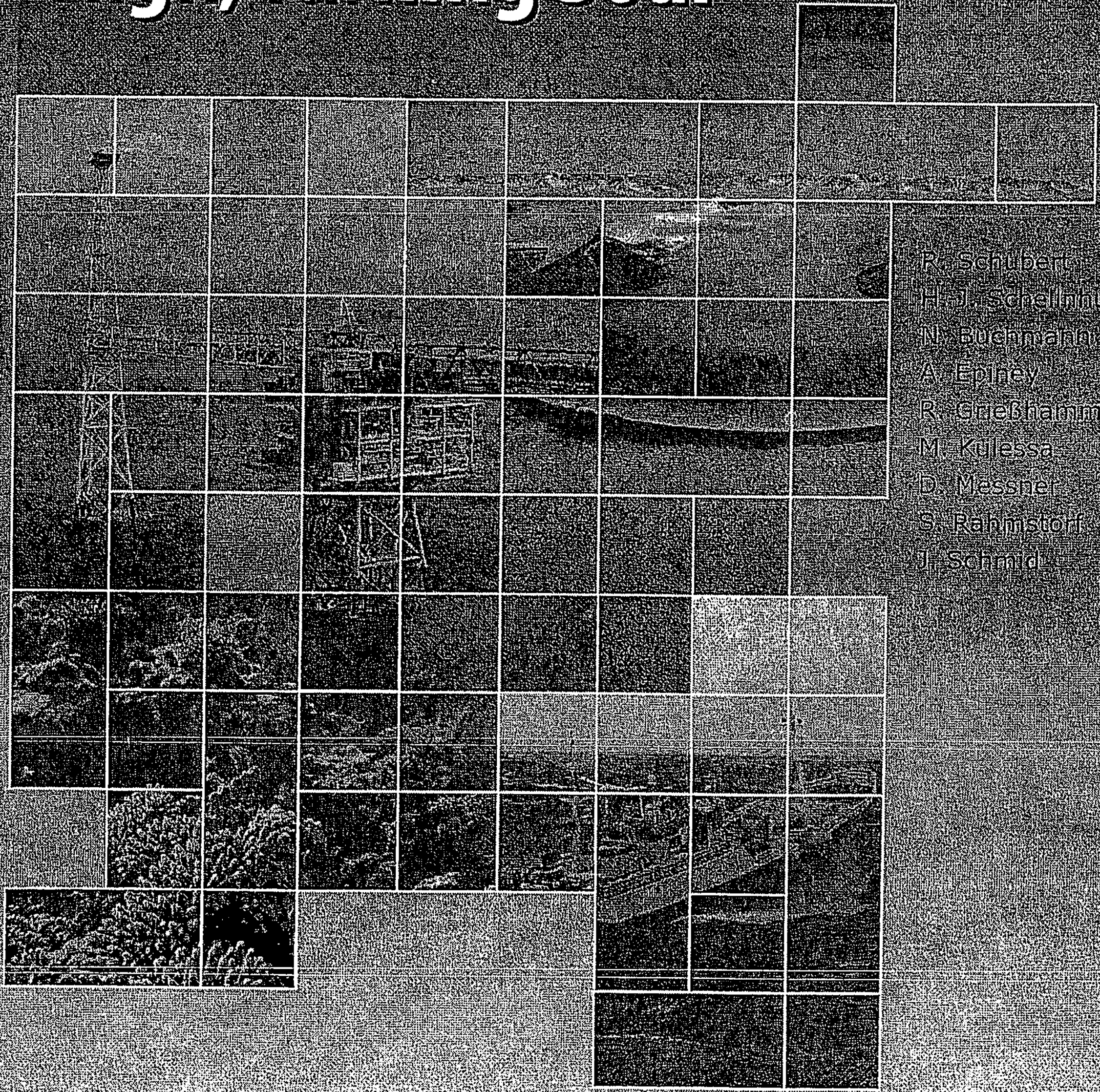

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German Advisory Council on Global Change

The Future Oceans – Warming up, Rising High, Turning Sour

Special Report

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Summary for policy-makers

The latest research findings show that climate change will subject the marine environment and the coasts to major change and damage that are likely to have severe consequences for humankind. Ocean surface waters are warming, the sea level is rising ever faster, the oceans are becoming increasingly acidic and marine ecosystems are under threat. Human activities are unleashing processes of change in the oceans that are without precedent in the past several million years. Due to the considerable geophysical time lags, these processes will determine the state of the world's oceans for millennia to come. Humanity is thus intervening in a pivotal mechanism of the Earth System, and many of the consequences cannot yet be predicted accurately. Resolute and forward-looking action is needed in order to ensure that the oceans do not overstep critical system boundaries. The way we handle the oceans will be a decisive test of humankind's ability to steer a sustainable course in the future.

Climate mitigation for marine conservation

Ocean warming, ocean acidification and a distinct sea-level rise are all already measurable. The causes are clear: elevated concentrations of greenhouse gases in the atmosphere caused by human activities have led to a global warming that has also increased temperatures in the surface waters of the oceans. This leads to rising sea levels due to thermal expansion of the water and due to melting ice masses. At the same time, the continuously rising carbon dioxide concentration in the air causes CO_2 to be absorbed by the sea where, through chemical reactions, the seawater acidifies. These changes can only be mitigated by means of drastic reductions in anthropogenic greenhouse gas emissions. Rapid action is therefore required:

- Ambitious climate protection measures are needed to limit the consequences of warming, acidification and sea-level rise for the marine environment and human society. WBGU therefore recommends that global anthropogenic greenhouse gas emissions must be approximately halved by 2050 from 1990 levels. Adaptation measures can only succeed if the present acceleration of sea-level rise and the increasing acidification of the oceans are halted.
- The guard rail already recommended previously by WBGU – namely limiting the rise in near-surface air temperature to a maximum of 2°C relative to the pre-industrial value while also limiting the rate of temperature change to a maximum of 0.2°C per decade – is essential not only to prevent dangerous climatic changes but also to maintain the state of the oceans.

Bolstering the resilience of marine ecosystems

Compared to terrestrial ecosystems, marine ecosystems respond much more sensitively and rapidly to climatic changes, for example through spatial shifts of populations. As a result, human-induced warming of the surface waters can cause changes in food webs and species composition that are difficult to predict. A further increase in water temperatures, in combination with continuing acidification, will have major overall impacts on marine ecosystems and also on fisheries.

The fisheries sector is thus facing two further threats in the future in the shape of climate change and ocean acidification, in addition to the consequences of overfishing, which are already drastic enough in themselves. Taken together, and in view of the continuing growth of the world population, these anthropogenic factors will jeopardize a sufficient supply of food from the oceans.

Tropical coral reefs, by far the most species-rich ecosystems in the ocean, are acutely threatened by climate change. Most reefs may be destroyed within the next 30–50 years, because many corals are not viable at higher water temperatures. The local ramifications are vast, reefs being indispensable for coastal protection and in supplying protein for millions of people.

One of the most visible consequences of warming is the retreat of Arctic sea ice. Over the past 30 years, summertime ice cover has declined by 15–20 per cent. Model scenarios for the future indicate that, unless action is taken to mitigate climate change, the Arctic Ocean will be practically ice-free in summertime by the end of the 21st century. This would have severe consequences for ecosystems and climatic processes.

- To preserve marine biodiversity and strengthen the resilience of marine ecosystems, WBGU proposes the following guard rail: at least 20–30 per cent of the area of marine ecosystems should be designated for inclusion in an ecologically representative and effectively managed system of protected areas. There is a particular need to enhance marine conservation significantly for coral reefs and areas that are nursery grounds for fish populations. Goals for marine protected areas already agreed by the international community need to be implemented, and the regulatory gap in this regard for the high seas should be closed by adopting an agreement under the United Nations Convention on the Law of the Sea (UNCLOS).
- Marine resource management should follow the 'ecosystem approach'. In particular, the publicly subsidized overfishing of the oceans must be terminated, not least in order to strengthen the resilience of fish stocks to the impacts of climate change. This necessitates not only removing fisheries subsidies, but also dismantling excess fishing capacity and taking measures to combat destructive fishing practices and illegal or unregulated fisheries.
- Our understanding of the linkages between anthropogenic disturbances, biological diversity and the resilience of marine ecosystems needs to be improved. Intensive monitoring is a precondition for the further development of coupled ecosystem-climate models.

Limiting sea-level rise and reorienting coastal zone management strategies

Climate change causes sea-level to rise, particularly due to ocean warming and the melting of inland glaciers and continental ice sheets. Throughout the 20th century, global sea-level rise averaged 1.5–2.0 cm per decade. Satellite measurements show that the decadal rate already reached 3cm in the past decade. If warming continues, there is a risk of further acceleration of sea-level rise. There are indications that the continental ice sheets on Greenland and in the Antarctic are beginning to disintegrate. This has the potential to cause several metres of sea-level rise in the next centuries.

Besides sea-level rise, the increasingly destructive force of hurricanes is a further factor threatening many coastal areas. Theory, observed data and mathematical models agree that while climate warming does not increase the number of hurricanes, it does boost their destructive energy. Tropical sea-surface temperatures have warmed by only half a degree Celsius, while an increase in the energy of hurricanes by 70 per cent has been observed.

Sea-level rise and extreme events such as hurricanes and storm surges are threatening the coasts. Coastal protection is thus becoming a key challenge for society, not least in economic terms. Past strategies for protecting and utilizing coastal areas fail to do justice to this development. Novel combinations of measures (portfolio strategies) are called for, whereby the options of protection, managed retreat and accommodation need to be weighed against each other. In particular, coastal protection and nature conservation concerns must be better linked, and the people affected by adaptation or resettlement measures need to be involved in decision-making on such measures.

- Guard rail: Absolute sea-level rise should not exceed 1m in the long term, and the rate of rise should remain below 5cm per decade at all times. Otherwise there is a high probability that human society and natural ecosystems will suffer unacceptable damage and loss.
- Because of anticipated sea-level rise, national and international strategies need to be developed for protection and accommodation, but also for a managed retreat from endangered areas.
- There is a need to improve the linking of nature conservation with coastal protection. The process of drawing up coastal protection plans and strategies for the sustainable use and development of coastal zones must integrate all key policy spheres (integrated coastal zone management).

Adopting innovative instruments of international law for refugees from sea-level rise

Sea-level rise will lead to the inundation of coasts and small island states and thus to migration of 'sea-level refugees'. Under international law as it stands at present, there is no obligation to receive refugees from coastal areas, nor is the question about costs resolved. In the long term, however, the international community will not be able to ignore the problem of refugees from coastal areas and will therefore need to develop appropriate instruments to ensure that affected people are received in suitable areas, ideally areas corresponding to their preferences.

- There is a need for agreements on the reception of refugees from coastal areas and on the apportionment of the associated costs, e.g. by means of a compensation fund. It would be expedient to develop a fair burden-sharing system, under which states make a binding commitment to assume responsibility for the migrants.
- To inform the policymaking process, studies should be undertaken in the fields of law and social sciences.

Halting ocean acidification in time

The dissolution of carbon dioxide in seawater leads to considerable acidification (decrease in pH) and thus to changes to the biogeochemical carbonate balance. The oceans have absorbed about one-third of all anthropogenic CO_2 emissions to date, which has already caused a significant acidification of seawater. Such emissions thus influence the marine environment directly – in addition to the route via climate change. Unabated continuation of this trend will lead to a level of ocean acidification that is without precedent in the past several million years and will be irreversible for millennia. The effects upon marine ecosystems cannot yet be forecast exactly but there is a risk of profound changes to the food web, as calcification of marine organisms may be impeded or in some cases even prevented. We are now seeing on a global scale problems similar to those that arose regionally when lakes acidified in the 1970s and 1980s ('acid rain').

- In order to prevent disruption of the calcification of marine organisms and the resultant risk of fundamentally altering marine food webs, the following guard rail should be obeyed: the pH of near surface waters should not drop more than 0.2 units below the pre-industrial average value in any larger ocean region (nor in the global mean).
- Engineering approaches to mitigate acidification, such as large-scale liming, are not feasible in the oceans. It is therefore important to ensure that anthropogenic CO_2 emissions are limited, regardless of reductions of other greenhouse gas emissions. WBGU thus recommends taking the special role of CO_2 compared to other greenhouse gases into account in the negotiations on future commitments under the United Nations Framework Convention on Climate Change. The consequences of acidification for marine ecosystems and for biogeochemical cycles are still insufficiently understood. Considerable further research is needed in this regard.

Regulating CO_2 storage

Engineering approaches can be used to capture the carbon dioxide arising from the utilization of fossil energy sources, and to compress it and transport it via pipelines or by ship to permanent repositories. CO_2 can be stored in geological formations on land or under the sea floor. Theoretically, the CO_2 could also be injected into the deep sea. Such approaches, however, involve a risk of continuous, slow release of the stored CO_2 into the atmosphere, which runs counter to long-term climate mitigation. The specific benefits and drawbacks of the technical and economic development of sequestration technologies therefore need to be balanced against other climate mitigation approaches such as improving energy efficiency or switching to renewable energy sources.

- The precautionary principle indicates that introducing CO_2 into seawater should be prohibited, because the risk of ecological damage cannot be assessed and the retention period in the oceans is too short.
- Storing CO_2 in geological formations under the sea floor can only be an 'emergency' solution for a transitional period. Permits for such measures should only be granted if they meet strict criteria with regard to technical safety and, above all, with regard to the permanence of storage and its low environmental impact. These criteria should also apply to the use of CO_2 for 'Enhanced Oil Recovery'. CO_2 sequestration must not lead to neglect of sustainable emissions reduction strategies (such as efficiency improvement and the promotion of renewable energies) and should therefore not be supported with public funds.
- Only a proportion of the CO_2 stored under the sea floor should be eligible as prevented emissions when drawing up emissions inventories and for the purposes of the flexible mechanisms in international climate policy. This is necessary in order to take the risk of leakage into account. Specific liability rules also need to be established.

Imposing strict conditions upon methane hydrate mining

Quantities of carbon are stored in the sea floor in the form of methane hydrates that are of the order of magnitude of total worldwide coal reserves. Methane hydrates are only stable under high pressure and at low temperature. Such conditions typically prevail on the sea floor from depths of around 500m downwards; in the Arctic this boundary is somewhat higher. The stability of methane hydrate stocks can be compromised by climate change, by disturbances resulting from mineral oil and natural gas production, or, in the future, possibly by direct mining of the hydrates themselves. WBGU takes the view that the hazard of a sudden release of larger, climate-relevant quantities of methane within this century is very small. Over the long term, however, the slow penetration of global warming to lower ocean layers and sediments could cause gradual methane releases over many centuries to millennia.

- Because of the potential instabilities of deposits, it is important to ensure even now that methane hydrate mining in the oceans is only permitted under very strict conditions. Existing regulatory systems governing ocean mining should be amended and adjusted accordingly.

Complementing the existing financing mechanisms

Measures to mitigate and cope with the anticipated adverse effects of climate change upon the marine habitat can be funded from existing international funds whose task is to finance emissions reductions or adaptation projects. It must be expected, however, that these resources will not suffice for the tasks outlined in the present report, above all because they do not budget for specifically ocean-related projects. To complement these resources, WBGU therefore recommends:

- Fisheries subsidies must be removed in order to avoid providing misplaced incentives for overfishing. The public funds thus released could then be invested partly in marine conservation.
- Charges should be levied on the use of the oceans by shipping, and the revenues earmarked.
- The establishment of microinsurance systems to protect individual assets should be supported as a component of a more comprehensive precautionary strategy, e.g. through public co-financing, especially in developing countries.
- Some of the official development assistance (ODA) resources presently deployed to provide emergency relief worldwide should be diverted into preventive measures.

With this special report, WBGU has taken up an issue that until now has attracted little attention, and whose profound implications are largely underestimated. The state of the marine environment is of elementary importance to the future of the blue planet Earth. Through overexploitation and pollution, humankind has already inflicted great damage on the oceans. Global climate change is presenting a further, completely new dimension of threat. The present report pinpoints the threats and identifies required actions and options that arise at the interface of climate change and the oceans. The report hopes to encourage policy-makers to tackle the necessary measures in time and with resolve, to prevent the oceans from becoming too warm, rising too high and turning too sour.

Introduction

1

The oceans are changing rapidly. Surface waters are warming, sea-level rise is accelerating and the oceans are becoming increasingly acidic, jeopardizing many marine ecosystems. Human activities are unleashing processes of change in the oceans that are without precedent in the past several million years. Humanity is thus interfering with pivotal mechanisms of the Earth System. The oceans play a key role in the carbon cycle of our planet and have absorbed about one-third of total anthropogenic CO_2 emissions until now. Covering more than two-thirds of the Earth's surface, the oceans initially take up the greater part of incoming solar heat and thus determine our climate system. Similarly, the global water cycle is driven mainly by evaporation from the oceans. Finally, the oceans harbour a great wealth of biological diversity and, through fisheries, supply humankind with vital proteins. An intact marine environment is also an important factor for economic development, social well-being and human quality of life.

Recent research is making it increasingly clear that climate change will change and damage the marine environment and the coasts. These effects will also impact severely upon human society. A large and growing part of the population now lives close to coasts. The threats posed to coastal populations and infrastructure by rising sea levels and extreme events such as storm surges or hurricanes will mount in coming decades. Furthermore, together with drastic overfishing, climate change and acidification can endanger food supply from the oceans. There is an urgent need for action now in order to limit the adverse effects of climate change upon ecosystems and human society, especially because, due to the considerable time lags, the present behaviour of humankind will determine the state of the world's oceans for millennia to come. A strong research effort is also needed, for the oceans are still terra incognita in many respects.

One important reason to produce this special report is the changed scientific understanding of sea-level rise and ocean acidification since the Intergovernmental Panel on Climate Change published its last assessment report (IPCC, 2001). Furthermore, recent events such as the unusual hurricane season of 2005, or the ongoing debate on methane hydrates and carbon storage, present a need for WBGU, the German Advisory Council on Global Change, to state its views. By analysing the climatic impacts upon the oceans, WBGU draws attention to the need for and urgency of efforts to engage in vigorous climate mitigation activities and develop appropriate adaptation strategies. WBGU also wishes to contribute its findings to the process of shaping a new European Union policy on seas and oceans.

This special report does not seek to paint a comprehensive picture of the state of the oceans. It does not, for instance, set out to recapitulate the many years of debate on ocean overfishing. WBGU concentrates instead on those key linkages between climate change and the oceans that are the topic of new scientific insights. These insights include new findings on warming, ocean currents, sea-level rise, carbon uptake and acidification, and on the impacts of these factors upon marine ecosystems. The report also discusses in detail the development of tropical cyclones, the issues surrounding carbon storage in the ocean or under the seabed, and the risks associated with methane hydrate deposits in the sea floor. Many of these issues are closely interlinked – coral reefs, for instance, are affected simultaneously by warming, sea-level rise, storms and acidification. Each theme is explored systematically, starting with the physical and chemical fundamentals, proceeding to the ecological impacts, moving on to the consequences for human society, and finally deriving policy and research recommendations on that basis. WBGU embeds its analysis within a normative framework that it has developed – the 'guard rail' approach (Box 1-1). Analogous to the 'climate guard rail' that it developed previously, WBGU now proposes a set of 'ocean guard rails' for the sustainable management of the oceans. These are quantitative boundaries that must not be overstepped.

Resolute and forward-looking action is needed to ensure that the oceans do not cross critical system boundaries within a matter of decades. Overstepping these boundaries would lead to severe and partly

Box 1-1

The guard rail concept

WBGU has developed the idea of guard rails to operationalize the concept of sustainable development (e.g. WBGU, 2004). Guard rails are limits on damage and can be defined quantitatively; a breach of these limits would give rise either immediately or in future to intolerable consequences so significant that even major utility gains in other fields could not compensate for the damage. Guard rails thus demarcate the realm of desirable and sustainable development trajectories. For instance, WBGU has argued repeatedly in previous reports that the average mean temperature should not be allowed to rise more than 2°C above the pre-industrial level. Beyond that value, a domain of climate change begins that is characterized by non-tolerable developments and risks.

The guard rail approach proceeds from the realization that it is scarcely possible to define a desirable and sustainable future in positive terms, in other words as a specific target or state that should be achieved. It is, however, possible to agree on the demarcation of a domain that is recognized as unacceptable and which society wishes to prevent. Within the guard rails, there are no further requirements at first. Society can develop in the free interplay of forces. Only if a system is on course for collision with a guard rail must measures be taken to prevent it crossing the rail. Compliance with all guard rails does not mean, however, that all socio-economic abuses and ecological damage will be prevented, as global guard rails cannot take account of all regional and sectoral impacts of global change. Moreover, knowledge is limited and misjudgement is possible. Compliance with guard rails is therefore a necessary criterion for sustainability, but it is not a sufficient one.

The analogy of road traffic may serve to illustrate the guard rail concept. Guard rails have a function similar to that of speed limits, e.g. a limit permitting a maximum of 50km per hour in built-up areas. The outcome of setting the limit at 40, 50 or 60km per hour can be determined empirically, but in the final analysis the choice of figure is a normative decision, representing an expedient way to handle a risk collectively. Compliance with the speed limit cannot guarantee that no serious accidents will occur, but it can keep the risk within boundaries accepted by society. The guard rails formulated by WBGU build upon fundamental norms and principles agreed by the international community in various forms. They can be no more than proposals, however, for the task of defining non-tolerable impacts cannot be left to science alone. Instead, it should be performed – with the support of scientists – as part of a worldwide, democratic decision-making process. For instance, compliance with the climate guard rail (no more than 2°C global warming) has now been adopted as a goal by the European Union.

GUARD RAILS FOR MARINE CONSERVATION

In the present report, WBGU applies its guard rail approach to the field of marine conservation. This builds upon earlier reports, in which WBGU has repeatedly argued for a two-fold climate guard rail (WBGU, 1995, 2003). The environmental changes in the oceans discussed in this report further underpin the need for the climate guard rail. In addition, the report develops further guard rails. Each is concerned with a specific aspect of the interplay between climate change and the oceans, and is elucidated and argued in a separate chapter. The full set of guard rails is as follows:

- *Climate protection*: The mean global rise in near-surface air temperature must be limited to a maximum of 2°C relative to the pre-industrial value while also limiting the rate of temperature change to a maximum of 0.2°C per decade. The impacts of climatic changes that would arise if these limits are exceeded would also be intolerable for reasons of marine conservation.
- *Marine ecosystems*: At least 20–30 per cent of the area of marine ecosystems should be designated for inclusion in an ecologically representative and effectively managed system of protected areas.
- *Sea-level rise*: Absolute sea-level rise should not exceed 1m in the long term, and the rate of rise should remain below 5cm per decade at all times. Otherwise there is a high probability that human society and natural ecosystems would suffer non-tolerable damage and loss.
- *Ocean acidification*: In order to prevent disruption of calcification of marine organisms and the resultant risk of fundamentally altering marine food webs, the following guard rail should be obeyed: the pH of near surface waters should not drop more than 0.2 units below the pre-industrial average value in any larger ocean region (nor in the global mean).

irreversible damage to nature and human society. The way we manage the oceans now will thus be a decisive test of humankind's ability to steer a sustainable course in the future.

Global warming and marine ecosystems

2

2.1
Climatic factors

2.1.1
Rising water temperatures

The temperatures in the ocean influence sealife as well as the solubility of carbon dioxide in the water. They change the density of seawater, thereby influencing the currents and the sea level: the thermal expansion of water contributes considerably to sea-level rise. The sea surface temperature also affects the atmosphere in a multitude of ways. The mild Atlantic air that is often felt in Europe during the winter obtains its heat from the relatively warm ocean. High water temperatures also lead to increased evaporation, which is an important energy source for the atmosphere (for example, in tropical cyclones) and a source of water for many intensive precipitation events (among others, the Elbe river flood of 2002 in Germany).

Significantly improved data sets of global ocean temperatures covering the past 50 years have become available to researchers in recent years through international efforts in the exchange of data (NODC, 2001). Based on over 7 million measured temperature profiles, Levitus et al. (2005) have reconstructed a time series of the heat content of the world ocean. They report an increase in the amount of stored heat of $15 \cdot 10^{22}$ joules from 1955 to 1998. This corresponds to an average heat absorption of 0.2 watts per m^2 for this time period when averaged across the entire surface of the Earth. For the period from 1993 to 2003 heat absorption was even greater, at 0.6 watts per m^2 (Willis et al., 2004). This increase of heat in the ocean indicates that the Earth is presently absorbing more energy from the sun than it can radiate back into space. This reveals a state of disequilibrium in the heat budget of the Earth, as is to be expected due to the anthropogenic greenhouse effect (Hansen et al., 2005).

Averaged globally and throughout the entire water column, the temperature of the ocean has only risen by 0.04°C since 1955. So far only the surface mixed layer with a thickness of a few hundred metres has warmed, while the average ocean depth is 3800m. The amount of sea-level rise caused by thermal expansion of the water so far is therefore only a small fraction of what will result when the warming extends into the deep sea over the coming centuries (Section 3.1.1).

Figure 2.1-1 shows the variation of the sea-surface temperature, which is very important for the climate system. It shows a strong similarity to the development of air temperatures, but the warming is not as pronounced (0.6°C since the beginning of the twentieth century). These two facts are not surprising. Thermally, the sea surface is closely coupled to the overlying atmosphere. Making up 30 per cent of the Earth's surface, the land masses, because of their lower heat capacity, warm up more quickly than the oceans, so the global mean air temperature rises generally more quickly than that of the ocean. A data set of air temperatures measured by ships at night above the sea surface (Parker et al., 1995) shows a pattern very similar to the water temperatures. These data support the fact of a warming trend in the ocean surface waters and once more confirm the global warming measured by weather stations.

Figure 2.1-2 shows the increase in surface temperatures in the North Atlantic, which in large part range between 0.3 and 1°C over the indicated time period. A significantly stronger warming of several degrees is seen in Arctic latitudes, primarily because of the positive (strengthening) feedback with the shrinking sea ice (Section 2.1.1). Some small areas, however, show a cooling trend due to dynamic changes in the sea. This is particularly true of the Gulf Stream region off the coast of the USA and in regions near Greenland. The reason is probably natural internal fluctuations in the circulation, which superimpose the general warming trend caused by greenhouse gases.

The increase of sea temperatures in tropical latitudes is of particular interest because it influences tropical storms. This will be discussed in Section 3.1.2.

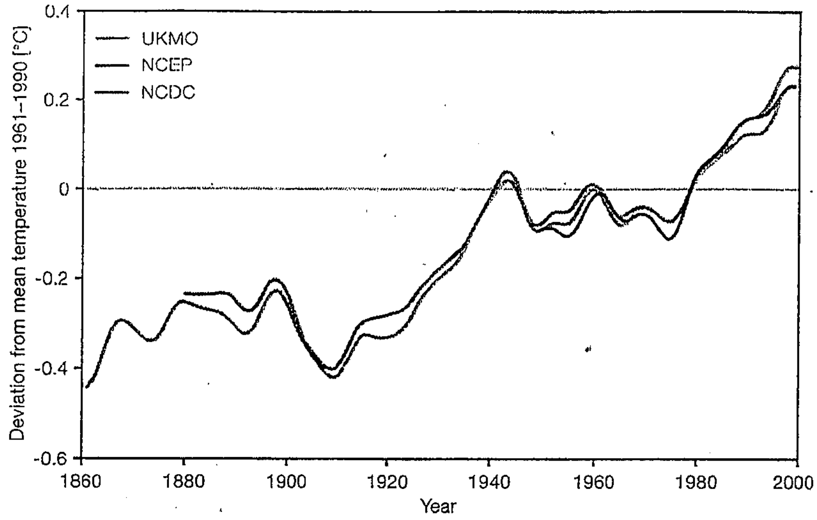


Figure 2.1-1
Globally averaged sea-surface temperature, according to three data centres: The UK Met Office (UKMO, blue), the US National Center for Environmental Prediction (NCEP, black), and the US National Climatic Data Center (NCDC, red).
Source: IPCC, 2001a

2.1.2
Retreat of Arctic sea ice

An especially strong warming of seawater has been observed in the Arctic region in recent decades. This was described in 2004 in detail along with its impacts in an international study (Arctic Climate Impact Assessment; ACIA, 2005).

The study concludes that a significant reduction of the Arctic sea ice has occurred that can not be explained by natural processes, but only by human influences. The ice retreat can be clearly seen in satellite photographs (Fig. 2.1-3). The satellite time series from 1979 to 2005 shows a decline in the ice area of 15 to 20 per cent. The lowest ice extent ever measured was recorded in September 2005. Using a compilation of observations from ships and coastal stations, this development can be extended back to the time before satellite measurements were available. These kinds of observations go back to the year 1900, and cover about 77 per cent of the area of the Arctic region. The long-term data strongly suggest that the present shrinking of the ice cover is a unique event in the past hundred years.

Changes in the thickness of Arctic ice are more difficult to observe than its lateral extent. With the end of the Cold War, measurements by military submarines that had patrolled beneath the Arctic ice became available. These data indicate that the ice thickness may have already decreased by 40 per cent (Rothrock et al., 1999). Other investigations suggest smaller decreases in the thickness. Johannessen et al. (2005) report a decrease of 8–15 per cent, so the actual changes still have to be regarded as uncertain.

Additional knowledge for the Arctic Ocean is obtained from computer models with high spatial resolution, driven by observed weather data. For

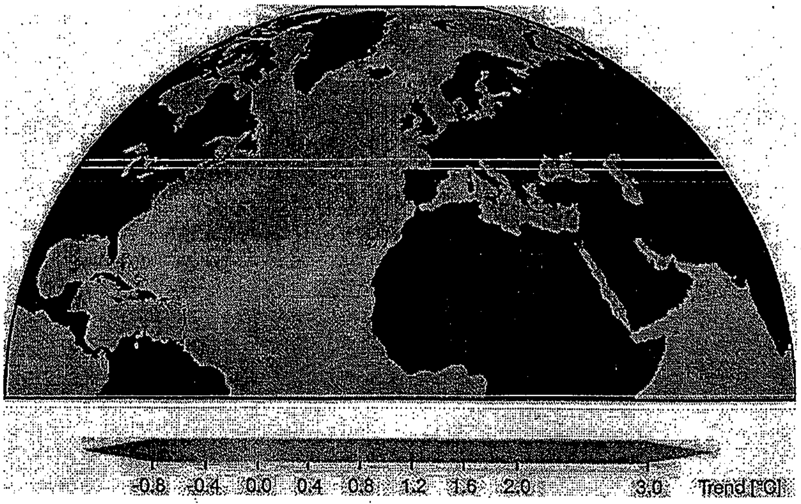


Figure 2.1-2
Development of sea-surface temperatures in the North Atlantic and European marginal seas. Temperature changes of the yearly average between 1978 and 2002 are shown (as a linear trend). Based on the GISST data set of the British Hadley Centre.
Source: PIK, based on Hadley Centre, 2003

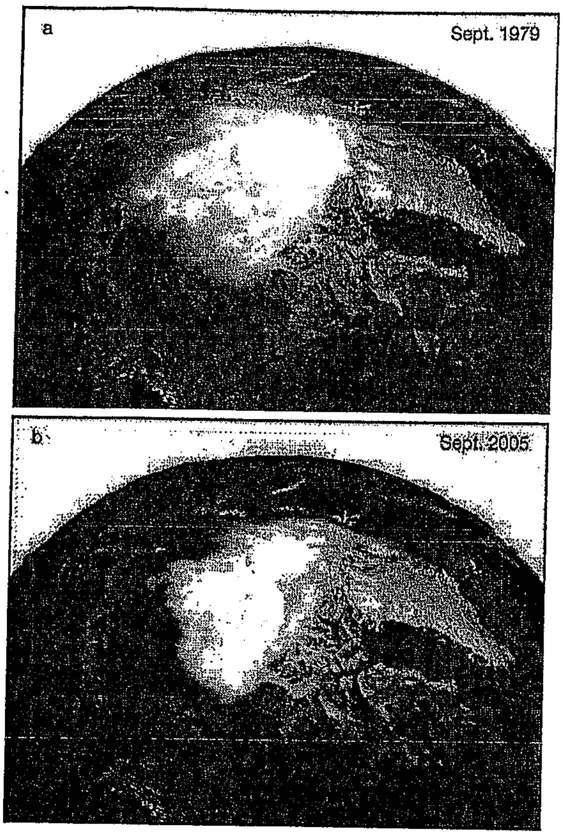


Figure 2.1-3
Satellite photos of the Arctic ice cover, (a) September 1979 and (b) September 2005.
Source: NASA, 2005

recent decades they show a decrease in ice extent that is in agreement with the satellite data as already discussed. In these models the ice thickness decreases more strongly, about 43 per cent since 1988 (Lindsay and Zhang, 2005). Maslowski et al. (2005) obtained similar numbers. If the warming continues unchecked, the scenarios produced by global models indicate that the Arctic Ocean will be practically ice-free in the summer by the end of this century (MPI für Meteorologie, 2005). According to the regional models mentioned, this condition could occur even earlier.

2.1.3
Changes in ocean currents

Since the 1980s scientists have begun to address the question of possible abrupt changes in Atlantic currents and their effects on the climate (Broecker, 1987). The basic problem – a possibly strong nonlinear response of the current to freshwater influx – was recognized as early as the 1960s (Stommel, 1961). In recent years there has been an increased focus by researchers on the probability and the possible impacts of such events. However, the research is still at an early stage and many questions have not yet been answered. The danger of changes in the marine currents was brought to the attention of the public through the 'Pentagon Report' by Schwarz and Randall (2003), which featured in the media in 2004. This report presented a worst-case scenario in which, during the next 10 to 20 years, the North Atlantic Current stops flowing, which would lead to a severe cooling in the North Atlantic region within just a few years. This is, however, a speculative and extremely improbable scenario. In the present situation there is no evidence to support an imminent change in the currents. But in the longer term, and with continued climate warming, this could develop into a serious danger by the middle of this century.

Huge masses of water currently sink from the surface to great depths in the Nordic Seas and the Labrador Sea. From there the water flows southwards at depths of 2–3km to the Southern Ocean (Figure 2.1-4). Balancing this loss of water, warm surface water flows from the south into the northern latitude regions. This results in a large-scale turnover of water in the Atlantic, in which around 15 million m^3 of water per second are transported. Like a central-heating unit, the ocean transports 10^{15} watts of heat to the northern Atlantic region through this process, which is equivalent to 2000 times the total output of Europe's power stations.

Global climate change affects this water flow by decreasing the density of seawater in two ways: first, the temperature increase causes a thermal expansion of the water and, secondly, increased precipitation and meltwater input dilute the seawater with freshwater. This density decrease can retard the sinking of water in the northern Atlantic, the so-called deep-water formation. Particularly in the Nordic Seas a salinity decrease has already been observed in recent decades (Curry and Mauritzen, 2005), although according to modelling calculations this trend is still too weak to have an impact on Atlantic current patterns.

British researchers have recently reported measurements suggesting that the circulation in the Atlantic may have already weakened by 30 per cent (Bryden et al., 2005). The interpretation of these data, however, is still contested in professional circles, in part because they do not agree with modelling calculations or with changes in sea-surface temperatures (Figure 2.1-2), where such a weakening of heat transport should be accompanied by a noticeable cooling. But if the trends of warming and salinity decrease should continue to strengthen in the coming

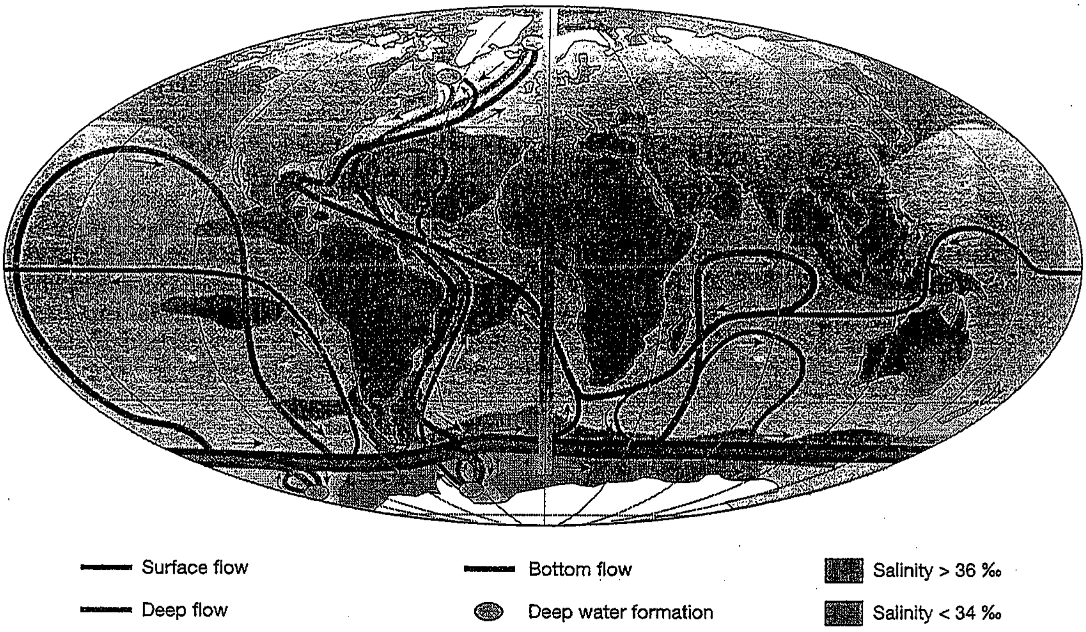


Figure 2.1-4
The system of global ocean currents, primarily showing the 'thermohaline' circulation that is driven by temperature and salinity differences.
Source: after Rahmstorf, 2002

decades, this may actually lead to a noticeable weakening of the Atlantic current over the course of this century, and in an extreme case possibly even to a total cessation of deep-water formation.

In all probability the consequences would be severe. The North Atlantic Current (not the Gulf Stream as is often too simply stated) and the greater part of the Atlantic heat transport would be shut down. This would significantly change the temperature distribution throughout the entire Atlantic region. Depending on the degree of warming that has taken place before, it could even lead to regional cooling to levels below today's temperatures. Southern Hemispheric warming would then be even stronger.

As a result of dynamic adaptation of the sea surface to the altered currents, sea level in the North Atlantic would quickly rise by up to 1m and slightly fall in the Southern Hemisphere. This redistribution of water would not have an immediate impact on the global sea-level average (Levermann et al., 2005). But over the long term the global average would rise by an additional 0.5m due to the gradual warming of the deep ocean after the loss of input of cold water. In addition, the tropical precipitation belt would very likely shift because the 'thermal equator' would drift southward (Claussen et al., 2003). This is indicated both by model simulations and historical climate data.

Initial simulation computations also show a reduction of the plankton biomass in the Atlantic by half (Schmittner, 2005; Section 2.2.2.2). Because of thermohaline circulation the Atlantic is presently one of the most fertile marine regions and most productive fisheries areas of the Earth. In addition, the interruption of deep-water formation would reduce the ocean's uptake of anthropogenic CO_2 (Chapter 4).

A breakdown of the North Atlantic Current is a risk that is difficult to calculate, but which would have severe adverse effects. One critical factor is the amount of freshwater that enters the northern Atlantic in the future. This will depend in large part on the speed at which Greenland's ice sheet melts. A reliable prediction is not possible with the present state of knowledge; at best, a risk estimation can be attempted. For this purpose the Potsdam Institute for Climate Impact Research together with the American Carnegie Mellon University questioned a dozen of the world's leading experts in the autumn of 2004, in detailed interviews lasting around six hours each. Their estimations of the risk of a total stop of deep-water formation and the associated currents varied considerably, but some were surprisingly high (Zickfeld et al., submitted). With an assumed global warming of only 2°C by the year 2100, four of the experts estimated the risk at greater than 5 per cent; with 3–5°C of warming, four of the experts indicated a risk exceeding 50 per cent.

2.2
Impacts of global warming on marine ecosystems

This section focuses on the impacts of climate warming (see Section 2.1) on marine ecosystems. WBGU considers this to include the entire marine realm, from the high seas to aquatically dominated coastal ecosystems. WBGU has deliberately only selected factors that are important to the subject of this special report. Overfishing, considered to be the most significant adverse anthropogenic impact today (Pauly et al., 2002; MA, 2005b), is not discussed. Also not treated here are direct destruction of marine ecosystems, pollution and alien species invasions (GESAMP, 2001; UNEP, 2002). Acidification of the sea is treated in Chapter 4. Togehter, these anthropogenic impacts have already strongly reduced the resilience of many marine ecosystems (Jackson et al., 2001).

The most productive areas in the oceans, the shallow continental shelves (<200m water depth) are the most intensely affected by these impacts. Although the shelves make up less than 7 per cent of the ocean's surface, this is where the greatest proportion of the primary and secondary production takes place, and where the most productive fishing grounds are found (Section 2.3). The primary production of the seas by algae (phytoplankton) is limited to the translucent upper water layer, the euphotic zone (down to approx. 200m water depth). A multitude of secondary producers live from these primary producers, especially zooplankton, fish and marine mammals, both in open water (pelagic) and at or below the sea floor (benthic). All organisms are linked to one another through a complex food web (Figure 2.2-1). For its energy source, the fauna of the dark deep sea is dependent on the organic carbon from the primary production, which sinks to the depths as dead biomass ('biological pump'). Only in the vicinity of hydrothermal vents in the deep sea do bacteria form an independent basis for higher life forms through chemosynthesis.

The coastal ecosystems are also of great biological and economical importance. In addition to their economic utility, some species-rich coastal systems such as wetlands, mangrove forests and coral reefs play a special role in protecting the coasts from flooding and erosion (Section 3.2).

2.2.1
Natural climate variability

The natural variability of abiotic factors in marine ecosystems such as water temperature or ocean currents is relatively great, and often follows non-linear or cyclic patterns. Studying the effects of natural climate variability can provide valuable information about the impacts of global warming. Compared to terrestrial systems, marine ecosystems react more sensitively and quickly to changes in climatic conditions, with unpredictable consequences for species compositions, spatial shifts of populations, or restructured food webs (Steele, 1998; Hsieh et al., 2005; overview by Brander, 2005). As Klyashtorin (2001) has shown, many Atlantic and Pacific fish stocks exhibit close correlations with climate patterns over many decades (Figure 2.2-2), for example, with the atmospheric circulation index, which describes atmospheric conditions in the Atlantic-Eurasian region. Even small natural climatic changes can have significant effects on marine ecosystems and fish stocks – through direct temperature effects, as a result of changes in primary production, or through impacts on important development stages (e.g., juvenile fish stages: Attrill and Power, 2002). For example, the cod stocks off Greenland reacted to a warming of the North Atlantic in the 1920s and 1930s with a rapid expansion to the north (approx. 50km per year) and a considerable increase of stock size, which later decreased again as a result of overfishing and deteriorating climatic conditions (Jensen, 1939). Plankton-feeding fish species in particular, such as sardines or anchovies, show strong natural stock fluctuations, in which large-scale climatic variations play an important role (Barber, 2001; PICES, 2004). The short-term disturbances of the ENSO events (El Niño/Southern Oscillation), for example, have far-reaching, 2- to 3-year effects on the marine ecosystems of the Peru-Humboldt current system (decreased nutrient supply causing lower primary production, partial collapse of fish populations: Barber, 2001) and on the most productive fish stock in the world (Peruvian anchovies: FAO, 2004; Bertrand et al., 2004). The impacts of the ENSO events are, however, reversible, with 'normal' conditions being re-established as a rule within a few years (Fiedler, 2002).

Ignoring small interannual variations, however, regional climatic conditions, along with the structure and dynamics of the ecosystems within a marine region, can also remain relatively stable over a period of many years or decades, defining what is generally referred to as a regime. When this kind of relatively stable situation changes rapidly, within the course of one or two years, it is called a 'regime shift' (King, 2005). Along with these regime shifts, considerable structural changes in the affected marine ecosystem occur, from the phytoplankton up to the highest trophic levels in the food web, including large predatory fish.

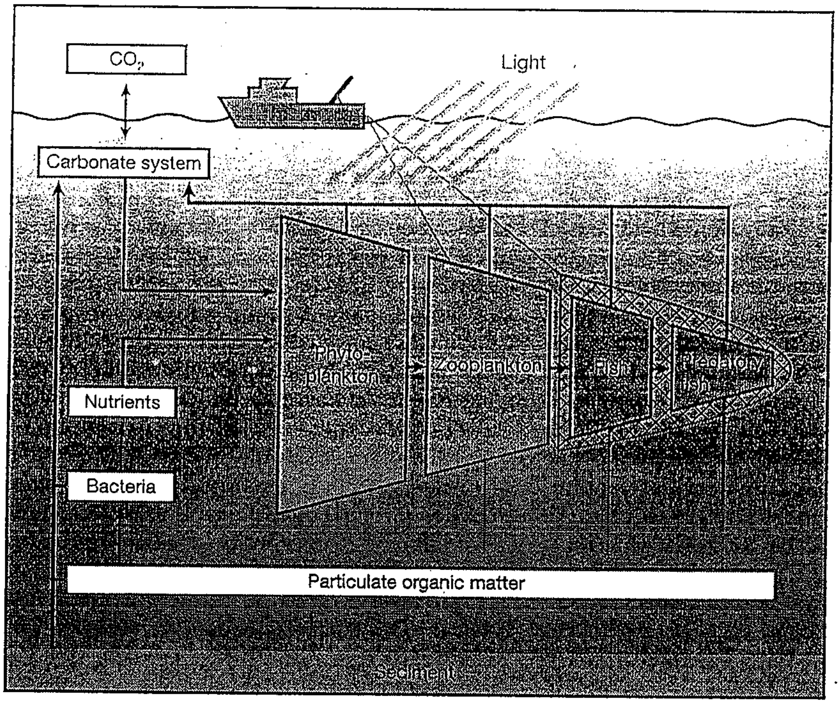


Figure 2.2-1
Schematic structure of a pelagic marine ecosystem. Green arrows: input to primary production; black arrows: interaction with the carbonate system; brown arrows: decomposition of biomass. In the interest of clarity, marine mammals and seabirds are not shown.
Source: WBGU

Regime shifts have been observed often and in various marine regions (King, 2005). In the North Sea in the late 1980s, for example, a regime shift occurred that was related to abrupt changes in surface temperature, wind conditions and a multitude of biological parameters (Reid et al., 2001; Beaugrand, 2004; Alheit et al., 2005). Due to an increase in westerly winds the influx of warm water into the North Sea was strengthened causing, among other things, a degradation of living conditions for North Sea cod. There is probably a connection between this persistent change in the North Atlantic Oscillation and anthropogenic climate warming (Gillett et al., 2003). In the North Pacific off the coast of California, alternating regimes with a period of around 60 years have been documented covering almost two millennia (Baumgartner et al., 1992). They cause a distinct restructuring of the marine ecosystems (Hare and Mantua, 2000; King, 2005).

How regime shifts are triggered and what effects they have in the food web of an ecosystem are not yet thoroughly understood, even though quite detailed observations of changing ecosystem structures do exist. The energy fluxes originating in the phytoplankton, at the base of the food web, often seem to play an important role ('bottom up' control: e.g., Richardson and Schoeman, 2004). However, structural changes can also be controlled 'top down', caused by the collapse of the population of predatory fish, either by overfishing (Worm and Myers, 2003; Frank et al., 2005) or by climatic changes (Polovina, 2005), and reaching down to the lower levels of the food web by trophic coupling.

2.2.2
Human-induced climate change

Although the natural variability can be very large regionally, the global warming trend already predominates in most areas (Figure 2.1-2). The anthropogenic impact on various climatic factors has already had observable effects on the distribution of marine organisms and the species assemblages of marine ecosystems (overview by Brander, 2005). Climate impacts have been described for all levels of the ecosystem, from primary production (Section 2.2.2.2) to zooplankton (e.g., Richardson and Schoeman, 2004) and small pelagic fish species (sardines), all the way up to the large predatory fish (tropical tuna: Lehodey et al., 2003).

2.2.2.1
Effects of water temperature on the physiology of marine organisms

According to the latest findings, temperature has a significantly greater influence on the distribution of animal and plant species than was previously assumed, and this is independent of the position of the organisms in the food web (Huntley et al., 2004).

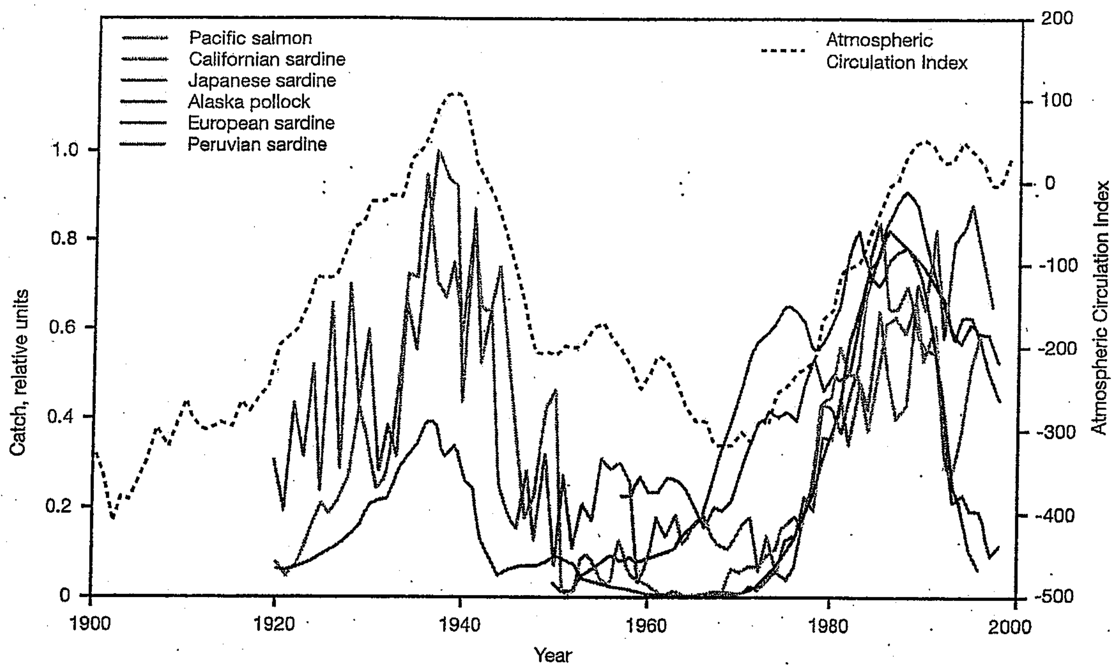


Figure 2.2-2
Correlation of the catch of various economically important fish stocks with the atmospheric circulation index.
Source: compiled on the basis of Klyashtorin, 2001

To a large degree, the window of thermal tolerance in which a species can survive, grow and reproduce determines its distribution (Pörtner, 2005). An increase in water temperature (Section 2.1.1) influences the life of marine organisms both directly and indirectly. A direct physiological impact is seen when the upper limit of the temperature tolerance range for a species is exceeded. This applies, for example, to tropical corals (Section 2.4.1). An indirect influence of increasing water temperature is observed, for example, when organisms previously available temporally and spatially as food for a species are no longer present due to changes in the species assemblage of an ecosystem caused by temperature differences (Section 2.2.2.5). Both of these effect chains can lead to shifts of populations, the invasion of alien species, and even the disappearance of species.

2.2.2.2
Phytoplankton and global primary production

The climatic factors altered by human activities (Section 2.1) initially affect the phytoplankton and therefore primary production. The total marine ecosystem, all the way up through the various trophic levels to the large predators such as tuna and sharks, feeds in principle from the primary production. Therefore, through this coupling, a change in primary production will have an effect on the higher trophic levels of the food web and will be reflected in changed species assemblages or biomasses in the total ecosystem. The primary production is influenced by many climatic factors (Fasham, 2003):

- *Temperature:* Growth and species composition of the phytoplankton are strongly dependent on temperature. Initially, primary production is directly stimulated through warming. But the increased temperature can also indirectly slow down production, for example due to a decrease in nutrient supply resulting from prominent temperature stratification.
- *Light:* Changes in the ice or cloud cover of the surface water have a direct influence on the primary production because the phytoplankton require light as an energy source. The light supply for phytoplankton also diminishes with increased mixing of the surface water.
- *Nutrients:* Climate change can also indirectly influence the supply of nutrients to the phytoplankton (primarily nitrogen and phosphorous, but also 'micronutrients' such as iron: Jickells et al., 2005). Through the sinking of dead organisms from the productive upper layer of the ocean, organic material and thereby nutrients are continuously exported to the deep sea ('biological

pump': Falkowski et al., 2003). The return transport to the upper layers occurs through upwelling currents and vertical mixing, which are influenced by climate in the form of temperature stratification, as well as wind and current conditions (for example, Sarmiento et al., 2003).

In addition to all these factors, climate warming is largely a result of rising CO_2 concentrations. In many phytoplankton species this leads to a direct increase in the rate of photosynthesis, although the various species groups benefit to differing degrees (Section 4.3.1). These various factors are also all coupled with one another. The warming of the surface layers not only increases photosynthesis rates, it also promotes a more stable layering of the water column, which decreases the nutrient supply and weakens the plankton production. The stronger stratification can also destabilize the dynamics of phytoplankton production (Huisman et al., 2006). An increased wind speed, on the other hand, counteracts the temperature effect upon stratification. In the northeast Atlantic the sum of these counteracting effects produces a net increase of phytoplankton in cold-water regions (because here with the good nutrient supply and higher turbulence the improved metabolism rates due to temperature increase are predominant), and a net decrease in warm-water regions (because stronger stratification, under limited nutrient availability, worsens the growing conditions; Richardson and Schoeman, 2004). It is therefore not surprising that these effects are difficult to model and vary greatly from region to region.

Satellite-based observations of the phytoplankton biomasses derived from the chlorophyll content of seawater reveal that the global annual primary production has decreased in nine of twelve ocean regions since the 1980s, and the global average by more than 6 per cent (Gregg et al., 2003). The high northern latitudes account for 70 per cent of the global decline, presumably caused by the worsening nutrient supply due to the rise in temperature. Only three tropical ocean regions (northern and equatorial Indian and the equatorial Atlantic) exhibited an increase. For the North Atlantic, long-term data series based on physical samples show an increase in phytoplankton north of 55 °N and a decrease south of 50 °N (Richardson and Schoeman, 2004). The projections for a future with global warming show contradictory trends. The modelling of Bopp et al. (2001) suggests a reduction of the global marine export production (which correlates well with primary production) by about 6 per cent in the next 65–75 years with a doubling of the atmospheric CO_2 concentrations. Production in the tropics would decline due to stronger stratification and the resulting decrease in nutrient supply, while increasing in the subpolar regions. In contrast, the models of Sarmiento et al. (2004), with large uncertainty, show a slight increase in the global primary production. Again, the effects are regionally highly variable. The authors of the Arctic Climate Impact Assessment consider it probable that moderate warming would promote primary production in the Arctic, mainly due to the reduction of sea ice (ACIA, 2005).

So the available findings are, at least in part, contradictory, and regional observations are not always in agreement with model prognoses. Obviously, our understanding of the critical processes, such as the temperature sensitivity of primary production, is insufficient. The quality of coupled climate, ocean, and ecosystem models presently does not allow any robust conclusions (Sarmiento et al., 2004), although some regional models are already able to represent the connections between the changes in ocean currents and primary production (examples in Brander, 2005).

It is improbable that climate change will lead to the breakdown of the North Atlantic Current, but this possibility cannot be excluded (Section 2.1.3; Rahmstorf, 2000; Curry and Mauritzen, 2005). The simulations of Schmittner (2005) show a completely altered ecosystem situation for this scenario: the biomasses of phyto- and zooplankton in the North Atlantic would decrease by half due to sharply reduced nutrient supply in the surface waters, with corresponding large impacts on ecosystem productivity and structure.

2.2.2.3
Zooplankton

Primary production by phytoplankton is the nutritional basis for the zooplankton (secondary production: often small crustaceans), which is in turn significant as food for the growth of fish populations. Fish larvae in particular are dependent on the synchronous and high availability of appropriate zooplankton, so that fish stocks can replenish and production is maintained. The following examples show that for the zooplankton too, noticeable changes can already be identified as a result of anthropogenic climate change.

In the North Atlantic the distribution of copepods, an important group in the marine food web, has shifted to the north by around 10° of latitude as a result of a combination of changes in the North Atlantic Oscillation (NAO) and human-induced climate change (Beaugrand et al., 2002). For the North Sea cod these changes, along with overfishing, have contributed to poor conditions encountered by the fish larvae and a steady decline of the population (Beaugrand et al., 2003).

Krill (*Euphausia superba*) in the Antarctic have declined significantly since 1976, while other zooplankton species (salps) have increased, which can probably be attributed to the climate-driven reduction of sea ice around the Antarctic peninsula (Atkinson et al., 2004). Because krill is an important food source for fish, penguins, seals and whales, this has led to significant changes in the food web in the Southern Ocean. Investigations of planktonic foraminifera in sediments covering the past 1400 years have revealed an anomalous change in the species assemblages in recent decades. This suggests that the anthropogenic warming of the ocean has already exceeded the range of natural variability (Field et al., 2006).

2.2.2.4
Marine mammals

The warming also causes a decrease in the geographic extent of the Arctic sea ice. This especially affects animals such as polar bears and ringed seals, which are directly dependent on this habitat in their feeding habits and for the rearing of their young (ACIA, 2005).

Polar bears feed almost exclusively on seals, which are bound to the ice habitat. Female polar bears bear their young in caves on the land. In the spring after their winter sleep, in order to reach their hunting areas on the ice, the mother and her young are dependent on ice corridors, because the young animals cannot cross large areas of open water. If the ice continues to recede, they will not be able to reach their hunting grounds. Adult polar bears are good swimmers, and can cover distances in the water of over 100km. Monnett et al. (2005), however, report a doubling of the number of polar bears sighted swimming in open water within a 20-year observation period, as well as most recent finds of four drowned polar bears near Alaska in a location where the ice was over 200km to the north of its normal seasonal limit. Around Canada's Hudson Bay, the area of their southernmost occurrence, the polar bear population has declined by 22 per cent since 1987 (Carlton, 2005). With the loss of the summer sea-ice cover, polar bears are forced into a life on land, where they encounter competition with brown and grizzly bears and increased contact with humans, which reduces the chances for survival of this species.

Scenarios for the Baltic Sea also indicate that the ice cover here will significantly decrease over the next 30 years. The Baltic ringed seal requires a firm ice layer with a snow cover for at least two months for rearing its young. Of the four former breeding areas in the Baltic Sea with separate populations only one suitable area will remain available in the future: the northern Bay of Bothnia (Meier et al., 2004). Initial observations have been reported in the Antarctic, too, that can be attributed to climatic changes. For the past 20 years birth rates of the cape fur seal have been in decline. This decrease correlates with unusually high temperatures of the surface water subsequent to the abundant El Niño events between 1987 and 1998, and it has presumably been intensified by the lowered nutrient supply – primarily krill – for the female seals (Forcada et al., 2005).

These examples illustrate how changes in the ice habitat caused by climatic change can drastically impact the highest trophic levels.

2.2.2.5
Ecosystem impacts

Temperature increases and other factors related to climate change affect groups of organisms in different ways, so that population shifts can occur at different rates and intensities to separate species that previously inhabited the same region or were present at the same time. This decoupling of previously synchronous trophic levels ('trophic mismatch') can produce considerable changes in the ecosystem structure (for example, in the North Sea: Edwards and Richardson, 2004). Climate-induced spatial changes in the phytoplankton distribution can affect both the herbivorous zooplankton and the carnivorous zooplankton, so that fish, seabirds and mammals also have to adapt to the new conditions (Richardson and Schoeman, 2004).

These kinds of large-scale shifts have already been observed at different levels in the food web, for example in the North Atlantic (Beaugrand and Reid, 2003). After an anomalous temperature increase in the 1980s, populations of cold-water species such as euphausids and copepods shifted northward and the stocks decreased, while the smaller warm-water species showed a corresponding increase (Beaugrand et al., 2002). This then led to a decline in the salmon population. For the future, Beaugrand and Reid (2003) expect a continuing decline in the number and distribution of the salmon population, especially at the southern edge of its geographic distribution (Spain and France).

As a result of the displacement of distribution areas of many species toward the poles, the pressure on marine ecosystems increases in the polar regions due to the immigration of new species, while the inhabitants of these regions, adapted to cold temperatures, cannot move to cooler latitudes. They are therefore particularly sensitive to climate change, so that losses of habitats and species are to be expected, especially in the polar marine sea-ice ecosystems (Smetacek and Nicol, 2005; ACIA, 2005). In addition, regional expressions of global warming are especially evident in the Arctic, in part because there is a particularly strong feedback with regional temperatures there as a result of the albedo changes due to retreating sea ice.

It is likely that primary production in the Arctic Ocean will increase due to climate warming, albeit from a low initial level (ACIA, 2005). The increased production can either be exploited by the zooplankton or fall out as sedimentation and provide nutrients for the benthic fauna. In regions with seasonal ice cover, a temporal shift could occur between the phytoplankton bloom and the massive occurrence of zooplankton as well as between the zooplankton and fish larvae due to the climate-dependent changes in the start of ice melting in spring. Such a lack of synchronization would result in a lower share of the primary production being available for higher levels of the food-web. Reliable predictions cannot be made, however, concerning the effect of increased primary production on fish, bird and mammal populations (ACIA, 2005).

An important question is whether anthropogenic climate change can influence naturally occurring regime shifts (Section 2.2.1). With the low resilience of marine ecosystem structures and the intensity of expected anthropogenic climate signals (Section 2.1.1) the possibility that regime shifts in the future will exhibit a different quality, occur more often or rarely, or occur in regions where they have not been previously seen can absolutely not be excluded. The observed acceleration in the periodicity of regime shifts in the North Pacific (King, 2005) could be indicative that there is a link with anthropogenic climate change, although a conclusive judgement cannot be made at this time (Brander, 2005).

The new findings in marine ecology support the increased climate change mitigation efforts that have been called for in previous WBGU reports (e.g. WBGU, 2003), because if climate warming continues unchecked, severe unpredictable and undesirable changes in marine ecosystems cannot be discounted.

2.3
In focus: Climate and fisheries

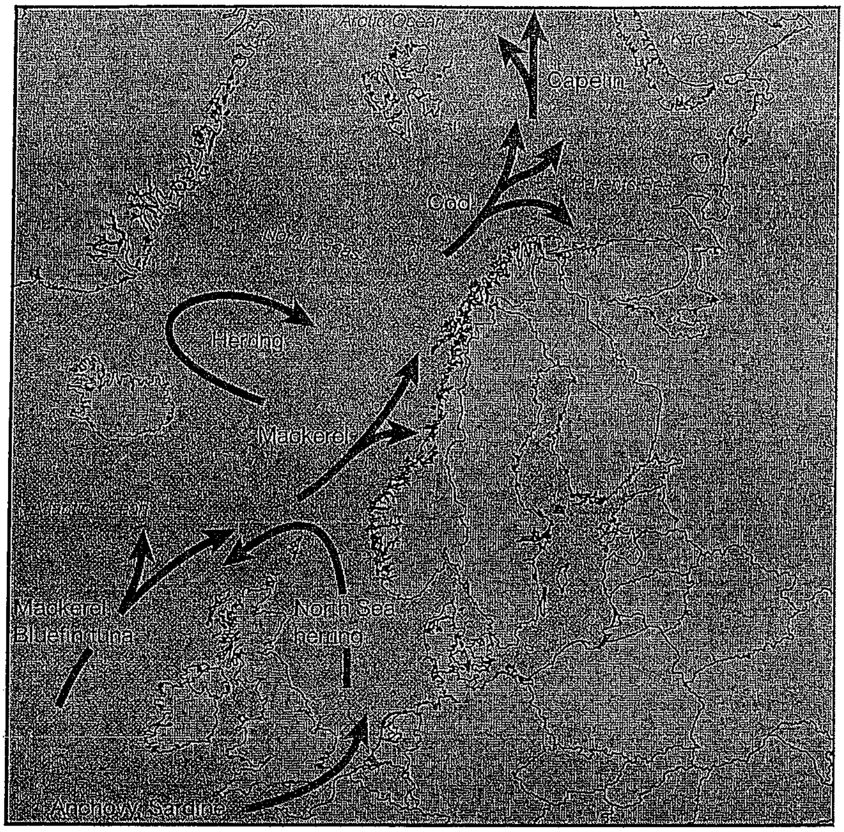
For over 2600 million people fish is the basis of at least 20 per cent of their protein supply (FAO, 2004). Industrial fisheries are growing and are coming into increasing competition with the 30 million traditional fishers, who are often faced with losses in income (World Bank, 2004). World fish production in recent years has remained stagnant at around 130 million tonnes per year, whereby the proportion of fish caught in the sea has slightly decreased and the share of aquaculture has risen (FAO, 2004). Fish stocks are very unequally distributed in the sea: less than 7 per cent of the ocean's area is represented by the continental shelves (water depths <200m), but these account for more than 90 per cent of the global fish catch (Pauly et al., 2002).

At the same time, the human impact on the marine ecosystems of the continental shelves is especially great: overfishing (FAO, 2004; MA, 2005b), including illegal or unregulated fishing (Gianni and Simpson, 2005), degradation and destruction of marine and coastal habitats (such as corals, Section 2.4), the invasion of alien species, pollution of the world's oceans (GESAMP, 2001), and, as a new threat, acidification (Chapter 4) endanger the health of the ecosystems and the sustainability of their use. Poor fisheries management and resulting overfishing are certainly more critical factors for the fish stocks than the anthropogenic climate change observed so far (Worm and Myers, 2004; ACIA, 2005). In the future, however, the latter could also cause a considerable additional burden for marine ecosystems (IPCC, 2001b; Richardson and Schoeman, 2004; Section 3.1.4).

2.3.1
Changes in fish populations

Similar to the terrestrial realm, the species in marine ecosystems often respond to anthropogenic warming with a poleward shift (Parmesan and Yohe, 2003). This is also the case for many of the fish populations in European shelf waters, with increasing evidence of a northward shift due to warming (Fig. 2.3-1). The stocks of cod in the North Sea are decreasing at a rate that cannot be explained by overfishing alone. Today, the upper limit of the thermal tolerance window has already been reached there, with the result that populations are moving northward. The decrease of cod correlates significantly with the changed species assemblage, stock decline and smaller average body size of the zooplankton (Beaugrand et al., 2003), which can probably be attributed to climate change. Fundamental changes in the pelagic ecosystem have been observed in the North Sea from 1925 to 2004, with a clear shift of many populations northward and the immigration of southern species (Beare et al., 2004). These systematic long-term trends correlate with the rising sea temperature. From observations in the North Sea, Perry et al. (2005) conclude that a further increase in temperature will result in additional changes in the species composition and ecosystem

Figure 2.3-1
Likely extension of the feeding area for some of the main fish populations if sea temperature increases.
Source: ACIA, 2005 modified after Blindheim et al., 2001



structure that cannot be predicted in detail, but will probably put considerable adaptive pressure upon commercial fisheries. In various Arctic marine regions, with a regional warming of 1–3 °C, northward displacements of fish populations can be expected, along with the establishment of discrete populations (e.g., cod near Greenland) as well as the immigration of southern species (ACIA, 2005).

2.3.2
Regional prognoses of impacts on fisheries

For some marine regions, especially for waters in the northern latitudes, our understanding of the ecosystem structures and their response to natural climate variability is good enough to discuss possible impacts of climate change. The Norwegian Sea, for example, is a very well studied area (Skjoldal, 2004). Based on experience with natural climate variability it can be assumed that regional temperature increases of 2–4 °C could increase the primary and secondary production of the sub-Arctic part of the Norwegian Sea and therefore improve conditions for fish production (Skjoldal and Sætre, 2004). At the same time, however, the spectrum of species would experience a shift, i.e. warm-water southern species would be introduced to the area.

The authors of the Arctic Climate Impact Assessment (ACIA) also assume that a regional warming of 1–3 °C would improve the conditions for some economically important fish populations, such as Atlantic cod or herring, because the retreat of sea ice would increase both the primary and secondary production as well as allowing these species to spread northward (ACIA, 2005).

Regime shifts with distinct changes in species composition (Section 2.2.1) are not ruled out by the ACIA, but its authors deem that the adaptation of the fisheries sector to the new conditions should not present a great expense. The ACIA comes to the general conclusion that the type and effectiveness of fisheries management – in particular the prevention of overfishing through application of the precautionary principle – will have a greater impact on production in the Arctic than the moderate regional climate change of 1–3 °C that is projected for the 21st century. Accordingly, significant economic or social effects at the national level are not expected, even though individual Arctic regions that are heavily dependent on fisheries could be clearly impacted.

This assessment changes, however, in the case of a more substantial regional climate change (>3°C). While the authors of the ACIA consider it possible that negative consequences could result for fisheries in some Arctic marine regions, they hesitate to make predictions for most Arctic regions due to the incomplete understanding of ecosystem structure and dynamics. Although the Arctic waters have been comparatively well studied, no reliable ecosystem model coupled with climate scenarios currently exists. The assessment of ecosystem impacts therefore must remain speculative. In order to answer the remaining questions, research efforts will have to take a more ecosystem-based approach. Improved numerical ecological models based on integrated environmental monitoring will make an important contribution (Skjoldal and Sætre, 2004; Section 2.7).

2.3.3
Global prognoses of impacts on fisheries

The Food and Agriculture Organisation of the United Nations (FAO) refers to future anthropogenic climate change as an example of the uncertainty justifying a precautionary approach to fisheries management (FAO, 2000). In its report 'The State of World Fisheries and Aquaculture 2002', FAO draws attention to the importance of natural long-term climate variability for the development of fish stocks in a chapter dedicated to this subject. It also points out that global warming could have significant impacts – positive or negative – on some, if not most of the commercial fish stocks (FAO, 2002). It concludes that stocks drastically reduced by overfishing are more vulnerable to climatic changes than sustainably exploited stocks (FAO, 2004). However, FAO's long-term projections are, even today, still based *inter alia* on the assumption that environmental conditions, including the climate, are not changing significantly.

The Intergovernmental Panel on Climate Change (IPCC, 2001b) points to the increasingly acknowledged relationship between natural climate variability and the dynamics of fish stocks and concludes that global warming complicates these relationships and will make fisheries management more difficult. Climate change therefore has the potential, during the coming decades, to become an important factor in the management of marine resources, although the effects will vary widely depending on the region and ecosystem characteristics (IPCC, 2001b).

The authors of the Millennium Ecosystem Assessment also warn about the consequences of climate change, although they have not carried out a detailed analysis. They describe current knowledge about the effects of climate change on marine ecosystems as inadequate. They point out in particular that the response of fish stocks to environmental influences depends, not least, on population size. Healthy stocks with large production of fish larvae can adapt better to population displacement and changes in ecosystem structure. Stocks that are greatly reduced due to overfishing respond more sensitively to environmental influences such as climate change (MA, 2005b) because there is a greater probability that the minimum stock level for reproduction is not attained.

Despite the lack of scientific data, several general recommendations for the management of marine ecosystems and fisheries management can be made. These will be discussed in Section 2.6.

2.4
In focus: Climate and coral reefs

Tropical coral reefs are recognized as the most species-rich of marine biotopes, not so much because of the abundance of species of the reef-building corals themselves (over 835 species have been described), but because of the biological diversity of organisms that live on and from coral reefs, representing an estimated 0.5–2 million species (Reaka-Kudla, 1997). Coral reefs provide important products such as fish and building materials (blocks of coral limestone). They also offer protection from the effects of tsunamis and coastal erosion, and at the same time, because of their aesthetic and cultural value, they are an important source of income from tourism. Although coral reefs only cover 1.2 per cent of the global continental shelves, it is estimated that more than 100 million people are economically dependent on them (Hoegh-Guldberg, 2005). A status report on worldwide coral reefs (Wilkinson, 2004) provides information on their development since the 1950s and raises vital concerns with its estimation of the future trends:

- 20 per cent of all coral reefs have been effectively destroyed and show no immediate prospects of recovery,
- 24 per cent of all coral reefs are under imminent risk of collapse through human pressures,
- a further 26 per cent are under a long-term threat of collapse.

The changes of the past 20–50 years are referred to as the 'coral reef crisis' because the adaptive capacity of corals and the animals and plants associated with them to changing environmental conditions has been exceeded worldwide (Hoegh-Guldberg, 1999; Pandolfi et al., 2003). The pressure from human activities is locally generated, first through poor land management practices, whereby sediments, nutrients and pollutants are released and washed into the sea and damage the reefs. In addition, overfishing, primarily the fisheries using destructive methods (dynamite, cyanide, heavy fishing rigs), reduces the populations of key species on the reef, damaging the function of the ecosystem and reducing productivity. After ecosystem damage, macroalgae have an advantage over the coral in their growth because the feeding pressure by selectively caught fish that normally feed on these algae declines.

In addition to the local stress factors, two results of global climate change are becoming increasingly important to the condition of coral reefs and will therefore be investigated in more detail in this section: the increase in seawater temperature and the acidification of seawater. These two factors contribute individually as well as synergistically, together with the local anthropogenic stressors, to the destruction of coral reefs.

It is only in recent decades that coral reefs were also discovered to exist in deep, dark, cold-water zones in practically all of the world's oceans (Freiwald et al., 2004). Their ecosystems and the serious dangers to them, particularly from bottom-trawl fishing, are currently being researched. Whether they are also threatened by the effects of climatic changes such as temperature change and changes in the availability of calcium carbonate is not clear.

2.4.1
Warming impact on corals

Coral reefs dominate tropical coasts at latitudes between 25°N and 25°S, which corresponds to a seawater temperature range of 18–30°C (Veron, 1986). Along with the atmosphere, the surface layers of the ocean have also warmed in recent decades (Section 2.1.1). In seven tropical regions where corals occur, a warming of 0.7–1.7°C has been measured in the 20th century (Hoegh-Guldberg, 1999).

Since 1979 a new phenomenon has been described with increasing frequency and geographic extent, called coral bleaching. This refers to the loss of single-celled algae that live in symbiosis with the corals. If a coral is subjected to a stress situation, which either in nature or in the laboratory can be produced by high or low temperatures, intensive light, changes in salinity or other physical, chemical and microbial stress factors, the algae will be expelled from the coral tissue. The living tissue of the corals is transparent without algae cells, so the white limestone skeleton will show through – hence the term coral bleaching. This phenomenon is to some extent reversible because algal cells can be taken up again by the body tissue. But after extended periods of coral bleaching the corals die.

Abundant occurrences of coral bleaching were first described in the scientific literature in the early 1980s. Strongly increasing worldwide occurrences correlate with higher surface temperatures of seawater and with disturbances related to El Niño events (El Niño/Southern Oscillation, ENSO). The most intense event by far occurred in 1997–1998, resulting in the death of 16 per cent of all tropical corals worldwide. Regionally the values were even higher, e.g. at 46 per cent in the western Indian Ocean (Wilkinson, 2004).

The strength and duration of the temperature anomalies are important values for predicting coral bleaching. The 'Degree Heating Weeks' (DHW), which aggregate the thermal stress over 12 weeks, were developed as an indicator. One DHW is equal to one week with a temperature of 1°C above the summer maximum during the previous 12 weeks. The USA's National Oceanic and Atmospheric Administration (NOAA) provides an operational early warning system for this. Analyses of the measurement series show that 8 DHW led to coral bleaching in 99 per cent of all cases. Coral bleaching can be predicted today with over 90 per cent probability several weeks before the event occurs (Strong et al., 2000). The worldwide area of coral reefs affected by DHW >4 is continuously increasing (Wilkinson, 2004). Modelling calculations based on IPCC scenarios indicate that between 2030 and 2050 events similar to the anomalous year of 1998 could occur annually, spelling the end of coral-dominated ecosystems (Hoegh-Guldberg, 2005). By combining the data of the NOAA early warning system with global circulation models, Donner et al. (2005) arrived at similar conclusions. According to their research, in 30–50 years coral bleaching will occur every one to two years in the large majority of all coral reefs if the corals do not adapt their temperature tolerance by 0.2–1°C per decade.

An important observation is that the threshold value of seawater temperature for triggering coral bleaching at many locations is only 1–2°C above the maximum summer temperature. Tropical corals are therefore living very close to the highest temperature at which they can survive (Hoegh-Guldberg, 1999). Assuming that the near-surface seawater temperatures will continue to increase, the question is how corals could respond to this temperature increase. Hughes et al. (2003) describe possible responses: a single threshold value for all coral species is unlikely; instead, the threshold values vary within a certain bandwidth depending on coral species, water depth and location. A model in which the different threshold values for the demise of the corals change with time through acclimatization and evolution seems to be most realistic. Symbiotic algae that occur in various genotypes are adapted to different upper temperature limits, for example. After coral bleaching has occurred, heat-tolerant algal groups could be taken up into the coral tissue, offering improved protection against future temperature peaks, and thereby providing some limited adaptation to climate change (Baker et al., 2004; Rowan, 2004). Hoegh-Guldberg (2005), however, expresses the concern that the evolutionary adaptation of corals and algae cannot keep pace with the rapid environmental changes taking place over just a few decades.

Coral reefs could also respond to increased seawater temperatures with a shift of their distribution or a change in their species assemblage. A poleward displacement of the distribution region, however, could only amount to a few degrees of latitude at most, because both the light (for photosynthesis of the symbiotic algae) and the aragonite supersaturation (for calcification) are limiting factors (Buddemeier et al., 2004).

2.4.2
Acidification impact on corals

The acidification of the sea through hydrolysis of CO_2 in seawater (Section 4.1) influences the carbonate chemistry and thereby also affects the corals, which produce skeletons of calcium carbonate (Orr et al., 2005). The formation of limestone (calcification) is not only the foundation for the growth of the coral reefs but also helps to counteract the process of reef erosion. The CO_2-determined impairment of calcification hampers the spread of coral reefs to cooler marine regions. Consequently, both increased temperatures and increased CO_2 concentrations must be expected to drastically constrain the distribution areas of the present-day coral reefs (Hoegh-Guldberg, 2005).

In laboratory experiments simulating a doubling of the CO_2 concentration in the atmosphere, the calcification rate for corals dropped by 11–37 per cent (Gattuso et al., 1999). Modelling calculations by Kleypas et al. (1999) confirm these results. According to their findings, calcification today has already fallen by 6–11 per cent compared to pre-industrial rates. With a doubling of CO_2, a further drop of 8–17 per cent compared to today's rates was calculated. Decreased calcification results in slower expansion of the coral skeleton and therefore a decreased competitive capacity for space in the coral reef. In addition, skeletons of lower density are produced, which are more delicate and vulnerable to erosion.

The calcification rate is influenced not only by CO_2 concentrations but also by water temperature. Increased seawater temperatures can lead to higher metabolic activity and increased photosynthesis rates of the symbiotic algae and thus to increased calcification by the corals (Lough and Barnes, 2000). McNeil et al. (2004) conclude from in-situ investigations and model calculations that the calcification rates of corals in the year 2100 could be at as much as 35 per cent above the pre-industrial rates in spite of decreasing aragonite saturation due to marine warming, presuming an adaptation of the corals to higher seawater temperatures. These hypotheses are scientifically contested (Kleypas et al., 2005). For calcification to increase over the long term the temperature rise of seawater has to remain below the thermal tolerance limit of the corals. So the key question here is whether the tropical corals and their symbiotic algae can genetically adapt their temperature tolerance quickly enough to keep pace with rising seawater temperatures. The question of possibly increased calcification would be moot if the corals die from heat stress.

2.4.3
Measures for coral conservation

Due to the specialization of tropical coral reefs within a narrow range of temperatures, aragonite supersaturation, and high light availability conditions, climate change, in addition to local anthropogenic stress factors, poses a great threat to them. Increasing occurrences of coral bleaching highlight the need for rigorous implementation of climate policy measures. Even the healthiest reefs are not immune to these impacts, as the status report on coral reefs points out (Wilkinson, 2004). It has, however, been found that 'healthy' reefs located in pristine areas have the greatest chance of surviving coral bleaching episodes. So it makes good sense to strengthen the resilience of coral communities through protective measures.

For this purpose the establishment of marine protected areas (MPAs) is considered to be especially effective, preferably in their most stringent form as No-Take Areas, which are closed to fishing (Hughes et al., 2003; Bellwood et al., 2004; Section 2.6.2). The focus on protected areas, however, should not lead to neglect of the remaining much larger reef areas that are not designated as protected. The critical functional groups (communities of particular, often regionally different species that maintain the ecosystem) have to be protected at a regional level; otherwise, the area loses resilience.

2.5
Guard rail: Conservation of marine ecosystems

2.5.1
Recommended guard rail

The guard rail concept devised by WBGU helps to operationalize the guiding principle of sustainable development (Box 1-1). A guard rail for conservation of marine ecosystems can be developed, although it will inevitably be temporary in nature because the scientific basis remains weak. Analogously to the ecological guard rail recommended by WBGU (2001) for terrestrial land and freshwater ecosystems, the Council recommends that at least 20–30 per cent of the area of marine ecosystems should be designated for inclusion in an ecologically representative and effectively managed system of protected areas.

2.5.2
Rationale and feasibility

The rationale behind this guard rail is, among other things, the realization that ecosystems and their biological diversity are vital for the survival of humankind because they fulfil a great variety of functions and provide a whole range of products and services (MA, 2005b). Ecosystem conservation is therefore an indispensable component of sustainable development. In its biosphere report, WBGU (2001) developed five principles that can provide a basis for sustainable management of ecosystems and serve as a background for developing a guard rail for protection of marine ecosystems: (1) preserve the integrity of bioregions; (2) safeguard biological resources; (3) maintain biological potential for the future; (4) preserve the global natural heritage; (5) maintain the regulatory functions of the biosphere.

Protected near-natural marine ecosystems fulfil many important functions for human society (Section 2.6). They play a major role in coastal protection (e.g. protecting coasts from sediment losses, wave erosion and flooding; Section 3.2), water purification, as a fisheries management instrument (Gell and Roberts, 2003; Section 2.6.2.1) and in tourism. They are also indispensable for conserving biological diversity and increasing the resilience of marine ecosystems to anthropogenic stress factors.

Developing a marine protected areas network by the year 2012 has now become an internationally recognized goal (Section 2.6.2.2). Although there is no dispute regarding the normative principles and the value or services provided by marine ecosystems, and the need to protect them, it is very difficult to translate this into a quantitative guard rail because the scientific basis for such quantification remains weak. Moreover, a simple global 'protection standard' is unlikely to meet the needs of different regions with vastly diverse ecological assets and situations. A standard of this sort can therefore only serve as a rough yardstick; it cannot be applied directly to all regions (Bohnsack et al., 2002; Agardy et al., 2003; Rodrigues et al., 2004). Conversely, the current practice of leaving almost all marine and coastal ecosystems open to overexploitation or destruction is certainly not a situation that can be considered tolerable. For this reason, a global guiding principle should be established that helps communicate the considerable deficits that currently exist and make initial progress at least towards slowing the continuing destruction of the natural resource base.

The IUCN World Parks Congress recommended protecting 20–30 per cent of each type of marine habitat (WPC, 2003a), and in the Convention on Biological Diversity this was also the target under consideration, although in the end it was not approved (CBD, 2003). At national level, similar coverage targets are under discussion: USA: 20 per cent (NRC, 2001), Great Britain: 30 per cent (Royal Commission on Environmental Pollution, 2004); the Bahamas, Canada and the Philippines, for example: 20 per cent (Agardy et al., 2003). Australia has demonstrated that these figures are not unrealistic by increasing the Great Barrier Reef protected area in recent decades from less than 5 per cent to 33 per cent. Due to the considerable uncertainties as regards scientific information, specific figures for coverage targets can only be temporary until better data and estimates become available.

Worldwide, significantly less than 1 per cent of the marine area is currently protected (Chape et al., 2005). In view of this fact, in addition to the need to establish a specific coverage target, there is considerable need for action, which is discussed in more detail in Section 2.6.2. As a basis for comparison: on land, around 12 per cent of land areas are protected (WPC, 2003b), which is much closer to the target coverage for ecosystem protection for terrestrial areas (10–20 per cent; WBGU, 2001). In terms of monitoring the implementation of coverage targets, the UNEP World Conservation Monitoring Centre and IUCN represent experienced and competent institutions that would be able to undertake monitoring activities if suitably equipped. There are also reporting obligations to be fulfilled, for example in the context of the Convention on Biological Diversity and the Ramsar Convention.

With coverage targets of this sort – as in the case of terrestrial areas – it cannot be emphasized too often that designation of protected areas is not sufficient in itself to ensure that protection actually takes place; good management and adequate funding are also prerequisites (WBGU, 2001). In addition, the remaining 70–80 per cent of the marine area not covered by protected area status must also be managed sustainably with integrated management concepts based on the ecosystem approach. Protected areas alone cannot stop the loss of biological diversity (WBGU, 2001), especially if overfishing is not halted and if there is a shift in climate zones. In the case of the ecosystems guard rail, moreover, the principle applies that adherence to the guard rail will only provide protection for marine ecosystems if the other guard rails too are implemented, especially the guard rails on climate protection (Box 1-1) and on ocean acidification (Section 4.4). Even the biggest and most proficiently managed protected areas system is only able to mitigate the consequences of unbridled climate change or extreme acidification to a very limited extent: the result would be an intolerable loss of ecological services over a large area.

2.6
Recommendations for action: Improving the management of marine ecosystems

Anthropogenic climate change has the potential to cause considerable additional stresses to marine ecosystems in future (Section 2.2–2.4). It is likewise possible that it will have an impact on commercial fishing, given that the naturally occurring variability in climate already plays a major role in the fluctuation of fish stocks. In some regions, anthropogenic temperature change is on the point of exceeding the highest levels ever reached by natural variability (e.g. in the Arctic: ACIA, 2005). Given the current state of knowledge, however, it is virtually impossible to make globally aggregated forecasts of the impact of climate change on marine ecosystems. As no comparable historical data or empirical figures are available, forecasts would amount to little more than speculation.

Mitigation of climate change, particularly by substantially reducing greenhouse gas emissions (WBGU, 2003; Schellnhuber et al., 2006), is crucial if additional stresses on marine ecosystems are to be limited. One mitigation option of direct relevance to oceans is sub-seabed storage of CO_2 (Chapter 5). Due to the geophysical lag effects of the climate system, however, adaptation measures will be unavoidable even if rigorous efforts are made to reduce emissions. For this reason, adaptation to climate change will be the focus of this section. Priorities set by WBGU in this context are fisheries management and marine protected areas. It makes sense to adopt adaptation measures for other reasons, too, as climate change is only one of many ways in which human influence degrades marine ecosystems (overfishing, destruction and pollution of marine ecosystems, invasion of alien species, etc.; GESAMP, 2001; UNEP, 2002). Even considered separately, each of these factors poses a considerable challenge to the international community.

Coupling and synergistic effects between the different factors call for particular attention (Brander, 2005). A coral reef that has suffered prior damage due to pirate fishing with poison or dynamite will be particularly sensitive to periods of unusually high temperatures (Section 3.3; Wilkinson, 2004). Where stocks of a species have been heavily depleted by overfishing, they will regenerate much more slowly if coastal ecosystems that serve as nursery grounds are exposed to severe stresses as a result of infrastructure measures or pollution, or if there is an additional stress in the form of warming. It is easy to find other examples to add to this list (for an overview, see Brander, 2005). Consequently, it is vital to consider the various factors in an integrated manner if management of marine ecosystems is to be successful. In the coming years, it will therefore become all the more important to rein in current overfishing practices and other destructive anthropogenic factors at the same time, so that marine ecosystems will have sufficient resilience to cope with climate change (Brander, 2005).

For these reasons, the ecosystem approach for promoting conservation and sustainable use of ecosystems and their living resources that was developed under the Convention on Biological Diversity and reaffirmed at the World Summit on Sustainable Development (WSSD) is vitally important (see e.g. OSPAR, 2003). In order to implement this approach, research and monitoring of marine ecosystems and ocean regimes must be improved and this knowledge applied to the assessment and management of fish species of commercial interest (FAO, 2003; Section 2.7). Current knowledge regarding the exceedingly complex interactions between climate, physical and chemical conditions in the sea, marine ecosystems and fishery is inadequate for making reliable predictions relating to how marine systems are likely to respond to climate change (ACIA, 2005; Section 2.7). Inadequate knowledge must not, however, serve as a pretext for delaying conservation and management measures. On the contrary: in accordance with the precautionary principle, action must be taken even if uncertainty prevails. This precautionary principle is already enshrined in multilateral fisheries policy, e.g., in the United Nations agreement on migratory fish stocks.

2.6.1
Fisheries management

National and international institutions face the challenge of dealing with the complex set of anthropogenic factors that currently characterizes the fisheries sector, of making decisions regarding sustainable management of the sector on this basis and, not least, implementing these decisions on the ground. Up to now, the situation has been less than satisfactory: calls for sustainable management of fish stocks, which we have been hearing for decades now and are reiterated time and again at international conferences, have hardly brought about any improvement in the overall situation (although there are some important regional exceptions) (Section 2.3). Half of all fish stocks are fully exploited, while a quarter of fish stocks have already collapsed as a result of overfishing (FAO, 2004). Illegal and unregulated fishing on the high seas continues to be an unresolved problem despite international efforts (FAO, 2001). In the future, this already very difficult situation will be exacerbated by climate change. In addition, new technologies have extended the boundaries of the feasible ever further in fishing, for example fish finding using much-improved sounding technology, and reaching great depths or particular stocks using modern catching methods. Nowadays, virtually no ocean habitat is inaccessible to fishing activities.

For these reasons, management of fishing grounds based on the ecosystem approach and on the precautionary principle is urgently needed in order to maintain the resilience of marine ecosystems (Scheffer et al., 2001; Pikitch et al., 2004). The Agreement on Conservation and Management of Straddling Fish Stocks and Highly Migratory Fish Stocks in the high seas applies the precautionary principle. In FAO programmes, too (e.g. in the Code of Conduct for Responsible Fisheries; FAO, 1995), the precautionary principle and ecosystem conservation have played a major role for some time. The EU's strategy for protection of the marine environment names the ecosystem approach as a key component (EU Commission, 2005), although it excludes fisheries policy from this strategy. Moreover, the binding requirements it sets out are very vague, with the result that the strategy's effectiveness is likely to depend largely on how it is implemented by the Member States.

Broad-based enforcement of sustainable fisheries management is long overdue (Fujita et al., 2004). The scientific and conceptual foundations have already been laid and have been reaffirmed repeatedly in the international policy arena. In many cases legislative provision at national and regional level is already adequate. In the European Union, for example, the Common Fisheries Policy has been endowed with a legal framework that is perfectly acceptable in environmental policy terms. It has yet to be rigorously implemented, however, most notably implementation of adherence to the scientifically-based recommendations from the International Council for the Exploration of the Sea regarding catch quotas. Rapid elimination of excess fishing fleet capacity has also yet to take place (SRU, 2004). It is not the purpose of this section to discuss all the issues relating to global fisheries management and its shortcomings. The aim is rather to formulate recommendations or reinforce existing recommendations relating to the additional problem of climate change and its impact on fisheries.

- A paradigm shift away from publicly subsidized overfishing (SRU, 2004) to a sustainable fisheries sector is long overdue. In order to achieve this, efforts must be urgently intensified to resolve the primary problems of the marine fisheries sector, namely excess fishing fleet capacity, destructive fishing practices, excessive bycatch, inflated catch quotas, illegal or unregulated fishing in the high seas, habitat destruction in coastal ecosystems, and pollution. An increased drive to promote labelling of sustainable marine products is also urgently needed. Implementation of the goals adopted by the World Summit on Sustainable Development (WSSD) is a key yardstick in this context.
- Eliminating subsidies in the fisheries sector is an effective means of slowing overfishing and putting an end to it altogether in the long term. Estimates of subsidies to the fisheries sector worldwide range from US$15–30 thousand million annually (Milazzo, 1998; Virdin and Schorr, 2001). These subsidies should be cut in order to reduce incentives to overexploit the marine environment. At the same time, public funds would be set free for investment in activities that include protecting the marine environment.
- Recent efforts to reduce fisheries subsidies in the context of the WTO are welcomed by WBGU. This relates particularly to subsidies in the OECD countries and especially in the EU (SRU, 2004). The possibility of negative social and ecological consequences arising as a result of cuts in subsidies, particularly in developing countries, due to the search for new ways of earning an income or alternative ways of exploiting the natural environment, must be explored and, where appropriate, taken into account. This must not, however, be allowed to hold up implementation of a swift and consistent change in international policy on subsidies.
- Due to the complex interaction of many factors, both anthropogenic and natural, the integrated

ecosystem approach for promoting conservation and sustainable use of ecosystems and their living resources developed under the Convention on Biological Diversity and reaffirmed at the WSSD is vitally important. On the one hand, monitoring of ocean regimes and ecosystem parameters (e.g. indicator species) must be improved; on the other, the resulting knowledge concerning the state of the ecosystem must be integrated into the process of assessing and managing commercially important fish stocks (FAO, 2003).

- The precautionary principle must be rigorously applied as the basis for fisheries management. Particularly when forecasting fish stock dynamics and calculating catch quotas on the basis of these, safety margins should be included to ensure that stocks do not fall below the minimum required for reproduction and that the age structure of the fish population remains healthy, even in the event of a regime shift induced by climate change (King, 2005). Fisheries management must be enabled to respond to regime shifts in good time and with appropriate strategies (Polovina, 2005). One example of the need to adapt in this way is the cod fishery in the North Sea (Section 2.3.1).
- For short-term management (1–5 years), although anthropogenic climate change will have relatively little impact, interannual variability and climatic events such as El Niño may trigger major effects (Barber, 2001). Assessing and forecasting these factors is an important area where research is needed.
- The role of the future climate is currently largely ignored when developing management strategies for the medium term (5–25 years), either because it is seen as something that can be disregarded or because it is considered impossible to foresee. Since climate change can have considerable impact on recruitment and distribution of fish stocks in the medium term, it will become necessary for fisheries management to take these effects into consideration. At present, the impact of climate variability and climatic events on fish stocks can only be analysed after the event. In view of the fact that climate change is already apparent, forecasting capacity needs to be developed in future and used to conduct risk analyses. This applies particularly to sensitive fish populations on the edge of their natural distribution area.
- When developing the models that are used as the basis for setting quotas, there needs to be a shift away from analysing and modelling individual fish populations of commercial interest to ecosystem-based models that take into account the dynamic interactions between climate, ocean and marine ecosystems (Pikitch et al., 2004). The usefulness of static concepts based on the assumption of unchanging environmental conditions is becoming increasingly questionable.
- In the case of terrestrial ecosystems, subdividing the area in question into zones with varying intensities of use is a long-established procedure for solving land-use conflicts (WBGU, 2001). For the oceans too, in the context of marine spatial planning systems, zoning is increasingly recognized as a useful instrument for sustainable, ecosystem-based fisheries management (Pauly et al., 2002; SRU, 2004; Pikitch et al., 2004; Boersma et al., 2004). Marine protected areas have a special role to play as a component of marine spatial planning in this context because, in conjunction with other measures, they represent an important tool for implementing the ecosystem approach. Recommendations relating to this are discussed in more detail in the next Section 2.6.2.

2.6.2
Marine protected areas

2.6.2.1
Definition and motivation

Climate change, ocean acidification and sea-level rise will have considerable impact on the marine environment (Sections 2.2–2.4). These 'new' anthropogenic factors, moreover, are affecting marine ecosystems which, in many regions, have already been significantly weakened by overfishing, contamination, invasive species and other human-induced influences. Recommendations for improving fisheries management were presented in Section 2.6.1 above. This section will deal with marine protected areas (MPAs), which – like their counterparts on land – are one of the most important instruments available for ecosystem protection (IUCN, 1994; Kelleher, 1999; Murray et al., 1999).

IUCN defines marine protected areas as 'any area of the intertidal or subtidal terrain, together with its overlying water and associated flora, fauna, historical and cultural features, which has been reserved by law or other effective means to protect part or all of the enclosed environment' (IUCN, 1988).

MPAs play a particular role in protecting the marine environment, as they are a direct means of implementing the ecosystem approach, and one of the easiest to apply (Royal Commission on Environmental Pollution, 2004). Although they cannot halt either climate change or acidification, nor altogether prevent invasion by alien or highly migratory species, they are an important tool for enhancing the resilience and adaptive capacity of ecosystems. They are also important because they allow mitigation of anthropogenic factors such as overfishing or habitat destruction within their boundaries by means of management or prohibition (e.g. Mumby et al., 2006). MPAs are thus the most important means, for example, of dealing with coral bleaching (Section 3.3.4), because although they do not tackle the underlying cause, they can enhance the general resilience of the reef (Grimsditch and Salm, 2005). However, enhanced scientific understanding of the relationship between resilience, anthropogenic influence and biological diversity is needed (Section 2.7). For coastal protection, near-natural ecosystems are also important: for example, the Asian tsunami of 26 December 2004 was able to penetrate much further inland in places where the mangroves or coral reefs had been destroyed than elsewhere (Danielsen et al., 2005; Fernando and McCulley, 2005). Protected coastal ecosystems are therefore also an important component of strategies for adapting to climate change (Section 3.4.1).

In addition to their role in ecosystem protection, MPAs can also be useful as a fishery management tool for conservation of commercial fish stocks; e.g. where traditional management has failed and overfishing has resulted, or to safeguard against future mistakes of this sort (Bohnsack, 1998; Pauly, et al., 2002; Gell and Roberts, 2003). Even conservation-based fishery can have a range of negative effects on marine ecosystems, and establishing MPAs can mitigate these (Palumbi, 2003). MPAs can also provide a retreat for species that are fished, but are not subject to monitoring or management. Coastal ecosystems and estuaries are also important for protecting the nursery grounds of many fish species against climate variability (Attrill and Power, 2002). MPAs should be viewed in conjunction with the traditional tools of fishery management, for one reason because quota setting could also be affected by the establishment of a large-scale network of MPAs if fishery activities are restricted to the areas outside MPAs (Hilborn, 2003).

A graded system of protected area management categories is applied in the marine environment too. This ranges from total protection (marine reserves where extractive use is prohibited) to areas serving primarily to uphold sustainable and/or traditional use of marine resources (IUCN, 1994). Areas that are closed to fishing activities (no-take areas) represent a special type of MPA. Different categories of protected area often sit side by side, with core areas under strict protection and peripheral zones with fewer restrictions relating to use (Agardy et al., 2003). The effectiveness of MPAs can be improved if they form part of a protected areas system geared towards ensuring ecological representativeness and creating networks.

Although differences of opinion still persist with regard to the optimum design and management of marine protected areas (NRC, 2001), there is broad consensus that adaptive management, linking of individual MPAs to protected areas systems, participation or co-management and an integrated view of the relationship between MPAs and the intensively exploited areas outside them are important aspects of MPA design and management.

2.6.2.2
International policy objectives

Because of the double use of MPAs for ecosystem conservation on the one hand and as a fishery management tool on the other (Lubchenko et al., 2003), as a guard rail, WBGU recommends designating 20–30 per cent of the marine area for inclusion in a linked system of MPAs (Section 2.5.1). Current protected areas coverage amounts to less than 1 per cent of marine habitats. Considerable catching up is therefore required and it is only very recently that this has led to the formulation of a number of policy objectives in this area:

- At the WSSD, the international community set itself the target of establishing an ecologically representative and effectively managed network of marine protected areas by 2012 (WSSD, 2002).
- The World Parks Congress reaffirmed this goal in 2003 and made it more specific with the recommendation that at least 20–30 per cent of every marine habitat should be strictly protected (WPC, 2003a).
- In the context of its programme of work on protected areas, the Convention on Biological Diversity has adopted the WSSD target for protected areas, albeit without specifying a coverage percentage (CBD, 2004a).
- A regional example is the OSPAR/HELCOM Convention, which has also set itself the target of creating a well managed and ecologically coherent system of marine protected areas by the year 2010 (OSPAR, 2003).

2.6.2.3
Present international law

Although the concept of MPAs or related strategies are used in the different international conventions, they are not used consistently and thus need to be expressed in more concrete terms (Agardy et al., 2003). Policy objectives are set out in the following provisions of international law:

- The Convention on Biological Diversity – whose objectives also cover marine ecosystems – envisages protected areas as an *in situ* conservation measure (Art. 8 a).
- The United Nations Convention on the Law of the Sea (UNCLOS) makes explicit mention of special protected areas only in the following context: Art. 211, para. 6 allows tightening of protective regulations in clearly defined areas in connection with measures to prevent pollution of the marine environment from vessels. Coastal states wishing to apply this provision can designate such an area within their respective exclusive economic zone, and apply to the competent international organization, the International Maritime Organization (IMO), requesting affirmation of the need for special measures to protect this area. Reasons may be related to the area's oceanographical and ecological conditions, its utilization or protection of its resources. Under this provision, however, special measures are restricted to regulations for the prevention of pollution from vessels.
- In various agreements in the field of international law on protection of the marine environment, there are terms and concepts that have similar objectives to MPAs. The International Convention for the Prevention of Pollution from Ships (MARPOL Convention), for example, provides for the establishment of 'Particularly Sensitive Sea Areas' (PSSAs). The purpose of the protected areas in this case is to ensure protection from pollution from ships in particularly vulnerable areas that are to be designated accordingly. Further examples are the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention) and the Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona Convention), both of which have a specific additional annex (OSPAR) or protocol (Barcelona Convention) on the establishment of 'Specially Protected Areas'. IMO has adopted a Resolution (A.885 (21)) setting out procedures for the establishment of PSSAs (Hohmann, 2001).

Requirements for designating protected areas vary according to the maritime area in question. The limits set out under international law depend primarily on the maritime area in which the protected area is to be established in a given case (Box 2.6-1; Proelß, 2004).

- In principle, in the case of internal waters and territorial sea, the coastal state has the freedom to decide on designation of MPAs. This may be limited to a certain extent, but only with regard to restrictions on shipping activities (Box 2.6-1).
- The legal situation with regard to exclusive economic zones (EEZ) is similar. UNCLOS accords particular sovereign rights to coastal states in this maritime area concerning exploitation and conservation of the living and non-living natural resources in the maritime area in question, including the seabed and its subsoil. In relation to establishing MPAs, this means that the coastal state has the freedom to adopt measures so long as these measures are aimed at restricting exploitation of natural resources. However, the establishment of an MPA in this area may not, for example, restrict the right of innocent passage of foreign vessels (Box 2.6-1).
- On the high seas, although the establishment of MPAs is not ruled out in principle (Proelß, 2004), it entails certain legal problems (Platzöder 2001; Warner 2001). These are discussed in Section 2.6.2.4.
- In contrast to agreements that are limited to particular regions (e.g. the OSPAR Convention, the Convention for the Protection of the Marine Environment of the Baltic Sea – the Helsinki Convention, or the Barcelona Convention) there is currently no global instrument of international law that specially promotes designation of cross-border MPAs or places any obligation on states to do so.

2.6.2.4

Marine protected areas in the high seas

There are significant deficits in the legislation pertaining to establishment of marine protected areas in the high seas (CBD, 2005a). The regional multi-functional maritime conventions only cover a very limited range of marine areas outside national jurisdiction, with the result that large areas of the world's oceans are not covered. In addition, existing regional fishery management regimes are limited to particular fished species such as tuna, while species that are not intensively fished are excluded. Application of the ecosystem approach under these regimes is also inadequate.

The United Nations Convention on the Law of the Sea (UNCLOS) reaffirms the right to freedom of navigation, which forms part of customary international law (i.e. it is a right that, in principle, cannot be restricted) (Art. 87 UNCLOS). It is thus out of the question to establish an MPA in the high seas that entails the prohibition or restriction of shipping activities. In addition, states may not conclude agreements establishing MPAs in the high seas that might

Box 2.6-1

Maritime zones under international law

The United Nations Convention on the Law of the Sea (UNCLOS) lays down the fundamental provisions under international law with respect to delimitation of maritime zones, and this is also relevant for designation of MPAs. In brief, the maritime zones under UNCLOS are organized as follows (Figure 2.6-1):

- *High seas:* According to Articles 86 and 89 UNCLOS, 'high seas' are those parts of the sea that are not subject to the sovereignty or jurisdiction of any state and as such constitute 'an area under international administration'. The principle of freedom of the high seas applies in this area. This comprises primarily freedom of navigation and of overflight, freedom to lay submarine cables and pipelines, freedom to construct artificial islands and other installations, freedom of fishing and freedom of scientific research. These freedoms may be exercised by all states, including land-locked states. In the area constituting the high seas, no state may validly purport to impose restrictions of any sort on other states relating to use of the high seas. Furthermore, international agreements between individual states can always only bind the states that are party to the agreement, and not third states.

A distinction is drawn between the high seas and maritime areas that are subject to varying degrees of territorial jurisdiction by the coastal state. According to Article 86 UNCLOS, the maritime areas over which the coastal state has varying degrees of jurisdiction are:

- *Exclusive economic zone:* Here, in the zone that lies on the boundary with the high seas, the coastal state begins to have the right to exercise jurisdiction based on its territorial rights. The corresponding rights of sovereignty, however, are limited insofar as they relate exclusively to exploitation and conservation of the living and non-living natural resources in the zone in question, including those in the seabed and its subsoil.
- *Continental shelf:* This term too is defined in terms of the right to exploit natural resources, although in this case it is specifically those of the seabed and subsoil close to the coast. Thus according to Article 77 para. 1 and 2 UNCLOS, the coastal state exercises over the continental shelf exclusive sovereign rights for the purpose of exploring it and exploiting its natural resources. The definition of resources that applies in the case of exploitation of the continental shelf, however, is somewhat restricted by comparison with that of the exclusive economic zone (non-living resources of the seabed and its subsoil and 'immobile' organisms).
- *Territorial sea:* Here, the special rights of coastal states are no longer limited to exploitation of marine resources, but are identical to actual territorial sovereignty.
- *Internal waters:* This is where the sovereign rights and jurisdiction of a coastal state are most extensive; this maritime zone forms an integral part of a state's territory.

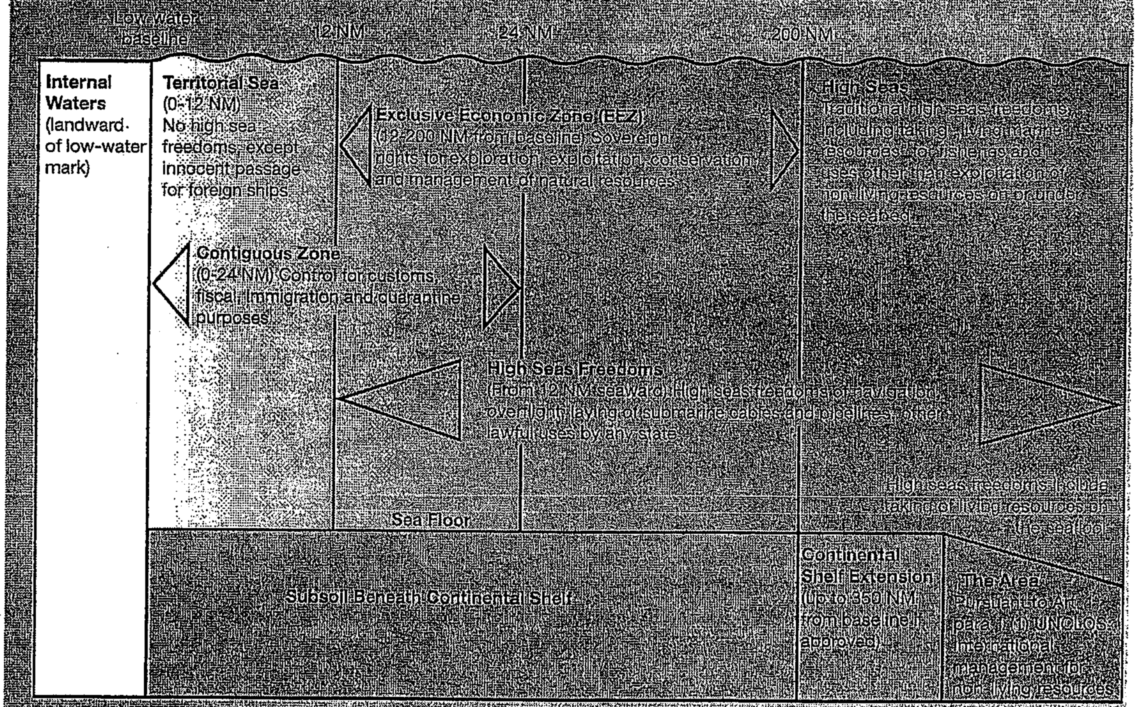


Figure 2.6-1
Maritime zones under the United Nations Convention on the Law of the Sea (UNCLOS). NM = nautical mile (1 NM = 1.852 km).
Source: Gorina-Ysern et al., 2004

be detrimental to third states that are not parties to the agreement. A corresponding commitment agreement among states in a particular region that are the main users of the high seas thus has no binding effect on third states. 'Freedom of the high seas' also includes, for example, the fundamental right of every state to use the marine resources of the high seas (e.g. fishing). In contrast to the case of freedom of navigation, however, this right is not unrestricted, and correspondingly there is a range of international conventions regulating the use of living marine resources in the high seas, especially relating to particular species. Examples include the prohibition on fishing of anadromous species (e.g. salmon, which spawns in freshwater but lives in seawater) in the high seas in accordance with Art. 66, para. 3(a) UNCLOS, or the whale sanctuaries provided for under the International Convention for the Regulation of Whaling (Gerber et al., 2005).

Urgent problems such as the increasing destruction due to fishery activities of sensitive undersea structures that are particularly rich in biological diversity (e.g. seamounts or cold-water coral reefs; UNGA, 2004; CBD, 2004b), and the scale of illegal and unregulated fishing (FAO, 2001), necessitate rapid identification and implementation of solutions for marine protection in the high seas. In view of the clear will of the international community to step up use of marine protected areas as a tool, action is needed to improve provisions pertaining to MPAs in the high seas under international law. In developing a regime for marine protected areas in the high seas, the following specific requirements should be met (CBD, 2005a):

- Moving beyond approaches that focus on specific species or regions, the aim should be to arrive at an integrated approach enabling the creation of large-scale networks for protecting marine ecosystems in the high seas too. Freedom of access to marine protected areas in the high seas should also be guaranteed for scientific research, insofar as this does not run counter to conservation objectives.
- In view of the problem of illegal and unregulated fishing in the high seas – which cannot be tackled by individual states because they do not have territorial jurisdiction to enforce the law in this maritime zone – mechanisms for enforcing the relevant conservation requirements in the high seas must be considered (Platzöder, 2001; Warner, 2001).
- In view of the need to create networks that cover a broad area, efforts should be made to ensure that the establishment of MPAs in the high seas – contrary to what has happened hitherto under the various specific conventions – takes place in a coordinated fashion (CBD, 2005b).

2.6.2.5
Negotiation processes

At global level, negotiations on MPAs are taking place notably in two parallel political processes:

- In the Convention on Biological Diversity, MPAs are on the agenda of a Working Group on Protected Areas, including protected areas beyond the limits of national jurisdiction. However, attempts to agree specific areas of the high seas that might be suitable for designation as MPAs or set a specific target of establishing 5–10 MPAs in the high seas by 2008 have so far failed due to resistance on the part of a few fishing nations (e.g. Iceland, Norway, New Zealand).
- In 2004 an informal Working Group of the General Assembly of the United Nations was established (UNGA, 2004) with a broad mandate relating to marine biodiversity conservation beyond areas of national jurisdiction. This Working Group convened for the first time in February 2006. Although the positions of the different country groups on MPAs still diverge widely, many states acknowledge the need to act to close this gap in international law.

2.6.2.6
Recommendations for action relating to marine protected areas

Despite the importance of marine protected areas, protection of the marine environment must not be reduced to this one instrument alone. Adherence to the ecological guard rail (20–30 per cent of marine ecosystem areas under protection; Section 2.5) is indispensable for conservation of the marine environment, but areas outside MPAs must also be managed sustainably using the ecosystem approach. A particularly important precondition for the success of MPAs is the urgently needed enforcement of sustainable fisheries management (Section 2.6.1). Another precondition is adherence to the guard rails on climate change and ocean acidification (Box 7-1), without which even an excellent protected areas system will lose most of its impact. In addition, it is not sufficient to plan, designate and link MPAs; they must also be well managed and adequately funded. Only in this way is there a chance that the target of significantly reducing the rate of loss of biological diversity by 2010 can be met in marine environments too.

IMPLEMENTING INTERNATIONAL TARGETS

- The rate of growth of MPA coverage, currently 3–5 per cent per year, is much too low to meet the internationally agreed targets on time, given that current coverage is less than one per cent (Wood et al., 2005). Efforts in this regard need to be intensified significantly.
- MPAs should be sufficiently large and linked with one another in protected area systems; they should encompass zones with different forms and intensities of use and be part of an integrated system of management that includes neighbouring continental shelf and coastal areas. In addition, they should be designed to be flexible and adaptive, since climate change may impose the need for reorganization if ecosystem processes change or shift in location (Soto, 2002). Improving the scientific basis in this context should be carried out in parallel with ongoing management activities. Adaptive management strategies and flexibility are crucial to deal with local impacts of climate change that are difficult to forecast.
- In the territorial sea and in EEZs, states can begin to implement international objectives now without coming up against problems relating to international law. The EU Habitats Directive and Birds Directive are both fully applicable in EEZs. In Germany this has already taken place: in the context of the Natura 2000 network, around 30 per cent of the German maritime area of the EEZ has been registered as protected areas with the European Commission. However, imposing restrictions on fishing is not a straightforward matter at present, as this is an area in which EU competences apply. MPAs should be used more effectively as a tool for sustainable fisheries, for example by setting long-term or temporary limits on fishing activities in protected areas (SRU, 2004).
- In developing countries particularly, there is a great deal of catching up to be done. In these countries, not only are there very few MPAs, but the designated protected areas in many cases amount to little more than 'paper parks' in which effective protection is not or cannot be enforced. Development cooperation should therefore make designation and management of MPAs a priority. In doing so, cooperation should take place between protected areas specialists and fishery representatives, and the local population should be involved in planning and management.

SECURING FUNDING

Due to the difference between the guard rail for protection of marine ecosystems (20–30 per cent coverage) and current coverage (less than 1 per cent of marine ecosystems are currently protected; Section 2.5.2), the need for additional funding is considerable. According to the findings of Balmford et al. (2004), the annual costs associated with protecting marine ecosystems on this scale would be in the region of US$5–19 thousand million. This figure includes both ongoing costs and one-off costs relating to implementation. Indirect costs, however, such as costs to businesses in the fisheries sector arising as a result of fishing exclusion, are not included.

- WBGU considers it to be the responsibility of national governments and the international donor community to ensure adequate funding for management of marine protected areas. Up to now, it has often proved impossible to ensure availability of adequate long-term financing: payments from public donors are often small and there are competing demands on these resources. The same applies to international transfer payments such as those made by the Global Environment Facility (GEF) or by donors in the context of bilateral development cooperation (OECD, 2002; GEF, 2005a). WBGU calls upon public donors to undertake additional efforts to make adequate funding available on a sustained basis. Complementary funding may be raised by means of instruments such as user charges or promoting private donations for conservation measures (Emerton, 1999; Morling, 2004).

PROTECTED AREAS IN THE HIGH SEAS: CLOSING GAPS IN INTERNATIONAL LAW

The ongoing process of political negotiations to develop an instrument for designating and managing protected areas in the high seas is to be welcomed, and the German Federal Government should give this process vigorous support. The basis for this is UNCLOS. Despite the fact that UNCLOS lays greater emphasis on rules pertaining to usage than on protection and conservation of marine resources, it nevertheless also provides the primary legal framework for protection of the marine environment (Platzöder, 2001). Fundamentally changing UNCLOS is not a political option, whereas adding moderate supplementary provisions to the current law of the sea seems feasible in both political and legislative terms. Options for doing this include the following:

- The primary task is to develop a multilateral agreement on designation of protected areas and corresponding systems in the high seas and append this to UNCLOS, either as an additional protocol or as a supplementary convention. A precedent already exists for this type of procedure in the form of the Agreement relating to the Conservation and Management of Straddling Fish Stocks and Highly Migratory Fish Stocks that is tied to UNCLOS, and which is concerned primarily with the exploitation of relevant fish species in areas outside national jusrisdiction.

- It would make sense to assign the monitoring and coordination tasks to the same – yet to be established – international regime. From a legal perspective, the mechanism should be laid down primarily in the above-mentioned multilateral agreement. With regard to this, the proposal to establish a Global Oceans Commission, put forward at the first International Marine Protected Areas Congress in 2005 in Geelong (Australia), can be considered as being along the right lines.
- The Convention on Biological Diversity (CBD) should also be amended or supplemented accordingly, whereby care will need to be taken to avoid overlap. The CBD has developed considerable expertise in the field of biodiversity conservation, and should therefore be involved in the UNCLOS negotiation process, for example by providing expert input. At the same time, the new regime's functions and areas of responsibility should be explicitly recognized by the CBD. In order to achieve this, the relevant CBD negotiation processes should be intensified with the aim of securing a key role for the CBD in the design of MPAs in the high seas in terms of content, e.g. deciding on appropriate instruments and criteria for the selection of MPAs. With a view to supporting cross-border conservation efforts, it would be useful to explore whether it would be worthwhile developing a protocol to the CBD on protected areas in the medium term based on the findings of the current Working Group. Such a protocol should cover the whole spectrum of protected areas and not merely MPAs.
- The informal Working Group of the General Assembly of the United Nations on marine biodiversity in areas beyond national jurisdiction has taken the first step towards closing the gap in international law regarding MPAs in the high seas. At the next UN General Assembly, the German Federal Government should urge that this sound basis be used to ensure continuation of the negotiation process.

2.7

Research recommendations

RESEARCH INTO CLIMATIC FACTORS

- *Behaviour of sea ice:* Possibilities for monitoring changes in the thickness of Arctic sea ice in particular remain inadequate, and sea ice simulation models need to be developed further in order to improve estimation of future sea ice dynamics.
- *Behaviour of continental ice:* The future behaviour of Greenland's continental ice sheet is likely to be decisive for the future dynamics of ocean currents in the Atlantic. Methods of modelling continental ice sheet dynamics need to be improved significantly.
- *Stability of Atlantic circulation and risks of changes in currents:* Climate models continue to differ considerably as regards the information they provide on the future stability of ocean currents. Reasons for this include internal oceanic processes (such as mixing), which as yet are poorly understood, and interactions with other climate components (e.g. the freshwater budget of the North Atlantic), which are difficult to quantify. Observation and enhanced modelling efforts could help to reduce the uncertainties in this area.

RESEARCH INTO MARINE ECOSYSTEMS, FISHERIES AND MARINE PROTECTED AREAS

- *Monitoring:* Observation data covering large areas of the oceans over long periods are vital, particularly as regards the nutrient situation and plankton (especially zooplankton). Because they provide, among other things, important inputs for modelling marine ecosystems, support should be given to appropriate monitoring programmes (e.g. using the Continuous Plankton Recorder).
- *Understanding the systems involved:* Too little is known about the structure and dynamics of marine ecosystems to be able to make reliable estimates of the impact of climate change. Examples include the significance of temperature effects on primary production, the impact of sea-ice retreat, or decoupling of trophic levels as a result of disparities in species' responses to climate change (e.g. migration, adaptation). Increased emphasis should be given to ecosystem-based research approaches with a view to enhancing understanding of the relationships between anthropogenic disturbance, biological diversity and resilience of marine ecosystems and incorporating this into new ecosystem models. The international research project GLOBEC and the new IMBER project have drawn up a detailed catalogue of issues (GLOBEC, 1999; IMBER, 2005). Promotion of these interdisciplinary research initiatives by national research promotion agencies should be stepped up.
- *Modelling marine ecosystems:* In order to gain a better understanding of the impact of changes in climatic factors (temperature, wind and ocean current patterns, etc.) on marine ecosystems, knowledge regarding the various ecosystem components must be integrated into improved ecosystem models and coupled with recent climate/ocean models.

- *Improving the basis of fisheries management:* In order to implement the ecosystem approach in fisheries management, there needs to be a shift in focus in terms of model development away from examination of individual fish species under the assumption of constant environmental conditions to a more integrated ecosystem modelling approach. Qualitative models should also be used to achieve this, incorporating expert knowledge regarding processes in dynamic systems (Kropp et al., 2005). Special attention should be paid to the impact of natural climatic variability and anthropogenic climate change on fish population dynamics, as well as to the socio-economic consequences and possible adaptation measures.
- *Design and management of marine protected areas:* Development of the theoretical basis for the design of marine protected areas should move away from the study of individual species towards multi-species, ecosystem approaches. Of particular importance in this context is the networking of MPAs with one another and with concepts for sustainable use of the surrounding coastal and marine areas. There are many unanswered questions regarding the design of MPAs in view of climate change and the potential for adaptation. In line with the principle of adaptive management, research and monitoring issues need to be given greater consideration in the design and management of MPAs. The basis for defining guard rails and coverage targets needs to be improved, particularly the basis for designating the proportion of an area that should be strictly protected (no-take areas). Furthermore, there is a need to increase research evaluating participatory approaches (e.g. community-based management) and the use of traditional knowledge, and to evaluate approaches that draw on management experience within the local population.

Sea-level rise, hurricanes and coastal threats

3

3.1
Climatic factors

3.1.1
Sea-level rise

3.1.1.1
Lessons from Earth's history

A rise in sea level is one of the unavoidable physical consequences of global warming. A close link between temperature and sea level is also evident in climate history. At the peak of the last ice age (around 20,000 years ago) sea level was around 120m lower than today, and the climate was about 4–7 °C colder. By contrast, during the last warm period, the Eem (120,000 years ago), the climate was slightly warmer than today (by approx. 1°C), but sea level was probably several metres higher – estimates vary from 2 to 6m (Oppenheimer and Alley, 2004). Going back farther into the Earth's history, one can find even warmer climate epochs. Three million years ago, during the Pliocene, the average climate was about 2–3 °C warmer than today and sea level was 25–35m higher (Dowsett et al., 1994).

The main reason for these large sea-level changes is the change in quantities of water that are tied up on the land in the form of ice. The 'sea-level equivalent' of the ice mass on Greenland equates to 7m, the West Antarctic ice sheet to 6m, and the East Antarctic ice sheet to more than 50m. Around 35 million years ago (in the Eocene) was the last time our planet was completely free of polar ice caps, thanks to high CO_2 concentrations related to the plate-tectonic situation at the time, and sea level was almost 70m higher than today (Zachos et al., 2001; Barrett, 2003). In this kind of time frame, however, volume changes in the ocean basins due to plate tectonics can also contribute to sea-level changes.

Plotting the values above on a graph (Fig. 3.1-1) reveals a relationship between temperature and sea level, where a global warming of 3 °C corresponds to a sea-level rise of several tens of metres. This is an order of magnitude more than the IPCC expects by the year 2100 (9–88cm; IPCC, 2001a). The main reason for this apparent discrepancy is that the relationship shown in the figure is based on a climate near equilibrium (following many millennia with relatively constant temperatures) – not during rapid changes as they are now occurring. The numbers give a general idea of how sea level would change after millennia with a 3 °C warming. But they do not allow any conclusions about how fast the ice masses could melt with warming and how quickly sea level could rise in response.

The end of the last ice age provides information about the possible rate of sea-level rise. At that time the global average temperature rose by around 4–7 °C, an amount that is also reached in pessimistic scenarios for the future. But the warming at that time took around 5000 years, which is much slower than the present trend. From 15,000 to 10,000 years ago sea level rose by around 80m, an average of 1.6m per century (Fairbanks, 1989). During some intervals

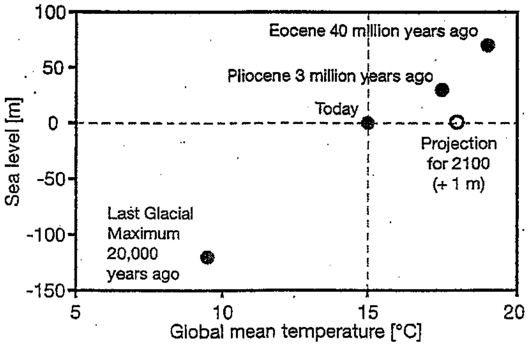


Figure 3.1-1
Mean global temperature and sea level (relative to today's) at different times in Earth's history, with the projection for the year 2100 (1m above today's sea level). For the long term a much higher sea-level rise probably has to be assumed than that predicted for 2100.
Source: after Archer, 2006

rates of up to 5m per century were reached (Clark et al., 2004).

These values cannot simply be applied to today's situation. The ice sheets at that time were considerably larger, which means the melting regions on the margins were greater, allowing a greater flow of meltwater. In addition, due to Earth's orbital cycles around the sun (Milankovich cycles; Ruddiman, 2000), the incoming solar radiation at high latitudes of the Northern Hemisphere was considerably stronger, a situation that cannot be directly compared with the global increase in greenhouse gas concentrations. These two factors suggest higher melting rates at the end of the ice age than during the present warming. The much slower warming at that time, by contrast, would suggest lower melting rates. In fact, the disappearance of ice sheets at that time for the most part kept pace with the gradual climate warming, so the assumption that ice masses would have melted significantly more rapidly with faster warming is quite plausible.

Two conclusions can be drawn from this discussion. Firstly, rates for sea-level rise of up to 5m per century are documented, and these probably do not represent an upper limit. Thus climate history shows that a much more rapid rise than that expected by the IPCC for the 21st century is possible. Secondly, such rates of sea-level rise suggest dynamic melting processes of the ice sheets, also taking account of the conditions at the end of the last ice age. This means there can be not only a simple melting through contact with warmer air, but also an accelerated flow of the ice into the sea.

3.1.1.2

Dynamics of the continental ice masses

The Earth presently has two large continental ice sheets with a thickness of 3–4km, in Greenland and Antarctica. Both are in a steady-state: in the centre new ice is continuously formed by snowfall, while ice flows away on the margins. Under persistently constant climatic conditions these processes are in balance and the size of the ice mass does not change. But in the Antarctic it is significantly colder than in Greenland. In Greenland, therefore, a large part of the ice at the margins melts while still on the land (like on a mountain glacier), while in the Antarctic it reaches the sea and tongues of the ice float on the water to form ice shelves.

It is still difficult to reliably measure changes in the total volume of these two ice masses. Efforts include elevation profiles taken from satellites and aeroplanes. There is still controversy over the margin of error of these measurements; they do not accurately record the craggy topography often found on the margins of the ice sheets. Newer techniques include satellite measurements of anomalies in the gravitational field. Changes at the margins of the ice masses are best obtained by local measurements and determination of the flow rate of the ice by satellites.

The various measurement methods provide the following qualitative picture for both ice sheets: in the past ten to twenty years, the thickness in the centre seems to be increasing somewhat, as should be expected with climate warming because of increased snowfall. On the other hand, increasing dynamic melting processes can be observed on the margins. The quantitative net balance of these processes is not exactly known, so a short discussion of the current measurement results follows.

In Greenland around half of the ice flows out of only 12 fast-moving outlet glaciers; the mass balance of the ice depends largely on changes in these ice flows (Dowdeswell, 2006). New data show that the flow rates of many of these glaciers (among others the Jakobshavn Isbrae) have doubled in recent years (Joughin et al., 2004; Rignot and Kanagaratnam, 2006). Furthermore, measurements of the melt area, which can be determined from satellite pictures, show an increase of around 25 per cent from 1979 to 2005 (Fig. 3.1-2); the area reached its highest extent ever in the year 2005 (Steffen and Huff, 2005). When the area that is affected by melting increases, it should cause a loss of mass in the ice cap. It has also been found that meltwater from the ice surface runs through holes (so-called glacier mills) to the base of the ice and acts like a lubricant there, accelerating the flow of the ice (Zwally et al., 2002).

Rignot and Kanagaratnam (2006) conclude that the acceleration of the ice flow represents a loss of mass corresponding to 0.5mm of sea-level rise per year, and that this value has doubled in the past ten years. This is equal to one-sixth of the current measured global sea-level rise (Fig. 3.1-4). This is in contrast to measurements of the elevation of the ice by satellite altimeters (Johanessen et al., 2005; Zwally et al., 2005), which indicate an increase in the mass of the Greenland ice (corresponding to a sea-level change of -0.03mm per year), but which do not accurately register the small-scale processes at the margins. Because this increase is significantly smaller than the loss observed by Rignot and Kanagaratnam, a net mass loss of Greenland ice has to be assumed, although there are considerable uncertainties in the numbers, and the various measurement methods yet need to be better reconciled.

More important, however, than the present changes in mass balance, which are still small and impossible to record accurately, is what is to be expected in the future with progressive warming.

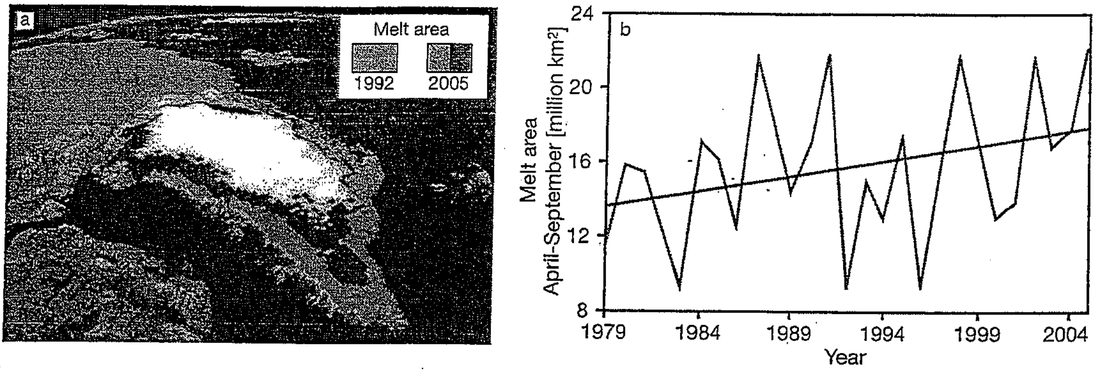


Figure 3.1-2
Extent of melt area on Greenland according to satellite data. The two extreme years 1992 (after the eruption of Pinatubo) and 2005 are shown (a), and the development over time (b).
Source: Steffen and Huff, 2005

Model calculations show that with a warming of the near-surface air layer above Greenland of about 2.7 °C or more, it is likely that the entire ice sheet will gradually melt (Gregory et al., 2004). Chylek and Lohmann (2005) estimate that the warming over Greenland is 2.2 times the global warming (a result of climate change feedbacks near the poles), so that the critical warming over Greenland could be reached with a global warming of only 1.2 °C.

The rate at which Greenland ice could melt – and therefore sea level could rise – is still an open question. The last IPCC report assumed a relatively simple model with conservative estimates using the difference between melting and snowfall, and concluded a duration for melting of several millennia (IPCC, 2001a). But that report did not consider the dynamic flow processes discussed above, which have since been observed and could imply a much faster reduction of the ice. This process is not taken fully into account in present ice models.

For the Antarctic ice masses the 2001 IPCC report predicted no melting, but, in contrast, a slight growth of ice due to increased amounts of snowfall. New data, however, also indicate a mass loss in the Antarctic and a dynamic response of the ice, especially in the smaller West Antarctic ice sheet. In February 2002 there was a spectacular collapse of the millennia-old Larsen B ice shelf off the Antarctic peninsula after warming in this region (Fig. 3.1-3). This has no direct effect on sea level, because ice shelves float on the sea and their mass displaces a corresponding amount of water. But it evidently has effects on the continental ice: the ice flows behind the Larsen B ice shelf which flow down from the continent have strongly accelerated since then (to up to eight times the speed: Rignot et al., 2004; Scambos et al., 2004). The floating ice shelves hang in part on projecting rocks, hence impede the flow of the ice into the sea. The flow of continental ice has also accelerated in other areas of the Antarctic, for example, in Pine Island Bay (Rignot et al., 2002). In addition, it has been shown that the melting rate of the ice flow where it reaches the sea is very sensitive to the sea temperatures: per 0.1 °C rise in the water temperature the melting rate increases by one metre per year (Rignot and Jacobs, 2002). Thus, if the water temperatures around the Antarctic increase or if large ice shelves like the Ross Ice Shelf should one day disappear, then one has to assume that there will be a corresponding acceleration of the flow of the West Antarctic ice sheet.

Latest data from the GRACE satellite, which can precisely measure anomalies in the gravitational field, indicate a shrinking of the Antarctic ice masses by 152km³ per year over recent years. This equates to a contribution to sea-level rise of 0.4mm per year (Velicogna and Wahr, 2006). The head of the British Antarctic Survey, Chris Rapley, has called the Antarctic in this respect an 'awakened giant'.

Overall, the new observations suggest that the last IPCC report could have underestimated the future sea-level rise. A dynamic disintegration of the ice sheets could possibly occur within a time frame of centuries instead of millennia. Unfortunately the presently available ice models do not permit a reliable prognosis for the further development of the ice sheets. This uncertainty weighs even heavier because, with the positive feedback processes, the deterioration of the ice sheets will be difficult to stop once it has begun. These feedback processes include the lubrication of the undersides of glaciers with meltwater from the surface and the frictional heat due to faster flowing, as well as the lifting of shelf ice from its resting points due to sea-level rise.

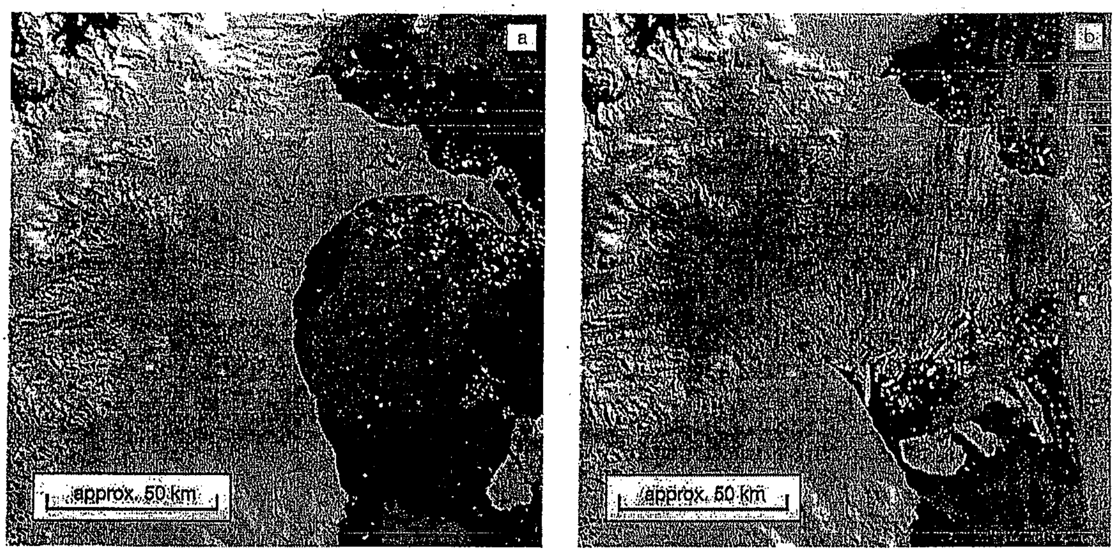


Figure 3.1-3
The Larsen B ice shelf off the Antarctic Peninsula in satellite photographs on 31 January (a) and 5 March 2002 (b).
Source: NSIDC, 2002

3.1.1.3
Further contributions to sea-level rise

Other contributing factors to global sea level are primarily the thermal expansion of water and the melting of smaller mountain glaciers. Regional sea levels are also influenced by changes in ocean currents and by geological processes (local uplift or subsidence of land masses). As long as the global trend is small the regional processes can still predominate. Satellite and water gauge measurements indicate that in spite of global sea-level rise there are still regions with falling sea level, e.g., in the Indian Ocean and around the Maldives (Cazenave and Nerem, 2004). But if global sea-level rise accelerates, it will eventually overcome the local effects and result in an overall rise.

According to water-gauge measurements, sea level on the coasts has risen globally by 20cm since 1870. That rise has accelerated throughout the 20th century, whereas the rate of rise was still near 0 at the beginning of the 19th century (Church and White, 2006). Over the past few millennia, according to geological data, sea level hardly rose at all (Peltier, 2004) – this is also confirmed by analyses of water levels at the time of the Roman Empire (Lambeck et al., 2004). Since 1993 it has been possible to measure sea level globally and precisely from satellites – over this time frame a rate of rise of 3cm per decade has been recorded (Fig. 3.1-4). Up to 5mm of the recent rise could be a fluctuation due to the eruption of the Pinatubo volcano in 1991 (Church et al., 2005). Independent estimates of the individual contributions currently give values of 1.6cm per decade (Willis et al., 2004) due to the warming of seawater, and 0.5cm per decade from mountain glaciers and smaller ice masses outside of Greenland and the Antarctic (Raper and Braithwaite, 2006). This leaves about one centimetre per decade for the two large continental ice masses, which is consistent with the discussion in Section 3.1.1.2. In light of the uncertainties in the individual contributions, however, it is still too early to derive a definitive balance of the present sea-level rise.

The various scenarios of the 2001 IPCC report yielded a rise of 9–88cm from 1990 to the year 2100. The lower of these values lie clearly below the rate of rise already measured. This also suggests that the IPCC has so far underestimated sea-level rise.

3.1.1.4
New estimates of sea-level rise

The physics of the observed dynamic processes in the continental ice discussed above are not adequately understood, and present continental-ice models do not yet consider these processes to a sufficient extent. There is an urgent need here for further research (Section 3.5). Improved estimates are difficult given the present state of knowledge, and are possible only with large uncertainties. Such an estimate, necessarily very rough, is attempted in the following.

Sea-level rise up to the year 2300 is considered, with a stabilization of warming at 3°C above the pre-

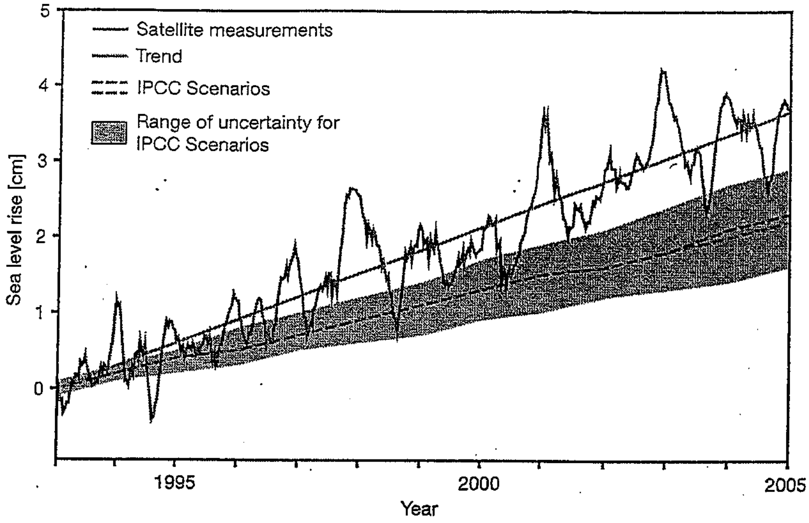


Figure 3.1-4
Global sea-level rise as recorded by satellite measurements (upper line with its linear trend), with the projections of the IPCC (2001a) and its range of uncertainty.
Source: Cazenave and Nerem, 2004

industrial value. The comparatively long time range was chosen because of the intrinsic time scales of the relevant processes, amounting to several centuries both for the melting of ice sheets and for thermal expansion of seawater. After stabilization of the greenhouse gas concentrations and the climate on the surface, the sea level will continue to rise for centuries. To estimate the impacts of anthropogenic emissions during the coming decades, therefore, a consideration only to the year 2100 is not enough.

At a medium climate sensitivity of 3 °C, this scenario corresponds to the effect of a doubling of the preindustrial CO_2 concentration, or a CO_2 equivalent of 560ppm. If the worldwide contribution of CO_2 to the radiative forcing due to anthropogenic greenhouse gas emissions remains at 60 per cent, the 560ppm CO_2 equivalent would correspond to a stabilization at 450ppm of CO_2.

- *Thermal expansion:* For this the values of the IPCC are adopted (0.4–0.9m: IPCC, 2001a, their Fig. 11.15a), which are derived from model simulations for a scenario with doubled CO_2.
- *Glaciers:* For the volume of all glaciers outside of Greenland and the Antarctic the same IPCC report gives a sea-level equivalent of 0.5m; with 3 °C of global warming one could expect a loss of 80 per cent of the glacial mass for the year 2300. A more recent study (Raper and Braithwaite, 2006), however, uses half of this value; therefore a range of 0.2–0.4m is applied.
- *Greenland:* The model presented by IPCC (2001a) for Greenland with a local warming of 5.5 °C (which is a plausible value with 3 °C global warming: Chylek and Lohmann, 2005) gives a sea-level rise contribution of 0.9m by the year 2300. The dynamic mechanisms mentioned above, however, are not considered, so this value represents a lower limit; therefore 0.9–1.8m is assumed here.
- *Antarctic:* The behaviour of the West Antarctic ice sheet (WAIS) is critical for the Antarctic. In 2001, IPCC considered the decay of this ice sheet to be very unlikely, because the then existing models suggested that the continental ice did not react to changes in the ice shelves floating in the adjacent sea. This now has to be considered as disproved, as the observations discussed above show. The disappearance of further ice shelves (like Larsen B: Fig. 3.1-3) due to warming of seawater means that the melting of the WAIS must be feared with a similar time frame as Greenland. For this, 1–2m of sea-level rise is assumed by the year 2300. At a constant rate this corresponds to the disappearance of the WAIS in a time frame of 900–1800 years – some glaciologists consider that broad destruction is even possible within 300–400 years.

The net result is a rise of around 3–5m by the year 2300. The value of 3m corresponds to a loss of one-sixth of each, the Greenland and the West Antarctic ice sheets; 5m corresponds to one-third of each (Table 3.1-1).

Table 3.1-1
Estimated global sea-level rise by the year 2300 with global warming limited to 3 °C (explanation in text).
Source: WBGU

Mechanism	Rise in m
Thermal expansion	0.4–0.9
Mountain glaciers	0.2–0.4
Greenland	0.9–1.8
West Antarctica	1–2
Total	*2.5–5.1*

The question arises whether these numbers are consistent with today's observed sea-level rise rate of 3cm per decade. Due to inertia and nonlinearity, and the initial slow start-up of the rise, this cannot yet be answered. At today's measured rate of rise, there would be an increase in sea level of only about 1m by 2300. The present rise, however, is a response to only 0.7°C global warming. At 3°C warming a pace four times faster is plausible for the rate of rise and would be consistent with the range estimated above.

This rough calculation, which does not represent a worst-case scenario, underscores the potential risk posed by sea-level rise, which could emerge to be one of the most severe consequences of global warming. More precise and robust estimates are therefore urgently needed. Research needs arise, above all, in the areas of continental ice mass dynamics and the dynamics of the ocean (especially ocean mixing), in order to reduce the uncertainty in the estimation of thermal expansion (Section 3.5).

3.1.2
Stronger tropical cyclones

Ocean-related impacts of climate change threaten humankind and ecosystems not only through the rise in sea level, but also through extreme weather events such as tropical cyclones. The 2005 hurricane season broke a series of records: not since the beginning of record keeping in the year 1851 have there been so many tropical cyclones in the Atlantic (27, six more than the previous record), have so many grown to full strength (15, four more than the previous record), and have there been three hurricanes of the most destructive category – category 5. A more intensive hurricane than Wilma, with a central pressure of only 882mb on 19 October 2005 has never been measured. And with Vince, the first tropical storm to approach Europe was seen; it developed into a hurricane near Madeira on 9 October 2005, and made landfall in Spain after weakening.

The hurricane season of 2004 was already extraordinary. For the first time Florida was hit by four hurricanes in one year, and for the first time Japan experienced ten typhoons, as hurricanes in the Pacific are called. Of even greater interest for climatologists was the fact that in March 2004, for the first time, a hurricane developed in the South Atlantic: Catarina. It formed in a region off the Brazilian coast, where a simulation calculated by the British Hadley Centre had indeed previously predicted that hurricanes would originate due to global warming (Met Office, 2006).

The question arises whether there is a connection between global warming and hurricanes. The central statement regarding this in the last IPCC report was that an increase in the number of tropical cyclones due to global warming is not to be expected, and that observational data also show no significant trend in the number of these storms.

Since this IPCC report was submitted there has been a series of new studies on this topic. They do not exactly contradict the IPCC statement, but they throw a completely new light on the question above, whereby the number of tropical storms is no longer the focus of interest but their strength. The two aspects are determined by different factors. Tropical storms arise from a small disturbance (such as a thunderstorm) over the tropical ocean. In the Atlantic this disturbance often originates on the African continent. What controls the frequency of such 'embryonic' hurricanes is not yet fully understood, but there is no evidence of a direct influence of global warming on this process.

The further development of a tropical storm after it has begun is, however, strongly determined by its surroundings, i.e., by the sea temperatures and the atmospheric circulation. The sea temperatures in particular are affected by anthropogenic warming. Whether the atmospheric circulation changes because of the warming, and to what extent this promotes or hinders the development of hurricanes is still unclear. Here one is dependent on simulations with global models, which, however, still have weaknesses with respect to the resolution of hurricanes. The following points are well-supported by measurement data:

1. Warmer sea temperatures lead to stronger hurricanes with more precipitation.
2. Sea temperatures in the tropics during the relevant season (around June to November) have increased and, in both the Atlantic and Pacific, are at their highest level since the beginning of measurements, which (although with decreasing quality) extend back into the 19th century.
3. The energy of hurricanes has increased both in the Atlantic and Pacific, to their highest values since the beginning of reliable data in the 1950s. While the total number of tropical storms has hardly changed, the number of especially strong hurricanes (category 4 and 5) has clearly increased.

The first point is well supported theoretically: warm temperatures are an energy source for hurricanes, which is why they are a tropical phenomenon. This fact is routinely applied in the predictions of the National Hurricane Center. Emanuel (2005) has verified this connection based on measurement data since 1950. He also defined an index for the strength of a hurricane, the 'Power Dissipation Index' (PDI), which is the cube of the wind speed added over the extent and duration of a hurricane. An increase in the

PDI therefore is seen for stronger, larger or longer-lasting hurricanes. The PDI can be interpreted as an approximate measure for the destructive potential of a hurricane.

Figure 3.1-5 shows the increase of the PDI over recent decades in the Atlantic; there is a similar development in the Pacific. In addition to the increase, the connection to the globally averaged near-surface air temperature is clearly recognizable. The increase of the PDI with temperature, however, is much stronger in the data than would follow from the theory of hurricane energy. This discrepancy is not yet understood. A conceivable hypothesis is that the warm surface layer is thickened, so that the quantity of heat accessible for the hurricane increases out of proportion with the temperature (Scharroo et al., 2005).

Another study (Webster et al., 2005), using satellite data, has shown that the number of category 4 and 5 hurricanes since 1970 has almost doubled globally (that is, in the Pacific, Atlantic and Indian Oceans), although the total number of tropical storms shows no significant trend during this time. This again confirms the statements of the IPCC (2001a), whereby the number does not change, and of Emanuel (2005), whereby the strength increases.

In several studies a working group in Princeton has investigated how global warming affects a hurricane model that is regularly employed for predictions by the National Hurricane Center (Knutson and Tuleya, 2004). The model was run under boundary conditions from several global climate models, both for today's climate and for a warming scenario. In these studies the frequency distribution of the hurricanes shifted clearly toward the stronger storms – the strongest hurricanes, those of category 5, occurred three times more often in the warming scenario than in the reference climate. Because global climate models themselves so far do not have sufficient resolution to describe hurricanes very well, these studies, with a regional, high-resolution prediction model are the strongest tools available to date for simulating the future development of these storms.

Theory, observational data and model calculations therefore indicate that climate warming leads to stronger hurricanes. The effects revealed by measured data are even stronger than theoretically expected. With a warming of the tropical sea-surface temperature of only 0.5°C the hurricane energy has increased globally by 70 per cent in recent decades, and by even more in the Atlantic (Emanuel, 2005). A new data analysis also confirms that the temperature rise is the main reason for this observed energy increase, while other factors play a minor role (Hoyos et al., 2006).

Yet, there are a few hurricane researchers in the USA who attribute the extreme year of 2005 to a natural cycle alone: to a fluctuation of the Atlantic currents ('thermohaline circulation'), which is discussed in Section 2.1.3. This is, so far, also the position of the National Hurricane Center of the USA. These hurricane researchers, however, do not reject the connection between higher temperatures and stronger hurricanes, rather they dispute that the warming itself is anthropogenic, and some of them even dispute anthropogenic climate change in general. Some studies will appear in the near future that analyse the anthropogenic contribution to the increased Atlantic temperatures more accurately.

A natural cycle, in addition to global warming, could have in fact contributed to the extreme year of 2005 in the Atlantic. But such a cycle cannot explain why the temperatures are higher now than ever since

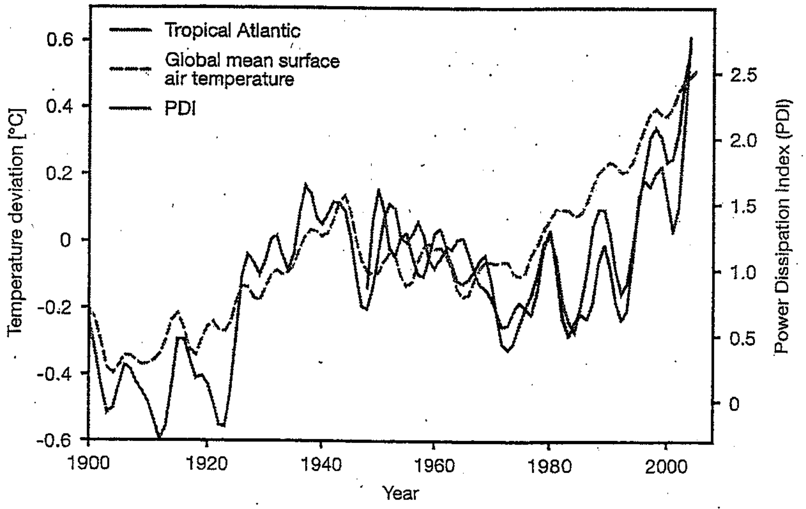


Figure 3.1-5
Temporal development of the energy of tropical storms (Power Dissipation Index – PDI, red) and the average sea-surface temperature in the tropical Atlantic from August to October (blue). For comparison the pattern of the globally averaged near-surface air temperature is shown (dashed grey line). Source: after Emanuel, 2005

the beginning of measurements (and than the last maximum of the cycle in 1950) nor can it explain the rise in the Pacific. There, where the majority of tropical storms occur, their energies have also shown an increasing trend for decades. In addition, the observed temperature development in the tropical Atlantic lies within the range of the global warming trend (Figs. 3.1-5, 2.1-1, and 2.1-2), and is consistent with that derived by modelling calculations as a result of anthropogenic emissions.

To resume, it can be said that among hurricane experts (most of whom are specialists in weather prediction and not climate research) there is a consensus that warmer sea temperatures strengthen tropical storms. Among climate experts there is a consensus that anthropogenic warming has contributed significantly to observed warming in the tropical oceans. A causal connection between global warming and stronger hurricanes is not proven by this and requires further research, but it has to be considered as very likely given the present state of knowledge.

3.2
Impacts on coastal regions

The consequences of climate change, whether in the form of sea-level rise or through greater frequency and force of extreme weather events, will directly affect the future development of coastal regions. The worldwide length of coastlines (excluding small protrusions of less than a few kilometres) is on the order of around one million kilometres. Coastal regions are of extreme importance for humankind. They offer settlement areas, are centres of economic activity (Turner et al., 1996) and, not least, harbour a rich abundance of biological diversity.

The direct effects of climate change, such as the extent and rate of sea-level rise, presently cannot be precisely determined. But it is very probable that the threat to coastal regions will increase considerably, as will the number of people affected by climate change. This is an obvious result of the fact that large numbers of settlements are located near the coasts. Eight of the world's ten largest cities today lie on the coast (UN, 2004), and according to estimates 21 per cent of the world's human population live less than 30km from the sea (Cohen et al., 1997; Gommes et al., 1998). The great attraction of coastal regions is also reflected in the large growth rates of populations there, which is around twice the global average (Bijlsma et al., 1996). The worldwide trend toward urbanization will amplify this development in the future. By the year 2030 approximately 50 per cent of the world population could be living within 100km of the coasts (Small and Nicholls, 2003).

How sea-level rise and weather extremes due to climate change will affect coastal regions and societies depends primarily on the kind and number of affected natural and social systems. The natural systems will mainly be represented by river deltas, low-lying coastal plains, coral islands and atolls, barrier islands and lagoons, beaches, coastal wetlands and estuaries (IPCC, 2001b). The following sections explore in detail which biogeophysical and socio-economic impacts can be expected and to what extent people are threatened.

3.2.1
Biogeophysical impacts

3.2.1.1
Inundation due to sea-level rise

The rise in mean sea level will result in the inundation of coastal areas and island groups in several regions of the world. Inundation here is defined as the permanent covering of land areas with water (as opposed to temporary, episodic flooding). Without counter-measures the result will be the irretrievable loss of this land.

In order to be able to estimate the total extent of the regions endangered by sea-level rise, Brooks et al. (2006) have compiled data on the global land-surface distribution with respect to the elevation above sea level. Figure 3.2-1 illustrates that large regions lie within the range of one metre above high water. Above the one-metre line, the land-surface distribution rises as an almost linear function of the elevation above the mean high water line. At an elevation of only 20m above sea level a total land area of 8 million km² would be affected.

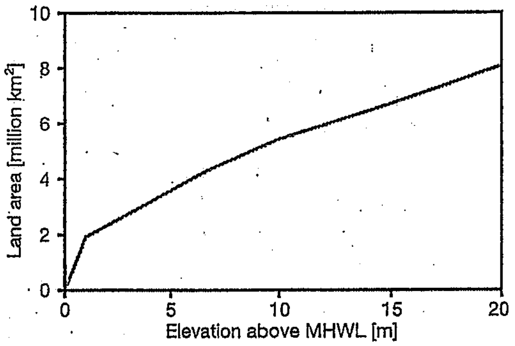


Figure 3.2-1
Distribution of land area, excluding Antarctica, as a function of elevation above present mean high water (MHW).
Source: ISciences, 2003

For purposes of illustrating the spatial distribution of these land areas, examples will be shown of regions that lie at elevations within 2m and within 20m above sea level. A rise of 20m (Fig. 3.2-2) represents an extreme scenario that could result from anthropogenic warming over a time frame of around 1000 years, in the event that the ice sheets of Greenland and west Antarctica should melt for the most part (Section 3.1.1). This long time frame has to be considered with sea-level rise because the relevant processes, such as melting of the ice sheets and mixing of the ocean, are slow geophysical processes. Because of the physical inertia in the marine system these processes will first come to a standstill centuries after stabilization of the greenhouse gas concentrations and the surface climate.

The particularly threatened areas in Europe with a rise of 20m would be mainly eastern England, the Po Delta in northern Italy, and the coastal strips running through Belgium, the Netherlands, north-western Germany, and into northern Denmark (Fig. 3.2-2).

A sea-level rise of 2m (Figs. 3.2-3 and 3.2-4) could occur in the coming century. As an illustration of the effects, Figure 3.2-3 depicts regions on the North Sea and the northern European coast. Because this kind of illustration is based on the absolute elevation above sea level, it also includes areas that are protected by dikes today. Some densely populated areas in the Netherlands, England, Germany and Italy today already lie below the normal high-water level (EEA, 2005). For these regions the sea-level rise is especially threatening. Here the question of the rate of change takes on a special importance, because a more rapid rise could hamper the implementation of adaptive strategies (Brooks et al., 2006).

In Asia, with a sea-level rise of 2m (Fig. 3.2-4), for example, the densely populated river delta of the Ganges-Brahmaputra-Meghna with its network of 230 rivers would be affected. The total river region covers an area of 175 million hectares and stretches from India and Bangladesh to Nepal, China and Bhutan (Mirza et al., 2003). Approximately 129 million people presently live in this river delta (Woodroffe et al., 2006), with a large portion of them in rural areas. With Dhaka and Kolkata (formerly Calcutta) there are already two fast-growing megacities here, that is, cities with more than ten million inhabitants.

3.2.1.2
Flooding as a result of storm surges

In most cases the most destructive results of sea-level rise will not be from the very slow rise of the mean water level, but in the increasing occurrences of storm surges.

The origin of storm surges is often related to the interplay of storm systems and tides. When storms push water onto the coasts at high tide it can lead to the flooding of large areas of land. Especially in river estuaries damage can occur over large inland distances (SwissRe, 1998). The word flooding here describes a temporally limited, partial or complete water cover of normally dry areas. This can be caused by the rise of surface water (still or flowing) over its banks, as well as by the results of strong precipitation (Münchener Rück, 1997).

Sea-level rise increases the exposure of coastal inhabitants to storm surges and storm waves, and with it the risk of flooding. The destructive force of these kinds of weather extremes increases as a direct consequence of sea-level rise (Jimenez and Sanchez-Arcilla, 1997). Higher waves will more easily reach the original coastline and also penetrate farther inland. Even the water levels of the two-metre scenario exceed today's standards for coastal defence structures. Although Great Britain, for example, has protective structures that reduce the wave height near the coasts, it is questionable whether these measures can provide long-term protection when the exceptional situation becomes the normal case. If water depths should change or shores become steeper, which would result in a direct energy increase for waves coming onto the land, then the existing structures would no longer be sufficient as coastal protection measures (Burgess and Townend, 2004).

Additional factors could significantly increase the risks from flooding: changes in oceanic and atmospheric circulation patterns caused by climate change can influence storms and their destructive potential at regional and local scale. For example, an increase in the strength of tropical cyclones is anticipated (Section 3.1.2). Furthermore, climate warming could contribute to intensification of the hydrological cycle, which makes increases in the frequency and intensity of extreme precipitation events likely (IPCC, 2001a).

For the consequences of sea-level rise it is less critical how much higher the average water height is than how frequent certain high levels are reached during storm surges. This can be estimated by a comparison of the expected average rise with statistics of past storm surges. Accordingly, the return periods, i.e., the time interval between certain critical gauge levels, could be strongly reduced in the future (Lowe et al., 2001). A model by the Hadley Centre for a region in eastern England, based on a combination of meteorological data and an assumed sea-level rise of 0.5m by 2100, shows a reduction in the return period

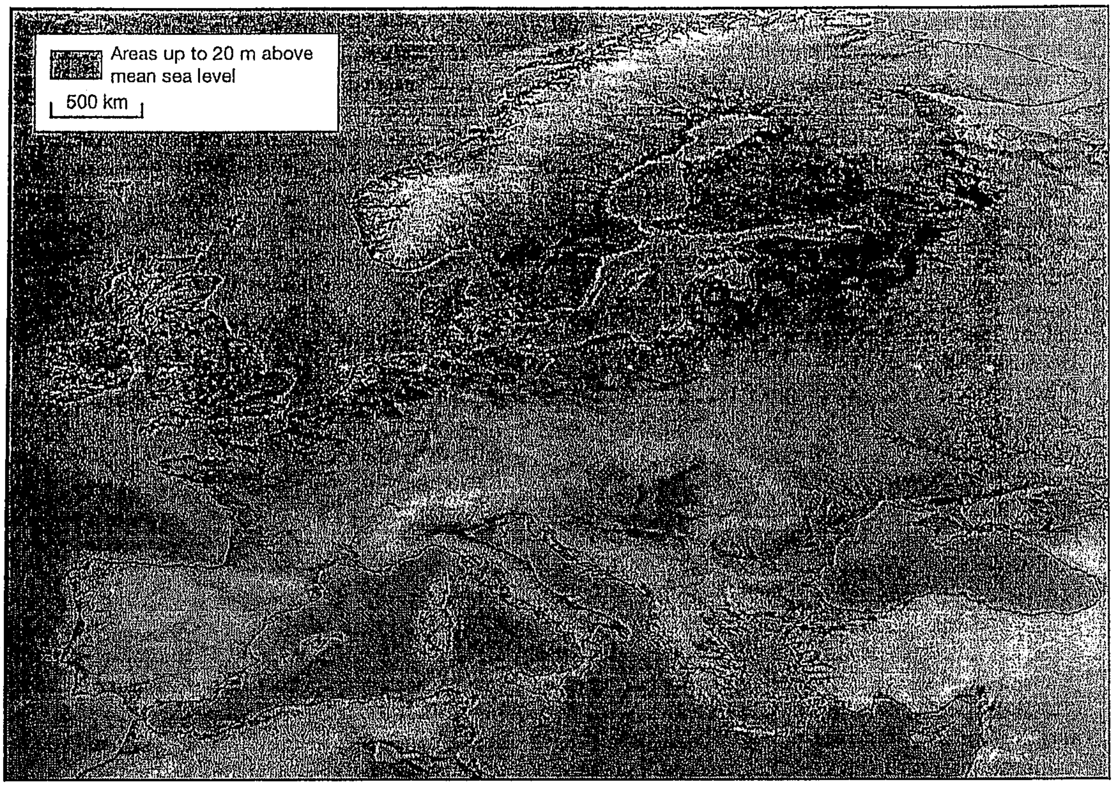


Figure 3.2-2
Coastal areas in Europe, parts of western Asia and North Africa. Areas below 20m elevation above the present mean sea level are coloured red (not taking future coastal defence measures into account).
Source: Brooks et al., 2006

Figure 3.2-3
Coastal areas along the North Sea. Areas below 2m elevation above the present mean sea level are coloured red (not taking future coastal defence measures into account).
Source: Brooks et al., 2006

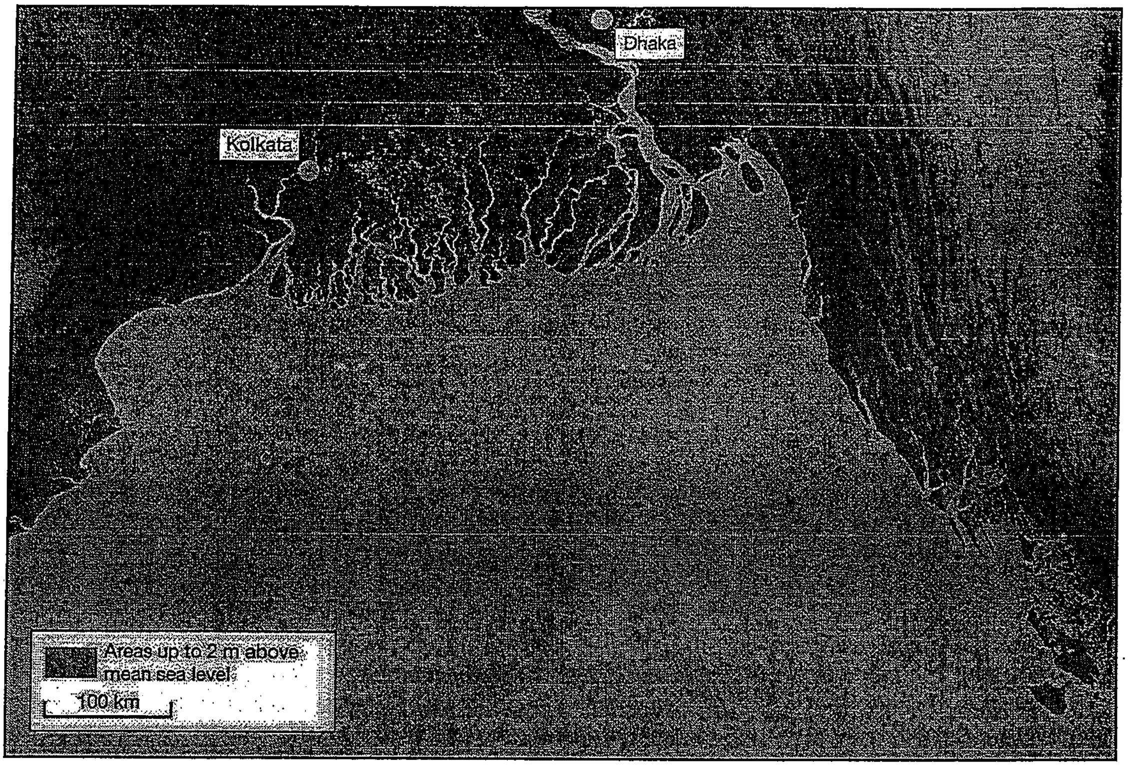


Figure 3.2-4
Coastal areas along the Gulf of Bengal and in the Ganges-Brahmaputra-Meghna River Delta. Areas below 2m elevation above the present mean sea level are coloured red (not taking future coastal defence measures into account).
Source: Brooks et al., 2006

of high-water events from 500 to 12 years (Lowe et al., 2001). Similar trends were calculated for the greater New York City area, based on various climate scenarios. According to these, with a sea-level rise of 24–95cm the return period of a 100-year flood in the 2080s is shortened to 4 to 60 years (Gornitz et al., 2002; Section 3.3). When the return periods of destructive extreme events become too short, the repeated repair of damaged infrastructures would no longer make sense, and they would have to be abandoned.

Land-use changes such as the clearing of forests, urbanization and the conversion of alluvial plains and wetlands can further increase the flooding risk, for example by weakening the water-retention capacity of the soil (Kundzewicz and Schellnhuber, 2004). Straightened or built-up rivers without natural forests and wetlands have less buffer capacity in extreme situations. The flow and sedimentation behaviour of rivers influenced by engineering measures often determines whether storm-caused flooding risks are amplified or attenuated.

3.2.1.3
Coastal erosion

In contrast to floods, which are relatively rare events with sometimes catastrophic results, erosion represents an episodically occurring process (Hall et al., 2002). During the erosion process, waves carry solid materials such as sand, mud and rocks away from the coast and redeposit them for the most part in other formations. A rise of sea level could accelerate these erosion processes (Zhang et al., 2004; Stive, 2004). In particular with a small rise, erosion may prove to be of greater importance than flooding (Smith and Lazo, 2001).

The erosion rates depend on the local conditions. If undercutting occurs along with the resulting collapse of steep coasts or coastal protection structures, erosion can represent a serious danger. In this connection it is important to note that above all the rates of sea-level rise are relevant to changes in coastal morphology. If sedimentation rates can keep up with the sea-level rise, then a new equilibrium can be established and this can have a stabilizing effect on the coastal processes. Sedimentation processes have contributed to coastal development since the beginning of the Holocene, and have been responsible for the preservation of land areas, especially during the inundation of river deltas (Brooks et al., 2006). However, if the sea-level rise accelerates so quickly that a new equilibrium cannot be established, or if sedimentation rates are significantly reduced due to management measures, then a loss of coastal strips will probably result. A well-known example is the Nile, where the sedimentation rates were decreased, primarily by the construction of the Aswan Dam, which led to accelerated erosion of the northern Nile Delta by tides (Stanley and Warne, 1998).

Many authors, including Zhang et al. (2004), refer to the Bruun Rule (Bruun, 1962) in their prognoses of the erosion of coastal regions caused by sea-level rise. This states that the erosion rates are approximately 50–100 times higher than the relative rate of sea-level rise, that is, a sea-level rise of 1m would result in the loss of a 50–100m wide coastal strip. Opinions about the general applicability of the Bruun Rule, however, vary widely, because it is based on the assumption of a simple, two-dimensional system, and the establishment of a sedimentation equilibrium in the bank area. These preconditions, however, can hardly be assumed in real situations. It therefore must be concluded that for estimating the results of erosion along the coastlines, more complex models have to be applied that also incorporate, for example, the sediment transport along the coasts and changes in sedimentation equilibrium, as would be the case with a sea-level rise.

3.2.1.4
Impacts on groundwater

The rise of sea level can also cause the groundwater level of a coastal region to rise. This is determined in part by geographic factors (e.g., elevation above sea level), and in part by geological factors (e.g., properties of rock and soil layers).

Above all, a rise in the groundwater level caused by sea-level rise could impact on river deltas up to 20–50km inland. This estimate is based primarily on the observation that groundwater along the coasts flows above a dense, landward-moving saltwater wedge. This balance between freshwater and saltwater is physically controlled by the relationship of the different water densities. With a rise of sea level, therefore, the overlying groundwater would also rise (Barlow, 2003). This can lead to a saturation of the soil. It produces impacts not only on the freshwater supply of a region, but also on agriculture (salinization risk), the stability of foundations, and the safety and functioning of dewatering and other underground systems such as subways.

In addition, a rise in sea level can promote the invasion of saltwater in coastal aquifers (seawater intrusion). Model simulations by Sherif and Singh (1999) concluded that a rise of 0.5m in the Mediterranean Sea would result in the intrusion of saltwater 9km into the coastal aquifers of the Nile Delta. With the same rise, however, in the Gulf of Bengal, only a zone of 0.4km landward would be affected. These processes would result in an increased salinization of the groundwater and surface waters, with considerable impacts on agriculture and the drinking-water supply. The intrusion of saltwater into the groundwater reservoirs of coastal zones can already be observed worldwide today, e.g. in China and India (Shah et al., 2000). Through the increasing overexploitation of freshwater resources in the densely populated coastal zones, this process can also be considerably amplified.

Although sea-level rise can cause the salinization of river estuaries and near-coastal groundwater reservoirs, this process is determined by a number of other factors. The run-off behaviour of precipitation and its contribution to groundwater recharging also controls seawater intrusion in coastal regions. An increase of freshwater runoff can counteract seawater intrusion. Seawater intrusion would have long-lasting effects. Some of these aquifers would require hundreds to thousands of years to reach a new harmonic equilibrium with the new sea level (Barlow, 2003).

3.2.1.5
Biological impacts

Besides temperature increase and acidification, the expected sea-level rise is an important additional stress factor for the often highly species-rich terrestrial coastal ecosystems or near-coast ecosystems. Two particularly relevant ecosystem types are coral reefs (Section 2.4) and mangrove forests, because they not only harbour great biological diversity, but at the same time play an important role in coastal protection. This latter was illustrated by the tsunami catastrophe in December 2004 in the Indian Ocean: on coasts with intact coral reefs and mangrove forests the flood wave was slowed considerably so that the damage was less disastrous (Fernando and McCulley, 2005; Dahdouh-Guebas et al., 2005; Danielsen et al., 2005).

How coral reefs will respond to sea-level rise can be derived by reconstructions of the past or by model simulations. The adaptive capacity of corals in prehistoric times varied greatly (Montaggioni, 2005).

The average vertical growth rate of coral reefs since the last ice age is reported as at most 10mm per year (IPCC, 2001b). But because the growth rate of corals is influenced by many factors (Section 2.4), and corals in this century will also be impaired by warming, acidification and other environmental factors, a prognosis for the adaptive capacity of these ecosystems cannot be made with respect to the rising water level.

Around 8 per cent of the coastlines worldwide today are bordered by mangroves. More than half of the mangrove forests have already disappeared (WRI, 2001). The observed decline can be attributed in large part to changes in human uses of coastal zones. A study on the changes of mangrove belts in the Amàzon region (Cohen and Lara, 2003) shows that sea-level rise can also have a local effect on the distribution of mangroves. The rise of sea level in the future will force the near-coastal mangrove belts farther inland. The mangroves, however, will only be able to survive in areas where enough space is left for them adjacent to the intensive human land use. For the preservation of this valuable ecosystem it is therefore urgently necessary to maintain protected areas or create new ones that include a wide buffer zone on solid land. With the help of the HadCM3 model, Nicholls (2004) evaluated the sensitivity of coastal regions to flooding under the different SRES scenarios (IPCC, 2000). In every case the sea-level rise results in the loss of wetland areas. This study also shows, however, that the direct destruction of wetlands by people could exceed the losses caused by climate change.

Changes in the tidal ranges and high-water levels caused by sea-level rise are an additional burden for coastal ecosystems. The consequences include changes in water depths, light and temperature, and current speeds, and a shift in the freshwater-saltwater distribution. These can lead to physiological burdens for some animal and plant species that could then require a habitat change. Studies show that even minor seawater intrusions into coastal seas lead to large disturbances in the structure and diversity of zooplankton populations. Accordingly, small salinity changes can result in a decline in the biodiversity of coastal ecosystems (Schallenberg et al., 2003). The functioning and preservation of ecosystems are therefore not only threatened by flooding because of sea-level rise, but also by changes in the frequency and strength of seawater intrusions.

The DIVA model (DINAS-COAST Consortium, 2004) is a new interactive tool for integrated analysis of the results of sea-level rise. The model simulates the effects of local sea-level rise (including tectonic rises and falls) on the ecosystems and populations of the coastal regions of the world, and incorporates different adaptive strategies. It is based on the analysis of the worldwide coast lines in more than 10,000 homogenous segments according to morphological and socio-economic aspects, a self-developed extensive worldwide database, and a series of coupled modules. For a scenario with a mean sea-level rise of 50cm by the year 2100 the model reports a loss of more than half of the freshwater wetlands in coastal regions, around 20 per cent of the coastal forests, and a quarter of the mangroves.

3.2.2
Socio-economic impacts

3.2.2.1
Impacts on people

The multiple effects of sea-level rise on the natural environment will have a major impact on people and the systems they depend on. It is likely that some of these effects will interact, intensifying each other, such as floods and erosion-related events. For inhabitants of coastal regions, sea-level rise will be the biggest challenge posed by global climate change (IPCC, 2001b).

The extent of climate-related hazard will also depend on the extent to which the ecosystems of the affected coastal regions have been exposed to prior damage. Pre-existing environmental problems often interact with the impacts of climate change. For instance, flood risk may be increased by changes in land use (deforestation, settlement, etc.) in hydrological catchment areas, or degradation of coastal ecosystems (coral death caused by marine pollution, logging of mangrove forests for building materials and to clear land for aquaculture installations, etc.). Moreover, it has been observed that in some cities the land mass is sinking below sea level. Contributing factors in this case include both the physical pressure of buildings and infrastructure and intensive urban management practices, combined with groundwater extraction, drainage and building activity. Nicholls et al. (1995) estimate that, at their most extreme, local rates of subsidence may be as much as 1m per decade. A rise in sea level then makes the risk of flooding in these regions even greater. The fact that a variety of factors are superimposed on each other – disappearance of natural barriers, sinking of land masses below sea level, and rising sea levels resulting from climate change – increases the risk to populations (Nicholls, 2003).

Based on 1995 population figures, there are currently 60 million people living below 1m elevation and 275 million below 5m elevation above mean sea level. If estimates are adjusted to take into account forecasts of population growth, the figures for the end of the 21st century rise to 130 million (below 1m elevation) and 410 million (below 5m elevation; Nicholls et al., 2005). A more recent study by Brooks et al. (2006) arrived at similar findings (Fig. 3.2-5).

How people in threatened areas will ultimately deal with the challenges of an accelerated sea-level rise is a complex and dynamic process. Migration away from threatened areas will depend on the particular situation in a given locality, and can range from planned migration based on risk assessments and economic considerations to the sudden displacement of people fleeing floods, storms, or sudden erosion-related events. Due to the likely increase in extreme weather events, the incidence of spontaneous migration following natural disasters will probably exceed that of planned migration (Brooks et al., 2006). This is especially likely to happen where a radical change in the landscape occurs and the costs of protecting the affected population become disproportionately high. People in low-lying coastal regions, especially river deltas and small island states, are particularly at risk in this regard (Nicholls, 2003). Studies show, for example, that unless costly protective measures are put in place, a sea-level rise of around 0.5m would put 1.5 million people at risk in the Egyptian governerates of Alexandria and Port Said (El-Raey et al., 1999). In the case of Europe, estimates suggest that 13 million people would be at risk in the event of a sea-level rise of 1m (EEA, 2005).

There is a whole range of model simulations designed to obtain a more precise estimate of the number of people exposed to flood risks. Using the FUND model, Nicholls et al. (2006), for example, have simulated the consequences of disintegration of the West Antarctic ice sheet and the resulting sea-level rise of 5m over a period of 100 to 1000 years beginning in the year 2030. The impact of coastal protection measures was evaluated using cost-benefit analysis. In all scenarios, population displacement reaches a peak between 2030 and 2060. Based on the (extreme) assumption that the ice sheet will disintegrate rapidly within 100 years, up to 350,000 persons per year will be forced to leave their homes over a period of ten years. This would give a total of 15 million people. However, these figures account for a mere 2–3 per cent of the total number of people at risk, because they are based on the assumption that coastal protection measures will be implemented on a large scale. In another study aimed at estimating flood risks, Hall et al. (2005) arrive at the conclusion that, under the A1 and A2-SRES scenarios, the number of people at risk in Britain in the 2080s compared to 2002 would double, rising from 0.9 million to 1.8 million.

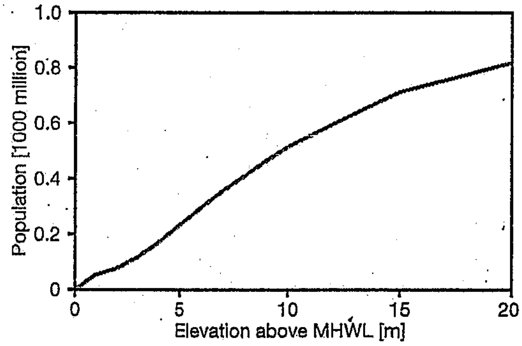


Figure 3.2-5
Population living below a certain elevation above mean high water (MHW) in 1995.
Source: Brooks et al., 2006

'Sea-level refugees'

Whether coastal dwellers who are forced to leave their homeland due to climate-related environmental changes ('sea-level refugees') return home or settle further away from the coast will depend on a whole host of factors. On the one hand, the decision will be influenced by whether coastal protection measures are put in place and how effective or reliable these are. On the other hand, the position adopted by local and regional government will also play a role, for example by discouraging or even prohibiting return to evacuated areas (Brooks et al., 2006). Actual numbers of sea-level refugees will ultimately be determined by the interplay of these factors and measures.

In any case, in the long term sea-level refugees will need to be resettled elsewhere, and this poses new challenges for policy. This is especially true in the case of the inhabitants of some of the low-lying atolls such as the Maldives, the Marshall Islands, Kiribati, Tuvalu or Tokelau. These island states, with a total population of more than 500,000 (CIA, 2005), lie a mere 2m above sea level on average and are therefore at risk of becoming uninhabitable or disappearing completely as a result of climate change. Their inhabitants face a constantly increasing risk of salinization and drinking water shortages and higher risk of storms and floods even if the 1m guard rail (Section 3.3) is successfully adhered to (Barnett and Adger, 2003). These factors are already making their impact felt: the first relocations to higher-lying land took place in December 2005 on the Pacific island of Vanuatu. In this particular case, decreasing intervals between storm surges had made it necessary to relocate the village of Lateu. The United Nations Environment Programme regards this case as probably the first formally recorded resettlement measure of its kind, resulting directly from the consequences of climate change (UNEP, 2005).

Official programmes are already in place to tackle the problem of sea-level refugees. New Zealand has reached agreement with the governments of Tuvalu, Fiji, Kiribati and Tonga on immigration regulations for their inhabitants under the 'Pacific Access Category'. Each year, a certain number of refugees whose status is a direct result of the consequences of climate change are granted a New Zealand residence permit. A whole set of conditions is attached to obtaining a residence permit under these arrangements, however, and older people and poor people are currently excluded (Friends of the Earth, 2005). The right of sea-level refugees to be granted refuge in other countries needs to be enshrined in international law (Section 3.4.2.3).

THREATS TO HUMAN HEALTH

In coastal areas, the primary threat to the lives and health of large numbers of people is posed by storms and floods. Even today, a total of 75 million people in coastal regions are exposed to the risk of storm-induced floods. Assuming a moderate climate change scenario with a sea-level rise of 0.4m by the 2080s, this figure would rise to an estimated 200 million (IPCC, 2001b; Patz et al., 2005).

When assessing health-related consequences of storm tides and floods, a distinction can be drawn between immediate, medium-term and long-term impacts. Immediate impacts refers to impacts arising during the event itself and which are due to the effects of flooding. These include death and injury due to drowning or collision with hard objects, and to hypothermia and cardiac arrest (WHO, 2002). In this context, the World Health Organization (WHO) has calculated that in the year 2030 the relative risk of death due to flooding in the coastal areas of the EUR-B Region will be 6.3 times higher than in the base years 1980–1999 (McMichael et al., 2004). Affected countries in the EUR-B Region include some of the former Soviet republics, several Balkan states, Turkey, Poland and the EU accession states Bulgaria and Romania.

The medium-term impacts of floods manifest themselves most notably in an increase in infectious diseases resulting from ingestion of or contact with contaminated water (e.g. cholera, hepatitis A, or leptospirosis), or respiratory infections due to overcrowded accommodation (IPCC, 2001b). The lack of properly functioning sanitary installations and public healthcare provision makes these risks even greater in poorer countries. Following the floods in Bangladesh in 1988, for example, the most common diseases were diarrhoea and respiratory infections, while the most frequent cause of mortality for all age groups under 45 years was acute watery diarrhoea (Siddique et al., 1991).

In the longer term, the consequences of sea-level rise could influence the frequency and distribution of disease vectors. Inundation of coastal regions, for example, affects the incidence of mosquito species that breed in brackish water, e.g. the malaria vectors *Anopheles subpictus* and *A. sundaicus* in Asia. Floods could, however, also destroy the natural habitat of some pathogens, such as the EEE virus (eastern equine encephalitis virus) found in freshwater swamp areas along the US coastline (IPCC, 2001b).

In addition, the rise in sea level and the consequences of storm surges and floods pose a risk to drinking water supplies and food security. This is a matter of increasing salinization of freshwater reservoirs, which not only affects drinking water supply, but can also adversely affect agricultural productivity in the vicinity of the coast. At the same time, floods can also lead to considerable crop losses, as for example in the case of the 1998 floods in Bangladesh, where rice losses accounted for more than half of total agricultural losses and resulted in annual agricultural production falling to a mere 24 per cent of the expected total. Potential consequences include food shortages and undernourishment (del Ninno et al., 2001; WHO, 2002).

As a result of the shock and the consequences of such events, floods can also have long-term effects on the psychological wellbeing of the people affected. Loss of family members and friends, social networks, property and employment can lead to post-traumatic stress syndrome. This manifests itself in feelings of anxiety, depression, psychosocial disorders, and indeed can lead to an increase in suicide rates. It must be taken into account that psychological problems of this sort may not emerge until months or years after an event of this sort (WHO, 2002).

According to a study by the World Health Organization, more than 150,000 people are already dying every year due to the consequences of climate change (WHO, 2002). The primary causes of mortality in this context are increased incidence of diarrhoea, malaria and undernourishment. WHO estimates suggest that additional health risks resulting from climate change will more than double worldwide by the year 2030 (McMichael et al., 2004). These estimates are based on forecasts of a sharp increase in the relative risk of floods, with smaller increases in malaria, undernourishment and diarrhoea. Although smaller relative changes in these phenomena are forecast, they have the potential to bring about disease on a much bigger scale. Infectious diseases thus seem to present a greater risk to humanity than the direct impact of sea-level rise. However, the models used at present do not take account of potential interactions among the various health risks.

3.2.2.2
Economic damage

Assessing the economic impact of climate change on coastal areas also presents scientists with considerable challenges. To be able to make any statement on the overall costs of the impact of sea-level related climate change requires detailed analysis that is also highly disaggregated in geographical terms so as to enable estimation of the expected damage. Such damage may take a wide variety of forms, ranging from damage to property to costs arising due to loss of human life or loss of biological diversity and ecosystem services. Table 3.2-1 gives examples of sectors of society affected by sea-level rise and of the damage and losses to be expected.

In order to assess potential physical damage and impacts on people, it must be borne in mind that a large number of megacities will be affected by a rise in sea level. Of the 20 megacities throughout the world, 15 are exposed to the sea (calculated on the basis of data from Klein et al., 2002; UN, 2004). These include Tokyo, Mumbai and New York. Since development of megacities often entails exacerbation of existing local environmental problems, such as lowering of the groundwater level, these areas often lack any natural buffering capacity to balance the consequences of a rise in sea level. In such cases, drinking water supplies could be jeopardized. This is an example of what is termed 'critical infrastructure' (Bruneau et al., 2003; DRM, 2006), a category that also includes transport, telecommunications and energy supply networks, and emergency, rescue and health services; it further includes the retail sector, public administration, banking and finance. Critical infrastructure refers to institutions that fulfil vital needs and guarantee public safety, uphold law and order and ensure provision of basic public services and a functioning economy (Commission of the European Communities, 2005a). Disruption or damage to this infrastructure can result in supply bottlenecks and significantly impair public safety (BBK, 2006), and may even have a destabilizing effect on a whole region. For example, a gradual rise in sea level and extreme events resulting from it could interfere with the functioning of major ports and at times bring them to a halt altogether, with a knock-on effect on regional trade and transport networks. Geophysical changes to coasts are thus also likely to have large-scale economic impacts on neighbouring and inland regions (Brooks et al., 2006).

In addition to the costs arising from physical damage or disruption to production, there are also costs resulting from the loss of ecosystem services. For example, the negative impact of sea-level rise on coastal ecosystems can adversely affect local fishing yields (Brooks et al., 2006). In many countries, especially poorer countries, the security of people's livelihoods often depends directly on the yield from these ecosystems. Any disturbance in the freshwater balance, for example by seawater intrusion (Section 3.2.1.4), can also affect agriculture. Increasing groundwater salinization has already damaged common agricultural land on the islands of Tuvalu (Friends of the Earth, 2005). As well as jeopardizing food supply, this also brings about a decline in local economic activity.

The overall costs of climate change include on the one hand the damage caused by climate change in monetary units, and on the other the costs of adapting to climate change. Adaptation measures must be implemented in accordance with the principle of economic efficiency so that the benefits of the measures (in the form of damage prevented) outweigh the costs (for example costs associated with construction and maintenance of sea walls). In other cases, it may be more sensible in strict economic terms to forego adaptation measures altogether and accept climate change-induced damage. A cost-effective portfolio of strategies will also depend on environmental and socio-economic conditions in a given region, and these can change over time. For planning strategies and decision-making, it is important that categories of costs and benefits associated are thoroughly explored and taken into account (Section 3.4.1.1).

Categories	Damage or losses
Infrastructure	Buildings, transport infrastructure (roads, rail networks, ports, airports), energy infrastructure, coastal protection structures
Economic sectors	Fisheries, agriculture, forestry (timber in mangrove forests), tourism, transport
Human wellbeing	Mortality, spread of diseases, migration/displacement of people, loss of landscapes and cultural assets
Ecosystems	Services from coastal ecosystems, biological diversity, including some species-rich islands, disruption of the freshwater/saltwater balance

Table 3.2-1
Classification of damage caused by a rise in sea level.
Source: adapted from Fankhauser, 1995

A great deal of data is required in order to assess the overall costs of climate change worldwide. Detailed information is particularly needed for identifying and assessing potential damage. Available information, however, is often far from comprehensive and indeed may be quite rudimentary, especially in developing countries. As shown in Table 3.2-1, damage may take a variety of forms and also includes goods that are not traded on the market and therefore have no price. This applies particularly to loss of ecosystem services and biodiversity, which may be quantified in economic terms with the aid of surveys and economic methods of estimation. However, this is an area that is fraught with uncertainty.

People will not simply put up with the effects of climate change. They will protect themselves from damage by putting measures in place to adapt. Economic analysis must therefore include exploring cost-effective combinations of strategies. To do this, models are needed that can simulate not only climate change but also national economic development worldwide. Although some models of this sort are already in use (Fankhauser, 1995; Yohe et al., 1999; Darwin and Tol, 2001), they are based on highly simplified assumptions, with the result that estimates of global costs can only be calculated very roughly and are therefore of limited expressiveness. Data from regional vulnerability analysis, however, enable more accurate estimation of the costs of climate change due to sea-level rise, at least in smaller areas (e.g. Box 3.4-2).

3.3
Guard rail: Sea-level rise

3.3.1
Recommended guard rail

WBGU recommends the following guard rail: absolute sea-level rise should not exceed 1m in the long term (even over several centuries), and the rate of rise should remain below 5cm per decade at all times. For comparison: total anthropogenic sea-level rise up to now has been 20cm; current rates are around 3cm per decade (Section 3.1).

3.3.2
Rationale

The recommended levels are based on WBGU's estimation that a higher or more rapid rise in sea level would in all probability cause damage and losses to humankind and nature that exceed tolerable levels. As is generally the case with guard rails, this estimation contains a normative component and is not solely based on scientific principles (Box 1-1), given that there continues to be considerable uncertainty surrounding the actual consequences of sea-level rise. WBGU hopes that this proposal will stimulate broad debate within society on what is an acceptable degree of sea-level rise and stimulate further research on its consequences.

As in the case of WBGU's climate guard rail on the increase in global temperature (a total of 2°C and not more than 0.2°C per decade; Box 1-1), the consequences of sea-level rise depend both on the overall figure and on the rate. Effects on structures that are non-moveable in the long term, such as cities and world cultural heritage sites, depend to a greater extent on the absolute figure, while the rate of rise tends to be more important for dynamic systems such as ecosystems, beaches and some coral atolls, which are able to adapt to some degree. Between the two – in other words between the overall figure and rate – there is a variable degree of trade-off, in the sense that a higher absolute value may be tolerated if the rate is slower, while the maximum rate is tolerable at best for a very short time.

ABSOLUTE RISE

In order to justify setting an absolute guard rail for sea-level rise that must be adhered to even in the long term, one must consider the consequences of a possible very slow rise in sea level. Based on current knowledge, in the view of WBGU a rise of more than 1m would be intolerable, because severe consequences would be virtually unavoidable even with a very long period of adaptation. This applies, for example, to a whole series of megacities in close proximity to the coast, such as New York, Lagos or Kinshasa.

New York City consists of several islands and peninsulas and has around 1000km of coastline (Bloomfield et al., 1999). Figure 3.3-1 shows the areas of southern Manhattan that would be inundated in the event of a 'one-hundred year flood' (water levels 3m above normal levels) at today's sea levels. In this case, massive damage could be expected to occur, with flooding of important infrastructure including some subway stations. Statistically, if there is a sea-level rise of 1m, this storm surge level would be attained not just once a century, but every four years. A 'one-hundred year flood' would then extend correspondingly further into the streets of Manhattan.

Similar storm problems are to be expected in other cities and in large river deltas (e.g. the Yellow River, the Yangtze, the Ganges-Brahmaputra, the Mississippi or the Nile). In developing countries,

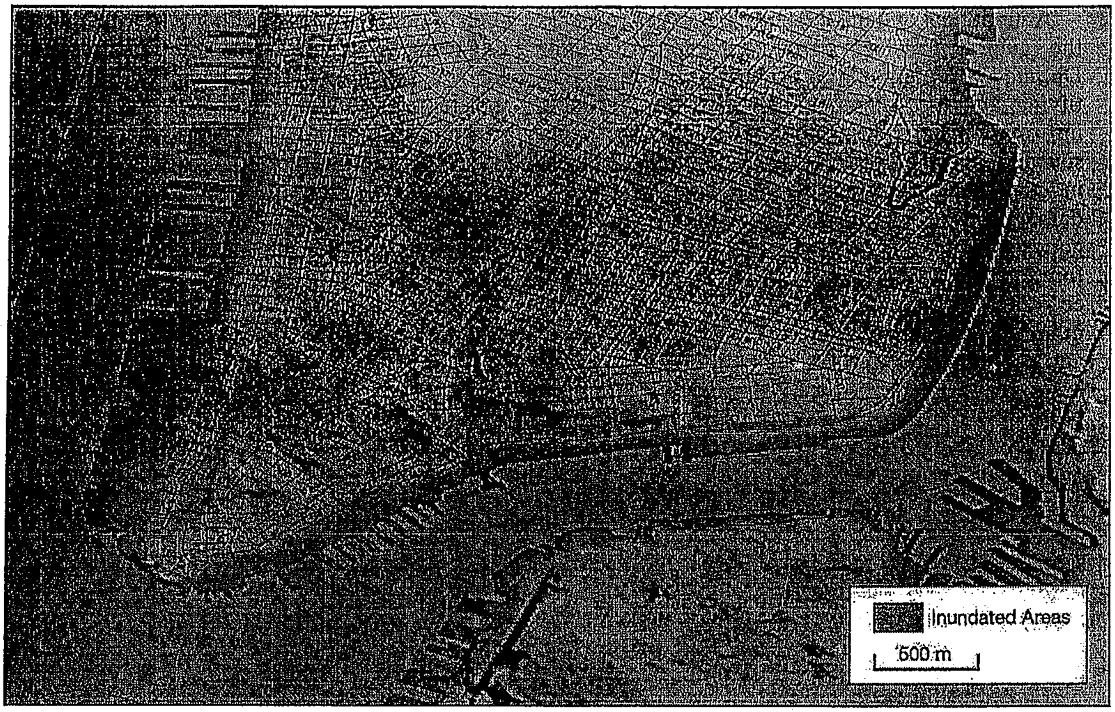


Figure 3.3-1
Inundated areas (blue) in lower Manhattan (New York) in a statistically typical one-hundred year storm event based on the present sea level. A sea-level rise of 1m would result in storm tides of this height approximately every four years.
Source: Rosenzweig and Solecki, 2001; data based on USGS, U.S. Army Corps of Engineers, Marquise McGraw, NASA GISS

poor population groups are often concentrated in these endangered areas.

In its first report, the IPCC listed a whole series of island states that would face a considerable threat from sea-level rise. Many small island states would lose a significant proportion of their land if the sea level rose by 1m (IPCC, 1990). Some of the islands are at risk of becoming uninhabitable due to storm surges resulting from a sea-level rise of this magnitude. Affected islands include, for example, the Maldives, Kiribati, Tuvalu and the Marshall Islands, with a total population of 523,000 people. These problems are exacerbated by the increase in tropical cyclone intensity (Section 3.1.2). Around another 380,000 people living on the Caribbean islands of Anguilla, Cayman Islands, Turks and Caicos Islands and the island state of the Bahamas would also be affected by this. Although some of these islands have high ground of up to 65m above sea level, with the rise in sea level, storm floods would penetrate further and further inland. In many cases, virtually the whole of the island's infrastructure (e.g. airports, roads) is located directly on the coast.

If the sea level rises by more than 1m, there is an additional risk that cultural heritage sites will be irretrievably lost. Cultural goods from the past possess 'outstanding universal value' (UNESCO, 1972). In view of this fact, in 1972 UNESCO adopted the International Convention for the Protection of the World Cultural and Natural Heritage. Some 180 countries are now signatories to this Convention. An important component of world heritage is its universality; it belongs to all individuals and peoples of the world, irrespective of the territory in which it is located.

Great importance should therefore be given to protecting these world heritage sites. A sea-level rise of more than 1m would pose a direct threat for example to the 12th century Shinto shrine of Itsukushima in Japan and the 8th century Shore Temple in Mahabalipuram in India. Both are important religious sites whose special character derives from their coastal location. To protect these sites from sea-level rise, one option might be to consider removing the monuments to another site. This would involve at least some loss, as the monuments are symbolically and historically rooted in their present environment.

A sea-level rise of 1m would also put, among other places, Venice and St. Petersburg at considerable risk. In the storms of 1966, when flood levels peaked at 2m above normal, large areas of Venice were submerged. Homes and businesses were destroyed as a result, but so too were valuable works of art (Nosengo, 2003). In

St. Petersburg too, storms could have devastating consequences. A researcher at the European Bank for Reconstruction and Development (EBRD) suggests that a storm-induced rise in water levels of 2.5m would inundate around 10 per cent of the city, while a rise in excess of this level could affect up to one-third of the city (Walsh, 2003). As a result of these dangers, extensive projects are currently under way to build protective structures; in the case of St. Petersburg, international funding is also involved.

Many valuable coastal ecosystems would also be threatened by a sea-level rise of this sort, for example the Kakadu National Park in Australia and the mangrove forests of the Sundarbans National Park in Bangladesh and India (UNESCO, 2006).

RATE OF RISE

The rate of sea-level rise should not overstretch the adaptive capacity of human society or marine and coastal ecosystems.

The adaptive capacity of ecosystems can be estimated using the example of coral reefs, mangrove forests and beaches. The last great rise in the sea level occurred at the end of the last Ice Age, over the period from 18,000 to 5,000 years before present. Since then, the rate of rise has always been less than 20cm per hundred years, and usually well below this (Walbroeck et al., 2002; Peltier, 2004). In the Holocene era, after this last great sea-level rise came to an end, coral reefs, beaches, mangrove forests and other ecosystems were able to become established again along the newly formed coastline.

The maximum vertical growth of coral reefs is estimated at 10cm per decade (IPCC, 2001b). If the conditions are highly favourable, they could therefore presumably keep pace with this rate of sea-level rise. Future growth rates will be markedly slower, however, due to ocean acidification and warming and other environmental stresses (Section 2.4).

The adaptive capacity of mangrove forests and beaches is highly dependent on sediment accretion. Sand beach loss already observed along many coastlines is considered to be a consequence of sea-level rise (Leatherman, 2001). Ellison and Stoddart (1991) analyse the development of mangrove forests during the Holocene and arrive at the conclusion that in a situation where there is little sediment accretion, even the current rate of sea-level rise places excessive demands on adaptive capacity and will result in the loss of mangrove forests. Other authors (Snedaker et al., 1994), meanwhile, argue that if the habitat is favourable, retreat of mangrove forests further inland could enable them to accommodate an even higher rate of sea-level rise. In many cases, however, such favourable conditions will not be present. Based on a scenario with an almost linear sea-level rise of 5cm per decade, the global DIVA model (Section 3.2.1.5) projects a continuous loss of mangrove forests whose adaptive capacity has thus already been exceeded. By 2100, according to this projection, a quarter of all mangrove forests would disappear.

According to the scenarios postulated by IPCC (2001a) the rate of sea-level rise towards the end of this century will be 3–7cm per decade, with up to 13cm per decade in the worst-case scenario. In view of these facts, WBGU recommends setting the guard rail for maximum sea-level rise at no more than 5cm per decade. It must be borne in mind, however, that even compliance with this guard rail will not provide protection from damage that is already significant, as is also the case with other WBGU guard rails (Box 1-1).

3.3.3
Feasibility

The current and foreseeable rise in sea level is almost entirely anthropogenic, and hence its future development can also be influenced by humankind. The ability to control it is limited on the one hand by the long time-scale required (centuries) for a response in terms of sea-level change. It is also limited by forecasting difficulties and by the potential for strongly non-linear behaviour on the part of the great continental ice sheets. Nevertheless, the recommended guard rails can be implemented, according to current knowledge, by means of an appropriate climate change mitigation strategy.

Stabilizing the global temperature at 2°C above pre-industrial levels, according to the mathematical models, would result in a sea-level rise of around 50cm in the long term (after 1000 years) simply due to thermal expansion. Mountain glaciers would add approximately another 20cm to this (Section 3.1.1.4). Prevention of large-scale melting of the continental ice sheets in Greenland and Antarctica would therefore be critical for compliance with the guard rail. Further research must establish the limit that needs to be set as regards the rise in global mean temperature in order to achieve this. It is conceivable that, in the long term, it may be necessary to reduce the temperature to below the 2°C threshold again.

In this century, the guard rail for the rate of sea-level rise would only be breached by the more pessimistic half of the IPCC scenarios (2001a); the more optimistic scenarios comply with the guard rail even without climate protection measures. It should be borne in mind, however, that the currently observed rate of rise of 3cm per decade is already clearly higher than all of these scenarios (Fig. 3.1-4). It must therefore be assumed that, in all likelihood, the IPCC

(2001a) has underestimated sea-level rise, and that climate mitigation measures are indeed required to comply with this guard rail. Based on the assumption that the change in sea-level rise will be relatively smooth and gradual, as depicted in all the scenarios, compliance with the guard rail for the rate of sea-level rise would mean a maximum rise in sea level of around 40cm in the 21st century. This would be double the sea-level rise that has taken place to date as a result of human activity.

The climate and sea-level rise guard rails are closely interlinked, since sea-level rise is directly caused by global warming. In the next few decades, the climate protection strategies required to meet the 2°C goal and to comply with the guard rails relating to sea-level rise will most likely be similar and compatible. Despite the long-term nature of sea-level rise and the uncertainties surrounding the behaviour of the continental ice sheets, these guard rails are not redundant. Even if the global warming guard rail is obeyed and lasting climate warming of 2°C takes place, this would be enough to cause melting of the Greenland ice sheets, thereby breaching the guard rail on sea-level rise. For this reason, it is conceivable that the guard rail on sea-level rise will lead to the imposition of strict limits on emissions, especially in the long term, in other words in the coming centuries, in order to stabilize the continental ice sheets.

This is why it is vital, as regards emissions, to embark on a path that will lead to stabilization of the global temperature at a low level after 2100, and if possible well below 2°C above the pre-industrial level. The guard rail on sea-level rise therefore determines in particular longer-term climate protection goals from the second half of the century onwards. In the coming decades, it is a key additional justification in support of the 2°C goal. If, on the other hand, the continental ice sheets of Greenland and Antarctica were to shrink suddenly and unexpectedly, the guard rail on sea-level rise could require tougher climate protection measures than the 2°C climate guard rail even sooner. It thus gives particular grounds for closer observation of the ice sheets in order to identify dangerous developments in time.

3.4
Recommendations for action: Develop and implement adaptation strategies

In its previous reports on climate policy, WBGU has made it clear that priority should be given to strategies for preventing greenhouse gas emissions. However, even if there is substantial success in preventing greenhouse gas emissions and complying with the guard rail on sea-level rise, it will no longer be possible to prevent some of the effects of climate change on coastal areas. Appropriate adaptation measures are required in order to cope with these effects. As regards strategies for adapting to sea-level rise and extreme weather events, WBGU focuses on two questions in particular:

1. How can the anticipated destruction of coastal infrastructure and settlements be coped with?
2. How can provision be made under international law to deal with land loss?

3.4.1
Adapting coastal regions to the consequences of climate change

3.4.1.1
Adaptation options: Classification and assessment

The extent to which the consequences of climate change will give rise to damage in coastal areas and turn hazards into disasters varies considerably from one region to another and depends on the vulnerability of the areas affected. This in turn depends on the susceptibility and resilience of natural, social, infrastructural, economic, institutional and cultural subsystems (Titus et al., 1991; Klein et al., 1999). Resilience in this context means the ability of subsystems to cope with repeated disruption so that key structures and processes remain intact (Burton and Lim, 2001; Burton et al., 2002; Adger et al., 2005).

Industrial countries will be better able to deal with hazards than developing countries, because they have more extensive capacities at their disposal, such as an efficient institutional infrastructure, technical know-how and financial resources. Hurricane Andrew, for example, a category 5 event on the Saffir-Simpson hurricane scale, cost the lives of 23 people in the USA in 1992. A typhoon of comparable strength that hit Bangladesh in 1991, meanwhile, led to extensive flooding that resulted in 100,000 deaths and millions of refugees (Adger et al., 2005).

The large number of influencing factors and interactions makes it essential to develop adaptation strategies that are tailored to the given context. Adaptation in this context needs to fulfil two purposes: on the one hand to reduce damage, and on the other to increase resilience of the above subsystems. There are basically three different options for adaptation in response to the hazards outlined above: 'protection', 'managed retreat' and 'accommodation' (IPCC, 2001b).

PROTECTION

Protection involves protecting coasts from rising sea levels by means of structural measures. These might include 'hard' engineering measures such as construction of sea walls, dykes, or flood defence systems, and 'soft' measures such as conservation or introduction of protective coastal ecosystems (e.g. wetlands, mangroves, islands) or beach nourishment as natural barriers. Hard structural adaptation measures are exceedingly cost-intensive in terms of construction and maintenance. In addition, they increase stress on neighbouring ecosystems; for example, they increase the threat of wetland loss. Without intervention, wetlands will tend, as a rule, to migrate inland in the event of floods. This autonomous adaptation is impeded by sea wall construction, because areas on the seaward side of sea walls become inundated, while on the landward side new wetlands are prevented from forming. In the case of US coasts, it is estimated that 50 per cent of all wetlands have disappeared as a result of this process (Titus, 1990). In the coastal regions of the EU, moreover, it has been observed that adaptation involving hard engineering measures can trigger or accelerate erosion processes in neighbouring coastal areas. This in turn can significantly impair the functioning of hard protection measures (Commission of the European Communities, 2005b; Brooks et al., 2006). Due to the multitude of problems associated with hard structural adaptation measures, preference is given nowadays to 'soft' measures wherever possible. Soft strategies interfere less with coastal ecosystems and permit a more flexible response to sea-level rise, the extent of which is fraught with uncertainty. Ultimately, however, the effectiveness of soft and hard measures will depend on the environmental and societal context.

MANAGED RETREAT

Managed retreat means that use of areas in proximity to the coast is reduced, or certain areas are relinquished completely. In this context, strategies might include moving buildings and settlements, and introducing government regulation on the use of vulnerable areas. Retreat may be enforced by means of public order legislation, e.g. by regulating land use under national construction and planning law. Another means is to provide incentives in favour of the decision to retreat voluntarily. Measures of this sort encourage households and private businesses to take account of all costs relating to use of the coast in their economic decisions to invest. A targeted information policy implemented by local public bodies could help to enhance awareness of the implications of climate-induced risks.

In certain cases, a sensible option may be to actively support resettlement of people from the coast to less threatened areas, for instance by providing grants via the regional administrative bodies, or within the framework of international development cooperation.

The issue of resettling communities and their residents arises in a very concrete way in the aftermath of a natural disaster, in other words, when infrastructure has been destroyed over a large area. A decision must then be made as to whether reconstruction is economically sensible according to the prognoses relating to future sea-level rise and the incidence and intensity of extreme weather events. The more residents can rely on the government to share the costs of protection measures, the more they will be inclined to remain in threatened regions. If, however, each individual is confronted with the costs of protection, the attractiveness of reconstruction decreases and more people will opt to migrate to less threatened areas. In order to provide the right incentives in such instances, therefore, government (and international) aid for reconstruction must be tied to a corresponding relocation condition. Municipalities, too, must weigh up their adaptation options and decide between protection and retreat. After a natural disaster, they will tend to rebuild destroyed infrastructure rapidly to be able to ensure continuity in public services. This is why it is important to develop strategies for resettlement for threatened areas before a natural disaster strikes (Brooks et al., 2006).

It is conceivable that, despite government incentives to encourage migration away from threatened coastal areas and an adequate information policy on the part of public institutions, some people will not agree to relocate on a voluntary basis. In such a situation, the government must decide whether it will permit the affected people to remain and face damage to property and life at their own risk, or whether it will forcibly relocate sections of the population. The latter option, of course, carries considerable potential for conflict (Box 3.4-1).

Government measures encouraging migration away from coastal areas should go hand in hand with measures limiting migration of people into these areas. For example, levying a tax that reflects the social costs resulting from migration of people into coastal areas ensures that these costs are included in an individual's calculation of the costs associated with migrating into the area, and thus become relevant for his decision.

Government regulation can thus fundamentally support the relocation of people in the desired direction. It is nevertheless possible to provide false incen-

Box 3.4-1

Potential for conflict over resettlement

Depending on regional scenarios of threat, policy-makers must consider the option of planned resettlement of population groups. However, a large number of projects in a great variety of socio-economic and political contexts demonstrate the many problems that can arise as a result of such measures. As examples, dam projects, mining and infrastructure projects (e.g. the Three Gorges Dam in China, lignite open-cast mining in Garzweiler, Germany, road construction in metropolitan Manila, etc.) can be cited.

Although resettlement of endangered coastal residents is generally a necessity in order to protect the affected people, there is also considerable potential for conflict in this situation. For example, decisions to protect important infrastructure installations may amount to unequal treatment of different population groups (populations in the proximity of a protected installation will be protected along with it, while other settlements are evacuated). In addition, exacerbation of conflicts relating to land use in the target area for resettlement may occur (conflicts between long-standing residents and new settlers). Massive resistance is most likely to occur, however, in regions where resettlement programmes were used in the past as a repressive measure by the government.

tives, for example, via interventions in insurance markets. Due to the increasing incidence of floods and cyclones, economic adjustments are in fact to be expected in the insurance markets: insurance premiums for flood damage will rise, and some private insurers will withdraw from the market. As a result, coastal areas lose their attractiveness as areas for settlement. If insurance premiums are kept artificially low by government subsidies, however, as is the case in the USA, prices are distorted and incentives to migrate away from coastal areas are reduced.

Accommodation

The third strategy, termed accommodation, involves modifying land use and subsystems to ensure that they take account of the new threats. Residents of threatened regions continue to use the threatened land, but without trying to protect it from inundation. This can take place, for example, by instituting disaster management systems (constructing emergency refuges, formulating plans of action, undertaking targeted public education and communication work). It is likewise possible to modify land use, for example by cultivating varieties of grain that are resistant to increasing salinization and inundation of the soil or by converting arable land to fish farming facilities. In addition, accommodation also includes engineering measures (such as increasing the height of buildings, making cellars and buildings water-tight).

Portfolio approach

It frequently happens that these options are implemented as a combined set of strategies rather than as alternatives. A 'portfolio approach' is pursued in order to respond adequately to the given conditions in a particular region. One possible combination of strategies involves partial retreat, where protective measures are applied only to areas where there is a high concentration of people, assets and functions. Flooding is allowed to take place in the other areas. Using this approach, implementation of protection measures would be prioritized, focusing on political and economic hubs such as cities, towns and industrial areas. A particular focus of attention in this context is protecting the 'critical infrastructure', in other words, infrastructure so essential that its destruction has a destabilizing impact on a country's public life and economy.

Another strategy that might be considered is to combine protection with accommodation. This could involve, for example, aiming to increase coastal resilience through conservation of mangrove forests as natural barriers. In the context of local land use planning, setback areas could be created or extended to permit ecosystems to shift landward, thereby enhancing an area's capacity for autonomous adaptation (Nicholls, 2003).

3.4.1.2
Choosing adaptation strategies

Cost-benefit analysis may be used (Box 3.4-2) to help choose appropriate adaptation strategies for a specific region. This requires comprehensive information on the state of coastal areas and on the impact of human activities. Assessment of the interaction of land and sea for commerce and industry, for port facilities, buildings, groundwater and extraction of construction material is also called for in this context (Kullenberg, 2001; SEEDS, 2005). The data required for this purpose are gathered and evaluated in the framework of vulnerability studies (Burton and Dore, 2000).

In contrast to prevention strategies, the effects of adaptation projects are essentially local; in other words, they have no direct global environmental benefit. Moreover, because the extent of the environmental effects is fraught with uncertainty, 'no-regret' measures should initially be identified and put in place. These are measures that bring a net benefit for stakeholders irrespective of any actually occuring climate-induced losses. Such measures tend to win greater support among affected stakeholder groups because they take into account the uncertainties of climate change and yield desirable results even if climate change were not to occur. An example might be a coastal region with pre-existing damage and a high population density, for which a rise in sea level would exacerbate existing problems. Improving planning relating to use of coastal areas would be an appropriate strategy here for dealing with sea-level rise. Moreover, it would still bring a positive net benefit even if the anticipated effects of climate change failed to materialize.

In practice, transaction costs, institutional failure or lack of information have frequently led to the shelving of such projects. Adaptation projects can help to dismantle these obstacles (Fankhauser, 1998). Implementation of integrated coastal zone management, for example, could help to improve the exchange of information among the different policymakers and thereby make it easier to carry out projects.

3.4.1.3
Implementing adaptation strategies

Adaptation requires more than simply implementing engineering options. Not only is the choice of strategies influenced by a multitude of factors; the strategies themselves impact on the subsystems of the region in which they are implemented. It is also necessary to reconcile the various responsibilities and interests of participating or affected groups in society (Nicholls, 2003).

RISK MANAGEMENT

Risk management provides an ideal means of implementing adaptation strategies. Risk management plans designate persons responsible (public and private, at municipal, national and international level) for all stages of an event – before, during and after. They describe what measures should be taken (strategic versus tactical measures) at what point in time, and the manner in which the responsible persons should respond and to whom they should report (Boyd et al., 2005). In many instances, policy-makers do not treat the issue of climate change as a priority, and as a result, climate-induced changes in the risk situation are not adequately taken into account. Risks are thus often graded as low and threats are considered as rather unlikely, with the result that the design of available risk management plans is inappropriate. The example of Hurricane Katrina, which caused destruction on an unprecedented scale on the US coast in August 2005, shows that inadequate planning can heighten the socio-economic impact of such events.

Formulating an appropriate risk management plan should ideally be a cyclic process. In advance of an extreme event, a planning phase (Phase 1) – in which preventative and reactive measures are devised – is followed by a preparatory phase (Phase 2). Measures included in this second phase are aimed at reducing the likelihood of potential hazards resulting in disasters. This may be done by establishing action plans, providing emergency training and conducting targeted public information and education campaigns, or by establishing agreements for international cooperation in the area of disaster assistance and for dealing with environmental refugees. If an event actually occurs, the response phase becomes relevant (Phase 3). This phase involves measures to be carried out during and after an event. Such measures include emergency response, measures to prevent consequential damage such as outbreaks of epidemics, or implementing measures aimed at speeding the recovery of affected areas. The reconstruction phase (Phase 4) concludes the process of managing such an event. All activities in this phase are aimed at restoring normal system functioning, via disbursal of insurance payments, setting up temporary emergency shelters or reconstructing the physical infrastructure. In addition to these four phases, problems are identified with regard to the handling of the event and mistakes are analysed. The experience gathered is then evaluated in a new planning phase and implemented in the form of improved strategies (Boyd et al., 2005).

In the case of slow onset hazards, on the other hand, the priority of risk management lies in regularly assessing the potential risks and identifying the most vulnerable individuals and regions. Risk management involves adaptation to constantly changing conditions. A high degree of flexibility in terms of strategies is needed to achieve this. Such strategies include in particular scientific monitoring, public education and communication and legislative provisions (Boyd et al., 2005).

INTEGRATED COASTAL ZONE MANAGEMENT

In order to take account of the highly complex, interconnected nature of impacts, adaptation measures should be very broad, in other words, they should be enshrined in all key areas of policy. Examples are coastal protection plans and strategies for sustainable development. Another term used in this context is 'integrated coastal zone management'. As part of this system of management, data on both ecosystems and social systems are collected and processed. Integrated coastal zone management as an instrument for managing risk in this context refers to a dynamic process developed and implemented on the basis of a

Box 3.4-2

Coastal management on the German North Sea coast

Global forecasts on the impact of sea-level rise are not directly applicable to regional or local circumstances. Even within Germany's coastal areas, major differences can be observed as regards the hazard situation and socio-economic resilience. To be able to put expedient measures in place to adapt to future consequences of climate change, therefore, small-scale, scenario-based studies need to be conducted that analyse both the natural and social characteristics of a given area. Studies of this sort have already been carried out for two regions of the German North Sea coast: for the island of Sylt and for the north-west German coastal region.

As a result of its particularly risky situation and economic productivity, the North Sea island of Sylt was analysed in the context of a study commissioned by the Federal Ministry for Education and Research (BMBF) entitled 'Climate change: consequences for people and coasts'. The island is an open system with a negative sediment balance in which erosion processes occur that result in a continuous reduction in land mass. Sea-level rise is expected to accelerate these processes. The economic structure of Sylt is heavily biased towards tourism, which is concentrated on the western side of the island.

Various scenarios were devised in order to estimate the consequences of climate change up to the year 2050. The scenario presented here is based on an assumed local sea-level rise of up to 25cm and changes in wind conditions, tidal range and swell (i.e. wave height, direction of approach and period). Extreme weather and its impacts on the natural environment and socio-economic structures were not considered, so further research is needed to explore these aspects. Based on the results of the model simulations, changes in sediment transport are to be expected on the west coast of the island, which would have a negative effect on the wave-attenuating impact of an offshore reef. The three municipalities of Rantum, Hornum and Wenningstedt are likely to be worst affected by this.

The study recommends adaptation of these coastal areas by adopting a portfolio approach, in other words by a combination of different component strategies. Consideration is given to the three components: protection, managed retreat and accommodation. A combination of 'soft' and 'hard' coastal protection measures was identified as the optimum strategy for protecting Sylt's current coastal form. The measures focus particularly on the environmentally sustainable option of beach nourishment, which is currently already being implemented on the west coast of the island.

To evaluate the recommended adaptation measures in economic terms, cost-benefit analysis was carried out for the west coast of the island. According to this analysis, adaptation costs would consist primarily of the costs of additional beach nourishment measures. At current values, the costs involved in the period up to 2050 are estimated at €33 million. The benefits of coastal protection in terms of prevented losses of assets, infrastructure, beaches and dunes must be balanced against this. The current value of this benefit is estimated at €381 million. The results of the analysis for this period thus show that the benefit-cost ratio of coastal protection for the island of Sylt is clearly positive. The scenario examined illustrates that the island of Sylt can probably be protected effectively against a small rise in sea level of 25cm by beach nourishment measures.

At the same time, it must be noted that Sylt represents a special case, with its particular geographical characteristics and its very high concentration of assets resulting from tourism. The recommended adaptation measures are unlikely to be applicable to the majority of the world's other coastal regions. Beach nourishment, for example, is only possible, and only makes economic and environmental sense, if sand is available within the coastal region in sufficient quantities. In addition, the estimated adaptation costs are based on a coastal protection strategy aimed primarily at protecting the main part of the island, which is higher-lying compared to the shore, from erosion. Beach nourishment would be unlikely to provide adequate protection for flatter sections of coast in the face of rising sea levels – especially in the event of extreme weather situations.

Building on the experiences of the Sylt study, the project 'Climate change and preventive risk and coastal protection management on the German North Sea coast' (KRIM) not only examines the consequences of accelerated sea-level rise for various stretches of coastline, but also the concomitant risks of extreme weather events. Using the same time horizon of 2050, this study analyses future consequences of climate change together with possible social adaptation measures and their impact.

The KRIM project assumes a regional increase in temperature of 2.8°C, a local sea-level rise of 55cm, and changes in mean tidal range, precipitation, swell, and winter wind velocity and direction. In addition, extreme weather conditions with flood levels of +200cm are also taken into account.

In order to analyse the consequences of this climate scenario for Germany's north-western coastal region, the resulting risks of extreme weather events were calculated and the costs and knock-on effects for the regional economy of possible coastal protection strategies were set against these. Alternative strategies were compared using cost-benefit analysis techniques. When assessing potential damage from storm surges, the KRIM project not only considered environmental damage and economic losses from damage to assets and infrastructure, but also the resulting losses to the national economy in terms of value-added activities, income and jobs. A mesoscale modelling technique was used to assess the value of economic losses, in other words aggregated data based on official regional statistics were used. Subsequent to the value assessment, losses were calculated as a function of flood levels.

Among other things, the study examined dyke-raising and construction of a second line of dykes as elements of a protection and accommodation strategy for the study area of Wangerland. The location of Wangerland (a region between river Weser and river Jade at the North Sea) is geographically very exposed, with long coastlines requiring protection, but it has relatively few assets. Based on the year 2010 as the assumed investment year (base scenario), the costs of dyke-raising were estimated at €10.5 million (for an average increase in height of 0.75m over a 28km stretch of dyke), while the costs of constructing a second line of dykes (variant II) were estimated at €20 million (for a 17km stretch of dyke with a height of 3m above mean sea level). The current value of economic losses in the KRIM climate change scenario, meanwhile, is estimated at €63 million (2000) – calculated using the flood simulations and for the period up to 2050. According to these calculations, the benefit-cost ratio is highest for the dyke-raising option, with the result that action was recommended to implement this coastal protection measure.

▶

The procedure followed in the KRIM project provides a guideline for handling climate change-induced uncertainties with regard to coastal management and shows how the economic future of coastal regions could be forecast and planned. There is still a great need for further research in this area, however: (1) to explore scenarios involving higher rises in sea level; (2) to extend existing insights regarding regional losses and the costs of different preventative strategies (e.g. for the managed retreat option); (3) to include other sections of coastline in this analysis. It will ultimately require a great many small-scale studies of this type in order to be able to make more reliable supra-regional predictions regarding the financial impacts of climate change, and to be better able to work out the possible options for action.

The cases described show that in these instances, where the rise in sea level is clearly below the WBGU guardrail on sea-level rise, the problems can probably be overcome by means of appropriate adaptation measures. Unfortunately, a rise in sea level of more than 1m was not studied for these regions; in many places, successful adaptation in the event of such a high sea-level rise would no longer be possible at an acceptable cost. In developing countries, meanwhile, the problem of financial feasibility would arise even with the scenarios and strategies presented above; the adaptation measures discussed above, therefore, do not represent strategies that are universally applicable.

Sources: Daschkeit and Schottes, 2002; Mai et al., 2004; Elsner et al., 2005

coordinated strategy with the aim of managing environmental, socio-cultural and institutional resources so as to ensure sustainable conservation of coastal areas and ensure that they can be used in a variety of ways in future (Fankhauser, 1998; Yeung, 2001).

Coordinating the sectoral, competing and in some cases overlapping competences of the various decision-making tiers and specialist areas within the administration presents a major challenge as regards devising an integrated coastal management system. Institutional fragmentation often gets in the way of providing adequate responses. WBGU therefore recommends creating integrated institutions that bring together all the key competences. Such institutions would also facilitate reconciliation of the diverse interests of affected groups in society. Municipalities and local administrative departments can play a key coordinating role. Providing for a high degree of local responsibility could help to ensure that available knowledge on coping strategies on the ground is used efficiently, that affected groups in society are appropriately involved in planning and decision-making processes, and, in doing so, that coastal management systems are accepted by the local population (SEEDS, 2005; WCDR, 2005; Box 3.4-2).

There is still a considerable degree of catching up to do in order to integrate information on the potential impact of climate change systematically into implementation of coastal management systems. Despite sound scientific findings regarding the potential consequences of climate change, there has been scant political effort so far to devise adequate strategies for action.

Against this background, the German Federal Government's national strategy for integrated management of German coastal areas is laudable (Bundesregierung, 2006). This strategy takes into account the many different players involved and brings together the competing interests of protection and utilization of Germany's coastal areas under a single, integrated concept. It certainly emphasizes climate change as a major component in the long-term orientation of precautionary planning at regional level. However, in view of the gravity of the anticipated consequences of climate change, it is necessary to improve the scientific basis for developing this strategy further. Measures aimed at adapting to the consequences of sea-level rise and extreme weather events will need to become the primary focus of future strategy.

3.4.1.4
Future challenges

Two issues relating to implementing adaptation strategies need to be emphasized here: the significance of proactive measures and the special challenges of implementing adaptation strategies in developing countries.

EARLY WARNING SYSTEMS

Risk management plans encompass both proactive and reactive components of adaptation. Proactive components are particularly important for cost-effective adaptation design, because they prevent or at least reduce the chance of a risk translating into a disaster. This is true particularly with regard to sudden onset hazards. In the past, priority in financing adaptation strategies was given to reactive measures such as financing reconstruction of damaged infrastructure in the wake of a natural disaster (WCDR, 2005). What appears to be needed, therefore, is a reorientation of funding resources combined with a shift in priorities when choosing appropriate adaptation strategies. At the World Conference on Disaster Reduction (WCDR) in 2005 in the Japanese city of Kobe, it was decided that 10 per cent of funds hitherto used for ex-post measures in the aftermath of natural disasters should be diverted into preventive measures over the next ten years (WCDR, 2005; Münchener Rück, 2005a). The significance of proactive measures is underlined by the plan adopted by the WCDR to promote an International Early Warning Programme (IEWP). The IEWP is aimed at identifying and closing existing gaps as regards early warning (UN ISDR, 2005c). Key elements for improving early warning systems include developing national, integrated risk reduction strategies, capacity-building in the field of risk management and improving technical equipment and training. In addition, strategies are to be developed to improve communication of warnings to affected communities. Early warning therefore comprises a range of aspects, from technical capacity to preparatory measures at municipality level. To date, however, this linking of planning and precautionary measures with adequate response strategies has often been flawed. In future this deficit in existing systems is also to be eliminated. In order to achieve the goals set out in Kobe, international cooperation is required particularly in the area of data exchange, dissemination of warnings and developing institutional structures. At the present time there is a particularly urgent need to raise governments' awareness of the problem and establish priorities for developing appropriate strategies of risk reduction.

SPECIAL CHALLENGES IN DEVELOPING COUNTRIES

Climate change will have a major impact on developing countries in particular. These countries account for 97 per cent of fatalities from natural disasters (Freeman et al., 2003). Damage resulting from natural disasters is a considerable impediment to economic development in these countries. Adaptation therefore has particular significance for these regions. Technical know-how, appropriate institutions and especially financial resources are lacking, however, to enable the necessary measures to be put in place. There is broad consensus in the international community that support should be given to help developing countries cope with the impact of climate change. In Article 4, para. 3 of the Framework Convention on Climate Change, the Parties to the Convention commit themselves to provide financial and technical support to affected countries. In the context of the 'Hyogo Framework for Action', the 10-year programme of action adopted at the WCDR, this commitment was reiterated (WCDR, 2005). In addition, in recent years there has been increasing recognition of the fact that strategies for adapting to natural disasters and slow onset hazards need to be made an integral part of sustainable development cooperation (UNFCCC, 1992; UN ISDR, 2005a, b).

3.4.1.5
Financing adaptation measures in developing countries

To provide financial support to enable developing countries to adapt to the general consequences of climate change, a variety of international funding institutions offer financial transfers at multilateral level.

INTERNATIONAL FUNDS

In recent years, international funding bodies have been set up to promote adaptation measures in developing countries. In the context of the Framework Convention on Climate Change, three funds have been established that provide funding for adaptation to climate change in general, in other words not specifically related to oceans: the Special Climate Change Fund (SCCF), the Least Developed Countries Fund (LDCF) and the Adaptation Fund (GEF, 2005b).

It is the explicit mandate of the SCCF to provide funding for adaptation projects and technology transfer. The fund was set up in 2003 to complement the Global Environment Facility (GEF) with a specific focus on climate change. By late 2004, the volume of funds in the hands of the SCCF in the form of voluntary contributions from OECD countries and other industrialized countries totalled US$34.7 million. SCCF has been in a position to provide effective support for projects since early 2005.

The LDCF gives particular priority to providing support for developing countries to formulate and implement National Adaptation Programmes of Action (NAPA). NAPAs identify areas where action relating to adaptation is most needed. Of the US$32.5 million already contributed to the fund, US$11 million has already been disbursed for the formulation of NAPAs.

The Adaptation Fund, lastly, was set up with the aim of implementing Article 12, para. 8 of the Kyoto Protocol. Its primary source of funds is a share in the proceeds of Clean Development Mechanism (CDM) project activities amounting to 2 per cent of the certified emission reductions issued for a project activity. Disbursal of payments from this fund is unlikely to begin before 2008, that is, before the start of the first commitment period under the Kyoto Protocol. While the revenue effect of this de facto taxation of prevention projects is welcome, its allocation effect must be viewed with considerable criticism.

In addition to the above, GEF also provides funds for projects under its Climate Change Focal Area. In this case, however, the focus is on prevention projects rather than adaptation projects.

EFFICIENT USE OF DEVELOPMENT COOPERATION FUNDS

As well as the above funds, international donors provide financial assistance to developing countries affected by natural disasters in the context of development cooperation. In recent years, for example, the share of funds made available by the World Bank for dealing with the consequences of natural disasters such as tropical cyclones has increased markedly, from 3 per cent to 8 per cent of the World Bank portfolio (Freeman et al., 2003). Financial resources are thus increasingly being earmarked for projects not aimed at fulfilling the original goal of promoting economic and social development.

If the aim of international development cooperation is to support the development of adaptive capacity in developing countries, then assistance must focus to a greater extent on preventative strategies than has hitherto been the case, e.g., on developing early warning systems. A partial shift of this sort from aftercare to hazard prevention takes on added significance against the background of expected intensification of climate-induced extreme events. In order to prevent a loss of efficiency, development cooperation should be brought into line with the policies of the special adaptation funds described above.

At the same time, while ironing out the issue of financing adaptation measures, it is important not to lose sight of the actual goal of development cooperation. Economic and social development in itself remains the best form of adaptation strategy, because it generally increases the adaptive capacity of a developing country and thereby reduces its vulnerability to the impacts of climate change (Schelling, 1992).

COMPLEMENTARY INSTRUMENTS: PRIORITIZING MICRO-INSURANCE

The funding required for adaptation measures cannot be quantified in any robust manner due to a lack of even moderately reliable damage estimates (Section 3.2). It can nevertheless be assumed that the above-mentioned financial resources will not be sufficient and that it would consequently be sensible to secure funding for adaptation measures in the broadest possible manner. For this reason, new funding mechanisms should be considered alongside existing funding instruments and reallocation of currently available resources (WBGU, 2002).

Another means is to promote micro-insurance in order to disperse the individual risk of hardship; in countries with low per capita incomes, this takes on added significance. Micro-insurance aims to provide insurance protection at extremely low premiums for households and small businesses with a low, and in some cases irregular, income and to increase available financial resources in the event of losses occurring. Micro-insurance, therefore, is not concerned with the national or international level, but is aimed at protecting individual assets (Münchener Rück, 2005b).

Micro-insurance experience already exists in some areas where individual risks occur independently of each other, e.g. risks relating to illness or accidents (Brown and Churchill, 1999, 2000; Ahmed et al., 2005; Cohen et al., 2005). Case studies carried out in India, Kenya or Uganda show that life insurance and health insurance in particular are already being used successfully (Brown and Churchill, 1999, 2000; Athreye and Roth, 2005). Micro-insurance for risks relating to natural disasters, on the other hand, is still being piloted. Applying micro-insurance to natural disasters is particularly difficult because large numbers of people are usually affected and the individual risk of loss to local policyholders thus depends on the risk for all the others. As a result, demands on the insurer are very high in the event of loss occurring, and may even exceed the insurer's capital stock. If the insurance provider opts for increasing his capital stock or reinsuring as a means of solving the problem, his capital costs increase and this is reflected in the price of the insurance policy. In these circumstances, many households and businesses with low incomes will ultimately forego private insurance altogether.

In order to be able put a reasonably-priced and effective insurance product within their reach despite the difficulties, existing micro-insurance systems for independent risks could be extended to cover losses arising as a result of natural disasters. The costs of insurance cover are kept low by developing effective institutional capacities and 'bundling' policyholders in groups and municipalities. In addition, governments could make it compulsory to take out insurance against natural disasters. This would enable a large number of policyholders to be recruited swiftly and achieve a broad geographical distribution of policyholders, which would greatly reduce the problem of correlated risks of individual losses. The question of whether compulsory insurance of this sort would be a sensible option – especially in countries where social insurance systems are still inadequate – should be investigated in the context of future research.

In order to ensure that providers of insurance for natural disasters operating at national or regional level are successful in the long term, it is important that they are linked to the international capital market. For example, against payment of a premium, reinsurance companies act as 'insurers of the insurers', assuming a proportion of the insurance provider's risk. Risks are thus spread more broadly and insurers are freed from the risk of facing extremely high payouts.

Micro-insurance programmes should be actively promoted by governments (public co-financing): alongside establishing the necessary legal framework, providing financial support might also be considered in the early stages, especially to develop the necessary institutional infrastructure, for example in the context of public-private partnerships and in cooperation with development organizations (Linnerooth-Bayer and Mechler, 2005).

3.4.2
The adoption of provisions governing loss of territory in international law

Adaptation strategies raise a number of legal issues as well. With steadily rising sea levels, it is likely that managed retreat will be the only option in many cases. In particular, national territories may well be lost completely or partially as a result of flooding, with people being forced to abandon settled areas. In terms of international law, this poses various challenges which relate, firstly, to the resettlement of the people displaced by sea-level rise, and secondly, the question of financial compensation in cases when states which are affected by the impacts of climate change-induced sea-level rise have not contributed significantly to its causes.

3.4.2.1
Reduction in the size of national territory

If a state's territory shrinks as a result of sea-level rise, this does not have any specific implications in terms of international law, aside from the issue of compensation (see Section 3.4.2.4). According to the relevant provisions of international law, in such a scenario, the constituent national territory is simply reduced in size. In individual cases, however, it may be necessary to amend specific commitments arising under international law, primarily those relating to the territory which is now submerged. In general, the relevant provisions of international law supply satisfactory solutions to the legal problems which can be anticipated here. It must be borne in mind that a reduction in the size of a state's national territory may result in a shift in the boundaries of its maritime jurisdiction as well, if the points used to position them have changed.

3.4.2.2
Submersion of (island) states

According to current knowledge, the survival of island states lying only a few metres above sea level is in acute jeopardy as a result of climate change-induced sea-level rise (CSD, 2004). These island states include the Maldives, an island group lying no more than 2m above sea level, and the Tuvalu, Kiribati and Tonga island groups, which are located on coral reefs. These small island states, which are also developing countries (Small Island Developing States – SIDS), have formed a community of interest which is making its presence felt as a political alliance in the international negotiations on the United Nations Framework Convention on Climate Change (UNFCCC) (Burns, 1997; Neroni Slade, 2001). Admittedly, the SIDS (along with countries with low-lying coastal areas) have been given special consideration in the UNFCCC; for example, Article 4, para. 8 (a) and (b) calls for consideration to be given to actions, including funding, insurance and the transfer of technology, which may be necessary to meet the specific needs and concerns of these countries. However, this vague reference comprises the full extent of the special consideration of island states contained in the UNFCCC. Indeed, Article 4, para. 8 of the UNFCCC defines the specific needs of other categories of developing countries in such broad terms that almost any developing country Party could claim to be particularly vulnerable in some way. In other words, no specific rights for the island states can be derived from these provisions of the Convention. The island states are not mentioned specifically in the Kyoto Protocol. In the supplementary agreements adopted by the Parties to operationalize the Kyoto Protocol, notably the Marrakech Accords, the needs of the island states are emphasized repeatedly, but this has yet to result in the adoption of any institutional or other specific provisions.

Other regional or global agreements, especially in the law of the sea, also fail to recognize, in any legally meaningful way, the status of island states as countries with special ecological or other problems. The same applies to the United Nations Convention on the Law of the Sea, even though islands play a key role in this Convention as a maritime geographical category of importance in determining maritime zones and related sovereign rights (Jesus, 2003).

From the perspective of international law, the existence of a national territory is a constituent element of the state, which means that submersion of a state's territory could result in its extinction. Nor does international law currently grant any entitlement to the allocation of any kind of 'replacement territory', although this would be possible in political terms. However, experience in the Middle East, not least, has shown that the creation of a state or new national territory may trigger considerable potential for conflict, especially given that hardly any unsettled territories are now available for consideration.

3.4.2.3
Dealing with 'refugees from sea-level rise'

If a state is submerged, its citizens become stateless. 'Refugees from sea-level rise' will probably seek refuge in neighbouring countries, perhaps greatly exceeding these countries' absorption capacities. WBGU therefore considers that formal provisions are required to regulate the legal status of these people.

WBGU recommends that the adoption of relevant provisions under international law be guided by the following principles. Basic provisions should establish the affected population's right to regulated refuge/resettlement. This raises the question of the obligations which would thus arise for potential host countries, whereby a distinction must be made between the practical reception of the refugees and the covering of costs. From a humanitarian perspective, the best option is for refugees to be received by countries in the geographical vicinity of, or with specific links to, the submerged state. The refugees should have a say in choosing their new living environment; forced resettlement should be avoided as far as possible. At the same time, however, an allocation formula should be developed in a process involving the wider international community, in order to ensure that individual host countries' capacities are not overstretched. Fair and efficient burden-sharing requires that the costs of receiving the refugees be allocated according to the 'polluter pays' principle. The allocation formula should thus be guided by the principle of common but differentiated responsibility enshrined in international law. This means that the heaviest burden must be borne by those countries which are making the largest contribution to global greenhouse gas emissions and which also have the greatest financial resources at their disposal (Principle 7 of the Rio Declaration, Article 3, para. 1 and Article 4, para. 1 of the UNFCCC; Kellersmann, 2000; Stone, 2004). It is important to bear in mind that the issue of sea-level refugees is universal, for it arises not only when an individual state is submerged but also when major climate change-induced flooding and devastation occur in states which continue to exist.

The development and application of the relevant legal provisions may prove to be problematical in practice, however. How can refugees who have lost their living environment as a result of climate change, making them dependent on assistance from others, be distinguished from other refugees? And how can the fundamental problem of causality be resolved? After all, hurricanes or extreme weather conditions which trigger refugee flows may not necessarily be caused by climate change but may simply be the result of the natural variability of the climate system (Section 3.1.2; Stone and Allen, 2005). Solutions to these problems must be found when formulating legal provisions governing the treatment of sea-level refugees. Against this background, WBGU recommends a significant increase in research in this area, especially the analysis and exploration of fair and effective burden-sharing systems.

A further difficulty arising in this context is that 'environmental refugees' do not fit into any accepted category in international refugee and migration law (GCIM, 2005). According to the Convention relating to the Status of Refugees (Geneva Refugee Convention), the term 'refugee' only applies to persons persecuted for reasons of race, religion, nationality, [or] membership of a particular social group or political opinion. It does not create any specific obligations under international law for the treatment of 'sea-level refugees'. In WBGU's view, this gap in international refugee law must be closed. One option is to establish bilateral agreements, e.g. with neighbour states, or to adopt a multilateral agreement. This raises the question whether the existing conventions, especially the Refugee Convention, can be amended appropriately without renegotiating the definition of 'refugee' itself, or whether the conclusion of a separate convention would be more appropriate. In line with the non-refoulement principle, persecuted persons may not be deported to a country where they may be subjected to torture or inhumane treatment. By the same token, states should undertake not to return sea-level refugees to their country of origin if climate change has rendered the conditions of life in these countries unsustainable, i.e. if the living conditions are incompatible with human dignity or basic economic survival cannot be guaranteed. The scope of such a new norm must therefore extend beyond the specific problem of sea-level refugees to encompass other forms of environmentally related migration as well.

3.4.2.4
Compensation for loss of land

Compensation issues play a key role in relation to the loss of territory and the submersion of island states. A distinction must be made between various scenarios here.

In cases when only the national level is affected, i.e. the damage is sustained by private individuals through the loss of their property or its value, or loss of income, national law applies; such cases are not relevant to this report. However, possible international conventions may have an impact on private actors if, for example, a state passes the responsibility for collecting the resources to cover international agreed compensation payments through taxes and levies to the private sector.

What is relevant, however, is whether and to what extent the international community or other individual states have an obligation to pay compensation if a country sustains damage directly or indirectly as a result of sea-level rise. According to current international law and practice and prevailing opinion, no such obligation exists: even though the problem of rising sea levels is rarely caused by the affected island or coastal states but is primarily due to greenhouse gas emissions in the industrialized and newly industrializing countries, an obligation to pay reparations or damages does not arise under current international law. The background to this issue is the problem of the cumulative effects of certain types of conduct – a question which has yet to be satisfactorily resolved in international law – and the causal links, which are sometimes difficult to establish. As international law stands, the ban on causing major transboundary environmental injury, recognized in customary international law, thus does not apply (Epiney, 1995; Beyerlin, 2000; Wolfrum, 2000; Sands, 2003). Nonetheless, cause and effect have been established in many instances, and there is no doubt that climate changed-induced sea-level rise is presenting some developing countries with problems which they lack the financial resources to cope with unaided.

Against this background, WBGU recommends the conclusion of an international convention which would oblige the industrialized countries in particular to guarantee adequate funding for an internationally administered compensation fund. Funding would be disbursed from this fund to countries particularly affected by rising sea levels. A country's contribution commitments should be weighted according to the greenhouse gas emissions it produces, so that payments can be regarded as compensation for a country's actual contribution to climate-related damage (Section 3.4.1.5). Once this compensation fund has been established as a means of providing assistance to the affected states, it could also take on a role in burden-sharing within the international community, e.g. managing the reception of refugees fleeing from sea-level rise and the payments made to host countries (Section 3.4.2.3).

Utilizing the mechanisms for the transfer of financial resources and technology established for the climate regime might also appear, at first sight, to be a viable option. For example, the Mauritius Strategy for the Further Implementation of the Programme of Action for the Sustainable Development of Small Island Developing States (para. 78(a)) posits, in the context of climate change adaptation and sea-level rise, that strategies can be developed with support from the Least Developed Countries Fund and the Special Climate Change Fund set up within the framework of the United Nations Framework Convention on Climate Change. The key objection here is that such support cannot be regarded as genuine compensation for climate-induced damage. A further possibility is for the United Nations Compensation Commission to take action in this area; for example, it recently adjudicated compensation for environmental damage caused in the 1990–1991 Gulf War (Sands, 2003). However, this particular instrument is not precise enough to pay targeted compensation for the damage caused by climate changed-induced sea-level rise. An existing body could at best be entrusted with the task of administering the separate compensation scheme outlined above.

3.5
Research recommendations

HURRICANE FORMATION AND STRENGTH

The links between hurricane activity and global warming need to be researched more thoroughly, both through further analysis of data gathered from past developments and by modelling the future development of the hurricane climate, including potential threats to areas not affected previously (South America, southern Europe).

EXTENT AND RATE OF SEA-LEVEL RISE

The greatest uncertainty surrounding future sea-level rise concerns the behaviour of continental ice sheets in Greenland and Antarctica. To reduce this uncertainty, there is a need to gain an improved understanding of ice dynamics; major progress is needed in continental ice modelling. These activities include researching the stability of the ice shelves as well as their interplay with continental ice. Further uncertainties surround ocean dynamics, especially the intensity of ocean mixing. Such dynamics greatly influence sea levels. There is a need to improve their characterization within global climate models.

GLOBAL POTENTIAL FOR DAMAGE CAUSED BY SEA-LEVEL RISE

The issue of 'dangerous sea-level rise' forms a sub-set of the wider question of 'dangerous climate change' and must be answered quantitatively if possible. To do so, there is a need to aggregate globally the health, socio-economic and ecological consequences associated with various scenarios (x metres rise in y years). Present assessments are not robust in this respect. They must be replaced by a new generation of impact analyses. This could produce a more precise definition of the provisional absolute guard rail proposed by WBGU (maximum of 1m sea-level rise).

VULNERABILITY OF COASTAL MEGACITIES IN DEVELOPING COUNTRIES

Climate change and urbanization are dominant trends of global change. The interplay of the two trends in the major coastal cities of the developing world could cause an almost unmanageable situation, particularly if the arsenal of responses is limited by social, economic and institutional deficits. There is an urgent need to conduct interdisciplinary studies in order to assess the severity of the problems for particularly critical megacities such as Lagos, Mumbai or Havana.

REGIONAL PORTFOLIO STRATEGIES FOR COASTAL MANAGEMENT

The dramatic geophysical impacts of climate change upon coastal zones (which will arise even if vigorous measures are taken to reduce global greenhouse gas emissions) mean that the traditional approaches to coastal management need to be revisited. There is a particular need to determine the priority given to the various strategic elements of protection, managed retreat and accommodation. To be able to conduct such an assessment, types of cost-benefit analysis must be developed that take account of the novel potential for damage. At present such analyses have only been carried out for limited sections of coasts, e.g. in Great Britain. There is an urgent need to conduct an integrated re-appraisal of robust and effective portfolio strategies for German coasts.

'SEA-LEVEL REFUGEESE': LEGAL AND INSTITUTIONAL ASPECTS

The threats presented to coastal regions and the potential destruction of entire state territories by climate-induced sea-level rise generate a novel migration problem whose legal dimensions have yet to be explored. There is a particular need for research on how to shape provisions under international law with respect to the reception of 'sea-level refugees', the payment of compensation, and burden-sharing in line with the 'polluter pays' principle. To resolve the legal problems, it is also very important to make progress in the scientific attribution of damage or territorial loss arising as a consequence of human-induced climate change. There is also a need to conduct operative appraisals, for instance to evaluate the capacity of the existing United Nations institutions to cope with refugee flows, especially given that needs will presumably grow exponentially in the future.

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4.1
Chemical changes in seawater

4.1.1
CO_2 input

The oceans hold around 38,000 gigatonnes of carbon (Gt C). They presently store about 50 times more CO_2 than the atmosphere and 20 times more than the terrestrial biosphere and soils (Fig. 4.1-1). However, the ocean is not only an important CO_2 reservoir, but also the most important long-term CO_2 sink. Driven by the difference in the partial pressure of CO_2 between the atmosphere and seawater, a portion of the anthropogenic CO_2 dissolves in the surface layer of the sea and, over periods ranging from decades to centuries, is finally transported into the deep sea by ocean currents.

There has already been a demonstrable increase in CO_2 concentrations in the upper layer of the sea over recent decades (Sabine et al., 2004) that can be attributed to the proportional rise of CO_2 in the atmosphere. The ocean is presently taking up 2Gt of carbon annually, which is equivalent to about 30 per cent of the anthropogenic CO_2 emissions (IPCC, 2001a). Altogether, between 1800 and 1995, the oceans have absorbed around 118Gt C ± 19Gt C. That figure corresponds to about 48 per cent of the cumulative CO_2 emissions from fossil fuels (including cement production), or 27–34 per cent of the total anthropogenic CO_2 emissions (including those from land-use changes; Sabine et al., 2004). The anthropogenic CO_2 signal in the sea can be traced, on the average, to a water depth of approximately 1000m. Due to the slow mixing of ocean layers it has not yet reached the deep sea in most parts of the ocean. In the North Atlantic, however, due to the formation of deep water there, the anthropogenic CO_2 signal already extends down to 3000m.

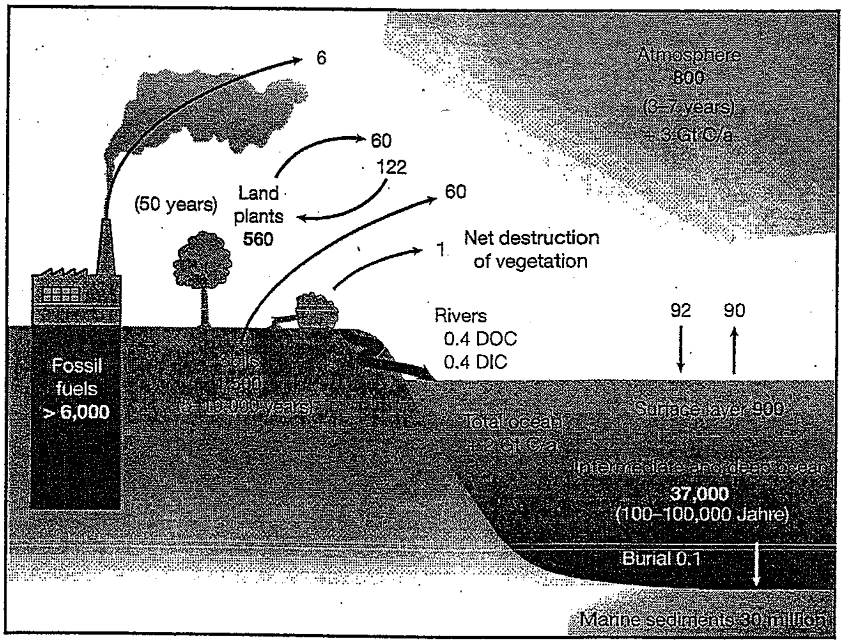

Figure 4.1-1
Overview of the global carbon cycle. Values for the carbon reservoirs are given in Gt C (numbers in boldprint). Values for the average carbon fluxes are given in Gt C per year (numbers in normal-print). Mean residence times are in parentheses. Flux into soils amounts to around 1.5Gt C per year. DOC = dissolved organic carbon, DIC = dissolved inorganic carbon. Sources: adapted after Schlesinger, 1997 and WBGU, 2003. Numbers expanded and updated for ocean and fossil fuels: Sabine et al., 2003; marine sediments: Raven et al., 2005; atmosphere: NOAA-ESRL, 2006

In the atmosphere CO_2 behaves chemically neutral, that is, it does not react with other gases, but it contributes to climate change through its strong interaction with infrared radiation. But in the ocean CO_2 is chemically active. Dissolved CO_2 contributes to the reduction of the pH value, or an acidification of seawater. This effect can already be measured: since the onset of industrialization the pH value of the ocean surface water has dropped by an average of about 0.11 units. This is equivalent to an increase in the concentration of hydrogen ions (H^+ ions) by around 30 per cent. Starting from a slightly alkaline pre-industrial pH value of 8.18 (Raven et al., 2005), the acidity of the ocean has thus increased at the surface. The various IPCC emission scenarios indicate that if the atmospheric CO_2 concentration reaches 650ppm by the year 2100, a decrease in the average pH value by 0.30 units can be expected compared to pre-industrial values. With an atmospheric concentration of 970ppm, the pH value would drop by 0.46 units. But if the CO_2 in the atmosphere can be limited to 450ppm, then the pH reduction will only amount to 0.17 units (Caldeira and Wickett, 2005).

4.1.2
Change in the carbonate budget

The carbon stored in the seas occurs in different chemical forms. A small part is stored in the biosphere and in organic compounds, but the greatest part by far is contained in inorganic compounds, which are referred to as DIC (dissolved inorganic carbon). Of these compounds, however, only 1 per cent is directly dissolved CO_2, 91 per cent occurs as bicarbonate (HCO_3^-), and 8 per cent as carbonate (CO_3^{2-}). The relationship of these three compounds can be represented by the equilibrium equation:

$$CO_2 + H_2O + CO_3^{2-} \leftrightarrow 2\,HCO_3^-$$

The relative proportions of these carbon compounds reflect the pH value of the water (Fig. 4.1-2). Only CO_2 can be exchanged with the atmosphere. Through the uptake of CO_2 the partial pressure of CO_2 increases in the seawater, and at the same time the equilibrium shifts in favour of bicarbonate and to the detriment of carbonate.

Due to the uptake of anthropogenic CO_2, the carbonate concentration in the ocean surface layer has already dropped by 10 per cent compared to the pre-industrial level (Orr et al., 2005).

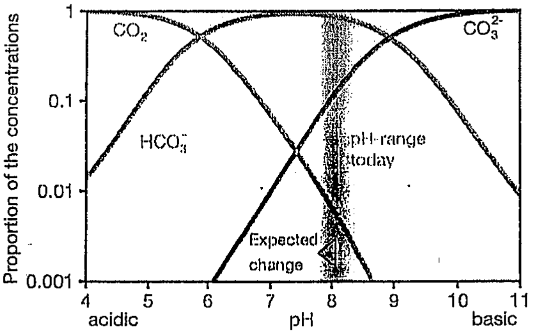

Figure 4.1-2
Carbonate system of seawater. Relative proportions of the three inorganic components CO_2, HCO_3^- und CO_3^{2-}. The blue shaded area shows schematically the pH range that occurs in today's ocean. The arrow shows the expected shift of the average pH value when the atmospheric CO_2 concentration reaches about 750ppm.
Source: Raven et al., 2005

The saturation of seawater with carbonate ions is especially important for marine organisms that build their shells or skeletons with lime (calcium carbonate, $CaCO_3$; Section 4.3.2). Calcium carbonate occurs in marine organisms primarily in the forms of aragonite and calcite, which differ in their crystal structures (Table 4.3-1). Seawater is supersaturated with respect to the more easily dissolved aragonite when the carbonate concentration lies above 66µmol per kilogram. If it falls below this value the aragonite formed by the organisms dissolves in the water – this is referred to as aragonite undersaturation. Because of the increasing solubility of calcium carbonate with decreasing temperature and increasing pressure, the deeper layers of the sea are, as a rule, undersaturated, that is, sinking $CaCO_3$ dissolves in the water at greater depths. The boundary between the undersaturated and super-saturated layers is referred to as the saturation horizon.

The present carbonate concentration in the sea surface layer varies among regions: the highest concentrations (averaging 240µmol per kilogram) occur in the tropics, while values in the Southern Ocean average only 105µmol per kilogram (Orr et al., 2005). With progressive CO_2 input into the sea, therefore, the marine organisms in the Southern Ocean are the first to be threatened by aragonite undersaturation (Section 4.3.2). Orr et al. (2005) calculate the possible future development of the carbonate concentration of the Southern Ocean for various emission scenarios. According to these calculations, under a 'business-as-usual' scenario it could already be undersaturated with respect to aragonite by the middle of this century (Fig. 4.1-3). With an atmospheric CO_2 concentration of approximately 600ppm or more, the greater part of the surface layer of the Southern Ocean would be undersaturated. But even before this threshold is reached the saturation horizon drifts upward, that is, the upper layer of the sea that is

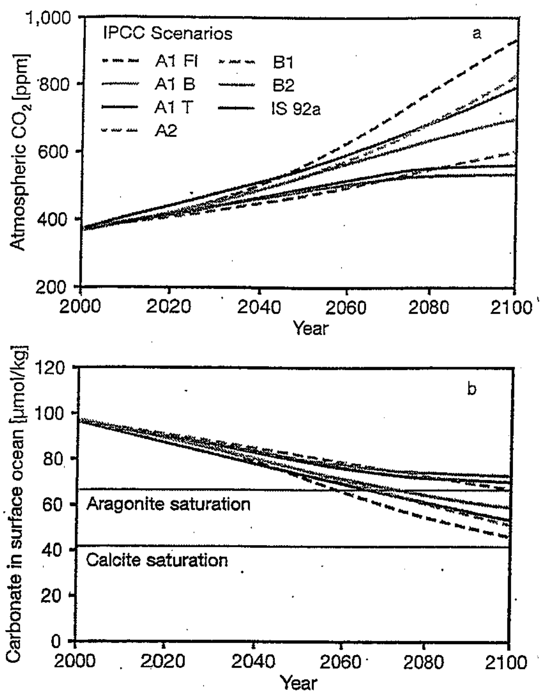

Figure 4.1-3
Projections of different CO_2 concentrations (a) and their effects on the carbonate budget of the Southern Ocean (b). The variation according to various IPCC scenarios is shown. Source: Orr et al., 2005

supersaturated with respect to aragonite becomes thinner, and $CaCO_3$ formation becomes more difficult. Individual parts of the surface layer would be affected even earlier. With respect to the less-soluble calcite the surface layer remains saturated despite higher CO_2 concentrations, but the calcite saturation horizon also shifts upward. With the displacement of the saturation horizon the conditions for biogenic $CaCO_3$ formation change, which can have considerable consequences for marine organisms and ecosystems (Section 4.3).

4.1.3
Special role of CO_2

The acidification of the sea is an effect that can be exclusively attributed to the CO_2 increase in the atmosphere. In this it is different from climate change, which is caused by the radiative effect of atmospheric CO_2 increase, but also of the increase of methane, nitrous oxide and several other radiatively active gases. With respect to climate change, calculations are often made in terms of CO_2 equivalents, that is, the radiative forcing attributable to the various gases is recalculated to the corresponding forcing of CO_2. The argument is that for climate protection it does not make any difference whether the radiative effect is caused by CO_2 or by any other emitted greenhouse gas. But this is not true for the effect of ocean acidification. To protect the oceans, reducing CO_2 emissions is relevant for two reasons: to limit both global warming and ocean acidification.

Acidification is, above all, a consequence of the rapid increase of the quantities of CO_2 in the ocean. With a slow input of CO_2, as has repeatedly occurred in the Earth's history (such as the end of the last ice age when the CO_2 concentration rose by 80ppm over a period of 6,000 years), or in climate epochs with elevated CO_2 concentrations (around 100–200 million years ago) the CO_2 mixes down into the deep sea, where a slow dissolution of carbonate sediments counteracts the acidification. In such constellations the pH value of the sea remains almost constant (Raven et al., 2005).

4.2
Future development of the oceans as a carbon sink

As discussed in Section 4.1, the oceans are the most important net sink for CO_2. Without oceanic uptake of anthropogenic CO_2, the relative CO_2 concentration in the atmosphere would lie more than 55ppm above the present level (Sabine et al., 2004). The future development of the oceans as a CO_2 sink will therefore determine in large part how strongly anthropogenic CO_2 emissions are reflected as an increase in the atmospheric concentration of carbon dioxide. Over the long term, that is, a period of several centuries (in which mixing takes place throughout the world's oceans), the ocean can take up about 65–80 per cent of the anthropogenic CO_2, depending on the total quantity of carbon emitted. At even longer time scales this proportion increases to 85–92 per cent due to the dissolution of carbonate sediments (Caldeira, 2005). In the coming decades and centuries, however, only a portion of this great sink potential can be effective: the limiting factor is the transport of carbon taken up at the surface into the deeper ocean layers. In fact, the oceans have so far only absorbed 30 per cent of the amount of anthropogenic carbon that they could take up over a long time period at present atmospheric concentrations (Sabine et al., 2004).

The great importance of the ocean as a sink is not applicable to the other greenhouse gases regulated by the Kyoto Protocol: the strongest sink for methane as well as for HFCs, for example, is the chemical reaction with the hydroxyl radical OH in the lower atmosphere, while N_2O is destroyed primarily in the stratosphere by UV radiation from the sun. The industrial gases PFCs and SF_6 do not decay until they are above the stratosphere. It is worth noting, however, that the sea is an important source of N_2O, whose future development in response to climate change is unclear.

Before industrialization the ocean was at a state of near equilibrium, and not a CO_2 sink. At its surface it gave off around 0.6Gt C annually to the atmosphere, while at the same time approximately the same amount of carbon entered the ocean from the terrestrial biosphere (and therefore ultimately from the atmosphere) in the form of organic matter flowing in from rivers (Watson and Orr, 2003). The proportion of atmospheric CO_2 did not change under these conditions, remaining constant over millennia at around 280ppm. The reason for the present function of the ocean as a sink is the anthropogenic perturbation of the carbon cycle: when the CO_2 concentration of the atmosphere increases, the ocean takes up CO_2 until the partial pressures of the surface water and the atmosphere are in equilibrium. Since the beginning of industrialization the atmospheric CO_2 concentration has risen almost exponentially. This has caused an annual increase in the CO_2 uptake by the oceans since that time, in quantities almost proportional to the atmospheric CO_2 concentrations, as model studies indicate (Gloor et al., 2003). For various reasons, however, this cannot be carried over into the future, which will be discussed below.

When one compares the quantities of CO_2 taken up by the ocean with anthropogenic emissions, the efficiency of the ocean sink appears to be falling already: Sabine et al. (2004), based on an analysis of observational data, show that from 1800 to 1994 the ocean absorbed 28–34 per cent of the anthropogenic emissions, while from 1980 to 1999 this value was only 26 per cent. Due to the large uncertainty in the determination of the global carbon balance, this decrease is not statistically significant, but on the basis of known geochemical processes it is also not unexpected. The more CO_2 that has been taken up by the ocean, the lower the carbonate concentration in the surface layer becomes (Section 4.1.2). This decreases its capacity to take up additional CO_2. Modelling studies show that the relative CO_2 uptake by the ocean (that is, the proportion of anthropogenic emissions absorbed by the ocean in the course of a few decades) is reduced by this effect by several per cent when an atmospheric CO_2 concentration of 450ppm is reached. At 750ppm of CO_2 in the atmosphere the relative CO_2 uptake falls by as much as 10 per cent (Le Quéré, personal communication). This geochemical effect is fully considered in models of the carbon cycle and is therefore rarely expressly discussed (Gruber et al., 2004). This effect is also active in the extreme long term, that is, time periods in which the ocean completely mixes, so that the proportion of anthropogenic CO_2 emissions remaining in the atmosphere continues to increase as more CO_2 has been emitted.

Climate change resulting from greenhouse gas emissions further affects the capacity of the ocean sink: the solubility of CO_2 in seawater decreases with rising temperature. Through this effect, by the end of this century the cumulative CO_2 uptake could fall by 9–14 per cent of what it would be without a temperature change (Greenblatt and Sarmiento, 2004). This effect is well-understood; the uncertainty predominantly results from the uncertainty of the degree of expected temperature change.

A further effect of climate change is an increasing ocean stratification, that is, the vertical mixing will be reduced. This has a number of complex effects. For one, the transport of carbon-enriched surface water to greater depths as well as the transport of carbon-depleted water to the surface will be weakened, resulting in an overall decrease of the sink effect of the ocean. For another, there could be changes in biological productivity through altered nutrient availability. Biological productivity is of great importance for the carbon balance of the ocean surface layer: CO_2 is taken up by marine organisms through photosynthesis and incorporated into organic substance; dead organisms sink and then decay in different water depths. Part of the released nutrients and carbon return to the surface through vertical mixing, but the net export to the deep sea is considerable. Ten gigatonnes of carbon are transferred annually by this 'biological pump' from the ocean surface layer to the deep sea. The combined effect of increased stratification and altered biological productivity on the sink effect of the ocean is highly uncertain. Greenblatt and Sarmiento (2004) give a range of -2 per cent (decreased sink function) to +10 percent (increased sink function) for the change in cumulative CO_2 uptake through this effect by the end of the century.

Many of the effects discussed are still difficult to quantify, but it is likely that climate change will contribute to a considerable overall weakening of the efficiency of the sea as a carbon sink. According to an overview based on various modelling studies by Greenblatt and Sarmiento (2004), the cumulative CO_2 uptake by the ocean could be 4–15 per cent lower by the end of the century due to the climate-related influences discussed above (temperature rise, increased stratification, and biological effects) than it would be without these. This attenuation of the CO_2 uptake has to be added to the geochemical effects that already lead to a weakening of the relative sink with a similar order of magnitude.

As already indicated, biological processes represent the greatest uncertainty in estimating the future development of the ocean sink. These biological processes include the impacts of anthropogenic interference with the atmosphere and ocean acidification on marine primary production, the biological pump and calcification (Section 4.3.5). A weakening of the ocean sink due to changes in the wind-driven rise of water at the equator ('equatorial upwelling') is a further aspect under debate (Winguth et al., 2005). In addition, non-linear events that are difficult to predict such as a strong decrease in oceanic convection or in the thermohaline circulation, or biological regime shifts (Section 2.2.1) could have a considerable influence.

In summary it can be stated that, with increasing atmospheric CO_2 concentrations, the proportion of anthropogenic CO_2 emissions taken up by the ocean will decrease, even if the absolute rate of uptake increases (IPCC, 2001a).

4.3
Effects of acidification on marine ecosystems

CO_2 input into the sea leads to shifts in the carbonate system of the seawater and to a decrease in pH value, and thus to acidification of the ocean (Section 4.1.1; Turley et al., 2006). Without counteractive measures this change in the carbonate system could reach a state during this century that has probably not been seen for several million years (Feely et al., 2004). Humans are significantly interfering with the chemical balance of the ocean, and this will not remain without consequences for marine organisms and ecosystems.

4.3.1
Physiological effects on marine organisms

A strong increase of CO_2 concentration (hypercapnia) has many adverse physiological effects that have been investigated experimentally on various marine organisms. Numerous changes in marine organisms have been identified, for example, in the productivity of algae, metabolic rates of zooplankton and fish, oxygen supply of squid, reproduction in clams, nitrification by microorganisms, and the uptake of metals (for a survey, see Pörtner, 2005). Many of these experiments, however, were carried out with CO_2 concentrations much higher than what could be expected in emission scenarios under discussion today for the time frame up to 2100. Further studies are therefore necessary in order to be able to estimate the short- and medium-term effects of acidification (Section 4.6). From today's viewpoint it seems improbable that marine organisms will suffer from acute poisoning at expected future CO_2 levels (Pörtner, 2005).

Doubling the present CO_2 concentration leads to an increase in the rate of photosynthesis in many phytoplankton species by about 10 per cent (Raven et al., 2005). However, the various groups of phytoplankton exhibit different sensitivities to increased CO_2 concentrations with respect to photosynthesis, which is due to differences in carbon uptake (CO_2 versus HCO_3^-) and a different saturation behaviour of the photosynthetic rates. The interactions between photosynthesis, primary production of phytoplankton, microbial respiration, and the resulting effects on the food web are, however, compounded by a number of other factors (temperature, light and nutrient supply, disparate feeding risk from zooplankton, adaptive processes, etc.). With the present state of knowledge no clear conclusions can be drawn regarding the effects of acidification on growth rates and assemblage compositions of the phytoplankton.

4.3.2
Effects on calcifying organisms

Next to photosynthesis, calcification is the most important physiological process influenced by the increase of CO_2 concentration. It has far-reaching consequences for the ecological function of marine ecosystems, and can also have feedbacks on the atmospheric concentration of CO_2 and thus on the climate system (Section 4.3.5).

For their skeletons or shell structure, many marine organisms use calcium carbonate, which has to be extracted from seawater. This is only possible while the seawater is supersaturated with calcium carbonate, which is why the increasing CO_2 concentration and falling pH value hampers calcification (Raven et al., 2005). This causes a weakening of the skeletal structure or – when a level below the saturation concentration is reached – even their dissolution. Calcium carbonate is employed as a construction material for organisms in different crystalline forms: aragonite and calcite are the two most important (Table 4.3-1). Organisms that use aragonite for their shells or skeletons are the first to be adversely affected by acidification, because aragonite dissolves more easily under the changing conditions due to its different crystal structure.

Acidification has an impact on all marine calcifying species, such as certain plankton groups, clams, snails and corals. Echinoderms (for example, starfish and sea cucumbers) are especially threatened, because their calcite structures contain larger amounts of magnesium and therefore dissolve even more easily than aragonite under increased CO_2 conditions (Shirayama and Thornton, 2005). Although corals are the most conspicuous and well-known marine calcifying organisms and are especially threatened by acidification as aragonite producers (Section 2.4), they only contribute 10 per cent of the annual global marine carbonate production of 0.64–2Gt C (Zondervan et al., 2001). The simulations of Guinotte et al. (2003) indicate that at an atmospheric CO_2 concentration of just under 520ppm, which could already be reached by the middle of this century, almost all of today's warm-water coral reef locations will barely still be suitable for coral growth because of insufficient aragonite saturation (Fig. 4.3-1).

Around three-fourths of the global marine calcium carbonate production is carried out by planktonic organisms, primarily coccolithophores, foraminifera, and pteropods. Of these, the coccolithophores are of particular importance because these one-celled primary producers, which can create large-area plankton blooms with only a few species, can greatly contribute to the export of calcium carbonate to the deep sea and thereby play a significant role in the global carbon cycle (Riebesell et al., 2000; Zondervan et al., 2001; Section 4.3.5). In experiments with both monocultures and natural plankton communities it has been shown that the calcification by coccolithophores clearly decreases with increased atmospheric CO_2 concentrations (Riebesell et al., 2000; Riebesell, 2004). Pteropods are important components of the marine food webs in polar and subpolar latitudes where they form dense populations (up to 1000 individuals per m^3) and serve as nutrition for the upper trophic layers of the food web. In these regions they are responsible for a significant portion of the export of particulate carbon to greater depths. When the carbonate saturation in seawater drops below a critical value, it is likely that these animals are no longer able to form a shell. For important parts of their habitat in the Southern Ocean an undersaturation with respect to aragonite (under assumptions of the IS92 scenario of the IPCC) is predicted beginning in 2050, so that their distribution area will be severely limited (Orr et al., 2005; Raven et al., 2005).

There is great uncertainty about the capacity of the organisms to adapt to these changes, as too few long-term experiments have been carried out (Raven et al., 2005; Pörtner, 2005).

4.3.3
Ecosystem structure and higher trophic levels

Over the course of this century the expected pH decreases could have a considerable impact on the calcifying organisms and thus on the total marine biosphere (Orr et al., 2005). Simultaneously, considerable climate-related warming is expected. The two effects are not independent of one another: the CO_2 increase, for example, could decrease the temperature tolerance of animals (Pörtner, 2005). The coral ecosystems in particular are an example of such synergistic negative effects (Section 2.4; Hoegh-Guldberg, 2005).

Acidification impacts on the food web are also conceivable. Different responses to increased CO_2 concentrations, with respect to growth rates or reproduction of an organism, could change the spatial as well as temporal distributions of the species through changes in competition (Rost and Sültemeyer, 2003). Impacts that have already been observed in primary producers include a difference in the magnitude of the CO_2 fertilization effect (which, for example,

Organisms	Photosynthetic	Crystal form of the carbonate	Habitat
Coccolithophores	yes	Calcite	Planktonic
Macroalgae*	yes	Aragonite or calcite	Benthic
Foraminifera	no some	Calcite Calcite	Benthic Planktonic
Corals			
warm-water	yes (in symbiosis)	Aragonite	Benthic
cold-water	no	Aragonite	Benthic
Pteropods	no	Aragonite	Planktonic
Non-pteropod molluscs*	no	Aragonite or calcite	Benthic or planktonic
Echinoderms	no	Mg-calcite	Benthic
Crustaceans*	no	Calcite	Benthic or planktonic

Table 4.3-1
Groups of calcifying marine organisms. Calcium carbonate occurs in different crystal forms. Aragonite dissolves more quickly than calcite at low carbonate ion concentrations, but more slowly than magnesium-rich calcite (Mg-calcite).
* not all species of this group are calcifiers.
Source: after Raven et al., 2005

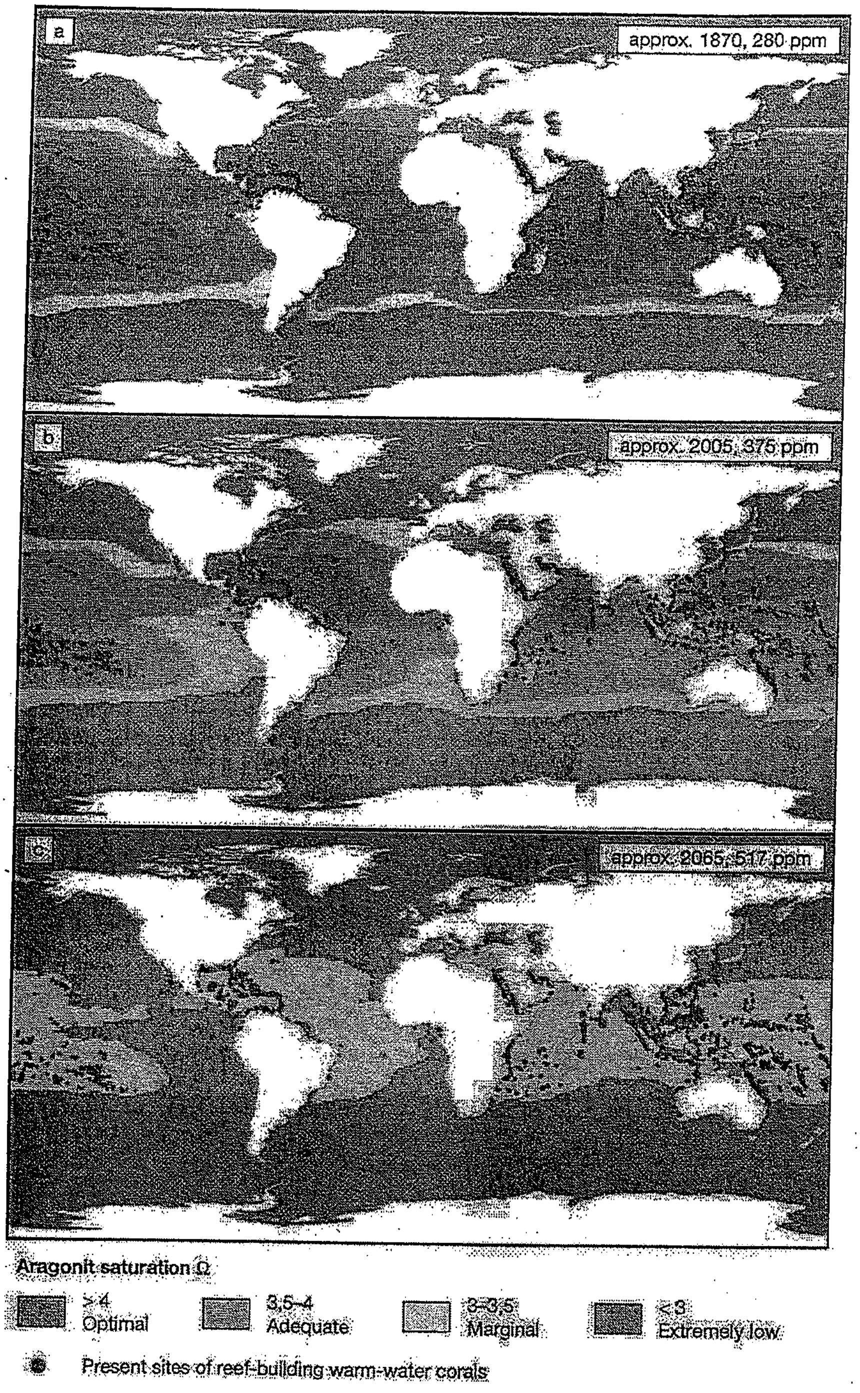

Figure 4.3-1
Aragonite saturation and present occurrence of reef locations for warm-water corals (blue dots). (a) pre-industrial values (around 1870, atmospheric CO_2 concentration 280ppm), (b) present (around 2005, 375ppm CO_2), (c) future (around 2065, 517ppm CO_2). The degree of aragonite saturation (Ω) indicates the relative proportion between the product of the concentrations of calcium and carbonate ions and the solubility product for aragonite. Locations with an aragonite saturation below 3.5 are only marginally suitable for reef-forming warm-water corals, below 3 they are not suitable.
Source: Steffen et al., 2004

favours coccolithophores over siliceous algae) and reduced calcification (which may be a disadvantage for coccolithophores: Riebesell, 2004). In long-term studies in the North Atlantic, it has been observed that changes in the phytoplankton, due to the close coupling with their predators, can be passed on first to the algae-feeding zooplankton and then further to the predatory zooplankton (Richardson and Schoeman, 2004). A change in the species composition of the phytoplankton can thus impact on the zooplankton. In polar ecosystems it is conceivable that reduced calcification by pteropods has effects on the higher levels of the food web, although this is speculative and not easily predictable (Orr et al., 2005).

Conclusions about possible adaptive processes at the ecosystem-structure level are also speculative, for example, whether gaps that are created by acidification impacts can be filled by other species without significant effects upon overall productivity.

4.3.4
Effects of acidification on fisheries

Acidification of the world's oceans could also have an impact on fisheries. Direct toxic effects of increased atmospheric CO_2 concentrations on fish are not expected because the threshold of acute sensitivity of fish to CO_2 is beyond the predicted concentrations (Pörtner, 2005; Section 4.3.1). When calcification is reduced, however, this can trigger changes in the species composition of the phytoplankton, and this, in turn, can have an impact all the way to the upper layers of the food web through trophic coupling (Richardson and Schoeman, 2004; Section 4.3.3). It cannot be ruled out that this kind of change in the structure and function of the marine ecosystems can have an impact on the pelagic fisheries, but with the present state of knowledge the prognosis remains very speculative (Raven et al., 2005).

Changes in growth and competitive conditions for the species in tropical coral reefs will probably also affect another important branch of fishery: millions of people depend on subsistence fishery on coral reefs for their protein supply (Raven, et al., 2005), and the coral reefs themselves are threatened by acidification (Section 2.4). A large-scale loss of coral habitats would doubtless have adverse effects upon this fishery, with socioeconomic consequences that are difficult to predict.

4.3.5
Feedback of changes in calcification on the carbon cycle

Overall, the ecological balances in the sea are shifting to the detriment of calcifying organisms, and this may affect even the global biogeochemical cycles through changes in species compositions in marine phytoplankton. The consequences of changing rates of plankton calcification described here represent only a small sample of all the interactions between the climate system and the ocean, which are reviewed in Section 4.2..

The annual primary production in the ocean is approximately 50 Gt C, of which approximately 10 Gt is exported to the deep sea by the biological pump. For this important process in the global carbon cycle, which contributes to the sink function of the ocean, it makes a great difference whether the production is by calcifying species like coccolithophores or by non-calcifying species, for example, siliceous algae.

Calcification by marine organisms always involves CO_2 production:

$$Ca^{2+} + 2\,HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$

This carbonate 'counter-pump' becomes stronger with increasing atmospheric CO_2 concentration as a consequence of the altered carbonate buffer capacity. Assuming constant calcification, this would cause a future weakening of the sink effect of the sea. But if biogenic carbonate formation is reduced as a result of a pH decrease, then this effect can be overcompensated so that the sink effect may even be strengthened. This would, however, only have a minor impact on the CO_2 uptake by the ocean (Zondervan et al., 2001). A number of other effects further complicate this picture (Riebesell, 2004): reduced calcification could also reduce the density and thus the sinking rates of particles to the deeper water layers, slowing the carbon export by the biological pump. On the other hand, there is a possible acceleration of the sinking rates caused by the increased formation of extracellular polysaccharides (Engel et al., 2004). Present-day plankton blooms of coccolithophores cover large areas of the sea, up to hundreds of thousands of km², and lighten the colour of the water because of their carbonate content. Their absence could therefore reduce the global albedo by up to 0.13 per cent, which would slightly accelerate global warming (Tyrell et al., 1999). The magnitude of some of these factors is not clear. The total effect of all of these factors on the interactions between atmospheric CO_2 concentration and marine biological production cannot currently be ascertained, which presents a need for increased research efforts in this area (Raven et al., 2005; IMBER, 2005).

4.4
Guard rail: Ocean acidification

4.4.1
Proposed guard rail

To prevent undesirable or high-risk changes to the marine food web due to aragonite undersaturation (Section 4.3), the pH value of near surface waters should not drop more than 0.2 units below the pre-industrial average value of 8.18 in any larger ocean region (nor in the global mean). A pH drop of 0.2 units would correspond to an increase in the H^+ ion concentration of around 60 per cent compared to pre-industrial values. The decrease in pH so far of 0.11 units since industrialization corresponds to a rise of the H+ ion concentration of around 30 per cent. The present average pH value of the ocean surface layer is 8.07 (Raven et al., 2005). Figure 4.4-1 illustrates the WBGU acidification guard rail.

It is necessary, however, to further specify the spatial and temporal averaging to which the guard rail refers, because the pH value is subject to strong natural variability. According to Haugan and Drange (1996), pH values vary up to 0.5 units worldwide, while local seasonal fluctuations can amount to around 0.1 pH units (in high-production regions even 0.2–0.3 units: Riebesell, personal communication).

According to simulations by Caldeira and Wickett (2005), a stabilization of the atmospheric CO_2 concentration of 540ppm by the year 2100 would already lead to a pH decrease of the ocean surface layer of 0.23 in the global average compared to the pre-industrial level, that is, at this CO_2 concentration the acidification guard rail would already be overstepped. A stabilization at 450ppm by 2100 reduces the pH value by 0.17, and so would presumably be consistent with the acidification guard rail. It still needs to be reviewed, however, whether at this stabilization value higher pH reductions could occur locally over longer time periods, which, especially in the Southern Ocean, could lead to undersaturation of the surface layer with respect to aragonite. It should be noted that this refers to the stabilization of CO_2 itself and not the stabilization level of greenhouse gases in total, which is described by the CO_2 equivalent.

4.4.2
Rationale and feasibility

The largest threat to marine organisms due to acidification is related to the solubility of calcium carbonate, which they need for the construction of their shells and skeletal structure (Section 4.3). The more easily dissolved variant of calcium carbonate is aragonite, which is used by corals and certain plankton species (Table 4.3-1). Calcifying marine organisms are important components of marine ecosystems, so their endangerment would represent a non-tolerable interference with the Earth System.

If the concentration of carbonate ions falls below the critical value of 66μmol per kilogram, then the seawater is no longer saturated with respect to aragonite, and marine organisms can no longer build their aragonite shells. This needs to be avoided above all in the surface layer where primary production takes place. The danger of undersaturation for aragonite is especially present in the Southern Ocean. According to Orr et al. (2005), simulations where the pH decrease averages about 0.25 already show a clear reduction of the vertical extent of the saturated layer, and undersaturation in some parts of the Southern Ocean. It is the view of WBGU that such a situation should be avoided.

The pH value is a critical variable not only for calcification, but also for many other processes in marine systems (for example, availability of nutrients). Within the past 23 million years the natural fluctuations of the average pH value between glacial and interglacial periods lay within a range of slightly more than 0.1 (Fig. 4.4-1), so that over a long time marine organisms were able to adapt to a fairly nar-

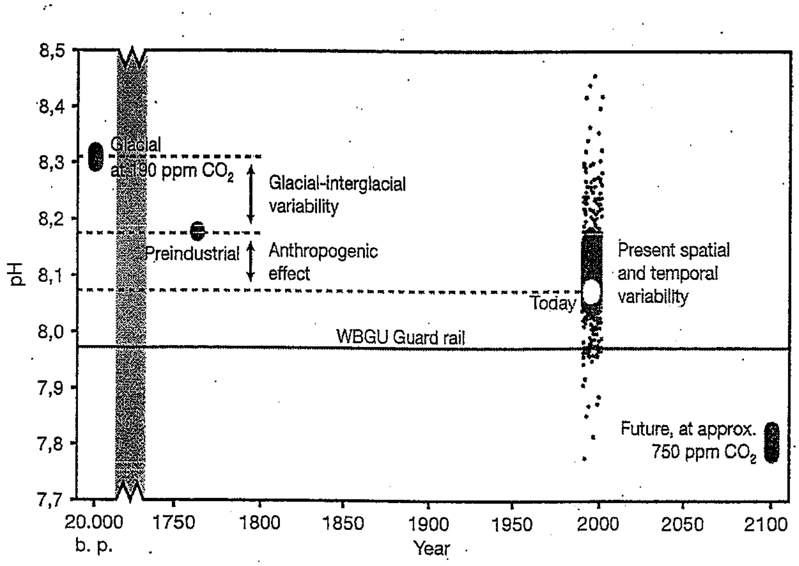

Figure 4.4-1
Variability of the average pH value of the oceans in the past and present, as well as a projection for the future for an atmospheric CO_2 concentration of approx. 750ppm. The red line indicates the WBGU guard rail.
Source: after IMBER, 2005

row pH span that very rarely dropped below the minimum in the surface-layer water (IMBER, 2005). This is a further argument for application of the precautionary principle, especially considering the gaps in the scientific knowledge about the impacts of acidification (Section 4.3).

Because of the importance of the consequences of ocean acidification, research in this area should be intensified considerably (Section 4.6). As long as there is no general scientific consensus about the tolerable limit for the effects of acidification, a margin of safety according to the precautionary principle should be observed. The suggestion of WBGU to prevent a pH decrease of more than 0.2 is oriented toward the goal of avoiding an aragonite undersaturation in the ocean surface layer. If it is found that other intolerable damages already occur before reaching aragonite undersaturation, then the guard rail will have to be adjusted accordingly.

Because the CO_2 input into the sea is caused by a rise in atmospheric CO_2 concentrations and therefore by anthropogenic CO_2 emissions, the pH drop in the ocean can be limited by reducing emissions. Once acidification has occurred, however, it is irreversible – as long as there is no possibility of lowering the atmospheric CO_2 concentration the pH value of the surface layer will not rise again in any foreseeable future. Overstepping the guard rail would thus be irreversible, which makes the precautionary principle particularly relevant to this problem.

Compliance with the guard rail can be verified reliably by scientific means: for one, the pH value of seawater can be determined directly, and for another, the average pH value of the sea can be derived from measurements of atmospheric CO_2 concentrations.

The acidification and climate guard rails could exhibit redundancies with regard to the measures required to obey them, but they are not replaceable by one another: human-induced global warming is caused by a group of greenhouse gases, with 60 per cent of the effect from CO_2. The only one of this group responsible for ocean acidification, however, is CO_2. Stabilization of CO_2 at 450ppm by 2100 would reduce the pH value by 0.17, therefore staying within the allowable range of the acidification guard rail. Compliance with the global warming guard rail of 2°C also requires a stabilization concentration of 450ppm or less, depending on climate sensitivity. Therefore, observance of the climate guard rail would incorporate the acidification guard rail, under the condition that CO_2 is adequately taken into account in the emissions reduction.

4.5
Recommendations for action: Linking climate protection with marine conservation

In the 1970s and 1980s, the phenomenon of 'acid rain' became widely known. This problem is caused by emissions of acid-forming gases (mainly SO_2 and NO_X) from the combustion of fossil fuels. The issue was taken up by the media under the catchphrase 'Waldsterben' (forest dieback), and exerted considerable pressure upon policymakers and industry. Great technical and financial effort was subsequently invested to fit large-scale power plants with flue gas scrubbers, mandate catalytic converters for cars, and embark upon broad-scale liming of forests and lakes. A comparison of the problem of acid rain with the already advancing acidification of the oceans shows the latter to be an issue significantly more serious. The media and policymakers, however, are expressing negligible interest compared to acid rain. Indeed, the problem is being practically ignored. Policymakers are therefore called upon to recognize the full impact of ocean acidification and to take measures of a scope and effectiveness comparable to those adopted to tackle acid rain.

4.5.1
Reappraising the role of CO_2 in climate protection policy

The release of CO_2 has particularly far-reaching consequences for marine ecosystems. Firstly, CO_2 acts as a greenhouse gas, altering the radiation balance of the atmosphere and thus contributing to global atmospheric warming and, as a further consequence, to the warming of the oceans. Secondly, a large proportion of the CO_2 emitted by human activities dissolves in seawater, where, in addition to the warming, it causes chemical changes. In view of these particularly harmful effects of CO_2 upon the oceans, it ~~is~~ essential that climate policy give special attention to this specific greenhouse gas.

Need for action

Compliance with the WBGU guard rail for ocean acidification will only be possible if the increase of the atmospheric CO_2 concentration is limited. Engineering approaches, such as liming the surface layers of the oceans, are unrealistic considering the scale of the problem (Raven et al., 2005). However, over a time scale of centuries, the acidified surface water will mix down into the deep sea through ocean currents. One option for action is to stabilize the atmospheric CO_2 concentration; this would lead over the long term to an acidification of deeper waters of the oceans until the pH of the surface layers is reached. An alternative option would be to agree a maximum limit on the total amount of CO_2 emitted to the atmosphere by human activities; that approach could cause the atmospheric CO_2 concentration to drop again over the medium term and could prevent the acidification of the deep sea.

LEGAL SETTING

The present climate policy instruments do not take into account the aspect of ocean acidification caused by CO_2 input. WBGU takes the view that the United Nations Framework Convention on Climate Change (UNFCCC) does indeed establish an obligation to take into account the impacts of climate change upon the oceans, regardless of the circumstance that this aspect was not a priority when the UNFCCC was concluded, and was not covered by the Kyoto Protocol when reduction commitments were set. The rationale is as follows: Under Art. 1 para. 3 UNFCCC, 'climate system' means the totality of the atmosphere, hydrosphere, biosphere and geosphere and their interactions. The term 'climate system' is thus defined in such a comprehensive way that it includes the oceans, which are a part of the hydrosphere, as well as the interactions of the oceans with the atmosphere and the biosphere. The UNFCCC objective established in Art. 2, 'stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system', thus also covers the impacts of increasing greenhouse gas levels upon the oceans. With respect to acidification, the meaning of Art. 2 UNFCCC can be concretized as follows: CO_2 is a greenhouse gas, and an excessive CO_2 concentration in the atmosphere leads to dangerous anthropogenic interference with marine ecosystems, for CO_2 dissolves in water and causes acidification (Sections 4.1 and 4.3). The oceans are a part of the hydrosphere, and marine organisms are a component of the biosphere. The problem of acidification is thus one of interaction among the atmosphere, hydrosphere and biosphere, all of which are components of the climate system (Art. 1 para. 3 UNFCCC). There can thus be no doubt that the objectives of the convention include preventing a dangerous acidification of the oceans. Furthermore, Art. 2 UNFCCC also states that ecosystems should be able to adapt naturally to climate change. The speed of acidification observed today calls compliance with this requirement into question: for instance, the adaptive capacity of marine ecosystems can be overstretched if the aragonite saturation horizons in the Southern Ocean rise to the surface (Section 4.3). This presents an immediate need to limit acidification and adopt appropriate measures under the UNFCCC.

RECOMMENDATIONS

WBGU argues against this backdrop that climate policy needs to take all impacts upon the marine habitat into account. In the negotiations on the second commitment period under the Kyoto Protocol now commencing, the German federal government should work to ensure that the direct adverse effects of CO_2 emissions upon the oceans are taken into account. The desired stabilization of atmospheric greenhouse gas concentrations should be set in such a way that ocean acidification is adequately limited. This implies that CO_2 should not be viewed only as part of a basket of various greenhouse gases. The atmospheric CO_2 concentration rather needs to be stabilized specifically, regardless of the reduction of other greenhouse gases – at a level permitting compliance with the WBGU acidification guard rail (Section 4.4).

To achieve this goal, it may be necessary to define a CO_2 emissions ceiling for individual states or groups of states in addition to existing reduction commitments. This CO_2 cap would then need to be observed as a complement to the other commitments. The precise effects of this and any further potential instruments still need to be clarified. A particularly important aspect in this regard is the possible need for adaptation of the existing flexible mechanisms (emissions trading, Clean Development Mechanism and Joint Implementation).

It would not, however, be necessary to define a separate ceiling for CO_2 if, firstly, the international community were to agree to reduce greenhouse gas emissions to a level ensuring compliance with the WBGU guard rail on climate protection, and, secondly, the relative proportion of CO_2 within overall greenhouse gas emissions does not change significantly. The CO_2 reduction needed in this case would most probably suffice to prevent transgression of the acidification guard rail.

4.5.2
Taking shipping sector emissions into account

As a part of efforts to stabilize the atmospheric CO_2 concentration, the CO_2 emissions generated by ocean shipping and international aviation should be integrated more closely into emissions reduction strategies. No quantitative reduction commitments have yet been agreed for either sector. WBGU recommends closing these regulatory gaps by integrating the CO_2 emissions generated by international shipping and aviation into negotiations on future reduction commitments within the Kyoto process. Present estimates suggest that worldwide CO_2 emissions from shipping amount to about 2 per cent of global emissions. Over the past decade, the rate of increase in shipping emissions was more than twice that for total emissions (Bode et al., 2002; IEA, 2002). This illustrates the urgent need for action.

Besides emitting CO_2, ocean shipping also generates pressures upon marine and coastal ecosystems by emitting pollutants, nutrients and sediment particles. Controls on ocean shipping thus present a starting point for linking climate protection with marine conservation at the level of legal instruments.

In view of the relatively good environmental performance and significant economic importance of ocean shipping, regulatory controls need not aim to reduce the volume of shipping traffic. The goal is rather to create incentives for technological innovations and improvements in environmental management that contribute both to abating ocean pollution and preventing atmospheric CO_2 emissions. As a means to this end, WBGU recommends levying charges on the use of the oceans by shipping (WBGU, 2002).

This instrument highlights the connection between the utilization of the environmental resources represented by 'the oceans' and 'the atmosphere' and the utilization-related impairment of these resources. A charge signals the scarcity of environmental resources and the cost of their provision. The economic players burdened by a charge receive an incentive to modify their utilization of global environmental goods and to make it more sustainable (WBGU, 2002).

WBGU has set out the options for designing a user charge system in detail elsewhere (WBGU, 2002). A proposed user charge regime applied to the European Union area alone could generate annual revenues of €400–700 million. WBGU proposes that the financial resources thus received be earmarked for marine conservation purposes, in order to create a substantive link between the generation and reduction of pressures upon the oceans (WBGU, 2002).

4.6
Research recommendations

ACIDIFICATION AND MARINE ECOSYSTEMS

The physiological effects of acidification on marine organisms, especially on calcifying ones, and the impacts on the marine ecosystem are insufficiently understood. Physiological experiments are needed with moderately increased CO_2 concentrations, as are experiments exploring the effects on marine food webs (trophic coupling among phytoplankton, zooplankton and fish), and studies of possible physiological adaptation processes on an evolutionary basis.

BIOGENIC CALCIFICATION AND THE CARBON CYCLE

Our understanding of the interactions between calcifying plankton, the biological pump, and the global carbon cycle shows similar gaps, so modelling of the net effect is not yet possible. Modelling studies therefore need to be carried out on the acidification-related reduction of biological export production due to decreased mineral ballast (carbonate shells).

FURTHER IMPACTS OF CLIMATE CHANGE

Acidification is probably just one of many changes that will take place in the biogeochemistry of the oceans due to anthropogenic greenhouse gas emissions, or through climate change. Other aspects, such as the effects on oxygen balance and nutrient supply in the sea, are poorly understood and urgently need further study in order to recognize critical developments in good time.

FUTURE CO_2 UPTAKE BY THE OCEAN

CO_2 uptake by the ocean plays a key role in climate change. Interactions among the atmospheric radiation balance, the chemical composition of the atmosphere and the physical, chemical, and biological changes in the ocean should therefore receive increasing attention.

INTERNATIONAL RESEARCH PROGRAMMES

Promotion of projects by international research programmes (e.g., SOLAS, 2004; IMBER, 2005) that address the questions above is recommended.

CO_2 AND CLIMATE PROTECTION

In the event that a specific reduction commitment for CO_2 proves to be necessary, the potential ways of designing such a commitment need to be developed and evaluated. In addition, the implications for Kyoto mechanisms (especially CDM and emissions trading) need investigation.

CO_2 storage in the ocean and under the sea floor

5

Great and growing hopes have been pinned of late upon the sequestration of CO_2 as a means of climate mitigation (IEA, 2004). IPCC discussed this theme in depth in a recent Special Report (IPCC, 2005). Estimates expect carbon dioxide capture and storage (CCS) to be market-ready by 2015 (IEA, 2004). Within 50 years, 20–40 per cent of the CO_2 emissions arising from the combustion of fossil fuels could be separated, captured and stored (IPCC, 2005), provided that research and development intensify significantly (IEA, 2004). Sequestration technology has direct relevance to the present report, as it also includes the storage of CO_2 in the ocean and under the sea floor (Box 5.3-1).

5.1
CO_2 sequestration

5.1.1
Potential and costs

The technology of carbon dioxide sequestration has three components: CO_2 capture, transport and storage (IEA, 2004). Storage locations under consideration include sub-seabed geological formations, the water column of the ocean, and onshore geological formations such as depleted oil and gas fields and unminable coal seams. Chemical fixation to metal oxides is conceivable, although this process is currently regarded as unsuitable in view of the enormous energy consumption and very high costs associated with it (IPCC, 2005).

The storage capacity of depleted oil and gas fields is approximately 30 to 40 times the current annual CO_2 emissions from the combustion of fossil energy carriers. The storage potential through Enhanced Oil Recovery (EOR), whereby CO_2 is injected into cavities in order to increase oil yield, is estimated as 3 to 5 times the annual CO_2 emissions. Estimates for absorption in coal seams vary between 13 per cent and nine times annual CO_2 emissions. Saline aquifers under the sea may be able to hold 40 times the annual CO_2 emissions or more (IPCC, 2005). However, with the exception of EOR, little practical experience relating to geological storage is available, and the suitability of potential reservoirs is not clear.

Large point sources such as large fossil power plants near potential storage locations are regarded as particularly attractive for CCS. Typically, 80–90 per cent of the CO_2 generated in fossil power plants could be captured. However, the process requires energy, resulting in an increase in fuel consumption by 16–31 per cent (or even 70 per cent if the technology is retrofitted to existing lignite-fired power plants). Transportation and injection of CO_2 require comparatively small amounts of energy. Compared to the amount of emissions avoided, about 20–40 per cent more CO_2 has to be put into storage – and more than twice the amount if existing lignite-fired power plants are retrofitted.

CO_2 emissions from large-scale biomass facilities would also be suitable for sequestration. This would create an actual CO_2 sink, since the carbon contained in the biomass was previously removed from the atmosphere via photosynthesis.

The costs of CO_2 capture are currently estimated at US$11–57 per t of CO_2, depending on the fuel, the age and type of the power plant, and the capture technology used (IPCC, 2005). Pipelines are state of the art for CO_2 transportation. In the USA alone, 40Mt CO_2 are transported each year via pipelines with an overall length of 2500km. However, for large distances transport by ship is more economic than pipelines. The costs for transporting 1 tonne of CO_2 by ship are approximately US$15–25 per 5000km, compared with US$4–30 per 1000km via pipelines (IEA, 2004; IPCC, 2005). The costs for injection and storage are comparatively low, estimated at US$0.5–8 per t of CO_2. In addition, there are minor costs for monitoring and maintenance of the reservoirs. The total costs of sequestration involving storage in the ocean or under the sea floor therefore range between US$20 and 100 per t of CO_2.

Based on current knowledge, sequestration of the CO_2 released during power generation would lead to increases in generating costs per MWh amounting to

US$12–34 in new power plants. For retrofitted lignite-fired power stations the cost increase is estimated at US$33–44 per MWh (IPCC, 2005). Current generating costs are around US$25–55 per MWh, depending mostly on fuel prices, which means that total generating costs including sequestration would be US$45–80 per MWh. This range is comparable with many wind and small-scale hydroelectric plants (Box 5.3-2). Sequestration would increase power generation costs in fossil power plants by 30–60 per cent for new plants. Retrofitting existing plants may triple costs. Optimistic forecasts assume that sequestration costs are likely to come down significantly by 2030. However, based on renewable electricity generating costs of US$10–20 per MWh (IEA, 2004) and expected increases in fossil fuel prices in the long term, electricity generation from renewables is likely to become an increasingly cost-effective option.

5.1.2
Risks and sustainability

The uncertainty regarding the environmental sustainability of sequestration is more significant than the uncertainties relating to cost development. A distinction has to be made between three types of risk.

1. *Risk of accidents:* Similar to natural gas pipelines, CO_2 pipelines may be affected by leakage. CO_2 concentrations of more than 7–10 per cent in air endanger health and life. However, experience with existing pipeline systems shows that major damage to pipelines is very rare. In addition, the risk can be reduced further through improved pipeline design and monitoring. Sudden escape of large quantities of CO_2 is also conceivable during CO_2 injection into the repository. In addition, similar to EOR or natural gas storage, stored CO_2 may escape abruptly, e.g. due to inadequate sealing of the repository (IPCC, 2005). However, this type of major accident is regarded as unlikely in conjunction with CO_2 storage. The immediate impacts of such an incident would be significantly lower at sea than in inhabited areas, where severe, in extreme cases fatal impact on humans would have to be expected.
2. *Potential impact on marine ecology:* This is mainly associated with CO_2 disposal in seawater, which WBGU regards as unacceptable. The issue is discussed in Section 5.2.
3. *Continuous slow escape of stored CO_2:* This risk is highly significant in the context of long-term climate change mitigation. While the IPCC Special Report (IPCC, 2005) contains no specific data on acceptable leakage rates, a simple rough calculation can provide some guidance. The cumulative emissions in the different SRES scenarios for 1990–2100 vary between 1000Gt C (B1 scenario) and 2200Gt C (A1FI scenario) (IPCC, 2000). In order to comply with the 2°C climate guard rail, the cumulative emissions to the atmosphere from the present need to be limited to 500Gt C (Meinshausen, 2006). Compared with a medium-level scenario assuming emission of 1500Gt C by 2100, around 1000Gt C would have to be mitigated. If this quantity were to be sequestered, with a leakage rate of 0.1 per cent per year (i.e. a retention period of 1000 years) 1Gt C would escape uncontrolled every year. However, in order to comply with the 2°C guard rail, a maximum of 1Gt C of total emissions per year would be acceptable in the long term (from about 2200), even for the case assuming an average climate sensitivity of 3°C (Caldeira et al., 2003). Thus even assuming a medium-level emissions scenario, which does not represent the worst case, leakage from CO_2 storage sites alone would represent 100 per cent of admissible CO_2 emissions in the long term. The situation is even more problematic if less optimistic assumptions are made: Climate sensitivity may prove to be higher, other greenhouse gases (e.g. methane, see Chapter 6) may contribute to warming more strongly than assumed, or the proposed 2°C guard rail may prove to be too high in the long term, e.g. in the event that it triggers the melting of Greenland ice (see Chapter 3). Overall, no more than one-tenth of the above-mentioned leakage rate would therefore appear to be acceptable, i.e. 0.01 per cent per year, corresponding to a retention period of 10,000 years. Therefore, sequestration can only be regarded as an acceptable climate mitigation technology if long-term CO_2 storage for at least 10,000 years can be guaranteed.

5.2
Ocean storage

Two basic options are under consideration for carbon sequestration in the ocean: physical-chemical dissolution in the seawater and, in the broadest sense, biological-engineered storage in marine ecosystems, primarily through iron fertilization. In the following, only the physical-chemical techniques will be discussed in detail. This report does not explore the concept of using permanent input of iron to trigger algal blooms and thereby increase the sink potential of the ocean in marine areas where the micro-nutrient iron is the limiting factor for primary production (notably the Southern Ocean). The expected quantitative effect is fairly low (as a comparison with palaeoclimatological data leads one to presume), and there is doubt that the permanence of storage is sufficient (Section 5.1.2). Furthermore, the risks of large-scale iron fertilization in terms of indirect effects on the marine ecosystem are hard to estimate. WBGU has already explained elsewhere the reasons for its rejection of iron fertilization of the ocean (WBGU, 2004).

5.2.1
Storage and residence time of CO_2

Direct injection into seawater is one form of CO_2 storage that is under discussion. The CO_2 content of the sea surface equilibrates relatively quickly with the atmosphere, so that an artificial increase of CO_2 in the surface water would result in outgassing to the atmosphere within a short time. Introduction into the deep sea could, in contrast, ensure a longer residence time of carbon in the sea. The CO_2 injected there could remain isolated from the atmosphere for several centuries (IPCC, 2005), but over longer time periods the equilibrium between atmospheric CO_2 concentration and that in the sea would be re-established. Then, depending on the atmospheric CO_2 concentration, between 65 and 80 per cent of anthropogenic CO_2 would be stored in the sea, regardless of whether the CO_2 has been emitted to the atmosphere or injected into the ocean (Caldeira et al., 2005). The injection of CO_2 into seawater could thus reduce a peak concentration of CO_2 in the atmosphere, but it has no influence on the long-term stabilization level of atmospheric CO_2. Thus, independent of the consequences for the marine ecology (Section 5.2.2), it does not represent a sustainable solution for the problem because future generations would be burdened with irreversible effects.

Another technological option would be the storage of CO_2 as a liquid or hydrate on the sea floor, which would only be possible in water depths below 3000m due to its greater density there. Without a physical barrier, however, the CO_2 would slowly dissolve from such reservoirs into the overlying water column. So this technology would also only lead to a postponement of the consequences of climate change, but not to their mitigation. None of the technological possibilities being discussed for storage in seawater have been tested in field studies at a meaningful scale. Approval has not been given for any of the research projects so far proposed, not even for injecting just a few tonnes of carbon dioxide into the deep sea.

5.2.2
Impacts of CO_2 storage on deep-sea organisms

Just as in the surface layer, the direct injection of CO_2 into the deep sea also changes the chemical and physical characteristics of the seawater. Initially this affects the direct surroundings of the location of introduction, for example, the end of the pipeline through which the liquid CO_2 flows into the deep sea. Here, as simulations indicate, dramatic changes in the local pH values of up to several units can occur. Through technical solutions that lead to faster dilution (such as a pipeline towed by a ship), the maximum local pH change can be reduced. In the somewhat broader surroundings (several kilometres), the rate of dilution is essentially determined by ocean currents, so that the chemical and physical impacts can be estimated with ocean circulation models. For example, with an input of 0.1Gt C per year (which is less than 2 per cent of the industrial emissions and around 5 per cent of the present CO_2 input through the sea surface caused by anthropogenic CO_2 level rise in the atmosphere), in up to 0.01 per cent of the ocean volume the pH value could drop by 0.3 units over a period of 100 years (Caldeira et al., 2005). CO_2 storage in the deep sea could thus have serious impacts on the deep-sea ecosystem. Deep-sea organisms develop very slowly, their metabolic rates are lower and life expectancy is greater than of organisms in other ocean layers (IPCC, 2005). During their evolution, the inhabitants of the deep-sea ecosystem have adapted to special living conditions, with typically very stable temperatures and pressures, and relatively constant CO_2 concentrations (except at volcanic CO_2 vents). Such constant environmental variables do not demand rapid adaptive strategies. Thus, it has to be expected for the possible storage of CO_2 on the sea floor, as well as for leakage of a storage reservoir below the sea floor, that the ecosystem affected will be critically damaged, or will take a long time to recover from a change in the environment (IPCC, 2005).

Very little is known about the organisms in the deep sea in general, their life forms and interactions. So far, the direct effect of CO_2 on marine organisms has mainly been investigated in the laboratory. Studies involving field observations are greatly lacking, except for a few experiments with small CO_2 plumes on the sea floor and investigations of volcanic CO_2 vents (Pörtner, 2005).

In one of these in-situ experiments off the coast of California, liquid CO_2 was injected at 3600m in order to study the survival and behaviour of the deep-sea fauna after direct contact with CO_2 (Barry et al., 2004). Depending on pH changes and distance from the CO_2 plume, the survival rate of the animals varied. Flagellates, amoebas and nematodes in the sediment zone near the CO_2 source showed a high mortality. In another study, the scents of prey animals were combined with the extrusion of CO_2 (Tamburri et al., 2000). Fish and invertebrates were attracted by the scents and appeared to some extent to remain relatively undamaged, even at a distance of just a few centimetres from the CO_2 source, in spite of the low pH value. Carrion-eating hagfish, attracted by the scent of the prey, did not seek to escape narcotization under the high CO_2 content. Tyler (2003) therefore fears that animals that die through contact with CO_2 introduced into the deep sea could attract larger carrion eaters, who would then likewise be killed by the CO_2 plume. Squid and other invertebrates may react more sensitively to high CO_2 concentrations than vertebrates (Pörtner et al., 2004) because their body fluids contain no haemoglobin, which helps protect the body from large pH fluctuations. So even a small, local CO_2 plume could have wide-reaching effects on its surroundings.

Risks also arise from outgassing into the atmosphere. Two catastrophes occurred in the 1980s when large CO_2 plumes from gas-saturated deep water escaped into the atmosphere from the volcanic Lakes Monoun and Nyos in Cameroon. The disaster at Lake Nyos had devastating consequences: around 80 million m^3 of CO_2 were expelled, taking the lives of at least 1700 people and several thousand animals up to a distance of 10km from the lake (Kling et al., 1987; Clarke, 2001). There is sparse information in the literature on whether Lake Nyos harboured life of any kind before the catastrophe, and how the gas plume affected this biotope. Freeth (1987) has reported that, in spite of otherwise favourable living conditions, the local population had neither seen fish in the lake before the catastrophe, nor were fish cadavers found after the event.

If a large plume of CO_2 pumped into the sea should rise to the sea surface or into higher water layers, the possible ecological results can only be speculated. In summary, the largely incalculable ecological risks also support a general prohibition of CO_2 storage in seawater.

5.2.3
Present international law

The relevant body of international law relating to CO_2 storage in the ocean and below the sea floor can be summarized as follows: according to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter – the London Convention of 1972 – the disposal of certain wastes and other matter (listed in Annex I to the convention) into the sea is forbidden. Further wastes and matter listed in Annex II to the convention may only be disposed of with prior special permission. Other wastes and matter may be disposed of under a prior 'general' permit. Since 1 January 1996, the 'black list' of Annex I includes industrial waste (No. 11), which means 'waste materials generated by manufacturing or processing operations'. It can be assumed that separated CO_2 is derived from such operations and is therefore industrial waste within the meaning of Annex I. However, with respect to matter whose discharge into the ocean is prohibited, the convention contains an important exception in connection with the extraction of mineral resources: according to Art. III, para. 1(c) of the London Convention, the 'disposal of wastes or other matter directly arising from, or related to the exploration, exploitation and associated offshore processing of seabed mineral resources' is not covered by the provisions of the convention. In other words, the disposal of CO_2 that is generated by the production of oil or natural gas at sea is permitted under the Convention, as long as the corresponding processing operations are carried out at sea.

Basically the same legal position exists under the Protocol of 1996, although the approach is different: the Protocol, which will replace the Convention in the future but has not yet been ratified by a sufficient number of signatories and is therefore not yet in force, contains a general prohibition of discharge into the sea, combined with a list (Annex 1) of exceptions. CO_2 is not included among these exceptions. This means that the discharge of CO_2 would be essentially prohibited under the Protocol once it enters into force. But, according to the Protocol, the discharge would still be allowed when the CO_2 is derived from the recovery of oil or natural gas at sea and the processing also takes place there (Art. 1, para. 4.3).

5.3
Sub-seabed geological storage

5.3.1
CO_2 injection into the geological sub-seabed

Injecting CO_2 into geological formations below the sea floor is basically no different than the procedure on land. Saline aquifers, for example, also provide repositories, and pressurized injection of CO_2 into oil formations could facilitate the extraction of oil. The technical systems just have to be adapted for the existing conditions. The appropriate monitoring techniques, however, are very different on land and in the sea. There are also some differences with respect to safety technology (Section 5.3.3.4).

Not only are great research efforts presently being carried out on CO_2 storage in the seabed (CSLF, 2005), but practical experience already exists in this field, and further projects are planned (Bellona Foundation, 2005; Deutsche BP, 2005). When charges on CO_2 or the prices for emission rights rise, sequestration becomes more economically attractive, and companies can be expected to apply increasing efforts in addition to the Sleipner project (Box 5.3-1) and EOR (Section 5.1). The Norwegian company Statoil is already considering the transport of 'foreign' CO_2 through pipelines to the company's Sleipner gas platform, and storing it there in the CO_2 formations already in use under the sea.

5.3.2
Risks and sustainability of CO_2 storage in the seabed

Various scenarios are imaginable for the escape of CO_2 from formations under the sea floor. If the CO_2 emerges at a depth where it occurs as hydrate, then the least damage can be expected. But when the CO_2 dissolves in water it contributes to acidification of the sea. The conceivable harmful consequences of leaks for marine organisms have already been described in Section 5.2.2. In cases of very large-volume leaks, the CO_2 could also reach the surface, which would, for one, contribute to the enrichment of CO_2 in the atmosphere and, for another, present a health risk in the immediate surroundings. But as long as the storage site is not directly on the coast near human settlements, the human health risk is significantly lower

Box 5.3-1

The Sleipner project

The Sleipner Platform in the North Sea is located approximately 250km from the coast of Norway. It is the first commercial project for CO_2 storage in a saline aquifer under the sea floor. CO_2 separated from natural gas here is transported locally to a depth 800m below the sea floor. The storage of CO_2 here is economically interesting because the separation of CO_2 from the gas is necessary in any case for later technical use, and the Norwegian government would tax its emission into the atmosphere. Since October 1996 around 1Mt CO_2 has been injected annually into the sub-seabed. By the beginning of 2005 more than 7Mt CO_2 had been injected into the aquifer. By the end of the project the total should be around 20Mt CO_2. The formation has a total capacity of 1–10Gt CO_2.

The project is being observed scientifically, in part to investigate safety and permanence of storage. Initial research results indicate that a dense cap rock seals the formation at the top, preventing the leakage of CO_2. Simulation calculations covering hundreds of thousands of years suggest that the CO_2 will dissolve in the pore waters and then sink to the bottom of the formation. The probability of long-term leakage is minimal, so that the gas, according to these calculations, should not escape into the North Sea for the next 100,000 years. Even after a million years, only a millionth of the CO_2 should escape. This storage could therefore fulfil the required holding time of more than 10,000 years (Section 5.1.2), but these conclusions will have to be better documented scientifically.

Sources: IPCC, 2005; Statoil, 2005

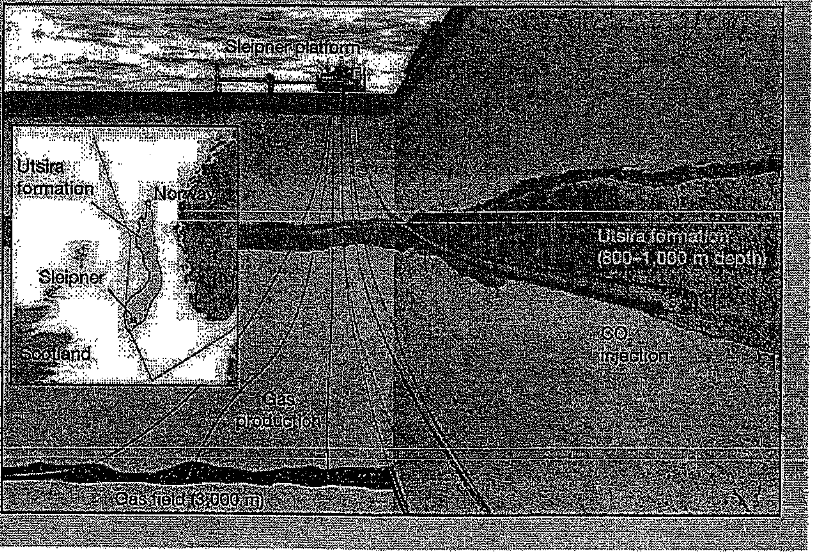

Figure 5.3-1
The Sleipner project in the North Sea, simplified representation. The gas production comes from the Sleipner East gas field. The captured CO_2 is injected into the Utsira sandstone formation. The small picture shows the position and extent of the Utsira formation in the North Sea.
Source: Statoil, 2005

than for storage on land. Even where people are in the vicinity, the probability of dangerously high CO_2 concentrations in the ocean environment is extremely low because, in contrast to the situation on land, CO_2 lakes cannot form. As a rule, such CO_2 lakes can only form and persist in depressions on land that have no or poor drainage.

As discussed in Section 5.1.2, a retention time for CO_2 of at least 10,000 years is required for long-term sustainability.

5.3.3
Regulating sub-seabed geological storage

Considering that global CO_2 emissions are rising, the option of storing CO_2 in geological formations deep below the sea floor should not be dismissed completely. However, such sub-seabed geological storage is not altogether unproblematic (Section 5.3.2). For one thing, a release of CO_2 to the atmosphere cannot be excluded entirely. This can be caused by technical faults or by accidents arising in the transport, injection and storage process. It may also be due to the selection of inappropriate geological formations. Current knowledge indicates that, under certain geological and technological preconditions, leakage rates may be acceptable (<0.01 per cent per year). There is a need for substantial further research, however, to be able to verify this with sufficient certainty. Issues in particular need of clarification include the criteria that geological formations must meet, and how any escape of the gas to seawater could be monitored and quantified.

Moreover, an all too strong political and economic focus on the sequestration option might cause neglect of far superior climate mitigation strategies, such as improving energy efficiency and switching to renewable energies. To attain the goal of sustainable energy systems, it is these superior options that particularly require political support, innovation and the employment of scarce resources (WBGU, 2004). A high renewable energy potential is available in the ocean and above the sea surface (Box 5.3-2).

WBGU therefore views sub-seabed storage of CO_2 as being, at most, a transitional option complementing other options (WBGU, 2004). Its deployment should be limited and regulated (Section 5.3.3.4).

5.3.3.1
Provisions under the international law of the sea

The 1972 London Convention and its 1996 London Protocol permit the storage of CO_2 in sub-seabed geological formations if the sequestered CO_2 originates in the course of processing the mineral resources of the seabed (Section 5.2.3; the same applies to placement of CO_2 in seawater). This is the case, for example, with the Sleipner project (Box 5.3-1).

In contrast, it has not yet been clarified unequivocally whether the 1972 London Convention or, in future, the 1996 London Protocol permits sub-seabed storage, for instance in saline aquifers, of CO_2 that was separated on land (IEA, 2005). Article III, para. 3, of the London Convention defines 'sea' as 'all marine waters'. There is some controversy as to whether this definition means that the seabed and the subsoil thereof fall within the scope of the convention. In response to a survey conducted by IMO, Germany argued in favour of construing the term 'all marine waters' to include the seabed and the subsoil thereof, as this would be in line with the history and purpose of the convention. The 1996 Protocol defines in Art. 1, para. 7, the term 'sea' more precisely, namely as 'all marine waters other than the internal waters of States, as well as the seabed and the subsoil thereof; it does not include sub-seabed repositories accessed only from land'. This definition, however, has also given rise to controversy over the depth to which the subsoil reaches. In the above-mentioned IMO survey, Germany argued in favour of construing the term as comprehensively as possible, too.

When construing the treaty wording, however, it needs to be taken into account that the issue of CO_2 sequestration, including CO_2 storage in the ocean or under the sea floor, was not on the agenda when the 1972 London Convention was negotiated, nor when its 1996 Protocol was elaborated. It is therefore not possible to draw conclusions from the wording of the treaty about the will of the participating states with respect to how to handle CO_2. The parties to the London Convention are now addressing this issue intensively (IMO, 2004), for instance at the 27th Consultative Meeting of the parties held in October 2005. In view of the numerous gaps in knowledge and the unresolved issue of whether placement of CO_2 in the seabed should be covered by the London Convention and/or the London Protocol, that meeting agreed to debate the issue in greater depth at the 28th Meeting. If the parties resolve to permit the placement in the seabed of CO_2 sequestered from separation processes on land, Annex 1 to the London Protocol may need to be amended; this would also be expedient in order to provide clarification. The pre-

Box 5.3-2

Marine renewables

In addition to their role within the climate system, the oceans offer options for active mitigation of anthropogenic climate change. On the one hand, increased utilization of renewables from the sea can substitute fossil energy carriers and therefore reduce associated CO_2 emissions. On the other hand, CO_2 storage in suitable geological formations in the seabed may offer an additional man-made sink for this greenhouse gas. The potential for marine renewables is briefly outlined below, followed by a rough comparison of the respective costs for the two options.

POTENTIAL FOR MARINE RENEWABLES

Commensurate with their proportion of the Earth's surface, the oceans receive more than 70 per cent of the solar insolation and almost 90 per cent of the wind energy (Czisch, 2005). They therefore hold the majority of the global renewables resources. However, from today's perspective only fractions of this theoretically available energy is technically and cost-effectively usable. In addition, the potential is reduced by a wide range of competing uses, particularly along densely populated coastlines. The sustainable potential is reduced further by the fact that environmental aspects have to be taken into account (WBGU, 2004). For example, any expansion of renewables must comply with the ecosystem guard rail (20–30 per cent of marine ecosystems designated as protected areas; Section 2.5). The overall area available for sustainable utilization of renewable energy is therefore reduced significantly.

- *Wind energy*: Studies on the European offshore wind energy potential (Sea Wind Europe, 2003) assume an installed capacity of 111GW and associated annual generation of 340TWh by 2015, equivalent to approximately 10 per cent of the technical potential. Siegfriedsen et al. (2003) conclude that outside the European Union approximately 4600TWh per year could be generated by offshore wind energy converters. With a total of 5000TWh per year, one third of current global electricity demand of approx. 15,500TWh per year would be covered by offshore wind energy. In 19 of 20 countries with the largest potential outside the EU, more than 10 per cent of electricity demand could be covered by offshore wind energy converters by 2020. Of the different energy forms examined, wind energy is the most significant one in terms of potential and implementation.
- *Wave energy*: Wavenet (2003) estimates the global technological potential as 11,400TWh per year. The global sustainable generating potential of wave energy is approx. 1700TWh per year, i.e. more then 10 per cent of current global electricity demand. An annual generation figure of 9TWh is assumed for the EU by 2020. Wave energy is not expected to make a significant contribution to global electricity demand until some time in the future.
- *Tidal energy*: Strong sea currents occur near coasts through tidal and other effects. The potential for energy generation from such currents in North America, Europe, South-East Asia and Australia is estimated at 120TWh per year. The total global sustainable potential is likely to be several hundred TWh per year. In 5–10 years' time, sea current turbines could experience a similarly dynamic development as that currently seen with offshore wind energy converters.
- *Energy from osmosis*: A further energy production technique is based on the utilization of osmotic pressure between freshwater and seawater (e.g. in estuaries) using special membranes with high salt retention. This technology is currently only available at the laboratory scale. Globally, a total of 730GW could be achievable from rivers with flows of more than $500m^3$ per second. The sustainable potential, taking into account ecological guard rails and shipping sector requirements, is estimated to be around 50 per cent of the technical potential, or 2000TWh per year.

Utilization of predominantly coastal marine areas that are currently regarded as technologically accessible would offer a global total potential of approximately 9000TWh per year from wind, waves, currents and osmosis, with wind power offering by far the biggest potential and quickest implementation. However, the issue of concurrent utilization of coastal marine areas through systems for power generation from wind and waves would have to be examined in more detail, because certain wave energy systems may be difficult to combine with wind farms. In addition, high-density installation of large numbers of systems would lead to significant habitat changes, e.g. through noise emissions, increased shipping traffic and other effects such as underwater cables, so that the overall effect caused by concurrent utilization of several technologies have to be regarded as unsustainable.

RENEWABLES VS CO_2 SEQUESTRATION

Generating costs for fossil power plants currently range between US$25 and 55 per MWh, for wind energy and small-scale hydroelectricity between US$35 and 90 per MWh (IEA, 2005). The additional costs for CO_2 sequestration relating to electricity production in fossil power plants range between 30 and 60 per cent, depending on the technology and underlying conditions. Assuming moderate future fuel price increases and further cost reductions for investments in both fossil power plants and renewables, sequestration with continued utilization of fossil energy carriers would very likely result in higher CO_2 avoidance costs than utilization of renewables in the medium and long term.

In addition, sequestration does not reduce dependence on fossil fuels and the potential for associated conflicts. Compared with CO_2 sequestration, intensive utilization of renewables is therefore regarded as the preferred option.

sent state of knowledge thus indicates that it would be necessary to take account of Art. 31, para. 1, of the Vienna Convention on the Law of Treaties, according to which a treaty shall be interpreted in good faith in accordance with the ordinary meaning to be given to the terms of the treaty in their context and in the light of its object and purpose.

5.3.3.2
UNFCCC and Kyoto Protocol

The production of the national emissions inventories in accordance with the United Nations Framework Convention on Climate Change and the Kyoto Protocol is based on the IPCC Guidelines for National Greenhouse Gas Inventories. At present, these Guidelines do not deal explicitly with the issue of sequestration. However, the IPCC Special Report on CSS (IPCC, 2005) provides for the option of applying the current framework provisions, principles and methods to sequestration activities. The Norwegian approach demonstrates how these general provisions could be applied to sequestration in practice: Norway reports the quantities of CO_2 sequestered at the offshore Sleipner facility (Box 5.3-1) and consistently factors any emissions leaked during the injection process into its national emissions (IPCC, 2005). The sequestered CO_2 is not added to the emissions inventory but is treated, in effect, as non-emitted. The Guidelines are due to be revised in 2006. It is likely that the current debate about standards for inventorizing sequestered CO_2 will flow into this process and relevant provisions will be adopted in the near future. Apart from the practical question of how to inventorize sequestered CO_2 in the national reports, a further issue to be clarified is whether, and how, sequestration projects should be integrated into the flexible mechanisms – emissions trading, the Clean Development Mechanism (CDM) and Joint Implementation (JI) (Bode and Jung, 2005; IPCC, 2005). The inclusion of sequestered CO_2 in the flexible mechanisms raises a variety of issues (Bode and Jung, 2005) which shall not be discussed in detail here. Matters become especially complicated in relation to the CDM if, for example, an Annex B country 'imports' CO_2 from developing countries which has been emitted on land and stores it in sub-seabed reservoirs which are already in use. Strictly speaking, such cases do not meet the CDM's additionality criterion, which means that in essence, no CDM emission credits can be issued. Nor does it necessarily promote technology transfer to developing countries, which is an explicit objective of the CDM. Similarly complex issues arise in relation to emissions trading and JI.

5.3.3.3
Instruments to regulate CO_2 storage in the seabed

WBGU considers that in view of the leakage risk, regulations are required for activities aimed at the storage of CO_2 in the seabed. Firstly, more rigorous minimum standards are needed, with mandatory compliance in order to minimize risks. Secondly, the use of quantity restrictions or liability-based instruments as a response to the risk of leakage would help ensure that lower-risk sustainable emissions avoidance options (e.g. increasing energy efficiency and the use of renewables) are not neglected.

GEOLOGICAL AND TECHNOLOGICAL MINIMUM STANDARDS

The rate of CO_2 leakage over the long term must be very low and must also be readily monitored and verified. Firstly, the retention period for stored CO_2 at the chosen site must be very long – at least 10,000 years. Our current state of knowledge indicates that it is possible to meet this criterion, at least in deeper aquifers (Ploetz, 2003; IPCC, 2005). Secondly, the CO_2 storage sites must be easily monitored, i.e. it must be possible to record both the leaked and the sequestered amount of CO_2 on a reliable basis. At present, however, adequate technologies to measure CO_2 leaks are not available.

INDIRECT QUANTITY RESTRICTIONS

The leakage risk in particular indicates that sequestered CO_2 cannot be viewed as fully 'avoided' CO_2 emissions in international climate agreements. In the setting and implementation of emissions reductions targets, storage should therefore only be eligible in part as avoided emissions. Various approaches can be considered in this context, both at international level (UNFCCC etc.) or solely for European climate policy at first. In the following, WBGU outlines various instruments which aim to restrict by indirect means the proportion of CO_2 storage. It offers an overview of possible approaches which could play an important role in relation to sub-seabed storage as well as sequestration in general. No conclusive evaluation of the instruments can be undertaken here, firstly because no policy decision has been taken on appropriate limitation targets, and secondly because there is still a considerable need for research in many areas (Bode and Jung, 2005; IPCC, 2005).

- *Adding leakage to total emissions:* Sequestered CO_2 would only be partly recognized as avoided emissions. The percentage of CO_2 which would be considered as having been emitted 'in practice' and which would have to be designated as such in the national reports would be determined at political level. However, this percentage should not merely reflect but should significantly exceed the probable leakage, in order to take appropriate account of the impacts of leakage on the marine environment.
- *Deductions in the context of the flexible mechanisms:* Emission rights arising from sequestration

could only be traded with substantial deductions. This would mean that a certificate based on one tonne of sequestered CO_2 would give rise to an emissions entitlement of less than one tonne of CO_2. The same principle would apply to CDM credits from sequestration activities in developing countries. CDM credits could also be granted for the storage of 'imported' CO_2 from developing countries, especially as this type of cooperative project would reduce global CO_2 emissions into the atmosphere – albeit without satisfying the current CDM criteria (Section 5.3.3.2), which is why a higher deduction would be justified. The decision which deduction rate would be reasonable in individual cases would largely depend on the climate policy assessment of the leakage risk and the impacts on marine ecology. There is a considerable need for further research in this area.

- *'Traditional Action'*: Countries would agree to meet a specific proportion of their emissions reduction commitments without recourse to subseabed or any other form of CO_2 sequestration. This approach would be analogous to the concept of 'domestic action'.

LIABILITY MECHANISMS

When applying the above-mentioned instruments to limit CO_2 sequestration, countries implicitly make their own assessment of the scale of the leakage risk and the likely damage that leakage would cause. By contrast, liability mechanisms are an alternative or supplementary approach relying on the market mechanism. An effective liability regime for sequestered CO_2 means establishing a transparent and credible system to determine who is responsible for discharged CO_2 and who is therefore liable to pay compensation: either through ex post adding to overall emissions, ex post acquisition of emission rights, or penalty payments which are used for climate and ocean protection. As long as the operator still exists, it may be comparatively easy to enforce liability. However, the long time scale of climate protection means that the issue of liability must be clarified and safeguarded over the long term. The issues surrounding the cleanup of contaminated sites at national level have shown that it is often the state which ultimately shoulders the financial burden. This applies similarly to cases involving private operators, especially if a defunct polluting company has no legal successor or the successor lacks the resources to pay damages.

'Carbon sequestration bonds' have emerged as a market-based solution in this debate (Edenhofer et al., 2005). Here, a firm which intends to sequestrate or store CO_2 has to deposit a sum of money with a designated authority, equivalent to the amount of sequestered CO_2 multiplied by the CO_2 certificate price (Edenhofer, 2003). The company would obtain interest for the bond, equivalent to the normal market rate of interest on long-term bonds. The authority – this could be the Climate Central Bank already proposed by WBGU (WBGU, 2003) – devalues the bond according to the fraction of leaked CO_2. The balance could be used to pay for emissions prevention measures, such as the promotion of renewable energies, or even the purchase and withdrawal of emissions rights. In the case of leaks from marine disposal sites in particular, the funding of marine conservation measures from these resources would be justified. As the value of the bond falls, the interest paid also decreases. No fixed price for the devaluation of the bond is set in advance; instead, the devaluation increases over time in line with the actual amount of leaked CO_2. The idea is that the company tries to sell the right to the interest accumulating on the deposit as a 'bond' on the financial markets. This can only be achieved if potential purchasers are offered a rebate on the value of the bond which is high enough to offset the risk of devaluation by the authority. During trading, the market value would reflect not only the devaluation of the deposited amount but also the capital market's assessment of the likely leakage risk in future. The concept of 'carbon sequestration bonds' is a very interesting and innovative approach to risk assessment and liability, and merits further research.

5.4
Recommendations for action: Regulating CO_2 storage

5.4.1
Prohibiting CO_2 injection into the ocean

WBGU firmly rejects the storage of CO_2 in the ocean, i.e. in the water column and on the sea floor. The ocean is in permanent exchange with the atmosphere, with the result that this option does not mitigate the long-term consequences of CO_2 emissions for future generations. It is therefore not a sustainable option. The risk that ecosystems will suffer appreciably under an elevated CO_2 concentration in the water is a further argument against the disposal of this greenhouse gas in seawater (Section 5.2.2; IPCC, 2005; Pörtner, 2005). Moreover, the international community will scarcely be able to control CO_2 lakes on the sea floor, and the release of this CO_2 to the atmosphere over the long term cannot be excluded. WBGU therefore recommends a full and comprehensive ban on CO_2 injection into the ocean, regardless of the territorial status of waters.

The 1972 London Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, in conjunction with its London Protocol (Section 5.3.3.1; the protocol has not yet entered into force) prohibit in principle the placement of CO_2 in the ocean. Both agreements, however, contain an important exception that needs to be firmly rejected in light of the above: both permit in their current wording the injection of CO_2 that arises from the production of mineral oil or natural gas, as long as the associated processing operations take place at sea. The prohibition on the injection of CO_2 arising from processing operations on land that is already implicitly in place should therefore be extended explicitly to such CO_2 that is separated in the course of seabed resource exploration and processing operations at sea. Such a prohibition could possibly be complemented by a corresponding arrangement under the Framework Convention on Climate Change; this could also serve to cover those states that do not ratify the London Protocol.

5.4.2
Limiting CO_2 storage in the seabed

The disposal of CO_2 in the seabed poses substantially less risk than its injection into the water column or on the sea floor. For that reason, and in view of the almost unavoidable rise in energy consumption especially in developing and newly industrializing countries, WBGU considers it acceptable for a transitional period to use injection into the geological sub-seabed as an option complementing more sustainable emissions reduction strategies.

WBGU accordingly recommends clarifying the issue of conformity of sub-seabed geological storage with the London Convention or London Protocol in the relevant bodies of the convention and protocol in such a way that CO_2 sequestration in sub-seabed geological formations is permissible regardless of the location of processing operations. If it should not prove possible to generate consensus on construing these legal provisions to mean that sub-seabed CO_2 disposal is permissible, then modifying or supplementing the London Protocol should be considered. WBGU also argues that such activities should only be permitted from the outset for a limited period, such as several decades.

Before the international law of the sea can be construed or supplemented in such a way, universal minimum technological standards would first need to be defined and complied with. These need to be developed specifically for marine transport, for CO_2 injection and storage, and for the characteristics and monitoring of geological disposal sites. As long as the problems currently associated with the measurement of CO_2 releases persist, WBGU advises applying exceedingly strict requirements upon geological disposal sites. WBGU takes the view that in this respect, too, the London Convention or London Protocol provides an appropriate framework for setting standards, underpinned by more comprehensive rules governing sequestration activities under the Framework Convention on Climate Change.

The IPCC Guidelines play an important role in this context. These guidelines govern the preparation of national emissions inventories. Their review is currently pending. WBGU shares the view of the IPCC Special Report (2005) that the present regulatory structure, including the flexible mechanisms, can in principle also be applied to sequestered CO_2. WBGU does not consider this expedient in all situations, but does regard it as purposeful in the case of CO_2 disposal in verified sub-seabed geological formations. WBGU recommends, however, that when sequestered CO_2 is integrated into inventories and into the flexible Kyoto mechanisms the risk of leakage be taken into account. This can be done through, for instance, deductions in emissions trading or from CDM credits, or through liability rules (Section 5.3.3.4).

5.5
Research recommendations

RISKS POSED BY THE USE OF GEOLOGICAL FORMATIONS FOR CO_2 STORAGE

There is a need for further research on the permanence of marine CO_2 storage in deep geological formations. The associated monitoring procedures also need further development. Furthermore, research should be conducted on the potential impacts of CO_2 leakage upon marine ecosystems and organisms.

The long-term effects of storage upon atmospheric CO_2 concentrations should also be studied. An issue of particular importance in this respect is which specifications a storage site needs to meet in order to ensure stable atmospheric CO_2 concentrations at a low level over the long term. This will require an improved understanding of the carbon cycle on a millennial time scale.

LEGAL SETTING

The instruments of international law governing the permissibility of CO_2 storage in deep sub-seabed geological formations need to be studied comprehensively. Not only the London Convention with its

1996 Protocol should be taken into account. It is equally important to analyse links to other regimes in international law – notably the Framework Convention on Climate Change with its Kyoto Protocol, and the United Nations Convention on the Law of the Sea (UNCLOS).

REGULATING CO_2 STORAGE IN THE SEABED

The manner in which geological storage of CO_2 in the seabed (and, it is worth noting, on land) may be eligible as a climate mitigation measure under the international climate protection regime needs to be clarified unequivocally in the near future. There is a need for research in the social sciences and economics on the issues surrounding the flexible mechanisms. Identifying which instruments for the limitation of sequestration are effective, efficient and enforceable in international law and policy is an issue of particular importance.

MARINE RENEWABLES

Great uncertainties still attach in some instances to the renewable energy potential of marine sources such as offshore wind, wave energy, salt gradient energy or ocean thermal energy conversion. There is a considerable need for further research in order to identify the sustainable global potential. This concerns both the methods and the impacts that need to be taken into account.

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Methane hydrates in the sea floor

6

Large quantities of carbon are stored in the sea floor in the form of methane hydrates, with an order of magnitude comparable to the global occurences of coal. There are risks associated with methane hydrates due to climate change as well as ocean mining. There are, however, considerable uncertainties and gaps in knowledge, so that only a preliminary evaluation of these risks is possible.

6.1

The methane hydrate reservoir

Gas hydrates – such as methane hydrates – are solids composed of water molecules that have gas molecules enclosed within their crystal lattices. Carbon dioxide, hydrogen sulphide and methane molecules have the right size to be trapped inside such a hydrate cage. Methane hydrates look like dirty ice and are flammable. They store large quantities of methane within a very small space: in the transition to the gas phase their volume increases by a factor of 170.

They are only stable under specific pressure and temperature conditions. The higher the ambient temperature, the higher the pressure has to be to prevent the methane hydrate from dissolving. The optimal conditions are typically found on the sea floor at water depths of at least around 500m, and in the Arctic starting already at lower water depth. Here, methane hydrate can form in the sediments provided sufficient quantities of methane are produced by the decomposition of organic carbon deposits. The carbon for the methane hydrate is ultimately derived from the biological production of the ocean, as dead biomass is deposited in the sediments and bacterially decomposed on the sea floor ('biogenic' methane). The formation of methane hydrates takes a very long time, so they cannot be considered as a renewable energy source: the present deposits have probably been formed over a period of several million years (Davie and Buffett, 2001). An additional, smaller hydrate source is found in leaking natural gas formations ('thermogenic' methane) from which methane bubbles rise through the sediments and under favourable conditions (i.e., in the hydrate stability zone in the cooler upper sediment layers) form hydrates with water. An example can be found in the Gulf of Mexico.

As the temperature in the sediment quickly rises with increasing depth due to the Earth's heat (at around 30°C per kilometre) but the pressure – also increasing – cannot compensate for the temperature increase, methane hydrates in marine sediments are only stable down to a certain depth in the sediments. Below the limit of this stability zone, typically several hundreds of metres thick, methane can again occur as a gas in the sediments.

Gaining evidence for the presence of methane hydrates, directly by drilling or indirectly with seismic techniques, is difficult. While the drilling that has been carried out up to now does not allow broad-area mapping of its occurrences, seismic methods can only identify the lower limit of the stability zone. On this basis, no conclusive statement can be made about the quantity of methane in sediments, because the volume of the hydrate remains unknown. These measurement problems mean that models must be used to estimate the global reservoir of methane hydrates. In the 1990s it was assumed that carbon quantities on the order of 10,000Gt C were stored in the form of methane hydrates (that equates to around twice the entire fossil energy resource: Rogner, 1997), but current estimates suggest a much lower value (500–3000Gt C: Buffett and Archer, 2004; Milkov, 2004). Klauda and Sandler (2005) presume that the largest hydrate occurrences are in the deep-sea basins rather than on the continental margins. They therefore also report a much higher estimation of 78,000Gt C, but this is based on unrealistic assumptions of the sedimentation rates of organic carbon in the deep sea. WBGU considers the estimate of 500–3000Gt C to be reliable. A comparable amount of methane is present again below the hydrates in the gaseous state (Archer, 2005). Here are some figures for comparison: at the end of 2004 the proven coal and natural-gas reserves amounted to 900Gt C and, respectively, 92Gt C (BP, 2005); the atmosphere contains 805Gt C of carbon dioxide, of which 210Gt C stem from anthropogenic emissions.

6.2
Methane release due to human intervention

The stability of methane hydrate deposits can be affected on the one side by global warming; on the other side, however, there are risks of an unintentional release of methane associated with the production of oil, natural gas, and possibly in the future of methane hydrate itself.

6.2.1
Response to pressure and temperature changes

Changes of pressure and temperature in the hydrate layer lead to changes in the stability zone, i.e., the depth interval in the sediment where methane hydrate is stable. Higher pressure stabilizes the methane hydrate, while warming reduces the thickness of the stability zone. Due to warming, methane hydrate will normally thaw from below (Fig. 6.2-1). Figure 6.2-1a uses a phase diagram to illustrate the stability zone in the ocean and in the underlying sediments. The red curve indicates temperature: in the ocean it decreases with increasing depth, and in the sediments it increases again due to the Earth's internal heat. The black curve shows the temperature below which methane hydrate is stable, as determined by the ambient pressure conditions. This means that methane hydrate can only exist in sediments within the depth interval where the actual temperature (red) is below the stability temperature (black). So the point where the two curves cross in the sediment represents the lower boundary of the stability zone.

If the ocean warms by 3°C, then the red temperature curve shifts by the corresponding amount to the right (Fig. 6.2-1b). The new point of intersection of the temperature and stability-temperature curves defines the new lower boundary of the stability zone, which has shifted upward. The amount of gaseous methane below the hydrate layer has also increased by the corresponding amount.

Figure 6.2-1c assumes that the ocean rapidly warmed by 8°C, so that the temperature curve is completely to the right of the stability-temperature curve, and therefore hydrate is no longer stable at any depth. Whereas with a 3°C ocean-temperature increase the total sediment depth down to the base of the stability zone first has to warm before the methane hydrate begins to dissolve at all, in the example with an 8°C increase the destabilization of the hydrate would begin at the sea floor, i.e., before the total sediment layer has warmed. In the course of the temperature rise the methane hydrates would dissolve completely from above.

6.2.2
Effects of climate change on methane hydrates

Global warming leads to temperature changes in the ocean as well as to changes in sea level, and therefore to pressure changes on the sea floor. Figure 6.2-2 provides an overview of the effects this can have on methane hydrate deposits.

In pessimistic IPCC scenarios the average sea-surface temperature increases by the end of this century to 5°C above the pre-industrial level. Regionally, for example in the Arctic, this value could be as great as 10°C. The high latitudes are of global importance

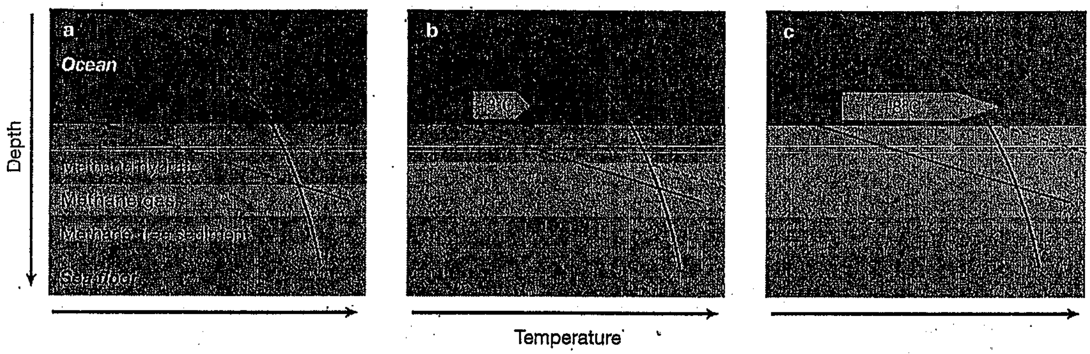

Figure 6.2-1
Changes in the methane hydrate layer due to warming. The black curve describes the stability temperature dependent on depth. The red curve shows the actual temperature; red dashed lines show schematic temperature profiles after a warming of 3°C (stability zone of hydrates becomes thinner from the bottom) and 8°C (stability zone completely disappears), respectively.
Source: WBGU

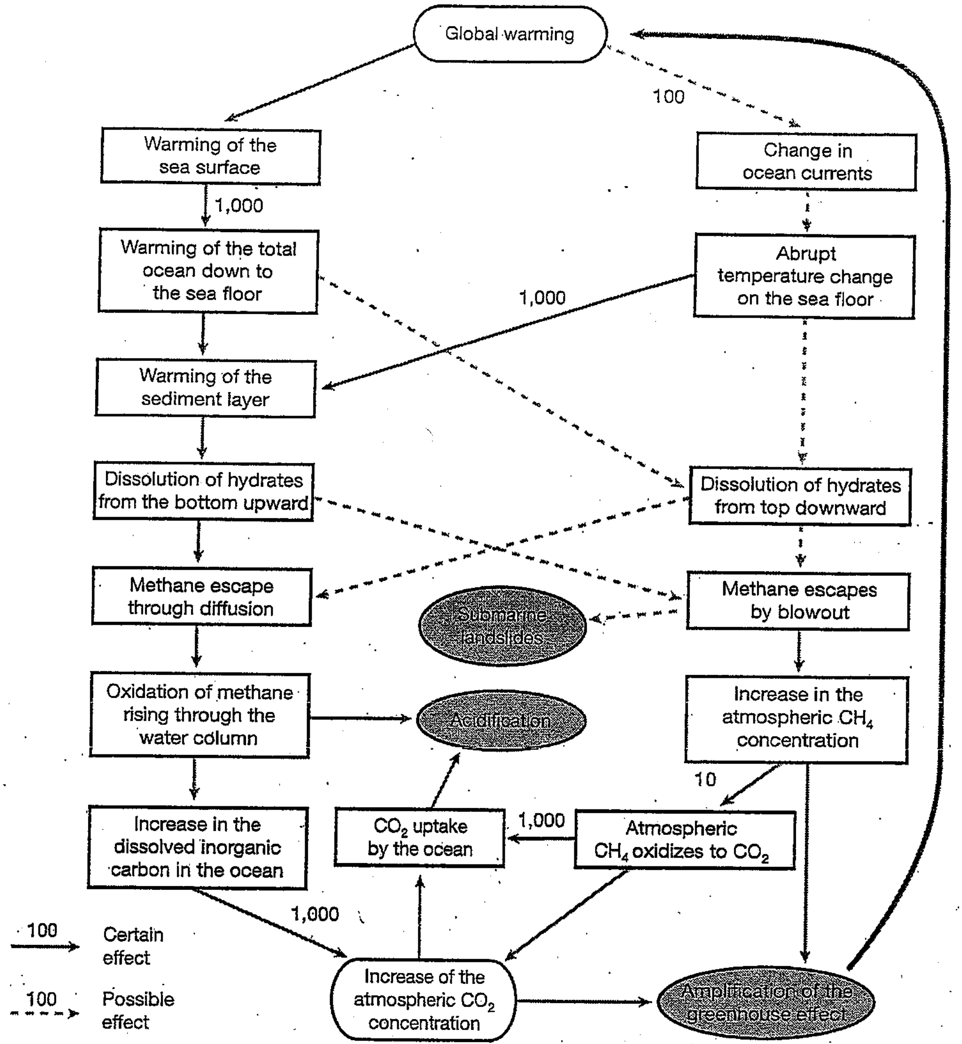

Figure 6.2-2
Causes and effects of methane hydrate destabilization. The mechanisms are discussed in the text. Numbers above the arrows indicate the respective time scale of the process in years (no number given = immediate effect).
Source: WBGU

because it is here that the cold-water masses originate that fill the deep sea worldwide. Because of the stable temperature layering and the slow mixing of the ocean, the warming, as a rule, will only penetrate to the sea floor very slowly, over the course of several centuries. Similar time frames are necessary in order to warm the sediment layers down to several hundreds of metres. Only under very special local conditions – with hydrate occurrences at shallow sea depths and in well-mixed marine regions – could hydrates become unstable in the short term (within this century) due to warming. An escape of hydrates on a large scale (that is, enough to have a noticeable impact on climate) is not an acute but a long-term danger. Over a period of centuries a reinforcing feedback loop with global warming could occur, which over time could become increasingly difficult to check.

Relatively rapid and intense local temperature changes could occur when marine currents are altered, a danger that is commonly discussed with respect to the northern Atlantic (Section 2.1.3). The development of temperature at the sea floor seems to depend strongly on how the circulation changes (Mignot et al., submitted) and is therefore difficult to predict. Simulations suggest, however, that after a breakdown of the deep-water formation in the Norwegian Sea the bottom temperature in some regions of the North Atlantic could quickly rise by over 7°C. Changes at this order of magnitude could then also destabilize hydrate reservoirs.

An additional factor is the rising sea level, which, by increasing the pressure on the sea floor, could in principle stabilize the hydrate deposits. Here only the volume of water released by melting land ice masses is relevant because thermal expansion would not increase the pressure. The effect, however, is very small: in water depths of 400m a pressure increase of 0.04MPa (corresponding to a sea-level increase of 4m) results in an increase of the destabilization temperature of less than 0.1°C. The long-term sea-level rise can therefore not compensate for the effect of the long-term warming on hydrate stability. The same is true for short-term relative changes in sea level resulting from circulation changes (Levermann et al., 2005), the results of which cannot compensate for the abrupt temperature changes they also cause.

If the methane hydrate stability zone is reduced, then methane gas forms below the hydrate layer. This gas can either penetrate through the hydrate layer and escape out of the sea floor through small channels or permeable sediment layers, or it can blast through the hydrate layer if sufficient quantities of gas collect below a continuously thinning layer. In such a blowout large amounts of methane gas are abruptly released. Because the shattered blocks of methane hydrate released are less dense than water, they rise to the surface and dissolve there.

The quantity of methane gas that would escape from the hydrate layers by one of these mechanisms in the future can presently only be roughly estimated, because the stability and permeability of sediment layers are dependent on highly variable local conditions.

6.2.3
Mining of methane hydrates

Methane hydrates represent a source of fossil fuel and can therefore be of interest for commercial exploitation. The economic feasibility of their recovery depends greatly on the available methane concentration in the hydrate. The few examples of practical experience obtained in exploiting methane from hydrate deposits are from the Messoyakha gas field (Siberia) and the Mallik (Alaska) research project. The Russian Messoyakha gas field is an occurrence below permafrost that was discovered as early as the 1960s. Not only were the mining costs here extremely high, but it has also come into question whether the methane recovered here in the 1970s really was, as claimed, retrieved from hydrate deposits (EIA, 1998; Schindler and Zittel, 2000a). Mallik 2002 is a drilling project on the Arctic coast of Canada, where the methane concentration of the hydrate is rated similar to that found in Japanese coastal waters. The project included gas hydrate production tests and is part of an international research consortium in which states (incl. USA, Japan, India and Germany) and companies are participating.

In principle, the mining of methane hydrates on the high seas would be possible. It is considered technically feasible to drill into the sea floor in water depths up to four kilometres. The technical and especially the economic practicability of potential recovery mining methods is a subject of research in which Japan and the USA are playing particularly important roles. The Japanese programme for methane hydrate mining (National Methane Hydrate Exploitation Program, MH21), among other aspects of methane hydrate research, is expressly pursuing the ambitious goal of beginning production tests in 2007 and is aiming to have the technology for commercial large-scale production by 2012 (MH21, 2005). Financing for the US American methane hydrate research programme (Methane Hydrate Research and Development Act of 2000) was extended through 2010 by the Energy Policy Act of 2005. Commercial mining of methane hydrate in US American waters is deemed possible by 2015 and large-scale mining by 2020 (DOE-NETL, 2005; Ray, 2005).

These expectations are compatible with the estimation that methane hydrate mining will be economically feasible in some regions within the next 5–10 years, while it would take 30–50 years before worldwide massive mining is possible (Methane Hydrate Advisory Committee, 2002; Collett, 2005). Methane hydrate exploitation in permafrost areas on land could reach industrial proportions more quickly than the exploitation from the sea (Johnson, 2004). That is because progress in the identification and evaluation of occurrences feasible for exploitation on land is ahead of that for occurrences beneath the sea. In addition, there has already been extensive experience gained in recovery and production technology on land (Mallik research drilling, Messoyakha gas field). The more favourable recovery conditions compared to the sea also make it likely that mining will first be carried out on land. In combination with economies of scale and learning effects, there could therefore be cost advantages. Overall, this means that there is an initial advantage for methane hydrate exploitation on land over that at sea. The predicted technological feasibility as well as the economic and energy-strategic potential of this kind of energy production, however, is critically questioned and considered to be clearly overestimated (Schindler and Zittel, 2000b).

Targeted research into the production of marine methane hydrate has been limited so far to a few pilot studies. They probably will not go beyond the stage of feasibility studies during this decade.

6.3
Possible results of methane release

The consequences of a release of methane gas from hydrates depend on the mechanism – 'diffusion' or 'blowout' – as well as the time scale of the release.

When methane gas diffuses through the hydrate layer and slowly escapes in small bubbles from the sea floor, a large portion of it will probably be dissolved in the water column as it rises. A new study shows, however, that methane bubbles could also possibly rise through the upper water layers and escape into the atmosphere (Sauter et al., 2006). Dissolved methane in the ocean has a lifetime of about 50 years before it oxidizes to H_2O and CO_2. A large portion of the released methane would therefore be released to the atmosphere before it oxidizes. Firstly, the remaining oxidized portion would increase the concentration of dissolved inorganic carbon in the ocean, which contributes to further acidification (Section 4.1). Secondly, an equivalent decrease in oxygen concentration would occur. For comparison: in order to exhaust all of the $2 \cdot 10^{17}$mol of oxygen contained in the ocean, it would have to react with 1000Gt of methane (Archer, 2005). Thirdly, in the long term, a new carbon-equilibrium state would be established between the atmosphere and ocean, over the course of about 1000 years, and about one-fifth of the carbon incorporated in the ocean released into the atmosphere. The concentration of CO_2 in the atmosphere would thereby increase, strengthening the greenhouse effect. Hence, over the long term, this effect would come about in any case: the result is the same whether methane escapes directly into the atmosphere and oxidizes there to CO_2, four-fifths of which is gradually taken up by the ocean, or if it is first released in the ocean, oxidized there, and one-fifth is given off to the atmosphere.

When large quantities of methane are suddenly released, most of it will reach the water surface and abruptly increase the methane concentration in the atmosphere. Because methane is a considerably more effective greenhouse gas than CO_2 (around 25 times stronger per molecule) due to its much lower concentration and therefore less saturated absorption bands, the effect of comparatively low amounts of methane is significant. But atmospheric methane quickly oxidizes (with an average residence time of eight years), to CO_2, which accumulates in the atmosphere due to its long life expectancy, so that in the long term the escaped methane after its oxidation to CO_2 has an even greater impact on climate than before.

Figure 6.3-1 shows how anthropogenic CO_2 emissions can lead to methane emissions from hydrate deposits over the coming millennia. A total emission of 1000Gt CO_2 is assumed. Figure 6.3-1a reveals how strongly this could cause the atmospheric methane concentration to increase, whereby the uncertainty of the time scale of the release is taken into account with three different assumptions.

Figure 6.3-1b illustrates the climatic consequences of the methane emissions for the 1000Gt of CO_2 scenario for the case of a methane release within 1000

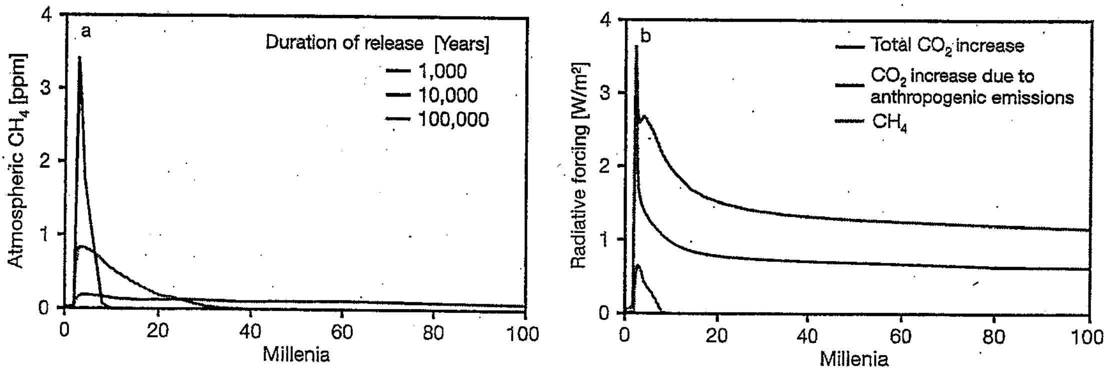

Figure 6.3-1
(a) Atmospheric methane concentration for a scenario with a total quantity of 1000Gt of anthropogenic CO_2 emissions. The curves describe the resulting methane release over different time frames (1, 10, and 100 thousand years). (b) Climate-impacting radiative forcing for the case of the shortest release period of 1000 years. This is a combination of the forcing due to methane itself (green; it gradually oxidizes to CO_2 and thus disappears), that due to anthropospheric CO_2 emissions (black), and CO_2 from the oxidation of methane. The last two together yield the radiative forcing due to the total increase of CO_2 (red).
Source: Archer und Buffet, 2005

years. The results are caused both directly through the increase in atmospheric methane concentration (green), as well as on a longer time scale by the increase of the CO_2 concentration (red). Although the direct methane effect is lower than that of the original anthropogenic CO_2 emission, the subsequent increase in CO_2 concentration through oxidation of the methane leads, over the long term, to a near doubling of the greenhouse effect.

Methane eruptions can also present other dangers. They can destabilize continental slopes and trigger large submarine landslides, which can then possibly result in the break-up of additional hydrates. Evidence of such slides can be found on the sea floor. For example, in the Storegga landslide off the coast of Norway around 8000 years ago, an average of 250m of the continental slope with a width of 100km were transported downslope (Archer, 2005). This event triggered a tsunami that was at least 25m high off the Shetland Islands and at least 5m high along the British coast (Smith et al., 2004). The amount of methane released by this landslide is estimated at 0.8Gt C (Archer, 2005). When this amount of methane directly enters the atmosphere, it can alter the radiative forcing by as much as 0.2W per m^2 (for comparison, today's radiative forcing due to anthropogenic greenhouse gases is 2.7W per m^2). This example illustrates that an abrupt release of methane, even in the case of a large catastrophic slide of the continental slope, would only have a relatively minor impact on climate.

6.4
Recommendations for action: Preventing methane release

Through the warming of seawater, anthropogenic climate change can lead to a destabilization of methane hydrate deposits on the sea floor. According to the present state of knowledge, however, the danger of a sudden release of large, climate-influencing quantities within this century is very small. Of much greater importance is the probability of a continuous methane release over many centuries to millennia due to the slow intrusion of global warming into the deeper ocean layers and sediments. The consequences of human actions persist in this respect not just over centuries, but could influence the Earth's climate over tens of thousands of years.

Limiting global warming follows once more here as a recommendation for action, because methane release from hydrates could further amplify climate change in the long term. This feedback effect presents the danger that humankind could lose control of the greenhouse-gas concentration in the atmosphere, as the outgassing of methane from the sea floor cannot be controlled or limited.

There is already a need today for institutional action with regard to marine methane hydrate deposits. This is with respect to, for one, the targeted mining of marine methane hydrates, and for another to the unintentional release of methane that could occur during sea-floor mining.

Theoretically, efforts to recover methane from hydrates could unintentionally trigger their release into the environment, in the worst case as a sudden eruption. The risks of this have not yet been sufficiently investigated (Archer, 2005). A leak of methane into the environment during mining would unnecessarily amplify global warming. In the worst case even a slope slide could be caused that could trigger a tsunami.

The risks associated with mining are very variable depending on the geological conditions. The risks of methane mining therefore have to be carefully reviewed for each individual case. An environmental impact assessment along with monitoring according to universal standards is necessary for every case. The International Seabed Authority, an institution of the international United Nations Convention on the Law of the Sea (UNCLOS), is responsible for methane hydrate deposits as well as for other resources on the sea floor outside the exclusive economic zone. The Authority grants mining licenses and monitors mining operations. Its regulations adopted in 2000 for the exploration of deep-sea mineral resources contain various environmental aspects. This is a starting point for agreement on concrete standards for mining marine methane hydrate on the high seas. In the opinion of WBGU it is furthermore necessary to improve and expand the monitoring system. It is, however, important to note here that so far 'only' about 150 countries have ratified UNCLOS, and of those only about 120 countries have ratified the rules governing seabed resources (those who have not signed include, for example, Iran and the USA). A framework within which more countries can be persuaded to accede to the agreements for maintaining universal standards in hydrate mining still needs to be worked out. Also needed are agreements binding under international law for the mining of methane hydrates in marine regions that lie within the territorial sovereign rights of coastal nations (Box 2.6-1). This is necessary considering that both the above-mentioned Japanese pilot project and American plans target future commercial methane production from hydrate deposits in national coastal waters.

The danger of methane hydrate release also exists in principle in other sea-floor mining activities. If methane were to be destabilized and unintentionally released in the mining of resources, these emissions would hardly be measurable, and therefore not accounted for in the emissions inventory of a country, or only insufficiently so. The applicable IPCC guidelines of 1996 for national emissions inventories do not include methane that is unintentionally emitted at sea. WBGU therefore recommends for the upcoming reworking of the guidelines in 2006 that this omission be corrected despite the difficulties in measurement. But at the very least a reporting obligation should be introduced for such releases of methane.

6.5
Research recommendations

Because estimates of the risks of methane release are still hampered by large uncertainties and gaps in knowledge, there is a significant need for research. To begin with, the methane occurrences need to be more extensively mapped and quantities estimated. The primary focus here should not be on the potential workable deposits, but on occurrences that could possibly become destabilized by climate change, and on the danger of slope slides. Furthermore, modelling studies should be employed to investigate which regions of the ocean show the greatest risk for hydrates to become destabilized through global warming.

While research on the long-term stability of marine methane hydrates and climate protection implications should continue to be strengthened, WBGU sees no need for government subsidies for applied research for the mining of marine methane hydrates. Public funding of such projects does not seem purposeful because mining poses considerable risks and methane hydrates do not represent a sustainable energy source.

There would, however, be a need for targeted natural science research if appropriate standards for the mining of marine methane hydrates need to be defined. Natural science investigations should be supplemented by social science and legal studies of the prospects for worldwide implementation of such standards.

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Core messages

Climate mitigation for marine conservation

The future of the marine environment will depend crucially upon whether human-induced disruption of the climate system can be limited to a tolerable level. It follows in WBGU's view that global anthropogenic greenhouse gas emissions will need to be approximately halved by 2050 from 1990. Because of the geophysical time lags, the climate protection policies adopted in the next few decades will determine the state of the oceans for millennia to come. Adaptation measures can only succeed if the present acceleration of sea-level rise and the increasing acidification of the oceans are halted.

WBGU has already formulated a 'climate guard rail' in earlier reports as a contribution to making a sustainable development pathway operable: to prevent dangerous climatic changes, the mean global rise in near-surface air temperature must be limited to a maximum of 2°C relative to the pre-industrial value and the rate of temperature change must be limited to a maximum of 0.2°C per decade. The present report shows that marine conservation is a further reason why it is essential to obey this guard rail.

Bolstering the resilience of marine ecosystems

Fish stocks and coral reefs will only retain their productivity and diversity if sustainable marine resource management is ensured worldwide. The mounting direct and indirect pressures generated by anthropogenic greenhouse gas emissions are making adoption of an 'ecosystem approach' for the conservation and use of the marine environment ever more important. To that end, the establishment of marine protected areas, an approach already agreed by the international community, must be pushed forward energetically, and the regulatory gap for the high seas must be closed by adopting a corresponding agreement within the framework of the United Nations Convention on the Law of the Sea (UNCLOS).

To conserve marine ecosystems and strengthen their resilience, WBGU proposes the following guard rail: at least 20–30 per cent of the area of marine ecosystems should be designated for inclusion in an ecologically representative and effectively managed system of protected areas.

Limiting sea-level rise and reorienting coastal zone management strategies

The strategies hitherto adopted to protect and utilize coastal areas are no longer adequate to cope with climate-driven sea-level rise and the mounting destructive force of hurricanes. Novel combinations of measures (portfolio strategies) are called for, whereby the options of protection, managed retreat and accommodation need to be weighed against each other. In particular, coastal protection and nature conservation concerns must be better linked, and the people affected by adaptation or resettlement measures must be involved in the planning and implementation of such measures. To this end, WBGU recommends creating integrative institutions that combine all key competencies.

To prevent severe damage and losses from occurring, and to avoid overstretching the adaptive capacity of coastal ecosystems and infrastructure, WBGU proposes the following guard rail for sea-level rise: absolute sea-level rise should not exceed 1 m in the long term, and the rate of rise should remain below 5 cm per decade at all times.

Adopting innovative instruments of international law for refugees from sea-level rise

At present no nation has any obligation under international law to receive migrants whose homeland has been lost due to climate-induced flooding. In the long term, however, the international community will not be able to ignore the issue of 'sea-level refugees' and will therefore need to develop appropriate instruments for the secure reception of affected people in suitable areas, ideally in areas that correspond to their preferences. It would be expedient to develop a fair burden-sharing system, under which states make a binding commitment to assume responsibility for these people in line with their greenhouse gas emissions. To inform the policymaking process, studies in the fields of law and social sciences should be undertaken.

Halting ocean acidification in time

The oceans have absorbed about one-third of all anthropogenic CO_2 emissions to date, which has already caused a significant acidification (decrease in pH) of seawater. These emissions thus influence the marine environment directly – in addition to the route via climate change. Unabated continuation of this trend will lead to a level of ocean acidification that is without precedent in the past several million years and will be irreversible for millennia. The effects upon marine ecosystems cannot be forecast exactly but profound changes to the food web are conceivable, as calcification of marine organisms may be impeded or in some cases even prevented. WBGU recommends fostering internationally coordinated research and monitoring programmes on this issue. Furthermore, the negotiations on future commitments under the United Nations Framework Convention on Climate Change need to take into account the special role of CO_2 compared to other greenhouse gases. Besides stabilizing the overall package of greenhouse gases, it will be important to also seek explicitly to stabilize CO_2 concentrations.

To protect the oceans against acidification, WBGU proposes the following guard rail: in order to prevent disruption to calcification of marine organisms and the resultant risk of fundamentally altering marine food webs, the pH of ocean surface waters should not drop more than 0.2 units below the pre-industrial level in any larger ocean region (i.e. also in the global mean).

References

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ACIA (Arctic Climate Impact Assessment) (2005) *Arctic Climate Impact Assessment*. Cambridge University Press, Cambridge, New York.

Adger, W N, Hughes, T P, Folke, C, Carpenter, S R and Rockström, J (2005) 'Social-ecological resilience to coastal disasters'. *Science* **309**: pp1036–9.

Agardy, T, Bridgewater, P, Crosby, M P, Day, J, Dayton, P K, Kenchington, R, Laffoley, D, McConney, P, Murray, P A, Parks, J E and Peau, L (2003) 'Dangerous targets? Unresolved issues and ideological clashes around marine protected areas'. *Aquatic Conservation Marine and Freshwater Ecosystems* **13**(4): pp353–67.

Ahmed, S, Mbasis, J, Moko, D and Ngonzi, A (2005) 'Health is wealth: how low-income people finance health care'. *Journal of International Development* **17**: pp383–96.

Alheit, J, Möllmann, C, Dutz, J, Kornilovs, G, Loewe, P, Mohrholz, V and Wasmund, N (2005) 'Synchronous ecological regime shifts in the central Baltic and the North Sea in the late 1980s'. *ICES Journal of Marine Science* **62**: pp1205–15.

Archer, D (2005) 'Destabilization of Methane Hydrates: A Risk Analysis'. Expertise for WBGU Special Report 'The Future Oceans – Warming Up, Rising High, Turning Sour'. WBGU website, http://www.wbgu.de/wbgu_sn2005_ex01.pdf.

Archer, D (2006) *Global Warming – Understanding the Forecast*. Blackwell Publishers, Oxford, UK.

Archer, D and Buffett, B (2005) 'Time-dependent response of the global ocean clathrate reservoir to climatic and anthropogenic forcing'. *Geochemistry Geophysics Geosystems* **6**(3): pp13.

Athreye, V and Roth, J (2005) *CGAP Working Group on Microinsurance. Good and Bad Practices. Case Study No. 14.* New Delhi: Tata-AIG Life Insurance Company Ltd.

Atkinson, A, Siegel, V, Pakhomov, E A and Rothery, P (2004) 'Long-term decline in krill stock and increase in salps within the Southern Ocean'. *Nature* **432**: pp100–3.

Attrill, M J and Power, M (2002) 'Climatic influence on a marine fish assemblage'. *Nature* **417**: pp275–8.

Baker, A C, Craig, J, Starger, T, McClanahan, R and Glynn, P W (2004) 'Corals' adaptive response to climate change'. *Nature* **430**: pp741.

Balmford, A, Gravestock, P, Hockley, N, McClean, C J and Roberts, C M (2004) 'The worldwide costs of marine protected areas'. *PNAS* **10**(1073): pp9694–7.

Barber, R (2001) 'Upwelling ecosystems'. In Steele, J H, Thorpe, S A and Turekian, K K (eds) *Encyclopedia of Ocean Sciences*. Academic Press, London, pp3128–35.

Barlow, P M (2003) *Ground Water in Freshwater-Saltwater Environments of the Atlantic Cost.* Circular 1262. US Geological Survey, Reston, Virginia.

Barnett, J and Adger, W N (2003) 'Climate dangers and atoll countries'. *Climatic Change* **61**: pp321–37.

Barrett, P (2003) 'Palaeoclimatology – cooling a continent'. *Nature* **421**: pp221–3.

Barry, J P, Buck, K R, Lovera, C F, Kuhnz, L, Whaling, P J, Peltzer, E T, Walz, P and Brewer, P G (2004) 'Effects of direct ocean CO_2 injection on deep-sea meiofauna'. *Journal of Oceanography* **60**: pp759–66.

Baumgartner, T R, Soutar, A and Ferreira-Bartrina, V (1992) 'Reconstruction of the history of pacific sardine and northern anchovy populations over the past two millennia from sediments of the Santa Barbara Basin, California'. *California Cooperative Oceanic Fisheries Investigations (ColCofi)* **33**: pp24–40.

BBK (Bundesamt für Bevölkerungsschutz und Katastrophenhilfe) (2006) 'Schutz kritischer Infrastrukturen'. Bundesamt für Bevölkerungsschutz und Katastrophenhilfe website, http://www.bbk.bund.de (viewed 15. February 2006).

Beare, D J, Burns, F, Greig, A, Jones, E G, Peach, K, Kienzle, M, McKenzie, E and Reid, D G (2004) 'Long-term increases in prevalence of North Sea fishes having southern biogeographic affinities'. *Marine Ecology Progress Series* **284**: pp269–78.

Beaugrand, G, Reid, P C, Ibanez, F, Lindley, J A and Edwards, M (2002) 'Reorganization of North Atlantic marine copepod biodiversity and climate'. *Science* **296**: pp1692–5.

Beaugrand, G and Reid, P C (2003) 'Long-term changes in phytoplankton, zooplankton and salmon related to climate'. *Global Change Biology* **9**: pp801–17.

Beaugrand, G, Brander, K M, Lindley, J A, Souissi, S and Reid, P C (2003) 'Plankton effect on cod recruitment in the North Sea'. *Nature* **426**: pp661–4.

Beaugrand, G (2004) 'The North Sea regime shift: evidence, causes, mechanisms and consequences'. *Progress in Oceanography* **60**: pp245–62.

Bellona Foundation (2005) *CO_2 for EOR on the Norwegian Shelf – the Environment and Economic Growth Hand in Hand.* Bellona Foundation, Oslo.

Bellwood, D R, Hughes, T P, Folke, C and Nystrom, M (2004) 'Confronting the coral reef crisis'. *Nature* **429**: pp827–33.

Bertrand, A, Segura, M, Gutiérrez, M and Vásquez, L (2004) 'From small-scale habitat loopholes to decadal cycles: a habitat-based hypothesis explaining fluctuation in pelagic fish populations off Peru'. *Fish and Fisheries*: pp296–316.

Beyerlin, U (2000) *Umweltvölkerrecht*. Beck, Munich.

Bijlsma, L, Ehler, C N, Klein, R J T, Kulshrestha, S M, McLean, R F, Mimura, N, Nicholls, R J, Nurse, L A, Perez Nieto, H, Stakhiv, E Z, Turner, R K and Warrick, R A (1996): 'Coastal zones and small islands'. In Watson, R T, Zinyowera, M C and Moss, R H (eds) *Impacts, Adaptations and Mitigation of Climate Change: Scientific-Technical Analyses.* Cambridge University Press, Cambridge, New York: pp289–324.

Blindheim, J, Toresen, R and Loeng, H (2001) 'Fremtidige klimatiske endringer og betydningen for fiskeressursene. Havets Miljø 2001'. *Fisken og Havet* 2: pp73–8.

Bloomfield, J, Smith, M and Thompson, N (1999) *Hot Nights in the City.* Environmental Fund, Washington, DC.

Bode, S, Isensee, J, Krause, K and Michaelowa, A (2002) 'Climate policy: analysis of ecological, technical and economic implications for international maritime transport'. *International Journal of Maritime Economics* 4: pp164ff.

Bode, S and Jung, M (2005) *Carbon Dioxide Capture and Storage (CCS) – Liability for Non-Permanence Under the UNFCCC.* Hamburgisches Welt-Wirtschafts-Archiv (HWWA), Hamburg.

Boersma, D, Ogden, J, Branch, G, Bustamante, R, Campagna, C, Harris, G and Pikitch, E K (2004): 'Lines on the water: ocean-use planning in large marine ecosystems'. In Glover, L K and Earle, S A (eds) *Defying Ocean's End. An Agenda for Action.* Island Press, Washington, DC: pp123–38.

Bohnsack, J A (1998) 'Application of marine reserves to reef fisheries management'. *Australian Journal of Ecology* 23: pp298–304.

Bohnsack, J A, Causey, B, Crosby, M P, Griffis, R B, Hixon, M A, Hourigan, T F, Koltes, K H, Maragos, J E, Simons, A and Tilmant, J T (2002) *A Rationale for Minimum 20–30% No-Take Protection. Paper Presented to the 9th International Coral Reef Symposium. Bali, Indonesia 23–27 October 2000.* Conference Secretariat, Bali.

Bopp, L, Monfray, P, Aumont, O, Dufresne, J-L, Le Treut, H, Madec, G, Terray, L and Orr, J C (2001) 'Potential impact of climate change on marine export production'. *Global Biogeochemical Cycles* 15(1): pp81–99.

Boyd, E, Clarke, J, Gray, G, Hodge, G B, Hurlston, L-A, Nicholson-Cole, S A, Tompkins, E L, Trotz, N and Varlack, L (2005) *Surviving Climate Change in Small Islands: A Guidebook.* Tyndall Centre for Climate Change Research, Norwich.

BP (British Petroleum) (2005) *Putting Energy in the Spotlight. BP Statistical Review of World Energy.* BP, London.

Brander, K M (2005) 'Assessment of Possible Impacts of Climate Change on Fisheries'. Expertise for WBGU Special Report 'The Future Oceans – Warming Up, Rising High, Turning Sour'. WBGU website, http://www.wbgu.de/wbgu_sg2005_ex02.pdf.

Broecker, W (1987) 'Unpleasant surprises in the greenhouse?' *Nature* 328: pp123.

Brooks, N, Nicholls, R and Hall, J M (2006) 'Sea Level Rise: Coastal Impacts and Responses'. Expertise for WBGU Special Report 'The Future Oceans – Warming Up, Rising High, Turning Sour'. WBGU website, http://www.wbgu.de/wbgu_sn2005_ex03.pdf.

Brown, W and Churchill, C F (1999) *Providing Insurance to Low-Income Households. Part 1: A Primer on Insurance Principles and Products.* Microenterprises Best Practices, Bethseda, MD.

Brown, W and Churchill, C F (2000) *Providing Insurance to Low-Income Households. Part 2: Initial Lessons from Micro-Insurance Experiments for the Poor.* Microenterprises Best Practices, Bethseda, MD.

Bruneau, M, Chang, S, Eguchi, R, Lee, G, O'Rourke, T, Reinhorn, A, Shinozuka, M, Tierney, K, Wallace, W and von Winterfelt, D (2003) 'A framework to quantitatively assess and enhance the seismic resilience of communities'. *EERI Spectra Journal* 19: pp733–52.

Bruun, P (1962) 'Sea level rise as a cause of shore erosion'. *Journal of Waterways and Harbours Division ASCE* (88): pp117–30.

Bryden, H L, Longworth, H R and Cunningham, S A (2005) 'Slowing of the Atlantic meridional overturning circulation at 25°N'. *Nature* 438: pp655–65.

Buddemeier, R W, Kleypas, J A and Aronson, R B (2004) *Coral Reefs and Global Climate Change: Potential Contributions of Climate Change to Stresses on Coral Reef Ecosystems.* Pew Center on Global Climate Change, Arlington.

Buffett, B and Archer, D (2004) 'Global inventory of methane clathrate: sensitivity to changes in the deep ocean'. *Earth and Planetary Science Letters* 227(3-4): pp185–99.

Bundesregierung (2006) *Integriertes Küstenzonenmanagement in Deutschland. Nationale Strategie für ein integriertes Küstenzonenmanagement.* Bundesregierung, Berlin.

Burgess, K and Townend, I (2004) *The impact of climate change upon coastal defence structures. Proceedings of the 39th Defra Flood and Coastal Management Conference.* Department for Environment, Food and Rural Affairs (Defra), London.

Burns, W C (1997) 'Global warming – the United Nations Framework Convention on Climate Change and the future of small island states'. *Dickinson Journal of Environmental Law and Policy* 6: pp147ff.

Burton, I and Dore, M H I (2000) 'The Costs of Adaptation to Climate Change in Canada: A Stratified Estimate by Sectors and Regions. First Deliverable: A Review of the Literature on the Costs of Adaptation to Climate Change'. Natural Resources Canada website, http://adaptation.rncan.gc.ca/app/filerepository/E74BFBF66A704A778C4D1AD4A8C4BFC2.pdf (viewed 19. January, 2006).

Burton, I and Lim, B (2001) *Adaptation Policy Framework. Draft Report.* United Nations Development Programme (UNDP), New York.

Burton, I, Huq, S, Lim, B, Pilifosova, O and Schipper, E L (2002) 'From impacts assessment to adaptation priorities; the shaping of adaptation policy'. *Climate Policy* 2: pp145–59.

Caldeira, K, Jain, A K and Hoffert, M I (2003) 'Climate sensitivity uncertainty and the need for energy without CO_2 emission'. *Science* 299: pp2052–4.

Caldeira, K, Akai, M, Brewer, P, Chen, B, Haugan, P, Iwama, T, Johnston, P, Kheshgi, H S, Q, L, Ohsumi, T, Pörtner, H O, Sabine, C, Shirayama, Y. and Thomson, J (2005): 'Chapter 6: Ocean Storage'. In Intergovernmental Panel on Climate Change (IPCC) (ed) *IPCC Special Report on Carbon Dioxide Capture and Storage.* Cambridge Unviversity Press, Cambridge, New York: pp4–41.

Caldeira, K and Wickett, M E (2005) 'Ocean model predicitions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean'. *Journal of Geophysical Research – Oceans* 110: ppC09S4, doi: 10.1029/2004JC002671.

Carlton, J (2005) 'Is Global Warming Killing Polar Bears?' The Wall Street Journal via AP website, http://reference.aol.com/article?id=20051216151609990001 (viewed 20. March 2006).

Cazenave, A and Nerem, R (2004) 'Present-day sea level change: Observations and causes'. *Reviews of Geophysics* 42(3): pp139–50.

CBD (Convention on Biological Diversity) (2003) *Integration of Outcome-Oriented Targets Into the Programmes of Work of the Convention, Taking into Account the 2010 Biodiversity Target, the Global Strategy for Plant Conservation, and Relevant Targets set by the World Summit on Sustainable Development.* UN Document UNEP/CBD/COP/7/20/Add.5. CBD Secretariat, Montreal.

CBD (Convention on Biological Diversity) (2004a) *Protected Areas (Articles 8 (a) to (e)). Decision VII/28.* UN Document UNEP/CBD/COP/7/21. CBD Secretariat, Montreal.

CBD (Convention on Biological Diversity) (2004b) *Marine and Coastal Biological Diversity. Decision VII/5.* UN Document UNEP/CBD/COP/7/21. CBD Secretariat, Montreal.

CBD (Convention on Biological Diversity) (2005a) *Ad Hoc Open-ended Working Group on Protected Areas: The International Legal Regime of the High Seas and Seabed Beyond the Limits of National Jurisdiction and Options for Cooperation for the Establishment of Marine Protected Areas in Marine Areas Beyond the Limits of National Jurisdiction.* UN Document UNEP/CBD/WG-PA/INF/2. CBD Secretariat, Montreal.

CBD (Convention on Biological Diversity) (2005b) *Ad Hoc Open-ended Working Group on Protected Areas: Options for Cooperation for the Establishment of Marine Protected Areas in Marine Areas Beyond the Limits of National Jurisdiction.* UN Document UNEP/CBD/WG-PA/1/2. CBD Secretariat, Montreal.

Chape, S, Harrison, J, Spalding, M and Lysenko, I (2005) 'Measuring the extent and effectiveness of protected areas as an indicator for meeting global biodiversity targets'. *Philosophical Transactions of the Royal Society* **360**: pp443–55.

Church, J A, White, N J and Arblaster, J M (2005) 'Significant decadal-scale impact of volcanic eruptions on sea level and ocean heat content'. *Nature* **438**: pp74–7.

Church, J A and White, N J (2006) 'A 20th century acceleration in global sea-level rise'. *Geophysical Research Letters* **33**(1): ppdoi:10.1029/2005GL024826.

Chylek, P and Lohmann, U (2005) 'Ratio of the Greenland to global temperature change: Comparison of observations and climate modeling results'. *Geophysical Research Letters* **32**: L14705.

CIA (Central Intelligence Agency) (2005) 'The World Factbook 2005'. CIA website, http://www.cia.gov/cia/publications/factbook/ (viewed 8. March 2006).

Clark, P U, McCabe, A M, Mix, A C and Weaver, A J (2004) 'Rapid rise of sea level 19,000 years ago and its global implications'. *Science* **304**: pp1141–4.

Clarke, T (2001) 'Taming Africa's killer lake'. *Nature* **406**: pp554–5.

Claussen, M, Ganopolski, A, Brovkin, V, Gerstengarbe, F-W and Werner, P C (2003) 'Simulated global-scale response of the climate system to Dansgaard/Oeschger and Heinrich events'. *Climate Dynamics* **21**(5-6): pp361–70.

Cohen, J E, Small, C, Mellinger, A, Gallup, J and Sachs, J D (1997) 'Estimates of coastal population'. *Science* **278**: pp1211–2.

Cohen, M C L and Lara, R J (2003) 'Temporal changes of mangrove vegetation boundaries in Amazonia: application of GIS and remote sensing techniques'. *Wetlands Ecology and Management* **11**: pp223–31.

Cohen, M, McCord, M J and Sebstad, J (2005) 'Reducing vulnerability: demand for and supply of microinsurance in East Africa'. *Journal of International Development* **17**: pp319–25.

Collett, T S (2005) 'Natural Gas Hydrates: Resource of the 21st Century?' American Association of Petroleum Geologists (AAPG) website, http://emd.aapg.org/technical_areas/gas_hydrates/resource_toc.cfm (viewed 22. November 2005).

Commission of the European Communities (2005a) *Grünbuch über ein Programm für den Schutz kritischer Infrastrukturen.* KOM(2005) 576 engültig. European Community (EC), Brussels.

Commission of the European Communities (2005b) *Thematische Strategie für den Schutz und die Erhaltung der Meersumwelt. Mitteilung der Kommission an den Rat und das Europäische Parlament.* KOM(2005)504 endgültig. SEC(2005)1290. European Community (EC), Brussels.

CSD (Commission on Sustainable Development) (2004) *Review of Progress in the Implementation of the Programme of Action for the Sustainable Development of Small Island Developing States.* Report of the Secretary-General. UN Document E/CN.17/2004/8. CSD, New York.

CSLF (Carbon Sequestration Leadership Forum) (2005) *CO_2 Capture and Storage Summary of Norway – Paper presented by Odd Sverre Haraldsen (Director General, Ministry of Petroleum an Energy) at the 1th International Workshop on CSLF Projects in Berlin, September 27-29, 2005.* CSLF, Washington, DC.

Curry, R and Mauritzen, C (2005) 'Dilution of the northern North Atlantic Ocean in recent decades'. *Science* **308**: pp1772–4.

Czisch, G (2005) *Szenarien zur zukünftigen Stromversorgung. Kostenoptimierte Variationen zur Versorgung Europas und seiner Nachbarn mit Strom aus erneuerbaren Energien. Doctoral Thesis.* University Kassel, Kassel.

Dahdouh-Guebas, F, Jayatissa, L P, Di Nitto, D, Bosire, J O, Lo Seen, D and Koedam, N (2005) 'How effective were mangroves as a defence against the recent tsunami?' *Current Biology* **15**: pp1337–8.

Danielsen, F, Sørensen, M K, Olwig, M F, Selvam, V, Parish, F, Burgess, N D, Hiraishi, T, Karunagaran, V M, Rasmussen, M S, Hansen, L B, Quarto, A and Suryadiputra, N (2005) 'The Asian Tsunami: a protective role for coastal vegetation'. *Science* **310**: p643.

Darwin, R F and Tol, R S J (2001) 'Estimates of the economic effects of sea level rise'. *Environmental and Resource Economics* **19**: pp113–9.

Daschkeit, A and Schottes, P (eds) (2002) *Klimafolgen für Mensch und Küste: am Beispiel der Nordseeinsel Sylt.* Springer, Berlin, Heidelberg, New York.

Davie, M and Buffett, B (2001) 'A numerical model for the formation of gas hydrate below the seafloor'. *Journal of Geophysical Research* **106**(B1): pp185–99.

del Ninno, C, Dorosh, P A, Smith, L C and Roy, D K (2001) *The 1998 Floods in Bangladesh: Disaster Impacts, Household Coping Strategies, and Response.* Research Report 122. International Food Policy Research Insitute (IFPRI), Washington, DC.

Deutsche BP (2005) 'BP plant Kraftwerk mit 90% weniger Emissionen. Pressemitteilung vom 06. Juli 2005'. Deutsche BP website, http://www.deutschebp.de/genericarticle.do?categoryId=2010149&contentId=7007117 (viewed 3. April 2006).

DINAS-COAST Consortium (2004) *DIVA 1.0. CD-Rom.* PIK Potsdam, Potsdam.

DOE-NETL (US Department of Energy National Energy Technology Laboratory) (2005) 'Program Facts – Methane Hydrates'. NETL website, http://www.netl.doe.gov/scngo (viewed 24. February 2006).

Donner, S D, Skirving, W J, Little, C M, Oppenheimer, M and Hoegh-Guldberg, O (2005) 'Global assessment of coral bleaching and required rates of adaptation under climate change'. *Global Change Biology* **11**: pp2251–65.

Dowdeswell, J A (2006) 'Atmospheric science – The Greenland Ice Sheet and global sea-level rise'. *Science* **311**: pp963–4.

Dowsett, H J, Thompson, R S, Barron, J A, Cronin, T M, Ishman, S E, Poore, R Z, Willard, D A and Holtz jr, T R (1994) 'Joint investigations of the middle pliocene climate I: PRISM paleoenvironmental reconstructions'. *Global and Planetary Change* **9**: pp169-95.

DRM (World Institute for Disaster Risk Management) (2006) 'Disaster Management for Critical Infrastructure'. DRM website, http://www.drmonline.det/projects/infrastructure.htm (viewed 19. January 2006).

Edenhofer, O (2003) 'Wege zu einer nachhaltigen Klima- und Energiepolitik'. *Aus Politik und Zeitgeschichte* 27: pp18–26.

Edenhofer, O, Held, H and Bauer, N (2005): 'A regulatory framework for carbon capturing and sequestration within the Post-Kyoto process'. In Rubin, E S, Keith, D W and Gilboy, C F (eds) *Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies. Volume 1: Peer-Reviewed Paper and Plenary Presentations, IEA Greenhouse Gas Programme. forthcoming.* Edward Elgar, Cheltenham, UK.

Edwards, M and Richardson, J (2004) 'Impact of climate change on marine pelagic phenology and trophic mismatch'. *Nature* **430**: pp881–4.

EEA (European Environment Agency) (2005) *Vulnerability and Adaptation to Climate Change in Europe.* EEA, Paris.

EIA (Energy Information Administration) (1998) *Natural Gas 1998: Issues and Trends.* EIA, Washington, DC.

Ellison, J C and Stoddart, D R (1991) 'Mangrove ecosystem collapse during predicted sea-level rise: holocene analogues and implications'. *Journal of Coastal Research* 7: pp151–65.

El-Raey, M, Dewidar, K R and El-Hattab, M (1999) 'Adaptation to the impacts of sea-level rise in Egypt'. *Mitigation and Adaptation Strategies for Global Change* **4**: pp343-61.

Elsner, W, Otte, C and Yu, I (2005) *Klimawandel und präventives Risiko- und Küstenschutzmanagement an der deutschen Nordseeküste (KRIM): Teilprojekt 5 – Endbericht. Klimawandel und regionale Wirtschaft. Vermögensschäden und Einkommensverluste durch extreme Klimaereignisse sowie Kosten-Nutzen-Analysen von Schutzmaßnahmen. Am Beispiel der nordwestdeutschen Küstenregion.* University Bremen, Bremen.

Emanuel, K (2005) 'Increasing destructiveness of tropical cyclones over the past 30 years'. *Nature* **436**: pp686–8.

Emerton, L (1999) *Economic Tools for the Management of Marine Protected Areas in Eastern Africa. Biodiversity Economics for Eastern Africa.* The World Conservation Union (IUCN), Gland.

Engel, A, Thomas, S, Riebesell, U, Rochelle-Newall, E and Zondervan, I (2004) 'Polysaccharide aggregation as a potential sink of marine dissolved organic carbon'. *Nature* **428**: pp929–32.

Epiney, A (1995) 'Das „Verbot erheblicher grenzüberschreitender Umweltbeeinträchtigungen": Relikt oder konkretisierungsfähige Grundnorm?' *Archiv des Völkerrechts* 33: pp309ff.

EU Commission (2005) *Thematische Strategie für den Schutz und die Erhaltung der Meeresumwelt. Mitteilung der Kommission an den Rat und das Europäische Parlament. EU Document KOM(2005)504 of 24.10.2005.* EU Commission, Brussels.

Fairbanks, R G (1989) 'A 17,000-year glacio-eustatic sea level record: influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation'. *Nature* **342**: pp637–42.

Falkowski, P G, Laws, E A, Baber, R T and Murray, J W (2003): 'Phytoplankton and their role in primary, new, and export production'. In Fasham, M J R (ed) *Ocean Biogeochemistry: The Role of the Ocean Carbon Cycle in Global Change.* Springer, Berlin, Heidelberg, New York: pp99–121.

Fankhauser, S (1995) *Valuing Climate Change: The Economics of the Greenhouse.* Earthscan, London.

Fankhauser, S (1998) *The Costs of Adaptation to Climate Change. GEF Working Paper 16.* Global Environment Facility (GEF), Washington, DC.

FAO (Food and Agriculture Organisation) (1995) *Code of Conduct for Responsible Fisheries.* FAO, Rome.

FAO (Food and Agriculture Organisation) (2000) *The State of World Fisheries and Aquaculture 2000.* FAO, Rome.

FAO (Food and Agriculture Organisation) (2001) *International Plan of Action to Prevent, Deter and Eliminate Illegal, Unreported and Unregulated Fishing.* FAO, Rome.

FAO (Food and Agriculture Organisation) (2002) *The State of World Fisheries and Aquaculture 2002.* FAO, Rome.

FAO (Food and Agriculture Organisation) (2003) *Fisheries Management 2: The Ecosystem Approach to Fisheries.* FAO Technical Report Nr. 4 (Suppl. 2). FAO, Rome.

FAO (Food and Agriculture Organisation) (2004) *The State of World Fisheries and Aquaculture 2004.* FAO, Rome.

Fasham, M J R (ed) (2003) *Ocean Biogeochemistry: The Role of the Ocean Carbon Cycle in Global Change.* Springer, Berlin, Heidelberg, New York.

Feely, R, Sabine, C, Lee, K, Berelson, W, Kleypas, J, Fabry, V J and Millero, F J (2004) 'Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans'. *Science* **305**: pp362–6.

Fernando, H J S and McCulley, J L (2005) 'Coral poaching worsens tsunami destruction in Sri Lanka'. *EOS* **86**: pp301–4.

Fiedler, P.C (2002) 'Environmental change in the eastern tropical Pacific Ocean: review of ENSO and decadal variability'. *Marine Ecology Progress Series* **244**: pp265–83.

Field, D B, Baumgartner, T R., Charles, C D, Ferreira-Bartrina, V and Ohman, M D (2006) 'Planktonic foraminifera of the California current reflect 20th-century warming'. *Science* **311**: pp63–6.

Forcada, J, Trathan, P N, Reid, K and Murphy, E J (2005) 'The effects of global climate variability in pup production of antarctic fur seals'. *Ecology* **86**: pp2408–17.

Frank, K T, Petrie, B, Choi, J S and Leggett, W C (2005) 'Trophic cascades in a formerly cod-dominated ecosystem'. *Science* **308**: pp1621–3.

Freeman, P K, Keen, M and Mani, M (2003) *Dealing with Increased Risk of Natural Disasters: Challenges and Options.* International Monetary Fund (IMF), Washington, DC.

Freeth, S J (1987) 'Life (and death) in Lake Nyos'. *Nature* **329**: pp491.

Freiwald, A, Fosså, J H, Grehan, A, Koslow, T and Roberts, J M (2004) *Cold-water Coral Reefs.* UNEP-WCMC, Cambridge, New York, UK.

Friends of the Earth (2005) 'A Citizen's Guide to Climate Refugees'. Friends of the Earth website, http://www.foe.org.au/download/CitizensGuide.pdf (viewed 15. February 2006).

Fujita, R, Bonzon, K, Wilen, J, Solow, A, Arnason, R, Cannon, J and Polasky, S (2004): 'Rationality or chaos? Global fisheries at the crossroads'. In Glover, L K and Earle, S A (eds) *Defying Ocean's End. An Agenda for Action.* Island Press, Washington, DC: pp139–49.

Gattuso, J-P, Allemande, D and Frankignoulle, M (1999) 'Photosynthesis and calcification at cellular, organismal and community levels in coral reefs. A review of interactions and control by carbonate chemistry'. *American Zoologist* **39**: pp160–83.

GCIM (Global Commission on International Migration) (2005) *Migration in an Interconnected World: New Directions for Action.* GCIM, Geneva.

GEF (Global Environment Facility) (2005a) *Producing Results for the Global Environment. Annual Report 2004.* GEF, Washington, DC.

GEF (Global Environment Facility) (2005b) *GEF Global Action on Climate Change. GEF Support for Adaptation to Climate Change.* GEF, Washington, DC.

Gell, F R and Roberts, C M (2003) 'Benefits beyond boundaries: the fishery effects of marine reserves'. *Trends in Ecology and Evolution* **18**(9): pp448–55.

Gerber, L R, Hyrenbach, K D and Zacharias, M A (2005) 'Do the largest protected areas conserve whales or whalers?' *Science* **307**: pp525–6.

GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection) (2001) *A Sea of Troubles.* GESAMP, The Hague.

Gianni, M and Simpson, W (2005) *The Changing Nature of High Seas Fishing: How Flags of Convenience Provide Cover for Illegal, Unreported and Unregulated Fishing.* Australian Department of Agriculture Fisheries and Forestry, International Transport Workers' Federation, WWF International, Sidney, London, Gland.

Gillett, N P, Graf, H F and Osborn, T J (2003): 'Climate change and the North Atlantic Oscillation'. In Hurrell, J W, Kushnir, Y, Ottersen, G and Visbeck, M (eds) *North Atlantic Oscillation: Climatic Significance and Environmental Impact.* American Geophysical Union, Washington, DC: pp193–209.

GLOBEC (Global Ocean Ecosystem Dynamics) (1999) *Implementation Plan.* IGBP Report Nr. 47. GLOBEC Report Nr. 13. IGBP Secretariat, Stockholm.

Gloor, M, Gruber, N, Sarmiento, J, Sabine, C L, Feely, R A and Rödenbeck, C (2003) 'A first estimate of present and preindustrial air-sea CO_2 flux patterns based on ocean interior carbon measurements and models'. *Geophysical Research Letters* **30**(1): pp10-11–10-14.

Gommes, R, du Guerny, J, Nachtergaele, F and Brinkman, R (1998) 'Potential Impacts of Sea-Level Rise on Population and Agriculture. FAO SD-Dimensions'. FAO website, http://www.fao.org/sd/eidirect/EIre0045.htm (viewed 22. February 2006).

Gorina-Ysern, M, Gjerde, K and Orbach, M (2004): 'Ocean governance: a new ethos through a World Ocean Public Trust'. In Glover, L K, Earle, S A and Kelleher, G (eds) *Defying Ocean's End. An Agenda for Action.* Island Press, Washington, DC: pp197–212.

Gornitz, V, Couch, S and Hartig, E K (2002) 'Impacts of sea level rise in the New York City metropolitan area'. *Global and Planetary Changes* **32**: pp61–88.

Greenblatt, J B and Sarmiento, J L (2004): 'Variability and climate feedback mechanisms in ocean uptake of CO_2'. In Field, C B and Raupach, M R (eds) *SCOPE 62: The Global Carbon Cycle: Integrating Humans, Climate and the Natural World.* Island Press, Washington, DC: pp257–275.

Gregg, W W, Conkright, M E, Ginoux, P, O'Reilly, J E and Casey, N W (2003) 'Ocean primary production and climate: global decadal changes'. *Geophysical Research Letters* **30**: p1809.

Gregory, J M, Huybrechts, P and Raper, S C B (2004) 'Threatened loss of the Greenland ice-sheet'. *Nature* **428**: p616.

Grimsditch, G D and Salm, R V (2005) *Coral Reef Resilience and Resistance to Bleaching.* The World Conservation Union (IUCN), Gland.

Gruber, N, Friedlingstein, P, Field, C B, Valentini, R, Heimann, M, Richey, J E, Romero Lankao, P, Schulze, E-D and Chen-Tung, A C (2004): 'The vulnerability of the carbon cycle in the 21st century: an assessment of carbon-climate-human interactions'. In Field, C B and Raupach, M R (eds) *The Global Carbon Cycle.* Island Press, Wasington, DC: pp45–77.

Guinotte, J, Buddemeier, R W and Kleypas, J (2003) 'Future coral reef habitat marginality: temporal and spatial effects of climate change in the Pacific basin'. *Coral Reefs* **22**: pp551–8.

Hadley Centre (2003) 'Global Sea Ice Coverage and Sea Surface Temperature Data (1856–Present)'. Meteorological Office – Hadley Centre website, http://badc.nerc.ac.uk/data/gisst (viewed 10. February 2006).

Hall, J W, Meadowcroft, I C, Lee, E M and van Gelder, P H A J M (2002) 'Stochastic simulation of episodic soft coastal cliff recession'. *Coastal Engineering* **46**: pp159–74.

Hall, J M, Sayers, P B, Walkden, M J A and Panzeri, M (2005) 'Impacts of climate change on coastal flood risk in England and Wales: 2030-2100'. *Philosophical Transactions of the Royal Society of London* **69**: pp343–65.

Hansen, J, Nazarenko, L, Ruedy, R, Sato, M, Willis, J, Del Genio, A, Koch, D, Lacis, A, Lo, K, Menon, S, Novakov, T, Perlwitz, J, Russell, G, Schmidt, G A and Tausnev, N (2005) 'Earth's energy imbalance: confirmation and implications'. *Science* **308**: pp1431–5.

Hare, S R and Mantua, N J (2000) 'Empirical evidence for Northeast Pacific regime shifts in 1977 and 1989'. *Progress in Oceanography* **47**(2-4): pp99–102.

Haugan, P and Drange, S (1996) 'Effects of CO_2 on the ocean environment'. *Energy Conversion and Management* **37**: pp1019–22.

Hilborn, R (2003) 'Marine reserves: the best option for our oceans?' *Frontiers in Ecology and the Environment* **1**(9): pp497–8.

Hoegh-Guldberg, O (1999) 'Climate change, coral bleaching and the future of the world's coral reefs'. *Marine Freshwater Resources* **50**: pp839–66.

Hoegh-Guldberg, O (2005) 'Low coral cover in a high-CO_2 world'. *Journal of Geophysical Research* **110**: in print.

Hohmann, H (2001): 'Weltweiter Schutz der Meeresumwelt unter besonderer Berücksichtigung des Schutzes von Nord- und Ostsee (einschließlich des Wattenmeeres)'. In Gesellschaft für Umweltrecht (ed) *Umweltrecht im Wandel.* Erich Schmidt, Berlin: pp99–128.

Hoyos, C D, Agudelo, P A, Webster, P J and Curry, J A (2006) 'Deconvolution of the factors contributing to the increase in global hurricane intensity'. *Science* **312**: pp94–7.

Hsieh, C-H, Glaser, S M, Lucas, A J and Sugihara, G (2005) 'Distinguishing random environmental fluctuations from ecological catastrophes for the North Pacific Ocean'. *Nature* **435**: pp336–40.

Hughes, T P, Baird, A H, Bellwood, D R, Card, M, Connolly, S R, Folke, C, Grosberg, R, Hoegh-Guldberg, O, Jackson, J B C, Kleypas, J, Lough, J, Marshall, P, Nystrom, M, Palumbi, S R, Pandolfi, J M, Rosen, B and Roughgarden, J (2003) 'Climate change, human impacts, and the resilience of coral reefs'. *Science* **301**: pp929–33.

Huisman, J, Nga, N, Thi, P, Karl, D M and Sommeijer, B (2006) 'Reduced mixing generates oscillations and chaos in the oceanic deep chlorophyll maximum'. *Nature* **439**: pp322–5.

Huntley, B, Green, R E, Collingham, Y. C, Hill, J K, Willis, S G, Bartlein, P J, Cramer, W, Hagemeijer, W J M and Thomas, C J (2004) 'The performance of models relating species geographical distributions to climate is independent of trophic level'. *Ecology Letters* **7**: pp417–26.

IEA (International Energy Agency) (2002) *CO_2 Emissions From Fuel Combustion 1971–2000.* IEA, Paris.

IEA (International Energy Agency) (2004) *Prospects for CO_2 Capture and Storage.* IEA, Paris.

IEA (International Energy Agency) (2005) *Legal Aspects of Storing CO_2.* IEA, Paris.

IMBER (Integrated Marine Biogeochemistry and Ecosystem Research) (2005) 'Science Plan and Implementation Strategy. IGBP Report No. 52'. IGBP Secretariat website, http://www.jhu. edu/scor/IMBER/IMBER_SPIS_Final.pdf (viewed 3. February 2006).

IMO (International Maritime Organization) (2004) *Report of the Twenty-Seventh Meeting of the Scientific Group.* IMO, London.

IPCC (Intergovernmental Panel on Climate Change) (1990) *Potential Impacts of Climate Change. Report of Working Group II to IPCC.* World Meteorological Organization (WMO), United Nations Environment Programme (UNEP), Geneva.

IPCC (Intergovernmental Panel on Climate Change) (2000) *Special Report on Emissions Scenarios.* Cambridge University Press, Cambridge, New York.

IPCC (Intergovernmental Panel on Climate Change) (2001a) *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the IPCC.* Cambridge University Press, Cambridge, New York.

IPCC (Intergovernmental Panel on Climate Change) (2001b) *Climate Change 2001: Impacts, Adaptation, and Vulnerability. Contribution of Working Group II to the Third Assessment Report of the IPCC.* Cambridge University Press, Cambridge, New York.

IPCC (Intergovernmental Panel on Climate Change) (2005) *Special Report on Carbon Dioxide Capture and Storage.* Cambridge University Press, Cambridge, New York.

Isciences (2003) *SRTM30 Enhanced Global Map Data. Elevation/Slope/Aspect.* Isciences, Ann Arbor, MI.

IUCN (The World Conservation Union) (1988) *Resolution 17.38 of the 17th General Assembly of the IUCN.* IUCN, Gland, Cambridge.

IUCN (The World Conservation Union) (1994) *Guidelines for Protected Areas.* IUCN, Gland.

Jackson, J B C, Kirby, M X, Berger, W H, Bjorndal, K A, Botsford, L W, Bourque, B J, Bradbury, R H, Cooke, R G, Erlandson, J, Estes, J A, Hughes, T P, Kidwell, S, Lange, C B, Lenihan, H S, Pandolfi, J M, Peterson, C H, Steneck, R S, Tegner, M J and Warner, R R (2001) 'Historical overfishing and the recent collapse of coastal ecosystems'. *Science* **293**: pp629–38.

Jensen, A S (1939) 'Concerning a change of climate during recent decades in the Arctic and Subarctic regions, from Greenland in the west to Eurasia in the east, and contemporary biological and geophysical changes'. *Biologiske Meddelelser. Kongelige Danske Videnskabers Selskab* **XIV**: p75.

Jesus, J L (2003): 'Rocks, new-born islands, sea level rise and maritime space'. In Frowein, J A, Scharioth, K, Winkelmann, I and Wolfrum, R (eds) *Verhandeln für den Frieden. Negotiating for Peace. Liber Amicorum Tono Eitel.* Springer, Berlin, Heidelberg, New York: pp579–603.

Jickells, T D, An, Z S, Andersen, K K, Baker, A R, Bergametti, G, Brooks, N, Cao, J J, Boyd, P W, Duce, R A, Hunter, K A, Kawahata, H, Kubilay, N, LaRoche, J, Liss, P S, Mahowald, N, Prospero, J M, Ridgwell, A J, Tegen, I and Torres, R (2005) 'Global iron conncections between desert dust, ocean biogeochemistry, and climate'. *Science* **308**: pp67–71.

Jimenez, J A and Sanchez-Arcilla, A (1997) 'Physical impacts of climatic change on deltaic coastal systems (II): driving terms'. *Climatic Change* **35**: pp95–118.

Johannessen, O M, Khvorostovsky, K, Miles, M W and Bobylev, L P (2005) 'Recent ice-sheet growth in the interior of Greenland'. *Science* **310**: pp1013–6.

Johnson, A H (2004) *Letter of the "Methane Hydrate Advisory Committee" to the US Department of Energy of 22.11.2004.* Methane Hydrate Advisory Committee, Washington, DC.

Joughin, I, Abdalati, W and Fahnestock, M (2004) 'Large fluctuations in speed on Greenland's Jakobshavn Isbrae glacier'. *Nature* 432: pp608–10.

Kelleher, G (ed) (1999) *Guidelines for Marine Protected Areas. Best Practice Protected Area Guidelines Series No. 3.* World Commission on Protected Areas of IUCN, Gland.

Kellersmann, B (2000) *Die gemeinsame, aber differenzierte Verantwortlichkeit von Industriestaaten und Entwicklungsländern für den Schutz der globalen Umwelt.* Springer, Berlin, Heidelberg, New York.

King, J R (2005) *Report of the Study Group on Fisheries and Ecosystem Responses to Recent Regime Shifts. PICES Scientific Report No. 28.* North Pacific Marine Science Organization (PICES), Sidney, BC, Canada.

Klauda, J and Sandler, S I (2005) 'Global distribution of methane hydrate in ocean sediment'. *Energy & Fuels* **19**(2): pp459–70.

Klein, R J T, Nicholls, R J and Mimura, N (1999) 'Coastal adaptation to climate change: can the IPCC Technical Guidelines be applied?' Mitigation and Adaptation Strategies for *Global Change* 4(3-4): pp239–52.

Klein, R J T, Nicholls, R J and Thomalla, F (2002): 'The resilience of coastal megacities to weather-related hazards: a review'. In Kreimer, A, Arnold, M and Carlin, A (eds) *Proceedings of The Future of Disaster Risk: Building Safer Cities.* World Bank, Washington, DC: pp111–37.

Kleypas, J, Buddemeier, R H, Archer, D, Gattuso, J-P, Langdon, C and Opdyke, B N (1999) 'Geochemical consequences of increased atmospheric carbon dioxide on coral reefs'. *Science* **284**: pp118–20.

Kleypas, J A, Buddemeier, R W, Eakin, C M, Gattuso, J-P, Guinotte, J, Hoegh-Guldberg, O, Iglesias-Prieto, R, Jokiel, P L, Langdon, C, Skirving, W and Strong, A E (2005) 'Comment on "Coral reef calcification and climate change: the effect of ocean warming"'. *Geophysical Research Letters* **32**: ppL08601.

Kling, G W, Clark, M A, Compton, H R, Devine, J D, Evans, W C, Humphrey, A M, Koenigsberg, E J, Lockwood, J P, Tuttle, M L and Wagner, G N (1987) 'The 1986 Lake Nyos gas disaster in Cameroon, West Africa'. *Science* **236**: pp169–75.

Klyashtorin, L (2001) *Climate change and long-term fluctuations of commercial catches. The possibility of forecasting.* FAO, Rome.

Knutson, T R and Tuleya, R E (2004) 'Impact of CO_2-induced warming on simulated hurricane intensity and precipitation'. *Journal of Climatology* **17**: pp3477–95.

Kropp, J, Eisenack, K and Scheffran, J (2005): 'Marine overexploitation: a syndrome of global change'. In Sonak, S (ed) *Multiple Dimensions of Global Environmental Change.* Teri Press, New Delhi: in print.

Kullenberg, G (2001) 'Contributions of marine and coastal area research and observations towards sustainable development of large coastal cities'. *Ocean & Coastal Management* **44**: pp283–91.

Kundzewicz, Z W and Schellnhuber, H-J (2004) 'Floods in the IPCC TAR perspective'. *Natural Hazards* **31**: pp111–28.

Lambeck, K, Anzidei, M, Antonioli, F, Benini, A and Espositol, A (2004) 'Sea level in Roman times in the central Mediterranean and implications for recent change'. *Earth and Planetary Science Letters* **224**: pp563–75.

Leatherman, S P (2001) *Sea Level Rise: History and Consequences.* Academic Press, San Diego.

Lehodey, P, Chai, F and Hampton, J (2003) 'Modelling climate-related variability of tuna populations from a coupled ocean biogeochemical-populations dynamics model'. *Fisheries Oceanography* **12**: pp483–94.

Levermann, A, Griesel, A, Hofmann, M, Montoya, M and Rahmstorf, S (2005) 'Dynamic sea level changes following changes in the thermohaline circulation'. *Climate Dynamics* **24**(4): pp347–54.

Levitus, S, Antonov, J and Boyer, T P (2005) 'Warming of the world ocean, 1955–2003'. *Geophysical Research Letters* **32**: L02604.

Lindsay, R W and Zhang, J (2005) 'The thinning of Arctic sea ice, 1988-2003: have we passed a tipping point?' *Journal of Climate* **18**: pp4879–94.

Linnerooth-Bayer, J and Mechler, R (2005) 'The potential benefits and limitations of micro-insurance as a risk transfer mechanism for developing countries. Viewpoint for International Day for Disaster Reduction'. MicroInsurance Centre website, http://www.microinsurancecentre.org (viewed 29. November 2005).

Lough, J M and Barnes, D J (2000) 'Environmental controls on growth of the massive coral Porites'. *Journal of Experimental Marine Biology and Ecology* **245**: pp225–43.

Lowe, J A, Gregory, J M and Flather, R A (2001) 'Changes in the occurrence of storm surges around the United Kingdom under a future climate scenario using a dynamic storm surge model driven by the Hadley Centre climate models'. *Climate Dynamics* **18**: pp179–88.

Lubchenko, J, Palumbi, S R, Gaines, S D and Andelman, S J (2003) 'Plugging a hole in the ocean: the emerging science of marine reserves'. *Ecological Applications* **13**(1): ppS3–S7.

MA (Millennium Ecosystem Assessment) (2005a) *Ecosystems and Human Well-Being: Summary for Decision-Makers.* Island Press, Washington, DC.

MA (Millennium Ecosystem Assessment) (2005b): *Ecosystems and Human Well-Being. Volume I: Current State and Trends.* Island Press, Washington, DC.

Mai, S, Elsner, A, Meyer, V and Zimmermann, C (2004) *Klimawandel und präventives Risiko- und Küstenschutzmanagement an der deutschen Nordseeküste (KRIM): Teilprojekt 2 – Endbericht. Klimaänderung und Küstenschutz.* Franzius Institute, University Hannover, Hannover.

Maslowski, W, Clement, J, Laxon, S and Jakacki, J (2005) 'The rate of change of the Arctic sea ice cover: 1979–2003 model results'. *Geophysical Research Abstracts* **7**: pp10380.

McMichael, A J, Campbell-Lendrum, D, Kovats, S, Edwards, S, Wilkinson, P, Wilson, T, Nicholls, R J, Hales, S, Tanser, F, Le Sueur, D, Schlesinger, M and Andronova, N (2004): 'Climate change'. In Ezzati, M, Lopez, A D, Rodgers, A and Murray, C J L (eds) *Comparative Quantification of Health Risks: Global and Regional Burden of Disease due to Selected Major Risk Factors.* World Health Organisation (WHO), Geneva: pp1543–649.

McNeil, B I, Matera, R J and Barnes, D J (2004) 'Coral reef calcification and climate change: the effect of ocean warming'. *Geophysical Research Letters* **31**: L22309.

Meier, H E M, Döscher, R and Halkka, A (2004) 'Simulated distributions of Baltic sea-ice in warming climate and consequences for the winter habitat of the Baltic ringed seal'. *Ambio* **33**(4-5): pp249–56.

Meinshausen, M (2006): 'What does a 2°C target mean for greenhouse gas concentrations? A brief analysis based on multi-gas emission pathways and several climate sensitivity uncertainty estimates'. In Schellnhuber, H-J (ed) *Avoiding Dangerous Climate Change.* Cambridge University Press, Cambridge, New York: pp265–79.

Met Office (2006) 'Catarina Hits Brazil. South Atlantic Hurricane Breaks all the Rules'. Met Office website, http://www.metoffice.com/sec2/sec2cyclone/catarina.html (viewed 14. February 2006).

Methane Hydrate Advisory Committee (2002) 'Report of the Methane Hydrate Advisory Committee on Methane Hydrate Issues and Opportunities – Including Assessment of Uncertainty of the Impact of Methane Hydrate on Global Climate Change, Dezember 2002'. U.S. Department of Energy (DOE) website, http://www.fe.doe.gov/programs/oilgas/hydrates/Methane_Hydrates_Advisory_Committee.html (viewed 24. February 2006).

MH21 (Research Consortium for Methane Hydrate Resources in Japan) (2005) 'Background and Organization'. MH 21 website, http://www.mh21japan.gr.jp/english/mh21-2. html (viewed 15. February 2006).

Mignot, J A, Ganopolski, A and Levermann, A (submitted) 'Atlantic subsurface temperature response to a shut-down of the overturning circulation'. *Journal of Climate.*

Milazzo, M (1998) *Subsidies in World Fisheries – A Reexamination.* World Bank Technical Paper 406. Fisheries Series. World Bank, Washington, DC.

Milkov, A V (2004) 'Global estimates of hydrate-bound gas in marine sediments: how much is really out there?' *Earth-Science Reviews* **66**(3-4): pp183–97.

Mirza, M M Q, Warrick, R A and Ericksen, N J (2003) 'The implications of climate change on floods of the Ganges, Brahmaputra and Meghna rivers in Bangladesh'. *Climatic Change* **57**: pp287–318.

Monnett, C, Gleason, J and Rotterman, L (2005) *Report at the 16th Biennial Conference on the Biology of Marine Mammals.* Conference Secretariat, San Diego, USA.

Montaggioni, L F (2005) 'History of Indo-Pacific coral reef systems since the last glaciation: Development patterns and controlling factors'. *Earth-Science Reviews* **71**: pp1–75.

Morling, P (2004) 'The economics of marine protected areas in the High Seas'. *The George Wright Forum* **21**(4): pp49–61.

MPI for Meteorology (2005) Klimaänderung so rasant wie noch nie. Press Release No. B62/C29/2005(146) of 29.9.2005. MPI for Meteorology, Hamburg.

Mumby, P J, Dahlgren, C P, Harborne, A R, Kappel, C V, Micheli, F, Brumbaugh, D R, Holmes, C E, Mendes, J M, Broad, K, Sanchirico, J N, Buch, K, Box, S, Stoffle, R W and Gill, A B (2006) 'Fishing, trophic cascades, and the process of grazing on coral reefs'. *Science* **311**: pp98–101.

Murray, S N, Ambrose, R F, Bohnsack, J A, Botsford, L W, Carr, M H, Davis, G E, Dayton, P K, Gotshall, D, Gunderson, D R, Hixon, M A, Lubchenco, J, Mangel, M, MacCall, A, McArdle, D A, Ogden, J C, Roughgarden, J, Starr, R M, Tegner, M J and Yoklavich, M M (1999) 'No-take reserve networks: sustaining fisheries populations and marine ecosystems'. *Fisheries* **24**(1): pp11–25.

Münchener Rück (1997) 'Überschwemmung und Versicherung'. Münchener Rück website, http://www.munichre.com (viewed 16. March 2006).

Münchener Rück (2005a) Wetterkatastrophen und Klimawandel. Sind wir noch zu retten? Münchener Rück, Munich.

Münchener Rück (2005b) 'Mikroversicherung wichtige Einrichtung zur Armutsbekämpfung'. Münchener Rück Stiftung website, http://www.epo.de (viewed 29. November 2005).

NASA (National Aeronautics and Space Administration) (2005) 'Arctic Sea Ice Continues to Decline, Arctic Temperatures Continue to Rise in 2005'. NASA Headquarters website, http://www.nasa.gov/centers/goddard/news/topstory/2005/arcticice_decline.html (viewed 13. March 2006).

Nicholls, R J (1995) 'Coastal megacities and climate change'. *GeoJournal* 37(3): pp369–79.

Nicholls, J R (2003) *Case Study on Sea-Level Rise Impacts. OECD Workshop on the Benefits of Cliamte Policy: Improving Information for Policy Makers.* Document ENV/EPOC/GSP(2003)9/FINAL. Organization for Economic Co-operation and Development (OECD), Paris.

Nicholls, R J (2004) 'Coastal flooding and wetland loss in the 21st century: changes under the SRES climate and socio-economic scenarios'. *Global Environmental Change* 14: pp69–86.

Nicholls, R J, Tol, R S J and Vafeidis, A T (2005) *Global Estimates of the Impact of a Collapse of the West Antarctic Ice Sheet: An Application of FUND.* Working Paper FNU-78. University Hamburg, Center for Marine and Atmospheric Sciences, Hamburg.

Nicholls, R J, Townend, I and Cooper, N (2006) 'Coastal engineering and management'. In Thorne, C R, Evans, E P and Penning-Rowsell, E C (eds) *Future Flood and Coastal Erosion Risks in the UK.* Thomas Telford, London.

NOAA-ESRL (Global Monitoring Division) (2006) 'Interactive Atmospheric Data Visualization. Mauna Loa, Hawaii, United States'. NOAA ESRL website, http://www.cmdl.noaa.gov/ccgg/iadv/ (viewed 20. March 2006).

NODC (National Oceanographic Data Center) (2001) *World Ocean Database 2001.* NODC, Silver Spring, MD.

Nosengo, N (2003) 'Save our city!' *Nature* 424: pp608–9.

NRC (National Research Council) (2001) *Marine Protected Areas: Tools for Sustaining Ocean Ecosystem. Committee on the Evaluation, Design, and Monitoring of Marine Reserves and Protected Areas in the United States.* Ocean Studies Board, National Research Council. NRC, Washington, DC.

NSIDC (National Snow and Ice Data Center) (2002) 'Larsen B Ice Shelf Collapses in Antarctica'. NSIDC website, http://nsidc.org/iceshelves/larsenb2002/ (viewed 24. January 2006).

OECD (Organisation for Economic Co-operation and Development) (2002): *Aid Targeting the Objectives of the Rio Conventions 1998–2000. A Contribution by the DAC Secretariat for the Information of Participants at the World Summit for Sustainable Development in Johannesburg in August 2002.* Paris, OECD.

Oppenheimer, M and Alley, R B (2004) 'The West Antarctic ice sheet and long term climate policy – An editorial comment'. *Climatic Change* 64(1-2): pp1–10.

Orr, J C, Fabry, V J, Aumont, O, Bopp, L, Doney, S C, Feely, R A, Gnanadesikan, A, Gruber, N, Ishida, A, Joos, F, Key, R M, Lindsay, K, Maier-Reimer, E, Matear, R, Monfray, P, Mouchet, A, Najjar, R G, Plattner, G-K, Rodgers, K B, Sabine, C L, Sarmiento, J L, Schlitzer, R, Slater, R D, Totterdell, I J, Weirig, M-F, Yamanaka, Y and Yool, A (2005) 'Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms'. *Nature* 437: pp681–6.

OSPAR (Oslo Paris Commission) (2003) *Joint Ministerial Meeting of the Helsinki and OSPAR Commissions (JMM), Bremen 25-26 June 2003. Declaration of the Joint Ministerial Meeting of the Helsinki and OSPAR Commissions.* OSPAR, Bremen.

Palumbi, S R (2003) *Marine Reserves: A Tool for Ecosystem Management and Conservation.* Pew Oceans Commission, Washington, DC.

Pandolfi, J M, Bradbury, R H, Sala, E, Hughes, T P, Bjorndal, K A, Cooke, R G, McArdle, D, McClenachan, L, Newman, M J H, Paredes, G, Warner, R R and Jackson, J B C (2003) 'Global trajectories of the long-term decline of coral reef ecosystems'. *Science* 301: pp955–8.

Parker, D E, Folland, C K and Jackson, M (1995) 'Marine surface temperature: observed variations and data requirements'. *Climate Change* 31: pp559–600.

Parmesan, C and Yohe, G (2003) 'A globally coherent fingerprint of climate change impacts across natural systems'. *Nature* 421: pp37–42.

Patz, J A, Campbell-Lendrum, D H, Holloway, T and Foley, J A (2005) 'Impact of regional climate change on human health'. *Nature* 438: pp310–7.

Pauly, D, Christensen, V., Guenette, S, Pitcher, T J, Sumaila, U R, Walters, C J, Watson, R and Zeller, D (2002) 'Towards sustainability in world fisheries'. *Nature* 418: pp689–95.

Peltier, W R (2004) 'Global glacial isostasy and the surface of the ice-age earth: The ice-5G (VM2) model and grace'. *Annual Review Of Earth And Planetary Sciences* 32: pp111–49.

Perry, A L, Low, P J, Ellis, J R and Reynolds, J D (2005) 'Climate change and distribution shifts in marine fishes'. *Science* 308: pp1912–5.

PICES (North Pacific Marine Science Organization) (2004) *Marine Ecosystems of the North Pacific.* PICES Scientific Report No. 1. PICES, Sidney, Canada.

Pikitch, E K, Santora, C, Babcock, E A, Bakun, A, Bonfil, R, Conover, D O, Dayton, P K, Doukakis, P, Fluharty, D L, Heneman, B, Houde, E D, Link, J, Livingston, P A, Mangel, M, McAllister, M K, Pope, J and Sainsbury, K J (2004) 'Ecosystem-based fishery management'. *Science* 305: pp346–7.

Platzöder, R. (2001): 'The United Nations Convention on the Law of the Sea and Marine Protected Areas on the High Seas'. In Thiel, H and Koslow, J A (eds) *Managing Risks to Biodiversity and the Environment on the High Sea, Including Tools Such as Marine Protected Areas – Scientific Requirements and Legal Aspects.* German Federal Agency for Nature Conservation, Bonn: pp137–42.

Ploetz, C (2003) 'Sequestrierung von CO_2: Technologien, Potenziale, Kosten und Umweltauswirkungen'. Expertise for the WBGU Report 'World in Transition: Towards Sustainable Energy Systems'. WBGU website, http://www.wbgu.de/wbgu_jg2003_ex07.pdf.

Polovina, J J (2005) 'Climate variation, regime shifts, and implications for sustainable fisheries'. *Bulletin of Marine Science* 76(2): pp233–44.

Pörtner, O H, Langenbuch, M and Reipschläger, A (2004) 'Biological impact of elevated ocean CO_2 concentrations: lessons from animal physiology and earth history'. *Journal of Oceanography* 60: pp705–18.

Pörtner, H O (2005) 'Auswirkungen von CO_2-Eintrag und Temperaturerhöhung auf die marine Biosphäre'. Expertise for WBGU Special Report 'The Future Oceans – Warming Up, Rising High, Turning Sour'. WBGU website, http://www.wbgu.de/wbgu_sn2005_ex04.pdf.

Prentice, I C, Farquhar, G D, Fasham, M J R, Goulden, M L, Heimann, M, Jaramillo, V J, Kheshgi, H S, Le Quéré, C, Scholes, R J and Wallace, D W R (2001): 'The carbon cycle and atmospheric carbon dioxide'. In Intergovernmental Panel on Climate Change (IPCC) (ed) *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the IPCC.* Cambridge University Press, Cambridge, New York: pp183–239.

Proelß, A (2004) *Meeresschutz im Völker- und Europarecht. Das Beispiel des Nordostatlantiks.* Duncker & Humblot, Berlin.

Rahmstorf, S (2000) 'The thermohaline ocean circulation: A system with dangerous thresholds? An Editorial Comment'. *Climatic Change* 46: pp247–56.

Rahmstorf, S (2002) 'Ocean circulation and climate during the past 120,000 years'. *Nature* **419**: pp207–14.

Raper, S C B and Braithwaite, R J (2006) 'Low sea level rise projections from mountain glaciers and icecaps under global warming'. *Nature* **439**: pp311–3.

Raven, J, Caldeira, K, Elderfield, H, Hoegh-Guldberg, O, Liss, P S, Riebesell, U, Shepherd, J, Turley, C and Watson, A J (2005) *Ocean Acidification Due to Increasing Atmospheric Carbon Dioxide.* Policy Document 12/05. The Royal Society, London.

Ray, P K (2005) 'Quantitative assessment of marine gas hydrates underway at mms'. The National Energy Technology *Laboratory Methane Hydrate Newsletter* (winter): pp5–7.

Reaka-Kudla, M L (1997): 'The global biodiversity of coral reefs: A comparison with rainforests'. In Reaka-Kudla, M L, Wilson, D E and Wilson, E O (eds) *Biodiversity II: Understanding and Protecting Our Natural Resources.* Joseph Henry/National Academy Press, Washington, DC: pp83–108.

Reid, P C, Holliday, N P and Smyth, T J (2001) 'Pulses in the eastern margin current and warmer water off the north west European shelf linked to North Sea ecosystem changes'. *Marine Ecology Progress Series* **215**: pp283–7.

Richardson, A J and Schoeman, D S (2004) 'Climate impact on plankton ecosystems in the Northeast Atlantic'. *Science* **305**: pp1609–12.

Riebesell, U, Zondervan, I, Rost, B, Tortell, P D, Zeebe, R E and Morel, F M M (2000) 'Reduced calcification of marine plankton in response to increased atmospheric CO_2'. *Nature* **407**: pp364–7.

Riebesell, U (2004) 'Effects of CO_2 enrichment on marine phytoplankton'. *Journal of Oceanography* **60**: pp719–29.

Rignot, E and Jacobs, S (2002) 'Rapid bottom melting widespread near Antarctic ice sheet grounding lines'. *Science* **296**: pp2020–3.

Rignot, E, Vaughan, D G, Schmeltz, M, Dupont, T and MacAyeal, D (2002) 'Acceleration of Pine Island and Thwaites Glaciers, West Antarctica'. *Annals Of Glaciology* **34**: pp189–94.

Rignot, E, Casassa, G, Gogineni, P, Krabill, W, Rivera, A and Thomas, R (2004) 'Accelerated ice discharge from the Antarctic Peninsula following the collapse of Larsen B ice shelf'. *Geophysical Research Letters* **31**(18): L18401.

Rignot, E and Kanagaratnam, P (2006) 'Changes in the velocity structure of the Greenland ice sheet'. *Science* **311**: pp986–90.

Rodrigues, A S L, Andelman, S J, Bakarr, M I, Boitani, L, Brooks, T M, Cowling, R M, Fishpool, L D C, da Fonseca, G A B, Gaston, K J, Hoffman, M, Long, J S, Marquet, P A, Pilgrim, J D, Pressey, R L, Schipper, J, Sechrest, W, Stuart, S N, Underhill, L G, Waller, R W, Watts, M E J and Yan, X (2004) 'Effectiveness of the global protected area network in representing species diversity'. *Nature* **428**: pp641–3.

Rogner, H-H (1997) 'An assessment of world hydrocarbon resources'. *Annual Review of Energy and the Environment* **22**: pp217–62.

Rosenzweig, C and Solecki, W D (eds) (2001) *Climate Change and a Global City: The Potential Consequences of Climate Variability and Change. Metro East Coast. Report for the US Global Change Research Program. National Assessment of the Potential Consequences of Climate Variability and Change for the United States.* Columbia Earth Institute, New York.

Rost, B and Sültemeyer, D (2003). 'Carbon acquisition of bloom-forming marine phytoplankton'. *Limnology and Oceanography* **48**(1): pp55–67.

Rothrock, D D, Yu, Y. and Maykut, G A (1999) 'Thinning of the Arctic sea ice cover'. *Geophysical Research Letters* **26**: pp3469–72.

Rowan, B (2004) 'Thermal adaptation in reef coral symbionts'. *Nature* **430**: pp742.

Royal Commission on Environmental Pollution (2004) *Turning the Tide: Addressing the Impact of Fisheries on the Marine Environment. Twenty-fifth Report.* Royal Commission on Environmental Pollution, London.

Ruddiman, W F (2000) *Earth's climate: past and future.* Freeman, New York.

Sabine, C S, Heimann, M, Artaxo, P, Bakker, C-T, Chen, A, Field, C B, Gruber, N, LeQuere, C, Prinn, R G, Richey, J E, Romero-Lankao, Sathaye, P J and Valentini, R (2003): 'Current status and past trends of the carbon cycle'. In Field, C B and Raupach, M R (eds) *Toward CO_2 Stabilization: Issues, Strategies, and Consequences.* Island Press, Washington, DC: pp17-44.

Sabine, C L, Feely, R A, Gruber, N, Key, R M, Lee, K, Bullister, J L, Wanninkhof, R, Wong, C S, Wallace, D W R, Tilbrook, B, Millero, F J, Peng, T-H, Kozyr, A, Ono, T and Rios, A F (2004) 'The oceanic sink for anthropogenic CO_2'. *Science* **305**: pp367–71.

Sands, P (2003) *Principles of International Environmental Law. Second Edition.* Cambridge University Press, Cambridge, New York.

Sarmiento, J L, Gruber, N, Brzezinski, M A and Dunne, J P (2003) 'High-latitude controls of thermocline nutrients and low latitude biological productivity'. *Nature* **427**: pp56–60.

Sarmiento, J L, Slater, R, Barber, R, Bopp, L, Doney, S C, Hirst, A C, Kleypas, J, Matear, R, Mikolajewicz, U, Monfray, P, Soldatov, V, Spall, S A and Stouffer, R J (2004) 'Response of ocean ecosystems to climate warming'. *Global Biogeochemical Cycles* **18**: ppGB3003.

Sauter, E J, Muyakshin, S I, Charlou, J-L, Schlüter, M, Boetius, A, Jerosch, K, Damm, E, Foucher, J-P and Klages, M (2006) 'Methane discharge from a deep-sea submarine mud volcano into the upper water column by gas hydrate-coated methane bubbles'. *Earth and Planetary Science Letters* **243**(3-4): pp354–65.

Scambos, T A, Bohlander, J A, Shuman, C A and Skvarca, P (2004) 'Glacier acceleration and thinning after ice shelf collapse in the Larsen B embayment, Antarctica'. *Geophysical Research Letters* **31**(18): ppL18402.

Schallenberg, M, Hall, C J and Burns, C W (2003) 'Consequences of climate-induced salinity increases on zooplankton abundance and diversity in coastal lakes'. *Marine Ecology Progress Series* **251**: pp181–9.

Scharroo, R, Smith, W H F and Lillibridge, J F (2005) 'Satellite altimetry and the intensification of Hurricane Katrina'. *Eos* **86**: pp366–7.

Scheffer, M, Carpenter, S, Foley, J A, Folkes, C and Walker, B H (2001) 'Catastrophic shifts in ecosystems'. *Nature* **413**: pp591–6.

Schelling, T C (1992) 'Some economics of global warming'. *American Economic Review* **82**(1): pp1–14.

Schellnhuber, H J, Cramer, W, Nakicenovic, N, Wigley, T and Yohe, G (2006) *Avoiding Dangerous Climate Change.* Cambridge University Press, Cambridge, New York.

Schindler, J and Zittel, W (2000a) *Fossile Energiereserven (nur Erdöl und Erdgas) und mögliche Versorgungsengpässe aus Europäischer Perspektive. Endbericht.* LB-Systemtechnik GmbH, Ottobrunn.

Schindler, J and Zittel, W (2000b) *Öffentliche Anhörung von Sachverständigen (17.10.2000) durch die Enquête-Kommission des Deutschen Bundestages „Nachhaltige Energieversorgung unter den Bedingungen der Globalisierung und der Liberalisierung" zum Thema „Weltweite Entwicklung der Energienachfrage und der Ressourcenverfügbarkeit".*

Schriftliche Stellungnahme zu ausgewählten Fragen der Kommission. LB-Systemtechnik GmbH, Ottobrunn.

Schlesinger, W H (1997) *Biogeochemistry. An Analysis of Global Change.* Academic Press, San Diego, London, Boston.

Schmittner, A (2005) 'Decline of the marine ecosystem caused by a reduction in the Atlantic overturning circulation'. *Nature* 434: pp628–33.

Schwartz, P and Randall, D (2003) 'An Abrupt Climate Change Scenario and Its Implications for United States National Security. A report commissioned by the U.S. Defense Department'. EMS website, http://www.ems.org/climate/pentagon_climatechange.pdf (viewed 13. February 2006).

Sea Wind Europe (2003) 'A Realistic Vision for the Development of Offshore Wind Power to 2020. Studie von Garrad Hassan und anderen im Auftrag von Greenpeace International'. Greenpeace International website, http://www.greenpeace.org/raw/content/usa/press/reports/ sea-wind-europe.pdf (viewed 8. March 2006).

SEEDS (Sustainable Environment & Ecological Development Society) (2005) *Strengthening the Resilience of Local Community in Coastal Areas to Water Related Natural Disasters. Integrating Risk Reduction in Recovery.* SEEDS, New Delhi.

Shah, T, Molden, D, Sakthivadivel, R and Seckler, D (2000) *The Global Groundwater Situation: Overview of Opportunities and Challenges.* International Water Management Institute, Colombo, Sri Lanka.

Sherif, M M and Singh, V P (1999) 'Effect of climate change on sea water intrusion in coastal aquifers'. *Hydrological Processes* **13**: pp1277–87.

Shirayama, Y. and Thornton, H (2005) 'Effect of increased atmospheric CO_2 on shallow water marine benthos'. *Journal of Geophysical Research* **110**: ppC09S8.

Siddique, A K, Baqui, A H, Eusof, A and Zaman, K (1991) '1988 floods in Bangladesh - pattern of illness and causes of death'. *Journal of Diarrhoeal Diseases Research* 9(4): pp310–4.

Siegfriedsen, S, Lehnhoff, M and Prehn, A (2003) 'Primary markets for offshore wind energy outside the European Union'. *Wind Engineering* 27(5): pp419–30.

Skjoldal, H R (ed) (2004) *The Norwegian Sea Ecosystem.* Tapir Academic Press, Trondheim.

Skjoldal, H R and Sætre, R (2004): 'Climate and ecosystem variability'. In Skjoldal, H R (ed) *The Norwegian Sea Ecosystem.* Tapir Academic Press, Trondheim: pp507–34.

Slade, N T (2001) 'Environmental concerns of small islands', *Environmental Policy and Law* **31**(3): 157–8.

Small, C and Nicholls, R J (2003) 'A global analysis of human settlement in coastal zones'. *Journal of Coastal Research* **19**: pp584–99.

Smetacek, V and Nicol, S (2005) 'Polar ocean ecosystems in an changing world'. *Nature* **437**: pp362–8.

Smith, J B and Lazo, J K (2001) 'A summary of climate change impact assessments from the US Country Studies Programme'. *Climatic Change* **50**: pp1–29.

Smith, D E, Shi, S, Brooks, C L, Cullingford, R A, Dawson, A G, Dawson, S, Firth, C R, Foster, I D L, Fretwell, P T, Haggart, B A, Holloway, L K and Long, D (2004) 'The holocene storegga slide Tsunami in the United Kingdom'. *Quaternary Science Reviews* **23**(23-24): pp2291–321.

Snedaker, S, Meeder, J, Ross, M and Ford, R (1994) 'Discussion of Ellison, Joanna C and Stoddart, David R, 1991: Mangrove ecosystem collapse during predicted sea-level rise: holocene analogues and implications'. *Journal of Coastal Research* **10**(2): pp497–8.

SOLAS (Surface-Ocean Lower-Atmosphere Study) (2004) *Science Plan and Implementation Strategy. IGBP Report 50.* IGBP Secretariat, Stockholm.

Soto, C G (2002) 'The potential impacts of global climate change on marine protected areas'. *Reviews in Fish Biology and Fisheries* 11: pp181–95.

SRU (Sachverständigenrat für Umweltfragen) (2004) *Meeresumweltschutz für Nord- und Ostsee. Sondergutachten.* SRU, Berlin.

Stanley, D J and Warne, A G (1998) 'Nile delta in its destruction phase'. *Journal of Coastal Research* **14**(3): pp794–825.

Statoil (2005) *CO_2 Capture and Underground Storage.* Presentation of Mr. Olav Kaarstad, held for WBGU in Stavanger, Norway, on 12.10.2005. Statoil, Stavanger.

Steele, J H (1998) 'Regime shifts in marine ecosystems'. *Ecological Applications* 8(1 supplement): ppS33–S6.

Steffen, W, Sanderson, A, Tyson, P D, Jäger, J, Matson, P A, Moore III, B, Oldfield, F, Richardson, K, Schellnhuber, H-J, Turner II, B L and Wasson, R J (2004) *Global Change and the Earth System. A Planet Under Pressure.* Springer, Berlin, Heidelberg, New York.

Steffen, K and Huff, R (2005) 'Greenland Melt Extent 2005'. Cooperative Institute for Research in Environmental Sciences (CIRES) website, http://cires.colorado.edu/ science/groups/steffen/greenland/melt2005/ (viewed 8. March 2006).

Stive, M J F (2004) 'How important is global warming for coastal erosion?' *Climatic Change* **64**: pp27–39.

Stommel, H (1961) 'Thermohaline convection with two stable regimes of flow'. *Tellus* **13**: pp224–30.

Stone, C D (2004) 'Common but differentiated responsibilities in international law'. *American Journal of International Law* **98**: pp276ff.

Stone, D A and Allen, M R (2005) 'The end-to-end attribution problem: from emissions to impacts'. *Climatic Change* **71**: pp303–18.

Strong, A E, Kearns, E J and Gjovig, K K (2000) 'Sea surface temperature signals from satellites: An update'. *Geophysical Research Letters* **27**: pp1667–70.

SwissRe (Schweizerische Rückversicherungs-Gesellschaft) (1998) 'Überschwemmungen: Ein versicherbares Risiko?' SwissRe website, http://www.swissre.com/INTERNET/pwsfilpr.nsf/vwFilebyIDKEYLu/WWIN-4V2BKW/$FILE/floods.Paras.0002.File.pdf (viewed 8. March 2006).

Tamburri, M N, Peltzer, E T, Friederich, G E, Aya, I, Yamane, K and Brewer, P G (2000) 'A field study of the effects of CO_2 ocean disposal on mobile deep-sea animals'. *Marine Chemistry* **72**: pp95–101.

Titus, J G (1990) 'Greenhouse effect, sea level rise, and land use'. *Land Use Policy* **7**(2): pp138–53.

Titus, J G, Park, R A, Leatherman, S P, Weggel, J R, Greene, M S, Mausel, P W, Brown, S, Gaunt, G, Trehan, M and Yohe, G (1991) 'Greenhouse effect and sea level rise: the cost of holding back the sea'. *Coastal Management* **19**: pp171–204.

Turley, C, Blackford, J C, Widdicombe, S, Lowe, D, Nightingale, P D and Rees, A P (2006): 'Reviewing the impact of increased atmospheric CO_2 on oceanic pH and the marine ecosystem'. In Schellnhuber, H J, Cramer, W, Nakicenovic, N, Wigley, T and Yohe, G (eds) *Avoiding Dangerous Climate Change.* Cambridge University Press, Cambridge, New York: pp65–70.

Turner, R K, Subak, S and Adger, W N (1996) 'Pressures, trends, and impacts in coastal zones: interactions between socioeconomic and natural systems'. *Environmental Management* **20**(2): pp159–73.

Tyler, P A (2003) 'Disposal in the deep sea: analogue of nature or faux ami?' *Environmental Conservation* **30**: pp26–39.

Tyrell, T, Holligan, P M and Mobley, C D (1999) 'Optical impacts of oceanic coccolithophore blooms'. *Journal of Geophysical Research* **104**(C2): pp3223–41.

UN (United Nations) (ed) (2004) *Human Settlements on the Coast. UN Atlas of the Oceans.* UN, New York.

UNEP (United Nations Environment Programme) (2002) *GEO – Global Environment Outlook 3. Past, Present and Future Perspectives.* London: Earthscan.

UNEP (United Nations Environment Programme) (2005) *Pacific Island Villagers First Climate Change „Refugees". UNEP News Release.* UNEP, Nairobi.

UNESCO (United Nations Educational Scientific and Cultural Organization) (1972) Übereinkommen zum Schutz des Kultur- und Naturerbes der Welt. Organisation der Vereinten Nationen für Bildung, Wissenschaft, Kultur und Kommunikation. Deutsche Übersetzung aus dem Bundesgesetzblatt, Jahrgang 1977, Teil II, Nr. 10. UNESCO website, http://www.unesco.de/c_bibliothek/info-welterbekonvention.pdf (viewed 8. March 2006).

UNESCO (United Nations Educational Scientific and Cultural Organization) (2006) World Heritage List. Results by Country. UNESCO website, http://whc.unesco.org/en/list/ (viewed 27. March 2006).

UNFCCC (United Nations Framework Convention on Climate Change) (1992) *Framework Convention on Climate Change.* United Nations (UN), New York.

UNGA (United Nations General Assembly) (2004) *Oceans and the Law of the Sea.* UNGA Resolution 59/24. United Nations (UN), New York.

UN ISDR (United Nations Interagency Secretariat of the International Strategy for Disaster Reduction) (2005a) *International Strategy for Disaster Reduction. Draft Resolution Submitted by the Vice-Chairman of the Committee, Mr. Stefano Toscano (Switzerland), on the Basis of Informal Consultations Held on Draft Resolution A/C.2/60/L.25.* UN ISDR, Geneva.

UN ISDR (United Nations Interagency Secretariat of the International Strategy for Disaster Reduction) (2005b) *Natural Disasters and Vulnerability. Draft Resolution Submitted by the Vice-Chairman of the Committee, Mr. Stefano Toscano (Switzerland), on the Basis of Informal Consultations Held on Draft Resolution A/C.2/60/L.27.* UN ISDR, Geneva.

UN ISDR (United Nations Interagency Secretariat of the International Strategy for Disaster Reduction) (2005c) *Progress Report: Worldwide Survey of Early Warning Systems. A Briefing Prepared for the EOSG by the ISDR Secretariat, 31 July 2005.* UN ISDR, Geneva.

Velicogna, I and Wahr, J (2006) 'Measurements of time-variable gravity show mass loss in Antarctica'. *Science* **311**: pp1754–6.

Veron, J E N (1986) *Corals of Austrakia and the Indo-Pacific.* Angus and Robertson, London, Sidney.

Virdin, J and Schorr, J (2001) *Hard Facts, Hidden Problems: A Review of current Data on Fishing Subsidies.* World Wildlife Fund, Brussels.

Waelbroeck, C, Labeyrie, L, Michel, E, Duplessy, J C, McManus, J F, Lambeck, K, Balbon, E and Labracherie, M (2002) 'Sea-level and deep water temperature changes derived from benthonic foraminifera isotopic records'. *Quaternary Science Reviews* **21**: pp295–305.

Walsh, N P (2003) 'St Petersburg races to halt floods'. The Guardian (29.07.2003), St. Petersburg.

Warner, R (2001): 'Marine protected areas beyond national jurisdiction: existing legal principles and a future international framework'. In Haward, M (ed) *Integrated Oceans Management: Issues in Implementing Australia's Oceans Policy.* Cooperative Research Centre for Antarctica and the Southern Ocean, Hobart: pp55–76.

Watson, A J and Orr, J C (2003): 'Carbon dioxide fluxes in the global ocean'. In Fasham, M J R (ed) *Ocean Biogeochemistry. The IGBP Series.* Springer, Berlin, Heidelberg, New York.

Wavenet (2003) 'Results from the Work of the European Thematic Network on Wave Energy'. Wavenet (European Wave Energy Thematic Network) website, http://www.wave-energy.net/Library/WaveNet_FullReport(11.1).pdf (viewed 27. May 2005).

WBGU (German Advisory Council on Global Change) (1995) *Scenario for the Derivation of Global CO_2 Reduction Targets and Implementation Strategies. Statement on the Occasion of the First Conference of the Parties to the Framework Convention on Climate Change in Berlin.* 1995 Special Report. WBGU, Bremerhaven.

WBGU (German Advisory Council on Global Change) (2001) *World in Transition: Conservation and Sustainable Use of the Biosphere.* 1999 Report. Earthscan, London.

WBGU (German Advisory Council on Global Change) (2002) *Charging the Use of Global Commons.* Special Report 2002. WBGU, Berlin.

WBGU (German Advisory Council on Global Change) (2003) *Climate Protection Strategies for the 21st Century: Kyoto and beyond.* Special Report 2003. WBGU, Berlin.

WBGU (German Advisory Council on Global Change) (2004) *World in Transition: Towards Sustainable Energy Systems.* 2003 Report. Earthscan, London.

WCDR (World Conference on Disaster Reduction) (2005) *Hyogo Framework for Action 2005–2015: Building the Resilience of Nations and Communities to Disasters. Extract From the Final Report of the World Conference on Disaster Reduction (Document A/CONF.206/6).* International Strategy for Disaster Reduction (ISDR), Kyoto.

Webster, P J, Holland, G J, Curry, J A and Chang, H-R (2005) 'Changes in tropical cyclone number, duration, and intensity in a warming environment'. *Science* **309**: pp1844–6.

WHO (World Health Organisation) (2002) Flooding: Health Effects and Preventive Measures. Fact Sheet 05/02. WHO, Copenhagen, Rome.

Wilkinson, C (2004) *Status of Coral Reefs of the World 2004.* Australian Institute of Marine Sciences, Townsville.

Willis, J K, Roemmich, D and Cornuelle, B (2004) 'Interannual variability in upper ocean heat content, temperature, and thermosteric expansion on global scales'. *Journal of Geophysical Research-Oceans* **109**: ppC12036.

Winguth, A, Mikolajewicz, U, Gröger, M, Maier-Reimer, E, Schurgers, G and Vizcaino, M (2005) 'Centennial-scale interactions between the carbon cycle and anthropogenic climate change using a dynamic Earth system model'. *Geophysical Research Letters* **32**: ppdoi:10.1029/2005GL023681.

Wolfrum, R (2000): 'International environmental law: purposes, principles and means of ensuring compliance'. In Morrison, F L and Wolfrum, R (eds) *International, Regional and National Environmental Law.* Kluwer Law International, The Hague, London, Boston: pp3–70.

Wood, L J, Fish, L, Laughren, J and Pauly, D (2005) *A Global Review Of Marine Protected Areas.* Abstract for the First International Marine Protected Areas Congress (Geelong, Australia 23–28 October 2005).

Woodroffe, C D, Nicholls, R J, Saito, Y, Chen, Z and Goodbred, S L (2006): 'Landscape variability and the response of Asian megadeltas to environmental change'. In Harvey, N (ed) *Global Change Implications for Coasts in the Asia-Pacific Region.* Springer, Berlin, Heidelberg, New York.

World Bank (ed) (2004) *Saving Fish and Fishers. Toward Sustainable and Equitable Governance of the Global Fishing Sector.* World Bank, Washington, DC.

Worm, B and Myers, R A (2003) 'Meta-analysis of cod-shrimp interactions reveals top-down control in oceanic food webs'. *Ecology* 84(1): pp162–73.

Worm, B and Myers, R A (2004) 'Managing fisheries in a changing climate'. *Nature* **429**: pp15.

WPC (World Parks Congress) (2003a) *Recommendations of the Vth IUCN World Parks Congress. 8–17 September 2003, Durban.* (IUCN) The World Conservation Union, Gland.

WPC (World Parks Congress) (2003b) *Message of the Vth IUCN World Parks Congress to the Convention on Biological Diversity.* (IUCN) The World Conservation Union, Gland.

WRI (World Resources Institute) (2001) *Pilot Analysis of Global Ecosystems. Coastal Ecosystems.* WRI, Washington DC.

WSSD (World Summit on Sustainable Development) (2002) *Plan of Implementation.* WSSD, Johannesburg, New York.

Yeung, Y. (2001) 'Coastal mega-cities in Asia: transformation, sustainability and management'. *Ocean & Coastal Management* **44**: pp319–33.

Yohe, G, Neumann, J and Marshall, P (1999): 'The economic damage induced by sea-level rise in the United States'. In Mendelsohn, R and Neumann, J E (eds) *The Impact of Climate Change on the United States Economy.* Cambridge University Press, Cambridge, New York: pp178–208.

Zachos, J, Pagani, M, Sloan, L, Thomas, E and Billups, K (2001) 'Trends, rhythms, and aberrations in global climate 65 ma to present'. *Science* **292**: pp686–93.

Zhang, K, Douglas, B C and Leatherman, S P (2004) 'Global warming and coastal erosion'. *Climatic Change* **64**: pp41–58.

Zickfeld, K, Levermann, A, Keith, D W, Kuhlbrodt, T, Morgan, M G and Rahmstorf, S (submitted) 'Experts' view on risk of future ocean circulation changes'. *Climatic Change.*

Zondervan, I, Zeebe, R E, Rost, B and Riebesell, U (2001) 'Decreasing marine biogenic calcification: a negative feedback on rising atmospheric CO_2'. *Global Biogeochemical Cycles* **15**(2): pp507–16.

Zwally, H J, Abdalati, W, Herring, T, Larson, K, Saba, J and Steffen, K (2002) 'Surface melt-induced acceleration of Greenland ice-sheet flow'. *Science* **297**: pp218–22.

Zwally, H J G, Mario, B, Jun, L, Cornejo, H G, Beckley, M A, Brenner, A C, Saba, J L and Donghui, Y. (2005) 'Mass changes of the Greenland and Antarctic ice sheets and shelves and contributions to sea-level rise: 1992–2002'. *Journal of Glaciology* **51**(175): pp509–27.

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Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals?

John M Guinotte[1,2], James Orr[3], Stephen Cairns[4], Andre Freiwald[5], Lance Morgan[1], and Robert George[6]

The answer to the title question is uncertain, as very few manipulative experiments have been conducted to test how deep-sea scleractinians (stony corals) react to changes in seawater chemistry. Ocean pH and calcium carbonate saturation are decreasing due to an influx of anthropogenic CO_2 to the atmosphere. Experimental evidence has shown that declining carbonate saturation inhibits the ability of marine organisms to build calcium carbonate skeletons, shells, and tests. Here we put forward a hypothesis suggesting that the global distribution of deep-sea scleractinian corals could be limited in part by the depth of the aragonite saturation horizon (ASH) in the world's oceans. Aragonite is the metastable form of calcium carbonate used by scleractinian corals to build their skeletons and the ASH is the limit between saturated and undersaturated water. The hypothesis is tested by reviewing the distribution of deep-sea, bioherm-forming scleractinian corals with respect to the depth of the ASH. Results indicate that > 95% of 410 coral locations occurred in saturated waters during pre-industrial times. Projections indicate that about 70% of these locations will be in undersaturated waters by 2099. Lab experimentation, in situ experimentation, and monitoring efforts are needed to quantify the effects of changing seawater chemistry on deep-sea coral ecosystems.

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Seawater chemistry and the calcium carbonate saturation state of the world's oceans are changing as a result of the addition of fossil fuel CO_2 to the atmosphere (Kleypas *et al.* 1999; Feely *et al.* 2004; Orr *et al.* 2005). The pH of surface oceans has dropped by 0.1 units since the industrial revolution and if fossil fuel combustion continues at present rates, the pH of the world's oceans will probably drop another 0.3 to 0.4 units by 2100 (Mehrbach *et al.* 1973; Lueker *et al.* 2000; Caldeira and Wickett 2003). "This influx of anthropogenic CO_2 is causing the world's oceans to become more acidic, to the detriment of corals and other marine calcifiers, including plankton, which occupies the base of marine food webs. Corals and some species of plankton (coccolithophores and foraminiferans) use carbonate ions obtained from the surrounding water to build their skeletons and protective shells. As oceanic pH and carbonate ions decrease as a result of rising fossil fuel CO_2 levels, the calcification mechanisms and abilities of many marine organisms will be negatively impacted.

In a nutshell:

- Anthropogenic CO_2 from the combustion of fossil fuels is altering the chemistry of the world's oceans
- Seawater chemistry changes have the potential to alter the distribution and abundance of marine organisms that use calcium carbonate to build their shells and skeletons (corals, plankton, etc) and the organisms that depend on them for survival (fishes, marine mammals, etc)
- Major funding and experimentation is needed to quantify the effects of changing seawater chemistry on marine calcifiers; experimentation should be a top priority for countries with commercial industries dependent on deep-sea coral bioherms
- The transition from fossil fuels to alternative "clean" sources of energy needs to occur as soon as possible

In recent decades, only half of anthropogenic CO_2 has remained in the atmosphere; the other half has been taken up by the terrestrial biosphere (20%) and the oceans (30%) (Feely *et al* 2004; Sabine *et al* 2004). This uptake initiates a series of chemical reactions, increasing the hydrogen ion concentration (H^+), lowering pH, and reducing the number of carbonate (CO_3^{2-}) ions available in seawater. All of this will make it more difficult for marine calcifying organisms to form biogenic calcium carbonate ($CaCO_3$). Although little is known about the effects of decreasing aragonite saturation state on deep-sea corals, lab experiments have conclusively shown that lowering carbonate ion concentration reduces calcification rates in tropical reef builders by 7–40% (Gattuso *et al.* 1999; Langdon *et al.* 2000, 2003; Marubini *et al.* 2003). In fact, all marine calcifying organisms tested to date have shown a similar negative response to decreasing carbonate saturation state. As the world's oceans become less saturated over time, corals are expected to build weaker

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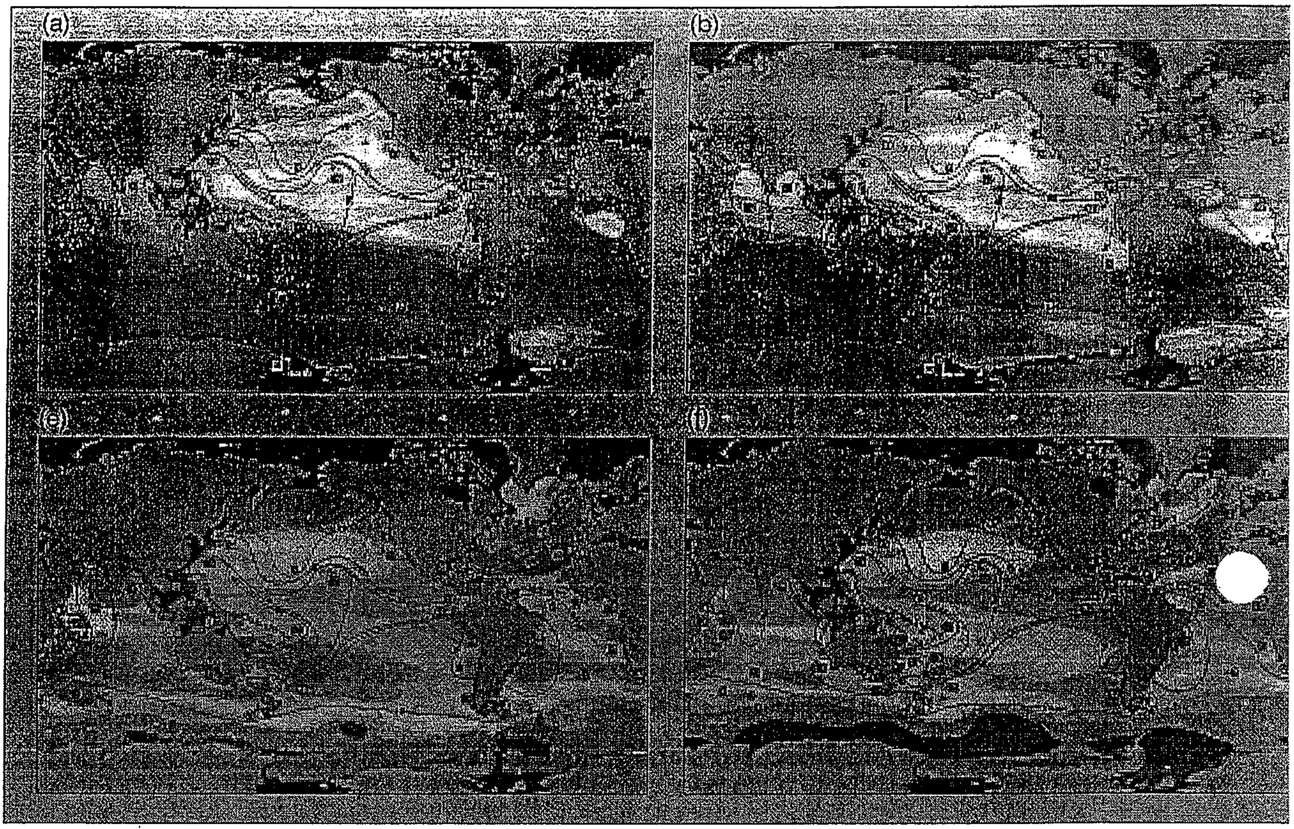

skeletons (a process similar to osteoporosis in humans) and/or experience slower growth rates (Buddemeier and Smith 1999; Gattuso *et al.* 1999; Kleypas *et al.* 1999; Guinotte *et al.* 2003). Both processes will make it more difficult for corals to withstand erosion and to retain a competitive advantage over other marine organisms.

Seawater chemistry: the movement of the aragonite saturation horizon (ASH)

Orr *et al.* (2005) calculated future changes in carbonate saturation state (aragonite and calcite) for the world's oceans and found that decreasing carbonate saturation state will not be limited to surface waters, but will occur in the deep sea as well. Orr's aragonite saturation horizon (ASH; the limit between saturation and undersaturation) projections were based on the Intergovernmental Panel on Climate Change (IPCC) IS92a scenario (788 ppmv in the year 2100). The IS92a scenario is generally regarded as the "business-as-usual" scenario, where nations do very little to curb emissions. These projections were incorporated in a geographic information system (GIS) with approximately 410 records of deep-sea bioherm-forming corals (*Lophelia pertusa*, *Madrepora oculata*, *Goniocorella dumosa*, *Oculina varicosa*, *Enallopsammia profunda*, *Solenosmilia variabilis*) provided by Andre Freiwald (Freiwald *et al.* 2004; Figure 1). Bioherm is defined as an ancient organic reef of moundlike form built by a variety of marine invertebrates, including corals, echinoderms, gastropods, mollusks, and others (Encyclopedia Britannica 2006). Cairns' (in press) diversity contours for 706 species of azooxanthellate scleractinian corals were overlayed on ASH projections to highlight the relationship between coral diversity and ASH depth.

The projections clearly show the ASH moving shallower over time as atmospheric CO_2 concentrations increase. Aragonite projections were used because aragonite is calcium carbonate mineral form deposited by scleracti corals to build their skeletons. Calcite, the less soluble form of $CaCO_3$ used by octocorals (soft corals) and other marine organisms, is not included in this study. It should be noted that the sclerites of octocorals are calcitic, but the axes may be composed of calcite, aragonite, or amorphous carbonate hydroxylapatite (Bayer and Macintyre 2001). The saturation depth for calcite is considerably greater than for aragonite because calcite is less soluble than aragonite in seawater. However, calcitic marine organisms will not be immune from saturation changes in the oceans because the depth of the calcite saturation horizon is also moving progressively shallower over time.

Based on 410 known locations of deep-sea, bioherm-forming corals obtained from Freiwald *et al.* (2004) and and the estimated pre-industrial (year 1765) ASH depth, >95% of the coral locations were found in areas that were supersaturated (omega > 1) in terms of aragonite (Figure 2). The mean omega value for all coral locations in pre-industrial times was 1.98 (supersaturated). By 2099, only 30% of coral locations remain in supersaturated waters, the vast majority of which are located in the North Atlantic,

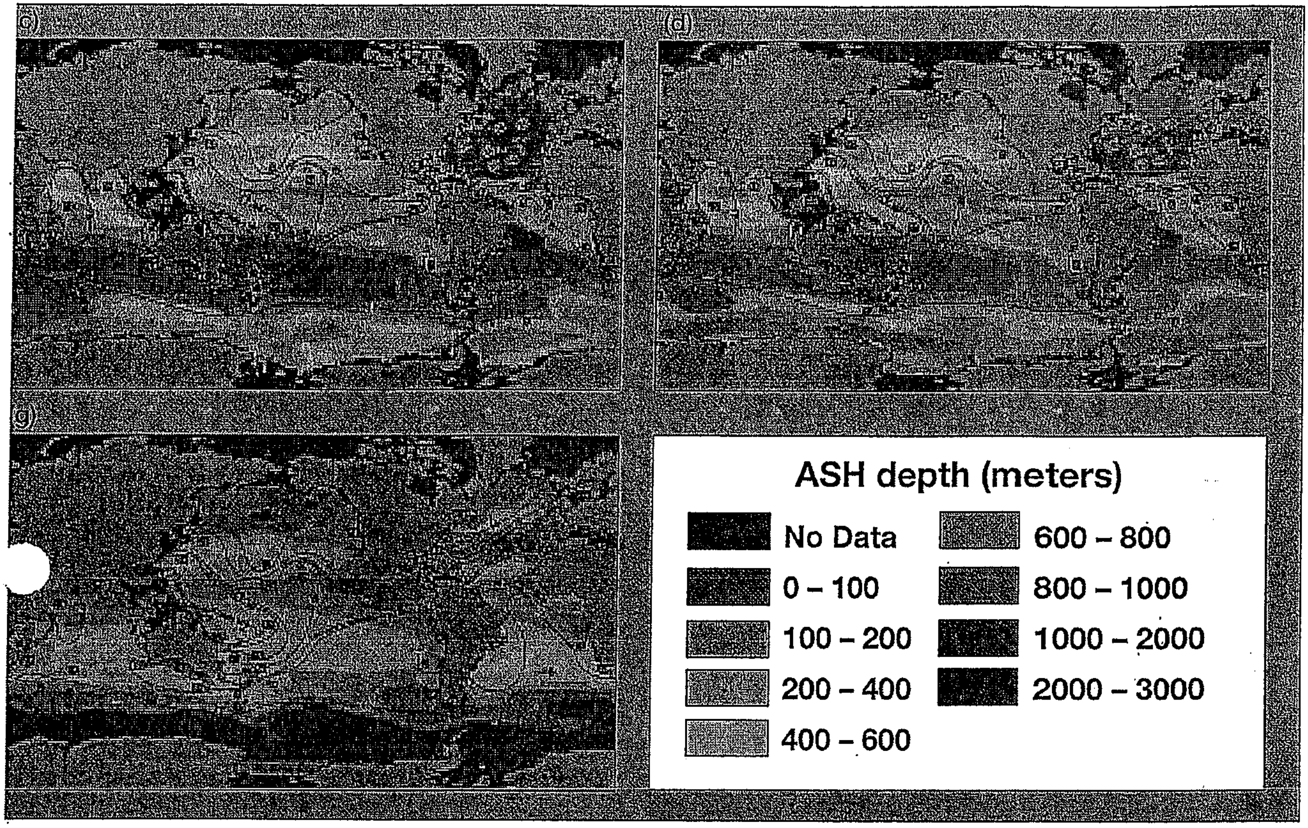

Figure 1. *Depth of the aragonite saturation horizon (ASH), locations of deep-sea bioherm-forming corals, and diversity contours for 706 species of azooxanthellate corals. (a) Projected ASH depth for year 1765; $pCO_2=278$ ppmv. (b) Estimated ASH depth for year 1995; $pCO_2=365$ ppmv. (c) Projected ASH depth for year 2020; $pCO_2=440$ ppmv. (d) Projected ASH depth for year 2040; $pCO_2=513$ ppmv. (e) Projected ASH depth for year 2060; $pCO_2=594$ ppmv. (f) Projected ASH depth for year 2080; $pCO_2=684$ ppmv. (g) Projected ASH depth for year 2099; $pCO_2=788$ ppmv. Green triangles are locations of the six deep-sea bioherm-forming coral species. Black areas appearing in the Southern Ocean in figures 1e–g and the North Pacific in Figure 1g indicate areas where ASH depth has reached the surface. Numerals not falling on diversity contours indicate number of azooxanthellate coral species.*

where the ASH remains relatively deep. Mean omega values for all coral locations in 2099 is 0.99 (undersaturated). Lab experiments performed on hermatypic, shallow-water corals in supersaturated waters have shown that relatively modest reductions in aragonite saturation state can cause substantial decreases in calcification (Langdon *et al.* 2003; Langdon and Atkinson 2005). If future experiments show the same is true for deep-sea, bioherm-forming corals, then calcification rates may decrease well before corals become undersaturated with respect to aragonite.

■ Deep-sea coral distributions in the Atlantic and Pacific

Deep-sea scleractinian corals are found in all ocean basins. Figure 1 shows that the center of species diversity for azooxanthellate corals are the waters surrounding the Philippines (~ 160 species), followed by New Caledonia (~ 140 species), and the Caribbean Sea (~ 80 species) (Cairns in press). The majority of deep-sea, bioherm-forming scleractinians have been discovered in the North Atlantic, which is probably a function of sampling bias, but may also be connected to the ASH depth. Extensive deep water surveys in the North Pacific (Aleutian and Hawaiian Islands; Baco pers comm; Stone pers comm) have not documented deep-sea scleractinian bioherms like those found in the North Atlantic, although some records of small pieces exist from collections (Rogers 1999). One possible reason for their absence in the North Pacific might be the shallow depth of the ASH throughout much of the region.

The ASH in the North Atlantic is very deep (> 2000 m) and many of the deep-sea scleractinians found in these waters are bioherm-forming, robust, and cover areas several kilometers in size. The *Lophelia pertusa* bioherms off the coasts of Norway and Sweden are prime examples of such corals; they cover large areas and occur at relatively shallow depths (Fosså *et al.* 2002). Deep-sea scleractinian accretion in the North Atlantic produces structures several meters in height, due to the corals' ability to grow on top of the dead skeletons (coral rubble) of their predecessors. Bioherm accretion in the deep sea is a slow process; the age of North Atlantic corals vary, but recent estimates indicate they are less than 10 000 years old (Schröder-Ritzrau *et al.* 2005).

North Pacific deep-sea coral ecosystems are quite unlike those found in the North Atlantic. Present-day ASH depth in the North Pacific is relatively shallow

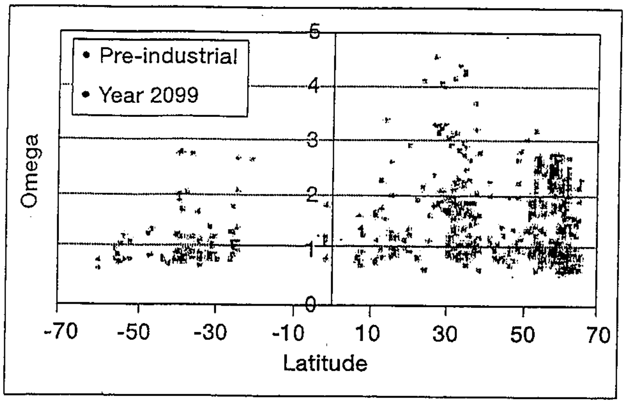

Figure 2. Projected ASH values for deep-sea coral locations in pre-industrial times (year 1765; black dots) and in the year 2099 (red dots). ASH (saturation boundary) is omega = 1; n = 410.

(50–600 m) and scleractinian corals found there do not form bioherms. North Pacific scleractinians tend to be found in solitary colonies and the region is dominated by octocorals (soft corals, stoloniferans, sea fans, gorgonians, sea pens) and stylasterids. Octocorals and a small percentage (about 10%) of stylasterid species use calcite to build their spicules and skeletons (Carins and Macintyre 1992). Cairns and Macintyre (1992) studied 71 stylasterid species, seven of which were from the temperate North Pacific. Remarkably, six of the seven species had calcitic skeletons (the less soluble polymorph), even though calcite is rare among the stylasterids. These calcitic stylasterids were found in abundance at depths of 50–500 m. The Aleutian Islands, a region where the approximate depth of the ASH is < 150 m, is one example of an area dominated by octocorals, stylasterids, and sponges.

The depth at which many azooxanthellate corals are found in the waters surrounding the Galápagos Islands lends further credence to the hypothesized ASH–scleractinian relationship. Figure 1 shows global diversity contours for 706 species of azooxanthellate corals, regardless of depth. Across all ocean basins, 91 of the 706 species (13%) occur exclusively in shallow water (0–50 m). However, 19 of the 42 species (45%) found in the waters off the Galápagos Islands are found in less than 50 m of water. This is interesting, given the fact that present-day ASH depth in the waters surrounding the Galapágos is quite shallow (< 300 m) due to upwelling.

Stony corals in the North Pacific are found in close proximity to, or at slightly shallower depths than, the ASH, suggesting that corals may be surviving in a marginal aragonite saturation state environment. Coral rubble fields are nonexistent in the North Pacific, where aragonite dissolution rates in the upper 1000 m are twice as high as the dissolution rates of the North Atlantic (Feely *et al.* 2004). The shallow depth of the ASH and the high dissolution rates in North Pacific waters could work synergistically to make bioherm accretion unlikely, if not impossible. Corals may have biophysical mechanisms which allow them to survive in close proximity to the ASH, but not to flourish and form accumulated structures such as those found in the North Atlantic, where the ASH is much deeper and dissolution rates are low.

The North Atlantic is not the only region where deep-sea scleractinians form bioherms. Such structures are also found in several ocean basins, where the ASH is deep and dissolution rates are low (eg the South Pacific and South Atlantic). Scleractinians are not known to form deep bioherms in the North Pacific or northern Indian Ocean, where the ASH is shallow and dissolution rates are high. A strong qualitative correlation exists between areas of low azooxanthellate coral diversity and areas where the present-day ASH is relatively shallow (Figure 1b). These areas include the temperate North Pacific, off the west coast of South America, the northern Indian Ocean, and off the southwest coast of Africa.

The exception to the low scleractinian diversity–shallow ASH relationship is the Southern Ocean, where scleractinian diversity is low (< 10 species) and the present-day ASH depth is relatively deep (> 800 m) for much o region. Low species diversity in the Southern Ocean is not due to lack of exploration in the region and it is generally accepted that the taxonomy of Antarctic scleractinians is fairly well known (Cairns pers comm). The reason(s) for this exception are not known, but possibilities include past and present barriers to coral recruitment and/or the extent of sea ice throughout geologic history.

■ Food availability

There is warranted concern that changing seawater chemistry could have an indirect, detrimental effect on deep-sea corals, by limiting the amount of food and nutrients available to deep-sea coral ecosystems. Very little information exists on the food sources of these organisms, but it is probable that they depend on suspended organic matter zooplankton for nourishment (Kiriakoulakis *et al.* 20 Since corals are sessile filter feeders, they can obtain nourishment either from organic matter falling from the surface or via currents that bring organic matter and zooplankton to the coral. Deep-sea corals are found in waters that have above-average surface primary productivity, indicating that food falling from the surface is important to their survival (Figures 3 and 4). There is also a strong correlation between chlorophyll-a concentration and particulate organic carbon (POC) in the world's oceans (Legendre and Michaud 1999; Gardner unpublished).

Many species of plankton (eg coccolithophores and foraminiferans) and pteropods (small gastropod mollusks), which form the base of marine food webs, use carbonate ions to build their $CaCO_3$ shells/tests and are sensitive to the seawater chemistry changes previously noted (Riebesell *et al.* 2000; Riebesell 2004; Orr *et al.* 2005). If changing seawater chemistry causes a reduction in phytoplankton and zooplankton production in surface waters, the feedback to deep-sea coral ecosystems will probably be negative, as deep-sea corals may not be able to attain their nutritional requirements.

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Figure 3. *Coral locations and global average chlorophyll-a concentration for the years 1997–2000. Red dots represent 1565 locations of the six deep-sea bioherm-forming coral species. Note: legend values for chlorophyll-a concentration range from 0–255; Data used was converted from mg/m^3 to a color unit scale, with 0 indicating no chlorophyll and 255 the highest chlorophyll concentration found in the oceans for this time period. Figures in parentheses indicate the percentage of total coral records within each concentration range. (Source: SeaWiFS Project, NASA/Goddard Space Flight Center.)*

■ Other factors

Changing seawater chemistry is not the only threat deep-sea corals face in the age of global climate change. These organisms have evolved in steady-state, cold, dark, nutrient-rich environments and it is possible that changes in temperature, salinity, or water motion may also have negative consequences. Model projections for these variables vary considerably, uncertainties are high, and the biological feedbacks to changes in these factors are poorly understood in terms of their effects on deep-sea corals. Nevertheless, worrisome physical changes are taking place in the world's oceans. Global sea temperatures are rising in the deep-sea, due to increasing amounts of anthropogenic CO_2 in the atmosphere (Barnett *et al.* 2005). Rising sea temperatures will probably influence deep-sea coral calcification rates, physiology, and biochemistry, even though specific ranges and thresholds are not yet known.

Climate change is also altering the salinity of the world's oceans (Curry *et al.* 2003). Increased evaporation in tropical waters has led to more saline conditions at lower latitudes, whereas glacial ice melt in polar waters has produced less saline conditions at higher latitudes. Freshwater inputs to high latitude waters are expected to increase as global temperatures continue to rise and the influx of freshwater may slow down water circulation, reduce upwelling, and/or alter the trajectory of present-day current patterns (Curry *et al.* 2003). Since deep-sea corals are sessile organisms that depend on currents to bring them food, any change in the direction and/or velocity of currents could have a serious impact on their distribution.

■ Summary

The oceans are changing both chemically and physically as a result of the uptake of anthropogenic CO_2. Shallow-water corals and other marine calcifiers react negatively when

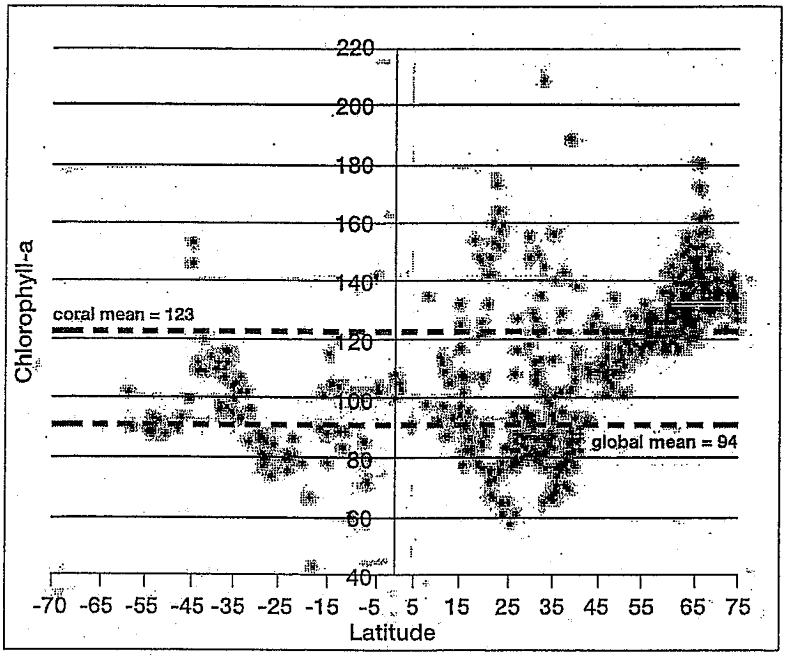

Figure 4. *Chlorophyll-a concentration for 1565 locations of the six deep-sea bioherm-forming coral species plotted with latitude.*

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exposed to reduced carbonate saturation state conditions. Biological feedbacks and the reactions of marine organisms to these changes will be complex and will probably affect all trophic levels of the world's oceans. Deep-sea coral ecosystems will not be immune from these changes and probably have not experienced the combination of chemical and physical stresses described for a very long time. The synergistic effects of these stresses occurring in concert are uncertain, but these changes will probably have serious implications for deep-sea coral ecosystems.

The effects of decreasing aragonite saturation state on deep-sea, bioherm-forming scleractinians are not well understood and further experimentation is warranted. Lab and in situ monitoring experiments are needed to help us understand and quantify how chemical changes might affect deep-sea coral ecosystems in the future. If (a) aragonite saturation state is as important to deep-sea scleractinians as it is to shallow-water hermatypic corals and (b) the depth of the ASH moves progressively into shallower waters as projected, then over time, deep-sea, bioherm-forming corals will be exposed to an increasingly marginal environment. If the hypothesis presented is valid and the shallow depth of the ASH in certain regions of the oceans (eg the North Pacific) is limiting deep-sea scleractinians from forming bioherms, then we can expect substantial changes in the distribution of deep-sea corals and the structures they form within this century. The upward migration of the ASH has the potential to alter the global distribution of deep-sea scleractinian bioherms and the organisms that depend on them.

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■ References:

Barnett TP, Pierce DW, AchutaRao K, *et al.* 2005. Penetration of human-induced warming into the world's oceans. *Science* **309**: 284–87.

Bayer FM and Macintyre IG. 2001. The mineral composition of the axis and holdfast of some gorgonacean octocorals (Coelenterata: Anthozoa), with special reference to the family Gorgoniidae. *Proc Biol Soc Wash* **114**: 309–45.

Buddemeier RW and Smith SV. 1999. Coral adaptation and acclimatization: a most ingenious paradox. *Am Zool* **39**: 1–9.

Caldeira K and Wickett ME. 2003. Anthropogenic carbon and ocean pH. *Nature* **425**: 365.

Cairns SD and Macintyre IG. 1992. Phylogenetic implications of calcium carbonate mineralogy in the Stylasteridae (Cnidaria: Hydrozoa). *Palaios* **7**: 96–107.

Cairns SD. Deep-water corals: a primer. *Bull Mar Sci.* In press.

Curry R, Dickson B, and Yashayaev I. 2003. A change in the freshwater balance of the Atlantic Ocean over the past four decades. *Nature* **426**: 826–29.

Encyclopedia Britannica. 2006. Bioherm. Encyclopedia Britannica Premium Service. www.britannica.com/eb/article-9079259. Viewed 15 February 2006.

Feely R, Sabine C, Lee K, *et al.* 2004. Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. *Science* **305**: 362–66.

Fosså JH, Mortensen PB, and Furevik DM. 2002. The deep-water coral *Lophelia pertusa* in Norwegian waters: distribution and fishery impacts. *Hydrobiologia* **471**: 1–12.

Freiwald A, Fosså JH, Grehan A, *et al.* 2004. Cold-water coral reefs. Cambridge, UK: UNEP–WCMC.

Gardner WD, Mishonov AV, and Richardson MJ. Global POC concentrations from in-situ and satellite data. Unpublished.

Gattuso J-P, Allemand D, and Frankignoulle M. 1999. Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: a review on interactions and control by carbonate chemistry. *Am Zool* **39**: 160–83.

Guinotte JM, Buddemeier RW, and Kleypas JA. 2003. Future coral reef habitat marginality: temporal and spatial effects of climate change in the Pacific basin. *Coral Reefs* **22**: 551–58.

Kiriakoulakis K, Harper E, Wolff GA, *et al.* 2005. Lipids and nitrogen isotopes of two deep-water corals from the North-East Atlantic: initial results and implications for their nutrition. In: Freiwald A and Roberts JM (Eds). Cold-water corals and ecosystems. Heidelberg, Germany: Springer Verlag.

Kleypas JA, Buddemeier RW, Archer D, *et al.* 1999. Geochemical consequences of increased atmospheric carbon dioxide or reefs. *Science* **284**: 118–20.

Langdon C and Atkinson MJ. 2005. Effect of elevated pCO_2 on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment. *J Geophys Res* **110**: C09S07. doi:10.1029/2004JC002576.

Langdon C, Broecker W, Hammond D, *et al.* 2003. Effect of elevated CO_2 on the community metabolism of an experimental coral reef. *Global Biogeochem Cy* **17**: 1–14.

Langdon C, Takahashi T, Sweeney C, *et al.* 2000. Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. *Global Biogeochem Cy* **14**: 639–54.

Legendre L and Michaud J. 1999. Chlorophyll-a to estimate the particulate organic carbon available as food to large zooplankton in the euphotic zone of oceans. *J Plankton Res* **21**: 2067–83.

Lueker TJ, Dickson AG, and Keeling CD. 2000. Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. *Mar Chem* **70**: 105–19.

Marubini F, Ferrier-Pages C, and Cuif JP. 2003. Suppressic skeletal growth in scleractinian corals by decreasing ambient carbonate-ion concentration: a cross-family comparison. *Proc R Soc Lond B* **270**: 179–84.

Mehrbach C, Culberson CH, Hawley JE, and Pytkowicz RM. 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressue. *Limnol Ocenaogr* **18**: 897–907.

Orr JC, Fabry VJ, Aumont O, *et al.* 2005. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* **437**: 681–86.

Riebesell U. 2004. Effects of CO_2 enrichment on marine phytoplankton. *J Oceanogr* **60**: 719–29.

Riebesell U, Zondervan I, Rost B, *et al.* 2000. Reduced calcification of marine plankton in response to increased atmospheric CO_2. *Nature* **407**: 364–67.

Rogers AD. 1999. The biology of *Lophelia pertusa* (Linnaeus 1758) and other deep-water reef-forming corals and impacts from human activities. *Internat Rev Hydrobiol* **84**: 315–406.

Sabine CL, Feely RA, Gruber N, *et al.* 2004. The oceanic sink for anthropogenic CO_2. *Science* **305**: 367–71.

Schröder-Ritzrau A, Freiwald A, and Mangini A. 2005. U/Th-dating of deep-water corals from the eastern North Atlantic and the western Mediterranean Sea. In: Freiwald A and Roberts JM (Eds). Cold-water corals and ecosystems. Heidelberg, Germany: Springer Verlag.

OSPAR Commission
for the Protection of the Marine
Environment of the North-East
Atlantic

Commission OSPAR
pour la protection du milieu marin de
l'Atlantique du Nord-Est

EFFECTS ON THE MARINE ENVIRONMENT OF OCEAN ACIDIFICATION RESULTING FROM ELEVATED LEVELS OF CO_2 IN THE ATMOSPHERE

Document prepared by an intersessional working group
convened by Norway and the United Kingdom
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Summary

1. Increasing levels of CO_2 in the atmosphere leads to CO_2 uptake across the air-sea interface and increased carbon concentrations in the ocean. This increases the acidity of the seawater, expressed by a reduced pH. Surface waters of the world oceans have already experienced a pH reduction of about 0.1 pH units. Further reductions of the order of 0.2-0.3 by 2100 are expected and even larger reductions may occur thereafter depending on future emission scenarios. The acidification occurs first in the surface mixed layer which is typically 50 - 200m deep, and with some delay to deeper waters. In regions with efficient ventilation to great depths, such as in the Greenland Sea, waters down to several thousand meters depth may experience acidification rates in this century approaching those of near surface water.

2. Changes in ocean carbon chemistry due to elevated atmospheric CO_2 are not restricted to increased acidity, i.e. reduced pH. An increased concentration of dissolved CO_2 in seawater also implies reduced concentration of carbonate ions. This has consequences for the carbonate saturation state of the seawater and implies that it is becoming gradually more difficult for marine organisms to build carbonate shells. Corals including those living in cold water coral reefs in the OSPAR maritime area, and some pelagic organisms, including potential key species of phytoplankton and zooplankton, are likely to be significantly negatively affected by the ongoing acidification.

3. Present changes in ocean carbon chemistry are rapid, at least 100 times more rapid than any experienced over the past 100 000 years. Individual species which may be especially vulnerable have little possibility to adapt, but some species which may exist in different forms e.g. with and without carbonate shells may shift towards dominance of the latter. Ecosystems are likely to change but in yet unpredictable ways. Subpolar marine ecosystems such as those within the OSPAR maritime area are characterized by long generation times and few key species. Chemical properties of the relatively cold water implies a more rapidly reducing carbonate saturation state than at lower latitudes.

4. It can be concluded with certainty that calcifying organisms will be negatively affected in the present century. However, detailed knowledge about possible other responses in different kinds of organisms to the ongoing changes is very limited. Few experiments have been made. There is basic mechanistic understanding of some physiological processes but no overall assessment of effects and poor baseline information in particular for polar and subpolar seas.

1. Introduction

5. Scientific knowledge about effects of elevated CO_2 in the ocean has a short history. Only very recently has the topic and the potential seriousness of direct consequences of anthropogenic CO_2 emissions on marine life through changes in the chemical state of seawater come to the full attention of scientists and policymakers worldwide. This means that the knowledge available is limited. The findings in the scientific

literature have in many cases had very short time to mature and come under scrutiny, and the state of knowledge is changing rapidly.

6. Available evidence comes from several sources. There have been some basic research activities notably within marine animal physiology. The total efforts have been limited with few active research groups, but the published understanding of mechanisms can be considered trustworthy. There have also been some important experiments exposing phytoplankton communities and different calcifiers to realistic future CO_2 levels and demonstrating clear effects. In many cases, however, the knowledge comes from experiments with either relatively rapid or relatively large amplitude environmental perturbations compared to those which are expected as a consequence of invasion of anthropogenic CO_2 from the atmosphere.

7. The lack of marine experimental data is in stark contrast to the situation for terrestrial systems, where a series of Free Air CO_2 Enrichment (FACE) experiments have been performed in many locations across the globe; a recent report (Ainsworth & Long, 2005) mentioned 120 peer review papers arising from 12 large scale FACE experiments in the past 15 years. In the marine realm, concern about rising levels of atmospheric CO_2 has primarily dealt with impacts of increasing ocean temperature and sea level, changing ocean currents, mixing and ventilation. But e.g. Hallock (2005) states that the most serious consequence of increasing atmospheric CO_2 concentrations for coral reefs is the one most commonly overlooked, i.e., alteration of ocean chemistry.

8. Unintentional leakage from subseabed disposal could give local change in ocean carbon chemistry with much larger local amplitude than that arising from invasion from the atmosphere. During the past 10 years there have been some research efforts devoted to the effects of direct ocean storage of CO_2 in the deep sea. Expected local effects may include acute mortality, see the Ocean Chapter of the recent IPCC Special Report on Carbon Dioxide Capture and Storage (Caldeira et al. 2005). In the case of leakage through the seabed, additional effects not addressed in the IPCC report could arise due to the difference between marine biota and environment in relatively shallow water above potential geological storage sites (of order 500m water depth) compared to those at the typical depths considered for ocean storage (3000m water depth). In case of leakage, and in contrast to the case of invasion from the atmosphere, monitoring in the ocean, similar to that envisioned for direct ocean storage schemes (Caldeira et al., 2005) could possibly be used to determine the location of the CO_2 source. To the best of our knowledge, monitoring of the effects on the marine environment of CO_2 from the atmosphere, has never been considered in detail. Effects on the marine environment of CO_2 leakage from seabed storage is not considered further in this report.

9. Emitted CO_2 spreads rapidly in the atmosphere and contributes to a pressure driving CO_2 into the ocean almost everywhere. The OSPAR maritime area is affected not only by air-sea exchange in the region but also by anthropogenic CO_2 taken up further south and carried by ocean currents into the area from lower latitudes (Lundberg & Haugan, 1996). This illustrates the global character of the ocean acidification problem.

10. According to the OSPAR convention the contracting parties shall take all possible steps to prevent and eliminate pollution in the area covered by the convention. Pollution here means the introduction by man, directly or indirectly, of substances or energy into the maritime area which results, or is likely to result, in hazards to human health, harm to living resources and marine ecosystems, damage to amenities or interference with other legitimate uses of the sea. It is not within the mandate of the working group to address possible implications of our findings for OSPAR or contracting parties. However, it should be noted that if it is concluded that ocean acidification e.g. leads to harm to marine ecosystems, our scientific understanding of the global carbon cycle suggests that implications ("all possible steps") should involve efforts to limit global CO_2 emissions. The effects on the OSPAR area of CO_2 emissions from elsewhere in the world will be identical to those arising from emissions in bordering countries or from ships or structures within the area.

2. Recent development of relevant assessments and research reports

11. The scientific literature contains references dating at least 10 years back pointing to possibly severe impacts and underlining the global scale and unprecedented rate of change in the marine environment due to global CO_2 emissions to the atmosphere. However, efforts to create global awareness and even to outline a work programme to the European Commission (Lie, 1998) met with limited response during the 1990s. The OSPAR Quality Status Report from 2000 elaborates on other issues including climate change and variability but does not mention direct CO_2 effects. Impact assessments from the Intergovernmental Panel on Climate

Change (IPCC) have so far not described ocean acidification. Climate change research programmes generally seem to have defined direct chemical effects of CO_2 as out of scope. The recent Arctic Climate Impact Assessment (ACIA) does not address acidification.

12. Despite limited funding, some researchers were able to perform very important work and the accumulated evidence grew, if slowly, around the turn of the century. Some of the available funding came from programs directed at investigating environmental effects of intentional direct ocean storage of CO_2 (Shirayama et al., 2004), but nevertheless provided background knowledge relevant also for atmospheric CO_2 effects. Turley et al. (2004) reviewed possible impacts after gradual or catastrophic release from storage. The IPCC Special Report on Carbon Dioxide Capture and Storage from December 2005 in its chapter on ocean storage (Caldeira et al., 2005) includes an up to date general discussion of biological consequences of elevated CO_2 in seawater. The focus of that report however is on consequences of intentional direct ocean storage, not atmospheric CO_2.

13. The recent report from the UNEP World Conservation Monitoring Centre on cold water coral reefs (Freiwald et al., 2004) mentions atmospheric CO_2 as a potential upcoming threat without going into details. A brief overview report of the general issue of ocean acidification (Haugan, 2004) was presented to OSPAR in early 2005. While it was not the result of another broad assessment, it contributed to the background for setting up the present working group.

14. Major events in 2004 and 2005 that created increased attention were the May 2004 IOC/SCOR Symposium and the June 2005 release of a Royal Society policy document. The report from a workshop in the US in April 2005 is likely to also become important, particularly for attention in North America and generally in scientific circles, once released in early 2006. In subsequent subsections we briefly describe these three events followed by two upcoming events in 2006. We note that of course it is the individual peer review papers which form the basis for any scientific assessment. Papers in high profile journals like Science and Nature (Riebesell et al., 2000, Caldeira et al., 2003, Feely et al., 2004, Sabine et al., 2004, Orr et al., 2005b) have stimulated much discussion and attention.

2.1 IOC/SCOR Symposium May 2004

15. Member states of the Intergovernmental Oceanographic Commission (IOC) of UNESCO expressed concerns over potential environmental consequences of using the deep ocean for intentional storage of CO_2. In order to be better informed on these isssues, IOC contacted the independent international Scientific Committee of Oceanic Research (SCOR) of the International Council of Scientific Unions (ICSU) to co-host a scientific symposium on ocean carbon sequestration science. In addition, a web site with a watching brief on ocean carbon sequestration (http://ioc.unesco.org/iocweb/co2panel/Sequestration.htm) was set up to provide an overview of the current scientific and legal issues of ocean sequestration of CO_2 for the Member States of the Intergovernmental Oceanographic Commission, as well as other policymakers and the general public.

16. The scientific program committee appointed by SCOR and IOC suggested to widen the scope of the scientific symposium to also include effects of atmospheric CO_2. This was approved by the sponsoring organizations and in May 2004 a symposium on The Ocean in a High CO_2 World (http://ioc.unesco.org/iocweb/co2panel/HighOceanCO2.htm) was held in Paris. A research priorities report is available on the web site and in addition two reports were published in EOS and The Oceanography Magazine, respectively (Cicerone et al., 2004a,b). Key scientific papers from the symposium were published in a special issue of Journal of Geophysical Research (Orr et al., 2005a).

2.2 Royal Society report June 2005

17. The Royal Society in the UK subsequently appointed an expert working group and solicited input from the scientific community to the production of a high profile policy document on ocean acidification due to increasing atmospheric carbon dioxide (Royal Society, 2005, also available on www.royalsoc.ac.uk). It provided an updated account of the science combined with specific policy recommendations such as the need to limit the cumulative CO_2 emissions to the atmosphere by 2100 to 900 GtC to avoid irreversible damage arising from ocean acidification. Scientific findings from this study are reflected in more detail in later sections.

2.3 US Workshop on impacts on coral reefs and other marine calcifiers

18. In April 2005 a Workshop on the Impacts of Increasing Atmospheric CO_2 on Coral Reefs and Other Marine Calcifiers was held in Petersburg, Florida, USA, sponsored by NOAA, NSF and USGS (http://www.isse.ucar.edu/florida/index.html). The full report is not yet available, but the organizers (Tedesco, Feely, Sabine and Cosca) have made available a popular summary report on http://www.oar.noaa.gov/spotlite/archive/spot_gcc.html. The following were some of the major conclusions of the workshop:

1. Ocean acidification is a predictable consequence of increased atmospheric carbon dioxide concentrations from human activities. Surface ocean chemistry CO_2 and pH changes resulting from these activities can be predicted with a high degree of confidence.
2. Ocean acidification means that there would be concern over carbon dioxide emissions independently and apart from any possible effects of carbon dioxide on the climate system. Ocean acidification and climate change are both effects of CO_2 emissions to the atmosphere, but they are completely different; ocean acidification depends on the chemistry of carbon dioxide; whereas climate change depends on temperature and freshwater changes resulting from the atmospheric carbon dioxide and other greenhouse gases.
3. If current trends in carbon dioxide emissions continue, the ocean will acidify to an extent and at rates that have not occurred for tens of millions of years. At present, ocean chemistry is changing at least 100 times more rapidly than it has changed in the 100,000 years preceding our industrial era.
4. Ocean acidification could be expected to have major negative impacts on corals and other marine organisms that build calcium carbonate shells and skeletons. When carbon dioxide reacts with seawater it forms carbonic acid, which is corrosive to calcium carbonate shells and skeletons. The impact is likely to be disruptions through large components of the marine food web. The potential for ecological adaptation is unclear at this time; however, both in today's ocean and over geologic time the rate of accumulation of shells and skeletons made from carbonate minerals shows a consistent relationship with ocean chemical conditions indicating that the success of these organisms is largely controlled by carbonate chemistry.
5. Research is needed to better understand the vulnerabilities, resilience, and adaptability of marine organisms and ecosystems. The science of understanding the biological consequences of ocean acidification, and placing these changes in a historical context, is in its infancy; initial information indicates that there is cause for great concern over the threat carbon dioxide poses for the health of our oceans.

19. While the topic of this workshop was restricted to calcifiers, the statements above resonate well with those that have emerged from other assessments.

2.4 Ongoing development of knowledge

20. At the biannual Ocean Sciences meeting in Honolulu in February 2006 hosted by the American Geophysical Union (AGU), the American Society of Limnology and Oceanography (ASLO) and The Oceanography Society (TOS), there will be a special session on "Observations of Anthropogenic Climate Change in the Oceans and Their Implications for Society II: Arctic and Ecosystem Responses". The session starts with an invited talk by Orr (with coauthors) entitled "Arctic Ocean Acidification" and includes talks by Langdon on "Possible consequences of increasing atmospheric CO_2 on coral reef ecosystems" and Caldeira on "Carbon Dioxide and Ocean Chemistry Change: What Does the Geologic Record Tell us About the Future?"

21. At the annual meeting of the European Geosciences Union in April 2006, for the first time there will be a separate session on the topic "Ocean acidification: chemistry, paleo-analogues, response of organisms and ecosystems, and modelling". The aim of the session is to review recent data on the chemical, biological, and geological consequences of rising atmospheric CO_2 and resulting ocean acidification. Submissions to this session from a broad geographic, thematic and instrumental range are encouraged by the conveners Jean-Pierre Gattuso (France), Joanie Kleypas (USA), Jim Orr (France) and Ulf Riebesell (Germany). Thus it can be stated that ocean acidification is rapidly becoming a mainstream topic in ocean science worldwide. Yet this research is difficult and it will take time and resources to provide more solid and broad knowledge.

22. We end this section with a quote from Jim Orr et al (abstract to AGU/ASLO/TOS Ocean Sciences 2006): "Decreases in Arctic carbonate ion concentrations are likely to affect many calcifying organisms, including aragonitic cold-water corals and shelled pteropods, calcitic coccolithophores and foraminifera, as well as high-Mg calcite producing coralline red algae and echinoderms. No data are available on the response of Arctic calcifiers to decreased carbonate saturation state, but evidence from lower latitudes suggests that at least some Arctic calcifiers will suffer reduced calcification, potentially affecting their competitiveness and survival. The added pressure of ocean acidification could reduce biodiversity and alter the food-web structure of both planktonic and benthic Arctic ecosystems. Unfortunately, our poor general understanding of Arctic calcifiers, e.g., even their baseline geographical distributions, means that future changes will be hard to detect." This study can be seen as a supplement or extension of the paper published in Nature in 2005 (Orr et al., 2005b) which described severe consequences in the world ocean, particularly the Southern Ocean, but where the Arctic was not included in the model studies or data analyses. Preliminary findings from the new study underline both the poor baseline knowledge and the potentially severe consequences that can be expected also in the high northern latitudes of particular relevance to OSPAR.

23. In combination, the references already mentioned document a fairly massive, though recent, consensus in the ocean science community that ocean acidification is a potentially critical issue for the future health of the ocean. The remainder of this report contains an overview of the present state of knowledge of relevance to OSPAR. References given above may be consulted for introduction to basic concepts and later references for more in depth information.

2. Changes in the chemical environment

24. As already mentioned, CO_2 emissions to the atmosphere spread rapidly. There is a north-south gradient in the atmosphere with higher CO_2 levels in the northern hemisphere than in the southern hemisphere due to emission patterns and oceanic and atmospheric transports. There is also a geographically dependent seasonal cycle both in the atmosphere and the ocean related to seasonal biology. And there are interannual variations in the atmospheric CO_2 trend due to phenomena such as El Nino which involves changes in sea surface temperatures in the Equatorial Pacific with implications for weather patterns and biological responses over large areas. However none of these variations can mask the fact that atmospheric CO_2 concentrations are rising in a geographically uniform way all over the globe on decadal and longer time scales due to the global anthropogenic emissions.

25. CO_2 enters the well mixed ocean surface layer whenever the partial pressure of CO_2 is higher in the overlying air than in water. The equilibration time is dependent on wind and sea state. But generally in the absence of deep mixing or upwelling, an ocean surface mixed layer of less than several hundred meters depth will have a partial pressure of CO_2, denoted pCO_2, which trails that of the atmosphere on time scales longer than a year. Surface exchange fluxes and the geographical distribution of anthropogenic CO_2 stored in the ocean is strongly affected by horizontal ocean currents, vertical exchange processes and the geographical distribution of biological agents which transform carbon back and forth between the organic and inorganic pools.

26. In the last 20 years efforts to map the distribution of carbon sources and sinks and the distribution of various forms of carbon in the ocean have been increasing. A consistent picture now emerges. The vertically integrated inventory of anthropogenic carbon per unit area in the ocean is clearly highest in the Northern North Atlantic compared to all other major ocean basins (Sabine et al., 2004). This is related to the relatively weak stratification in the area and the character of the mean ocean circulation which converts surface water to deep water in the Nordic Seas, the Labrador Sea and generally in the subpolar gyre. This allows deep penetration of the surface signature in anthropogenic CO_2. Much of the anthropogenic CO_2 in the northern parts enters the area via the dominating inflowing current system from the south rather than via local air-sea uptake (Lundberg & Haugan, 1996).

27. In order to understand past changes in ocean carbon cycling and study future scenarios, numerical ocean circulation carbon cycle models are used (Caldeira & Wickett, 2003, 2005, Heinze, 2004, Orr et al., 2005b). These uniformly predict a continued uptake of anthropogenic CO_2 in the oceans in the future. Assuming fossil fuel reserves corresponding to total emissions of 5270 GtC since pre-industrial times and distributing the emissions over time based on observations up to now, IPCC emission scenario IS92a until 2100, and a logistic function thereafter, Caldeira & Wickett (2003) obtained surface pH reduction of more than 0.7 in year 2300, noting that the surface ocean may then become more acidic than during the past 300 million years with the possible exception of rare, extreme events.

28. As the ocean becomes more acidic due to higher carbon content, its ability to take up CO_2 reduces. While the chemistry of this buffer effect are well understood, the future uptake may also depend on poorly understood possible responses to increased greenhouse effect such as changes in ocean circulation and ice cover, and indeed on possible changes in ocean biology including such changes which are discussed in the present report. However, even if the ocean in the future may take up a slightly smaller fraction of the emissions on annual basis than the present situation, on a 1000 year time scale, 70-90 % of the cumulative emissions are likely to reside in the ocean. Thus we can be confident that the ocean acidification process will not stop in the future. It will increase in amplitude and be with us for centuries.

29. Simple calculations suffice for estimating the equilibrium carbon system response in surface water to specified atmospheric partial pressure (Haugan & Drange, 1996, Brewer, 1997). These are suitable for global averages. More detailed calculations for the future can be made in numerical models which account for ocean circulation and represent geographical variations in temperatures and chemical state. Orr et al. (2005b) used such models and found that the Southern Ocean was particularly vulnerable to changes in carbonate saturation state with severe implications for calcifiers (see later sections). Bellerby et al. (2005, Fig. 1b below) focussed on an area relevant to OSPAR, and found that the future pH changes are not expected to be uniform. The main regional gradients are associated with the transition between Atlantic and Arctic waters.

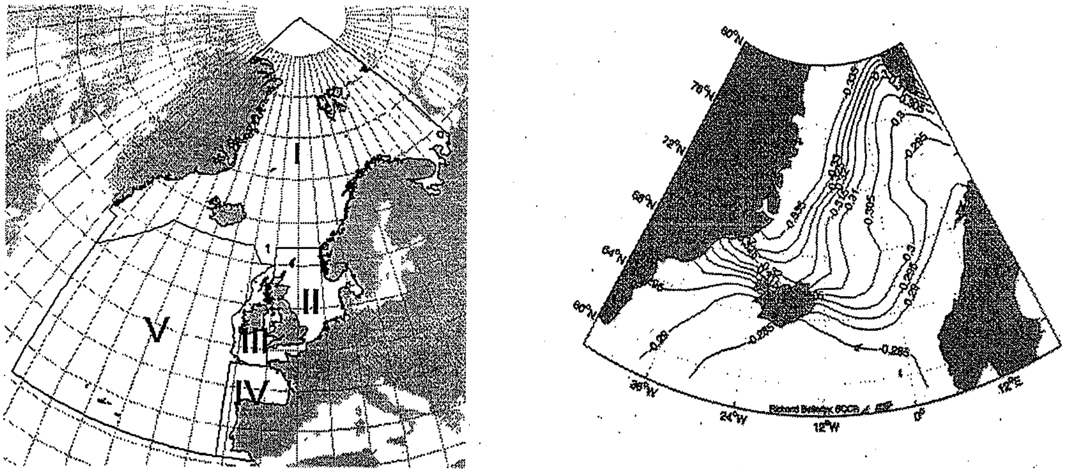

Figure 1a) showing the OSPAR regions and 1b) showing the predicted reduction in surface pH from 1997 to 2067 in a scenario in which atmospheric CO_2 doubles during that time (approximately 1% increase per year). The physical ocean state is taken from coupled climate model run and the surface ocean carbon chemistry from empirical correlations with the physical state. From Bellerby et al. (2005).

30. Overviews of ocean carbon chemistry can be found in textbooks such as Zeebe & Wolf-Gladrow (2001). A brief introduction focussed on the issues associated with adding CO_2 to seawater and an overview of scenarios can be found in the IPCC report (Caldeira et al., 2005). Other reports also contain introductory material. A one-page primer on relevant carbon chemistry is included in Haugan (2004). Noting that the pH scale is logarithmic (so that a pH reduction of 1.0 corresponds to a 10-fold increase in the concentration of H^+), the essence for our purposes are contained in the equation given in section 4.1, showing that addition of CO_2 reduces availability of carbonate ion (CO_3^{2-}).

4. CO_2 effects on marine organisms and ecosystems: physiological background and affected processes

31. Biogeochemical processes that regulate the earth system are determined by the ecosystem functioning and the biodiversity within the ecosystem. Loss or change in biodiversity could therefore have impacts on ecosystem functioning, its biogeochemistry and regulation of the earth system.

32. So far there are no field observations to prove specific effects of CO_2 in marine ecosystems. Statements on the effect of CO_2 on marine organisms are therefore based on experimental studies in laboratories or, lately, in mesocosms. They are also based on experiments in areas with volcanic CO_2 emission or on few observations after releasing CO_2 into the deep sea. Known effects range from the

molecular to the cellular and whole organism level and relate to processes and mechanisms in phytoplankton and some groups of animals. General principles of the effects of CO_2 in all organisms are to be distinguished from those specific and typical for certain groups. This is especially valid in case of animals. Apart from more recent mesocosm studies (Riebesell, 2004) experimental investigations of the effect of CO_2 at ecosystem level are completely missing. Existing mesocosm studies focus on CO_2 effects on primary production and the export of organic material.

33. In the light of complete lack of field observations, scenarios of CO_2 effects on marine ecosystems developed based on laboratory, mesocosm or even experimental field data will only be reliable when based on a mechanistic cause and effect understanding elaborated in physiological and biochemical studies. In view of the large gaps in knowledge, there is considerable demand for research in this area (Cicerone et al., 2004a,b, Raven et al., 2005, Orr et al., 2005b) to reach predictability. As per latest findings, the effects of CO_2, temperature and oxygen are interacting (Reynaud et al., 2003, Hoegh-Guldberg, 2005, Pörtner et al., 2005d). This requires an integrated analysis of these effects to evaluate the role of CO_2 as well as its interaction with other changing factors more precisely.

34. Considering the importance of organismic physiology and biochemistry for the understanding of causes and effects, the physiology of the effects of temperature and CO_2 shall be dealt with first. This knowledge includes whether, how and to what extent organisms acclimatize or adapt on evolutionary time scales to changing CO_2 levels. Only with such baseline knowledge, can the sensitivity of higher level processes be understood beyond empirical or modelling studies. Higher level processes comprise changes in biogeographical distribution, in how organisms and their interactions shape biogeochemical processes, in biodiversity and last not least in availability of marine resources for fishery.

35. When organisms (here marine microorganisms, phytoplankton and water-breathing animals) are surrounded by increased CO_2–concentrations, these conditions are called hypercapnia. Knowledge of the unifying physiological effects of CO_2 on individual organisms is equally important for understanding CO_2 effects on organisms at the ocean surface as on benthic and deep-sea organisms. In surface oceans, photosynthetically active marine organisms, especially phytoplanktonic organisms, are the basis for 99 % of the organic material which enters the seas' food chains. By fixation of about 47 Gt C per year, phytoplankton contributes to nearly half the primary production on earth, macroalgae, sea grass and corals produce additional 1 Gt C per year (Field et al., 1998). Mostly microorganisms (del Giorgio und Williams, 2005), but also zooplankton and larger animals consume the organic carbon, which passes through complex food chains for the higher trophic levels, animals. A change in ocean chemistry affects all organisms directly, heterotrophic organisms like animals are also indirectly affected through changes in the food chain. Feeding pressure on phytoplankton or other organisms may change due to direct CO_2-effects on plankton grazers.

36. Some CO_2 effects are elicited through changes in water pH. The effect of lowered pH-values (without simultaneous CO_2 accumulation) was mostly investigated in fresh water organisms and to a lesser extent in marine organisms (Wolff et al., 1988). Effects caused by pH changes comprise changes of productivity in algae (e.g. through changes in the rate of cell division; Hinga, 2002) and in heterotrophic microorganisms (Archaea, bacteria, fungi and protozoans), altered rates of biological calcification and decalcification as well as changes in the rates of metabolism of zooplankton, benthic species and fish. Lowered pH-values in the water impair reproduction of animals in fresh water and in the sea. A low pH in the water leads to smaller egg sizes and delayed hatching (Vinogradov and Komov, 1985). Egg fertilization in mussels is most successful at slightly alkaline pH (Alvarado-Alvarez et al., 1996). Even slight lowering of pH may reduce reproductive success (e.g. Desrosiers et al., 1996). In sturgeons (*Acipenser transmontanus*) sperm mobility is reduced at both low pH as well as at increased pCO_2 (Ingermann et al., 2002).

37. The ability to adapt to increasing CO_2 concentrations on evolutionary time scales is unclear for all groups of organisms. However, the ancestors of extant forms lived under higher CO_2 levels. For marine organisms it is also completely unclear to what extent adaptation to today's values is based on irreversible specialisation on certain windows of CO_2 concentrations. Available tests of experimental evolution (Collins and Bell, 2004) have limited applicability in natural environments.

38. Results obtained in phytoplankton and macroalgae support an integrative concept for the effects of CO_2 on primary production. This concept is not yet complete, but interprets some phenomena at organismic and ecosystem levels through enzymatic characteristics and cellular transport phenomena and thus shows a way to understanding causes and effects. Such an integrative concept is not yet available for animals, but similar principles may be operative as under the effect of temperature changes (e.g. Pörtner, 2002, Pörtner et

al., 2004). Several components and processes have become known in animals, and, as in case of temperature, many CO_2-effects at molecular and cellular levels may finally lead to a lowering of aerobic capacity and scope of animals and thus a restriction of whole animal performance capacity (Pörtner et al., 2005).

4.1 Calcification and calcifying organisms

39. When CO_2 is dissolved in seawater, there will be a decline in carbonate ion (CO_3^{2-}) concentrations as they react with increased concentrations of anthropogenic CO_2:

$$CO_2 + CO_3^{2-} + H_2O \Rightarrow 2HCO_3^-$$

40. The net effect is removal of carbonate ions and production of bicarbonate ions (HCO_3^-) and a lowering in pH (Turley et al. 2004 and 2006). This in turn will encourage the dissolution of more calcium carbonate ($CaCO_3$). Indeed, the long-term sink for anthropogenic CO_2 is dilution in the oceans and reaction with carbonate sediments. The decline in carbonate ions will make it more difficult for calcifying organisms to form biogenic calcium carbonate and it is predicted that that this situation will continue for 100's of years (Kleypas et al. 1999; Broecker & Peng 1979; Feely et al. 2004; Orr et al. 2005b). Organisms form their calcium carbonate shells, tests or liths either in the form of calcite (e.g. coccolithophores) or the less stable form of aragonite (e.g. low latitude corals or pteropods). Orr et al. (2005b) highlighted their particular concern for high latitude calcifiers. Initially, the most vulnerable are species that form aragonite shells and live in high latitudes (polar and sub polar surface waters) where aragonite undersaturation will occur by around 2050 (at around 2 x CO_2, equivalent to 560 ppm). Those that form calcite shells and live in high latitudes will become increasing vulnerable after a further 50-100 years as calcite becomes undersaturated.

41. For example, the shallowing of the aragonite saturation horizon in the Southern Ocean is likely to have serious consequences on the aragonite shell producing pteropods which are the dominant calcifiers in these waters and a key food resource for higher organisms, including zooplankton, fish (including commercial fish such as salmon, mackerel, herring, cod) and baleen whales. Marked dissolution of shells of living pteropods were found when incubated for only two days at concentrations of CO_2 predicted to occur in 2100 (Orr et al. 2005b). The authors asked the question of whether these key organisms can survive in these waters in the future and indeed whether they can shift their range to warmer, lower latitude waters that remain supersaturated in aragonite. Pteropods also dominate the flux of carbonate and/or organic carbonate from the surface of the ocean in the Ross Sea and South of the Polar Front (Orr et al. 2005b). Loss of these organisms may therefore impact the biological pump and removal of carbon from the surface of the ocean.

42. The calcifying phytoplankton group, the coccolithophores play a varied and complex role in the global carbon cycle and are thought to be the most important calcite producer on the planet. They produce calcite platelets or liths and their blooms can cover 100,000's of square km (Holligan et al., 1993). Reduced calcification in cultures of two species of coccolithophores has been observed when grown at 750 ppm CO_2 (Riebesell et al. 2000). A reduction in coccolithophorid global coverage may decrease flux of CO_2 to the atmosphere through reduced calcification, decrease flux to the sea through decreased primary production (although other organisms may replace them) and decrease ballast and thus removal of carbon from the surface ocean. The combined impacts are uncertain (Chuck et al. 2005) as are the consequences on the rest of the marine food web. Other non-calcifying organisms may grow in their place and impact the structure and processes occurring in the whole ecosystem. Impacts of high CO_2 on benthic calcareous organisms are dealt with below.

43. The sensitivity of calcifiers to acidosis and CO_2 varies among species depending on the degree of calcification and the calcite structure: If CO_2 was a key factor in the Perm-Trias Mass mass extinction, the stronger, but more sensitively calcificated corals, bryozoans and echinoderms were especially affected, while molluscs, arthropods including crustaceans as well as the chordates reacted less strongly (Knoll et al., 1996). It remains unclear whether crustaceans, which also display CO_2 effects on calcification (Wickins, 1984), are more sensitive after moulting due to repeated demand for calcium and bicarbonates for mineralizing their exoskeleton. Generally, the CO_2-induced reduction of carbonate super-saturation in the water can weaken carbonate-containing skeleton structures and make them less resistant against physical and biological erosion. When pCO_2 increases, the existing calcium carbonate structures finally dissolve (e.g. Bamber, 1987; Shirayama, 1995). These disturbances, also caused by lowered pH, are combined with a reduction of growth and reproduction (Bamber, 1987, 1990, Michaelidis et al., 2005).

44. CO_2 effects on phytoplankton already start when the CO_2 concentration is slightly increased, and such effects seem to have already played a role in the course of corresponding CO_2 variations in earth's history. Barker and Elderfield (2002) showed that CO_2 variations in the ice ages and inter-ice ages of the latest 50000 years correlated with the shell weights of fossile planktic foraminifers. These observations prove that marine calcification is already influenced by small fluctuations in atmospheric CO_2 values. Therefore, effects will progressively intensify with increasing CO_2 values. The capacity of sea water buffers to reduce pH alterations decreases with increasing CO_2 accumulation in the ocean. As a consequence less CO_2 is stored (cf. Fung et al., 2005) and biological effects increase more strongly.

4.2 Primary production and phytoplankton

45. Around half of global primary production is carried out by microscopic plants, the phytoplankton, which grow and die within a matter of days (Field et al. 1998). Their response to changing environmental conditions can therefore be very rapid. They also provide 99% of the organic matter used by marine food webs. A decline in oceanic primary production, either through reduced photosynthesis or through being less effective at nutrient uptake would have consequences on the rest of the food web. The Royal Society (2005) concluded that unlike land plants, most marine phytoplankton are thought to have mechanisms to actively concentrate CO_2 so that changes in seawater pH and CO_2 have little (<10%) if any direct effect on their growth rate or their elemental composition (Burkhardt et al. 1999; Gervais and Riebesell 2001; Beardall and Raven 2004; Schippers et al. 2004; Giordano et al. 2005). Although some studies have shown a change in the C:N:P composition in response to increasing CO_2 with large species-specific differences this may not have a significant effect on the global carbon cycle (Burkhardt and Riebesell 1997; Burkhardt et al. 1999). However, whilst taxon specific differences in CO_2 sensitivity have been observed in laboratory culture (Rost et al. 2003) it is currently unknown whether a reduction of the advantage of possessing a CO_2 concentrating mechanism will impact phytoplankton species diversity in the natural environment. This is a possibility and, should it occur, may impact the contribution of different functional group, primary production, food web structure and marine biogeochemical cycles. Exceptionally the coccolithophore, *Emiliania huxleyi,* increased its rate of photosynthesis in elevated CO_2 (Rost and Riebesell 2004). Considering it was also observed to decrease its rate of calcification at higher CO_2 (Engel et al. 2005) it is unsure whether this may offset the organisms directly benefit from increasing CO_2 (Riebesell et al. 2000). The Royal Society (2005) reported that most of the experiments on marine phytoplankton have been short term and did not provide sufficient time for any genetic modification that might enable them to adapt, some were carried out by artificially altering pH and therefore do not mimic the situation in the real world or were at pH's unlikely to be seen in future scenarios.

46. Nutrients such as nitrogen, phosphorus and iron often limit phytoplankton growth in major parts of the World's oceans. The lower pH expected over the next 100 years can theoretically impact the speciation of many elements (including oxidation states) (Zeebe and Wolf-Gladrow 2001; Turley et al. 2004). These include key nutrients (N, P, Si) and micronutrients (Fe, Co, Mn etc). For instance, a decrease in pH of 0.3 units could reduce the fraction of NH_3 by around 50% (Raven 1986). In contrast, the proportion of soluble iron may increase which might be beneficial to the 10% of the oceans where iron is thought to limit primary production. Clearly, unravelling the combined impacts of declining pH on nutrient concentration and speciation, on nutrient uptake by natural phytoplankton assemblages, their primary production or their nutritional value to the organisms that feed on them will be a challenge.

47. While the majority of primary production is carried out by microscopic planktonic algae, benthic primary producers play a key role in coastal areas providing habitats and breeding grounds and reducing coastal erosion through the dissipation of wave action. The Royal Society (2005) concluded that there was little data on the consequences of higher CO_2 concentrations on the photosynthetic or growth rates or composition of seaweeds or seagrasses although data available did indicate increased rates of photosynthesis at CO_2 concentrations higher than present (Beer et al. 2002). This may be because they may take up CO_2 by diffusion rather than through a concentrating mechanism. Kubler et al. (1999) found significant increases in the growth rate of a red seaweed at double today's concentration of CO_2. However, elevated CO_2 inhibited calcification in the coralline seaweed, *Corallina pilulifera* (Gao et al. 1993).

4.3 Microheterotrophic processes and bacteria, archaea and the microbial loop

48. Non-photosynthetic bacteria and archaea are important components of the marine environment and play a key role in major biogeochemical processes (e.g. decomposition of organic matter, nutrient regeneration, carbon remineralization and biogas production) and are an important food resource for small heterotrophic zooplankton and benthic detrital and suspension feeders (Azam et al. 1983). The main source of energy for planktonic heterotrophic bacteria is dissolved organic carbon released by phytoplankton. Phytoplankton production of organic carbon may change in high CO_2 waters (Engel et al. 2004) and if this occurs it seems likely that bacteria would respond rapidly to their main energy source. Bacteria also require nutrients for their growth and compete with phytoplankton for a range of nutrients. Any change in the speciation and supply of nutrients will also affect these groups of micro-organisms. We can find no data on the impacts of low pH/high CO_2 on elements of the microbial loop or bacteria-phytoplankton interactions. There is an urgent need to invest in our understanding of the impacts of a high CO_2 world on this fundamental part of the foodweb that drives so many key processes.

49. Coffin et al. (2004) investigating the potential impacts of direct deep ocean sequestration found that bacterial production rates were reduced in elevated CO_2 while Takeuchi et al. (unpublished) found potential activities of bacterial ectoenzymes and bacterial biodiversity were sensitive to elevated CO_2. However, there is little information available on the effect of CO_2 concentrations due to ocean uptake of anthropogenic atmospheric CO_2 on surface ocean heterotrophic bacteria. Experiments carried out in the Bergen mesocosms may soon reveal CO_2 induced changes in their diversity (M Muhling, PML, unpublished).

50. Huesemann et al. (2002) found rates of nitrification were reduced by ~ 50% at pH 7 with inhibition at pH 6. This may result in a reduction of ammonia oxidation rates, the accumulation of ammonia instead of nitrate (that is, increasing the NH_4:NO_3 ratio). Depending on the nutrient requirements and uptake abilities of different species this has the potential to impact the growth and biodiversity of phytoplankton and bacteria. It should be noted that these pH levels are far lower than those predicted by ocean uptake of atmospheric CO_2. Further research is required on the impact of more realistic decreases (of 0.4-0.8 pH units from pre-industrial levels) in pH on nitrification. Also see section 4.6.

4.4. Secondary production, larval settlement and zooplankton

51. Impacts of high CO_2 and low pH on calcifying phytoplankton (such as the coccolithophores), zooplankton (such as pteropods) and heterotrophic micro-organisms (bacteria and archaea) and key biogeochemical processes are dealt with above. However, most benthic fauna have a planktonic larval phase to enhance their dispersal.

52. Larval settlement is a driver in the distribution and abundance of benthic populations (Gaines and Roughgarden 1985). Planktonic larval behaviour is important in the transport, delivery and settlement to the benthos and their response to changing environmental conditions may have a substantial effect on their settlement (Annis 2005). Juvenile forms of calcareous organisms may be less tolerant to changes in pH than adults. Indeed, greater than 98% of the mortality of settling marine bivalves occurs within the first few days or weeks after settling (Green et al. 2004). This is thought to be in part due to their sensitivity to the carbonate saturation state at the sediment-water interface. Compared to controls larvae of sea urchins grown at pH 7.8 (+500ppm) were smaller and those grown at pH 7.6 were also deformed (Kurihara and Shirayama 2004; Kurihara et al. 2004a). The authors postulate that this may be due to reduced rates of calcification of their calcium carbonate shells. The higher seawater CO_2 concentrations that will occur in the future may therefore enhance shell dissolution and impact recruitment success and juvenile survival.

53. Experiments associated with the concept of ocean sequestration of CO_2 have revealed the oceanic zooplankton (Adams et al. 1997; Yamada and Ikeda 1999) including those inhabiting the deep-sea (Watanabe et al. 2001) are sensitive to low pH. Sub-lethal effects on marine planktonic copepods may also be of concern including egg production rate and early development (Kurihara et al. 2004b). Foraminifera in the geological past have been sensitive to changes in oceanic pH, for example 55 Mya during the Palaeocene/Eocene thermal maximum (PETM) when ocean pH declined due to excessive CO_2 probably caused by release of methane hydrates (Zachos et al.). The shell weight of *Orbulina univera*, a planktonic foraminifer, was reduced under elevated CO_2 (Bijma et al. 2002).

54. However, further research is required in this area using pH values reflecting those predicted to occur through ocean uptake of anthropogenic CO_2 rather than the lower pH levels predicted from ocean disposal. Kurihara and Shirayama (2004) also call for experiments using CO_2, rather than acid, to reduce pH as there is higher sensitivity to high CO_2.

4.5 Water-breathing animals

4.5.1. Direct effects

55. Present knowledge can already negate any conjecture that higher life forms like animals may only be affected by CO_2 enrichment through the food chain. In water-breathing animals processes like calcification, growth, reproduction and activity are directly affected by increased CO_2 partial pressures. Effects already set in with an increase to 560 µatm (see below). The principle question is whether these most complex life forms, animals, may be most sensitive to these disturbances in similar ways as they are most sensitive to temperature (Pörtner, 2002)? Further knowledge needs to be developed to answer this question. Effects on animals are also in the foreground when evaluating scenarios of CO_2 dumping or leakage in the deep ocean.

56. Disturbances of respiration, narcosis and mortality are short-term effects on animals in case of strongly increased CO_2 concentrations. Lower concentrations of CO_2 can, however, cause long-term effects which remain sublethal at first and affect processes like muscular activity, behaviour, growth, reproduction and finally life spans, with corresponding consequences at the level of population and ecosystem. There are also specific sensitivities in different life stages like eggs, larvae and juveniles. Juvenile stages are usually more sensitive than the adults (Pörtner et al., 2005d). Long-term effects beyond the duration of a reproduction cycle or individual lifespan are likely to be overlooked, but can finally have drastic effects on an ecosystem. Unifying mechanisms of CO_2 effects can be studied in animals from the intertidal zone, because these organisms even survive higher contents for a long time. Some of the invertebrates and fish examined up to now, however, live at depths below 2000 m or in permanently cold waters (e.g. Langenbuch und Pörtner, 2003, 2004), so that preliminary statements regarding effects on the physiology of animals in deeper or polar waters seem possible.

57. At first the sensitivity against increased CO_2 values was attributed to acidification (lowering of water pH) (cf. Shirayama, 1995, Auerbach et al., 1997). Specific effects by CO_2 and bicarbonate, however, must be considered in a complete analysis (Pörtner und Reipschläger, 1996). At least on short time scales there are considerable differences between experiments in which the same degree of acidification was either caused by hydrochloric acid alone (CO_2 released from carbonates was removed by aeration) or by increasing the CO_2 partial pressure. Only under CO_2 an immediate mortality of fish larvae was observed (Ishimatsu et al., 2004). In sea water acidified by hydrochloric acid (with a constant pCO_2) damages developed over longer periods. One reason certainly is that the highly diffusive CO_2 rapidly enters the body fluids via all epithelia and disperses into all body compartments. This internal accumulation of CO_2 causes most of the effects observed in animals (reviewed by Pörtner und Reipschläger, 1996, Seibel und Walsh, 2001, Ishimatsu et al., 2004, 2005; Pörtner et al., 2004a, 2005d). The CO_2 concentration to which an organism is acclimated will influence its acute critical tolerance limit. The capacity for acclimatisation and associated shifts in tolerance limits, however, has not yet been examined.

58. In Teleostei and Elasmobranchii ventilation is not only stimulated by hypoxia but also through increased CO_2 concentrations (Burleson and Smatresk, 2000; McKendry et al., 2001, McKenzie et al., 2002), with consequences for the energy budget of animals, i.e. the distribution of metabolic energy among energy consumers in the animal. Due to low CO_2 gradients between organism and water, water-breathing animals have a limited capacity to compensate disturbances in acid-base status by ventilation (Scheid, 1989). Upon ambient CO_2 accumulation an increase in CO_2 content in the organism cannot be avoided. Therefore, water-breathing animals nearly always use ion exchange mechanisms to compensate for hypercapnic disturbances of the acid-base status.

59. An increase in pCO_2 leads to acidification (the pH value decreases), and the content of bicarbonate increases, depending on the effect of other buffering substances (non-bicarbonate buffers), which are titrated by the increase in the content of carbonic acid. The decrease in pH is larger, and the increase of bicarbonate levels less in fluids with low buffering capacity. The passive increase in bicarbonate levels caused by the increase in pCO_2 is thus lower in sea water than in extracellular body fluids, and here considerably lower than in the intracellular space. Conversely, the strongest decrease is in sea water pH due to small quantities of non-bicarbonate buffers and the smallest decrease occurs in intracellular pH due to non-bicarbonate buffer

values about five times higher than in the extracellular space. In most animals, invertebrates and vertebrates, the extracellular pH value is set at 0.5-0.8 pH units above the intracellular pH value (with the exception of squid and other cephalopods, here, intra- and extracellular pH values are nearly the same in many cases). Consequently, there are usually higher bicarbonate concentrations in extracellular than in intracellular space.

60. There have been many analyses of CO_2 effects on acid-base regulation of animals (Egginton et al. 1999), but only in few species were these combined with metabolic analyses (e.g. Reipschläger et al., 1997). Changes in metabolic rate are caused by changes in acid-base parameters (e.g. pH, bicarbonates) in one or more body compartments (Pörtner and Reipschläger, 1996, Pörtner et al., 2000, Langenbuch and Pörtner, 2002). The processes of transmembrane ion regulation react to respiratory or metabolic acid loads or to changes in the acid-base status so that new acid-base equilibria develop, which are associated with shifts in e.g. the pH value. In marine fish transfer of acid-base equivalents are always connected with disturbances in osmotic regulation (salt-water balance), because of the required intake of counter-ions, which leads to an additional up to 10 % higher load of sodium chloride (Evans, 1984). A strong relation between acid-base status and ion regulation was also found in decapod crustaceans. Compensation of CO_2-induced acidification causes large and possibly unfavourable changes in the ion composition of plasma and other body fluids (Cameron und Iwama, 1989, Whiteley et al., 2001).

61. In all animals examined up to now, hypercapnic disturbances of acid-base status are compensated for by accumulation of bicarbonate-anions (Heisler, 1986b, Pörtner et al., 1998, Wheatly, 1989). This happens very effectively in the intracellular, but not always as effectively in the extracellular compartment. In fish, compensation in both compartments often is nearly complete (Larsen et al., 1997), while extracellular pH reaches the control value more slowly than intracellular pH, together with a slower increase in extracellular bicarbonate content (Heisler, 1986a). In contrast to many fish species, extracellular pH in marine invertebrates usually does not completely return to its original value. For example, compensation is by only 30 % in a marine worm (Pörtner et al., 1998) and is near 0% in *Mytilus galloprovincialis* (Michaelidis et al. 2005). A limiting factor for the extent of compensation could be, how much bicarbonate is available from the surrounding medium for extracellular compensation or from the extracellular fluid (blood, haemolymph) for intracellular compensation (Heisler, 1993; Pörtner et al., 1998). The newly established pH values affect transmembrane ion exchange mechanisms (Pörtner et al. 2000), oxygen transport and metabolic equilibria, which are important for growth or modulate the concentrations of neurotransmitters. An overview figure of CO_2 effects and affected mechanisms is given in Pörtner et al. (2005d). Based on these effects we expect that functional rates of the respective mechanisms as well as oxygen or energy turnover are mostly suppressed by high CO_2 and low pH values. Decreasing rates of protein synthesis affect functions like growth and reproduction (Langenbuch und Pörtner 2002, 2003). Finally, mortality increases (Kikkawa et al., 2004, Langenbuch und Pörtner, 2004), however, factors causing mortality are only known for acute effects of high CO_2 levels but not those causing mortality after long term exposure to moderately elevated CO_2 levels.

62. Many of these results were found in CO_2 concentrations which exceed by far those levels expected by 2100. Accordingly, further investigations are necessary to elaborate the potential influence of future atmospheric CO_2 levels on fish and other marine resources. Based on present knowledge, it cannot be excluded that marine living resources will diminish due to the generally depressing effect of CO_2 on physiological performances. However, no generalized statement on the extent of this depression can yet be made.

4.5.2 Short- and long-term effects of CO_2 in animals

63. To be able to assess the significance of CO_2 effects and affected processes at ecosystem levels, we must find out the advantages of effective acid-base regulation and the effects which changes in the acid-base parameters have under stress due to new environmental conditions, e.g. in case of increased CO_2 concentrations. Furthermore, CO_2 affects animals through physiological processes which differ depending on concentration and time scale (Pörtner et al., 2005d). It is possible that not all of these effects are elicited via disturbances in the acid-base status. The sensitivity against CO_2 also depends on lifestyle and energy turnover of the animals as well as on the physiological-functional characteristics of the respective phylum. Benthic animals show lower energy turnover than pelagic animals and may therefore be less sensitive. Especially in the tidal zone they are more adapted to variable environmental conditions like hypoxia, hypercapnia or extreme temperatures. Squid, however, are especially sensitive cephalopods, last not least because of their metabolic rate which is considerably higher than that of e.g. fish. The most active squid live in the pelagic areas of the open oceans and show levels of activity comparable to those of fish of similar size (O'Dor und Webber, 1986). The squid's high demand for oxygen is explained by their lifestyle and their

cost-intensive swimming by jet propulsion (O'Dor und Webber, 1986). A similar understanding of CO_2 effects is not available for other organisms.

64. Acute sensitivities to CO_2, caused by effects on blood gas transport, are only important in scenarios in which CO_2 is discharged into the sea and can locally reach very high concentrations. Acute effects (within minutes or hours) mainly occur in response to high CO_2 concentrations and are to be considered near volcanic sources of CO_2 or during CO_2 disposal in the deep ocean. For many groups of animals it has been known for a long time that strongly increased CO_2 concentrations can cause acute decreases in metabolic rate or even anaesthesia. This is also confirmed by investigations of deep-sea fish (Tamburri et al., 2000). The acute sensitivity of some squid against increased CO_2 concentrations is due to the extreme dependence of oxygen transport by the extracellular pigment haemocyanin on well controlled changes in pH between arterial and venous blood. Such high pH sensitivity of haemocyanin can be explained by limited haemocyanin levels and the necessity to make maximum use of blood bound oxygen transport. Only in case of exactly controlled variations in blood pH, the pigment is loaded with oxygen at the gills and discharged completely in tissues (Pörtner, 1990, 1994). Of course, this system is very sensitive to CO_2 and the resulting pH disturbances (Pörtner und Zielinski, 1998).

65. Accordingly, the number of species showing acute sensitivity already in case of relatively low CO_2 concentrations of several thousand ppm is relatively small. In *Illex illecebrosus* a moderate decrease of the pH value by 0.15 pH units, caused by an increase in pCO_2 over 2 000 µatm, would limit oxygen availability to tissues and lower the capacity to use aerobic metabolism, i.e. aerobic scope. In case of a stronger increase of pCO_2 over 6 700 µatm a decrease of arterial blood pH by approx. 0.25 pH units is to be expected. This would lower oxygen binding capacity by approx. 50 % and possibly cause death by suffocation (Pörtner und Reipschläger, 1996). Other squid like *Loligo pealei* die at CO_2 partial pressures of 26 500 µatm (ppm), for similar reasons (Redfield and Goodkind, 1929). In fish the acutely effective concentration of CO_2 (after 72 h) is even higher, at 30 000 to 50 000 ppm (µatm, Crocker and Cech, 1996, Ishimatsu et al., 2004). Sensitivity is increased in early life stages (eggs, sperm, larvae, juveniles) (Crocker and Cech, 1996, Ingermann et al., 2002; Kikkawa et al., 2003, Ishimatsu et al. 2004), which display lethal limits at between 13 000 and 28 000 ppm in fish larvae.

66. Compared to squid, fish are much more protected against CO_2 effects due to their functional characteristics. They have a lower metabolic rate, a venous oxygen reserve and, above all, their haemoglobin is available at high concentrations in blood cells (erythrocytes) and is thus highly protected from disturbances of extracellular pH, mostly due to the high capacity of intracellular pH regulation. Compared to marine invertebrates, the fish's capacity to (nearly) fully compensate for an extracellular acidosis is generally much more developed. Accordingly, it is not the disruption of oxygen transport by the pigment, but rather the disturbance of cardio-circulatory function system which are finally lethal at high CO_2 levels in fish (Ishimatsu et al., 2004).

67. The general conclusion that the number of acutely sensitive animals is rather small is, however, debatable, especially if CO_2 levels increase in the deep sea. In fact, some deep-sea animals show a rather strong dependency of oxygen transport on pH, combined with a high oxygen affinity of their respiratory pigments. Seibel and Walsh (2001) therefore postulated that deep-sea animals, e.g. fish, would experience severe insufficiency in oxygen transport under increased CO_2 concentrations. However, their examples include organisms from the oxygen minimum layer at intermediate depths, like the mysid *Gnathophausia ingens* or some fish species (Childress and Seibel, 1998; Sanders and Childress, 1990). These species are adapted to ambient hypoxia and neither typical for the deep sea nor for other groups of fish.

68. Antarctic animals are more suitable animal models for deep sea organisms. Also, blood oxygen transport in Arctic cephalopods (e. g. octopods) is dependent on pH, but the pH-dependent regulation of oxygen transport becomes less important at reduced activity levels and decreasing temperatures (Zielinski et al., 2001). Nevertheless, this indicates that groups may react sensitively to increased CO_2 concentrations even in the cold. In Antarctic fish, however, the role of oxygen transport via haemoglobin is strongly reduced, compared to fish from warmer areas. The concentration of haemoglobin is lower, oxygen transport by the pigment is less dependent on pH. These results comply with lower levels of motor activity in cold oxygen-rich waters (Wells et al., 1980, D'Avino and DeLuca, 2000; Tamburrini et al., 1998). These characteristics resemble those of deep-sea fish (from oxygen-richer regions below the oxygen minimum layer), where Graham et al. (1985) also found low contents of haemoglobin. Generally, fish (and squid) below 300 - 400 m lead an energy-saving, rather passive life (Childress, 1995; Seibel et al., 1997), which makes them less sensitive to acute effects of CO_2.

69. CO_2 effects on long time scales (weeks, months, years), however, are also to be expected for many other groups of animals and even at CO_2 concentrations which will be reached in the near future during continuing anthropogenic CO_2 release and adsorption into ocean surface waters. This was already explained for effects on calcification (4.1.). Accordingly, long-term investigations under moderately increased CO_2 concentrations are required for a better understanding of affected mechanisms and to understand and quantify ecological effects.

70. Animals that are not dependent on calcification processes also react to long-lasting increases in CO_2 concentrations. In *Sipunculus nudus* CO_2 causes a long-term suppression of aerobic energy turnover. The degree of depression depended on concentration and reached up to 35 % at 20 000 µatm pCO_2 (water pH ~ 6.6). Unter normo- as well as under hypercapnia the non-compensated acidosis in the extracellular space could be identified as one cause of the decrement in metabolic rate (Reipschläger and Pörtner, 1996). In parallel with the decrease in extracellular pH the transmembrane exchange rate of proton-equivalent ions fell, consequently, less natrium was pumped through the Na^+/K^+-ATPase, thereby lowering the energy demand of acid-base regulation (Pörtner et al., 2000).

71. Further study showed, however, that the modulation of acid-base regulation cannot fully explain the suppression of metabolic rate. Ventilation is also reduced under hypercapnia, indicating that a central nervous mechanism is involved (Pörtner et al., 1998). In fact, an accumulation of the neurotransmitter adenosine occurred in the nervous tissue of *S. nudus* under CO_2. Infusions of adenosine caused a suppression of metabolism (Reipschläger et al., 1997). Similar effects were also found in some vertebrates under anoxia (e.g. freshwater fish and turtles) (Lutz and Nilsson, 1997). The role of adenosine or other neurotransmitters in marine fish under hypercapnia still requires investigation.

72. Further results show an increasing degradation of protein under hypercapnia. At the same time the rate of protein synthesis fell (Langenbuch and Pörtner, 2002), as a major process contributing to growth and reproduction. This effect would explain the decrease in growth seen in mussels under hypercapnia (Michaelidis et al., 2005). Reduced growth rates were also found in crustaceans and fish. Many marine fish, however, react differently to hypercapnia than marine invertebrates, because their metabolic rate is not slowed down, and at the same time ventilation rate may increase. Considering the high energy cost of ventilation in water breathers the associated shift in energy budget can explain the observed reduction of growth.

73. In animals from the intertidal zone the suppression of metabolic rate under CO_2 appears adaptive, because it helps to passively survive unfavourable environmental conditions. In the long term (after several weeks at 10 000 ppmv CO_2), however, increased mortality was observed in the sipunculid, with unclear cause and effect relationships (Langenbuch and Pörtner, 2004). Investigations in mussels from the Mediterranean Sea suggest that the effects on calcification as well as metabolic depression and the shift in energy allocation occur in parallel (Michaelidis et al., 2005). Consequently, both the slow-down of somatic growth as well as reduced calcification are involved in growth reduction. These effects are drastic, i.e. a growth reduction by more than 50 % was found in mussels kept under CO_2 at pH 7.3, a pH value expected for the year 2300. As mentioned above, other investigations already show a significant reduction of growth and survival in echinoderms and gastropods from the Pacific at CO_2 concentrations just 180 ppm (µatm) above today's values (section 4.1). As per present scenarios of increasing anthropogenic production of CO_2, such effects will already set in 10 - 20 years from now.

74. Long-term effects of hypercapnia are also to be expected in deep-sea organisms, with corresponding effects on geographic species distribution and their population structures. Their low metabolic rate suggests that the capacities and efficiencies of cellular and organismic acid-base regulation are reduced compared to organisms from the photic zone (Seibel and Walsh, 2001). A lower intracellular buffer capacity (Seibel et al., 1997) and reduced rates of ion exchange at the gills (Goffredi and Childress, 2001) could be typical for deep-sea fauna, with the above mentioned consequences for acid-base, ion and metabolic equilibria. Reduced energy turnover rates and thus limitations of growth and reproduction would have to be expected on long time scales.

75. The conclusion from previous investigations is that many organisms can tolerate CO_2-induced acidification to pH values of 7 to 6.5 for limited time, but a small increase of atmospheric CO_2 levels beyond today's values may already cause metabolic shifts in some animals (especially echinoderms, molluscs), associated with reduced rates of growth and reproduction as well as increasing mortality.

76. At first sight, the effects of CO_2 described here comply with a key role of CO_2 during mass mortality in Permian-Triassic mass extinctions (cf. Knoll et al., 1996). Here pCO_2 values are postulated for the surface layers of the seas, which correspond to those reached locally in CO_2 discharge scenarios. However, the hypothesis of Knoll et al., that mainly animals without gills and with low capacity of circulation and low metabolic rates have been affected, is not supported by the physiological findings discussed here. As explained above, ventilatory compensation plays a small role in more active water breathers. It rather seems to be the extent of calcification, the sensitivity of skeleton structures and the dependence of organismic functions on calcified structures, e.g. in echinoderms, bryozoans and corals which contributes to increased CO_2 sensitivity of these organisms.

4.6 Benthic biogeochemistry and fauna

77. With increasing CO_2 and declining seawater pH the average carbonate saturation state of shallow sea sediment pore waters could decline significantly, inducing dissolution of metastable carbonate phases within the pore-water-sediment system (Andersson et al. 2003). Shallow sea benthic ecosystems, such as in the North Sea, may be particularly sensitive to reducing seawater pH (Turley et al. 2006; The Royal Society 2005) as they are already characterised by strong geochemical gradients, including pH (Fenchel and Riedl 1970). Benthic communities have adapted to these gradients with different species occupying different depth horizons (Barnes and Hughes 1988) so even though benthic systems as a whole are already subject to a relatively large range in pH, many of the organisms and processes that exist within them are not. The surface layer is most densely inhabited, whilst only those species capable of oxygenating their immediate environment, for example through ventilated burrows, are able to dwell below the redox discontinuity depth (Furukawa 2001). Microbial communities and the processes they carry out (e.g. nitrification and denitrification) also differ considerably between the oxic surface sediments and the deeper anoxic layers. Consequently, animals which inhabit permanent burrows may have a greater tolerance to changes in pH than non-burrow builders.

78. Burrowing and bioturbating benthic organisms alter the physical and chemical characteristics of their immediate environment (Rhoads and Young 1970) and thereby the rate of nutrient flux at the sediment/water interface (Nedwell and Walker 1995; Banta et al. 1995; Widdicombe and Austen 1998; Howe et al. 2004) and the maintenance of biodiversity (Widdicombe et al. 2000). Some of these key "ecosystem engineers" have calcareous structures (e.g. heart urchins, sea urchins, starfish, brittle stars and molluscs) and may be particularly vulnerable to the decline in carbonate ions (see section 4.1). Sea urchins appear particularly susceptible even at CO_2 concentrations (550ppm) likely to be reached by around 2050 (Shirayama and Thornton, 2005). Even amongst such organisms which depend on calcium carbonate structures variability in tolerance has been observed with echinoderms showing less tolerance to pH change than molluscs (Shirayama et al. 2004). This potential difference in pH tolerance between benthic species could lead to the selection of more tolerant species and thereby substantial changes in the structure and function of sediment communities in the face of changing levels of pH. Although we are unaware of published work on impact of high CO_2 on benthic diversity and ecosystem function, work has just started on this at Plymouth Marine Laboratory.

79. Pelagic and benthic ecosystems are closely coupled, even in the deep ocean seas (Turley 2000). Sinking particles produced initially by primary production in the photic zone act as the main food resource for sediment dwelling organisms. In shallow coastal seas, up to 80% of the nitrogen required by photosynthesis comes from microbial regeneration of organic matter within sediments (Dale and Prego 2002). Changes to the rate of benthic regeneration of nutrients through changes in the benthic species composition and their function could therefore impact pelagic production. Conversely, changes to rates of primary production, the composition of the primary producers and the rate and timing of their flux to the sea bed could impact the food resources for the sediment dwellers and nutrient regeneration. Also see "Biological pump" (section 4.7).

80. Decreasing pH is likely to result in changes to the speciation and oxidation states of metals (Turley et al. 2004; 2006 and refs therein). Theoretical models predict that decreasing pH generally increases the proportion of free dissolved metal species by reducing the concentration of particulate, immobile metal species. In lakes, a decline in pH from 8 to 6 increased the percentage of free copper from 3 to 73% (Morel et al. 1975). It is generally thought that the free dissolved form of metals have a higher toxicity than particulate forms when present at high concentrations (e.g. copper and zinc). A decrease in pH may also change the nature and form of particle surfaces and therefore metal partitioning (Mouvet and Bourg 1983)

such that there may be release of previously bound metals from the sediment to the seawater. This could be of particular importance in shallow seas with high sediment loadings of bound metals but we are unaware of current research in this area. In vast areas of the open ocean primary production is limited by iron (Coale et al. 1996; Boyd et al. 2000). Theoretically, lower pH could make iron more bioavailable through changing its speciation and thereby reduce its limitation to phytoplankton growth in these regions (Morel et al. 2001; Turley et al. 2004).

4.7 The biological pump, carbon flux and delivery of food to the benthos

81. The global ocean sink for anthropogenic CO_2 is thought to be around half of that produced by human activities since pre-industrial times (Sabine et al. 2004). Organisms fix and export carbon to the deep sea, either as organic carbon (the organic carbon pump which causes a net draw down of CO_2 from the atmosphere into the oceans) or as calcium carbonate (the carbonate counter pump which causes a net release of CO_2 to the atmosphere). The ratio between these two processes (the rain-ratio) determines the flux of CO_2 between the surface ocean and the atmosphere (Riebesell 2004). This biological pump is an important part of the global carbon cycle as over long time scales calcium carbonate is the major form in which carbon is buried in marine sediments (Royal Society 2005). The substantial and rapid changes to the carbonate chemistry of the system may affect plankton species composition by inhibiting calcifying organisms such as coccolithophores, pteropods, gastropods, foraminifera and corals in waters with high CO_2 (Riebesell 2004; Engel et al. 2005; Orr et al. 2005; Royal Society 2005). Engel et al. (2004) reported increased transparent exopolymer particle (TEP) production with elevated CO_2. Since TEP enhances aggregation of cells its increased production could increase the biological pump while decreased calcification by planktonic organisms would reduce the input of ballast and the rate of sinking (Klaas and Archer 2002). Mesocosm experiments of a bloom dominated by *E. huxleyi* indicated that at CO_2 concentrations predicted for 2100 there was a delay in the onset of calcification, a 40% reduction in net community calcification and enhanced loss of organic carbon from the water column implying a shift in the rain ratio (Delille et al. 2005). The behaviour of key calcifiers to higher CO_2 concentrations will determine the future strength of the biological pump (Riebesell 2004), the delivery of food to deeper waters and to benthic organisms (Turley 2000), the global carbon cycle and climate regulation (Archer and Maier-Reimer 1994). Also see section 4.6.

4.8 Adaptation

82. Assuming the IPCC (2002) predicted concentration of atmospheric CO_2, the changes in seawater chemistry that will occur by 2100 or even by 2050 could well influence the structure of marine ecosystems, their biodiversity and impact many trophic levels. Phenotypic adaptations to raised CO_2 over multiple generations needs to be studied (Collins and Bell 2004) under natural environmental conditions (Royal Society 2005). The outstanding question is whether organisms and ecosystems can adapt to these rapid and challenging environmental changes.

5. Other changes to marine systems and their synergistic impacts

83. Apart from ocean acidification, other important changes to the oceans are predicted to occur over the same period of time which could have synergistic impacts on marine ecosystems. Surface water temperature is already increasing and predicted to increase further, accompanied by changes in ocean carbon cycling (Denman et al. 1996; Boyd and Doney 2003) while changes in rainfall and land run off will impact salinity and nutrient input to coastal seas. Increases in temperature (and salinity) will increase the degree of stratification of the water column (unless currents and wind mixing increase to balance this). Increases in temperature, stratification and nutrient input from land run-off could increase the potential risk of hypoxia or anoxia in shelf sea ecosystems. Increased stratification would reduce the influx of nutrients from below the thermocline that sustain primary production and the drawdown of CO_2. As the oceans, and organisms within them, are a major source of other atmosphere changing gases (Nightingale and Liss 2002) changes to the biology could impact their production and cycling.

84. The combined impact of ocean acidification and other global changes could well influence the relative composition, productivity, timing, location and predominance of the major functional groups of phytoplankton and zooplankton and thereby impact the rest of the food web. Models that consider the key interactions of these functional groups and their response to a high CO_2 world are key to making predictions of the overall impact on marine biogeochemical cycles and food webs (Boyd and Doney 2002; Legendre and

Rivkin 2005; Turley et al. 2006). Experimentalists will need to consider multi-factorial impacts to help provide information to drive or test the models.

85. As discussed in section 4.5, the relative role of increased CO_2 and other environmental changes for the Permian-Triass mass extinction is debated. The analysis by Knoll et al. (1996) neglects the role of temperature and its variability which most probably contributed considerably to mass mortalities. In the marine realm, mass mortalities were often connected with strong, long-term and recurrent climate variations and especially with cooling events (Stanley, 1987, Ivany et al., 2000, Pörtner, 2001, 2004). In this context it is important that, according to the principle of oxygen-limited temperature tolerance, the animals' thermal tolerance window is determined by the integrated capacity of ventilatory and cardio-circulatory functions for the uptake and distribution of oxygen in the body (Pörtner, 2001, 2002). This capacity is increased in cold-adapted eurytherms, combined with an increase in energy turnover. The question arises whether CO_2 might influence these relationships.

86. A recent analysis of the marine fossil record showed that mass mortalities repeatedly led to a drastic increase of the fraction of mobile animals in the marine fauna (water breathers) (Bambach et al., 2002). This pattern shows that the most active marine animals survived. According to the concept of oxygen-limited temperature tolerance, the most active animals are those which are especially cold-eurytherm, i.e. tolerant to large temperature variability (Pörtner 2002b, 2004). The most active and eurytherm animals are also those with the highest energy turnover. This effect is to be expected in a similar way in all taxa. CO_2 accumulation and hypoxia alone cannot have caused these effects, because they have a depressing effect on many physiological rates and favour those forms which survive in hypoxic and hypercapnic surroundings at low rates of energy turnover. This would rather lead us to expect the opposite, survival of the less active. However, if there were extreme variations in temperature at the same time, CO_2 enrichment and hypoxia could have influenced the extent of eurythermy and thus have exacerbated mass mortality so that only the most eurythermal animals survived.

87. This hypothesis is supported by the extant significance of interactions between temperature, CO_2 enrichment and hypoxia in marine ecosystems: The present anthropogenic warming and eutrophication trends are combined with a decrease in oxygen contents (hypoxia), especially in coastal zones. All three factors, warming, accumulation of CO_2 in surface layers and increasing hypoxia events combine in their effects on marine fauna. The depressing effect of CO_2 and hypoxia on the animal's aerobic capacity results in a narrowing of the thermal tolerance window, i.e. in a higher sensitivity to extreme temperatures (Pörtner et al., 2005d). This would cause a decreasing range of biogeographical distribution in a climate gradient. Such effects will have a particularly negative influence on populations at the limit of their geographical distribution. Recent study confirms the narrowing of the temperature window under CO_2 (unpublished), quantitative statements, however, are not possible yet. These effects will concern stenotherms and also the most eurythermal animals, but the narrowing of their geographical distribution range may be less fatal, because they start from a larger area of distribution.

88. The negative interactions between temperature extremes and CO_2 are particularly acute in coral reefs. If the atmospheric CO_2 content stabilizes at 550 ppm, a marginalisation of these habitats is already impending (Hoegh-Guldberg, 2005). This would be the result of the combined burden by increased temperatures and CO_2. Increased temperatures are declared responsible for the (six) recurrent bleaching events since 1979. The endosymbiontic zooxanthellae leave their host, the coral bleaches. For the year 1998, the loss of live corals was estimated at 20% worldwide. The increase in CO_2 in parallel to warming trends leads to a decrease in the over-saturation degree of aragonite. This over-saturation is important for the velocity of the calcification process. Calcification is not only the basis for the growth of coral reefs, it also counteracts the erosion process. The CO_2-related slow-down of the calcification rate also hinders the retreat of coral reefs into cooler areas of the sea, so that, as per present perspectives, increased temperatures and CO_2 contents will drastically limit the distributional areas of today's coral reefs (Hoegh-Guldberg, 2005). A comparison with earth history raises the question of why coral reefs could exist e.g. in the Siluric in spite of high atmospheric CO_2 levels. At that time, the calcium contents in sea water were 2 to 2.5 times higher (Arp et al., 2001) and thus provided the required super-saturation values of carbonates.

89. Due to their specialization on a narrow temperature range, on aragonite saturation and on high concentrations of light, today's coral reefs are among the most endangered ecosystems. Nothing can be said, however, on the sensitivity of the insufficiently explored cold-water corals. Besides, there are potentially much endangered species in all ecosystems (Benthic infauna and epifauna and pelagic fauna), especially among echinoderms and pteropods. Changing composition of species communities due to warming are

already being observed and might already be influenced synergistically by previous CO_2 accumulation in the ocean.

6. Research priorities

90. The Royal Society (2005) recognised the seriousness of CO_2 induced acidification, the infancy of research in this area and recommended that a major international research effort should be launched on a scale to that expended on climate change. Key research areas highlighted in the report were the effects of enhanced atmospheric CO_2 on ocean chemistry and the resulting impacts on sensitive organisms, functional groups and ecosystems. The report recommended the need to focus on establishing a better understanding of the various metabolic processes at different parts of the life cycle and how these are expressed at the ecosystem level and developing models that include effects of pH over a range of scales from the level of the organism to that of the ecosystem and the need to include synergistic impacts with those of climate change.

91. The Integrated Marine Biogeochemistry and Ecosystem Research (IMBER) project is an international and multi-disciplinary activity jointly sponsored by the International Geosphere-Biosphere Programme (IGBP) and the Scientific Committee on Oceanic Research (SCOR). The IMBER (http://www.imber.info/) project goal is to understand how interactions between marine biogeochemical cycles and ecosystems respond to and force global change. Ocean acidification is one of the global change priorities that IMBER recognises as important to address.

92. The Scientific Committee on Oceanic Research (SCOR) and the Intergovernmental Oceanographic Commission (IOC) of UNESCO convened an open symposium on *The Ocean in a High-CO2 World* on 10-12 May 2004 in Paris, France at UNESCO Headquarters (http://ioc.unesco.org/iocweb/co2panel/HighOceanCO2.htm). The symposium participants identified the research agenda/priorities related to the ocean in a high-CO_2 world, without mitigation, with attention to both biogeochemical and organismal/ecological aspects. It therefore represents a collective view of research priorities in this area. The following is taken from the report.

6.1 Forcing factors

93. The most obvious forcing factor on the ocean in a high-CO_2 world is increased atmospheric pCO_2, which will increase the surface ocean (and eventually deep ocean) pCO_2 and lower pH. A major research priority will be to conduct research and modelling that will allow predictions of changes in ocean carbonate chemistry, and on how these changes will differentially affect calcitic and aragonitic organisms. As pCO_2 is increasing, other environmental variables will also change as a result. For example, likely changes that will accompany increased pCO_2 include increased temperature, changes in availability of nutrients (due to changes in redox conditions, ocean mixing, patterns of precipitation, dust inputs, and increased stratification), decreased O_2 in the warmer water, changes in salinity due to heating and precipitation effects, and changes in ocean mixing, circulation and wind. It will be very important to consider, in research, observational, and modelling activities, how these changes interact to affect marine biogeochemical processes and feed back to the Earth system. It also will be important to consider regional differences and to consider the combined effects of higher pCO_2 levels, higher temperature, and low O_2 concentrations.

6.2 Ecological/organismal aspects

94. Keeping in mind the forcing factors described above, it will be necessary to conduct research on both ocean biology and biogeochemistry. In terms of biology, effects are naturally expected for calcifying organisms, but it is also important to study the effects of increasing ocean pCO_2 and associated environmental changes on non-calcifying organisms. Interactions and synergies among variables (e.g., pCO_2 and temperature) are particularly important. Specifically, research should include

- Effects on community structure and composition (including how species-specific responses will affect community composition), from bacteria to vertebrates.
- Effects on genetic diversity, species diversity, and the diversity of functional groups.
- Microevolutionary potential and rate of evolutionary change—Earth's temperature and atmospheric CO_2 concentrations have changed in the distant past, but not at the rapid pace that is now occurring, nor at the high CO_2 levels now encountered.
- Many organisms were probably able to evolve quickly enough to adapt to global changes in the past. Will they be able to adapt to the more rapid pace of change now occurring? Can adaptation

occur under a continually and rapidly changing environment versus one that eventually stabilizes?

- Sub-lethal effects—Most effects are likely to be sub-lethal, including decreased reproductive potential, slower growth, and increased susceptibility to disease.

6.3 Key biogeochemical processes

95. Increasing surface ocean pCO_2 and decreasing pH can affect a variety of processes that are important in regulating the oceanic cycles of carbon, nitrogen, and other elements. New research is needed to understand how the ocean will respond to increasing atmospheric CO_2, particularly related to:

- Primary production—Will increasing pCO_2 in the surface ocean fertilize phytoplankton? If so, which species? What effects will this have on higher trophic levels? Since CO_2 generally is not a limiting resource for phytoplankton, production might not increase much, due to limitations in other elements. CO_2 fertilization may affect elemental stoichiometry (C/N/P).
- Remineralization—Auto- and heterotrophic processes are likely to respond differently to environmental changes (e.g., due to differences in temperature dependency). What effect will this have on the balance between primary production and remineralization?
- Will changes in nitrogen fixation, denitrification and nitrification be induced by changes in phytoplankton species composition and changes in oxygen levels?
- DOM transformations (aggregation, solubilization, biological turnover)—Will increasing pCO_2 change the proportion or type of carbon that enters the DOM pool? How will this affect the dynamics of dissolved organic material and particles?
- How does increasing pCO_2 impact the precipitation of $CaCO_3$ by planktonic and benthic calcifiers? What are the current dissolution kinetics of aragonite and calcite and how might they change under different scenarios of increased pCO_2? What impact will increasing pCO_2 and decreasing pH have on dissolution of $CaCO_3$ in the upper ocean, throughout the water column, and in ocean sediments? Will there be an impact on the $CaCO_3$ compensation depth?
- How will changes in the above processes affect export production and the rain ratio?

6.4 Key types of ecosystems/species to be investigated

96. Some ecosystems are more likely to be affected than others by increasing oceanic pCO_2 and decreasing pH, or may have more significant feedbacks to the Earth system. These ecosystems are priority areas for study:

- Ecosystems dominated by and/or structured by calcifying organisms such as coccolithophores, foraminifera, pteropods, and coral reefs (including different species and strains). There is some evidence that increasing pCO_2 would prevent the colonization of corals in new environments (within the temperature tolerance of the corals) because it will cause a decrease in the saturation of $CaCO_3$ in seawater.
- Ecosystems dominated by and/or structured by other biogeochemically relevant functional groups (pelagic and benthic) and "ecosystem engineers"/"keystone species".
- Intertidal and shallow subtidal areas.
- The mesopelagic zone.
- The Southern Ocean and subarctic Pacific Ocean.

6.5 Approaches

97. Discussion group participants identified a set of promising approaches to study how the ocean might respond in a high-CO_2 world. These approaches range from small-scale laboratory experiments to open-ocean perturbation studies:

- Laboratory experiments—Small-scale studies in the laboratory can help isolate various factors to increase the understanding of results from larger-scale field studies and to guide planning for mesocosm and field studies.
- Mesocosm experiments—Experiments in mesocosm enclosures have produced useful results about how species composition changes in carbon-altered ecosystems. These experiments make it possible to create experimental designs with replication and controls on a larger scale and

more realistic conditions than in the laboratory. An important activity will be to design standard experimental protocols that will make these experiments more reproducible.

- Short-term open-ocean perturbation experiments—Large-scale open-ocean iron fertilization experiments have yielded significant new knowledge about ocean ecosystems in the past decade. Short-term additions of carbon dioxide to various ecosystem types should result in similar information gains related to effects of carbon on the ocean.
- FACE-like experiments— Free Air CO_2 Enrichment (FACE) experiments are currently being conducted at many sites worldwide, in a variety of terrestrial, non-agricultural ecosystems. These experiments involve additions of carbon dioxide to research plots continuously for several years to maintain elevated atmospheric CO_2 levels that mimic levels that will be experienced under likely future scenarios. These experiments have demonstrated how plant communities will respond in both the short and long term. The continuity of these experiments is an important feature, because some long-term effects have been shown to differ from short-term effects on the same parameters. Both SOLAS and the IMBER project have proposed FACE-like experiments for the ocean. The benefit of such experiments is that they are more likely to show the actual long-term effects that will occur in the future. The major anticipated drawback is that it might be impossible to use for pelagic communities without enclosing them in some way or somehow using a Lagrangian approach. There is a need to start with a feasibility study because the amount of CO_2 or acid required for a full-scale pelagic FACE experiment may be very high. The other drawback is the public perception problem. This drawback might be approached by pointing out that the effects of elevated CO_2 under "business as usual" scenarios may be so severe that understanding them might cause policymakers to think more carefully about emission controls or other mitigation methods.
- Model development— Ongoing development of models should be pursued, to assess the role of climate feedback and elevated CO_2 levels on ocean ecosystems and biogeochemistry. This will require the reconsideration of the distinction between the euphotic zone and the underlying waters (above the permanent pycnocline). Models should consider the high-CO_2 world in an Earth system context, where feedbacks and indirect effects are important and are often the dominant drivers, and disciplinary distinctions between functional biodiversity, ecosystem functioning and the fluxes of elements and associated feedbacks are no longer appropriate.

98. Other important research and observation approaches that should be explored include:

- Encouraging experimentalists, field researchers, and modelers to work together.
- Using specific locations that are acid- or CO_2-rich due to human effects or natural factors (e.g., the Rio Tinto, outlets of power stations, and natural CO_2 vents such as on Loihi Seamount).
- Adding stable pH sensors to Argo profiling floats.
- Studying interactions between coastal areas and the open ocean, and between the seafloor and water column.
- Following-up on the symposium with international working groups to focus on specific implementation tasks, though SOLAS and IMBER, the International Ocean Carbon Coordination Project, and/or SCOR working groups.

6.6 Additional areas of research

99. The authors of this report to OSPAR BDC recognise additional areas of research since the above 2004 meeting. Impacts studies should also take into account the more subtle effects such as on intracellular processes, cell or metabolic efficiency and indirect effects such as their ability to compete for resources, cope with other environmental stressors, reproduce and adapt. They are:

- Impacts on zooplankton
- Impacts on predator-prey interactions
- Impacts on larval development, settlement and recruitment
- Impacts on primary and secondary production and remineralization
- Impacts on higher trophic groups such as sea mammals and birds
- Impacts on socio-economics including aquaculture and fisheries
- Impacts on services provided by marine systems
- Understanding past geological analogues

- What are the relative impacts of mitigation methods and how do these measure against non mitigation?
- What are the synergistic impacts of ocean acidification and other serious climate change variables
- Feedback to the Earth system

7. References

Adams, E.E., Caulfield, J.A., Herzog, H.J. and Auerbach, D.I. (1997) Impacts of reduced pH from ocean disposal of CO_2. In: Battaglia, B. and Beardmore, J.A. (eds). Ocean storage of carbon dioxide. Workshop 2-Environmental impact. Plenum Press, New York, 41-55.

Ainsworth, E.A. and S.P. Long (2005) "What have we learned from 15 years of free-air CO2 enrichment (FACE)? A meta-analytic review of the responses of photosynthesis, canopy." New Phytologist 165(2): 351-371.

Andersson, A. J., Mackenzie, F. T and Ver, L.M., 2003. Solution of shallow-water carbonates: An insignificant buffer against rising atmospheric CO_2. Geology 31(6): 513-516.

Annis, E.R. 2005. Temperature effects on the vertical distribution of lobster postlarvae (*Homarus americanus*). Limnology & Oceanography, 50(6), 1972-1982.

Archer, D. and Maier-Reimer, E. (1994) The effect of deep-sea sedimentary calcite preservation on atmospheric CO_2 concentrations. *Nature*, 367, 260-263.

Arp, G., A. Reimer, J. Reitner (2001): Photosynthesis-induced biofilm calcification and calcium concentrations in Phanerozoic oceans. *Science*, **292**, 1701-1704.

Auerbach D., J.A. Caulfield, E.E. Adams and H.J. Herzog (1997): Impacts of ocean CO_2 disposal on marine life: I. A toxicological assessment integrating constant-concentration laboratory assay data with variable-concentration field exposure. *Env. Model. Assessment* **2**, 333-343.

Azam, F. et al. 1983. The ecological role of water-column microbes in the sea. Mar. Ecol. Prog. Ser. 10: 257-263.

Bambach R.K., A.H. Knoll and J.J. jr. Sepkowski (2002): Anatomical and ecological constraints on Phanerozoic animal diversity in the marine realm. *Proc. Natl. Acad. Sci.* USA **99**, 6845-6859.

Bamber R.N. (1987): The effects of acidic sea water in young carpet-shell clams, *Venerupis decussata* (L.) (Mollusca: Venracea). *J. Exp. Mar. Biol. Ecol.* **108**, 241-260.

Banta G T, Giblin A E, Hobbie J E & Tucker J (1995). Benthic respiration and nitrogen release in Buzzards Bay, Massachusetts. Journal Marine Research 53, 107–135.

Barker S. and H. Elderfield (2002): Foraminiferal calcification response to glacial-interglacial changes in atmospheric CO_2. *Science* **297**, 833-836.

Barnes RSK & Hughes RN (1988) An Introduction to Marine Ecology. Blackwell Scientific Publications. 351pp

Beardall J & Raven J A (2004). The potential effects of global climate change in microalgal photosynthesis, growth and ecology. Phycologia 43, 31–45.

Beer S, Bjork M, Hellblom F & Axelsson L (2002). Inorganic carbon utilization in marine angiosperms (seagrasses). Functional Plant Biology 29, 237–240.

Bellerby, R.G.J, A. Olsen, T. Furevik and L.G. Anderson 2005. Response of the Surface Ocean CO_2 System in the Nordic Seas and Northern North Atlantic to Climate Change. In H. Drange et al (Ed.) The Nordic Seas: An Integrated Perspective. Geophysical Monograph Series 158, American Geophysical Union, p. 189-197.

Bijma J, Hönisch B & Zeebe R E (2002). Impact of the ocean carbonate chemistry on living foraminiferal shell weight: comment on 'Carbonate ion concentration in glacial-age deep waters of the Caribbean Sea' by Broecker W S & Clark E -art no 1064. Geochemistry Geophysics Geosystems 3, 1064–1064.

Bopp L, Aumont O, Belviso S & Monfray P (2003). Potential impact of climate change on marine dimethyl sulfide emissions. Tellus 55B, 11–22.

Boyd P & Doney S C (2003). The impact of climate change and feedback process on ocean carbon cycle. Ocean Biogeochemistry: In Ocean Biogeochemistry: the role of the ocean carbon cycle in global change (ed Fasham M J R) 157–193., Germany.

Boyd P W, Watson A J, Law C S, Abraham E R, Trull T, Murdoch R, Bakker D C E, Bowie A R, Buesseler K O, Chang H, Charette M, Croot P, Downing K, Frew R, Gall M, Hadfield M, Hall J, Harvey M, Jameson G, LaRoche J, Liddicoat M, Ling R, Maldonado M T, McKay R M, Nodder S, Pickmere S, Pridmore R, Rintoul S, Safi K, Sutton P, Strzepek R, Tanneberger K, Turner S, Waite A, & Zeldis J (2000). A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. Nature 407, 695–702.

Boyd, P. W. and Doney S. C., 2002. Modelling regional responses by marine pelagic ecosystems to global climate change. Geophysical Research Letters 29(16): art. no.-1806.

Brewer, P. G. 1997. Ocean chemistry of the fossil fuel CO_2 signal: The haline signal of "business as usual". *Geophysical Research Letters* **24** (11), 1367-1369.

Broecker W. and Peng T. H. (1979) Gas exchange rates between air and sea Tellus 26, 21-35.

Burkhardt S. and Riebesell U. (1997) CO_2 availability affects elemental composition (C:N:P) of the marine diatom *Skeletonema costatum*. Mar. Ecol. Prog. Ser. 155, 67-76.

Burkhardt S, Zondervan I & Riebesell U (1999). Effect of CO_2 concentration on C:N:P ratio in marine phytoplankton: a species comparison. Limnology and Oceanography 44, 683–690.

Caldeira, K. and M.E. Wickett 2003. Anthropogenic carbon and ocean pH. *Nature* **425**, 365.

Caldeira, K. and M.E. Wickett 2005. Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean. J. geoph. res. 110, C09S04, doi:10.1029/2004JC002671

Caldeira, K., M. Akai, P. Brewer, B. Chen, P. Haugan, T. Iwama, P. Johnston, H. Kheshgi, Q. Li, T. Ohsumi, H. Poertner, C. Sabine, Y. Shirayama, J. Thomson, 2005: Ocean storage. In: IPCC, 2005: IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate

Change [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp.

Cameron J.N. and G.K. Iwama (1989): Compromises between ionic regulation and acid-base regulation in aquatic animals. *Can. J. Zool.* 67, 3078-3084.

Childress J.J. (1995): Are there physiological and biochemical adaptations of metabolism in deep-sea animals? *Trends Ecol. Evolut.* **10**, 30-36.

Childress J.J., R. Lee, N.K. Sanders, H. Felbeck, D. Oros, A. Toulmond, M.C.K. Desbruyeres and J. Brooks (1993): Inorganic carbon uptake in hydrothermal vent tubeworms facilitated by high environmental pCO_2. *Nature* **362**, 147-149.

Childress J.J. and B.A. Seibel (1998): Life at stable low oxygen levels: adaptations of animals to oceanic oxygen minimum layers. *J. Exp. Biol.* **201**, 1223-1232.

Chuck, A., Tyrrell, T., Totterdell, I.J. and Holligan, P.M. 2005. The oceanic response to carbon emissions over the next century:investigation using three carbon cycle models. Tellus, 57B, 70-86.

Cicerone, R., J. Orr, P. Brewer, P. Haugan, L. Merlivat, T. Ohsumi, S. Pantoja, H.-O. Poertner 2004a. Meeting report: The Ocean in a High CO_2 World. EOS Transactions AGU 85(37), 351-353.

Cicerone, R., J. Orr, P. Brewer, P. Haugan, L. Merlivat, T. Ohsumi, S. Pantoja, H.-O. Poertner, M. Hood, E. Urban 2004b. The Ocean in a High CO_2 World. Oceanography 17(3), 72-78.

Coale K H, Johnson K S, Fitzwater S E, Gordon R M, Tanner S, Chavez F P, Ferioli L, Sakamoto C, Rogers P, Millero F, Steinberg P, Nightingale P, Cooper D, Cochlan W P, Landry M R, Constantinou J, Rollwagen G, Trasvina A, Kudela R (1996). A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific-Ocean. Nature 383, 495–501.

Coffin, R.B., Montgomery, M.T., Boyd. T.J. and Masutani, S.M. (2004) Influence of ocean CO_2 sequestration on bacterial productivity. Energy 29, 1511-1520.

Collins S & Bell G (2004). Phenotypic consequences of 1000 generations of selection at elevated CO_2 in a green alga. Nature 431, 566–569.

Crocker C.E. and J.J. Cech (1996): The effects of hypercapnia on the growth of juvenile white sturgeon, *Acipenser transmontanus*. *Aquaculture* **147**, 293-299.

Dale A W & Prego R (2002). Physico-biogeochemical controls on benthic-pelagic coupling of nutrient fluxes and recycling in a coastal upwelling system. Marine Ecology Progress Series 235, 15-8.

Del Giorgio P.A. and P.J. Williams LeB (2005): The global significance of respiration in aquatic ecosystems: from single cells to the biosphere. In: Respiration in Aquatic Ecosystems (eds P.A. Del Giorgio & P.J. LeB Williams) Oxford University Press: Oxford

Delille, B., Harlay, J., Zondervan, I., Jacquet, S., Chou, L., Wollast, R., Bellerby, R.G.J., Frankignoulle, M., Borges, A.V., Riebesell, U. and Gattuso, J-P., 2005. Response of primary production and calcification to changes of pCO_2 during experimental blooms of the coccolithophorid *Emiliania huxleyi*. Global Biogeochemical cycles, 19, GB2023 10.1029/2004GB002318.

Denman K, Hofmann E & Marchant H (1996). Marine biotic responses to environmental change and feedbacks to climate In: Climate change 1995, the science of climate change (eds Houghton J T, Meira Filho L G, Callander B A, Harris N, Kattenberg A, Maskell K) Cambridge University Press: 483–515.

Engel A, Thoms S, Riebesell U, Rochelle-Newall E & Zondervan I (2004). Polysaccharide aggregation as a potential sink of marine dissolved organic carbon. Nature 428, 929–932.

Engel A, Zondervan I, Aerts K, Beaufort L, Benthien A, Chou L, Delille B, Gattuso J-P, Harly J, Heemaan C, Hoffmann L, Jacquet S, Nejstgaard J, Pizay M-D, Rochelle-Newall E S, Schneider U, Terbrueggen A & Riebesell U (2005). Testing the direct effect of CO_2 concentration on marine phytoplankton: a mesocosm experiment with the coccolithophorid Emiliania huxleyi. Limnology and Oceanography 50(2), 493–507.

Evans D.H. (1984): The roles of gill permeability and transport mechanisms in euryhalinity. p. 239-283. In *Fish Physiology*, Vol. XA, ed. by W.S. Haar, D.J. Randall, Academic Press, New York.

Feely R A, Sabine C L, Lee K, Berelson W, Kleypas J, Fabry, V J & Millero F J (2004). Impact of anthropogenic CO_2 on the $CaCO_2$ system in the ocean. Science 305, 362–366.

Fenchel T M & Riedl R J (1970). The sulfide system: a new biotic community underneath the oxidized layer of marine sand bottoms. Marine Biology 7, 255–268.

Field C B, Behrenfield M J, Randerson J T & Falkowski P (1998). Primary production of the biosphere: integrating terrestrial and oceanic components. Science 281, 237–240.

Freiwald, A., Fosså, J.H., Grehan, A., Koslow, T., Roberts, J.M. 2004. Cold-water Coral Reefs. UNEP-WCMC, Cambridge, UK.

Furukawa, Y. (2001). Biogeochemical consequences of macrofauna burrow ventilation. Geochemical Transactions (supplement). ACS Division of Geochemistry Symposium, Biogeochemical consequences of dynamic interactions between benthic fauna, microbes and aquatic sediments, San Diego, CA.

Fung I.Y., S.C. Doney, K. Lindsay, and J. John (2005): Evolution of carbon sinks in a changing climate. *Proc. Natl. Acad. Sci.* USA **102**, 11201–11206.

Gaines, S, and Roughgarden, J. 1985. Larval settlement rate: a leading determinant of structure in an ecological community of the marine intertidal zone. Proc. Natl. Acad. Sci. USA 82: 3707-3711.

Gao K., Aruga, Y., Asada, K., Ishihara, T., Akano, T. and Kiyohara, M. (1993) Calcification in the articulated coralline alga *Corallina pilulifera*, with special reference to the effect of elevated CO_2 concentration. Mar. Biol. 117, 129-132.

Gervais F & Riebesell U (2001). The effect of phosphorus limitation on elemental composition and stable carbon isotope fractionation in a diatom growing under different CO2concentrations. Limnology and Oceanography 46, 497–504.

Giordano M, Beardall J & Raven J A (2005). CO_2 concentrating mechanisms in algae: mechanism, environmental modulation, and evolution. Annual Review of Plant Biology 56, 99–131.

Goffredi S.K. and J.J. Childress (2001): Activity and inhibitor sensitivity of ATPases in the hydrothermal vent tubeworm *Riftia pachyptila*: a comparative approach. *Mar. Biol.* 138, 259-265.

Graham M.S., R.L. Hädrich and G.L. Fletcher (1985): Hematology of three deep-sea fishes: a reflection of low metabolic rates. *Comp. Biochem. Physiol. A* 80, 79-84.

Green M A, Jones M E, Boudreau C L, Moore P L, Westman B A (2004) Dissolution mortality of juvenile bivalves in coastal marine deposits. Limnology and Oceanography 49(3), 727–734.

Hallock, P. (2005) "Global change and modern coral reefs: New opportunities to understand shallow-water carbonate depositional processes." Sedimentary Geology 175(1-4): 19-33.

Haugan, P.M. and H. Drange 1996. Effects of CO_2 on the ocean environment. *Energy Convers. Mgmt.* 37 (6-8), 1019-1022.

Haugan, P.M. 2004. Possible effects of ocean acidification. Reports in Meteorology and Oceanography 2-2004. Geophysical Institute, University of Bergen, Norway ISSN 1502-5519, ISBN 82-8116-002-0.

Heinze, C. 2004. Simulating CaCO3 export production in the greenhouse. *Geophysical Research Letters* **31** L16308, doi:10.1029/2004GL020613.

Heisler N. (1986a): Acid-base regulation in fishes. p. 309-356. In *Acid-base Regulation in Animals,* ed. by N. Heisler, Elsevier Biomedical Press, Amsterdam.

Heisler N. (1986b): Comparative aspects of acid-base regulation. P. 397-450. In *Acid-base Regulation in Animals,* ed. by N. Heisler, Elsevier Biomedical Press, Amsterdam.

Heisler N. (1993): Acid-base regulation. P. 343-377. In *The physiology of fishes*, ed. by D.H. Evans, CRC Press Inc., Boca Raton (FL), U.S.A.

Hinga K.R. (2002). Effects of pH on coastal phytoplankton. *Mar. Ecol. Progr. Ser.* **238**, 281–300.

Hoegh-Guldberg O. (2005): Low coral cover in a high-CO_2 world. *J. Geochem. Res. – Oceans* **110**, C09S06, doi:10.1029/2004JC002528.

Holligan P M, Fernandez E, Aiken J, Balch W M, Boyd P, Burkill P H, Finch M, Groom S B, Malin G, Muller K, Purdie D A, Robinson C, Trees C C, Turner S M & van der Wal P. (1993). A biogeochemical study of the coccolithophore, Emiliania huxleyi, in the North Atlantic. Global Biogeochemical Cycles 7(4), 879–900.

Howe R L, Rees A P & Widdicombe S (2004). The impact of two species of bioturbating shrimp (Callianassa subterranea and Upogebia deltaura) on sediment denitrification. Journal of the Marine Biological Association of the United Kingdom 84, 629–632.

Huesemann M H, Skilmann A D & Crecelius E A (2002). The inhibition of marine nitrification by ocean disposal of carbon dioxide. Marine Pollution Bulletin 44, 142–148.

Ingermann R.L., M. Holcomb, M.L. Robinson and J.G. Cloud (2002): Carbon dioxide and pH affect sperm motility of white sturgeon (*Acipenser transmontanus*). *J. Exp. Biol.* **205**, 2885-2890.

IPCC (2000). Special Report on Emission Scenarios. A Special Report of Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK.

Ishimatsu A., T. Kikkawa, M. Hayashi, K-S. lee and J. Kita (2004): Effects of CO_2 on marine fish: larvae and adults. *J. Oceanogr.* **60**, 731-741.

Ishimatsu A., M. Hayashi, K.-S. Lee, T. Kikkawa and J. Kita (2005): Physiological effects on fishes in a high-CO_2 world. *J. Geochem. Res. – Oceans 110*, C09S09, doi:10.1029/2004JC002564.

Ivany L.C., W.P. Patterson and K.C. Lohmann (2000): Cooler winters as a possible cause of mass extinctions at the Eocene/Oligocene boundary. *Nature* **407**, 887-890.

Kikkawa T., A. Ishimatsu and J. Kita (2003): Acute CO_2 tolerance during the early developmental stages of four marine teleosts. *Env. Toxicol.* **18**, 375-382.

Klaas C & Archer D E (2002). Association of sinking organic matter with various types of mineral ballast in the deep sea: implications for the rain ratio. Global Biogeochemical Cycles 16, article number 1116.

Knoll A.K., R.K. Bambach, D.E. Canfield and J.P. Grotzinger (1996): Comparative earth history and late Permian mass extinction. *Science* **273**, 452-457.

Kübler J E, Johnston A M & Raven J A (1999). The effects of reduced and elevated CO_2 and O_2 on the weed Lomentaria articulata. Plant Cell and Environment 22, 1303–1310.

Kurihara H, Shimode S & Shirayama Y (2004a). Sub-lethal effects of elevated concentration of CO_2 on planktonic copepods and sea urchins. Journal of Oceanography 60, 743–750.

Kurihara H, Shimode S & Shirayama Y (2004b). Effects of raised CO_2 concentration on the egg production rate and early development of two marine copepods (Arctia steuri and Acartia erythraea). Marine Pollution Bulletin 49, 721–727.

Kurihara, H. and Shirayama, Y. (2004) Effects of increased atmospheric CO_2 on sea urchin early development. Mar. Ecol. Prog. Ser. 274, 161-169.

Langenbuch M. and H.O. Pörtner (2002): Changes in metabolic rate and N-excretion in the marine invertebrate *Sipunculus nudus* under conditions of environmental hypercapnia: identifying effective acid-base parameters. *J. Exp. Biol.* **205**, 1153-1160.

Langenbuch M. and H.O. Pörtner (2003): Energy budget of Antarctic fish hepatocytes (*Pachycara brachycephalum* and *Lepidonotothen kempi*) as a function of ambient CO_2: pH dependent limitations of cellular protein biosynthesis? *J. Exp. Biol.* **206**, 3895-3903.

Langenbuch, M. and H.O. Pörtner (2004): High sensitivity to chronically elevated CO_2 in a eurybathic marine sipunculid. *Aquatic Toxicol.* **70**, 55–61.

Larsen B.K., H.O. Pörtner and F.B. Jensen (1997): Extra- and intracellular acid-base balance and ionic regulation in cod (*Gadus morhua*) during combined and isolated exposures to hypercapnia and copper. *Mar. Biol.* **128**, 337-346.

Legendre, L. and Rivkin, R.B. (2005) Integrating functional diversity, food web processes, and biogeochemical carbon fluxes into a conceptual approach for modeling the upper ocean in a high CO_2 world. J. Geophysical Res. 110, C09S17, doi:10.1029/2004JC002530, 1-17.

Lie, U. (Ed.) 1998. CO_2 and marine life. Report from a workshop in Bergen, Norway, 16-18 February 1998. Centre for Environment and Resources, University of Bergen, SMR-report 30/99. ISSN 0803-7132, 42 pp.

Lundberg, L. and P.M. Haugan 1996. A Nordic Seas - Arctic Ocean Carbon Budget From Volume Flows and Inorganic Carbon Data. *Global Biogeochemical Cycles* 10(3), 493-510.

Lutz P.L. and G.E. Nilsson (1997): Contrasting strategies for anoxic brain survival - glycolysis up or down. *J. Exp. Biol.* **200**, 411-419.

McKendry J.E., W.K. Milsom and S.F. Perry (2001): Branchial CO_2 receptors and cardiorespiratory adjustments during hypercarbia in Pacific spiny dogfish (*Squalus acanthias*). *J. Exp. Biol.* **204**, 1519-1527.

McKenzie D.J., E.W. Taylor, A.Z. Dalla Valle and J.F. Steffensen (2002): Tolerance of acute hypercapnic acidosis by the European eel (*Anguilla anguilla*). *J. Comp. Physiol.* B **172**, 339-346.

Michaelidis, B., C. Ouzounis, A. Paleras and HO. Pörtner (2005): Effects of long-term moderate hypercapnia on acid-base balance and growth rate in marine mussels (*Mytilus galloprovincialis*). *Mar. Ecol. Progr. Ser.* **293**, 109-118.

Morel F M, Milligan A J & Saito M A (2003). Marine bioinorganic chemistry: the role of trace metals in the oceanic cycles. In The Oceans and Marine Geochemistry Treatise on Geochemistry (eds Holland H D & Turekian K K). Elsevier-Pergamon: Oxford, UK.

Morel F.M.et al. (1975) Fate of trace metals in Los Angeles County waste water discharge. Environ. Sc. And Technol. 9, 757-761.

Mouvet C & Bourg A C M (1983). Speciation (including adsorbed species) of copper, lead, nickel and zinc in the Meuse River: observed results compared to values calculated with a chemical equilibrium computer program.Water Research 17, 641–649.

Nedwell D B & Walker T R (1995). Sediment - water fluxes of nutrients in an Antarctic coastal environment: Influences of bioturbation. Polar Biology 15, 57–64.

Nightingale, P. D. and Liss P. S., 2003. Gases in seawater In The oceans and marine geochemistry. Ed. H. Elderfield, A Treatise on Geochemistry, Vol 6, Elsevier.

O'Dor R.K. and D.M. Webber (1986): The constraints on cephalopods: why squid aren't fish. *Can. J. Zool.* **64**, 1591-1605.

Orr, J.C., S. Pantoja and H.-O. Poertner 2005a. Introduction to special section: The Ocean in a High CO_2 World. J. geoph. res. 110, C09S01, doi:10.1029/2005JC003086.

Orr, J. C. *et al.* (2005b). Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* **437**, 681-686.

Pörtner H.O. (1990): An analysis of the effects of pH on oxygen binding by squid (*Illex illecebrosus, Loligo pealei*) haemocyanin. *J. Exp. Biol.* **150**, 407-424.

Pörtner H.O. (1994): Coordination of metabolism, acid-base regulation and haemocyanin function in cephalopods. *Mar. Freshw. Behav. Physiol.* **25**, 131-148.

Pörtner H.O. (2001): Climate change and temperature dependent biogeography: oxygen limitation of thermal tolerance in animals. *Naturwissenschaften* **88**, 137-146

Pörtner H.O. (2002a): Climate change and temperature dependent biogeography: systemic to molecular hierarchies of thermal tolerance in animals. *Comp. Biochem. Physiol.* **132**, A739-761.

Pörtner H.O. (2002b): Physiological basis of temperature dependent biogeography: tradeoffs in muscle design and performance in polar ectotherms. *J. exp. Biol.* **205**, 2217-2230.

Pörtner H.O. (2004): Climate variability and the energetic pathways of evolution: the origin of endothermy in mammals and birds. *Physiol. Biochem. Zool.* **77**, 959-981.

Pörtner H.O. and M.K. Grieshaber (1993): Characteristics of the critical PO_2(s): gas exchange, metabolic rate and the mode of energy production. pp. 330-357. In *The vertebrate gas transport cascade: adaptations to environment and mode of life*, ed. by J:E.P.W. Bicudo, CRC Press Inc., Boca Raton FL, U.S.A.

Pörtner H.O. and A. Reipschläger (1996): Ocean disposal of anthropogenic CO_2: physiological effects on tolerant and intolerant animals. pp. 57-81. In *Ocean Storage of CO_2. Environmental Impact*, ed. by B. Ormerod and M. Angel, Massachusetts Institute of Technology and International Energy Agency, Greenhouse Gas R&D Programme, Cheltenham/Boston.

Pörtner H.O. and R. Playle (eds.) (1998): Cold Ocean Physiology. Cambridge University Press, Cambridge, 489 pp.

Pörtner H.O. and R. Knust (2005): Effects of climate change on marine fishes: Explaining field observations from physiology. Manuskript.

Pörtner H.O., A. Reipschläger and N. Heisler (1998): Metabolism and acid-base regulation in *Sipunculus nudus* as a function of ambient carbon dioxide. *J. Exp. Biol.* **201**, 43-55.

Pörtner H.O. and S. Zielinski (1998): Environmental constraints and the physiology of performance in squids. In *Cephalopod Biodiversity, Ecology and Evolution*, ed. by A.I.L. Payne, M.R. Lipinski, M.R. Clarke, and M.A.C. Roeleveld. *South African Journal of Marine Science* **20**, 207-221.

Pörtner, H.O., L. Peck, S. Zielinski, and L.Z. Conway (1999): Intracellular pH and energy metabolism in the highly stenothermal Antarctic bivalve *Limopsis marionensis* as a function of ambient temperature. *Polar Biol.* **22**, 17-30.

Pörtner, H.O., B. Berdal, R. Blust, O. Brix, A. Colosimo, B. De Wachter, A. Giuliani, T. Johansen, T. Fischer, R. Knust, G. Lannig, G. Naevdal, A. Nedenes, G. Nyhammer, F.J. Sartoris, I. Serendero, P. Sirabella, S. Thorkildsen and M. Zakhartsev (2001): Climate induced temperature effects on growth performance, fecundity and recruitment in marine fish: developing a hypothesis for cause and effect relationships in Atlantic cod (*Gadus morhua*) and common eelpout (*Zoarces viviparus*). *Cont. Shelf Res.* **21**, 1975-1997.

Pörtner H.O., C. Bock and A. Reipschläger (2000): Modulation of the cost of pHi regulation during metabolic depression: a ^{31}P-NMR study in invertebrate (*Sipunculus nudus*) isolated muscle. *J. Exp. Biol.* **203**, 2417-2428.

Pörtner H.O., M. Langenbuch, and A. Reipschläger (2004a): Biological impact of elevated ocean CO_2 concentrations: lessons from animal physiology and earth history? *J. Oceanogr.* **60**, 705-718.

Pörtner H.O., F.C. Mark, and C. Bock (2004b): Oxygen limited thermal tolerance in fish? Answers obtained by Nuclear Magnetic Resonance techniques. *Respiratory Physiology & Neurobiology* **141**, 243–260.

Pörtner, H.O., D. Storch, and O.Heilmayer (2005a): Constraints and trade-offs in climate dependent adaptation: energy budgets and growth in a latitudinal cline. *Scientia marina,* in press

Pörtner H.O., Lucassen M. and Storch D. (2005b): Metabolic biochemistry: its role in thermal tolerance and in the capacities of physiological and ecological function. In *The Physiology of Polar Fishes* (Guest editors: J. F. Steffensen and A. P. Farrell) To appear in 2005 as volume 22 in the series Fish Physiology - Series editors W.S. Hoar, D.R. Randall and A.P. Farrell

Pörtner H.O., A.F. Bennett, F. Bozinovic, A. Clarke, M.A. Lardies, M. Lucassen, B. Pelster, F. Schiemer and J.H. Stillman (2005c): Trade-offs in thermal adaptation: the need for a molecular to ecological integration. *Physiol. Biochem. Zool.*, in press

Pörtner H.O., M. Langenbuch and B. Michaelidis (2005d): Synergistic effects of temperature extremes, hypoxia and increases in CO_2 on marine animals: from earth history to global change. *J. Geochem. Res. – Oceans*, in press

Raven J A (1986). Physiological consequences of extremely small size for autotrophic organisms in the sea. In Photosynthetic Picoplankton 214. (eds Platt T & Li W K W) 583. Canadian Bulletin of Fisheries and Aquatic Sciences: Ottawa, Canada.

Raven J., K. Caldeira, H. Elderfield, O.Hoegh-Guldberg, P. Liss, U. Riebesell, J. Shepherd, C. Turley and A. Watson (2005): Ocean acidification due to increasing atmospheric carbon dioxide. Policy document 12/05, www.royalsoc.ac.uk, The Royal Society, UK.

Redfield A.C. and R. Goodkind (1929): The significance of the Bohr effect on the respiration and asphyxiation of the squid, *Loligo pealei. J. Exp. Biol.* **6**, 340-349.

Reipschläger A., G.E. Nilsson and H.O. Pörtner (1997): Adenosine is a mediator of metabolic depression in the marine worm *Sipunculus nudus. Am. J. Physiol.* **272**, R350-R356.

Reynaud S., N. Leclercq, S. Romaine-Lioud, C. Ferrier-Pagès, J. Jaubert and J.P. Gattuso (2003): Interacting effects of CO_2 partial pressure and temperature on photosynthesis and calcification in a scleratinian coral. *Global Change Biol.* **9**, 1-9.

Rhoads D C & Young D K (1970). The influence of deposit-feeding organisms on sediment stability and community trophic structure. Journal Marine Research 28, 150–178.

Riebesell U, Zondervan I, Rost B, Tortell P D, Zeebe R & Morel F M (2000). Reduced calcification of marine plankton in response to increased atmospheric CO_2. Nature 407, 364–367.

Riebesell, U. (2004) Effects of CO_2 enrichment on marine phytoplankton. J. Oceanogr. 60, 719-729.

Rost B, Riebesell U (2004). Coccolithophores and the biological pump: responses to environmental changes pp76–99. In: Coccolithophores – From molecular processes to global impact. Springer.

Rost B, Riebesell U, Burkhardt S & Sültemeyer D (2003). Carbon acquisition by bloom-forming marine phytoplankton. Limnology and Oceanography 48, 55–67.

Royal Society, 2005. Ocean acidification due to increasing atmospheric carbon dioxide. Policy document 12/05 Royal Society: London.

Sabine C L, Feely R A, Gruber N, Key R M, Lee K, Bullister J L, Wanninkhof R, Wong C S, Wallace D W R, Tilbrook B, Millero F J, Peng T H, Kozyr A, Ono T & Rios A F (2004). The oceanic sink for anthropogenic CO_2. Science 305, 367–371.

Sanders N.K. and J.J. Childress (1990): A comparison of the respiratory function of the hemocyanins of vertically migrating and non-migrating oplophorid shrimps. *J. Exp. Biol.* **152**, 167-187.

Scheid P., H. Shams and J. Piper (1989): Gas exchange in vertebrates. *Verh. Dtsch. Zool. Ges.* **82**, 57-68.

Seebacher F., W. Davison, C. J. Lowe, and C. E. Franklin (2005): A falsification of the thermal specialization paradigm: compensation for elevated temperatures in Antarctic fish. *Biology Letters* **1**, in press

Seibel B.A., E.V. Thuesen, J.J. Childress and L.A. Gorodezky (1997): Decline in pelagic cephalopod metabolism with habitat depth reflects differences in locomotory efficiency. *Biol. Bull.* **192**, 262-278.

Seibel B.A. and P.J. Walsh (2001): Potential impacts of CO_2 injections on deep-sea biota. *Science* **294**, 319-320.

Shirayama Y. (1995): Current status of deep-sea biology in relation to the CO_2 disposal. In *Direct ocean disposal of carbon dioxide*, ed. by N. Handa and T. Oshumi, Terra Scient. Publ. Comp., Tokyo, p. 253-264.

Shirayama, Y. et al 2004. Special Section on Advances in Biological Research for CO2 Ocean Sequestration, *Journal of Oceanography* **60** (4), 691-816.

Shirayama, Y.; Thornton, H. (2005) Effect of increased atmospheric CO_2 on shallow water marine benthos. J. Geophys. Res., Vol. 110, No. C9, C09S08 10.1029/2004JC002618

Stillman J.H und C.A. Reeb (2001): Molecular phylogeny of Eastern Pacific porcelain crabs, genera *Petrolisthes* and *Pachycheles*, based on the mtDNA 16S rDNA sequence: phylogeographic and systematic implications. *Molecular Phylogenetics and Evolution* **19**, 236-245.

Sundby S. (2000): Recruitment of Atlantic cod stocks in relation to temperature and advection of copepod populations. *Sarsia* **85**: 277-298.

Takeuchi, K., Sugimori, M., Furukawa, S., Fujioka, Y and Ishizaka, J. Impacts of CO_2 on microbial communities in a mesocosm experiment. (unpublished)

Tamburri M.N., E.T. Peltzer, G.E. Friedrich, I. Aya, K. Yamane and P.G. Brewer (2000): A field study of the effects of CO_2 ocean disposal on mobile deep-sea animals. *Mar. Chem.* **72** 95-101.

Tamburrini M., M. Romano, V. Carratore, A. Kunzmann, M. Coletta and G. diPrisco (1998): The hemoglobins of the Antarctic fishes *Artedidraco orianae* and *Pogonophryne scotti. J. Biol. Chem.* **273**, 32452-32459.

Turley, C., Blackford, J., Widdicombe, S., Lowe, D., Nightingale, P.D. and Rees, A. P. (2006)Reviewing the impact of increased atmospheric CO_2 on oceanic pH and the marine ecosystem. In: Avoiding Dangerous Climate Change, Schellnhuber, H J., Cramer,W., Nakicenovic, N., Wigley, T. and Yohe, G (Eds). Cambridge University Press, 8, 65-70.

Turley, C., Nightingale, P., Riley, N., Widdicombe, S., Joint, I., Gallienne, C., Lowe, D., Goldson, L., Beaumont, N., Mariotte, P., Groom, S., Smerdon, G., Rees, A., Blackford, J., Owens, N., West, J Land, P. and Woodason, E. (2004) Literature Review: Environmental impacts of a gradual or catastrophic release of CO_2 into the marine environment following carbon dioxide capture. (DEFRA: MARP 30 (ME2104) 31 March 2004.

Turley, C.M. .(2000) Bacteria in the deep-sea benthic boundary layer and sediment water interface of the NE Atlantic: A Review. FEMS Microbiol. Ecol. 1154, 1-11.

Vinogradov G.A. and V.T. Komov (1985): Ion regulation in the perch, *Perca fluviatilis*, in connection with the problem of acidification of water bodies. *J. Ichthyol.* **25**, 53-61.

Watanabe, Y., Ishida, H. Yamaguchi, A and Ishizaka, J. (2001) Effects of high concentration of CO_2 on deep-sea plankton. In: CO_2 ocean sequestration and its biological impacts. Bull Jpn Soc Sci Fish 67 (4), 764-765.

Wells R.M.G., M.D. Ashby, S.J. Duncan and J.A. Macdonald (1980): Comparative study of the erythrocytes and haemoglobins of nototheniid fishes from Antarctica. *J. Fish Biol.* **17**, 517-527.

Wheatly M.G. (1989): Physiological response of the crayfish *Pacifasticus leniusculus* (Dana) to environmental hypoxia. I. Extracellular acid-base and electrolyte status and trans-branchial exchange. *J. Exp. Biol.* **57**, 673-680.

Whiteley N.M., J.L. Scott, S.J. Breeze and L. McCann (2001): Effects of water salinity on acid-base balance in decapod crustaceans. *J. Exp. Biol.* **204**, 1003-1011.

Wickins J.F. (1984): The effect of hypercapnic sea water on growth and mineralization in penaeid prawns. *Aquaculture* **41**, 37-48.

Widdicombe S & Austen MC (1998). Experimental evidence for the role of Brissopsis lyrifera (Forbes, 1841) as a critical species in the maintenance of benthic diversity and the modification of sediment chemistry. Journal of Experimental Marine Biology and Ecology 228(2), 241–255.

Widdicombe S, Austen M C, Kendall M A, Warwick R M & Jones M B (2000). Bioturbation as a mechanism for setting and maintaining levels of diversity in subtidal macrobenthic communities. Hydrobiologia 440, 369–377.

Wolf-Gladrow, D. A., Riebesell, U., Burkhardt, S and Bijma, J.,1999. Direct effects of CO_2 concentration on growth and isotopic composition of marine plankton. Tellus Series B-Chemical and Physical Meteorology 51(2): 461-476.

Yamada, Y. and Ikeda T (1999) Acute toxicity of lowered pH to some oceanic zooplankton. Plankton Biol Ecol 46 (1), 62-67.

Zachos, J.C., Wara, M.W., Bohaty, S., Delaney, M.L., Petrizzo, M. R. Brill, A., Bralower, T.J. and Premoli-Silva I. (2005) A Transient Rise in Tropical Sea Surface Temperature During the Paleocene-Eocene Thermal Maximum. Science 28 November 2003: Vol. 302. no. 5650, 1551–1554.

Zeebe RE & Wolf-Gladrow D (2001) CO_2 in Seawater: Equilibrium, Kinetics, Isotopes. Elsevier Oceanography Series Vol.65, 360pp.

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Review

Effects of CO_2 on Marine Fish: Larvae and Adults

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CO_2-enriched seawater was far more toxic to eggs and larvae of a marine fish, silver seabream, *Pagrus major*, than HCl-acidified seawater when tested at the same seawater pH. Data on the effects of acidified seawater can therefore not be used to estimate the toxicity of CO_2, as has been done in earlier studies. Ontogenetic changes in CO_2 tolerance of two marine bony fishes (*Pag. major* and Japanese sillago, *Sillago japonica*) showed a similar, characteristic pattern: the cleavage and juvenile stages were most susceptible, whereas the preflexion and flexion stages were much more tolerant to CO_2. Adult Japanese amberjack, *Seriola quinqueradiata*, and bastard halibut, *Paralichthys olivaceus*, died within 8 and 48 h, respectively, during exposure to seawater equilibrated with 5% CO_2. Only 20% of a cartilaginous fish, starspotted smoothhound, *Mustelus manazo*, died at 7% CO_2 within 72 h. Arterial pH initially decreased but completely recovered within 1–24 h for *Ser. quinqueradiata* and *Par. olivaceus* at 1 and 3% CO_2, but the recovery was slower and complete only at 1% for *M. manazo*. During exposure to 5% CO_2, *Par. olivaceus* died after arterial pH had been completely restored. Exposure to 5% CO_2 rapidly depressed the cardiac output of *Ser. quinqueradiata*, while 1% CO_2 had no effect. Both levels of ambient CO_2 had no effect on blood O_2 levels. We tentatively conclude that cardiac failure is important in the mechanisms by which CO_2 kills fish. High CO_2 levels near injection points during CO_2 ocean sequestration are likely to have acute deleterious effects on both larvae and adults of marine fishes.

Keywords:
- Physiological effects of CO_2,
- CO_2 mortality,
- marine fish,
- developmental stage,
- acid-base regulation,
- blood circulation.

1. Introduction

Although fish physiologists have investigated the effects of environmental hypercapnia (elevated ambient CO_2) on several physiological functions of this major group in the aquatic environment, studies have dealt mostly with freshwater species and not much with marine species (Ishimatsu and Kita, 1999). Apart from the relative inaccessibility of marine species in most laboratories, there has been little incentive for the reseachers to study effects of CO_2 on marine fish, because under natural conditions, both aquatic hypercapnia and hypoxia (low ambient O_2) are more common in freshwater environments, most typically in stagnant water bodies in the tropics, but are relatively infrequent in marine environments (see Dejours, 1988).

However, the idea of CO_2 ocean sequestration as a method to mitigate adverse effects of global warming has created an urgent need for a thorough understanding of how elevated levels of CO_2 in the ocean affect marine life. CO_2 causes a wide range of mostly negative influences on many aspects of animal physiology (see Pörtner *et al.*, 2004). Short-term effects, for example, include disturbance of acid-base status, respiration, blood circulation and nervous activities of the exposed animals, while long-term effects include reduced growth rate, reproduction, and calcification, although there are few data available on the long-term effects of CO_2 (Ishimatsu and Kita, 1999).

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When a fish is exposed to environmental hypercapnia, body fluid pH rapidly decreases due to increased body fluid PCO_2, but is subsequently compensated by accumulation of bicarbonate ions in body fluids as long as PCO_2 remains sublethal. The gills are the principal site of bicarbonate uptake from and/or hydrogen ion excretion into the ambient water (Heisler, 1986). Marine fish generally show faster pH compensation than freshwater species because of the higher bicarbonate (Heisler, 1993) and sodium chloride concentrations (Iwama and Heisler, 1991) of seawater. Hypercapnia generally enhances gill ventilation of fish. It has been postulated that the CO_2-driven hyperventilation is due to lowered blood oxygen content caused by both Bohr and Root effects, but recent evidence has demonstrated that CO_2 itself stimulates gill ventilation (Burleson and Smatresk, 2000; McKendry *et al.*, 2001). Chemoreceptors responsible for the response appear to reside in the gills. Cardiovascular responses to hypercapnia have not been examined until relatively recently. Studies reported variable cardiac and blood pressure responses, probably due to interspecific variability of CO_2 sensitivities and the different experimental protocols used (Perry and Gilmour, 2002).

Much less is known on the effects of higher, possibly lethal levels of CO_2 on fish. Cruz-Neto and Steffensen (1997) reported a decrease of oxygen uptake in freshwater European eel, *Anguilla anguilla*, subjected to water PCO_2 of 4.0 kPa, while McKenzie *et al.* (2002) reported no effect of water PCO_2 of up to 10.66 kPa on oxygen uptake, arterial PO_2 and cardiac output for the same species. Under extremely high CO_2 concentrations, fish will be anesthetized (Yoshikawa *et al.*, 1994; Bernier and Randall, 1998), and eventually die (Takeda and Itazawa, 1983).

This paper summarizes our recent findings on the effects of both lethal and sublethal levels of CO_2 on marine larval and adult fish. Fish in the early developmental stages are generally more susceptible to environmental toxicants than adults (McKim, 1977). It is therefore conceivable that CO_2 exerts greater negative impacts on fish eggs, larvae and juveniles, but this was a totally unexplored area before we started CO_2 exposure studies on the early stages (Kikkawa *et al.*, 2003, 2004). Even if the severity of environmental hypercapnia due to CO_2 sequestration is made tolerable to adults, a gradual reduction of population size, and changes in marine ecosystem structures are unavoidable consequences when young individuals cannot survive. Therefore, evaluation of both acute and chronic influences of CO_2 on marine animals should take all life stages of susceptible marine species into consideration.

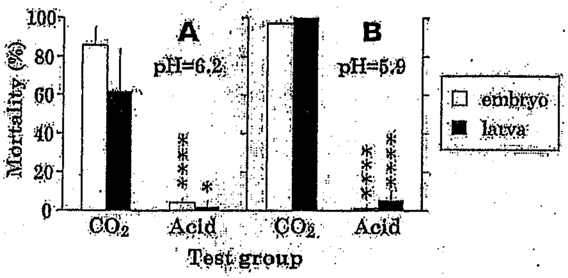

Fig. 1. Comparison of mean mortalities of embryo ($n = 5$) and larva ($n = 3$) of silver seabream, *Pagrus major*, exposed to two seawater pH levels lowered by either CO_2 or HCl (Condition A: pH 6.2, Condition B: pH 5.9 in Table 1). Exposure periods for embryo and larva were 6 h and 24 h, respectively. Asterisks show significant difference between test groups (A: Welch's t-test, B: Student's t-test, *: $p < 0.05$, ****: $p < 0.0001$, from Kikkawa *et al.*, 2004).

Table 1. Seawater carbonic systems of CO_2 and acid groups.

Parameters	Condition A		Condition B	
	CO_2 (5%)	Acid	CO_2 (10%)	Acid
pH	6.16	6.19	5.86	5.87
$[H^+]$ (mmol L^{-1})	$6.92 \cdot 10^{-7}$	$6.46 \cdot 10^{-7}$	$1.38 \cdot 10^{-6}$	$1.35 \cdot 10^{-6}$
PCO_2 (kPa)	4.95	0.037	9.90	0.037
$[CO_2]$ (mmol kg^{-1})*	1.58	$1.17 \cdot 10^{-2}$	3.16	$1.17 \cdot 10^{-2}$
$[HCO_3^-]$ (mmol kg^{-1})	2.16	$1.71 \cdot 10^{-2}$	2.16	$0.82 \cdot 10^{-2}$
$[CO_3^{2-}]$ (mmol kg^{-1})	$2.05 \cdot 10^{-3}$	$1.74 \cdot 10^{-5}$	$1.03 \cdot 10^{-3}$	$4.00 \cdot 10^{-6}$

pK_1 (6.026) and pK_2 (9.181) from Mehrbach *et al.* (1973). CO_2 solubility (0.03241 mol $kg^{-1}atm^{-1}$) from Weiss (1974). *Includes negligible concentration of H_2CO_3 (Heisler, 1986). Assuming atmospheric pressure of 101.3 kPa. From Kikkawa *et al.* (2004).

2. Larvae

2.1 *Acid and* CO_2

We exposed eggs and larvae of silver seabream, *Pagrus major*, to seawater pre-acidified either by equilibrating with a CO_2 gas mixture or addition of hydrochloric acid to give the same pH levels (pH 6.2 and 5.9). Eggs were judged dead if hatching did not occur, while the death of larvae was judged on cessation of heartbeat. When tested at the same pH levels, seawater acidified by elevated PCO_2 exerted a far more severe effect on survival of eggs (Fig. 1A) and larvae (Fig. 1B) than seawater acidified by addition of hydrochloric acid. Mortalities were significantly higher in the CO_2 groups than in the acid groups, irrespective of developmental stage. The use of acid toxicity data of nonvolatile acids, such as HCl or H_2SO_4, would therefore greatly underestimate the impacts of CO_2, as has been done in earlier studies (Auerbach *et al.*, 1997). CO_2 must be used in both laboratory and field experiments to properly assess the environmental impacts of CO_2 ocean sequestration on marine organisms, and we must urgently accumulate CO_2 toxicity data for various species with different physiological and ecological characteristics under different environmental conditions, e.g. temperature, pressure, and dissolved O_2 levels.

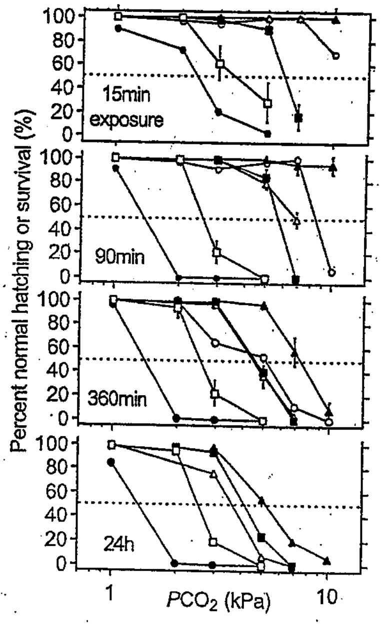

Fig. 2. Percent normal hatching or survival of eggs, larvae and juveniles of *Pagrus major* in hypercapnic seawater for 15 min to 24 h exposure. Vertical lines indicate standard deviation. Solid circles: cleavage stage, open circles: embryo stage, solid triangles: preflexion stage, open triangles: flexion stage, solid squares: postflexion stage, open squares: juvenile stage (from Kikkawa *et al.*, 2003).

Table 1 lists the calculated concentrations of CO_2-derived molecular species in the test seawater. All CO_2-derived molecular species were ca. 130-fold (5%) and 260-fold (10%) higher in the CO_2 group than in the acid group, while the H^+ concentration was nearly identical for each pH level. Compared with HCO_3^- and CO_3^{2-} ions, uncharged CO_2 molecules readily diffuse through the epithelium into the body according to PCO_2 gradient (Vandenberg *et al.*, 1994), and then hydrate to form carbonic acid, which immediately dissociates into H^+ and HCO_3^-, the latter further dissociating into H^+ and CO_3^{2-}. Thus, elevation of ambient PCO_2 will rapidly increase H^+ concentrations of body fluids and decrease their pH. The resulting intracellular acidosis will affect a number of physiological processes (Roos and Boron, 1981), to the extent that it may be lethal to marine organisms. In addition to these acidic toxicities, CO_2 itself may be toxic to animal cells (Max, 1991).

2.2 *Ontogenetic changes in* CO_2 *susceptibility*

Both hatching (for cleavage and embryo stages) and survival (preflexion stage and thereafter) declined with water PCO_2 and exposure period when *Pag. major* was exposed to different levels of ambient CO_2 levels for varying periods of time (Fig. 2). The effects of water PCO_2 on percentage hatching and survival of Japanese sillago, *Sillago japonica*, were generally similar to those for *Pag. major*, although the trend was less clear.

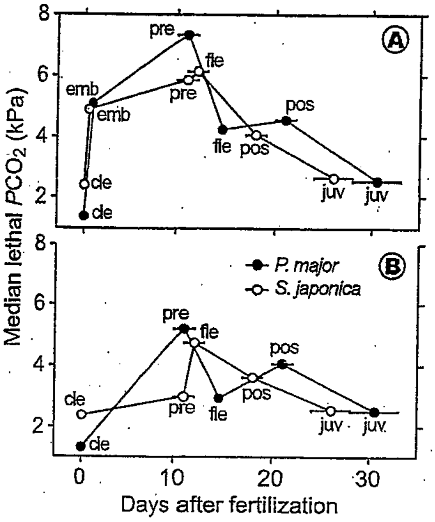

Fig. 3. Ontogenetic changes of the median lethal PCO_2 in *Pagrus major* (solid circles) and *Sillago japonica* (open circles). Horizontal lines show range. A: 360 min exposure, B: 24 h exposure. cle: cleavage stage, emb: embryo stage, pre: preflexion stage, fle: flexion stage, pos: postflexion stage, juv: juvenile stage (from Kikkawa *et al.*, 2003).

Table 2. Median lethal $P\mathrm{CO}_2$ of four teleosts.

Species	Stage	Median lethal $P\mathrm{CO}_2$ (kPa)							
		15 min	90 min	360 min	1000 min	24 h	45 h	48 h	72 h
Pagrus major	Egg (cleavage)	2.20	1.35	1.38	—	1.31	—	—	—
	Egg (embryo)	>9.90	8.39	5.08	—	—	—	—	—
	Larva (preflexion)	>9.90	>9.90	7.33	—	5.22	—	—	—
	Larva (flexion)	>6.93	6.84	4.24	—	2.94	—	—	—
	Larva (postflexion)	5.96	5.68	4.56	—	4.09	—	—	—
	Juvenile	3.56	2.56	2.54	—	2.52	—	—	—
Sillago japonica	Egg (cleavage)	2.52	2.39	2.40	2.38	—	—	—	—
	Egg (embryo)	>9.80	>9.80	4.88	—	—	—	—	—
	Larva (preflexion)	>9.80	>9.80	5.87	—	2.98	—	—	—
	Larva (flexion)	>9.80	9.10	6.13	—	4.73	—	—	—
	Larva (postflexion)	>4.90	4.34	4.06	—	3.63	—	—	—
	Juvenile	3.72	2.81	2.66	—	2.57	—	—	—
Paralichthys olivaceus	Egg (cleavage)	>7.95	2.93	2.78	—	2.82	2.29	—	—
	Young	>6.95	>6.95	>6.95	—	4.96	—	4.61	4.61
Euthynnus affinis	Egg (cleavage)	>14.75	9.96	11.84	—	9.28	—	—	—

From Kikkawa *et al.* (2003).

The pattern of ontogenetic changes in CO_2 tolerance, expressed as median lethal $P\mathrm{CO}_2$ ($P\mathrm{CO}_2$ at which 50% of test animals die in a specified exposure period), was similar for *Pag. major* and *Sil. japonica*, in that median lethal $P\mathrm{CO}_2$ peaked in the preflexion stage (*Pag. major*) or one day after, i.e. the flexion stage (*Sil. japonica*), with CO_2 sensitivity much higher in the preceding and following stages (Table 2 and Fig. 3). This pattern was especially clear when median lethal $P\mathrm{CO}_2$ was calculated for 360 min, and might be common among temperate shallow-water teleosts, considering the different taxonomy and life histories of the two species; *Pag. major* migrates between the coast and adjacent shelf waters while *Sil. japonica* is a coastal demersal fish.

It is currently unclear why CO_2 susceptibility changes during early development. Our hypothesis is that developmental changes in ion-transporting chloride cell population and respiratory surface area are responsible for the changes. We postulate that gill chloride cells are involved in pH regulation in marine species (see Subsection 3.1 Acid-base regulation). Chloride cells develop in the embryo stage in a number of teleosts (Kaneko *et al.*, 1995; Shiraishi *et al.*, 1997; Sasai *et al.*, 1998; Katoh *et al.*, 2000), and this may explain the observed enhanced tolerance to CO_2 from the cleavage to the embryo stages. Our recent studies have demonstrated a significant increase in chloride cell size in the yolk sac membrane of *Sil. japonica* exposed to 1% CO_2 for 21 h and in the gills of young *Pag. major* subjected to both short-term (1% CO_2 for 24 h) and long-term (0.6 and 1.1% CO_2 for 30 days) hypercapnia (Kikkawa *et al.*, unpublished).

The gradual fall in CO_2 tolerance from the larval to juvenile stage may result from the development of gill lamellae in the preflexion stage (*Pag. major*: Oikawa *et al.*, 1999; *Sil. japonica*: Oozeki *et al.*, 1992), which dramatically increases the surface area available for diffusion. In these early developmental stages, gas transfer across the body surface should be diffusion-limited (Perry and Gilmour, 2002).

3. Adults

3.1 Acid-base regulation

Teleosts died during 5% CO_2 exposure (water $P\mathrm{CO}_2$ 4.9 kPa): cumulative mortality was 17% at 8 h, 33% at 24 h and 100% at 48 h for the bastard halibut (*Paralichthys olivaceus*), whereas the Japanese amberjack (*Seriola quinqueradiata*) died considerably earlier (20% mortality recorded at 3 h and 100% at 8 h). In contrast, a cartilaginous fish, the starspotted smooth-hound (*Mustelus manazo*), died only at 7% CO_2 (6.9 kPa) with 20% mortality recorded at 72 h. Thus, *M. manazo* was more tolerant to CO_2 than the two teleosts, although pHa (arterial pH) regulation was less efficient in this fish than in the teleosts (see below). This may indicate that blood pH itself is not a direct cause of acute fish death during hypercapnia.

Figure 4 summarizes acid-base changes during CO_2

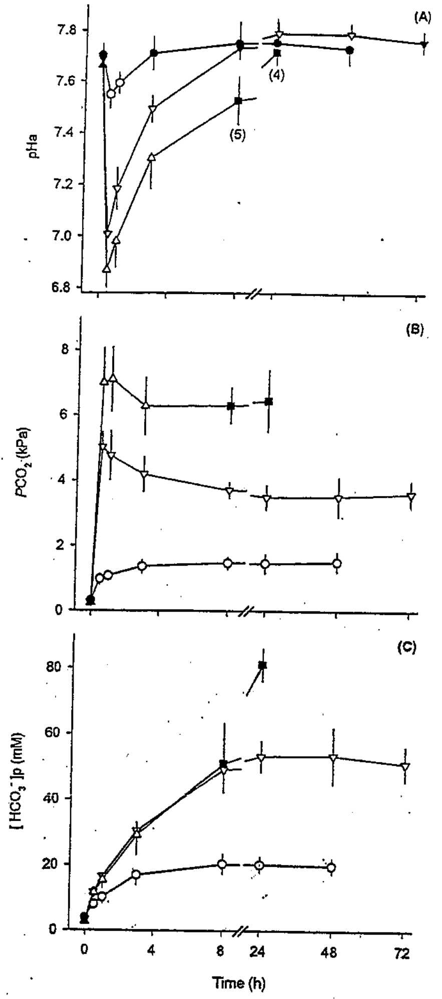

Fig. 4. Arterial pH (A), PCO_2 (B) and hematocrit (Hct, C) of *Paralichthys olivaceus* during exposure to seawater equilibrated with 1% (circles), 3% (upward triangles) and 5% CO_2 (downward triangles) in air ($N = 5$). Open symbols indicate significant differences from corresponding 0-h values ($p < 0.05$; Dunnett test). N decreased due to mortality at 5% (squares), to which no statistical comparison was applied (from Hayashi *et al.*, 2004).

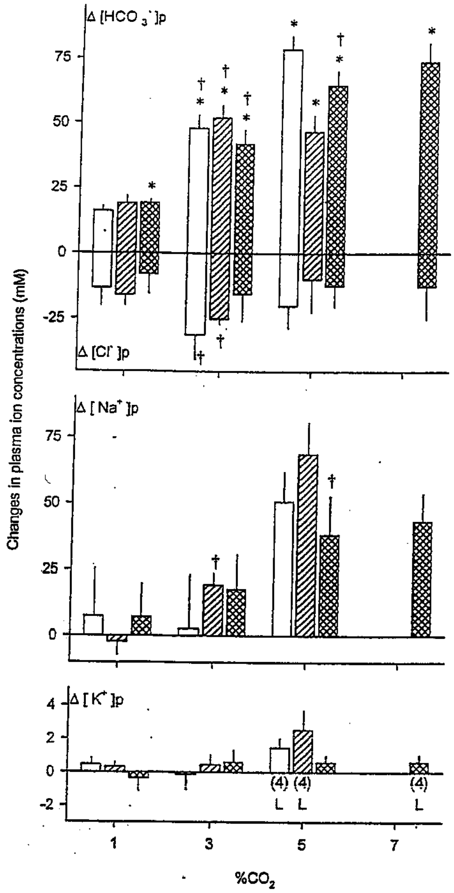

Fig. 5. Changes in plasma ion concentrations in response to environmental hypercapnia for *Paralichthys olivaceus* (open bars, $N = 6$), *Seriola quinqueradiata* (hatched bars, $N = 5$), and *Mustelus manazo* (cross hatched bars, $N = 5$). The data are shown as differences between normocapnic control values and data obtained at the end of each CO_2 exposure (72 h for sublethal exposures and the last sampling time for lethal exposures (L), i.e. 5% for *Par. olivaceus* and *Ser. quinqueradiata*, and 7% for *M. manazo*). Numbers in parentheses indicate the numbers of fish at the last sampling time. Vertical lines indicate SD. Asterisks indicate that absolute changes in [HCO_3^-]p were significantly different from those in [Cl^-]p under the same condition ($p < 0.05$; paired t-test). Daggers represent significant differences from the corresponding 1% values ($p < 0.05$; Dunnett test, no comparison from 1% values was applied where partial mortality occurred: from Hayashi *et al.*, 2004).

exposure for *Par. olivaceus*. When exposed to elevated ambient CO_2, PCO_2 gradient is transiently reversed until a new steady-state condition is established by continued production of metabolic CO_2 to resume outward diffusion of CO_2 through the gills. Elevations of blood PCO_2 resulted in a transient but significant drop of pHa, which was subsequently recovered within 3 to 24 h by CO_2-dependent increases in plasma [HCO_3^-] ([HCO_3^-]p). Importantly, fish died at 5% CO_2 after pHa had already been completely restored to the pre-exposure level within 24 h. Qualitatively, two other fish (*Ser. quinqueradiata* and *M. manazo*) showed a similar pattern of pHa recovery during CO_2 exposure. However, there were noticeable quantitative differences in acid-base and plasma ion changes during CO_2 exposure among fish as well as among applied CO_2 levels (Table 3). The pHa recovery found in this study is relatively more rapid than those

Table 3. Depression (ΔpHa) and recovery time (R.T.) of pHa during CO_2 exposure.

Experimental fish	Water temp. (°C)	%CO_2	ΔpHa	R.T. (h)	References
Halibut (SW)	20	1	−0.16 ± 0.06 a	3	Hayashi *et al.*, 2004
		3	−0.68 ± 0.05 b	8	
		5	−0.80 ± 0.08 c	24	
Amberjack (SW)	20	1	−0.10 ± 0.03 a	1	Hayashi *et al.*, 2004
		3	−0.27 ± 0.03 d	8	
		5	−0.45 ± 0.10 d	No recovery	
Smooth-hound (SW)	17	1	−0.33 ± 0.03 d	72	Hayashi *et al.*, 2004
		3	−0.68 ± 0.05 b	72 (−0.14 ± 0.04)	
		5	−0.82 ± 0.04 c	72 (−0.19 ± 0.05)	
		7	−0.96 ± 0.10 d	No recovery	
Conger (*Conger conger*) (SW)	17	1	−0.40	10	Toews *et al.*, 1983
Cod (*Gadus morhua*) (SW)	12	1	−0.20	24	Larsen *et al.*, 1997
Carp (*Cyprinus carpio*) (FW)	15	1	−0.22	>456	Claiborne and Heisler, 1986

Recovery time is defined as the time it needed before pHa became insignificantly different from the control, pre-exposure value. ΔpHa values at the same CO_2 levels with same letters are not significantly different from each other ($p < 0.05$; Tukey test). From Hayashi *et al.* (2004).

previously reported, especially compared with the freshwater carp (Table 3).

Figure 5 compares changes in plasma ion concentrations from respective control values during exposure (Δ[ions]p). The data are calculated as the difference between the final values (72 h for sublethal conditions or the last sampling time for lethal conditions) and the corresponding pre-exposure values. As far as water PCO_2 remains at sublethal levels, Δ[HCO_3^-]p increased in a CO_2-dependent manner for all fish, values being more or less similar at a given CO_2 level. Δ[Cl^-]p was significantly more negative at 3% than at 1% for the teleosts, whereas Δ[Cl^-]p was nearly constant irrespective of water CO_2 levels for *M. manazo*. At 1% CO_2, Δ[HCO_3^-]p was significantly larger than −Δ[Cl^-]p only for *M. manazo*, while this was the case at higher CO_2 levels for all fish. Δ[Na^+]p values were significantly larger at 3% (*Ser. quinqueradiata*) and 5% (*M. manazo*) than corresponding 1% values. There were no significant differences in Δ[K^+]p. Exposure to lethal levels of hypercapnia resulted in further increases in Δ[HCO_3^-]p for *Par. olivaceus* and *M. manazo*, but not for *Ser. quinqueradiata*. Δ[Cl^-]p did not show any further decrease. Δ[Na^+]p increased substantially for the teleosts but not for *M. manazo*. Δ[K^+]p increased only in the teleosts during lethal CO_2 exposure.

A net absorption of HCO_3^- from and/or an excretion of H^+ ions to surrounding water across the gills are responsible for pHa recovery during hypercapnia in both marine teleosts (Toews *et al.*, 1983) and elasmobranchs (sharks and rays, Claiborne and Evans, 1992). The transport of HCO_3^- and/or H^+ across the body surface inevitably accompanies transport of counterions to maintain the electroneutrality of body fluids, but the precise mechanisms of, and the cell types responsible for the transport process have yet to be firmly established, particularly for marine fish. For freshwater fish, the role of H^+-ATPase coupled with Na^+ channels for acid-base regulation has gained growing support in recent years, but the role of H^+-ATPase in marine fish is generally thought to be minor (Claiborne *et al.*, 2002). The current model of acid-base regulation in marine fish emphasizes Na^+/H^+ exchange brought about by Na^+/H^+ ion exchangers (Claiborne *et al.*, 2002). However, it should be noted that [Cl^-]p invariably decreases with a nearly equimolar increase in [HCO_3^-]p under low (1 to 2%) levels of hypercapnia in both freshwater and marine teleosts, with little or no change in [Na^+]p (Toews *et al.*, 1983; Larsen *et al.*, 1997). This attests to the importance of Cl^- ions as the main counterion accompanying acid-base compensation at least at sublethal moderate levels of hypercapnia.

Marine fish actively secrete Na^+ and Cl^- through chloride cells to counterbalance diffusional entry of the ions (Zadunaisky, 1984). We have recently found that Na^+/K^+ ATPase activity in the gills increased significantly upon exposure to 1% and 5% CO_2 and that apical opening area of branchial chloride cells increased significantly upon exposure to 5% CO_2 in *Par. olivaceus* (Hayashi *et al.*, unpublished). Hypercapnia also increased chloride cell size in larval *Sil. japonica* and young *Par. major* (Kikkawa *et al.*, unpublished). In addition, there is some morphological evidence for the involvement of chloride cells in acid-base regulation in freshwater fish. Goss *et al.* (1995) demonstrated that decreases in $[Cl^-]p$ during hypercapnic exposure in brown bullhead, *Ictalurus nebulosus*, coincided with a reduction in chloride cell surface area caused by the extension of adjacent pavement cells, thereby limiting active uptake of the ion. Kaneko *et al.* (1999) found a remarkable proliferation of branchial chloride cells in Japanese dace, *Tribolodon hakonensis*, in acid water. We speculate that the lowering of $[Cl^-]p$ observed in marine fish during hypercapnia was brought about by stimulated chloride cell activity.

Most previous studies employed only moderate levels of hypercapnia (mostly 1 to 2% CO_2), and few data are available on acid-base responses and plasma ion status under different levels of hypercapnia. No direct comparison has been made on acid-base adjustments among different groups of fish under various CO_2 conditions. At 3% or higher CO_2 conditions, a Na^+-involving mechanism appears to participate in pHa recovery as attested by the significant rise in $[Na^+]p$ (Fig. 5). Grøttum and Sigholt (1996) also reported a 20 mM rise in $[Na^+]p$ during 7% CO_2 exposure for the seabass, *Dicentrarchus labrax*, when $[Cl^-]p$ decreased by about 50 mM. Elasmobranch fish appear to employ different acid-base regulatory mechanisms, because responses of plasma sodium and chloride ion concentrations to different levels of hypercapnia differ from those in teleosts (Fig. 5). Previous studies on elasmobranchs reported either no change in $[Cl^-]p$ during 1% hypercapnia for a skate, *Raja ocellata* (Graham *et al.*, 1990), and 0.7% for a dogfish, *Scyliorhinus stellaris* (Randall *et al.*, 1976), or a small but significant decrease for a dogfish, *Squalus acanthias* (Cross *et al.*, 1969).

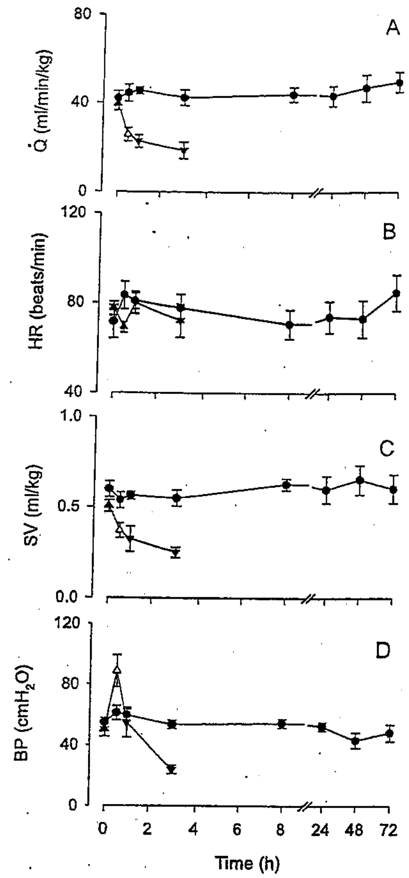

Fig. 6. Time-dependent changes in cardiac output (Q: A), heart rate (HR: B), stroke volume (SV: C) and arterial blood pressure (BP: D) in *Seriola quinqueradiata* exposed to two levels of hypercapnia. Circles represent data at 1% CO_2 (water $PCO_2 = 0.9$ kPa, $N = 5$), and triangles data at 5% CO_2 (water $PCO_2 = 5.1$ kPa, $N = 6$). Open symbols indicate a significant difference from control values ($P < 0.05$). Downward triangles indicate that N was decreased due to fish death. No statistical analysis was applied to these points. Means ±SEM. From Lee *et al.* (2003).

3.2 Cardiovascular function

No Japanese amberjack, *Seriola quinqueradiata*, died at 1% CO_2 until the end of the exposure (72 h), while all fish died within 8 h at 5%. The exposure to 5% CO_2 had deleterious effects on cardiac function (Fig. 6). Cardiac output (Q) and strike volume (SV) rapidly decreased, while heart rate (HR) was maintained throughout the experiment.

Neither arterial PO_2 (PaO_2) (Fig. 7A) nor oxygen content (CaO_2) (Fig. 7B) changed significantly during exposure to either level of hypercapnia. Hematocrit (Hct) increased significantly only at 5% CO_2 (Fig. 7C). Acid-base responses were essentially the same as reported above. Although the oxygen affinity of amberjack blood is sensitive to CO_2/pH (Bohr factor −0.74, Lee *et al.*, 2003), CaO_2 was probably maintained by the release of stored red blood cells into circulation, as suggested by the large increase in hematocrit. The pHa was only about 0.3 pH unit lower than the pre-exposure level before the fish died at 5% CO_2, making it unlikely to be the cause of CO_2 mortality. In addition, *Par. olivaceus* died during exposure to 5% CO_2, when pHa had already been restored to the normocapnic level (Fig. 4). From these findings, we tentatively conclude that cardiac failure, and not blood acidosis, is the major physiological perturbation leading

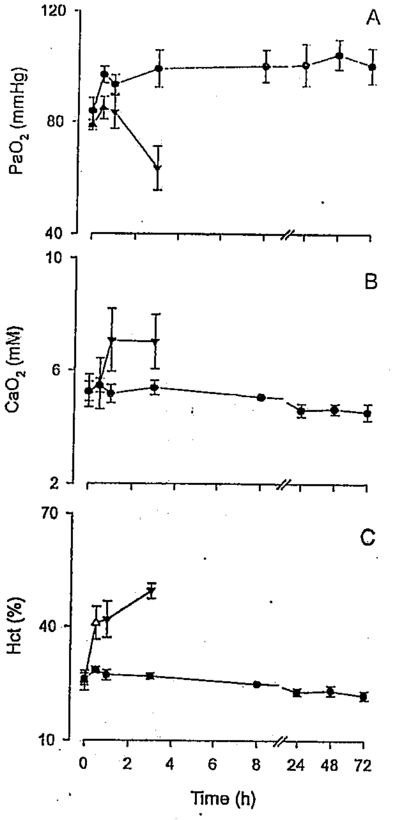

Fig. 7. Time-dependent changes in arterial PO_2 (PaO_2: A), arterial oxygen content (CaO_2: B) and hematocrit value (Hct: C) in *Seriola quinqueradiata*. Symbols are the same as in Fig. 6. From Lee *et al.* (2003).

to death of fish subjected to lethal levels of environmental CO_2 pressures.

Hypercapnic acidosis is known to negatively affect contraction of fish cardiac muscle cells (myocardium) *in vitro* (see Farrell and Jones, 1992 for review). The high solubility of CO_2 will rapidly lower intracellular pH of the myocardium, reducing contractility through an antagonism between hydrogen ions and intracellular calcium ion (Gesser and Poupa, 1983). It is conceivable, therefore, that the reduced myocardial contractility is responsible for the observed lowering of stroke volume. As shown above, CO_2 tolerance varied among fishes, i.e. the starspotted smooth-hound (*M. manazo*) being the most tolerant, followed in turn by *Par. olivaceus* and *Ser. quiqueradiata* (Hayashi *et al.*, 2004). In this context, it may be worth pointing out that a flounder (*Platichthys* (=*Pleuronectes*) *flesus*) is exceptional among fish in that myocardial contractility restores under sustained *in vitro* hypercapnia, as in mammalian myocardium (Gesser and Poupa, 1983). Therefore, the higher tolerance of *Par. olivaceus*, compared with that of *Ser. quinqueradiata*, might be due to this exceptional capacity of myocardial cells. However, one should be somewhat cautious about extrapolating these *in vitro* findings to *in vivo* conditions because these *in vitro* experiments compared myocardial forces at 2–3% CO_2 and above 10% CO_2, the former "low" CO_2 level already being far higher than *in vivo* CO_2 levels under normocapnic conditions.

In spite of the established negative inotropic effect (i.e. reduction of contractility) of hypercapnia on fish myocardium *in vitro*, *in vivo* cardiac responses to hypercapnia varied among fishes (see Perry and Gilmour, 2002 for review). Perry *et al.* (1999) reported that rainbow trout (*Oncorhynchus mykiss*) exposed to water PCO_2 of 0.8 and 1.2 kPa for 30 min experienced no change in cardiac output, a 15–26% increase in stroke volume, but a significant drop in heart rate. In contrast, white sturgeon (*Acipenser transmontanus*) exposed to water PCO_2 of 2.6 kPa for 2 h showed a 31% increase in cardiac output, a 41% increase in stroke volume, and a smaller but significant (8%) increase in heart rate (Crocker *et al.*, 2000). McKendry *et al.* (2001) demonstrated that hypercapnia (water PCO_2 0.9 kPa for 20 min) elicited a 30% decrease in cardiac output, and a 64% reduction in heart rate in the Pacific spiny dogfish (*Squalus acanthias*), indicating that stroke volume was increassed. McKenzie *et al.* (2002) reported acute cardiorespiratory responses of freshwater eel, *Anguilla anguilla*, to graded levels of CO_2, and found no significant effect on cardiac output up to water PCO_2 as high as 10.7 kPa; a significant rise in stroke volume at PCO_2 higher than 5.33 kPa accompanied by a corresponding fall in heart rate. Obviously, *in vivo* cardiovascular responses to hypercapnia varies with the severity as well as the duration of hypercapnia imposed on fish, let alone interspecific variability, and probably experimental temperature. Furthermore, the above studies all examined an acute response (commonly shorter than 30 min), and no information is available on the effects of long-term exposure, during which respiratory acidosis is compensated, as described earlier. This may be particularly relevant in considering cardiac function under sustained hypercapnia because the *in vitro* depression of myocardial contractility by hypercapnic acidosis depends on bicarbonate concentration in the bathing medium. Therefore, cardiac output depressed by hypercapnia may be restored as bicarbonate concentration is increased by the acid-base compensation unless hypercapnic stress is so severe that death would ensue in a short time.

In vivo blood pressure responses to hypercapnia are similarly variable. Trout showed a significant increase in the dorsal aortic pressure at water PCO_2 of above 0.47 kPa accompanied by a water PCO_2-dependent increases in systemic vascular resistance (Perry *et al.*, 1999). Changes in dorsal aortic pressure in white sturgeon were significant, but only marginal, i.e. from 2.92 ± 0.093 kPa during normocapnia to 3.00 ± 0.11 in 2 h of hypercapnia. Systemic resistance decreased significantly (20%, Crocker *et al.*, 2000). The dogfish showed a small but significant decrease (11%) in dorsal aortic pressure, with no change in systemic resistance (McKendry *et al.*, 2001). The dramatic increase in dorsal aortic pressure during exposure to 5% CO_2 indicate a considerable hypertention of the ventral aorta, although no data are available for the latter. The very high pressure level is likely beyond the range of homeometric regulation, with which stroke volume is maintained over a range of output pressure (Fig. 6, see Farrell and Jones, 1992). In fact, cardiac output began to fall before blood pressure started to rise (Lee *et al.*, 2003). Certainly, more study is needed to understand neural and hormonal cardiovascular regulation during hypercapnia.

4. Future Studies

Environmental factors that should be considered in estimating the lethal effect of CO_2 at depth are low temperature and high pressure. Water temperature in the ocean declines rapidly with depth, and is below 4°C at depths at which CO_2 sequestration is being proposed (Lerman, 1986). Therefore, CO_2 exposure tests should be conducted at low temperatures, or results obtained at higher temperatures should be somehow extrapolated to low temperatures. Another complicating factor is that the taxonomy of bathypelagic and epipelagic fish differs greatly (Weitzman, 1997). Although the susceptibility of bathypelagic fishes to CO_2 is conceivably different from that of epipelagic species, it may be logistically very difficult to use these fishes for experiments, particularly individuals in early developmental stages. However, we have recently found that adults of some deep-sea fish can be captured and kept alive under atmospheric pressure, such as rough snailfish, *Careproctus trachysoma* (Liparididae, distribution: 300–800 m), and Tanaka's eelpout *Lycodes tanakai* (Zoarcidae, distribution: >300 m) in Japan Sea (water temperature 1–2°C below depths of larger than 200 m). We have recently conducted a preliminary CO_2 exposure experiment on *C. trachysoma* using a high pressure chamber (max. pressure 50 MPa) at 5°C. Special care was necessary when handling the fish, but we successfully recorded electrocardiograms from fish exposed to seawater equilibrated with 1% CO_2 at 10 MPa (Ishimatsu *et al.*, unpublished).

Alternatively, the CO_2 susceptibility of deep-sea fishes may be estimated indirectly by using some morphological characteristics that correlate with CO_2 susceptibility. Our recent results suggest that chloride cell activity is stimulated by hypercapnia (Hayashi *et al.*, unpublished). Further, exceptionally CO_2-tolerant larval fish had a high density of chloride cells (Kikkawa *et al.*, unpublished). Thus, if interspecific correlation between chloride cell morphometry and CO_2-susceptility is established, then it may be possible to estimate the CO_2 susceptibility of deep-sea fishes without having live materials for experimental evaluation.

Finally, it should be noted that animals would be subjected to fluctuating PCO_2 when CO_2 droplets are released from the lower end of a pipe used for CO_2 ocean sequestration (Sato and Sato, 2002). Our preliminary studies indicated that mortality differed considerably when fish is exposed to unsteady levels of environmental CO_2 conditions, as compared with data obtained using steady CO_2 protocols (Kikkawa *et al.*, unpublished). This should also be included in experimental protocols to assess the effects of CO_2 under realistic conditions of CO_2 ocean sequestration.

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References

Auerbach, D. I., J. A. Caufield, E. E. Adams and H. J. Herzog (1997): Impacts of ocean CO_2 disposal on marine life: I. A toxicological assessment integrating constant-concentration laboratory assay data with variable-concentration field exposure. *Environ. Model. Assess.*, **2**, 333–343.

Bernier, N. J. and D. J. Randall (1998): Carbon dioxide anaesthesia in rainbow trout: effects of hypercapnic level and stress on induction and recovery from anaesthetic treatment. *J. Fish Biol.*, **52**, 621–637.

Burleson, M. L. and N. J. Smatresk (2000): Branchial chemoreceptors mediate ventilatory responses to hypercapnic acidosis in channel catfish. *Comp. Biochem. Physiol.*, **125A**, 403–414.

Claiborne, J. B. and D. H. Evans (1992): Acid-base balance and ion transfers in the spiny dogfish (*Squalus acanthias*) during hypercapnia: A role for ammonia excretion. *J. Exp. Zool.*, **261**, 9–17.

Claiborne, J. B. and N. Heisler (1986): Acid-base regulation and ion transfers in the carp (*Cyprinus carpio*): pH compensation during graded long-and short-term environmental hypercapnia, and the effect of bicarbonate infusion. *J. Exp. Biol.*, **126**, 41–61.

Claiborne, J. B., S. L. Edwards and A. I. Morrison-Shetlar (2002): Acid-base regulation in fishes: cellular and molecular mechanisms. *J. Exp. Zool.*, **293**, 302–319.

Crocker, C. E., A. P. Farrell, A. K. Gamperl and J. J. Cech, Jr. (2000): Cardiorespiratory responses of white sturgeon to environmental hypercapnia. *Am. J. Physiol.*, **279**, R617–R628.

Cross, C. E., B. S. Packer, J. M. Linta, H. V. Murdaugh, Jr. and E. D. Robin (1969): H^+ buffering and excretion in response to acute hypercapnia in the dogfish *Squalus acanthias*. *Am. J. Physiol.*, **216**, 440–452.

Cruz-Neto, A. P. and J. F. Steffensen (1997): The effects of acute hypoxia and hypercapnia on oxygen consumption of the freshwater European eel. *J. Fish Biol.*, **50**, 759–769.

Dejours, P. (1988): *Respiration in Water and Air: Adaptations-Regulation-Evolution*. Elsevier, New York, 179 pp.

Farrell, A. P. and D. R. Jones (1992): The heart. p. 1–73. In *Fish Physiology Vol. XIIA*, ed. by W. S. Hoar, D. J. Randall and A. P. Farrell, Academic Press, San Diego.

Gesser, H. and O. Poupa (1983): Acidosis and cardiac muscle contractility: comparative aspects. *Comp. Biochem. Physiol.*, **76A**, 559–566.

Goss, G. G., S. F. Perry and P. Laurent (1995): Ultrastructural and morphometric studies on ion and acid-base transport processes in freshwater fish. p. 257–284. In *Fish Physiology Vol. 14: Cellular and Molecular Approaches to Fish Ionic Regulation*, ed. by C. M. Wood and T. J. Shuttleworth, Academic Press, San Diego.

Graham, M. S., J. D. Turner and C. M. Wood (1990): Control of ventilation in the hypercapnic skate *Raja ocellata*: I. Blood and extradural fluid. *Respir. Physiol.*, **80**, 259–277.

Grøttum, J. A. and T. Sigholt (1996): Acute toxicity of carbon dioxide on European seabass (*Dicentrarchus labrax*): Mortality and effects on plasma ions. *Comp. Biochem. Physiol.*, **115A**, 323–327.

Hayashi, M., J. Kita and A. Ishimatsu (2004): Acid-base responses to lethal aquatic hypercapnia in three marine fish. *Mar. Biol.*, **144**, 153–160.

Heisler, N. (1986): Acid-base regulation in fishes. p. 309–356. In *Acid-Base Regulation in Animals*, ed. by N. Heisler, Elsevier, Amsterdam.

Heisler, N. (1993): Acid-base regulation. p. 343–378. In *The Physiology of Fishes*, ed. by D. H. Evans, CRC Press, Boca Raton.

Ishimatsu, A. and J. Kita (1999): Effects of environmental hypercapnia on fish. *Japan. J. Icthyol.*, **46**, 1–13.

Iwama, G. K. and N. Heisler (1991): Effect of environmental water salinity on acid-base regulation during environmental hypercapnia in the rainbow trout (*Oncorhynchus mykiss*). *J. Exp. Biol.*, **158**, 1–18.

Kaneko, T., S. Hasegawa, Y. Takagi, M. Tagawa and T. Hirano (1995): Hypoosmoregulatory ability of eyed-stage embryos of chum salmon. *Mar. Biol.*, **122**, 165–170.

Kaneko, T., S. Hasegawa, K. Uchida, T. Ogasawara, A. Oyagi and T. Hirano (1999): Acid tolerance of Japanese dace (a cyprinid teleost) in lake Osorezan, a remarkable acid lake. *Zool. Sci.*, **16**, 871–877.

Katoh, F., A. Shimizu, K. Uchida and T. Kaneko (2000): Shift of chloride cell distribution during early life stages in seawater-adapted killifish, *Fundulus heteroclitus*. *Zool. Sci.*, **17**, 11–18.

Kikkawa, T., A. Ishimatsu and J. Kita (2003): Acute CO_2 tolerance during the early developmental stages of four marine teleosts. *Env. Toxicol.*, **18**, 375–382.

Kikkawa, T., J. Kita and A. Ishimatsu (2004): Comparison of the lethal effect of CO_2 and acidification on red sea bream (*Pagrus major*) during the early developmental stages. *Mar. Pol. Bull.*, **48**, 108–110.

Larsen, B. K., H.-O. Pörtner and J. B. Jensen (1997): Extra- and intracellular acid-base balance and ionic regulation in cod (*Gadus morhua*) during combined and isolated exposures to hypercapnia and copper. *Mar. Biol.*, **128**, 337–346.

Lee, K. S., J. Kita and A. Ishimatsu (2003): Effects of lethal levels of environmental hypercapnia on cardiovascular and blood-gas status in yellowtail, *Seriola quinqueradiata*. *Zool. Sci.*, **20**, 417–422.

Lerman, M. (1986): *Marine Biology*. The Benjamin/Cummings Publishing Company, California, 534 pp.

Max, B. (1991): This and that: the neurotoxicity of carbon dioxide. *Trends Pharmacol. Sci.*, **12**, 408–411.

McKendry, J. E., W. K. Milsom and S. F. Perry (2001): Branchial CO_2 receptors and cardiorespiratory adjustments during hypercarbia in Pacific spiny dogfish (*Squalus acanthias*). *J. Exp. Biol.*, **204**, 1519–1527.

McKenzie, D. J., E. W. Taylor, A. Z. Dalla Valle and J. F. Steffensen (2002): Tolerance of acute hypercapnic acidosis by the European eel (*Anguilla anguilla*). *J. Comp. Physiol.*, **172B**, 339–346.

McKim, J. M. (1977): Evaluation of tests with early life stages of fish for predicting long-term toxicity. *J. Fish. Res. Board Can.*, **34**, 1148–1154.

Mehrbach, C., C. H. Culberson, J. H. Hawley and J. E. Pytkowwicz (1973): Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limonol. Oceanogr.*, **18**, 897–907.

Oikawa, S., M. Hirata, J. Kita and Y. Itazawa (1999): Ontogeny of respiratory area of a marine teleost, porgy, *Pagrus major*. *Ichthyol. Res.*, **46**, 233–244.

Oozeki, Y., P.-P. Hwang and R. Hirano (1992): Larval development of the Japanese whiting, *Sillago japonica*. *Japan. J. Ichthyol.*, **39**, 59–669.

Perry, S. F. and K. M. Gilmour (2002): Sensing and transfer of respiratory gases at the fish gill. *J. Exp. Zool.*, **293**, 249–263.

Perry, S. F., R. Fritsche, T. M. Hoagland, D. W. Duff and K. R. Olson (1999): The control of blood pressure during external hypercapnia in the rainbow trout (*Oncorhynchus mykiss*). *J. Exp. Biol.*, **202**, 2177–2190.

Pörtner, H.-O., M. Langenbuch and A. Reipschläger (2004): Biological impact of elevated ocean CO_2 concentrations: Lessons from animal physiology and earth history. *J. Oceanogr.*, **60**, this issue, 705–718.

Randall, D. J., N. Heisler and F. Drees (1976): Ventilatory responses to hypercapnia in the larger spotted dogfish *Scyliorhinus stellaris*. *Am. J. Physiol.*, **230**, 590–594.

Roos, A. and W. F. Boron (1981): Intracellular pH. *Physiol. Rev.*, **61**, 296–434.

Sasai, S., T. Kaneko and K. Tsukamoto (1998): Extrabranchial chloride cells in early life stages of Japanese eel, *Anguilla japonica*. *Ichthyol. Res.*, **45**, 95–98.

Sato, T. and K. Sato (2002): Numerical prediction of the dilution process and its biological impacts in CO_2 ocean sequestration. *Mar. Sci. Technol.*, **6**, 169–180.

Shiraishi, K., T. Kaneko, S. Hasegawa and T. Hirano (1997): Development of multicellular complexes of chloride cells in the yolk-sac membrane of tilapia (*Oreochromis mossambicus*) embryos and larvae in seawater. *Cell Tiss. Res.*, **288**, 583–590.

Takeda, T. and Y. Itazawa (1983): Possibility of applying anesthesia by carbon dioxide in the transportation of live fish. *Nippon Suisan Gakkaishi*, **49**, 725–731.

Toews, D. P., G. F. Holeton and N. Heisler (1983): Regulation of the acid-base status during environmental hypercapnia in the marine teleost fish *Conger conger*. *J. Exp. Biol.*, **107**, 9–20.

Vandenberg, J. I., J. C. Metcalfe and A. A. Grace (1994): Intracellular pH recovery during respiratory acidosis in perfused hearts. *Am. J. Physiol.*, **266**, C489–C497.

Weiss, R. F. (1974): Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.*, **2**, 203–215.

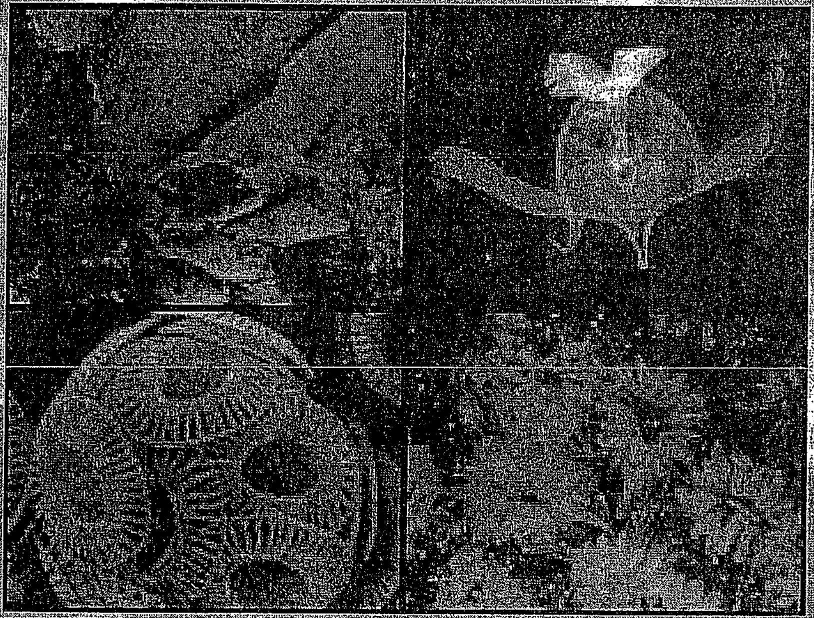
Weitzman, S. H. (1997): Systematics of deep-sea fishes. p. 43–78. In *Fish Physiology, Vol. XVI. Deep-Sea Fishes*, ed. by D. J. Randall and A. P. Farrell, Academic Press, San Diego.

Yoshikawa, H., F. Kawai and M. Kanamori (1994): The relationship between the EEG and brain pH in carp, *Cyprinus carpio*, subjected to environmental hypercapnia at an anesthetic level. *Comp. Biochem. Physiol.*, **107A**, 307–312.

Zadunaisky, J. A. (1984): The chloride cell: The active transport of chloride and the paracellular pathways. p. 130–176. In *Fish Physiology, Vol. 10B*, ed. by W. S. Hoar and D. J. Randall, Academic Press, Orlando.

IMPACTS OF OCEAN ACIDIFICATION ON CORAL REEFS AND OTHER MARINE CALCIFIERS

A GUIDE FOR FUTURE RESEARCH



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Impacts of Ocean Acidification on Coral Reefs and Other Marine Calcifiers: A Guide for Future Research

A report from a workshop sponsored by the National Science Foundation, the National Oceanic and Atmospheric Administration, and the U.S. Geological Survey

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Contents

Executive Summary

RESEARCH FINDINGS of the past decade have led to mounting concern that rising atmospheric carbon dioxide (CO_2) concentrations will cause changes in the ocean's carbonate chemistry system, and that those changes will affect some of the most fundamental biological and geochemical processes of the sea. Thanks to the efforts of large-scale physical and biogeochemical ocean programs such as WOCE, JGOFS, and OACES, ocean-wide changes in the carbonate system are now well documented. Since 1980 ocean uptake of the excess CO_2 released by anthropogenic activities is significant; about a third has been stored in the oceans. The rate of atmospheric CO_2 increase, however, far exceeds the rate at which natural feedbacks can restore the system to normal conditions. Oceanic uptake of CO_2 drives the carbonate system to lower pH and lower saturation states of the carbonate minerals calcite, aragonite, and high-magnesium calcite, the materials used to form supporting skeletal structures in many major groups of marine organisms.

A variety of evidence indicates that calcification rates will decrease, and carbonate dissolution rates increase, as $CaCO_3$ saturation state decreases. This evidence comes from principles of thermodynamics, the geologic record, and the evolutionary pathways of $CaCO_3$ secreting organisms. Further evidence, from controlled experiments of biocalcification under increased CO_2 conditions, confirms that calcification rates of many organisms decrease with decreasing $CaCO_3$ saturation state. Extrapolation of these results to the real world suggests that calcification rates will decrease up to 60% within the 21st century. We know that such extrapolations are oversimplified and do not fully consider other environmental and biological effects (e.g., rising water temperature, biological adaptation); nor do they address effects on organism fitness, community structure, and ecosystem functioning. Any of these factors could increase or decrease the laboratory-based estimates, but it is certain that net production of $CaCO_3$ will decrease in the future.

The St. Petersburg Workshop, sponsored by NSF, NOAA, and the USGS, and held at the USGS Center for Coastal and Watershed Studies on 18–20 April 2005, was designed to take the next step toward understanding the response of marine calcification to increasing atmospheric CO_2 concentration. The aims of the workshop were to summarize existing knowledge on the topic, reach a consensus on what the most pressing scientific issues are, and identify future research strategies for addressing these issues. Although workshop participants were drawn from a wide range of scientific disciplines, there was a clear convergence on the major scientific issues that should be pursued over the next 5–10 years. These include:

- Determine the calcification response to elevated CO_2 in benthic calcifiers such as corals (including cold-water corals), coralline algae, foraminifera, molluscs, and echinoderms; and in planktonic calcifiers such as coccolithophores, foraminifera, and shelled pteropods;
- Discriminate the various mechanisms of calcification within calcifying groups, through physiological experiments, to better understand the cross-taxa range of responses to changing seawater chemistry;
- Determine the interactive effects of multiple variables that affect calcification and dissolution in organisms (saturation state, light, temperature, nutrients) through continued experimental studies on an expanded suite of calcifying groups;
- Establish clear links between laboratory experiments and the natural environment, by combining laboratory experiments with field studies;
- Characterize the diurnal and seasonal cycles of the carbonate system on coral reefs, including commitment to long-term monitoring of the system response to continued increases in CO_2;
- In concert with above, monitor in situ calcification and dissolution in planktonic and benthic organisms, with better characterization of the key environmental controls on calcification;
- Incorporate ecological questions into observations and experiments; e.g., How does a change in calcification rate affect the ecology and survivorship of an organism? How will ecosystem functions differ between communities with and without calcifying species?

- Improve the accounting of coral reef and open ocean carbonate budgets through combined measurements of seawater chemistry, $CaCO_3$ production, dissolution and accumulation, and, in near-shore environments, bioerosion and off-shelf export of $CaCO_3$;
- Quantify and parameterize the mechanisms that contribute to the carbonate system, through biogeochemical and ecological modeling, and apply such modeling to guide future sampling and experimental efforts;
- Develop protocols for the various methodologies used in seawater chemistry and calcification measurements.

Some of these research objectives require technological development, but others can be addressed immediately. While much work remains toward answering the fundamental question: "How will marine calcification rates respond to increasing atmospheric CO_2 concentrations," we need to begin investigations that look forward to answering the question: "What are the consequences of reduced calcification in both planktonic and benthic calcifying communities and ecosystems?" We should not wait until we answer the former question before tackling the latter.

This report is intended as a guide to program managers and researchers toward designing research projects that address these important questions. It is written with the detail and references needed to serve as a resource for researchers, including graduate students, who wish to tackle projects within the sometimes confusing topic of marine carbonate chemistry and calcification.

1. Introduction

1.1 Background

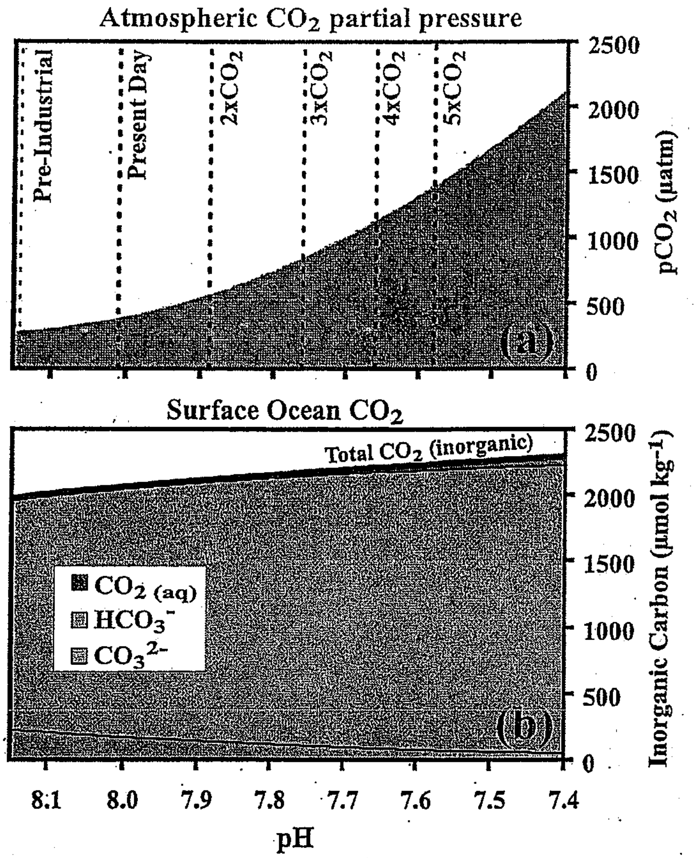
Carbon dioxide (CO_2) is one of the most important gases in the atmosphere, affecting the radiative heat balance of the earth as well as the calcium carbonate ($CaCO_3$) equilibrium of the oceans. For 650,000 y (650 ky) prior to the Industrial Revolution, atmospheric CO_2 concentrations remained between 180 to 300 parts per million by volume (ppmv) (Petit *et al.*, 1999; Augustin *et al.*, 2004; Siegenthaler *et al.*, 2005). Increased fossil fuel burning associated with industrialization, cement production, and land use changes associated with agricultural activities are causing atmospheric CO_2 concentrations to rise, and at increasing rates (rates of increase have risen from 0.25% y^{-1} in the 1960s to 0.75% y^{-1} in the last five years). The current atmospheric CO_2 concentration is about 380 ppmv and is expected to continue to rise by about 1% y^{-1} over the next few decades (Houghton, 2001) (**Figure 1–1**). The rate of current and projected CO_2 increase is about 100x faster than has occurred over the past 650,000 years and the rising atmospheric CO_2 levels are irreversible on human timescales (Royal Society, 2005).

Over the two decades of the 1980s and 1990s only about half of the CO_2 released by human activity has remained in the atmosphere, with the oceans having taken up about 30% and the terrestrial biosphere 20% (Sabine *et al.*, 2004). Similar partitioning of anthropogenic CO_2 is expected to continue with the result that the partial pressure of CO_2 (pCO_2) dissolved in the surface ocean is likely to double its pre-industrial value within the next 50 years. Over the next millennium, the ocean will absorb about 90% of the anthropogenic CO_2 released to the atmosphere (Archer *et al.*, 1998).

Increasing the amount of CO_2 dissolved in the ocean lowers the pH, and decreases the availability of carbonate (CO_3^{2-}) ions and lowers the saturation state of the major shell-forming carbonate minerals (**Box 1**). Tripling the pre-industrial atmospheric CO_2 concentration will cause a reduction in surface ocean pH that is almost three times greater than that experienced during transitions from glacial to interglacial periods. This is often termed "ocean acidification" because it describes the process of decreasing pH. Current projections of ocean acidification suggest that the pH of surface ocean waters will continue to decline. However, the term can also lead to confusion when it is wrongly assumed that the oceans will become acidic, when in reality, ocean pH is never expected to fall below 7.0; i.e., the oceans are becoming less basic, but not acidic. Such a phenomenon could only occur in the unlikely event that CO_2 emissions reach more than 10,000 Pg C (Caldeira and Wickett, 2005). In this report, we use the term "ocean acidification" to conform with current terminology, with the recognition that it refers to the process rather than an end state.

There is clear evidence that the carbonate equilibrium of the oceans is shifting in response to increasing atmospheric CO_2 concentrations. Carbonate chemistry measurements at the Hawaiian Ocean Time-series (HOT), the Bermuda-Atlantic Time-series (BATS), and the European Station for Times Series in the Ocean at the Canary Islands (ESTOC) show a shift in carbonate equilibrium consistent with increases in atmospheric CO_2 (**Figure 1–2**) (Bates, 2001; Gruber *et al.*, 2002, González-Dávila *et al.*, 2003; Brix *et al.*, 2004). Over the last two decades, several large-scale programs (Joint Global Ocean Survey, World Ocean Circulation Experiment, Ocean-Atmosphere Carbon Exchange Study) have measured the carbonate chemistry (mainly the total dissolved inorganic carbon, DIC, and the total alkalinity, A_T) along multiple ocean transects. These measurements allowed quantification of the anthropogenic carbon in the oceans, regionally and with depth (Sabine *et al.*, 2004) (**Box 2**), and have been used to estimate changes in the calcite and aragonite saturation states (Feely *et al.*, 2004).

Potential long-term impacts of anthropogenic CO_2 on the calcite and aragonite saturation state of the oceans have been discussed in detail (Broecker *et al.*, 1979; Feely and Chen, 1982; Feely *et al.*, 1984; Feely *et al.*, 1988; Kleypas *et al.*, 1999; Broecker, 2003; Caldeira and Wickett, 2003; Feely *et al.*, 2004; Caldeira and Wickett, 2005; Orr *et al.*, 2005). Past, present, and future aragonite saturation horizons have been modeled based on historical data and IPCC "business-as-usual" CO_2 emission scenarios (Orr *et al.*, 2005) (**Figure 1–3**). These results indicate that in the cold high-latitude surface waters typical of the subarctic North



Parameter	Symbol	Unit	Glacial	Preindust.	Present	2 × CO_2	3 × CO_2
Temperature	T	°C	15.7	19	19.7	20.7	22.7
Salinity	S	ppt	35.5	34.5	34.5	34.5	34.5
Total alkalinity	A_T	μequiv kg^{-1}	2356	2287	2287	2287	2287
pCO_2 in seawater	pCO_2	μatm	180	280	380	560	840
			-56	0	35.7	100	200
Carbonic acid	H_2CO_3	μmol kg^{-1}	7	9	13	18	25
			-29	0	44	100	178
Bicarbonate ion	HCO_3^-	μmol kg^{-1}	1666	1739	1827	1925	2004
			-4	0	5	11	15
Carbonate ion	CO_3^{2-}	μmol kg^{-1}	279	222	186	146	115
			20	0	-16	-34	-48
Hydrogen ion	H^+	μmol kg^{-1}	4.79×10^{-03}	6.92×10^{-03}	8.92×10^{-03}	1.23×10^{-02}	1.74×10^{-02}
			-45	0	29	78	151
Calcite saturation	Ω_{calc}		6.63	5.32	4.46	3.52	2.77
			20	0	-16	-34	-48
Aragonite saturation	Ω_{arag}		4.26	3.44	2.9	2.29	1.81
			19	0	-16	-33	-47
Dissolved inorganic carbon	DIC	μmol kg^{-1}	1952	1970	2026	2090	2144
			-1	0	2.8	6.1	8.8
Total pH	pH_T		8.32	8.16	8.05	7.91	7.76

Figure 1–1: (a) Increasing atmospheric CO_2 partial pressure and (b) associated changes in the surface ocean carbonate chemistry. Table shows carbon system parameter and temperature changes in surface seawater based on IPCC IS92a CO_2 emission scenario (Houghton *et al.*, 2001), assuming $PO_4 = 0.5$ μmol L^{-1}, Si = 4.8 μmol L^{-1}; and using the carbonic acid dissociation constants of Mehrbach *et al.* (1973) as refit by Dickson and Millero (1987). pH_T is based on seawater scale. Percent change from pre-industrial values are in magenta.

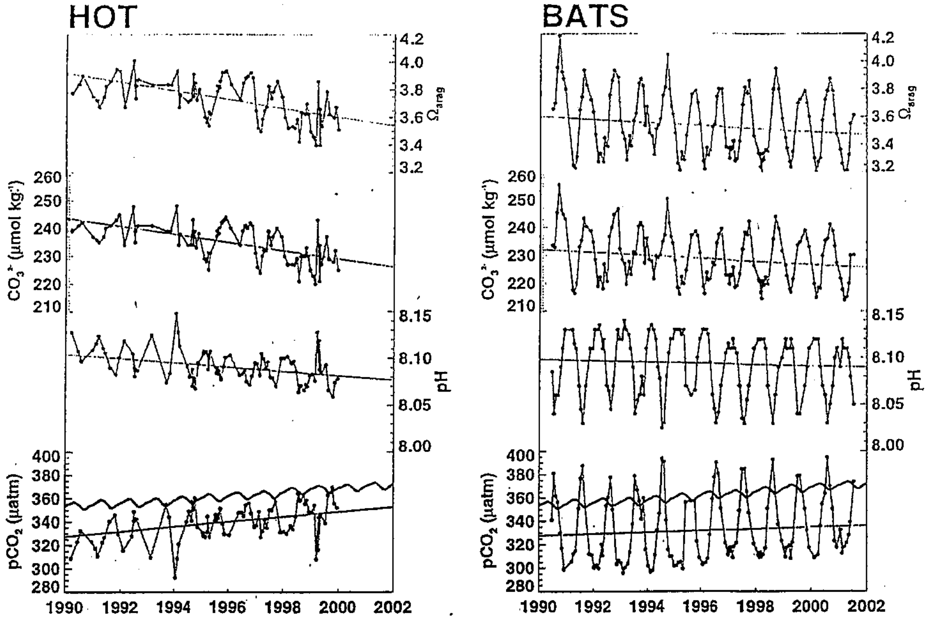


Figure 1–2: Monthly carbon-system parameters at two time-series stations in subtropical gyres: HOT (Hawaii Ocean Time-series station) and BATS (Bermuda-Atlantic Time-series Station). The lowest plot in each graph includes both the surface water pCO_2 (line with dots), and the Mauna Loa atmospheric CO_2 record (line without dots).

Pacific and North Atlantic, and the sub-Antarctic and polar regions of the Southern Ocean, aragonite and calcite undersaturation will occur when pCO_2 reaches 600 and 900 μatm, respectively. In the warm tropical and subtropical waters undersaturation will occur when pCO_2 values reach about 1700 and 2800 μatm, respectively. If CO_2 emissions continue as projected, aragonite undersaturated regions will develop in the sub-Arctic, sub-Antarctic, and polar surface waters by the end of the 21st century. This would occur first in the wintertime when surface water temperatures are coldest and pCO_2 values are highest due to wind-driven mixing of subsurface waters into the mixed layer. Undersaturated regions would then expand toward the equator, although it is unlikely that the tropical and warmest subtropical surface waters will ever become undersaturated with respect to calcite, as model projections of CO_2 emissions predict an upper limit of atmospheric CO_2 concentration of about 2000 ppmv (Caldeira and Wickett, 2003).

Calcifying organisms of both neritic and pelagic environments are sensitive to changes in saturation state; calcification rates of several major groups of marine calcifiers decrease as the carbonate ion concentration decreases (**Figure 1–4**; **Table 1.1**). There is also evidence that dissolution rates of carbonates will increase in response to CO_2 forcing. Even small changes in CO_2 concentrations in surface waters may have large negative impacts on marine calcifiers and natural biogeochemical cycles of the ocean (Gattuso *et al.*, 1998; Wolf-Gladrow *et al.*, 1999; Langdon *et al.*, 2000; Riebesell *et al.*, 2000; Marubini *et al.*, 2001; Zondervan *et al.*, 2001; Reynaud *et al.*, 2003). For example, decreased carbonate ion concentration significantly reduces the ability of corals to produce their calcium carbonate skeletons. This affects individual corals and the ability of the reef to maintain a positive balance between reef building and reef erosion (Kleypas *et al.*, 2001). New research is necessary to gain a better understanding of how ocean biology and chemistry respond to higher CO_2 and lower pH conditions, so that predictive models can include appropriate mathematical representations of these processes.

1.2 Geologic Context

Anthropogenic changes in atmospheric composition are forcing Earth's climate and ocean chemistry toward conditions that have not occurred over geologic timescales of millions of years (My) (**Figure 1–5**) (Caldeira and Wickett, 2003). When viewed against the Pleistocene record of atmospheric CO_2 variability, the increase in atmospheric CO_2 over the past century constitutes an unprecedented spike in greenhouse gas concentration which is certain to increase with continued fossil fuel burning. The best records of

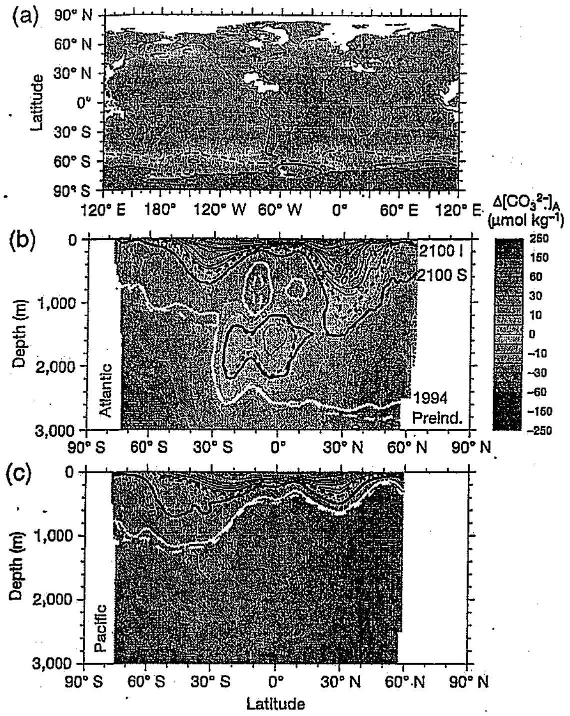


Figure 1–3: Median concentrations of $\Delta[CO_3^{2-}]$ (in situ $[CO_3^{2-}]$ minus $[CO_3^{2-}]$ for aragonite-equilibrated sea water) for the year 2100 under scenario IS92a, based on model results from the Ocean Carbon Model Intercomparison Project (OCMIP-2). (a) Surface map, and zonal averages for (b) Atlantic, and (c) Pacific. Thick lines indicate the aragonite saturation horizons for the pre-industrial, 1994, and 2100 (using scenarios S650 and IS92a). Reprinted from Orr *et al.* (2005) with permission from *Nature*, copyright 2006.

past atmospheric concentrations are from direct sampling of air bubbles trapped within ice cores. The Vostok and EPICA Dome Concordia ice core records, of which the past 650 ky have been analyzed, indicate that atmospheric CO_2 concentrations remained between 180 and 300 ppmv over eight major glaciations (Petit *et al.*, 1999; Siegenthaler *et al.*, 2005). These values are supported by leaf stomatal index data for the last interglacial (115–130 ka), which indicate more variable but similarly low atmospheric concentrations (Rundgren and Bennike, 2002).

CO_2 data extending back millions of years are scarce. Leaf stomatal index data from fossil trees dating from about 50–60 millions of years ago (Ma) indicate that atmospheric CO_2 concentrations in the early Tertiary remained between 300 and 450 ppmv, only slightly higher than that of recent interglacials (Royer *et al.*, 2001). Data from the marine environment, however (e.g., calcium isotopes (De la Rocha and DePaolo, 2000), boron isotopes (Pearson and Palmer, 2000; Pearson *et al.*, 2001), and alkenones (Pagani, 2002)) all indicate that atmospheric CO_2 concentrations were probably much higher in the early Tertiary and by the Early Miocene (24 Ma) had likely decreased to below 300 ppmv. The GEOCARB model, which hindcasts atmospheric CO_2 levels over the past 600 My by combining geological, geochemical, biological, and climatological data, suggests that early Tertiary CO_2 levels were up to five times that of pre-industrial levels (Berner, 1994, 1997; Berner and Kothavala, 2001).

CO_2 levels are only one parameter controlling ocean carbonate chemistry, however; alkalinity also determines the carbonate ion concentration. Ocean alkalinities could have been higher during periods with high CO_2 levels, since higher CO_2 levels accelerate rock weathering and $CaCO_3$ dissolution, which raises alkalinity. Over long timescales, this feedback tends to maintain a balance between atmospheric CO_2 and oceanic alkalinity. At the current rate of atmospheric CO_2 increase, however, this feedback operates too slowly to raise alkalinity significantly.

The suite of marine calcifiers has evolved considerably since the Cretaceous. For example, most of today's important reef-building coral families appeared sometime in the Eocene, and acroporids (fast-growing, branching corals common on reefs today) were not dominant on coral reefs until the late Oligocene (23–28 Ma, Schuster, 2002). Coccoliths first appear in the fossil record in the Late Triassic (Bown *et al.*, 2004), although their abundance is most evident in the large, Cretaceous chalk deposits of northern Europe and other regions. Only about 20% of extant coccolithophore species are known from Quaternary records (Young, 1994), and today's most common coccolithophore, *Emiliania huxleyi*, evolved less than 300,000 years ago (Thierstein *et al.*, 1977). Similar to corals, modern thecosomatous pteropod families appeared in the Eocene and Miocene (cf., Lalli and Gilmer, 1989). Geologic deposits produced by calcifying ecosystems of the early Tertiary (Paleocene and Eocene, ca. 65–35 Ma), when atmospheric CO_2 levels were probably at least 500 ppmv, may provide important clues regarding calcification/dissolution patterns, distribution patterns, etc., but they are less useful for providing information about ecological response because the community composition and ecological relationships were probably quite different from those of present-day ecosystems.

The most recent time period when oceanic carbonate chemistry could have approached those of today is the Paleocene/Eocene Thermal Maximum (PETM) about 55 Ma (Kennett and Stott, 1991; Zachos *et al.*, 1993; Zachos *et al.*, 2003; Zachos *et al.*, 2005). This boundary is characterized by an anomalous depletion in ^{13}C indicative of a rapid release of ^{13}C-

Table 1.1: Measured biogenic calcification responses to increased $p\mathrm{CO}_2$.

		Approx. % change in calcification when $p\mathrm{CO}_2$ is			
Organism/System	Mineralogy	2x preind.	3x preind.	References	Notes
Coccolithophores					
Emiliania huxleyi	Calcite	−25		Sciandra *et al.*, 2003	
E. huxleyi	"	−9	−18	Riebesell *et al.*, 2000; Zondervan *et al.*, 2001	Decrease in $\mathrm{CaCO_3}$/cell
Gephyrocapsa oceanica	"	−29	−66	"	"
Foraminifera					
Orbicula universa	Calcite	−8	−14	Spero *et al.*, 1997; Bijma *et al.*, 1999; Bijma *et al.*, 2002	Decrease in shell weight
Globigerinoides sacculifer	"	−4 to −6	−6 to −8	Bijma *et al.*, 1999; Bijma *et al.*, 2002	Decrease in shell weight
Scleractinian corals					
Stylophora pistillata	"	−14	−20	Gattuso *et al.*, 1998b	Curve was nonlinear, linear fit was made for Ω_{arag} from 2.0–3.9
S. pistillata	"	0 to −50		Reynaud *et al.*, 2003	Level of response is temperature-dependent
Acropora cervicornis	Aragonite	−40	−59	Renegar and Riegl, 2005	
Acropora eurystoma	"	−38	−56	Schneider and Erez, 2006	
Acropora verweyi	"	−12	−18	Marubini *et al.*, 2003	
P. compressa + *Montipora capitata*	"	−40	−59	Langdon and Atkinson, 2005	
Porites compressa	"	−17	−25	Marubini *et al.*, 2001	
P. lutea	"	−38	−56	Ohde and Hossain, 2004	
P. lutea	"	−33	−49	Hossain and Ohde, in press	
P. porites	"	−16		Marubini and Thake, 1999	
Pavona cactus	"	−14	−20	Marubini *et al.*, 2003	
Fungia sp.	"	−47	−69	Hossain and Ohde, in press	
Galaxea fascicularis	"	−12	−18	Marubini *et al.*, 2003	
G. fascicularis	"	−56	−83	Marshall and Clode, 2002	
Turbinaria reniformis	"	−9	−13	Marubini *et al.*, 2003	
Coralline red algae					
Porolithon gardineri	High-Mg calcite	−25		Agegian, 1985	
Mesocosms and field studies					
Biosphere 2	Mixed	−56	−83	Langdon *et al.*, 2000	Dominated by coralline red algae
Monaco mesocosm	"	−21		Leclercq *et al.*, 2000	
Monaco mesocosm	"	−15		Leclercq *et al.*, 2002	
Bahamas Bank	"	−57	−85	Broecker and Takahashi, 1966	
Rukan-sho, Okinawa	"	−45	−67	Ohde and van Woesik, 1999	

Box 1—Controls on Marine Carbonate Chemistry

Marine carbonate chemistry is a complex but predictable series of chemical equilibria, governed mainly by the total concentration of dissolved inorganic carbon species (DIC or TCO_2, the molar sum of the carbonate species: dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}), and total alkalinity (A_T, the concentration of all the bases that can accept H^+, when a titration is made with HCl to the carbonic acid endpoint). Processes that increase DIC (e.g., adding CO_2 to the water column) shift the equilibrium toward lower pH and lower CO_3^{2-} concentration, while processes that increase A_T (e.g., the dissolution of calcium carbonates) shift the equilibrium toward higher pH and higher CO_3^{2-} concentration. Photosynthesis and respiration primarily affect DIC, while calcification and dissolution affect both DIC and A_T (see right-hand figure). Marine calcification draws down A_T twice as fast as it draws down DIC, and thus leads to a decrease in pH, which decreases the capacity of the upper ocean to take up atmospheric CO_2. Dissolution of marine carbonates has the opposite effect, and neutralizes CO_2 via the reaction:

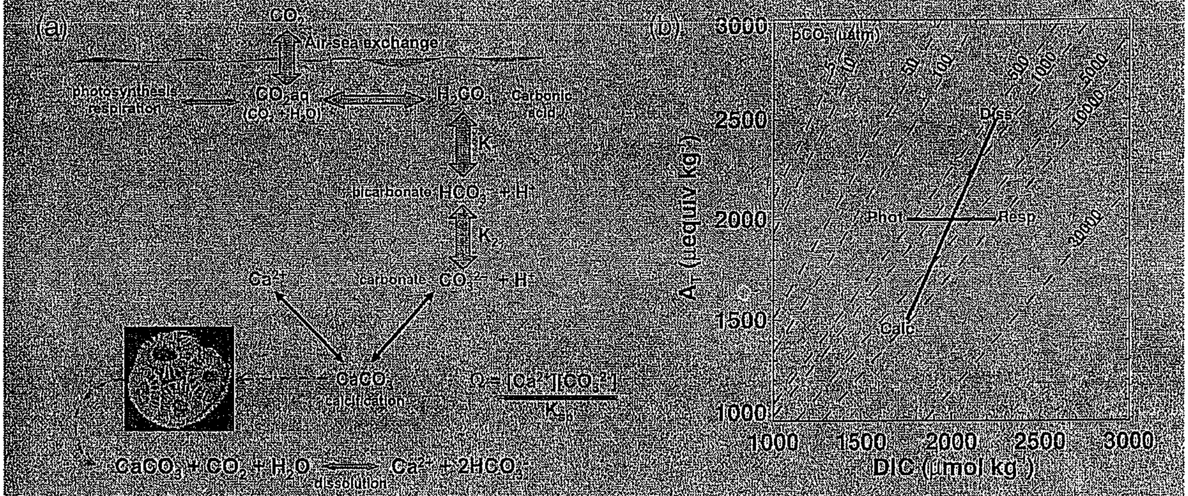
$$CaCO_3 + CO_2 + H_2O \leftrightarrow 2HCO_3^- + Ca^{2+} \tag{1}$$

The degree of saturation of seawater with respect to calcite and aragonite is the ion product of the concentrations of calcium and carbonate ions, at the in situ temperature, salinity, and pressure, divided by the stoichiometric solubility product (K^*_{sp}) for those conditions:

$$\Omega_{arag} = [Ca^{2+}][CO_3^{2-}]/K^*_{sp_{arag}} \tag{2}$$

$$\Omega_{calc} = [Ca^{2+}][CO_3^{2-}]/K^*_{sp_{calc}} \tag{3}$$

where the calcium concentration is either measured or estimated from the salinity and the carbonate ion concentration is calculated using known relationships between two carbonate system parameters (pCO_2, DIC, A_T, pH). Since the calcium to salinity ratio in seawater does not vary by more than 1.5%, variations in the ratio of $[CO_3^{2-}]$ to the stoichiometric solubility product primarily govern the degree of saturation of seawater with respect to magnesian calcite, aragonite, and calcite.



(a) A simplified diagram of the carbonate system in seawater. K_1 and K_2 are the dissociation constants for H_2CO_3 and HCO_3^-, respectively. (b) pCO_2 concentration (dashed lines) as a function of A_T and DIC. Photosynthesis and respiration affect only DIC, while calcification and dissolution affect both DIC and A_T.

depleted carbon (e.g., release of bacterially produced methane stored as gas hydrates (Dickens *et al.*, 1995), or thermogenic methane associated with volcanism (Svensen *et al.*, 2004)), and is accompanied by a sharp rise in sea surface temperatures (5–9°C) over a short time period (~100–1000 y). There is also evidence that the oceans experienced a simultaneous decrease in ocean pH during this event; the deep ocean's calcite saturation horizon shallowed at least 2 km, suggesting >2000 Pg of carbon dissolved into the ocean over a relatively short period of time (1,000–2,000 y) (Zachos *et al.*, 2005). Sedimentary data and model results suggest the ocean required 10–15 ky to again accumulate $CaCO_3$ at 1500 m depth and as much as 60 ky for the deep ocean to attain saturation levels. The increase in atmospheric CO_2 associated with this event is esti-

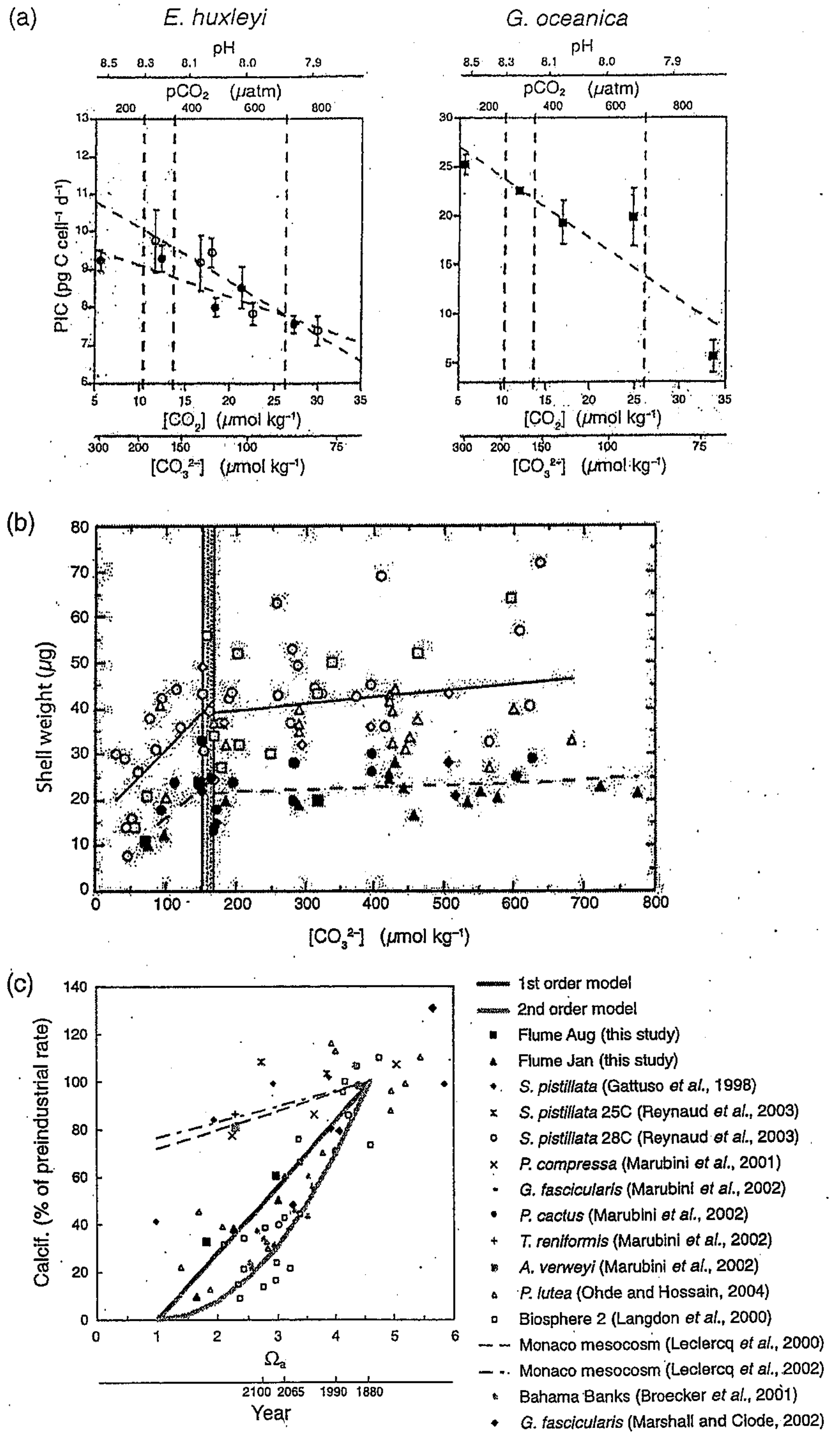
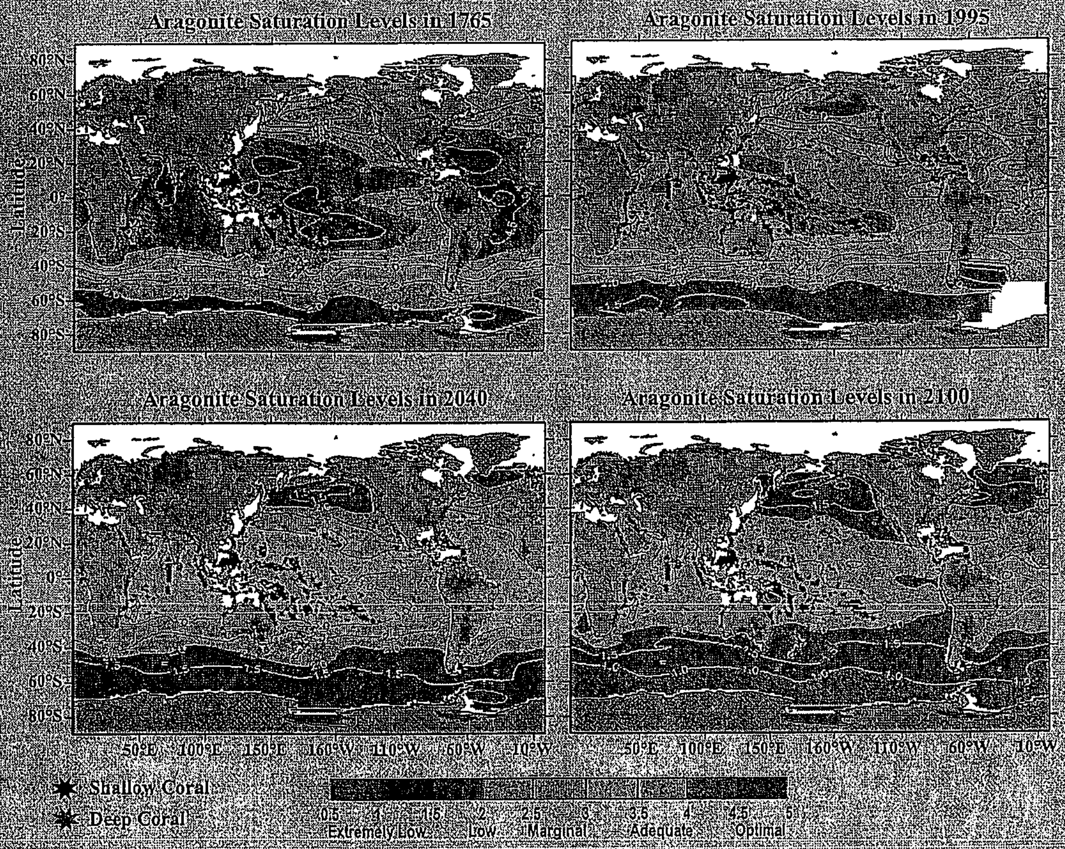


Figure 1–4: Calcification and shell growth rates reported as a function of a variety of carbonate chemistry parameters: (a) Coccolithophore calcification per cell as a function of carbonate ion concentration for *Emiliania huxleyi* and *Gephyrocapsa oceanica* (modified from Zondervan *et al.*, 2001). (b) Shell weight of the foraminifera *Orbulina universa* as a function of carbonate ion concentration, grown in high light (open symbols) and in the dark (closed symbols). Circles = constant alkalinity conditions; triangles = constant DIC conditions; squares = constant pH conditions. Shaded vertical bar indicates range of ambient conditions (reprinted from Bijma *et al.*, 1999, with kind permission of Springer-Verlag and Business Media). (c) Calcification rates (relative to pre-industrial values) of corals, coral mesocosms, and on the Bahama Banks, as a function of aragonite saturation state (reprinted from Langdon and Atkinson, 2005).

Box 2—Anthropogenic Carbon in the Oceans, and Shoaling of Aragonite and Calcite Saturation Horizons

In the 1990s, several agencies supported an international effort to survey inorganic carbon of the oceans (WOCE, JGOFS, OACES). This produced observations from more than 72,000 locations collected on over 95 expeditions. These observations were analyzed with a tracer-based separation technique to estimate the global content of anthropogenic CO_2 in the oceans that had accumulated over the period 1800–1994 (Sabine *et al.*, 2004), and showed that the distribution of anthropogenic CO_2 in the ocean is not uniform. Over half of the 118 ± 19 petagrams of anthropogenic carbon that has accumulated in the ocean is stored in the upper 10% of the ocean water column (upper 400 m). The largest column inventories of anthropogenic CO_2 are observed in areas where surface waters are transporting carbon into the ocean interior (see **Figure 2–1**). The oceanic sink accounts for ~48% of the total fossil fuel and cement manufacturing emissions, implying that the terrestrial biosphere was a net source of CO_2 to the atmosphere of about 39 ± 28 Pg C for this period. Thus, the ocean has been the only long-term sink for CO_2 released to the atmosphere by human activity.

This uptake is affecting the saturation horizons (the depth where saturation state = 1) of both calcite and aragonite (Feely *et al.*, 2004). There is natural shoaling of both the aragonite and calcite saturation horizons from the Atlantic through the Indian to the Pacific, because of the higher DIC/A_T ratios in the intermediate and deep waters of the Indian and Pacific relative to the Atlantic. This is the result of the cumulative large-scale enrichment of DIC relative to A_T due to respiration processes as ocean water circulates along the deep conveyor belt from the Atlantic to Indian and Pacific (Broecker and Peng, 1982; Broecker, 2003; Broecker and Clark, 2003). The intermediate waters of the North Pacific show evidence for undersaturation in the shallow waters between approximately 200 m and 1000 m where they have also been impacted by anthropogenic CO_2 (Feely *et al.*, 2004). Surprisingly, however, portions of the northern Indian Ocean and southeastern Atlantic Ocean are also undersaturated with respect to aragonite at shallow depths and these regions appear to be increasing in areal extent as a consequence of anthropogenic CO_2 accumulations (Feely *et al.*, 2002; Sabine *et al.*, 2002; Chung *et al.*, 2003; Feely *et al.*, 2004).



Estimated aragonite saturation states of the surface ocean for the years 1765, 1995, 2040, and 2100 (Feely *et al.*, submitted), based on the modeling results of Orr *et al.* (2005) and a Business-As-Usual CO_2 emissions scenario. The distributions of deep-sea coral banks are from Guinotte *et al.* (2006).

Box 2—(contined)

For example, Figure 1–3 shows a comparison of the pre-industrial, 1994, and 2100 saturation horizons for the Atlantic and Pacific based on the modeling results of Orr *et al.* (2005). There are several distinct regions where the undersaturation zone has already expanded or could significantly expand in the future. Similarly, additional modeling efforts (Feely *et al.* submitted) for surface waters indicate significant reductions in aragonite saturation state of the tropical and subtropical oceans over the 21st century (see figure on the previous page). Superimposed on the maps are locations of present day shallow and deep-water coral ecosystems (after Guinotte *et al.*, 2006). The color coding provides an indication of the conditions for coral calcification (Langdon *et al.*, 2003; Langdon and Atkinson, 2005). Subtropical regions would decrease from an optimal degree of saturation level >4 to marginal levels <3.0. These conditions will have significant impacts on the ability of coral reef ecosystems to maintain their structures against the forces of erosion and dissolution. For deep-water scleractinian corals, vertical migration of the aragonite saturation horizons means that more than 70% of these corals would be subjected to undersaturated conditions by 2100 (Guinotte *et al.*, 2006).

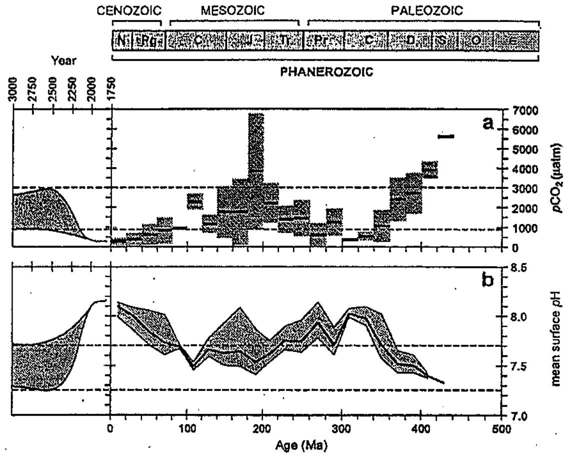


Figure 1–5: Geologic history (right-hand side of figure) and projection (left-hand side) of (a) atmospheric pCO_2 and (b) modeled changes in pH over the same time period. Horizontal dashed lines indicate the range of predicted pCO_2 peak atmospheric CO_2 concentration over the next century. Dark lines are average historical pCO_2 values, while gray shading indicates ± one standard deviation. Reprinted from Ridgwell and Zeebe (2005), with permission from Elsevier.

mated to have been only about 70–160 ppmv, which may be too low to have caused the dramatic temperature increase recorded by marine organisms. This has led to speculation about the sources of the light carbon, whether CH_4 oxidation occurred in the ocean or atmosphere (Dickens, 2001; Zachos *et al.*, 2003), and whether other mechanisms (e.g., ocean circulation changes (Tripati and Elderfield, 2005)) could have contributed to the warming. Thus while the PETM may provide clues toward our understanding of rapid perturbations to the global carbon cycle, this period may not be an ideal analog for present-day changes due to fossil fuel combustion.

The geologic record suggests that even earlier in Earth history, carbonate sedimentation was abruptly interrupted during periods of rapid increases in pCO_2. For example, a rapid volcanogenic increase in pCO_2 at the Triassic-Jurassic boundary (Palfy, 2003) coincides with a major extinction event, a worldwide interruption of carbonate sedimentation, and an evolutionary replacement of aragonite with calcite (Palfy, 2003; Hautmann, 2004). Furthermore, there is evidence that groups of calcifying organisms have become more or less dominant over geologic time, depending on CO_2 levels, and is likely linked to their utilization of dominant carbonate species in the ocean. For example, comparison of atmospheric CO_2 fluctuation from the Cambrian through the Cenozoic, to dominance trends for cyanobacterial and algal calcifiers, demonstrate that cyanobacteria dominate during periods of high CO_2, while algae dominate in periods of relatively lower CO_2, when HCO_3^- is more abundant (Yates and Robbins, 2001).

1.3 History of the CO_2-Marine Calcification Issue

The realization that atmospheric CO_2 concentrations can affect marine calcification rates emerged about 40 years ago (**Table 1.2**). Probably the first paper to address this issue was that of Wally Broecker and Taro Takahashi (Broecker and Takahashi, 1966), who based their conclusions on a time series of carbon system measurements over the Bahamas Bank. In the following decade, several authors presented calculations suggesting that the surface ocean would become undersaturated with respect to calcite by the year 2000, and that this would likely affect shell formation in many marine calcifying organisms (Fairhall, 1973a, 1973b; Zimen and Altenhein, 1973). However, these early calculations did not properly account for the carbon system equilibrium in seawater, and later calculations revealed that atmospheric CO_2 concentrations would have to reach nearly ten times that of pre-industrial levels to cause calcite undersaturation in the tropical oceans (Whitfield, 1974; Skirrow and Whitfield, 1975).

In the 1980s, predictions based on field studies of the carbonate system in the Pacific Ocean forecast that surface waters of the North Pacific would become undersaturated with respect to aragonite (which is more soluble than calcite) sometime in the 21st century (Feely and Chen, 1982; Feely *et al.*, 1984; Feely *et al.*, 1988). At the same time, laboratory and field studies demonstrated that calcification rates in many marine organisms varied in response to the *degree* of $CaCO_3$ saturation, even in supersaturated waters. Smith and Buddemeier (1992) explicitly stated that increased CO_2 could cause seawater chemistry changes that would lead to reduced calcification rates, and numerous laboratory studies showed that calcification rates of reef-building corals and algae could decline by 10–50% under doubled CO_2 conditions (Gattuso *et al.*, 1998b; Langdon *et al.*, 2000; Leclercq *et al.*, 2000; Marubini *et al.*, 2001; Leclercq *et al.*, 2002; Langdon *et al.*, 2003; Marubini *et al.*, 2003; Langdon and Atkinson, 2005). Similarly, experiments with laboratory cultures and field populations revealed that calcification rates of two coccolithophore species decreased by 9–29% when pCO_2 was two times higher than pre-industrial levels (Riebesell *et al.*, 2000; Zondervan *et al.*, 2001; Sciandra *et al.*, 2003; Delille *et al.*, 2005; Engel *et al.*, 2005).

1.4 The Next Step—Development of a Research Strategy

Several previous workshops and meetings were explicitly dedicated to addressing how marine biological processes (primarily calcification) will respond to future changes in ocean CO_2 chemistry. A U.S. JGOFS workshop on marine calcification (Iglesias-Rodriguez *et al.*, 2002) focused on the effects on open ocean calcifiers and how reduced calcification would affect the ocean carbon cycle. In May 2004, the Scientific Committee on Oceanic Research (SCOR) and the Intergovernmental Oceanographic Commission (IOC) of UNESCO sponsored the symposium *The Ocean in a High-CO_2 World* that addressed the "biological and biogeochemical consequences of increasing atmospheric and oceanic CO_2 levels, and possible strategies for mitigating atmospheric increases." This workshop identified priority research areas regarding organismal and ecosystem responses to increased CO_2, and also recommended approaches to study them from small-scale laboratory experiments to large-scale field experiments, and modeling (Cicerone *et al.*, 2004). The Royal Society Report, *Ocean Acidification Due to Increasing Atmospheric Carbon Dioxide* (Royal Society, 2005), described the potential impacts of ocean acidification on ocean ecosystems and the resulting socio-economic impacts on the global economy. The report recommended that these potential risks to the ocean environment be considered by national and international policy makers involved in discussions of climate change issues. A recent report by the Integrated Marine Biogeochemistry and Ecosystem Research program of the IGBP (IMBER, 2005) lists "the effects of increasing CO_2 levels and decreasing pH" as a major scientific issue, with three priorities: (1) the effects of CO_2-driven changes in carbonate chemistry, (2) the effects of pH changes on the speciation of nutrients and trace metals, and (3) the sensitivity of organisms to changes in pH and CO_2.

The present report summarizes findings from a workshop (hereafter referred to as the "St. Petersburg Workshop") jointly sponsored by NOAA, NSF, and the USGS entitled "The Effects of Increased Atmospheric CO_2 on Coral Reefs and Other Marine Calcifiers," held in St. Petersburg, Florida, 18–20 April 2005. Some fifty participants gathered to address the next steps toward understanding the future of marine calcification and calcifying communities:

- identification of specific, testable hypotheses;
- evaluation of existing and promising methodologies for testing those hypotheses; and
- recommendations for streamlining research, from coordination of research across agencies to identification of specific locations where the most information can be obtained.

We present the scientific basis for building a realistic research strategy for understanding the interactions between ocean carbonate chemistry and marine calcification, and ultimately toward predicting marine ecosystem response to future increases in atmospheric CO_2. Although marine calcification occurs in virtually every marine environment, the focus of this document is on shallow benthic calcifying ecosystems (primarily coral reefs) and planktonic calcifying organisms (primarily planktonic foraminifera, coccolithophorids, and euthecosomatous (shelled) pteropods).

1.5 The Overall Scientific Issues

The St. Petersburg Workshop was stimulated by a need to consolidate current understanding of future changes in seawater carbonate chemistry and the response of marine calcification to those changes; and

Table 1.2: Chronological summary of significant research findings relevant to the relationship between carbonate chemistry of seawater and marine calcification.

Reference	Finding
Broecker and Takahashi, 1966	Illustrated dependency of calcification rates on $CaCO_3$ saturation state, in field study across the Bahama Banks
Smith and Pesret, 1974	Illustrated interaction between calcification and carbonate chemistry in Fanning Island Lagoon
Zimen and Altenhein, 1973 Fairhall, 1973a	Predicted increasing atmospheric CO_2 concentrations would cause surface ocean to become undersaturated with respect to calcite by year 2000
Skirrow and Whitfield, 1975 Whitfield, 1975	Corrected calculations showed that calcite undersaturation would not occur until atmospheric CO_2 was 10x pre-industrial levels
Feely and Chen, 1982 Feely *et al.*, 1984	Predicted surface waters of northern Pacific Ocean could become undersaturated with respect to aragonite in the 21st century
Smith and Roth, 1979 Borowitzka, 1981 Agegian, 1985 Gao *et al.*, 1993	Multiple studies illustrated that calcification rates in corals and coralline algae vary with the degree of $CaCO_3$ saturation
Smith and Buddemeier, 1992	Review called attention to potential role of decreasing $CaCO_3$ saturation state on future coral calcification rates
Gattuso *et al.*, 1998b	First controlled experiment showing calcification rate in a coral decreases with decreasing saturation state
Gattuso *et al.*, 1999a	Predicted 9–30% reduction in calcification rates between years 1990 and 2100
Kleypas *et al.*, 1999	Predicted that globally, coral reef calcification will decline by 14–30% under doubled CO_2 conditions
Marubini and Thake, 1999 Marubini *et al.*, 2001 Marubini *et al.*, 2003	Multiple studies showed effects of lower pH (or decreased carbonate ion concentration) on calcification in individual corals
Langdon *et al.*, 2000 Langdon *et al.*, 2003	Showed significant decline in calcification in CO_2 manipulations of the Biosphere 2 coral reef mesocosm. Illustrated that calcification rates were controlled by the ion concentration product of $[Ca^{2+}]$ and $[CO_3^{2-}]$ rather than pH, pCO_2, or $[CO_3^{2-}]$ alone.
Leclercq *et al.*, 2000 Leclercq *et al.*, 2002	Coral mesocosm studies showed decline in calcification under increased atmospheric CO_2 conditions
Riebesell *et al.*, 2000 Zondervan *et al.*, 2001 Riebesell, 2004	Showed significant reductions in calcification of two coccolithophorid species under increased atmospheric CO_2 conditions
Lough and Barnes, 2000	Analyzed dozens of *Porites* cores which did not reveal significant decline in coral calcification between early 20th and late 20th century
Feely *et al.*, 2004 Sabine *et al.*, 2004	Synthesized observations from 10 years of ocean carbon chemistry measurements; established role of oceans as carbon sink; addressed future changes in calcium carbonate saturation state profiles
Orr *et al.*, 2005	Predicted surface waters of Southern Ocean and subarctic Pacific will become undersaturated with respect to aragonite by year 2100

to identify the most important unknowns. This issue naturally cuts across physical, chemical, biological, and geological disciplines. Considerable effort has gone into understanding the patterns of open ocean carbonate chemistry and biogeochemical feedbacks to the global carbon cycle; and some major findings have arisen from that effort (e.g., quantitative estimates of ocean carbon uptake (Sabine *et al.*, 2004); the potential role of calcium carbonate as mineral ballast for organic carbon to the deep sea (Armstrong *et al.*, 2002; Klaas and Archer, 2002; Barker *et al.*, 2003)). Much less effort has gone into investigating the response of marine calcifying organisms to future changes in carbonate chemistry, and almost no research has tackled the longer timescales necessary to determine ecosystem responses.

Many benthic and planktonic calcifiers of both neritic and pelagic communities display a similar response to increased CO_2 forcing. There are important differences between the two (**Table 1.3**) that will dictate different approaches toward assessing the potential effects of reduced calcification on ecosystem structure and function, and how the effects could cascade to other ecosystems and the ocean carbon cycle. However, there is opportunity for researchers of planktonic and benthic communities to exchange ideas and technology and thus streamline their respective research. For the most part, planktonic and benthic calcification are addressed separately in this report. Regardless of differences between the two groups, there are certainly common questions:

1. What are the most important hypotheses within the overall question of "What are the ecological consequences of increasing atmospheric CO_2 on marine calcifying organisms and communities?"
2. What information is currently available for synthesis and guiding future research?
3. What information can be gained from monitoring natural temporal and spatial variations?
4. What scientific hypotheses will require testing with experimental manipulations in the field and laboratory?
5. Which ocean regions will be first to experience large changes in carbonate chemistry? Over what timescales?
6. What are the technical needs to address these research questions in these environments?
7. Based on the above, what are the priority research areas?
8. Where can we take advantage of existing observing systems, and with what technology, for both monitoring and experimental testing of hypotheses? Where can we capitalize on existing efforts by developing partnerships?

1.6 Relevant U.S. Agencies and Programs

1.6.1 National Science Foundation (NSF)

Determining the effects of rising atmospheric CO_2 on marine ecosystems—an interdisciplinary challenge—has relevance in several National Science Foundation programs, and particularly within the Division of Ocean Sciences (OCE). The Biological Oceanography Program supports investigations of the biology, ecology, and biogeochemistry of planktonic and benthic systems of both the open ocean and coastal regions, while the Chemical Oceanography Program has a strong emphasis on the formation and fate of both organic and inorganic geochemical materials. This topic also falls under the Marine Geology and Geophysics (MGG), Earth System History (ESH), and Geobiology and Low-Temperature Geochemistry (GG) programs. MGG considers the genesis, chemistry, and mineralogical evolution of marine sediments, as well as interactions of continental and marine geologic processes; ESH addresses the mechanisms and feedbacks that drive the Earth's climate system and determine its natural variability; and GG promotes studies of the interactions between biological and geological systems at all space and timescales (and several other research objectives relevant to this report). Finally, NSF's Long-Term Ecological Research Program (LTER) supports the type of long-term interdisciplinary research necessary to understand the consequences of decreased calcification rates at the ecosystem scale.

1.6.2 National Oceanic and Atmospheric Administration (NOAA)

On 23 December 2000 the U.S. Congress enacted the Coral Reef Conservation Act of 2000 (CRCA; Public Law 106-562). The CRCA authorized the Secretary of Commerce to establish a National Program and conduct mapping, monitoring, assessment, restoration, scientific research, and other activities that benefited the understanding, sustainable use, and long-term conservation of U.S. coral reef ecosystems. As authorized by the CRCA, the Secretary of Commerce established the National Oceanic and Atmospheric Administration Coral Reef Conservation Program to carry out the mandates laid out in the CRCA, including supporting effective ecosystem-based management and sound science to preserve, sustain, and restore the condition of coral reef ecosystems. NOAA's Coral Reef Conservation Program is implemented by four NOAA line offices—the National Ocean Service (NOS), the National Marine Fisheries Service (NMFS), the National Environmental, Satellite, and Data Information Service (NESDIS), and the Office of Oceanic and Atmospheric Research (OAR). In June 2002 NOAA, in collaboration with the United States Coral Reef Task Force, published "A National Coral Reef Action Strategy" as required by the CRCA to: provide information on major threats and needs; identify priority actions to achieve the goals outlined in the National Action Plan and the CRCA; and track progress in achieving these goals and objectives. Regarding research, the National Action Strategy identified two needs: (1) conduct strategic research to provide critical information on the underlying causes of reef decline; and (2) increase understanding of the social and economic factors of conserving coral reefs.

1.6.3 U.S. Geological Survey (USGS)

The USGS mission is to provide sound scientific knowledge and information needed to understand environmental quality and preservation on regional,

Table 1.3: Comparison of benthic and planktonic calcifying ecosystems.

	Benthic	Planktonic
Ecology		
Habit	Mostly stationary or sedentary as adults; $CaCO_3$ accumulation provides structural ecosystem framework	Nonstationary; $CaCO_3$ accumulation physically separate from ecosystem
Domain	Continental shelves <100 m deep; mostly at low latitudes	Upper ocean; present data suggest mostly at high latitudes
Nutrient limitation	Usually low	Variable
Light limitation	Many species are photosynthetic or have photosynthetic symbionts	Many species are photosynthetic or have photosynthetic symbionts
Temperature limitation	Directly affected by changing temperature	Indirectly affected by changes in thermal stratification, upwelling
Biodiversity or functional diversity?	High, but differs between ocean basins	High at low latitudes; generally lower at high latitudes
Dominant calcifiers	Low latitudes: coelenterates/algae Temperate latitudes: bryozoans, molluscs, forams, algae	Algae, protists, molluscs
Food web	Mostly primary producers	Primary producers or consumers
Competition	Potential to be outcompeted by noncalcifying species	Potential to be outcompeted by noncalcifying species
Capacity to adapt to elevated pCO_2	No evidence of adaptation in corals, coralline algae	Unknown; short generation times may enhance ability to adapt
Calcification		
Production cycle/generation times?	Relatively constant production; Regeneration times usually years to decades	Variable production cycle from bloom-forming to relatively constant; Regeneration times usually days to months[1]
Mineralogy	Low latitudes: mainly aragonite (corals) and high-Mg calcite (calc. algae) High latitudes: mainly calcite (bryozoans, forams) and mixed arag/calcite (molluscs)	Mainly calcite (coccolith; forams) Some aragonite (pteropods; heteropods) Some high-Mg calcite[2]
Area[3]	$\sim 1 \times 10^{12}$ m^2	$\sim 300 \times 10^{12}$ m^2
Calcification rate[3]	10–180 g C m^{-2} y^{-1}	1–2 g C m^{-2} y^{-1} Wide range in literature for coccolithophores; hard to measure in many planktonic calcifiers
Net $CaCO_3$ production[3]	0.02–0.1 Pg C y^{-1}	0.29–1.1 Pg C y^{-1}
Net $CaCO_3$ accumulation[3]	0.01–0.1 Pg C y^{-1}	0.1 Pg C y^{-1}
Carbonate System Behavior		
pCO_2 variability	High	Low?[4]
Influence of sedimentary processes	High	Low
Carbon Cycling		
Role in carbon cycle	Increases atmospheric CO_2 — "coral reef hypothesis"	Affects C_{org}:C_{CaCO_3} of deep ocean

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[1] Two coccolithophorid species can have episodic blooms but there are many other species that may be important in terms of $CaCO_3$ flux.

[2] In some regions, such as Sargasso Sea.

[3] Estimates from Milliman and Droxler (1996) and Lee (2001).

[4] At high latitudes there are pronounced differences between summer/winter seasons.

national, and when appropriate, global scales. A number of programs within the USGS address such needs, including the Coastal and Marine Geology Program, Earth Surface Dynamics and Climate Change, and various USGS Biology Programs. Within the marine realm, the Coastal and Marine Geology Program in the USGS recognizes a need for scientific research linking changes in atmospheric CO_2 to marine ecosystem responses because of significant resource management implications. Coastal and marine ecosystems, including coral reefs, bays, and estuaries, and continental margins are particularly sensitive to climatic and CO_2 changes. Therefore, USGS research will continue to provide fundamental information on CO_2 cycling in these societally important areas and these data will feed development of models that describe ecosystem responses to CO_2 changes in the ocean.

1.6.4 Other U.S. Agencies

Several other agencies have programs that are relevant to investigations of changes in carbonate chemistry of the ocean and the effects on marine organisms. The Earth Science mission of the National Aeronautics and Space Administration (NASA) is to "understand and protect our home planet by using the view from space to study the Earth system and improve prediction of Earth system change." Much of NASA's contributions to ocean research are through their support of remotely sensed observations from space-based and sub-orbital platforms, such as SeaWiFS, MODIS/Aqua, QuikSCAT, and TOPEX/Poseidon, to name but a few. NASA also supports basic research and data analysis, modeling, applying research results in decision support, and scientific assessment. Specific applications of satellite-based data to derive calcification rates in both open ocean and shallow water environments are described in section 4.1.4 of this document.

The Environmental Protection Agency (EPA) has a long history of supporting ecosystem research. For example, EPA's National Center for Environmental Research (NCER) sponsors the Science to Achieve Results (STAR) program, which engages scientists and engineers in targeted research that complements existing research within EPA as well as that of other federal agencies. NCER recently sponsored a research program on the "Effects of Climate Change on Ecosystem Services Provided by Coral Reefs and Tidal Marshes." NCER also periodically establishes large research centers in specific areas of national concern, such as the National Center for Caribbean Coral Reef Research (NCORE). NCER lists several "opportunities" presented by these centers that would greatly accelerate research on the effects of ocean acidification on marine calcifiers; these include:

- provide for multidisciplinary interactions in a wide range of scientific areas—informing state-of-the-art research programs for a specific purpose;
- establish a national network that fosters communication, innovation, and research excellence;
- improve study designs, resulting from intra-Center, multi-disciplinary integration and cross-disciplinary work;
- ability to pursue "higher-risk" efforts in methods development, validation, and pilot studies, providing a greater potential for innovation; and
- longer term continuity (i.e., for five years) allows long-term planning and research implementation.

2. Future Carbonate Chemistry of the Oceans

2.1 Open Ocean

2.1.1 Background

The ocean is the largest labile reservoir for carbon on decadal to millennial timescales, acting as a variable sink for atmospheric CO_2 and other climate-relevant trace gases (e.g., Siegenthaler and Sarmiento, 1993). Model projections suggest that on millennial timescales the ocean will be the ultimate sink for about 90% of the anthropogenic carbon released to the atmosphere (Archer *et al.*, 1998). On shorter timescales, however, the rate of ocean uptake can vary substantially. Estimates of the ocean CO_2 uptake for the last 20 years amount to about a third of the CO_2 released from fossil fuel burning (Prentice *et al.*, 2001). However, a recent estimate of the ocean anthropogenic CO_2 inventory for the mid 1990s accounts for nearly half of the fossil fuel CO_2 released between 1800 and 1994 (Sabine *et al.*, 2004). The net ocean uptake of anthropogenic carbon appears to be controlled over the historical period and at present by ocean physics (**Figure 2–1**), namely the ventilation and exchange of surface waters with the thermocline and intermediate to deep waters (Sarmiento and Gruber, 2002). The study of purely physical transport processes in the ocean is a huge endeavor in itself and is arguably further advanced than the study of ocean ecosystems and their effect on the carbon cycle.

Distinguishing a human-induced signal from natural decadal variability is often singularly difficult given the relatively short length of most oceanographic data records. Recent geochemical studies indicate a 0.1 unit drop in surface ocean pH and a shoaling of aragonite saturation depths by as much as 200 m since the pre-industrial period (Feely *et al.*, 2004; **Box 2**). Model projections indicate that these chemical changes will accelerate in concert with increases in atmospheric CO_2, and the human signal will become increasingly evident in the near future. A recent study projects that surface waters around Antarctica and the North Pacific could become undersaturated with respect to aragonite by the end of the 21st century (Orr *et al.*, 2005).

Decadal timescale ocean biological responses (e.g., changes in nutrient stocks and community structure) to climate change and ocean acidification are not well characterized. There is, however, evidence for large-scale biogeochemical regime shifts (or perhaps secular trends) (Karl, 1999) and changes in nutrient distributions (Emerson *et al.*, 2001). Under future greenhouse warming climate scenarios, the ocean's physical uptake of anthropogenic carbon is expected to decline over the next few decades because of surface warming, increased vertical stratification, and slowed thermohaline circulation (Sarmiento *et al.*, 1998; Matear and Hirst, 1999). In coupled simulations with simple biogeochemical models, these physical effects are partly compensated by increased uptake from changes in the strength of the natural biological carbon pump. The biogeochemical response is governed by two opposing factors: (1) a reduction in the upward nutrient supply due to increased stratification, which leads to decreased export production of organic matter and CO_2 uptake, and (2) a decrease in the upward vertical flux of dissolved inorganic carbon. The latter factor generally dominates in the present simulations, so that the effect of altered biogeochemistry is a net positive CO_2 uptake. These studies, however, only consider overall productivity and not the potential impact of changes in ecosystem structure if, for example, calcifying organisms were more strongly impacted than other marine producers. Given the low level of biological sophistication used in these early simulations, such projections must be considered preliminary. They do, however, demonstrate the potential sensitivity of the system and pose important questions to be addressed through future research.

2.1.2 Evidence and gaps in current knowledge

A wide variety of mechanisms have been identified that could alter ocean carbon uptake, but in many cases even the sign of the biogeochemical response, let alone the magnitude, is uncertain (Denman *et al.*, 1996; Doney and Sarmiento, 1999). Potential effects include:

- Decreased CO_2 released to the seawater environment because of lower calcification due to anthropogenic CO_2 uptake (Gattuso *et al.*, 1999b;

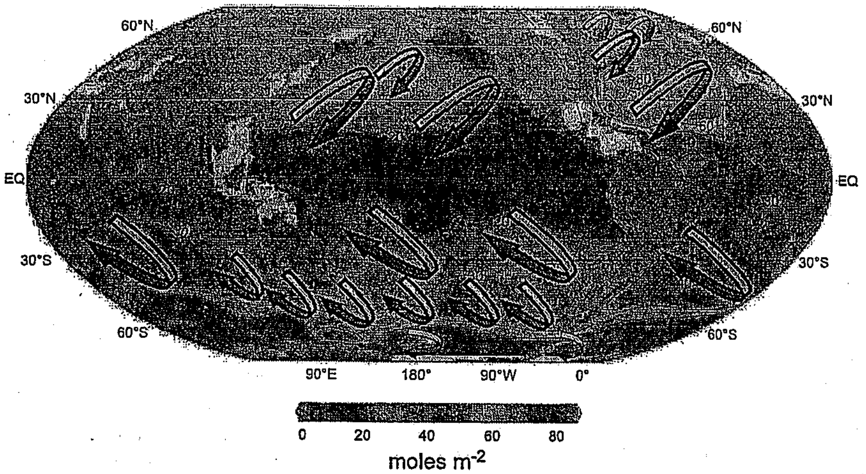

Figure 2–1: Comparison of estimated mode, intermediate, and deep water formation regions (Talley, 1999) and regions with large column inventories of anthropogenic CO_2 (Sabine *et al.*, 2004). The largest arrows indicate deep and bottom water formation regions, the medium-size arrows are intermediate water formation regions, and the smallest arrows indicate mode water formation regions. The water mass formation regions are areas where anthropogenic CO_2 is moved into the ocean interior.

Riebesell *et al.*, 2000; Zondervan *et al.*, 2001; Barker *et al.*, 2003);

- Altered carbon export rates because of lower vertical nutrient supply and in some regions enhanced, effective-surface-layer light supply leading to often opposing regional changes in primary productivity (Bopp *et al.*, 2001);
- Alterations in the spatial patterns of carbon uptake and export due to stratification-induced changes in community composition of marine biomes (Boyd and Doney, 2002);
- Altered carbon uptake and export in high nitrate-low chlorophyll (HNLC) regions such as the Southern Ocean, and possible changes in subtropical nitrogen fixation, due to changes in dust deposition and iron fertilization; and
- Decoupling of carbon and macronutrient cycling because of shifts in the elemental stoichiometry of surface export and differential subsurface remineralization.

Accounting for such hypotheses in future climate projections is problematic given our current understanding and modeling tools (Doney, 1999; Falkowski *et al.*, 2000).

Calcium carbonate is thought to play a role in organic carbon transport to the deep ocean (Armstrong *et al.*, 2002; Klaas and Archer, 2002), but the mechanism for this has not been determined (Passow, 2004). Predictions of the response of the ocean carbon cycle to increased atmospheric CO_2 are thus poorly constrained. Reduced calcification and/or increased calcium carbonate dissolution in the ocean will increase its capacity to take up atmospheric CO_2. A complete shutdown of calcification would lower surface ocean pCO_2 by about 10–20 μatm (Gruber *et al.*, 2004) and oceanic uptake of CO_2 would slightly *increase*. However, calcium carbonate is also thought to serve as a "ballast" for organic carbon transport to the deep ocean (Armstrong *et al.*, 2002); so a reduction in ballast could *decrease* ocean uptake of CO_2.

Mechanisms for dissolution of particulate inorganic carbon (PIC) in the water column, above the aragonite and calcite saturation horizons, are poorly understood. The dissolution of PIC affects the carbonate chemistry of the water column, and thus affects the rate of carbon uptake from the atmosphere, the calcification rates of organisms, and the translocation of carbon to deeper depths. PIC composition, grainsize, aggregation (Jackson, 1990; Jackson and Burd, 1998), sinking rate (e.g., Pilskaln *et al.*, 1998; Berelson, 2002), and carbonate saturation state of the water column are all factors affecting PIC dissolution, as well as biological factors such as microbial activity, ingestion by organisms, and the presence of biologically produced materials such as transparent exopolymer particles (TEP) (Passow, 2002). These processes and how they will change in response to future CO_2 increases must be better understood in order to obtain a global carbonate budget and to predict the future state of ocean seawater chemistry. Without this understanding, we cannot close the global carbonate budget or have a proper understanding of how ecosystem changes might impact the calcium carbonate cycle. Similarly, the role of PIC dissolution in open oceans needs to be quantified; e.g., what are the rates of change in carbonate dissolution?

Dissolution of open-ocean carbonate sediments needs further study. Over glacial-interglacial timescales, preservation and dissolution of $CaCO_3$ in ocean sediments act to maintain a constant ocean alkalinity ("calcium carbonate compensation") that provides a significant negative feedback on changes in atmospheric CO_2 (Archer, 1996). On shorter timescales, the rates of dissolution are too slow to effectively counter the current increase in atmospheric CO_2. However, dissolution rates of these sediments are likely to increase as the saturation horizons of the carbonate minerals begin to shoal and expose more sediments to undersaturated conditions, which will affect the rates of alkalinity fluxes across the water-sediment interface. Similar to the controls on PIC dissolution in the water column, a variety of factors can affect benthic dissolution rates, from organic carbon content (Jahnke *et al.*, 1994) to bioturbation and dissolution in the guts of deposit feeders (Jansen and Ahrens, 2004). Factors that affect solubility and dissolution kinetics of carbonate sediments are also not fully understood (Gehlen *et al.*, 2005a, b). Predicting how the rates of carbonate sediment dissolution may change in response to water column chemical changes and how this will affect carbonate chemistry of the overlying water column are important objectives toward improved understanding of the global $CaCO_3$ budget.

2.2 Coastal Ocean

2.2.1 Background

Little attention has been given to the role of the carbon cycle of shallow-water ocean margins and their modeling in the context of global change, despite their documented importance in the global carbon cycle (Gattuso *et al.*, 1998a; Ver *et al.*, 1999; Chen, 2003; Chen *et al.*, 2003; Chen *et al.*, 2004). The shallow-water ocean environment (i.e., bays, estuaries, lagoons, banks, and continental shelves) constitutes only 7% of global ocean surface area, but supports approximately 10–30% of the world's marine primary production. Eighty percent of inputs from land to sea are deposited here, and 85% of organic carbon and 45% of inorganic carbon are buried in the ocean margin sediments (Gattuso *et al.*, 1998a; Wollast, 1998; Chen *et al.*, 2003). Carbonate accumulation in coral reef environments alone accounts for an estimated 20–30% of the global ocean accumulation (Milliman and Droxler, 1996). Ocean margins are also heavily impacted by human activities, as nearly 40% of the global population lives within 100 km of the coastline (Cohen *et al.*, 1997). Since the onset of the Industrial Revolution, burning of fossil fuels and land-use changes have caused substantial increases in both atmospheric CO_2 concentration and in the delivery of organic matter and nutrients to ocean margins (Mackenzie, 2003). Such changes could alter the role of this system and considerably affect important processes such as air-sea CO_2 exchange.

Model calculations for a "business as usual" CO_2 emissions scenario suggest that global coastal ocean seawater marine carbon chemistry could change significantly and that the saturation state of the surface waters with respect to aragonite and calcite could decline 45% by the year 2100 and 73% by the year 2300 (Caldeira and Wickett, 2005; Andersson *et al.*, 2006). Because of this and increases in water temperature, the $CaCO_3$ production rate (mainly biogenic calcification) in coastal seawater could decrease by 40% by 2100 and by 90% by 2300 (**Figure 2–2**). By 2150, because of increases in atmospheric CO_2, temperature and loading of the coastal ocean with nutrients and organic carbon, the $CaCO_3$ production rate in the global coastal ocean is predicted to fall below the $CaCO_3$ dissolution rate; that is, $CaCO_3$ would be dissolving faster than it is being produced (Andersson *et al.*, 2006).

2.2.2 Evidence and gaps in current knowledge

Pre-industrial carbon cycling in the coastal zone is not well understood because human activity has already significantly altered the natural carbon cycle. Without a clear understanding of how the coastal carbon system operated prior to human alteration, it is difficult to understand how the system will change in the future. For example, we do not fully understand the potential role of sediment (including suspended sediment) dissolution in benthic environments.

Measurements of coastal zone carbon fluxes are currently insufficient to determine the response of coastal carbonate systems. At present it is difficult to determine from either syntheses of field observations or modeling whether global coastal ocean waters are a net source or sink of CO_2 to the atmosphere. This is particularly true in tropical and subtropical zones and estuaries. Upscaling of air-water CO_2 fluxes measured in the coastal ocean is hampered by the poorly con-

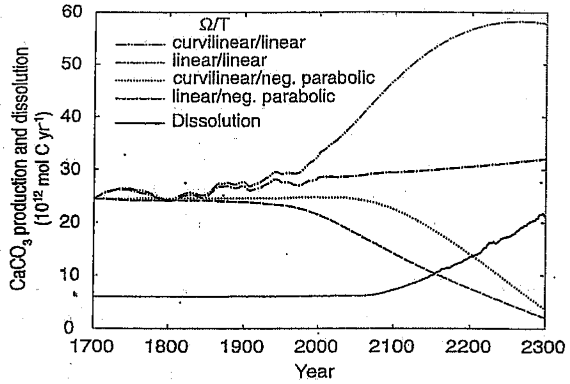

Figure 2–2: Model calculations showing changes in $CaCO_3$ production and dissolution rates in global coastal ocean surface waters depending on various relationships between carbonate production rate, temperature (T), and saturation state (Ω). For the most likely scenario of a linear relationship between saturation state and production and a negative parabolic relation between production and temperature, the calculations indicate that by 2150 under a business as usual scenario, global coastal ocean carbonates will be dissolving faster than they are produced. Reprinted from Andersson *et al.* (2006) with permission from the American Journal of Science.

strained estimate of the surface area of inner estuaries (Borges, 2005), and some regions are net sinks and others net sources of CO_2 to the atmosphere. Coastal oceans are characterized by extreme spatial and temporal heterogeneity, and by high rates of primary production, fluxes from land, and burial of organic and inorganic carbon. Quantifying these rates and detecting a response to CO_2 forcing are difficult and require a well-designed, coordinated monitoring network. As atmospheric CO_2 continues to rise, there is a strong need for such data to (1) resolve the direction and magnitude of the CO_2 flux in coastal waters, (2) assess the effects of the rise on the carbonate saturation state of coastal waters, and (3) identify response of coral and other shallow-water carbonate ecosystems to this perturbation. Estimates from modeling are not very robust at present but suggest that the global coastal ocean several hundred years ago was a net source of atmospheric CO_2, and has recently or will soon become a net sink (Mackenzie *et al.*, 2004; Andersson *et al.*, 2005).

3. Calcification/Dissolution Response

Research into the effects of increased atmospheric CO_2 on marine calcifiers has concentrated on two research questions: (1) how do calcification rates vary with calcium carbonate saturation state, and (2) what are the effects of changing calcification and dissolution rates on the ocean carbon cycle and the capacity of the ocean to take up CO_2 from the atmosphere? How decreased calcification rates affect biological functioning or organism survival, however, is essentially unstudied. Carbonate dissolution also remains poorly determined; i.e., the controls on dissolution rates in the water column and in sediments, how dissolution affects alkalinity fluxes, and the potential role of dissolution in buffering the carbonate system.

Biogenic calcification[1] evolved sometime during the Cambrian period, coincident with a sudden rise in Ca^{2+}. Because high Ca^{2+} is toxic to cellular processes, it has been proposed that calcification may have arisen as a detoxification mechanism (Brennan *et al.*, 2004). Organisms have since evolved to put these $CaCO_3$ secretions to good use as skeletal support, protection, and many other functions (**Table 3.1**). Predictions about how reduced calcification will affect organisms are therefore based on the fact that secretion of calcium carbonate by organisms serves some function (or multiple functions) that benefits the organism.

3.1 Coral Reefs and Other Benthic Calcifying Systems

The major benthic calcifying organisms on coral reefs are corals, calcifying macroalgae, benthic foraminifera, molluscs, and echinoderms (**Figure 3–1**). In the tropics, scleractinian corals and calcareous green and red algae are important to the building and cementation of the massive carbonate framework that forms the habitat for coral reef organisms. In colder deep (50–1000 m) waters of the continental shelves and offshore canyons, deep-sea corals build carbonate thickets or groves of high complexity that provide habitat for many other organisms. To date, studies of the effects of elevated CO_2 have been confined to a few species of coral and/or algae, and there remain large voids in our knowledge of the physiological and ecological impacts of increasing pCO_2 on other benthic calcifiers such as benthic foraminifera, echinoderms, molluscs, and deep-sea corals. For example, some deep-sea corals will experience waters with $\Omega_{arag} < 1$ as early as 2020 (Guinotte *et al.*, 2006); these organisms may thus be impacted by undersaturated waters before we can determine their potential ecological and economical importance as fish habitat.

The following addresses the evidence and gaps in our current knowledge of how increasing ocean acidification will affect benthic calcifying ecosystems in terms of: (1) calcification response, (2) organism response, (3) ecosystem response, and (4) dissolution and reef-building response. We focus here on coral reefs and other benthic calcifying systems of the tropics, but many other calcifying systems should be included in future studies. Some temperate shelves, for example, support a wealth of benthic calcifiers and calcifying communities, many of which are of economic importance either directly (shellfish) or indirectly (supporting fish habitat and fisheries). Finally, although not addressed here, calcification by benthic microbial communities is recognized as a potentially important component of the overall $CaCO_3$ budget. Microbial communities are of particular interest because they tend to have biologically induced rather than biologically controlled calcification (Weiner and Dove, 2003), and are thus more likely to respond to changing carbonate chemistry.

3.1.1 *Calcification response*

Multiple taxa of benthic calcifiers have shown a significant calcification response to carbonate chemistry. Most studies have concentrated on reef-associated taxa such as coralline red algae (articulate and encrusting) and hermatypic corals (branching, massive, and solitary). The two most soluble phases of the $CaCO_3$ mineralogy (aragonite and high-Mg calcite) are represented in this suite. Decreases in calcification rates across a suite of benthic species and calcifying systems range from 3% to 60% for a doubling

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[1] Biological precipitation of $CaCO_3$, which is often termed "biocalcification" or, given that almost all $CaCO_3$ precipitation is biologically induced or mediated, simply "calcification."

Table 3.1: Proposed functions of calcification in organisms. Not all suggested functions are supported by experimental evidence.

Function	Planktonic	Benthic
Protection	all groups	all groups
Buoyancy regulation	coccolithophores, foraminifera	
Light modification	coccolithophores	corals
Provide protons for conversion of HCO_3^- to CO_2 for photosynthesis	coccolithophores	calcareous algae?
Facilitate bicarbonate-based photosynthesis	coccolithophores	
Aid in capture of prey	foraminifera	
Reproduction	foraminifera, some pteropod species	corals?
Prevention of osmotically induced volume changes	coccolithophores	
Extension into hydrodynamic regime		corals, calc. algae, bryozoans
Anchoring to substrate		corals, calc. algae, bryozoans
Competition for space		corals, calc. algae, bryozoans

in pCO_2 (34% reduction in saturation state) (**Figure 1–4**). The average response of corals is a 30% decline in calcification in response to a doubling in pCO_2 (**Table 1.1**).

Exposure to elevated CO_2 can affect physiology as well as calcification rate in many other benthic organisms. Several studies have demonstrated physiological stress in organisms exposed to very high pCO_2 levels that would be expected from direct CO_2 disposal in the ocean (see, for example, the special issue on ocean sequestration of CO_2 (Brewer *et al.*, 2004)). Two recent studies have investigated both physiological and calcification effects of long-term exposure of molluscs and sea urchins to much lower elevations of CO_2. Specimens of *Mytilus galloprovincialis* that were maintained for three months at pH = 7.3 (consistent with a pCO_2 of about 1900 μatm) experienced a significant reduction in growth, as well as shell dissolution, in response to reduced haemolymph bicarbonate levels (Michaelidis *et al.*, 2005). In another study, specimens of two species of sea urchin (*Hemicentrotus pulcherrimus* and *Echinometra mathaei*) and one gastropod mollusc (*Strombus luhuanus*) that were exposed for six months to CO_2 levels elevated by 200 ppmv over normal levels had smaller size and body weight, and in *E. mathaei* a thinning of the $CaCO_3$ tests was observed (Shirayama and Thornton, 2005). Many other calcifying taxa are important ecologically, economically, and as components of the marine $CaCO_3$ cycle (e.g., calcareous green algae, echinoderms, benthic molluscs and foraminifera, bryozoans, ahermatypic corals), but few have been tested for their physiological and calcification responses to elevated CO_2.

The interactive effects of saturation state, temperature, light, and nutrients, are important factors in calcification rates of reef organisms. Human activities are causing changes in all of these factors and light, temperature, and nutrients have all been demonstrated to affect calcification rates of corals, either singly or in combination with saturation state. As described below, there are very few studies that have examined the combined effects of these variables, and the results have been difficult to interpret.

Coral calcification responds to both light and saturation state but the effects do not seem to be strongly interactive, as coral calcification decreases under increased pCO_2 conditions over the full range of light intensity that corals experience (Marubini *et al.*, 2001), and dark calcification shows the same sensitivity.

Only two studies have tested the combined temperature-saturation state effect on coral calcification, and these have produced confusing results. Reynaud *et al.* (2003) observed a strong interaction between temperature and saturation state while Langdon and Atkinson (2005) observed little or no interaction. Coral calcification increases with increasing temperature up to a thermal optimum and then declines rapidly (Coles and Jokiel, 1977; Jokiel and Coles, 1977; Marshall and Clode, 2004; Al-Horani, 2005). As a result, increasing temperature could mask, partially offset, or reinforce the effect of elevated pCO_2, depending on where the temperature falls on the bell-shaped calcification-temperature response curve.

Two studies have measured the effects of combined nutrient concentrations and saturation state on corals. In one experiment, the calcification rate in *Porites porites* was more sensitive to changes in aragonite saturation state under increased nutrient conditions (Marubini and Thake, 1999), while in another, calcification rates of the corals *P. compressa* and *Mon-*

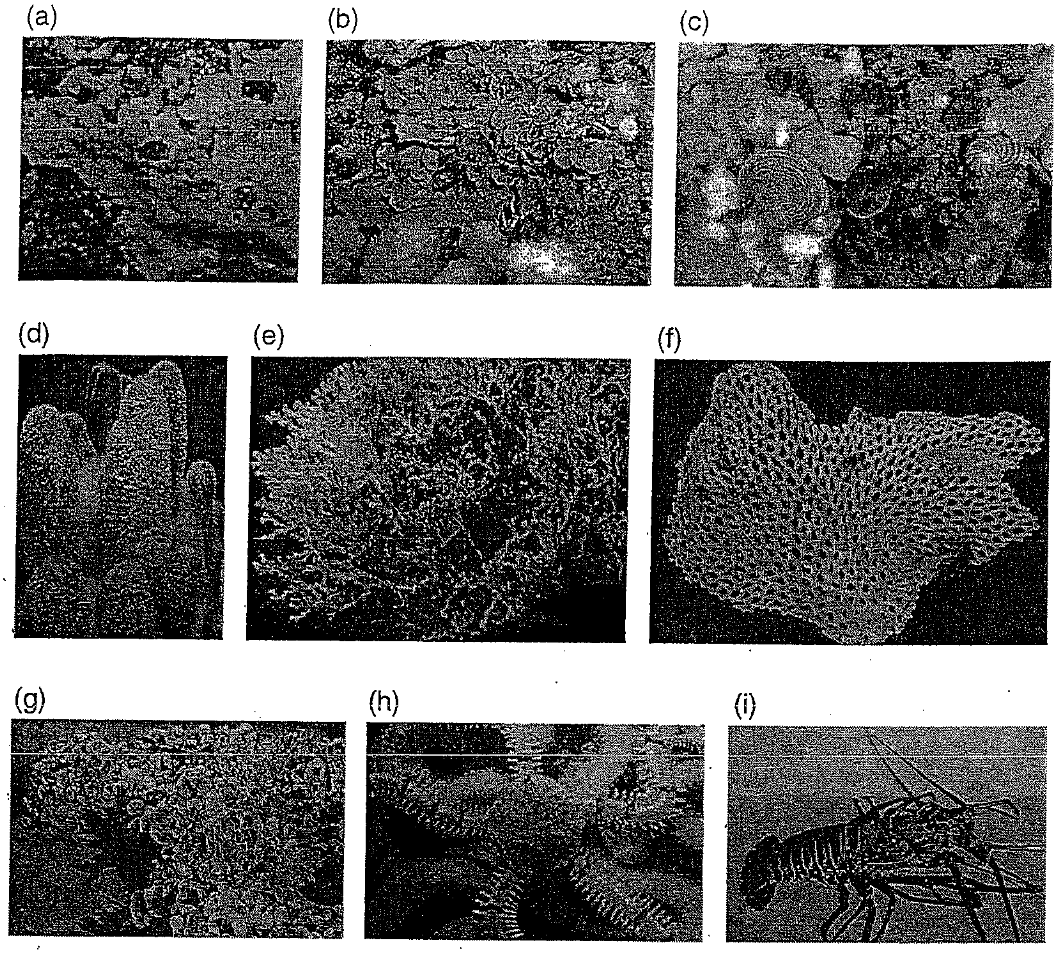


Figure 3–1: Representatives of major benthic calcifiers: (a) coralline algae (photo by Nancy Sefton; courtesy NOAA/CORIS); (b) *Halimeda* (photo by James Watt; courtesy NOAA/NMFS); (c) benthic foraminifera (courtesy P. Hallock); (d) reef-building coral (*Dendrogyra cylindrus*; Cmdr William Harrigan, NOAA Corps; courtesy Florida Keys National Marine Sanctuary); (e) deep-water coral (*Lophelia pertusa*; from 413 m depth off North Carolina. Large red crab is *Eumunida picta*; urchin below it is *Echinus tylodes*; courtesy S.W. Ross, K. Sulak, and M. Nizinski); (f) bryozoan (courtesy NOAA/Ocean Explorer); (g) mollusc (oyster reef; courtesy South Carolina Department of Natural Resources); (h) echinoderm (brittle star; Larry Zetwoch; Florida Keys National Marine Sanctuary); (i) crustacean (lobster; Dr. James P. McVey, NOAA Sea Grant Program). The calcification responses of many of these groups have not been investigated.

tastraea capitata were much less sensitive to changes in saturation state under increased nutrient conditions. The experimental designs of these two studies were very different, however, which is a likely factor in the mixed results.

Identification of a "CO_2 signal" is difficult because calcification rates in the field are a response to multiple variables (light, temperature, nutrients, etc.), and particularly to rising temperature. If seawater chemistry was the only variable affecting calcification, then calcification records from corals and other organisms should show a decrease in calcification over the past century. While some individual calcification records from massive corals do reveal a decrease in calcification rate over the past century, on average they do not (Lough and Barnes, 1997, 2000), and this is believed to reflect the effects of other variables on calcification. In particular, calcification rates in these and other massive corals show a strong correlation with temperature (Lough and Barnes, 1997, 2000; Bessat and Buigues, 2001; Carricart-Ganivet, 2004).

Boron isotopic analysis of a massive *Porites* coral core from Flinders Reef in the southwest Pacific indicates that seawater pH in this region fluctuated between about 7.9 and 8.2 units over the last 300 years, in 50-year cycles consistent with circulation changes associated with the Interdecadal Pacific Oscillation (Pelejero *et al.*, 2005). The authors also found that calcification rates for this core were not correlated with the derived pH values.

Carbonate chemistry measurements of waters overlying reefs and reef flats often show extreme diurnal variability, due to the effects of calcification-dissolution and photosynthesis-respiration of the coral community (Gattuso *et al.*, 1993b; Kayanne *et al.*, 1995; Frankignoulle *et al.*, 1996; Bates *et al.*, 2001; Kayanne *et al.*, 2005). Such high variability illustrates that many factors affect seawater chemistry both spatially and temporally on coral reefs, and attributing a change in calcification rate to a single factor is difficult. Future experiments that monitor diurnal to seasonal environmental fluctuations on a coral reef and compare them to calcification rates of resident organisms (e.g., as recorded in coral cores) would certainly shed light on the cumulative impact of multiple variables on coral calcification.

The relationship between photosynthesis and calcification in benthic calcifiers remains poorly understood. There is strong evidence that calcification rates in coralline algae and corals are enhanced by photosynthesis, with a mean light:dark ratio of about 3 (Gattuso *et al.*, 1999a), but the stimulating mechanism remains poorly known (Cohen and McConnaughey, 2003). The assumption that photosynthetic removal of CO_2 simply elevates the carbonate saturation state (Goreau, 1959) does not seem to hold. The opposite notion—that calcification stimulates photosynthesis by supplying CO_2—has also been proposed but is not widely accepted (Gattuso *et al.*, 2000; Cohen and McConnaughey, 2003; McConnaughey, 2003; Cohen, 2004; Marshall and Clode, 2004), although a recent study supports it (Schneider and Erez, 2006). Finally, photosynthesis and calcification may not be connected through carbonate chemistry, but rather because photosynthesis provides energy for calcification (Muscatine, 1990), or because calcification stimulates nutrient uptake (Cohen and McConnaughey, 2003).

Based on a small number of studies, net photosynthetic rates of corals show either no response to increased pCO_2 or a slight increase (Burris *et al.*, 1983; Goiran *et al.*, 1996; Langdon and Atkinson, 2005; Schneider and Erez, 2006). There is also empirical evidence that photosynthesis and calcification vary inversely when exposed to elevated CO_2 or nutrients (Hoegh-Guldberg and Smith, 1989; Stambler *et al.*, 1991; Marubini and Davies, 1996; Marubini and Thake, 1999; Langdon and Atkinson, 2005). Clearly, research is required on the molecular and biochemical pathways of the photosynthesis-calcification relationship before the effect of environmental changes on coral physiology can be deciphered.

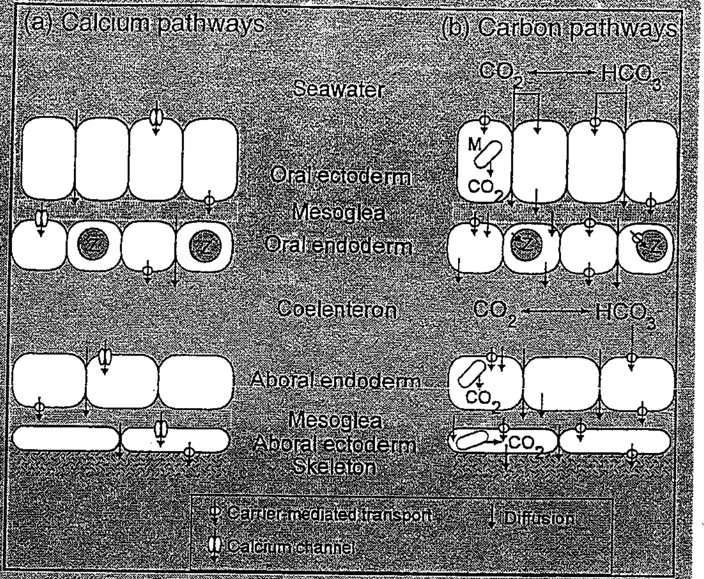
Identifying the various calcification mechanisms across taxa can streamline efforts to understand future responses to saturation state. The degree of biological control of calcification varies between taxonomic groups. The most passive mechanism, termed "biologically induced calcification" (Lowenstam and Weiner, 1989), occurs as a consequence of an organism's metabolic effects on the environment (e.g., photosynthesis absorbs CO_2 and raises saturation state). Calcification in most benthic calcifiers, including corals, is "biologically controlled," that is, cellular processes are directly involved in mineral nucleation, growth, and placement (Weiner and Dove, 2003). Even amongst taxa with biologically controlled calcification, the degree of control varies considerably. Calcification rates in those taxa with biologically induced or weakly controlled calcification are likely to be more sensitive to seawater chemistry changes than in other groups. For example, the mineralogy, skeletal amounts, and overall volumes of $CaCO_3$ produced by "hypercalcifiers" (e.g., corals, coccolithophores, and phylloid algae) have varied over geologic time in concert with changes in the seawater Mg:Ca ratio (Stanley and Hardie, 1998; Stanley *et al.*, 2005).

Beyond this broad classification, some of the biocalcification processes of corals can be pieced together from existing studies. For example, both dark and light calcification in corals are affected by a change in saturation state of the seawater, which implies that there is either significant exchange with the external environment or some indirect control by the external seawater chemistry on the carbonate chemistry of the internal calcifying space (**Box 3**). While HCO_3^- is the preferred substrate for coral photosynthesis (Al-Moghrabi *et al.*, 1996; Goiran *et al.*, 1996; Allemand *et al.*, 1998), coral calcification uses both HCO_3^- from seawater and metabolic CO_2 as sources of carbon (Erez, 1978; Furla *et al.*, 2000). Most models assume that the calcifying fluid is isolated from external seawater. This is supported by microelectrode observations that show that the pH of the calcifying space is elevated relative to external waters (as high as 9.3) (Al-Horani *et al.*, 2003) and by the well-known fractionation of oxygen and carbon isotopes in the calcifying fluid.

The component of the carbonate system—CO_3^{2-}, saturation state, pH—that controls calcification rate has not been adequately determined. Although biochemical studies fail to provide any evidence that

Box 3—Coral Calcification

Coral calcification was reviewed by Gattuso *et al.* (1999a), Cohen and McConnaughey (2003), and Allemand *et al.* (2004). A coral is a colonial organism made up of many polyps. The anatomy of a polyp can be simply described as a "bag" enclosing a coelenteric cavity or gut open to the surrounding seawater by a mouth. The walls of the polyp are made of two single-cell thick epithelial layers, the ectoderm (outer layer) and the endoderm (inner layer), separated by a thin connective layer, the mesoglea. The two layers against the skeleton are the aboral endoderm and ectoderm, and the two layers in closest contact to seawater are the oral endoderm and ectoderm. A schematic of the polyp geometry is shown below. In reality, the geometry is much more complex: the coelenteric cavities of neighboring polyps are connected, the shape of the "bag" conforms to the complex skeletal structure of the calyx or calcium carbonate "cup" that each polyp occupies, the "bag" is compartmentalized into mesenteries and tentacles, and it contains cilia that are capable of generating water movement.



(a) Calcium and (b) carbon pathways involved in calcification and photosynthesis in scleractinian corals. Anatomy is greatly simplified. The extracytoplasmic calcifying fluid is located between the aboral ectoderm and the skeleton. Every possible pathway is shown; the actual transport mechanisms for each of the four cell layers can be transcellular or paracellular, or a combination of both. M = mitochondria; Z = zooxanthellae. Reprinted from Gattuso *et al.* (1999a).

The zooxanthellae, symbiotic plant cells, are mainly located in the oral endoderm. The zooxanthellae supply during the day much of the polyp's energy requirements through the process of photosynthesis. Calcification occurs in the extracellular calcifying fluid (ECF) located between the aboral ectoderm and the dead skeleton. The cells of the aboral ectoderm, called calicoblastic cells, are thought to be intimately involved in skeletogenesis, the process whereby crystals of calcium carbonate produced by calcification are grown into the complex architecture characteristic of each coral species. The distance separating the processes of photosynthesis and calcification is approximately 25 μm.

The diagram summarizes the many pathways via which calcium ion and inorganic carbon could reach the site of calcification. For each there are diffusive or active pathways that have been demonstrated by physiological and pharmacological studies. Diffusive pathways involve molecular diffusion through the lateral cell junctions termed paracellular transport while active pathways occur via an energy-dependent transcellular transport mechanism. The chemical composition of the coelenteric fluid is influenced by photosynthesis, calcification, and advective exchange of seawater through the mouth and transepithelial transport of ions by enzyme-mediated mechanisms. This fluid in turn supplies the Ca^{2+} and inorganic carbon to the ECF. The source and pathways of inorganic carbon are particularly complex because they can exist in three different forms and can be produced metabolically within the cells in addition to diffusing into the cells from the seawater or being actively transported in the form of $[HCO_3^{2-}]$. Several studies suggest that metabolic CO_2 is the major source of carbon for calcification (Erez, 1978; Furla *et al.*, 2000). The current model of coral calcification emphasizes the active uptake of Ca^{2+} from the coelenteric fluid by calicoblastic cells in which two major transporter proteins, the Ca^{2+}-channel allowing Ca^{2+} entry into the cells and the Ca^{2+}-ATPase allowing its active secretion toward the site of calcification, have been characterized and localized (Allemand *et al.*, 2004). It has been demonstrated that these cells are responsible for the secretion of macromolecules, called organic matrix, involved in the control of calcification (Puverel *et al.*, 2005).

CO_3^{2-} plays a direct role in coral calcification, results from experiments that specifically control the concentrations of the various components of the carbonate system (e.g., maintaining constant pH while varying $[CO_3^{2-}]$) suggest that coral calcification responds to $[CO_3^{2-}]$ rather than pH or some other component of the surrounding seawater environment (Langdon, 2002; Schneider and Erez, 2006). Many calcification data sets are well described by the rate law: $R = k(\Omega - 1)^n$, where R is rate of calcification, k is the rate constant, Ω is the saturation state, and n is the order of reaction. Two data sets have shown that an increase in $[Ca^{2+}]$ has the same effect on calcification as an increase in $[CO_3^{2-}]$ (Gattuso *et al.*, 1998b; Langdon *et al.*, 2000), lending support to the hypothesis that it is the ion concentration product, $[Ca^{2+}][CO_3^{2-}]$, and not the change in carbonate chemistry per se that is affecting the rate of calcification. In normal seawater, $[Ca^{2+}]$ is much higher than $[CO_3^{2-}]$ and is not considered limiting to calcification. Changes in Ω are thus primarily a function of $[CO_3^{2-}]$ changes.

3.1.2 *Organism response*

How decreased calcification rates will affect the long-term survival of benthic calcifiers is unknown. The effects of reduced calcification on an organism's fitness and survivorship have been hypothesized based on the perceived functions of $CaCO_3$ in that organism. In corals and coralline algae, for example, skeletal growth is thought to elevate the organism above the substrate and into higher light and better flow conditions, provide anchoring/rigidity against hydrodynamic forces, increase competitiveness for space, increase light gathering, and provide protection (**Table 3.1**). Reproductive success of some coral species could be affected by slower or more fragile growth. Reproductive maturity in *Goniastrea aspera*, for example, is achieved by size rather than age (Sakai, 1998a, b), and increased skeletal fragmentation in *Acropora palmata* can promote asexual propagation, but can also lower the potential for sexual reproduction of the species (Lirman, 2000).

The role of calcification in multiple life stages may play a critical role in organism survival. For many organisms, the function of $CaCO_3$ varies with life cycle stage (e.g., planktonic stages, recruitment), but almost all studies of CO_2 effects on calcification have focused on adults. One study (Agegian, 1985) noted that recruitment of coralline algae on aquarium walls was reduced in experiments with elevated pCO_2, and another (Green *et al.*, 2004) found that newly settled larvae of the mollusc *Mercenaria mercenaria* experienced higher shell dissolution and mortality rates when the pore-water interface was undersaturated with respect to aragonite.

Several years may be necessary to determine whether benthic calcifiers can adapt or acclimate to different carbonate chemistry conditions. There is no experimental evidence from either single organisms or multispecies mesocosms that corals or coralline algae can acclimate or adapt to lowered saturation state. However, most experiments have been conducted over hours to months, and based on isotopic evidence corals appear to calcify with natural "biorhythms" for up to two years after being introduced into a new environment (P. Swart, personal communication). Another unexplored mechanism for adaptation may be to secrete less soluble skeletons. The solubility of high-Mg calcite, for example, increases with increasing Mg content, and several taxa are known to vary the Mg content of their skeletons in response to several environmental variables (Chave, 1954; Stanley *et al.*, 2002). This ability to secrete skeletons with lower Mg content (and lower solubility) provides some organisms the potential to "adapt" to decreasing saturation state. Finally, some species may be able to adapt to lower calcification rates by adopting different morphologies or growth strategies.

3.1.3 *Ecosystem response*

The effects of changing calcification and dissolution on reef ecosystem functioning are unknown. This includes (1) the interactions of organisms, (2) food web dynamics, (3) basic cycling of carbon and nutrients through the ecosystem, and (4) the services that these ecosystems provide. The role of inorganic cementation in stabilization of organisms, communities, and reef structures has not been quantified; nor has the extent to which inorganic cementation may be affected by a lowered saturation state. Inorganic cementation is considered another component of ecosystem development, as it plays a role in the resilience of coral skeletons and reef structures.

The effects of reduced saturation state on bioerosion rates are unknown. Bioerosion is another prevalent, natural process in coral communities. All benthic calcifiers experience skeletal bioerosion simultaneously with growth, from a wide variety of both chemical and physical bioeroders, both macroscopic (e.g., molluscs and sponges) and microscopic (e.g., fungi and microalgae). Will bioerosion rates change in response to lower calcification rates, or increase in the presence of less dense skeletal material; and how will this affect the structure and functioning of benthic ecosystems?

3.1.4 Dissolution and reef-building response

The role of reef-building in coral reef ecosystem functioning is complex and not fully understood. Reef-building supports many functions of a coral reef community: (1) the ability to keep up with sea level rise, (2) the creation of spatial complexity that supports diversity, (3) the depth gradient that also supports diversity, and (4) the structural influence on the local hydrodynamic regime. A better understanding of the second point, in particular, is key to predicting coral reef community response to elevated CO_2.

Dissolution in reef environments is expected to increase. Net carbonate dissolution is observed in many reef environments at night when respiration elevates the local pCO_2 of the water column. Measured dissolution rates range from 0.1–20 mmol $CaCO_3$ m^{-2} h^{-1} and average 2 ± 5 mmol $CaCO_3$ m^{-2} h^{-1} (**Table 3.2**). Dissolution is likely occurring all the time in sediments and carbonate framework of the reef but is only evident at night when it is not masked by a higher rate of carbonate precipitation. Mass loss of red algal carbonate substrates (18% Mg-calcite) embedded in Florida reef tract sediments suggest a dissolution rate of 10–19 mmol $CaCO_3$ m^{-2} d^{-1} of this most soluble form of biogenic carbonate.

Rates of dissolution in the sediments and reef framework are expected to increase as the overlying water becomes less supersaturated. This is because respiratory CO_2 produced by microorganisms living in the sediments produces a profile of saturation state that is initially equal to the overlying water at the sediment-water interface and then declines to undersaturation with increasing depth. As the saturation state of the overlying water declines due to uptake of anthropogenic CO_2, the pore water profile of saturation state will become more uniform. This will cause the saturation horizon to rise closer to the surface, and the degree of undersaturation in the deeper sediments will increase. The combined result is likely to be more dissolution and a greater flux of Ca^{2+} and CO_3^{2-} ions into the overlying water.

Model calculations that account for changing saturation state of the overlying water, and the organic carbon and mineral characteristics of the sediments, predict that by the year 2300 under a business-as-usual scenario, dissolution of carbonate minerals, particularly of high-Mg calcite, will increase by more than 200% (Andersson *et al.*, 2006).

Conditions controlling sediment dissolution (including suspended sediment) and the potential impact on coral reef carbonate chemistry are poorly understood. Increased dissolution of coral reef sediments (particularly high-Mg calcite) may provide some buffering of the carbonate system in coral reef waters that have low exchange rates with the open ocean. Modeling of this process, however, has shown that dissolution of shallow-water carbonates will not significantly counteract the effects of rising CO_2 (Andersson *et al.*, 2003). Quantifying the effects of dissolution would greatly benefit from better determination of the thermodynamic constants for high-Mg calcite, which can vary by an order of magnitude.

Reef building requires reef calcification to exceed reef dissolution, but dissolution is likely to exceed calcification at some threshold value of pCO_2. Coral reefs by definition produce more calcium carbonate than is removed, but reef-building is expected to decrease in the future as calcification rates decline and dissolution rates increase (Kleypas *et al.*, 2001). The net response of coral reef calcification to changing seawater chemistry will be the sum of many interrelated processes such as (1) the response of calcifying organisms, (2) changes in inorganic processes of carbonate precipitation and dissolution, and (3) the response of bioeroders to changes in community structure and perhaps in cementation patterns. To predict how rates of reef building will change in the future, the calcium carbonate budgets of coral reefs, particularly across environmental gradients, need to be better quantified.

The threshold pCO_2 value where dissolution exceeds calcification will vary from reef to reef with changes in community structure and environmental conditions. In experiments where calcification and dissolution were measured using sealed enclosures placed over the reef or associated seafloor, the threshold value where calcification = dissolution occurred at pCO_2 levels of 467–1003 μatm (Yates and Halley, submitted).

3.2 Coccolithophores, Foraminifera, Pteropods, and Other Planktonic Calcifying Organisms and Systems

The major planktonic calcifying organisms are coccolithophores and foraminifera, both of which secrete calcite, and euthecosomatous pteropods, which form shells of aragonite (**Figure 3–2**). While many other calcifying invertebrate and protist taxa also have planktonic stages, these three groups largely account for the majority of the total $CaCO_3$ produced by planktonic organisms. The major planktonic calcifying groups differ with respect to size, trophic level, generation time, and other biological attributes (Ta-

Table 3.2: Carbonate dissolution rates reported from reef environments and mesocosms.

	CaCO$_3$ dissolution rate			
Location	mmol m^{-2} h^{-1} at night	mmol m^{-2} night^{-1}	mmol m^{-2} 24 h^{-1}	Source
Moorea sandy bottom reef flat and lagoon	0.8	9.4	2.4	Boucher *et al.*, 1998
Hawaiian patch reef 22% coral cover	1.5*	17.7		Yates and Halley, 2003
Hawaiian patch reef 10% coral cover	1.1*	13.0		"
Hawaiian coral rubble	1.2*	14.1		"
Hawaiian sand bottom	0.3*	3.3		"
Florida patch reef 10% coral cover	0.5*	5.5		"
Florida patch reef top	0.1*	1.1		"
Florida seagrass	0.4*	4.7		"
Florida sand bottom	0.3*	3.0		"
Reunion Island Back reef zone summer	7.0			Conand *et al.*, 1997
Rib Reef flat, GBR in March	4.0		97.0	Barnes and Devereux, 1984
Biosphere 2 mesocosm hi Mg-calcite sediments	0.2*		4.7	Langdon *et al.*, 2000
One Tree Island, GBR back reef zone	3.0*			Kinsey, 1978
Monaco mesocosm sand community	0.8*			Leclercq *et al.*, 2002
Florida Bay	0.8		19.0	Walter and Burton, 1990
Average	**2.3**	**8.0**	**42.6**	
Standard deviation	**4.8**	**5.5**	**42.0**	

* derived rates

Table 3.3: Characteristics of major calcifying groups.

Group	Trophic Level	Mineral Form	Generation Time	Approx. No. of Extant Species
Coccolithophores	autotrophic	calcite	day(s)	200
Foraminifera	heterotrophic many with autosymbionts	calcite	weeks	35
Euthecosomatous pteropods	heterotrophic	aragonite	Months to >1 year?	34
Coralline algae	autotrophic	high-Mg calcite	days	~20 genera
Halimeda	autotrophic	aragonite	weeks	25–30
Zooxanthellate corals	hetotrophic with autosymbionts	aragonite	months–years	~1000

ble 3.3). However, quantitative data on the distribution and abundance of these major groups are lacking, and estimates of their contributions to global calcification rates are poorly constrained. Analysis of sediment trap data indicates that the relative proportion of each of these major groups varies regionally. For example, at the Ocean Flux Program (OFP) site in the Sargasso Sea, the total CaCO$_3$ fluxes at 1500 and 3200 m of 8.0 g m^{-2} y^{-1} consist primarily of calcite (75–79%) composed mainly of foraminifera and coccolithophores with a lesser amount of aragonite (13–15%) produced by planktonic pteropod and heteropod snails (1.2 g m^{-2} y^{-1}), and high-Mg calcite (8–10%) possibly produced by bryozoans attached to floating *Sargassum* (Deuser and Ross, 1989; Fabry and Deuser, 1991) (**Table 3.4**). In contrast, at the high-latitude site of Ocean Station Papa in the North Pacific, the aragonite flux of a single pteropod species was 2.5 g CaCO$_3$ m^{-2} y^{-1}, about twice the total aragonite flux in the Sargasso Sea (Tsurumi *et al.*, 2005).

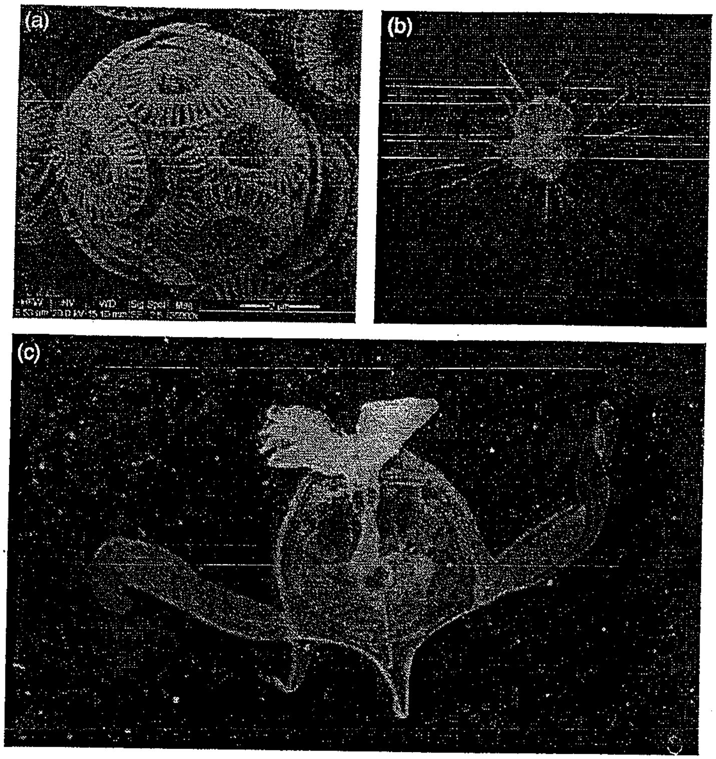


Figure 3–2: Representatives of major planktonic calcifiers: (a) the coccolithophore *Emiliania huxleyi* (courtesy V. Fabry) ; (b) planktonic foraminifer (courtesy A. Alldredge); and (c) the euthecosomatous pteropod *Cavolinia tridentata* (courtesy V. Fabry).

Table 3.4: Contributions of various planktonic groups and $CaCO_3$ mineral phases to the total $CaCO_3$ fluxes measured with sediment traps at 1500 and 3200 m in the Sargasso Sea (after Deuser and Ross, 1989 and Fabry and Deuser, 1991).

	Calcite[a]		Aragonite[b]		High-Mg calcite[c]		
Depth (m)	Flux ($g\ m^{-2}\ y^{-1}$)	% of total $CaCO_3$	Flux ($g\ m^{-2}\ y^{-1}$)	% of total $CaCO_3$	Flux ($g\ m^{-2}\ y^{-1}$)	% of total $CaCO_3$	Total $CaCO_3$ flux ($g\ m^{-2}\ y^{-1}$)
1500	6.0	75	1.2	15	0.8	10	8.0
3200	6.3	79	1.1	13	0.6	8	8.0

[a] Primarily foraminifera and coccoliths
[b] Pteropod and heteropod shells
[c] Containing >5 mole% $MgCO_3$

The physical, chemical, and biological factors that drive biogenic calcification and population dynamics in coccolithophores, foraminifera, and pteropods are little understood. To date, few studies have investigated the response of planktonic calcifiers to elevated pCO_2, and most of these have involved a single coccolithophore species, *Emiliania huxleyi*. There are clear needs for research on the physiological and ecological impacts of increasing pCO_2 on planktonic calcifying organisms and marine systems, and these are presented below. The evidence and gaps in our current knowledge of how increasing ocean acidification will affect planktonic calcifiers are addressed below in terms of: (1) calcification response, (2) organism response, (3) ecosystem response, and (4) dissolution.

3.2.1 Calcification response

Calcification in three major groups of planktonic calcifiers—coccolithophores, foraminifera, and pteropods—has been shown to respond to changes in the carbonate system. However, most studies have been performed on bloom-forming coccolithophores, and there are very limited observations of other planktonic groups. Several laboratory and field studies show that two coccolithophore species have reduced calcification rates at elevated pCO_2, even when the calcite saturation state is >1 (Riebesell *et al.*, 2000; Zondervan *et al.*, 2001; Zondervan *et al.*, 2002; Sciandra *et al.*, 2003; Delille *et al.*, 2005; Engel *et al.*, 2005). In a mesocosm bloom experiment with *E. huxleyi* cultured at glacial, present-day, and year 2100 CO_2 values, organic carbon production did not change, but calcification decreased under the projected year 2100 levels (Delille *et al.*, 2005). Contrary to findings in laboratory experiments (e.g., Riebesell *et al.*, 2000), no malformations of the coccospheres were observed, but coccospheres and coccoliths were smaller and coccoliths weighed less when grown under high pCO_2 levels (Engel *et al.*, 2005). In laboratory experiments with three species of planktonic foraminifera, shell mass in two species decreased as the carbonate ion concentration of seawater decreased (Spero *et al.*, 1997; Bijma *et al.*, 1999; Bijma *et al.*, 2002). Data for a single species of shelled pteropod suggest that net shell dissolution occurs in live pteropods when the aragonite saturation is forced to <1 (Feely *et al.*, 2004; Orr *et al.*, 2005).

The response of planktonic calcifying organisms to elevated pCO_2 is likely to vary between and within taxonomic groups. The limited number of studies and species investigated, however, preclude identification of widespread or general trends. Furthermore, all data collected from foraminifera and pteropods to date have come from mature specimens. Hence, there is a need for quantitative, direct measurements of calcification rates over a range of taxa and life stages, as well as over a range of elevated pCO_2 values.

While the relationship between calcification and carbonate ion concentration appears to be linear in corals, the response of other major groups of planktonic calcifiers may not be linear, and additional studies are needed to better determine the nature of the response. Some experimental data suggest, for example, that calcification in coccolithophores and foraminifera may respond asymptotically to carbonate ion concentration, implying that reduction of the carbonate saturation state below a threshold value will lead to large decreases in calcification rates.

The synergistic impacts of increased pCO_2 with light, nutrients, and temperature are largely unknown. For example, de Villiers (2005) found that shell weight of marine foraminifera was better correlated with "optimum growth conditions" defined by a suite of environmental factors than by saturation state alone. Light intensity was shown to be an important factor in laboratory experiments with *E. huxleyi*, with calcification rates decreasing with increasing CO_2 concentrations only under saturating light intensities (Zondervan *et al.*, 2002). Nutrient limitation may also be important, as experiments with *E. huxleyi* cultured under nitrogen limitation showed that calcification rates decreased with increasing CO_2, but that organic carbon production decreased only in response to limited nitrogen (Sciandra *et al.*, 2003) (in contrast to nitrogen replete experiments which show an increase in organic carbon production under increased pCO_2 (Riebesell *et al.*, 2000; Zondervan *et al.*, 2001; Zondervan *et al.*, 2002; Delille *et al.*, 2005; Engel *et al.*, 2005)). Finally, trace metal limitation has been shown to affect *E. huxleyi* calcification and growth (Schulz *et al.*, 2004). Iron limitation affected both calcification and organic carbon production, while zinc was limiting to organic carbon production but not to calcification.

Calcification and photosynthesis in coccolithophores and foraminifera are poorly understood. The few studies on the relationship between calcification and photosynthesis in these two groups suggest that the two processes may not be coupled. In laboratory experiments with *E. huxleyi*, calcification does not stimulate photosynthesis (Paasche, 1964; Herfort *et al.*, 2002) and, although calcification rates are greater in light than in dark, increased rates of calcification are not necessarily accompanied by higher photosynthetic rates (Paasche, 1964; Herfort *et al.*, 2004; Rost and Riebesell, 2004). In foraminifera, photosynthesis by symbiotic algae enhances calcification (e.g., Anderson and Faber, 1984; Lea *et al.*, 1995); however, calcification rates in symbiont-bearing species are similar to those of nonsymbiont foraminifera and photosynthesis is not necessary for calcification (Zeebe and Sanyal, 2002).

The molecular and physiological mechanisms that control the calcification response in planktonic organisms to changes in the CO_2 system are poorly understood. Results from several studies indicate that the substrate for calcification in *E. huxleyi* is HCO_3^- (cf., Paasche, 2001), which *increases* under elevated pCO_2 conditions, suggesting that calcification in this coccolithophore should increase under high CO_2 conditions, rather than decrease as observed. In foraminifera, one hypothesis is that if HCO_3^- is the substrate, then a proton pump is required to remove excess H^+ formed during calcification, and the pump does not operate as efficiently when external pH is lower (Zeebe and Sanyal, 2002). In addition, it is unclear why calcification rates in foraminifera decrease in response to surrounding seawater carbonate chemistry when the pH at the shell surface ranges from 8.8 during the daytime when symbiont photosynthesis is active, to 7.9 when respiration processes dominate (Rink *et al.*, 1998).

The suite of planktonic calcifiers includes larval stages of many benthic invertebrates but almost no information exists on how these early calcifying stages may be affected by decreased carbonate saturation state. Larval stages of two sea urchins showed smaller calcitic skeletons, as well as decreased developmental rates and larval size, under high pCO_2 conditions (Kurihara and Shirayama, 2004).

3.2.2 *Organism response*

It is not known whether planktonic calcifiers require calcification to survive (Seibel and Fabry, 2003). The response will almost certainly vary among taxa and the function of the $CaCO_3$ precipitation (**Table 3.1**). For example, if $CaCO_3$ provides protection, then the species may be more subject to predation or microbial infections; if $CaCO_3$ provides ballast, then the species may be less able to maintain its position in the water column. Some coccolithophore species have a non-calcifying stage in their life cycles (e.g., Green *et al.*, 1996; Houdan *et al.*, 2004) and many laboratory cultures of coccolithophores grow well without calcifying (cf. Paasche, 2001). In field samples, the presence of such naked coccolithophore cells cannot readily be identified by traditional microscopy, but may be accomplished with the use of molecular markers, such as immunofluorescence probes (e.g., Campbell *et al.*, 1994).

The capacity for planktonic organisms to adapt to lower saturation states (or reduced calcification rates) has not been investigated. The few studies of the response of planktonic calcifying organisms to increased pCO_2 and decreased carbonate saturation state have been short term, and have not detected adaptations that would allow organisms to calcify at "normal" rates under decreased saturation states. Natural variation within species and sister species indicates that some species may be favored over others. For example, specimens of the foraminifer *Globigerina bulloides* from Chatham Rise (east of New Zealand) are much larger and heavier than those from Catalina Island (west of California), despite the waters around Catalina Island having a higher CO_3^{2-} concentration. One explanation is that *G. bulloides* may be a complex of sister species (Darling *et al.*, 2000); and "adaptation" in the future may reflect replacement by species better adapted to lower saturation state.

While little is known about the ability of planktonic calcifiers to adapt to the high pCO_2 ocean of the future, there is evidence suggesting that at least one coccolithophore species may have the capacity to adapt to changing pCO_2 over long time periods. Experimental manipulations show that *Calcidiscus leptoporus* exhibits highest calcification rates at present-day CO_2 levels, with malformed coccoliths and coccospheres at both lower and higher pCO_2 (Langer *et al.*, in press). However, since no malformed coccoliths are observed in sediments from the Last Glacial Maximum (when pCO_2 levels were about 200 ppm), the authors conclude that *C. leptoporus* has adapted to present-day CO_2 levels.

Long-term impacts of elevated pCO_2 on reproduction, growth, and survivorship of planktonic calcifying organisms have not been investigated. Existing studies on the impacts of ocean acidification on calcareous plankton have been short-term experiments, ranging from hours to weeks. Chronic exposure to increased pCO_2 may have complex effects on the growth and reproductive success of $CaCO_3$-secreting plankton. No studies have investigated the possibility of differential impacts with life stage or age of the organism.

3.2.3 *Ecosystem response*

If reduced calcification decreases a calcifying organism's fitness or survivorship, then such calcareous species may undergo shifts in their latitudinal distributions and vertical depth ranges as the CO_2/carbonate chemistry of seawater changes (Seibel and Fabry, 2003). To date, no quantitative data exist with which to test this hypothesis. This emphasizes the need for high-quality data on the vertical distributions and abundances of foraminifera, shelled pteropods, and coccolithophores, particularly in those oceanic regions which are expected to experience the greatest changes in carbonate saturation states.

The potential impacts of increased CO_2 on planktonic ecosystem structure and functions are unknown. It is possible that CO_2-sensitive species will be outcompeted by non-calcifying species and/or those not sensitive to elevated pCO_2. The synergistic effects of elevated pCO_2 with other stressors such as increased water column stratification and decreased upwelling could result in substantial changes in species diversity and abundances in many regions. Species interactions may be altered on multiple trophic levels, potentially impacting ecosystem productivity as well as the cycling of organic carbon and carbonate carbon.

3.2.4 Dissolution response

Decreased saturation states can affect both the production and dissolution of biogenic $CaCO_3$, yet most studies have neglected dissolution rates. One study observed dissolution of the aragonitic shells of live pteropods exposed to a degree of aragonite undersaturation that is projected to occur in surface waters of the Southern Ocean by 2100 under the IPCC business-as-usual CO_2 emissions scenario (IS92a) (Feely et al., 2004; Orr et al., 2005).

$CaCO_3$ dissolution is substantial in the upper water column, but little is known about the mechanisms that control this dissolution or how they may change with future increased CO_2. Dissolution rates are unexpectedly high in the upper ocean, even in supersaturated waters. From mass balance estimates, up to 70% of the export production of calcite and aragonite dissolves before it reaches the lysocline (Milliman *et al.*, 1999; Feely *et al.*, 2002; Feely *et al.*, 2004), and process studies in the equatorial Pacific and Arabian Sea suggest that 75–80% of the calcite flux dissolves in the upper 800–900 m of water (Balch and Kilpatrick, 1996; Balch *et al.*, 2000). Several mechanisms for these high dissolution rates have been proposed but have not been adequately quantified or tested. Mechanisms include microbial processes (e.g., Buitenhuis *et al.*, 1996; Troy *et al.*, 1997; Schiebel, 2002) and dissolution in acidic zooplankton guts (Bishop *et al.*, 1980; Harris, 1994; Pond *et al.*, 1995). Improved understanding of these processes is needed to predict how upper ocean dissolution rates will change with increased ocean acidification.

3.3 Linkages Between Communities and Ecosystems

Calcifying organisms affect processes in different communities and ecosystems, thereby creating linkages between marine systems. For example, species diversity in the deep ocean has been linked to surface ocean productivity (Gage and Tyler, 1991). Thus, if increased pCO_2 decreases calcification rates and abundance of calcifying planktonic organisms in the upper ocean, there could be cascading effects on deep sea biodiversity and ecology. Further examples of the connectivity between ecosystems are the lateral, offshore transport of alkalinity from shallow coral reef systems to the open ocean (Sabine *et al.*, 1995; Mackenzie *et al.*, 2004), and between sea-grass beds and coral reefs (Burdige and Zimmerman, 2002). Such community and ecosystem linkages are undoubtedly important in the overall cycling of carbon and nutrients across large spatial scales, but are among the least understood aspects of the calcium carbonate cycle.

3.4 Effects on Carbon Cycle

3.4.1 The coral reef hypothesis

Shallow-water deposition of calcium carbonate has changed dramatically with the flooding and drying of continental shelves during glacial-interglacial fluctuations in sea level. The "coral reef hypothesis" (Berger, 1982) states that flooding of continental shelves during postglacial sea level rise provided large surface areas for reef growth and $CaCO_3$ production, which released significant amounts of CO_2 to the atmosphere. Several modeling efforts confirm that this mechanism is probably a significant component of the global carbon cycle (Opdyke and Walker, 1992; Archer *et al.*, 2000), including one that estimates that the 20 ppmv increase in atmospheric CO_2 in the late Holocene was primarily due to increased shallow water $CaCO_3$ deposition (Ridgwell *et al.*, 2003).

3.4.2 The open-ocean $CaCO_3$ budget

The biological pump removes carbon from surface waters in organic ("soft tissue pump") and inorganic ("hard tissue pump") forms. The inorganic form is predominantly $CaCO_3$. Although both pumps transport carbon from the surface to the deep ocean, their net effect on the partitioning of CO_2 between the atmosphere and the ocean is different. While the hard tissue pump increases pCO_2 of the surface ocean and thus decreases its ability to absorb atmospheric CO_2, the soft tissue pump has the opposite effect. Thus, changes in the carbon export ratio between the hard and soft tissue pumps may have major consequences for the upper ocean pCO_2 and the air-sea CO_2 flux. Furthermore, only the soft tissue pump is directly coupled to the biological uptake of nitrogen, phosphorus, and iron. Growing evidence suggests a linkage between the vertical remineralization length-scales of organic matter and the sinking fluxes of $CaCO_3$ and biogenic silica. While the basic chemical and biological processes driving both biological pumps are known, current understanding of the environmental factors that control variations in the ratio between both pumps remains limited.

Quantitative accounting of the global $CaCO_3$ budget was first addressed by Milliman (1993) and Milliman and Droxler (1996), and those estimates continue to be refined (Iglesias-Rodriguez *et al.*, 2002; Feely *et al.*, 2004). Elements of this budget were derived through a variety of techniques, including direct measurements (e.g., calcification rates, sediment calculations). Pelagic $CaCO_3$ production is estimated to be between 0.5 and 2.0 Pg C y^{-1}, based on direct measurements and modelling studies. Alkalinity-based estimates seem to narrow this estimate down to between 0.72 Pg C y^{-1} (Morse and Mackenzie, 1990) and 1.1 ± 0.3 Pg C y^{-1} (Lee, 2001); while the globally integrated trap-based estimate of $CaCO_3$ flux at 2000 m is 0.41 Pg C y^{-1} (Iglesias-Rodriguez *et al.*, 2002). This suggests that at least half of the pelagic production dissolves in the water column, between 100–1500 m depth. $CaCO_3$ accumulation rates at the seafloor (data from some 3000 deep-sea cores (Catubig *et al.*, 1998) indicate a present-day global measured accumulation rate of 0.1 Pg C y^{-1}, which implies that about 90% of surface $CaCO_3$ production dissolves in the water column, at the sediment-seawater interface, or within the sediment column.

3.4.3 Composition of the open-ocean $CaCO_3$ flux

Calcifying organisms in the open ocean are represented by at least ten different phyla including coccolithophorids, planktonic foraminifera, and pteropods, and the life cycles of each affects their potential contribution to the carbonate flux. The distribution of coccolithophorids in the oceans is not well mapped, but some general patterns are known. *Emiliania huxleyi* and *Gephyrocapsa oceanica* are cosmopolitan species that can form large blooms visible in satellite imagery (Brown and Yoder, 1994). *Florisphaera profunda* lives in the deep photic zone (about 150–200 m) in low to mid latitudes, and can be extremely abundant in low- to mid-latitude sediments (Winter and Siesser, 1994). *Coccolithus pelagicus* is a cold-water species dominant from sub-polar to polar waters in the northern Atlantic (McIntyre and Bé, 1967). *Calcidiscus leptoporus* ranges from equatorial to polar waters, although it never constitutes a large part of the living flora (McIntyre and Bé, 1967).

Satellite observations suggest that the greatest spatial extent of surface coccolithophorid blooms are in subpolar and polar regions and are largely represented by *E. huxleyi* (Brown and Yoder, 1994; Balch *et al.*, 2005). While *E. huxleyi* is the numerically dominant coccolithophore species on a global basis, in situ data suggest that other coccolithophore species such as *Coccolithus pelagicus* in the North Atlantic or *Florisphaera profunda* in the tropics may also be important components of the $CaCO_3$ flux in those regions (Broerse *et al.*, 2000).

The contribution of heterotrophic calcifiers to the open-ocean carbonate flux has often been overlooked (understandably so, as it is much easier to parameterize calcifying primary producers as a function of nutrients, light, etc. than higher trophic-level calcifiers such as pteropods and planktonic foraminifera). Foraminifera tend to produce flux pulses of calcite that are related to their reproduction cycles (Bijma, 1991; Bijma and Hemleben, 1994; Bijma *et al.*, 1994; Schiebel *et al.*, 1997) and are difficult to detect. Most, if not all, spinose planktonic foraminifera seem to follow a lunar or semi lunar reproduction cycle (Spindler *et al.*, 1979; Bijma *et al.*, 1990; Erez *et al.*, 1991). Non-spinose species have probably longer cycles (Hemleben *et al.*, 1989). In at least a few spinose species, two modes of carbonate transport have been distinguished (Bijma and Hemleben, 1994) associated with juvenile and adult mortality. Due to high juvenile mortality, a large number of smaller shells sink in association with the cytoplasm. The cytoplasm counteracts the negative buoyancy of the shell and the spines provide "drag," hence the shells settle slowly and bacterial infestation might result in dissolution and break up of the shells at intermediate depth. Adult specimens that undergo gametogenesis produce spineless and empty shells that have an additional carbonate phase ("gametogenetic calcite," up to 30% by weight) that causes the shells to sink rapidly into the abyss (Bé, 1980).

On a global basis, it is generally assumed that euthecosomatous pteropods constitute 10–15% of the total $CaCO_3$ flux (Fabry and Deuser, 1991; Milliman, 1993; Milliman and Droxler, 1996), although few studies have provided high-quality quantitative information on annual pteropod mass fluxes. In most ocean areas, pteropod aragonite dissolves in the water column or soon after reaching the seafloor, and does not accumulate in sediments. In polar and subpolar regions, the aragonitic shells of pteropods are important components of the $CaCO_3$ flux (e.g., Accornero *et al.*, 2003; Collier *et al.*, 2000; Honjo *et al.*, 2000; Tsurumi *et al.*, 2005), and can include mass sedimentation of pteropods after the summer growing season.

3.5 Misconceptions

The previous sections have outlined the current state of knowledge of ocean carbonate chemistry and the effects of ocean acidification on calcifying marine organisms. These issues are complicated and have led to several misconceptions about the future response of marine calcifiers to increasing atmospheric CO_2, which we address here.

Misconception 1. Increasing atmospheric CO_2 will *increase* rather than decrease pH of marine waters

This argument is based on an incorrect assumption that the coupled processes of photosynthesis and calcification increase pH of the water. Release of CO_2 via calcification on reefs, for example, generally exceeds CO_2 uptake by photosynthetic processes, so that reef waters tend to have elevated pCO_2 and lower pH than surrounding oceanic waters (Gattuso *et al.*, 1996a; Gattuso *et al.*, 1996b; Gattuso *et al.*, 1997; Kawahata *et al.*, 1997; Gattuso *et al.*, 1998a; Gattuso *et al.*, 1999a; Gattuso *et al.*, 1999b; Kawahata *et al.*, 2000; Suzuki *et al.*, 2001; Suzuki *et al.*, 2003). Although biological processes can modify the carbonate system in seawater (see section 4.1), the thermodynamic effect of increasing atmospheric CO_2 on surface ocean pH outweighs the ability of marine photosynthesis to take up that excess CO_2 and thus raise the pH (see below for related discussion). Long-term measurements of the carbonate system in seawater illustrate that ocean pH is decreasing (sections 1.1 and 2.1).

Misconception 2. CO_2 fertilization of zooxanthellae will lead to an increase in coral calcification

A common misconception is that an increase in CO_2 will increase photosynthesis of coral symbionts, which will then enhance coral calcification. This is based on two assumptions about the coral/algal symbiotic relationship: (a) that zooxanthellar photosynthesis will increase with rising CO_2, and (b) that increased photosynthesis increases calcification rates.

The first assumption assumes that, like land plants, zooxanthellae use CO_2 as the substrate for photosynthesis, so an increase in CO_2 concentrations will increase photosynthesis. Seagrasses are an example of a marine plant that also directly uses CO_2 for photosynthesis and which may benefit from increased CO_2 concentrations (Zimmerman *et al.*, 1997; Invers *et al.*, 2001; Invers *et al.*, 2002). However, almost all marine autotrophs, including zooxanthellae, are algae that primarily use HCO_3^- for photosynthesis, and HCO_3^- concentrations will increase only about 14% under doubled CO_2 conditions. Photosynthetic rates of corals have shown little to no response to increased pCO_2 (Burris *et al.*, 1983; Goiran *et al.*, 1996; Langdon and Atkinson, 2005; Schneider and Erez, 2006).

The second assumption is based on the fact that zooxanthellate corals calcify about 3x faster in the light than in the dark (Gattuso *et al.*, 1999a). The photosynthetic activity of zooxanthellae is the chief source of energy for the energetically expensive process of calcification, and much evidence suggests that calcification rates generally rise in direct proportion to increases in rates of primary production both at the organismal and community scale (Gattuso *et al.*, 1999a), at least under normal conditions. Although a shutdown in photosynthesis leads to slower calcification rates, the inverse—that an increase in photosynthesis will lead to increased calcification—is not evident. In virtually all studies that have measured both photosynthesis and calcification in corals, any stimulation of photosynthesis by increased pCO_2 was accompanied by a decrease rather than an increase in calcification (for example):

1. Reynaud *et al.* (2003) exposed *Stylophora pistillata* to two levels of pCO_2 (380 and 750 μatm) and two temperatures (25 and 28°C). There was no significant increase in symbiont photosynthesis with a doubling in pCO_2 at either temperature. At 25°C there was also no significant change in calcification. However, at 28°C they observed a 50% decrease in calcification.
2. Langdon *et al.* (2003) subjected a coral reef community in a mesocosm to pCO_2 of 400 and 660 μatm for one to two months of preconditioning and then measured the rates of net primary production and calcification for seven days. They found no significant change in the rate of net primary production and an 85% decrease in calcification.
3. Langdon and Atkinson (2005) exposed an assemblage of *Porites compressa* and *Montipora capitata* in an outdoor flume to two pCO_2 levels (380–460 and 733–789 μatm), and observed the rates of symbiont net primary production and calcification. At the higher pCO_2 level, they found a 22–26% increase in the rate of net primary production and a 44–80% decrease in calcification, depending on the time of year.

In all but one case a doubling in pCO_2 resulted in a 40–80% decrease in calcification (in the exceptional case there was no significant change in calcification). Such results may be due to competition between zooxanthellae and the host for the same internal pool of dissolved inorganic carbon—a mechanism first suggested to explain the observation that nutrient enrichment stimulates photosynthesis but causes a decrease in calcification (Hoegh-Guldberg and Smith, 1989; Stambler *et al.*, 1991; Marubini and Davies, 1996; Marubini and Atkinson, 1999; Ferrier-Pagès *et al.*, 2000).

Misconception 3. Warmer water temperatures will significantly offset decreases in saturation state

Two consequences of rising atmospheric CO_2 affect the seawater CO_2 system: (1) increasing partial pressure of CO_2 drives more CO_2 into seawater, but (2) the greenhouse effect also warms the ocean, and warmer waters can hold less CO_2. However, the ameliorating effect of warming is small. At constant temperature of 27°C and a typical oceanic A_T of 2300 μmol kg^{-1}, a doubling in pCO_2 results in a 37% decrease in carbonate saturation state. If one includes the effect of a 5°C warming in ocean temperature over the same period (an extreme case) the net decrease in saturation state would be 25%.

Misconception 4. The effect of global warming on calcification will outweigh the effects of decreased saturation state

Records from massive coral colonies in the Western Pacific (Lough and Barnes, 1997, 2000; Bessat and Buigues, 2001) and Caribbean (Carricart-Ganivet, 2004) do not show a decrease in calcification in recent decades as would be expected from increased atmospheric CO_2 concentrations, but rather a statistically significant positive correlation with temperature. This has led some to conclude that, under future ocean temperature and chemistry conditions, the effects of increasing temperature on coral calcification will outweigh the effects of decreasing carbonate saturation state and coral calcification will increase rather than decrease (McNeil *et al.*, 2004). This conclusion ignores three important points (Kleypas *et al.*, 2005). First, the calcification response of corals to temperature almost always follows a Gaussian function rather than a linear function (Coles and Jokiel, 1977; Houck *et al.*, 1977; Jokiel and Coles, 1977; Marshall and Clode, 2004), and will reverse once the optimum temperature is reached (the optimum temperature is often close to ambient summertime temperatures). Second, the temperature increase necessary to outweigh the effects of ocean acidification exceeds the threshold for coral bleaching (1–2°C above average maximum), which will shut down coral calcification rather than enhance it. Indeed, given the recent increase in coral bleaching episodes, further increases in tropical sea surface temperature are considered a major threat to the future of coral reefs (Wilkinson, 2004). Third, the temperature:calcification relationship from massive corals, which are longer-lived and more tolerant of environmental perturbations, may not be representative of the bulk of reef-building species.

Temperature is certainly a major control on metabolism and growth, and the above misconception simply arises from extrapolating the positive benefits of temperature beyond biological thresholds. This highlights the need to study coral calcification response to the combination of rising temperature and declining saturation state within a wide range of coral taxa.

Misconception 5. Carbonate dissolution in coral reef sediments will buffer the overlying seawater

Dissolution of carbonate minerals releases alkalinity and increases the carbonate saturation state of the surrounding water column. Dissolution is a prevalent process in reef environments (see section 3.2.2), but the misconception relates to the extent to which dissolution can bring the system toward pre-industrial conditions. Empirical evidence illustrates that dissolution rates are much slower than calcification rates and do not fully restore the carbonate chemistry of coral reef systems (Gattuso *et al.*, 1995, 1996a; Kawahata *et al.*, 1997; Gattuso *et al.*, 1999b; Kawahata *et al.*, 2000; Suzuki *et al.*, 2003). Total alkalinity and carbonate saturation state of most reef waters primarily reflect the balance between precipitation and dissolution of $CaCO_3$. Total alkalinity and saturation state are both lower in reef waters than in the nearby open ocean, and the magnitude of the difference is proportional to the residence time of water on the reef. The departure from oceanic conditions is small in systems with short residence times, but can be significant in lagoons or on reefs with long residence times (Gattuso *et al.*, 1997; Boucher *et al.*, 1998; Conand *et al.*, 1997; Yates and Halley, 2006a,b), illustrating that rates of dissolution are much slower than rates of calcification.

With increased pCO_2, net calcification rates on coral reefs are likely to decline, partly due to slower calcification rates and partly due to faster dissolution. At some point in time and space, we can expect that some reef systems will shift from net calcification to net dissolution; i.e., shift from being a sink to a source of alkalinity to the surrounding ocean (see Section 3.1).

3.6 Critical Research Needs

Based on the identified knowledge gaps listed above, the St. Petersburg Workshop participants identified critical research needs. Although the following list is not exhaustive, we believe it captures the most pressing research needs for the next 5–10 years.

- Determine the calcification response to increased CO_2 in additional species of coccolithophores, foraminifera, and shelled pteropods, and benthic calcifiers such as corals (including cold-water corals), coralline algae, foraminifera, molluscs, and echinoderms. Where applicable, studies should address calcification within multiple life stages of organisms. In particular, experiments to quantify the effect of elevated pCO_2 on calcification in two major groups—shelled pteropods and deep-sea scleractinian corals—are considered urgent. These two aragonite-secreting organisms will be the first to experience carbonate saturation states <1 within their current geographical ranges;

- Discriminate the various mechanisms of calcification within calcifying groups through physiological experiments, and thus better understand the cross-taxa range of responses to changing seawater chemistry;
- Continue experimental studies that combine multiple variables affecting calcification in marine organisms: saturation state, light, temperature, and nutrients, and extend the range of calcifying groups tested;
- Combine laboratory experiments with field studies. Analogous to the CO_2 enrichment experiments performed in terrestrial systems, develop and deploy technology for continuous field monitoring and experiments. Focus on multiple oceanic areas, including regions where substantial changes in seawater CO_2 chemistry will occur in the near future (e.g., Southern Ocean), regions where naturally high pCO_2 conditions are found (e.g., Galápagos Islands), and regions that are readily accessible or have on-going, related monitoring programs (e.g., Station Papa, HOTS, BATS, Florida Keys, CREWS stations);
- Characterize the diurnal and seasonal cycles of the carbonate system on coral reefs, including a commitment to long-term monitoring. Focus on collecting information from a variety of ocean settings that cover the important environmental ranges and seawater chemistry conditions, as well as the range of reef settings (e.g., well-mixed open ocean versus lagoonal) and reef zones (e.g., forereef, reef flat, lagoonal);
- In concert with above, monitor in situ calcification and dissolution in planktonic and benthic organisms, with better characterization of the key environmental controls on calcification, and supplement and cross-check present-day measurements with coral skeletal records of calcification and skeletal geochemical proxies (stable isotopes, metals, etc.);
- Incorporate ecological questions into observations and experiments; e.g., How does a change in calcification rate affect the ecology and survivorship of an organism? At the ecosystem scale, what are the ecological differences between communities with and without calcifying species?
- Improve the accounting of coral reef and open ocean carbonate budgets through combined measurements of biogenic $CaCO_3$ production, seawater chemistry, $CaCO_3$ dissolution and accumulation, and, in near-shore environments, bioerosion and off-shelf export of $CaCO_3$.
- Apply biogeochemical and ecological modeling to quantify the mechanisms that contribute to the carbonate system, and to guide future sampling and experimental efforts.
- Develop protocols for the various methodologies used in seawater chemistry and calcification measurements. Establish the pros and cons of each procedure, and, when possible, how each measurement can be related to the others.

The following section summarizes the research techniques and designs to be considered when addressing these research needs.

4. A Guide to Improve Research on Increasing Atmospheric CO_2 on Marine Calcifiers

4.1 Field Monitoring and Surveys

4.1.1 *What variables should be monitored?*

PRECIPITATION AND DISSOLUTION of $CaCO_3$ occurs both inorganically and through biological processes. $CaCO_3$ precipitation is driven mainly by organisms, with inorganic cementation contributing a fraction of the total oceanic $CaCO_3$ precipitation. $CaCO_3$ dissolution is primarily an inorganic process, although microbial films, borings, and bioerosion may play a significant role in determining dissolution rates. $CaCO_3$ precipitation/dissolution thus lies along a continuum of biological and inorganic processes, and therefore many variables need to be considered when monitoring a system's calcification response to increased atmospheric pCO_2.

Monitoring the inorganic carbon system requires measuring at least two of the following: pCO_2, DIC, pH, A_T, as well as temperature and salinity. In regions where calcification rates are high and water exchange is low, measurements of the calcium ion may also be required. Calculation of air-sea CO_2 exchange rates also require measurements of atmospheric and oceanic CO_2 concentrations, barometric pressure, and wind speed. Other important physical variables include surface seawater temperature and salinity.

Field monitoring of ecosystems should minimally include calcification rates of key individual organisms, community structure, and, if appropriate, primary production and sedimentary characteristics (mineralogical composition, accumulation rates, and dissolution rates). Calcification rates should include measurements of both extension rates and density. In planktonic systems, the vertical distributions of calcifying organisms should be tracked and related to vertical profiles of the $CaCO_3$ saturation state. When measuring ecological response, it is important to also monitor the response of multiple life stages of organisms, including larval recruitment, age to sexual maturity, and fecundity. Biological measurements of calcification in the field should be closely coupled with measurements of the seawater CO_2 chemistry.

The temporal and spatial scales over which monitoring should be conducted vary widely across environments. The coastal ocean requires high-frequency monitoring because of high spatial and temporal variability (**Figure 4–1**). High-frequency monitoring of the reef waters of Ishigaki, Palau, and South Florida, for example, revealed rapid and large fluctuations (e.g., a diurnal range in pCO_2 an order of magnitude greater than that of adjacent open-ocean waters) that allowed an analysis of how various physical and biological factors affected organic and inorganic carbon cycling in coastal systems (Kayanne *et al.*, 2005; Yates and Halley, 2006b). Monitoring of coastal waters should be augmented with measurements from nearby offshore waters, preferably from a reference station (e.g., time-series station ALOHA as an open-ocean reference for coastal environments of Hawaii, and the BATS station as a reference for those of Bermuda).

4.1.2 *Priority environments for future monitoring or research*

Organisms/Ecosystems. Priority ecosystems for studying the effects of increased CO_2 on marine calcification include those with high calcification rates or where calcification is an integral part of the ecosystem, and organisms or ecosystems which may be particularly threatened by lowered $CaCO_3$ saturation states. Because calcification is often linked to photosynthesis, studies of the effects of CO_2 on marine calcification have concentrated on photosynthetic organisms, and have thus been confined to the photic zones of the ocean, although many calcifying organisms are not phototrophic.

In neritic regions, the major benthic calcifiers are the reef-forming organisms (corals and calcareous algae), the aragonite secreting algal species of the genus *Halimeda*, benthic foraminifera, bryozoans, molluscs, and echinoderms (**Figure 3–1**). Coral reefs have received the most attention regarding the effects of changing saturation state. Reefs and *Halimeda* bioherms have high calcification rates, a wide distribution in the tropics, and produce the bulk of continen-

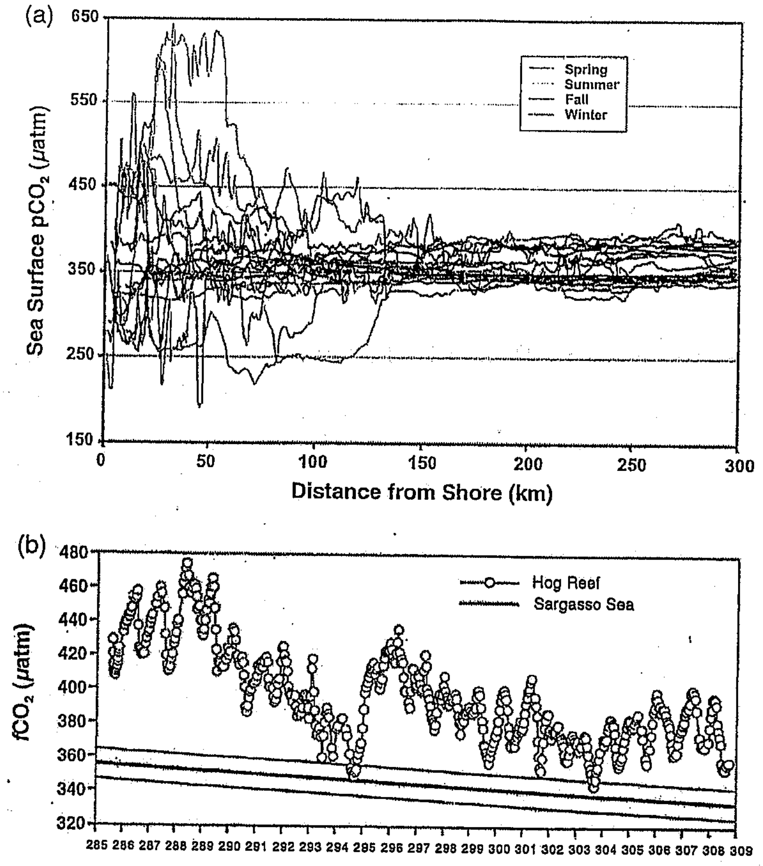


Figure 4–1: pCO_2 variability of surface waters: (a) pCO_2 variability in surface waters across the continental margin of the west coast of the United States, showing the high degree of variability in coastal upwelling regions out to a distance of about 150 km from the coast (courtesy Francisco Chavez; modified from Pennington *et al.*, in press); and (b) Time series of seawater fCO_2 from Hog Reef Flat in Bermuda, and the Sargasso Sea. The curve for the Sargasso Sea reflects the mean seawater fCO_2 observed over 1994–1998 (reprinted from Bates *et al.*, 2001; copyright by the American Society of Limnology and Oceanography, Inc.).

tal shelf $CaCO_3$ production and accumulation (Milliman and Droxler, 1996). Deep-water coral bioherms are another important neritic calcifying ecosystem. These corals are non-photosynthetic, and occur on continental slopes often at depths near the saturation horizon. These bioherms may be particularly vulnerable to shoaling of the saturation horizon (Guinotte *et al.*, 2006).

In the open ocean, the major planktonic calcifiers are coccolithophores, foraminifera, and pteropod molluscs (**Figure 2–2**), and members within each of these groups are considered sensitive to carbonate saturation. Coccolithophorids are calcitic, autotrophic, and are often the most prominent planktonic calcifiers, in part because of their visibility in surface waters during blooms, and because of their estimated importance in global calcium carbonate budgets. Planktonic foraminifera are calcitic and heterotrophic, although many species have photosynthetic symbionts, and are widely distributed latitudinally. Pteropods are aragonitic, heterotrophic, planktonic gastropods widely distributed in the oceans and may be quantitatively important in maintaining the alkalinity flux in several major ocean regions (Betzer *et al.*, 1984; Fabry, 1990). While all of the major planktonic calcifiers most frequently occur in the upper 500 m, baseline data on their present-day vertical distributions and abundances are insufficient to detect possible changes that may result from ocean acidification.

Natural gradients. Natural gradients in carbonate chemistry can affect biological calcification rates, as well as inorganic processes of dissolution and perhaps inorganic cementation (**Table 4.1**). The obvious gradients in $CaCO_3$ saturation are with latitude and depth (**Figure 4–2**), but there are also gradients associated with major upwelling regions and biological processes (Feely *et al.*, 2004).

Depth gradients in seawater carbonate chemistry occur as a consequence of (1) biological processes that take up carbon, such as photosynthetic organic carbon production and calcium carbonate production, (2) remineralization of those products through respiration and dissolution, and (3) physical processes that mix the surface ocean and increase air-sea CO_2 exchange. The typical profile of carbonate chemistry in the open ocean is where alkalinity increases rapidly with depth (due to the solubility pump), as does dissolved inorganic carbon (due to the organic carbon pump). The distribution of planktonic organisms with depth gradients in carbonate chemistry are essentially unknown, although rates of dissolution of their shells with depth have been investigated (Byrne *et al.*, 1984; Feely *et al.*, 1988). Obvious targets for future monitoring are the depths of the aragonite, calcite, and high-Mg saturation horizon. The depth distribution of carbonate chemistry parameters on coral reefs or other benthic calcifying ecosystems has not been investigated.

Latitudinal gradients in seawater carbonate chemistry in the surface ocean occur primarily in concert with temperature change. Because the surface ocean is so well mixed, processes that affect alkalinity and air-sea CO_2 exchange also affect the rate of CO_2 uptake by the surface ocean, but the effects on latitudinal gradients in carbonate chemistry are secondary to those of ocean temperature and physics (Takahashi *et al.*, 1997).

In a few areas, upwelling processes bring deep CO_2-rich waters to the surface, and this dominates surface carbonate chemistry. The best example of this is the equatorial upwelling region in the eastern Pacific (Feely *et al.*, 2002). pCO_2 in the Galápagos Islands often exceeds 500 μatm (Millero *et al.*, 1998; Sakamoto *et al.*, 1998), with high spatial and temporal variability. Coral reefs in the Galápagos are considered marginal in terms of their development, probably owing to many factors such as cooler temperature and low diversity, but the role of lower saturation state of the waters should also be considered.

Natural gradients in carbonate chemistry also occur because of calcification itself, which draws down the alkalinity. Broecker and Takahashi (1966) documented such a gradient on the Bahama Banks, and a recent study (Kawahata *et al.*, 2000) documented a similar gradient between open ocean waters and those of the Great Barrier Reef lagoon.

Some information about possible future changes can be gained by examining how calcium carbonate production varies across these natural gradients. At higher latitudes, for example, corals and other reef-building organisms exist and even comprise coral reef communities, but their carbonate accumulation (i.e., the balance between $CaCO_3$ production and its removal) is not sufficient to build reefs. Carbonate production also decreases dramatically with depth, presumably because of light limitations, as the main $CaCO_3$-producing organisms are photosynthetic or have photosynthetic endosymbionts.

The main disadvantage of using natural gradients to examine the control of carbonate saturation state on $CaCO_3$ production, within both the planktonic and benthic environments, is the difficulty of finding regions where carbonate chemistry does not co-vary with other parameters that affect calcification rates (e.g., temperature, irradiance, nutrients). Temperature, for example, decreases with depth, latitude, and in upwelling regions. Irradiance also decreases with latitude and depth, but less so in upwelling regions. Where gradients are due to calcification, such as in coral reef regions, the carbonate chemistry gradient reflects an alkalinity change as well as changes in DIC, and thus does not exactly mimic the carbonate chemistry changes expected from increased pCO_2.

Practical considerations. Because biological processes dominate marine calcification, environmental monitoring should include not only carbonate chemistry parameters, but also parameters that affect biological processes. These include oceanographic parameters such as temperature, irradiance, hydrodynamics, and nutrients; and atmospheric parameters such as surface winds and pressure. Carbonate chemistry parameters are routinely measured as part of the International Repeat Hydrography and Carbon Program (Feely *et al.*, 2005), and at a handful of open ocean time-series stations (**Table 4.2**). A few of the time-series stations have monitored seawater chemistry for more than a decade.

Several efforts are currently underway to expand these observations in the coastal zone and in specific ecosystems. For example, the implementation strategy for the Ocean Carbon and Climate Change report (Doney *et al.*, 2004) calls for expanding CO_2 system measurements at existing time-series stations, and augmenting additional time-series sites and moored buoys with automated CO_2 system measurements. Also, NOAA is establishing monitoring stations in several tropical coral reef locations as part of the Integrated Coral Observing Network/Coral Reef Early Warning System (ICON/CREWS; **Figure 4–3**). Existing ICON/CREWS stations collect both meteorological and oceanographic data, and could easily be augmented with autonomous carbon system instrumentation.

Table 4.1: Major processes that create natural gradients in seawater carbonate chemistry.

Process	Effects on carbonate parameters	Notes	Gradients
Physical			
atmospheric pCO_2	controls air-sea equilibrium CO_2	equilibrium generally achieved within 1 year	minor; CO_2 is well mixed in the atmosphere
temperature	determines CO_2 solubility	solubility decreases with increasing temperature	latitude and depth
pressure	determines CO_2 solubility	solubility increases with increasing pressure	
upwelling	delivers CO_2-rich waters to surface	also cold and nutrient-rich	upwelling gradients
$CaCO_3$ dissolution	removes CO_2 releases alkalinity	through reaction $CaCO_3 + CO_2 + H_2O \rightarrow 2HCO_3^- + Ca^{2+}$	depth, and other carbonate chemistry gradients
Biological			
photosynthesis	removes CO_2	through formation of organic matter	depth, and other irradiance gradients
respiration	releases CO_2	through remineralization of organic matter	biological—mostly microbial
calcification	decreases alkalinity increases CO_2	through reaction $2HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + CO_2 + H_2O$	biological—across calcifying zones

4.1.3 Skeletal records and isotopic/elemental analyses

Calcification records from corals and other calcifying organisms. Skeletal records provide climatological and oceanographic histories as well as information about the response of the organism to environmental change (e.g., changes in calcification rates). A wealth of potential information on coral calcification exists within the large inventory of coral cores collected in recent decades. Such measurements tend to be confined to a few massive species of corals, such as *Porites*, *Montastrea*, and *Diploria*. Branching corals, by nature of their growth form, do not offer a clear yearly record of skeletal growth. Some calcitic sponges also record environmental information in their skeletons (Böhm *et al.*, 2002).

Annual density bands in massive corals allow retrospective monitoring of coral growth rates over several centuries and can provide information about the response of such corals to environmental stress and change. The most easily measured growth parameter in coral skeletons is annual linear extension rate, which can be measured from X-radiographs of coral slices, but deriving annual calcification rates also requires measuring skeletal density (**Figure 4–4**). This can be measured using gamma densitometry (Chalker and Barnes, 1990) and optically from X-radiographs (Helmle *et al.*, 2002). Calcification rate is thus calculated as the product of skeletal extension and skeletal density. It is probable that changes in coral calcification rate will be reflected as changes in density in some species, and in linear extension in others. In some species, such as the commonly used Indo-Pacific coral, *Porites*, variations in annual calcification rate are dominated by changes in linear extension rate and the latter (most easily measured parameter) can be used as a proxy for calcification rate (Lough and Barnes, 2000).

In recent years, most studies using massive corals have focused on geochemical records contained within the coral skeletons rather than analyses of coral growth rates. Although extracting geochemical proxies for various climatic and environmental parameters is important, there is a large number of massive coral cores already collected that could be exploited to assess possible changes in coral growth due to changing carbonate chemistry (see coral records data base at NOAA Paleoclimatology Data Center, `http://www.ncdc.noaa.gov/paleo/index.html`). Such existing coral material could be used for retrospective coral growth analyses, including annual density, extension, and calcification. These would provide long-term information on changes in coral growth rates, important baselines for assessing future changes, and would also allow spatial comparisons between regions. Coral calcification rates vary with average water temperature, and in several massive species have so far responded more to rising water temperature than to changes

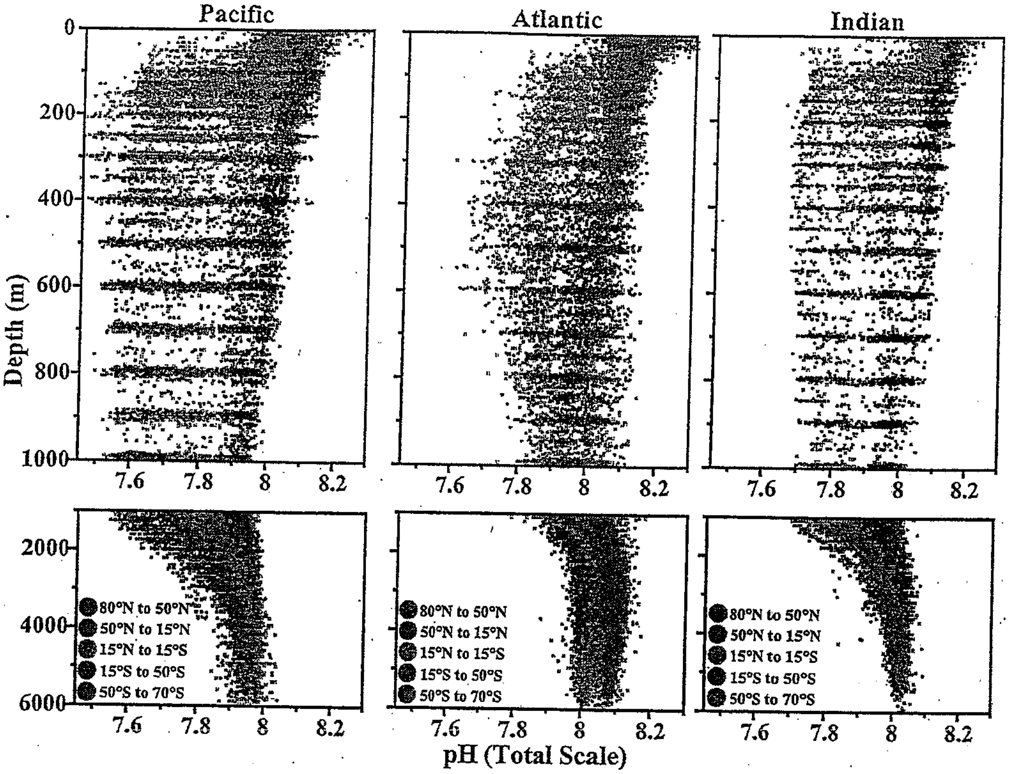


Figure 4–2: Natural gradients in ocean pH (total scale) across the Pacific, Atlantic, and Indian Ocean basins, showing the natural variation with both depth and latitude, for the period 1990–1998. Data from GLODAP (`http://cdiac.esd.ornl.gov/oceans/glodap/Glodap_home.htm`); after Feely *et al.* (submitted).

in ocean chemistry (Lough and Barnes, 2000; Bessat and Buigues, 2001). Observed and modeled future changes in water temperature and ocean chemistry would allow targeting of particular regions where, for example, either parameter is more or less important. Coral growth rates could then be analyzed either from the existing international archive or through collection of new coral cores. Future efforts to document calcification histories should also include both non-massive coral species and other major calcifiers.

Stable isotopes and other environmental proxies. The use of stable isotopes and trace elements from $CaCO_3$ skeletal material has been common in environmental reconstructions, particularly of temperature and salinity, and more recently of carbonate chemistry (**Figure 4–5**). Several geochemical tracers have been used to reconstruct past environmental conditions. For example, massive dissolution events that occurred in the past have been examined using both isotopes ($\delta^{18}O$, $\delta^{13}C$, $\delta^{11}B$) and trace elements (U/Ca, Sr/Ca, Mg/Ca) to describe the environmental setting and to reveal mechanisms for the dissolution events. $\delta^{13}C$ of corals and sponges has also been developed as a proxy for the penetration of anthropogenic pCO_2 in the ocean (Quinn *et al.*, 1998; Böhm *et al.*, 2002). In addition, the $\delta^{13}C$ of skeletal material may reflect differences in physical mixing in environments, since pCO_2 in closed systems tends to show greater changes than in open-ocean environments (P. Swart, personal communication; **Figure 4–6**).

Skeletal chemistry can also record ocean carbonate chemistry. For example, the Zn/Ca ratio in benthic forams appears to covary with the carbonate ion concentration of bottom waters (Marchitto *et al.*, 2000; Marchitto *et al.*, 2005). More widely used as a proxy for ocean pH is the boron isotope ratio (Sanyal *et al.*, 1995; Sanyal *et al.*, 2001). A recent analysis raises concerns about large uncertainties in the technique (Pagani *et al.*, 2005); however, boron isotope fractionation in corals has been shown to be strongly dominated by pH control (Reynaud *et al.*, 2004), and a recent analysis of boron isotopes in a massive coral from the western Coral Sea provided multi-century, annually resolved reconstructions of pH (Pelejero *et al.*, 2005) (**Figure 4–5b**). The signal appeared to reflect variations in ocean circulation and flushing rate

Table 4.2: Locations where carbonate chemistry parameters are currently or have been routinely measured.

Location	Ocean	Lat.	Lon.	Time Period	Frequency (per year)
Atlantic Ocean					
Ocean Weather Station M	Norwegian Sea	66°N	2°E	1992–present	4
Irminger Sea	Irminger Sea	60°N	36°W	1990–present	limited
Ocean Weather Station Bravo	Labrador Sea	57°N	53°W	1980s–present	1
BATS (Bermuda-Atlantic Time-series)	NW Atlantic	31°50′N	64°10′W	1988–present	12
Hydrostation S	N Pacific	31°50′N	64°10′W	1983–present	12
ESTOC (European Station for Time-series in the Ocean Canary Islands)	NE Atlantic	29°N	16°W	1994–present	12
CARIACO (CArbon Retention In A Colored Ocean)	Atlantic	10°30′N	64°40′W	1995–present	intermittent
DYFAMED (Dynamics of Atmospheric Fluxes in the Mediterranean sea)	Mediterranean	43°25′N	7°52′E	1995–1997 2003–present	intermittent 4
Pacific Ocean					
OSP/Line P (Ocean Station PAPA)	Gulf of Alaska	50°N	145°W	1970s–present	4
KNOT (Kyodo N Pacific Ocean Time-series)	N Pacific	44°N	155°E	1999–2002	12
HOT (Hawaii Ocean Time-series)	Pacific	22°45′N	158°00′W	1988–present	12
TAO/TRITON mooring (pCO_2 only)	Tropical Pacific	2°S	170°W	1997–present	continuous
"	"	0°S	170°W	2005–present	continuous
"	"	0°	155°W	1997–present	continuous
"	"	0°	140°W	2003–present	continuous
"	"	0°	125°W	2003–present	continuous
Kuroshio Extension Observatory (pCO_2 only)	N Pacific	32°18′N	144°30′E	2006–present	continuous
Kaneohe Bay, Oahu Hawaii	N Pacific	21°24′N	157°W	2005–present	continuous
Monterey Bay, California	N Pacific	36°48′N	122°W	1989–present	12
Santa Monica Bay, California	Pacific	33°56′N	118o43′W	2001–present	continuous
Indian/Southern Oceans					
KERFIX	Indian Ocean	50°S	68°E	1990–1995	intermittent

related to natural, approximately 50-year climatic oscillations. The variations of approximately 0.3 pH units equate to a variation in Ω_{arag} of approximately 3–4.5, but had no apparent impact on coral extension or calcification rates. The authors concluded that this *Porites* coral was well adapted to maintain its calcification over the natural range of variability. Application of this technique to *Porites* from around the Indo-Pacific basin and to other corals elsewhere should provide an exciting source of data on the response of corals to a wide range of natural saturation states.

An important need in correlating skeletal records with environmental change requires a combination of experimental and sclerochronological studies. Both calcification and isotopic records from free-living corals should be compared with those from massive corals used in experimental studies to understand how well the techniques capture the relationship, for example, between pH and calcification.

4.1.4 Remote sensing

Satellite observations can be used to estimate the distribution of particulate inorganic carbon (PIC, which is primarily composed of $CaCO_3$), in the global oceans (**Figure 4–7a**). This includes calcite biomass of coccolithophores (in the upper 20 m of the ocean), suspended PIC due to phenomena such as whitings and resuspended PIC in the coastal ocean, and submerged accretions in shallow tropical coral reefs. Satellite and airborne remote sensing tools, once calibrated against field measurements of PIC, can be used to investigate long-term changes in abundance and lateral ex-

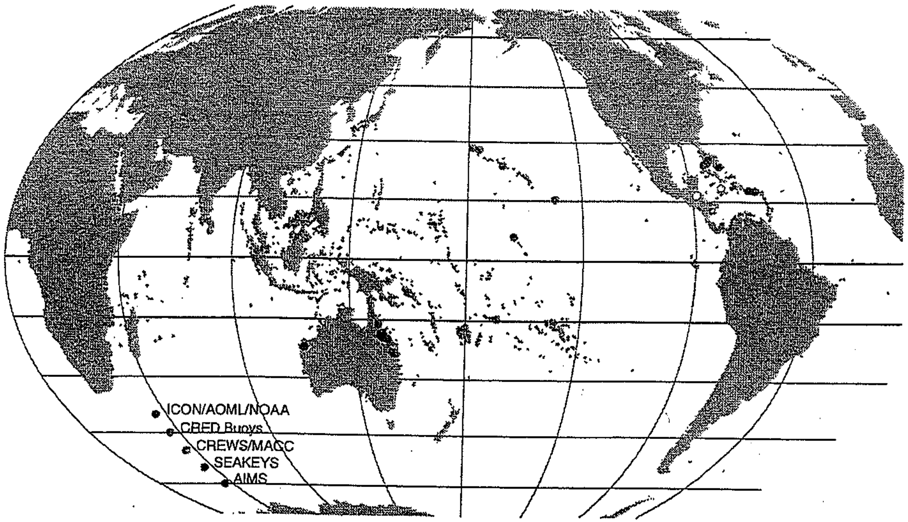


Figure 4–3: Existing and proposed stations within NOAA's Coral Reef Conservation Program; ICON = Integrated Coral Observing Network; AOML = Atlantic Oceanographic and Meteorological Laboratory (NOAA); CREWS = Coral Reef Early Warning System; CRED = Coral Reef Ecosystem Division (NOAA); MACC = Mainstreaming Adaptation to Climate Change; AIMS = Australian Institute of Marine Science. Solid symbols are existing sites; open symbols are proposed sites (data courtesy Eric Stabenau and Jim Hendee, NOAA/AOML).

port. New instruments that will become available in the next 10 years will provide better spatial and temporal resolution, and development and application of these data should prioritize quantifying $CaCO_3$ production in both the open and coastal oceans.

Remote sensing of suspended calcite. This is a relatively new addition to the suite of space-based measurements available to oceanographers. NASA has kept ocean color sensors in space beginning with the Coastal Zone Color Scanner (CZCS) mission from 1978–1986, and continuing with the Sea Wide Field of view Sensor (SeaWiFS; 1997–2004), and the Moderate resolution Imaging Spectrometer (MODIS; 1999–present) aboard the Terra (1999–present) and Aqua (2002–present) platforms. Originally considered as "contamination" in the ocean color spectrum, suspended PIC (mainly calcite from coccolithophores and other micron-sized particles, rather than forams and pteropods; Balch *et al.*, 1996) can now be quantified through 2-band and 3-band PIC algorithms of remotely sensed water-leaving irradiances (**Box 4**). These techniques are mainly limited to coccolithophorid blooms, and can only estimate $CaCO_3$ standing stock rather than $CaCO_3$ production. However, these advances provide a valuable baseline for tracking changes in the upper few meters of the water column, and for quantifying $CaCO_3$ production in the future.

Remote sensing of $CaCO_3$ production in benthic communities. Previous studies based on very few in situ measurements demonstrated that shallow tropical coral reefs may be both sources and sinks of carbon depending on the patchiness of the community components (corals, algae, sediments), and on the condition of the reef (Kayanne *et al.*, 2005). Further, short-term perturbations (rainfall, river discharge) may invalidate the assumption that carbonate equilibrium of seawater above reefs is principally controlled by respiration, photosynthesis, and solution and calcification of the reef. Assessing these conditions requires tools that address both large-scale as well as local forcings and changes in the reef over both short and longer time periods. Satellite observations have the potential to address these questions, and also obtain reliable estimates of the total extent of calcification and associated biogeochemistry by:

1. Better defining spatial constraints of locations and surface area of shallow tropical reef communities;
2. Assessing the diversity of habitats associated with coral reefs around the world, and quantifying the carbonate content and calcification associated with each;
3. Assessing disturbance on reefs, from regional-scale climatic/environmental factors to local-scale anthropogenic and natural phenomena; and assessing the resistance and resilience of coral communities to perturbation;

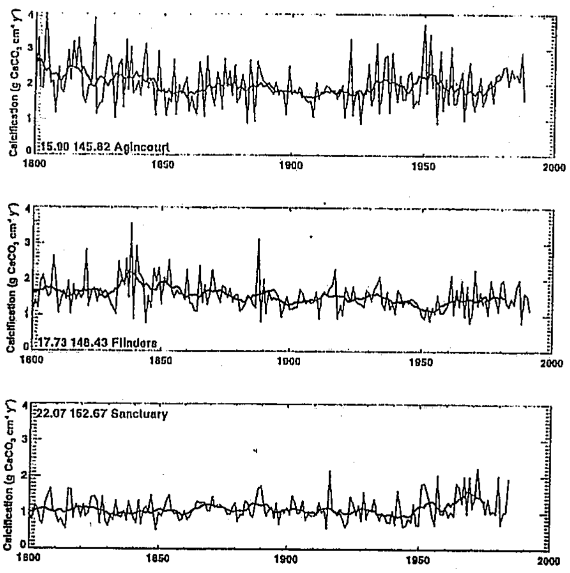


Figure 4–4: Calcification records from massive *Porites* corals of several outer reefs of the Great Barrier Reef. The thin line indicates raw data; thick line is a running 10-year average; data obtained from Lough and Barnes (2000; `http://coris.noaa.gov/metadata/records/html/paleoclimatology_masthead_2001.html`). Calcification records reflect decrease in calcification with increasing latitude, as well as very different calcification trends over the last century.

4. Detecting change in calcification rates and other biogeochemical impacts on communities and the water column at local, regional, and global scales.

A variety of strategies can be used to address these questions. One strategy would be to map global coral reef communities using high-resolution LANDSAT 7 ETM+, IKONOS, and other high spatial resolution satellite images. A basic global coral reef LANDSAT 7 ETM+ dataset has been assembled under NASA's Millennium Coral Reef Mapping Project (**Figure 4–7b**). Such high-resolution imagery, if complemented with time series of specific oceanographic environmental variables around selected reefs (e.g., temperature, sea-surface height, rainfall, wind speed and direction, phytoplankton pigment, colored dissolved organic matter and suspended solid concentrations, photosynthetically active radiation, cloud cover), allows assessment of the effects of large-scale processes, from short-term weather events to long-term climate forcing, that may cause stress and/or affect coral reef $CaCO_3$ budgets.

A number of representative reefs should be selected where in situ air-sea CO_2 fluxes are to be measured at least seasonally. Pairing these measurements with high-resolution satellite images will enable large-scale integration and scaling-up of metabolic rate estimates (**Box 5**), rates of export of suspended sediment plumes from shallow water to deep areas, and biogeochemical impacts on the overlying water column and vice versa.

4.2 Experimental Approaches

Testing the response of calcifying organisms to increased CO_2 concentrations has primarily been conducted under controlled, laboratory conditions. Most of these experiments have also been conducted over short periods (days to weeks), and otherwise have not been designed to detect adaptation or acclimation. Given the scarcity of data on many marine organisms, workshop participants expressed a real need to continue laboratory-based experiments, and to establish guidelines for designing such experiments. Such guidelines should include recommendations and standards for:

1. acclimatization periods for organisms;
2. length of experiments;
3. methods for manipulating carbonate chemistry;
4. ranges for carbonate chemistry manipulations; and
5. measuring and reporting of seawater chemistry and calcification rates.

For example, experimental manipulations should cover the natural range of atmospheric CO_2 conditions between the minima of past glacial periods through the values predicted from different emissions scenarios and ocean models (e.g., 180–2000 ppmv; Caldeira and Wickett, 2003), while ensuring that the other carbonate chemistry variables are maintained within the associated natural ranges.

Experimental approaches to advance our understanding of the future of $CaCO_3$-secreting organisms requires a suite of experimental designs spanning a range of space and timescales (**Table 4.3**). These and other approaches are roughly outlined below based on whether they are generally laboratory-based, microcosm/mesocosm-based, or field-based.

4.2.1 Laboratory experiments

Most research on calcification of marine calcifiers to increased CO_2 has been laboratory based. Additional laboratory work is necessary to expand our knowledge of calcification response across the major planktonic calcifying groups (corals, benthic calcifying algae, coccolithophorids, foraminifera, pteropods,

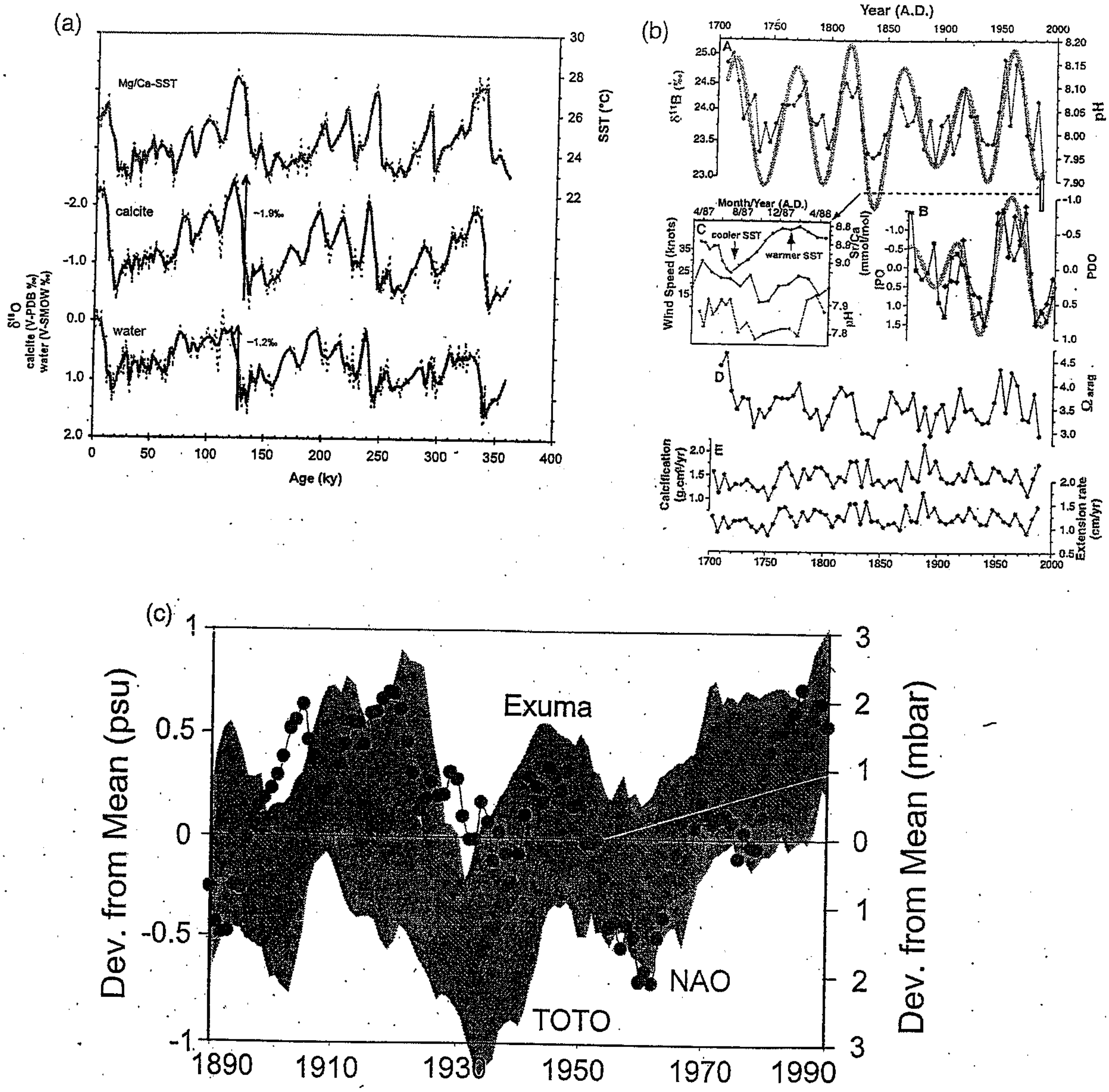


Figure 4–5: Environmental records from calcifying organisms: (a) A 350-ky paleo-SST record from deep-sea sediments at Cocos Ridge based on $\delta^{18}O$ isotope and Mg/Ca ratios of the planktonic foram *Globigerinoides ruber*; dashed lines are measured and calculated data while heavy lines are filtered to remove higher frequency components (reprinted from Lea *et al.*, 2002, with permission from Elsevier); (b) A 300-y reconstruction of surface-ocean pH at Flinders Reef, Australia, based on boron isotope ($\delta^{11}B$) data retrieved from a 300-y-old *Porites* coral. Gray line in top figure is the Interdecadal Pacific Oscillation (IPO). Also shown are aragonite saturation state (Ω_{arag}) calculated from the boron isotope-derived pH and assuming constant alkalinity, and the measured extension and calcification rates of the corals (reprinted from Pelejero *et al.*, 2005, copyright AAAS). (c) A 100-y paleo-salinity record for the North Atlantic, based on a combination of Sr/Ca and $\delta^{18}O$ isotope from the aragonitic sclerosponge *Ceratoporella nicholsoni* (reprinted from Rosenheim *et al.*, 2005 with permission from *Geophys. Res. Lett.*).

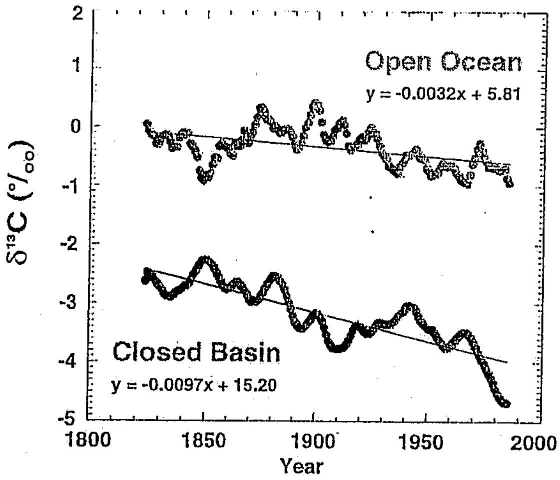


Figure 4–6: δ^{13}C records from South Florida coral skeletons, one from a well-mixed open ocean setting, and the other from a closed basin with restricted circulation. The closed system coral shows changes in δ^{13}C that is 5x greater than that of the open system (figure courtesy of Peter Swart, University of Miami).

echinoderms), and determine the various mechanisms of calcification. Priority should be given to molecular and physiological studies of species within these major groups to determine:

1. transport mechanisms of ions to the site of calcification;
2. efficiency of the proton pump;
3. pH at the site of calcification;
4. how the above are affected by changes in pH and carbonate system parameters of seawater; and
5. the interaction of carbonate chemistry with other environmental parameters, such as temperature, nutrient concentrations, and light.

Laboratory studies should continue to investigate both the photosynthesis-respiration and calcification-dissolution responses of calcifiers to combinations of saturation state, temperature, light, and nutrients. Field monitoring should be used to guide these studies; e.g., using organisms that show natural variations in calcification rates between different geographic regions.

Genomic sequencing of key calcifying organisms may lead to the identification of genes involved in calcification and how they are regulated by environmental parameters such as pCO_2, temperature, light, and nutrients. Since 2004, the National Human Genome Research Institute of the National Institutes of Health has been considering proposals to sequence a coral genome, and solicited recommendations of which species to use. Most coral researchers prefer *Porites lobata* as the likely candidate, because it is widespread and well researched, but other well-studied "lab rat" species have also been recommended (e.g., species of *Acropora*, *Montastrea*, and *Pocillopora*). Among planktonic calcifiers, the mitochondrial genome of *E. huxleyi* was the first to be sequenced (Sanchez Puerta *et al.*, 2004) and additional genomic sequencing is being conducted through the Department of Energy's Microbial Genomics Program (`http://www.jgi.doe.gov/sequencing/why/microbesseq.html`). Because of the genetic diversity and the possibility of pseudo-cryptic speciation in coccolithophores and foraminifera (De Vargas *et al.*, 1999), markers need to be developed for different genotypes, so that changes in dominance due to competition and/or adaptation can be tracked during experiments.

Cultured strains of coccolithophores may have low genetic diversity, and experiments with such cultures can lead to biased results. Thus, there is a need to broaden the genetic diversity of culture stocks. Some cultured strains of calcifiers actually lose their ability to calcify (cf. Paasche, 2001), but it has not been determined whether this is a laboratory artifact or a natural adaptation that occurs in the field.

Finally, there is a need to commit to long-term experiments (>1 year), for the major calcifying taxa, and particularly benthic species that require a year to form a complete skeletal band. Studies to determine the calcification response of deep-water corals (non-symbiont bearing corals that form deep-water reefs and support important fisheries) to increased CO_2 are also recommended.

4.2.2 *Aquaria, flumes, microcosms, and mesocosms*

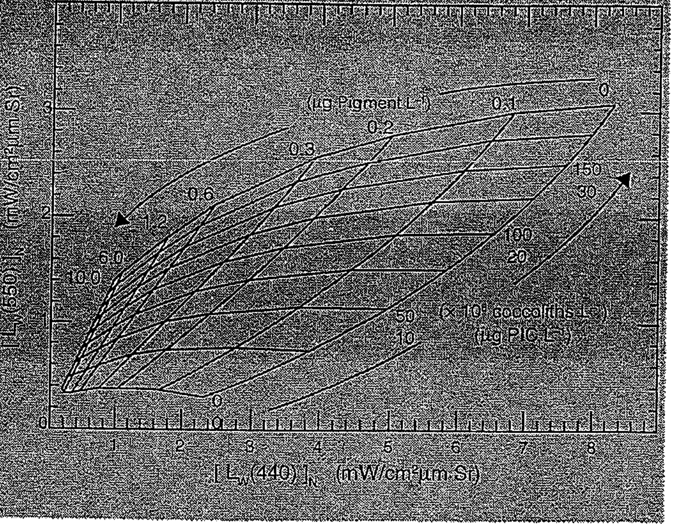
Microcosms are small, aquarium-sized (<1 m^3) experimental systems that allow species assemblages and environmental conditions to be controlled. Mesocosms are larger (>1 m^3) with less control on the ecosystems and environmental conditions. Mesocosms range from very large aquaria, to corrals and bags, to natural enclosures with known dimensions, physics, and chemistry. In general, the larger the system, the greater its complexity and the difficulty to control it; for example, many mesocosm experiments occur under natural lighting and temperature conditions.

Most physiological studies of planktonic calcifiers have been conducted on single species in aquaria or physiological chambers with tightly controlled envi-

Box 4—Recent Advances in Remote Sensing Techniques to Measure Suspended Calcite

Determination of suspended calcite from satellite imagery has been performed with algorithms that rely on either two remotely sensed reflectances or three. The 2-band PIC algorithm relies on absolute remote-sensing reflectance of the 440 nm and 550 nm wavelengths (not ratios). The normalized water-leaving radiance (L_W) is related to the absorption and scattering properties of the biogenic components of the water, phytoplankton, and their associated detritus (Gordon *et al.*, 1988). Balch *et al.* (1991) showed that the backscattering coefficient at 436 and 546 nm of detached coccoliths could be approximated along with the wavelength dependence of calcite backscattering. The 2-band PIC algorithm iteratively solves for both chlorophyll (Chl) and calcite concentrations (C_{cc}) using a standard ratio algorithm as well as the absolute water-leaving irradiances, but is sensitive to chlorophyll concentration (sensitivity of radiances to C_{cc} decreases by ~2x from high to low Chl; see figure below). The 2-band algorithm produces (1) coccolith concentration (assumed to be *Emiliania huxleyi* coccoliths), (2) equivalent PIC concentration, and (3) chlorophyll concentration. The conversion of coccolith concentration to suspended PIC is based on the carbon content in coccoliths, 0.2 pg PIC coccolith^{-1} (Balch *et al.*, 1991; Fernandez *et al.*, 1993; Balch *et al.*, 1999); however, PIC per coccolith can vary with environmental conditions (Paasche *et al.*, 1996; Paasche, 1999), and represents a potential source of error.

A 3-band calcite algorithm (670, 765, and 865 nm) has been devised that reduces errors associated with chlorophyll and CDOM (chromophoric dissolved organic matter) (Gordon *et al.*, 2001; Balch *et al.*, 2005). SeaWiFS trials of this algorithm in dense coccolithophore blooms show promise, and without contaminating effects of chlorophyll and CDOM. Ongoing validation activities for both the 2-band and 3-band algorithms are demonstrating that the two algorithms produce similar results, and further validations are planned for the future.



$[L_W(550)]_N$ as a function of $[L_W(440)]_N$ for various combinations of chlorophyll and C_{cc} (coccolith concentration). The less sloped lines are lines of constant C_{cc} ranging from 0 (bottom) to 200×10^9 coccoliths m^{-3} (top) in steps of 25 $\times 10^9$ coccoliths m^{-3}. The more sloped lines are lines of constant chlorophyll. The chlorophyll concentrations are 0.03, 0.1, 0.2, 0.3, 0.6, 1, 2, and 6 mg m^{-3} from right to left (see isopleth markings). From Balch *et al.* (2005).

ronmental conditions. Investigations of the collective response of planktonic calcifying communities to increases in pCO_2 require microcosm or mesocosm experiments; for example, the mesocosm "bag" experiments on induced *E. huxleyi* blooms (**Figure 4–8**) (Delille *et al.*, 2005) could measure not only primary production and calcification, but also the vertical fluxes of organic and inorganic carbon in the water column. Other species may be well suited for mesocosm studies similar to those on *E. huxleyi.* Pteropods may be good candidates, as they can be collected and placed in mesocosm bags, and have long life cycles for extended study. Foraminifera are thought to be poor candidates for mesososms because they normally occur in low densities, and the environmental conditions to induce population explosions are poorly known.

Studies of the calcification response of benthic calcifiers have mostly been measured with individual species in aquaria or chambers, but a few studies have included microcosm studies of communities dominated by corals (Leclercq *et al.*, 2000, 2002; Reynaud *et al.*, 2003; Yates and Halley, 2003), mesocosms dominated by corals and/or coralline algae (Langdon *et al.*, 2000; Yates and Halley, 2003) and coral-lined flumes (Langdon and Atkinson, 2005) (**Figure 4–9**). Usually the experiments are carried out under controlled conditions in the laboratory, but some have been conducted in situ using microcosm-size chambers (e.g., Dodge *et al.*, 1984; Gattuso *et al.*, 1993a)

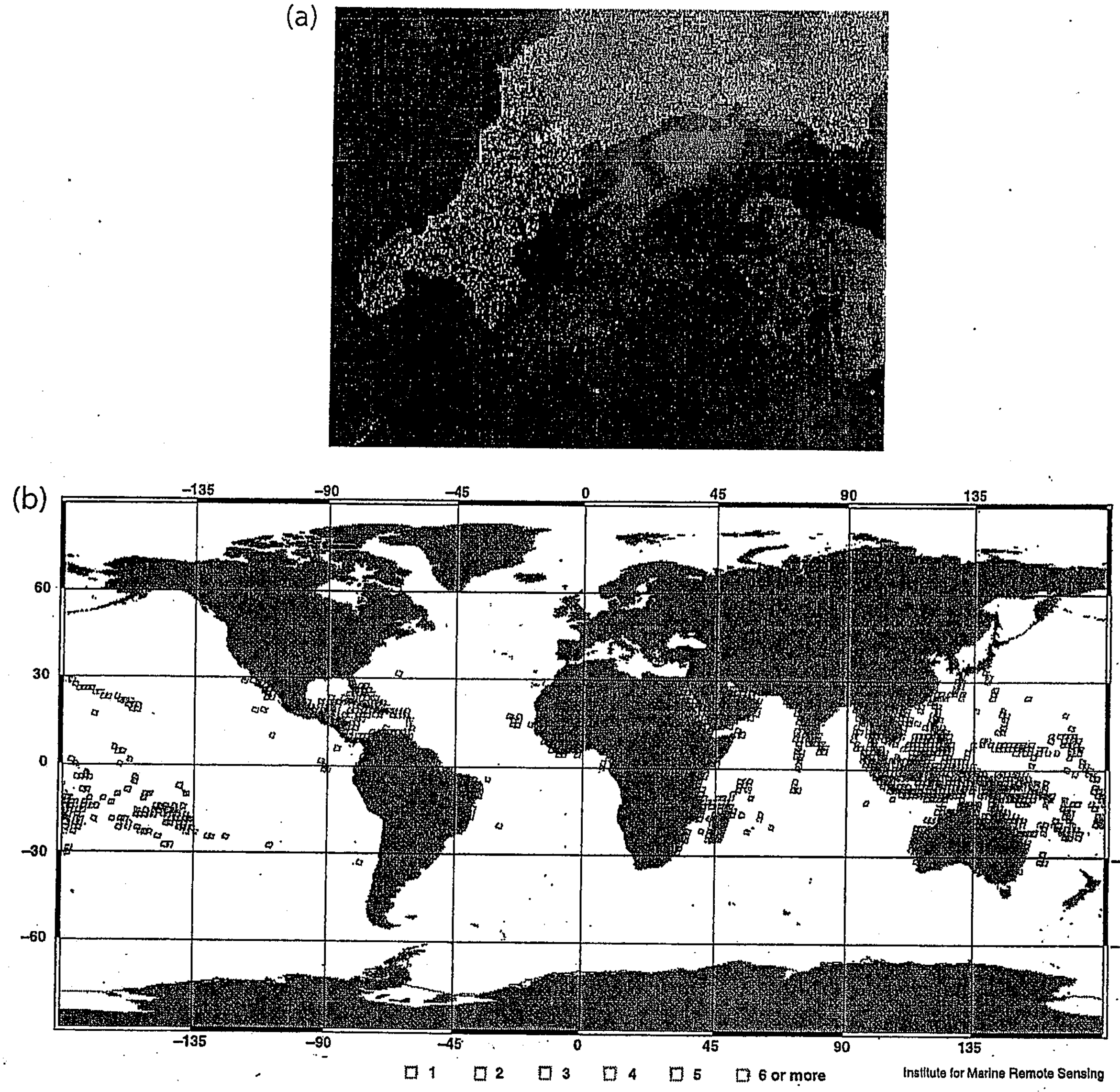


Figure 4–7: Remote sensing of marine calcium carbonate. (a) Remotely sensed image of a coccolithophorid bloom (image courtesy of Steve Groom and Andrew Wilson, Plymouth Marine Laboratory). (b) Location of shallow tropical coral reefs. Numbers of images in the LANDSAT-7 ETM+ holdings of the Millennium Coral Reef Mapping Project are shown as squares of different colors. Each square represents a LANDSAT-7 ETM+ scene. From University of South Florida, France's Institut de Recherche pour le Développement, and NASA's Johnson Space Center and the Goddard Space Flight Center (image courtesy of Frank-Muller Karger; see `http://imars.usf.edu/corals/index.html` and `http://eol.jsc.nasa.gov/reefs/`).

or enclosures such as the SHARQ (Submerged Habitat for Analyzing Reef Quality) chamber system developed by the USGS (Yates and Halley, 2003). Besides reef-building corals and coralline algae, other critical groups of benthic calcifiers that should be investigated include major carbonate producers such as *Halimeda,* and key ecosystem components such as benthic forams and deep-water corals.

All of these laboratory and in-situ approaches are overlapping in scale, and many of the pressing research questions identified in Section 3 will be best answered through multiple approaches. Scaling is an important concern when designing these systems, particularly when considering the timescales over which organisms can acclimatize or adapt to new conditions. Most planktonic calcifiers are microscopic and have generation times of days to

Box 5—Remote Sensing Applications to Coral Reef Production and Calcification

Remote sensing can be used to scale up coral reef production and calcification measurements to reef scales. Below is a classification of Moorea Island (French Polynesia) reefs (a and b) produced using high-resolution remote sensing data (Andréfouët and Payri, 2001). The main zonation patterns of the reefs are clearly visible, showing large sedimentary areas of low productivity (yellow), coral-dominated regions (blue), etc. Profiles of gross production and calcification are also shown along the profile plotted over the map (the corresponding reef is stylized in the upper-right panel). Excess production (gross production minus respiration) for the first full-resolution profile (i) is slightly positive for the barrier reef. Profiles are averaged at 100 and 300 m resolutions (h, f), and for the entire reef width (d). The spatial variability of metabolism is still distinct at 300 m resolution, which is easily accessible by LANDSAT or IKONOS imagery. At the island scale (over 35 km^2 of coral reef environment) metabolic performances were estimated for gross production (93,560 10^3 kg C y^{-1}), excess production (10,017 10^3 kg C y^{-1}), and calcification (165,348 10^3 kg $CaCO_3$ y^{-1}) (figures reprinted from Andréfouët and Payri, 2001, with kind permission from Springer Science and Business Media).

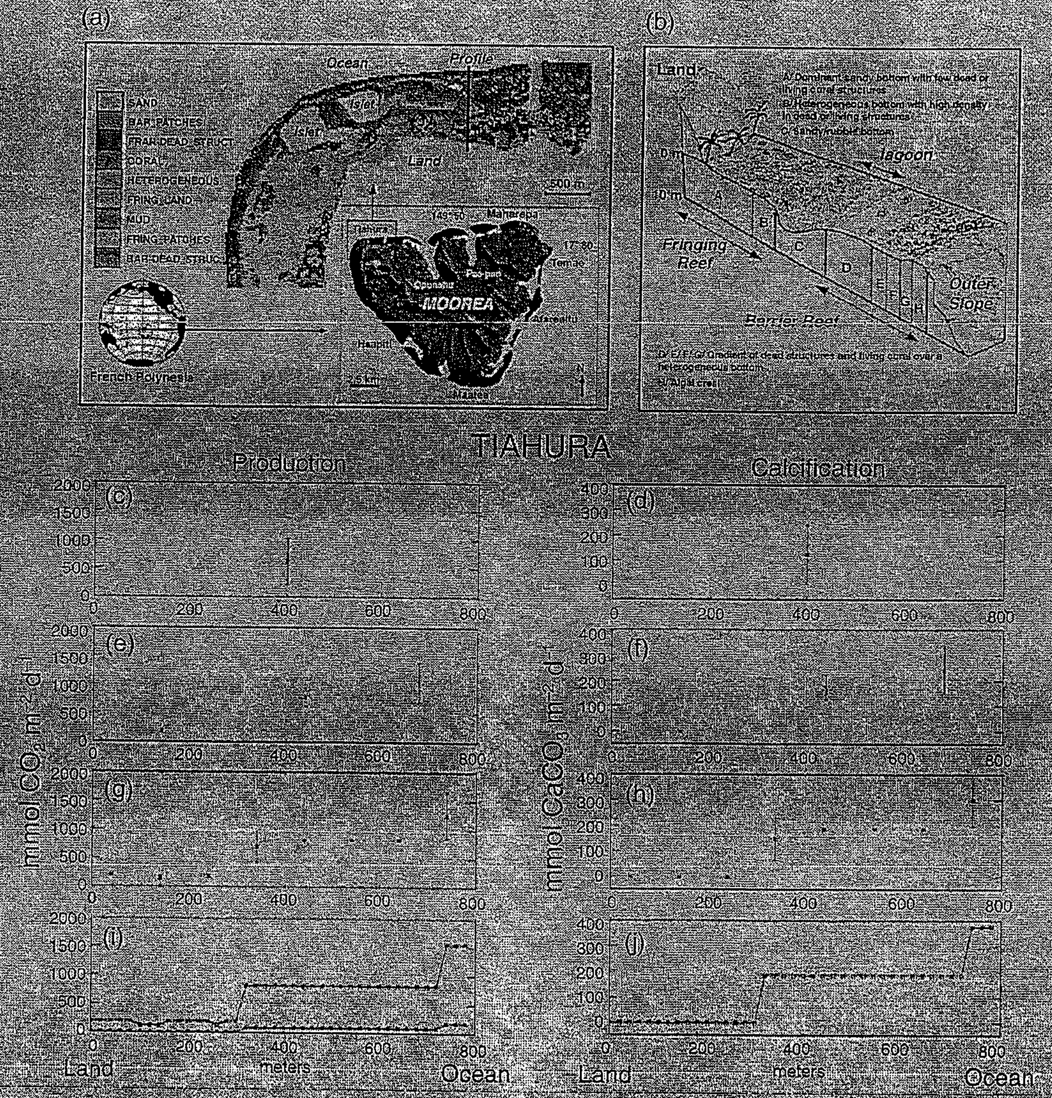


Table 4.3: What will it take to answer the pressing questions? Major research questions regarding the response of marine calcifiers to increased atmospheric CO_2, and the primary types of experiments and experimental settings necessary to address those questions.

Calcification Response	Types of Experiments	Experimental Settings
Organisms		
Determine the relationship between photosynthesis and calcification.	Physiological Biochemical	Laboratory manipulations
Discriminate mechanisms of calcification within calcifying groups; identify cross-taxa range of responses to changing seawater chemistry.	Physiological Biochemical	Laboratory manipulations
Measure response of other taxa and other life stages to elevated pCO_2.	Physiological Skeletal records	Laboratory manipulations Field monitoring Field manipulations
Determine interactive effects of multiple variables that affect calcification in organisms: saturation state, light, temperature, nutrients.	Physiological Skeletal records	Laboratory manipulations Mesocosm manipulations Field monitoring Modeling
Test for adaptation: Several years may be necessary to determine whether calcifying taxa can adapt or acclimate to different carbonate chemistry conditions.	Physiological monitoring Skeletal records	Laboratory manipulations Field manipulations and monitoring
Ecosystems		
Determine how calcification in organisms affects: (1) species interactions, (2) food webs, (3) regional productivity, (4) carbon and nutrient cycling through the ecosystem, and (5) ecosystem services.	Ecosystem monitoring Ecosystem manipulations	Mesocosm manipulations Field monitoring and manipulations Ecosystem modeling
Determine role of inorganic cementation in resiliency of coral skeletons and reef structures and how inorganic cementation will be affected by lowered saturation state.	Geochemical Documentation of cementation patterns versus environment	Laboratory studies
Determine how bioerosion rates will be affected by reduced saturation state.	Bioerosion studies Ecosystem manipulations	Field surveys Field manipulations
Dissolution and Carbonate Budgets		
Quantify dissolution rates and chemical mass balances in pelagic systems, and characterize factors that control them.	Biogeochemical	Laboratory Field
Quantify $CaCO_3$ budgets of coral reefs, *Halimeda* bioherms, and temperate and cool-water benthic carbonate-producing systems.	Sedimentological and geochemical surveys and monitoring	Field Modeling
Commit to long-term monitoring for detecting response of the seawater carbonate system to continued increases in CO_2, across a variety of planktonic and benthic settings.	Geochemical	Field Measurements
Determine role of excess $CaCO_3$ production ("reef building") in supporting: (1) vertical accretion, (2) spatial complexity that supports diversity, (3) depth gradient that also supports diversity, and (4) structural influence on hydrodynamic regime.	Combined ecological, environmental and geological studies	Field measurements and manipulations Modeling
Determine the dissolution = calcification threshold in benthic calcifying communities, and how it varies under different environmental conditions.	Geochemical Seawater chemistry monitoring	Field measurements and manipulations Modeling

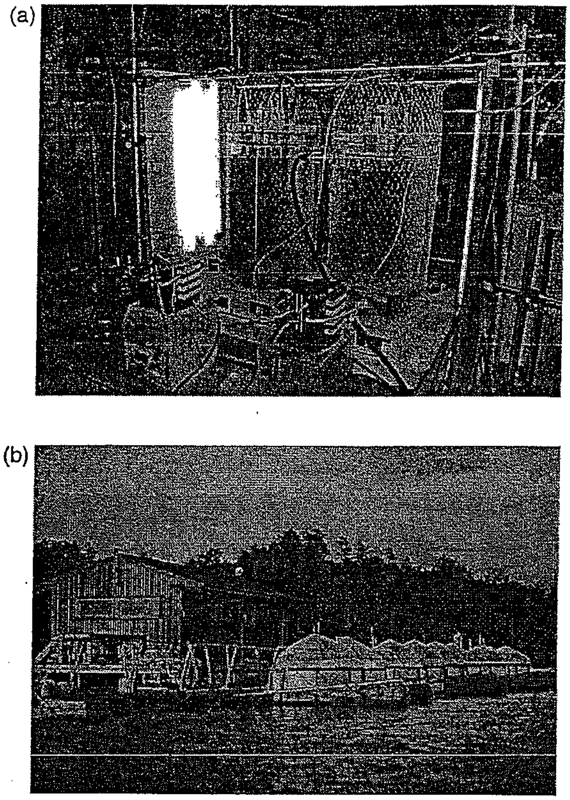


Figure 4–8: Experimental setup for measuring *E. huxleyi* calcification under different environmental conditions. (a) Laboratory experiments with a "chemostat" (Sciandra *et al.*, 2003) (photo courtesy of J.-P. Gattuso, CNRS). (b) Mesocosms in Norway (Delille *et al.*, 2005; Engel *et al.*, 2005) (photo courtesy of Ulf Riebesell, GEOMAR).

months, so that the potential for genetic adaptation is greater than for slower-growing macroinvertebrates that dominate benthic systems. Microcosm and mesocosm experiments of many benthic organisms may require timescales of a year or more to determine the potential rates of acclimation and adaptation to elevated pCO_2.

4.2.3 Field experiments

Manipulative field experiments have the advantage of closely mimicking the real world, and may be one of the few ways to obtain realistic assessments of the ecological consequences of decreased calcification rates. Field experiments avoid the problem of co-variation between important parameters (temperature, saturation state, and light), and biases introduced in controlled laboratory experiments. For example, a field experiment where a patch of water in the open ocean or overlying a benthic community is enriched with pCO_2 while keeping all other variables natural would provide key insights into future responses of the calcifying community, particularly in terms of subtle changes such as species interactions, community structure, bioerosion, and dissolution..

Ideally, experimental field settings should range from naturally enclosed water bodies (natural embayments, lagoons) to open ocean. Such experiments (particularly the open-boundary experiments) are difficult to conduct because the environmental variable of interest—seawater carbonate chemistry—is difficult to control, as are other conditions such as temperature, nutrients, and light. Those environmental variables that cannot be controlled will have to be monitored and then factored into the overall response. Field studies should, therefore, be augmented with controlled laboratory and mesocosm experiments.

Two types of field experiments that could be adapted for examining calcification response of planktonic communities include (1) the IronEx and similar experiments where a large patch of seawater was fertilized with iron, and then tracked and monitored for several weeks to examine community and biogeochemical response (Martin *et al.*, 1994; Coale *et al.*, 1996; Boyd *et al.*, 2000; Coale *et al.*, 2003) (**Figure 4–10a**); and (2) FACE (Free Air Carbon dioxide Enrichment), the terrestrial field experiments which increase ambient CO_2 concentrations using controlled inputs of CO_2 directed toward the center of an experimental plot (Hendrey and Kimball, 1994) (**Figure 4–10b**). "CO_2Ex" studies could be conducted at a variety of scales in benthic communities, particularly with restricted water masses (from patch reefs to atoll lagoons and large embayments). A CO_2Ex study could be performed within a planktonic calcifying community, although additional manipulations may be necessary to induce calcifiers to bloom. For benthic calcifying systems, coral reef lagoons (e.g., within an atoll) are one example of naturally enclosed systems in which CO_2 chemistry manipulations could be contained.

An ocean version of a FACE experiment requires considerable engineering design, mainly because of challenges associated with hydrodynamics and with CO_2 supply to the water column. Some progress in such designs has been made already (**Figure 4–11**; Kirkwood *et al.*, 2005). A FACE-like experiment for shallow benthic systems would be easier than in the open ocean, as it could be permanently secured to the ocean floor and the organisms would remain in place (as opposed to open ocean systems, in which a system would have to be deployed and maintained within a bloom of calcifiers in order to obtain measurable results).

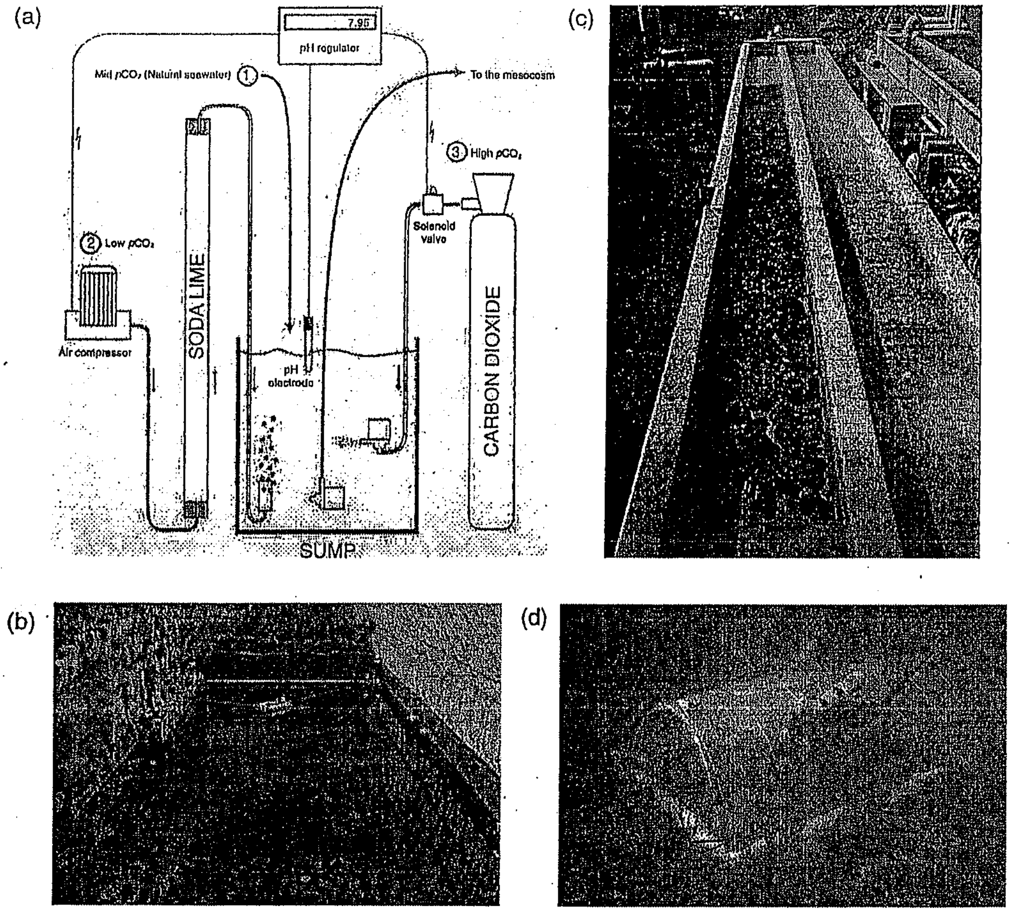


Figure 4–9: Mesocosm experiments for conducting calcification experiments on benthic communities. (a) Diagram of the Monaco coral community microcosm (reprinted from Leclercq *et al.*, 2002; copyright by the American Society of Limnology and Oceanography, Inc.). (b) Biosphere 2 coral reef mesocosm (Langdon *et al.*, 2000; Langdon *et al.*, 2003). (c) Hawaii Marine Biological Institute flume studies on coral communities (Langdon and Atkinson, 2005). (d) SHARQ (Submersible Habitat for Analyzing Reef Quality) chamber experiments conducted in situ (reprinted from Yates and Halley, 2003, with kind permission from Springer Science and Business Media).

Both CO_2Ex and FACE-like experiments require pumping large quantities of CO_2 into seawater. This is a technological challenge, and may also be harmful in some environments. Alternatively, technology and techniques to conduct CO_2-*removal* experiments (e.g., to mimic ice-age concentrations) should also be considered in future design.

4.2.4 Target organisms for research

Most research on marine calcifiers has been on three major taxa: coccolithophorids, foraminifers, and scleractinian corals. Continued research on these groups is likely because they are ecologically and biogeochemically important, but also to take advantage of the existing database. Research on many other groups is badly needed, however. Little research has been conducted on organisms that secrete high-Mg calcite, or commercially important species such as bivalves and crustaceans. Selection of target species for laboratory experiments should consider a range of features (**Table 4.4**), including:

1. ecological importance;
2. different calcification mechanisms (i.e., from organisms with low biological control over calcification to those with high biological control);
3. different skeletal structures (e.g., dense versus porous);
4. different mineralogies (e.g., aragonite versus high-Mg calcite);

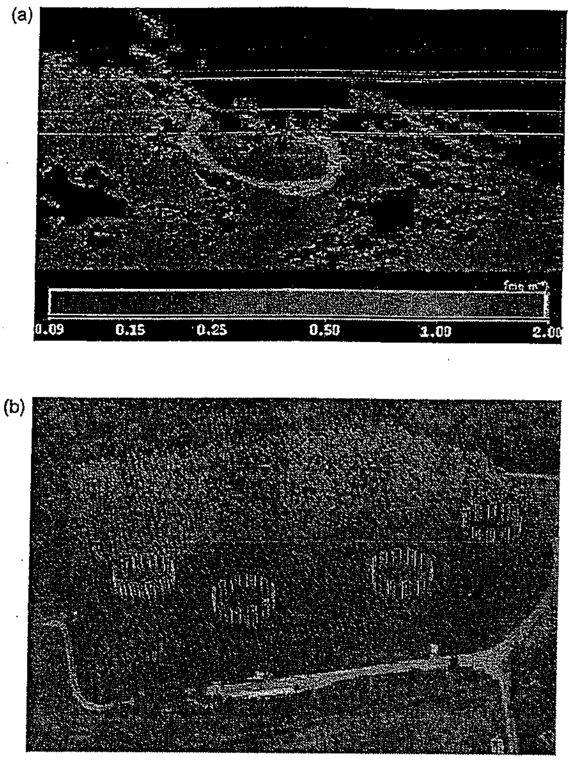


Figure 4–10: Examples of large-scale field experiments that could be modified for open-ocean studies on calcifying communities: (a) Satellite picture of a phytoplankton bloom in the Southern Ocean induced by iron fertilization during the SOIREE experiment (from `http://www.awi-bremerhaven.de/Biomeer/southern-ocean-top01-e.html`); and (b) the Free-Air Carbon-dioxide Enrichment (FACE) experimental design for terrestrial systems.

5. different capacities for adaptation (e.g., from variable and/or marginal environments); and
6. ease of culture.

For example, the coccolithophorid *E. huxleyi* is the best-studied of the planktonic calcifiers, owing to its prominence in the open ocean, its importance in marine ecosystems and biogeochemical cycling, and the relative ease of maintaining it in culture. Many aspects of *E. huxleyi* physiology are well understood, but the underlying mechanisms of its calcification are not. Many common coccolithophore species differ substantially from *E. huxleyi* in calcification and other physiological processes, and the response of such species to decreased carbonate saturation state should be investigated. Among benthic organisms, massive *Porites* and branching *Stylophora pistillata* and *Acropora* spp. are often considered the "lab rats" among corals, but many other benthic calcifiers should be considered target species for future research.

Many organisms within these groups have multiple life stages, but most studies have concentrated on adults. Calcification could play a critical role in planktonic larval stages (e.g., ballast or protection), and when benthic organisms initially calcify to a substrate at the time of settlement (see "Organism Response" under Section 3.1).

4.2.5 *Dissolution in the water column and sediments*

Both field and laboratory measurements are useful and necessary to understand rates and processes affecting carbonate dissolution. In some basic ways, our understanding of carbonate dissolution is limited; for example, there is still debate concerning the kinetic expression defining the relationship between calcite dissolution and degree of saturation (Morse and Arvidson, 2002; Gehlen *et al.*, 2005a). Aragonite and high-Mg calcite dissolution kinetics are even more poorly understood. Measuring dissolution in the field has been tackled in both the water column and in sediments. In the open ocean, quantification of carbonate particle dissolution may be achieved using an array of techniques:

1. *Hanging particles on a wire* and determining dissolution rates over time (Peterson, 1966; Troy *et al.*, 1997). An advantage of this approach is its elegant simplicity. A drawback is that the impact of hydrodynamics and fouling are difficult to assess and that a mooring is required.
2. *Sediment trap fluxes* provide a measure of net dissolution. The change in flux between two trap horizons, in a simple 1-dimensional mass balance, defines the rate of dissolution between two depths in the water column (Walsh *et al.*, 1988; Feely *et al.*, 2002). This approach can be widely applied throughout the global ocean as there are data from many trap arrays, yet the 1-dimensional flux assumption is problematic, especially in assessing trap data from depths shallower than 1000–2000 m. Hence, obtaining an accurate measurement of dissolution in the shallow ocean requires the use of traps free of hydrodynamic biases. Neutrally buoyant traps may provide a partial solution to this dilemma. Another problem with trap budget approaches is the difficulty in assessing whether captured particles swam or fell into the trap.
3. *Water chemistry mass balance.* Feely *et al.* (2004) provides a clever method of establishing disso-

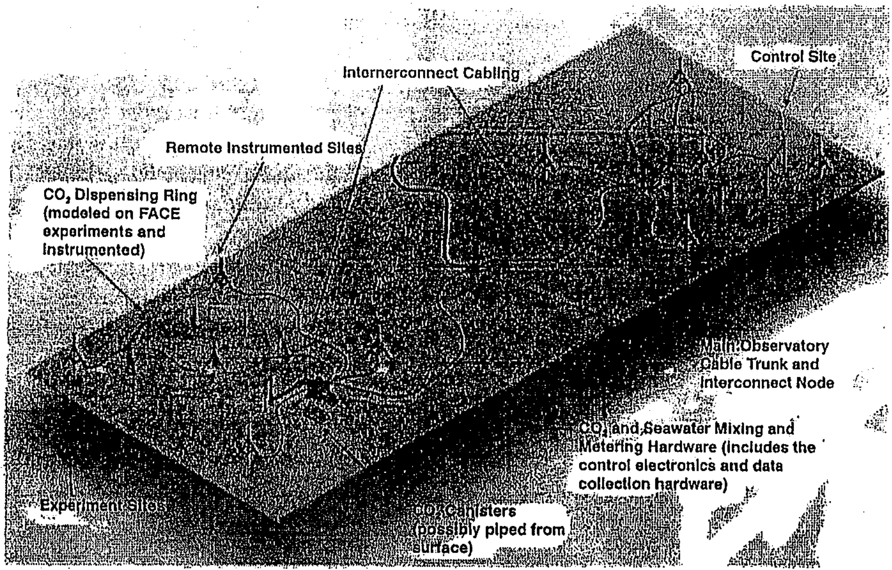


Figure 4–11: Diagram of FACE-like technology adapted for benthic marine studies (figure reprinted from Kirkwood *et al.*, 2005, courtesy of Bill Kirkwood and Peter Brewer, MBARI).

lution rates in parcels or discrete water masses. Here, the age of a water mass is established from tracer modeling (Chlorofluorocarbons, tritium, ^{14}C) and the "in-growth" of "excess" alkalinity or calcium is determined. The method to define the excess alkalinity in a water mass is not simple—it relies on two model-dependent determinations—but its applicability to deriving global estimates of dissolution makes it a powerful tool.

4. *Particle tracers.* The mass of foraminifera tests (Broecker and Clark, 1999) has been used as a proxy for dissolution (simple weight loss) as has the change in Mg/Ca ratios in forams. While these proxies have been more often applied to studies of carbonate dissolution within sediments, they may also serve to constrain dissolution as it occurs within the water column.
5. *Bulk water measurements.* Capturing a volume of water, incubating it, and determining the change in carbonate chemistry is a direct measure of dissolution or precipitation rate (Byrne *et al.*, 1984; Feely *et al.*, 1988; Buitenhuis *et al.*, 1996). This approach requires high precision measurements to detect the small changes in the CO_2/carbonate system that occur during incubation.

Field methods to study carbonate dissolution on the sea floor include both "active" experimentation which captures reactions occurring over timescales of days, and integrative measurements which capture reactions occurring over much longer timescales, often integrating processes that have been active over hundreds to thousands of years.

1. *Benthic flux chambers* are deployed in situ to capture and incubate water in contact with the sediment-water interface. Changes in alkalinity and/or calcium with time provide a direct measure of sea floor dissolution rates (Berelson *et al.*, 1994; Jahnke *et al.*, 1994; Martin and Sayles, 1996). This approach has had limited application in the field and some consider chamber fluxes suspect due to hydrodynamic interferences and because dissolution is determined over short timescales.
2. *In situ microelectrode profiles* of pH and/or pCO_2 have been applied to study carbonate diagenesis in sediments (Hales *et al.*, 1994). Data are interpreted with the use of transport-reaction models to predict carbonate dissolution rates, and resulting flux estimates are subject to the uncertainties inherent in model assumptions.
3. *Proxies for dissolution,* including those mentioned above, provide a measure of dissolution occurring on the timescale of sediment accumulation, mixing, and sample resolution. Other proxies for dissolution include the degree of foram fragmentation, trace metal ratios (McCorkle *et al.*, 1995), and the ratio between more soluble and less soluble species.

Table 4.4: Examples of targeted organisms and taxa for research on impacts of increasing atmospheric CO_2 on calcification. Note that a lack of notes under "Cons" does not necessarily indicate the taxon is highly suitable for research, but rather a lack of information in this regard.

Taxon	Pros	Cons
Planktonic		
Coccolithophores	Abundant with global distributions Some species are bloom-forming and blooms can be induced Some species are easy to maintain in lab Importance in carbon cycle Potential importance in food webs Some species well studied Common in calcareous sediments	Complex life cycles Difficult to identify species without using SEM
Planktonic foraminifera	Abundant and widespread Calcification mechanism in many taxa uncomplicated by photosynthesis Some species can be cultured in lab Common in calcareous sediments	Difficult to culture
Euthecosomatous pteropods	Widespread and regionally abundant Importance in carbon cycle Importance in food webs Only aragonitic member of the major planktonic calcifiers Calcification mechanism uncomplicated by symbiotic algae	Normal behavior is often disrupted in captivity
Benthic		
Halimeda	Abundant and widespread in tropics Simple calcification mechanism Easy to maintain in lab Prolific calcifier Importance in carbon cycle	
Coralline algae	Abundant and widespread Secrete most soluble form of $CaCO_3$ Easy to maintain in lab Importance in carbon cycle Reef-builder	
Benthic foraminifera	Abundant and widespread Important component of carbonate sediments Symbiotic and asymbiotic forms High-Mg and low-Mg taxa Some species well studied and easy to maintain in the lab Diverse calcification mechanisms Diverse habitats (infaunal, epifaunal, sessile, motile)	
Zooxanthellate coral, *Stylophora pistillata*	Abundant and widespread Easy to maintain in lab Established history in laboratory experiments	Branching coral—not well suited to skeletal records Typically non-reef-forming
Zooxanthellate coral, massive *Porites* spp.	Abundant and widespread Calcification rates and isotopic signals recorded in skeletal bands Major reef-builder	Slow-growing Difficult to culture and maintain
Azooxanthellate corals	Calcification mechanism uncomplicated by symbiotic algae Some species form significant deep-water reefs Some species may occur near saturation horizon (most vulnerable) Low environmental variability may allow clean signal of calcification rate changes over time	Slow-growing Usually non-reef-building Ability to culture unknown?
Echinoderms	Abundant and widespread Can be maintained in culture (larvae of some species are used in bioassay work) High-Mg calcite	

Table 4.4: Continued.

Taxon	Pros	Cons
Bryozoans	Abundant and widespread Both shallow-water and deep-water taxa Aragonite, high-Mg calcite, and calcite taxa	
Molluscs	Abundant and widespread Some species house zooxanthellae Many species commercially important Some taxa easy to culture (e.g., several bivalve taxa are aquacultured) Calcification rates and isotopic signals recorded in skeletal bands Some taxa secrete aragonite and calcite in proportions that may reflect saturation state	

4. *The amount of C_{org}* raining to the sea floor affects the rate of carbonate dissolution (Emerson and Bender, 1981; Archer and Maier-Reimer, 1994). Subtle changes in how much organic matter gets mixed into surface sediments, as opposed to sitting in a fluff layer on top of the sediments, is thought to be an important factor in controlling net dissolution.
5. *The mass balance approach*, which determines net dissolution as the balance between sedimentation and burial rates, generally requires a loss term. Mass balances constructed over short time periods for a section of sea floor and water column require high-frequency determinations of carbonate parameters and good control on water circulation. This approach could be more frequently applied as technologies improve in Doppler current meters and pCO_2 and pH detectors.

In addition to the methods listed above, there are emerging research needs that will require creative research designs. At the smallest biological scales in ocean ecosystems, the rôle of viruses, bacteria, and *Archaea* in affecting carbonate precipitation, dissolution, or preservation is poorly known, but likely important (Fabry and Robbins, 1994; Robbins *et al.*, 1997; Yates and Robbins, 1999). Methods to measure dissolution inside the guts of zooplankton and larger organisms should be refined (Bishop *et al.*, 1980; Harris, 1994; Milliman *et al.*, 1999), and measurements of particle dissolution in the water column require better ways of estimating particle residence time in different water masses.

4.3 Target Regions for Research

Potential locations of future research studies were recommended at the St. Petersburg Workshop. These recommendations were based on several factors, including:

1. ecologically important systems (e.g., high biodiversity, food-chain support);
2. ecological systems particularly sensitive to carbonate chemistry changes;
3. regions likely to experience the most dramatic change in carbonate chemistry (e.g., high latitudes, deep-sea coral reefs near the aragonite saturation horizon);
4. regions which already experience high pCO_2, or have strong natural gradients in carbonate chemistry (see section 4.1.2);
5. regions that permit combined pelagic and benthic experiments;
6. remoteness from human activities;
7. regions with existing long-term environmental information (existing time-series stations, LTER sites);
8. regions with existing infrastructure for performing the research (e.g., marine laboratories, ocean observing systems).

Based on these criteria, some regions identified as being particularly suitable for future field research. The list below is biased toward coral reef locations, which were the priority benthic ecosystem considered at the workshop; however, we stress the need to also consider temperate calcifying environments. Among the pelagic systems, workshop participants focused on high-latitude regions, particularly those most likely to experience undersaturated surface waters within decades, and regions with natural gradients in CO_2 chemistry.

Galápagos Islands (0°30′N 91°W). The Galápagos Archipelago in the eastern Pacific lies in a region of strong equatorial upwelling. pCO_2 of upwelled waters is naturally high (often exceeding 500 μatm), and in many locations these waters penetrate the thermocline and reach the surface, particularly along the western sides of the islands. Anecdotal evidence supports the notion that lower saturation states of these waters may have been a factor in the marginal coral reef development here (although other factors, such as low water temperature, certainly play a role as well). The Galápagos Archipelago also has strong lateral gradients in carbonate chemistry which could be taken advantage of in experimental designs, and offers the opportunity to study both planktonic and benthic calcifying systems, and sedimentation (sedimentation rates at Cocos Ridge are about 15 cm ky^{-1}). There are existing research facilities and low levels of human influence. All of the major groups of planktonic calcifiers commonly occur here and have high species diversity. Coral reefs of the Galápagos experienced severe bleaching during the 1982–1983 El Niño event, and moderate bleaching in the 1997–1998 event. While many of the reefs experienced dramatic bioerosion following these events, coral recruitment continues and offers the opportunity to examine coral reef development in an elevated-pCO_2 environment.

Bahamas Bank (22–27°N 72–75°W). In contrast to the Galápagos, the Bahamas Bank is a region where saturation states are naturally high, although strong gradients do occur across the Banks because of calcification processes that draw down the alkalinity (e.g., Broecker and Takahashi, 1966; Broecker *et al.*, 2001). This region has been a Mecca for carbonate research, as there is a suite of biologically produced and inorganically precipitated carbonates (ooids and whitings). Ocean chemistry has been measured nearly annually at various locations in the Bahamas since 1980 (Frank Millero, University of Miami, personal communication). It is also a region of high ecological importance and most of the Bahama Islands experience low human impact. Several research stations are active in the Bahamas (e.g., Perry Institute for Marine Science on Lee Stocking Island; the Bahamian Field Station on San Salvador Island) and offer good infrastructure for supporting research and monitoring.

Florida Keys and Dry Tortugas (24°25′–25°45′N 80–83°W). The primary advantage of conducting research in the Florida Keys is access to excellent research facilities and expertise on the carbonate system from various Florida marine science laboratories. While most of the Keys are heavily impacted by human activities, the Dry Tortugas are more remote and isolated from land activities.

Bermuda (32°20′N 64°40′W) and **Hawaiian Islands** (19–28°N 155–177°W). Both Bermuda and the Hawaiian Islands are located in mid-ocean gyres, and have extensive coral reefs. Bermuda is located at the northern limit of reef development in the Atlantic, while the Hawaiian Islands extend across nearly 10° latitude. Both locations have a long history of reef and oceanic research, and have time-series stations that have tracked open ocean carbonate chemistry for more than 15 years (HOT and BATS, see **Table 4.2**). Each site has well-equipped laboratories for carbonate chemistry analyses. Bermuda's coral reefs have been studied for more than a century, with intensive ecological studies being conducted since the 1960s, mainly through the Bermuda Biological Station for Research (BBSR). Several studies have already been conducted on the carbonate chemistry of Bermudan reef waters (Bates *et al.*, 2001; Bates, 2002). Hawaiian coral reefs are similarly well studied, particularly those of Kaneohe Bay, site of the Hawaiian Institute of Marine Biology research station, where experiments have been conducted on the effects of increased pCO_2 on coral calcification (Langdon and Atkinson, 2005). NOAA has recently established an extensive monitoring program in Kaneohe Bay and the NW Hawaiian Islands.

Many other coral reef locations may be well suited for research on the effects of increased pCO_2 on calcifying communities. These include the Great Barrier Reef, French Polynesia (which has recently established a Long-Term Ecological Research site), and Ryukyu Islands of Japan, among many other coral reef regions.

Deep-sea coral communities. Deep-sea coral communities are distributed throughout the world oceans, in relatively constant environments, and usually at 200–600 m depth. Deep-sea corals are non-zooxanthellate, slow-growing, and can live for over a century. Because of the low environmental variability, the long-lived nature of the corals, and their proximity to carbonate saturation horizons, these communities may be ideal for monitoring changes in saturation state.

Southern Ocean. In the Southern Ocean, the aragonite saturation horizon is expected to shoal from a mean present-day depth of 730 m to the surface in less than 100 y (Orr *et al.*, 2005). The very large changes in carbonate chemistry that this high latitude region will experience make it a high priority study area. The McMurdo and Palmer Stations in Antarctica have excellent research facilities for monitoring field populations of both planktonic and benthic calcifiers, and conducting manipulative experiments.

Subarctic Pacific. Similar to the Southern Ocean, parts of the subarctic Pacific are expected to experience aragonite undersaturation in surface waters within 100 years (Orr *et al.*, 2005); calcite undersaturation is predicted to lag that of aragonite by 50 to 100 years. The major planktonic calcifying groups commonly occur here and occasionally experience population explosions (e.g., coccolithophores, pteropods). Ocean Station Papa and the Line P have a long history of hydrographic and biological measurements, and researchers at Canada's Institute of Ocean Science (IOS) have monitored carbonate chemistry for many years. The ongoing monitoring activities by IOS, coupled with the large changes in carbonate saturation states that are expected to occur within the 21st century, make this an ideal region to study planktonic calcification and dissolution processes.

Large Scale Mesocosm Facilities, Bergen, Norway. This facility at the Marine Biological Station of the University of Bergen consists of nine polyethylene enclosures moored to a raft in the Raunefjorden (60.3°N, 5.2°E). In previous experiments, the volume of each enclosure was 11 m^3 or 20 m^3. The enclosures are filled with fjord water and coccolithophore blooms are induced by addition of nutrients. This mesocosm facility provides the ability to manipulate complex ecosystems in a semi-natural setting, providing a critical bridge between laboratory studies and mesoscale in situ experiments.

4.4 Modeling Opportunities and Needs

Modeling will be an important component of future research on CO_2 effects on marine calcifiers. Such modeling efforts need to focus on three arenas:

1. physical and chemical environment (hydrodynamics, sediments, carbonate system);
2. biological and ecological response (physiological response; community interactions);
3. coupling of global-coastal processes.

4.4.1 *Current modeling efforts*

Modeling efforts of the ocean carbon system have focused on the biogeochemical response of the global carbon cycle to increased CO_2, and the consequent feedbacks to future atmospheric CO_2 concentrations (**Box 6**; **Figure 4–12**). Global models of the open-ocean system can capture the main physical and biogeochemical processes that control the marine carbon cycle. For the present-day ocean, global models simulate large-scale regional changes in saturation state and saturation horizons that roughly match observed changes. Such models can therefore guide laboratory and field studies and make predictions of large-scale changes over at least the 21st century. These models are designed only for the open ocean, however, and they do not include coastal processes. Also the ecological components of the models are probably too simple to adequately predict biogenic calcium carbonate production under higher atmospheric CO_2 levels.

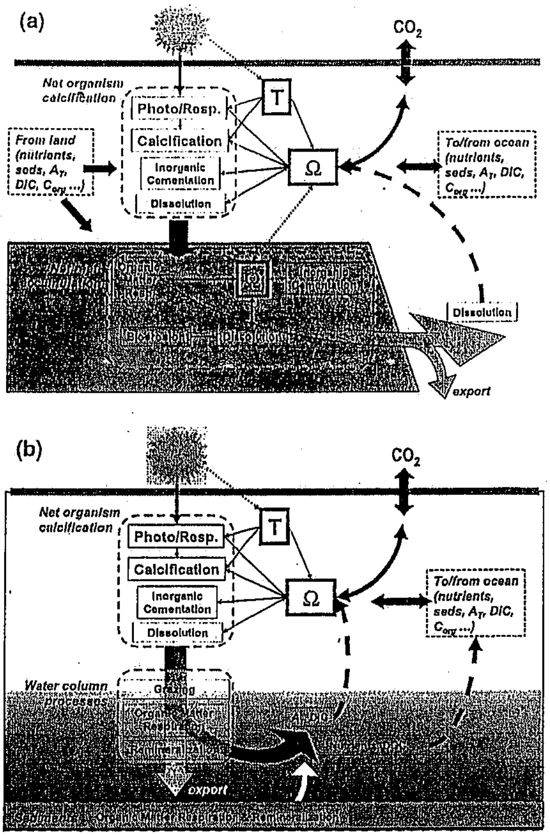


Figure 4–12: Comparison of the major processes that need to be considered in modeling the carbonate system in (a) a shallow benthic system (<100 m depth) and (b) an open ocean system (up to 6000 m depth). These are oversimplified representations. For example, the dissolution component in both systems involves complicated processes that include differences in mineralogies, organic matter respiration, etc.

Few coastal carbon system models have been developed. Coastal modeling is inherently more difficult than open-ocean modeling, because, in addition to water column processes and air-sea gas exchange, coastal models must include land-based inputs and sediment interactions (**Figure 4–12a**) as well as much higher spatial and temporal variability. Coastal models must also be validated site by site. One example of a coastal biogeochemical model is the Shallow Ocean Carbon Model (SOCM) developed by Fred Mackenzie and colleagues (e.g., Andersson *et al.*, 2003). This

Table 4.5: Priority modeling needs, example topics, and whether the question relates primarily to physical-chemical or biological-ecological questions.

Modeling Priority	Example Topics	Physical-Chemical	Biological-Ecological
Guidance on field design	• best regions for monitoring/experiments	×	×
	• constraining ranges of measurements, expected variability in parameters	×	×
	• determining best frequency/spatial scale for data collection	×	×
Dissolution and remineralization	• C_{org}:C_{CaCO3} rain ratio	×	×
	• settling rates	×	×
	• controls on dissolution rates within the water column	×	×
	• changes in carbonate chemistry profile with depth	×	
Sedimentary response	• sedimentation rates	×	×
	• advection of alkalinity from sediments to coastal and open ocean	×	
	• mineralogical controls on sedimentary response	×	×
	• hydrodynamic controls on fluxes (especially flow through porous media)	×	
	• relative effects of organic matter respiration on dissolution versus changing saturation state of overlying water column	×	×
Mineralogical	• conditions affecting the balance between calcification/dissolution	×	×
	• kinetics of high-Mg calcite precipitation and dissolution	×	×
Organism response	• organism production, respiration, calcification rates	×	×
	• competitiveness		×
	• potential role of adaptation		×
	• changes in reproductive success		×
Ecosystem response	• community production, respiration, calcification rates	×	×
	• competitive interactions		×
	• predator-prey interactions		×
	• cascading effects due to removal of key calcifiers		×
Global-coastal model coupling	• need for coupling coastal processes with open ocean	×	×
	• to what extent can shallow water sediments affect global changes in carbonate saturation (open ocean, coastal)?	×	×
	• scaling up from local/regional to global	×	×
	• driving regional models with global model	×	×
	• incorporating more realistic coastal circulation; predicting future changes in circulation	×	

model could be adapted for studying both future biogeochemical changes in coastal carbonate systems, and ecosystem response to those changes.

Even fewer models have addressed $CaCO_3$ production at smaller scales, varying from the organism to the ecosystem, or how changes in calcification rates might affect future ecosystem composition and functioning. For example, some coral species propagate by skeletal fragmentation. If reduced calcification leads to less dense skeletons, would this increase propagation of this species, and if so how would such changes affect long-term community composition? In the pelagic realm, can we use ecological modeling to predict how a change in pteropod abundance or distribution (Orr *et al.*, 2005) would affect food webs that depend on them?

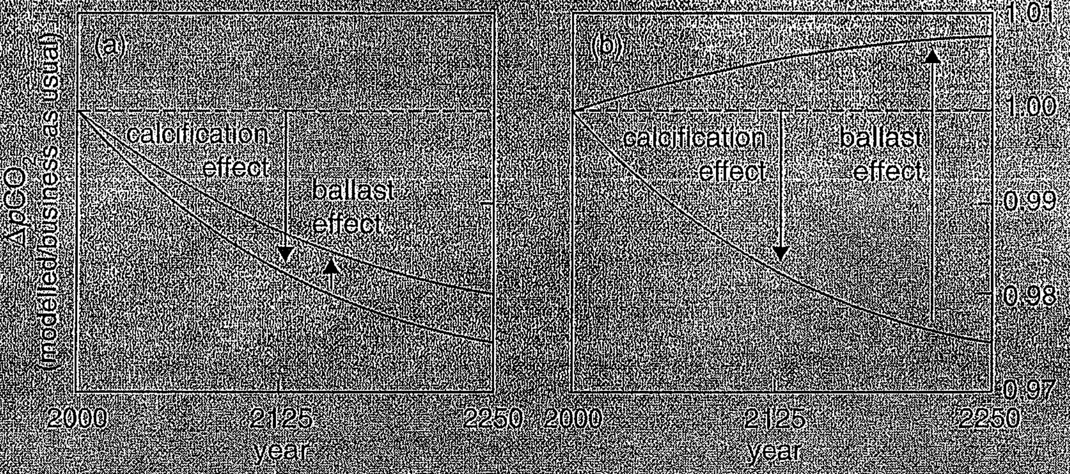
4.4.2 Modeling priorities

A successful research strategy requires modeling be included from the outset. In the early stages, models can guide research design (experiments and observations; sensitivity tests to bound particular processes), and field designs should specifically address activities for model validation. The obvious first step toward this greater integration of modeling is to conduct a census of available models—hydrodynamic through ecological—and data available for input and valida-

Box 6—Current Modeling of $CaCO_3$ Processes Within the Global Carbon Cycle

Most modeling efforts addressing calcium carbonate production have focused on the role of $CaCO_3$ production, export, and dissolution on the marine carbon cycle. The state-of-the-art technique for predicting biogenic $CaCO_3$ production is ecosystem modeling (imbedded within ocean general circulation models) that typically contain two to five functional types of phytoplankton (Moore *et al.*, 2002; Bopp *et al.*, 2003; Aumont and Bopp, in press). $CaCO_3$ export (and its ratio with POC) may be modeled as competition between a functional calcifier and the other plankton (e.g., silicifiers) where dominance is determined by differential grazing pressures and physical oceanographic conditions. However, the calcifier is always patterned after the bloom-forming coccolithophore *E. huxleyi*, which may or may not be the dominant producer of $CaCO_3$.

The traditional alternative to complex ecosystem formulations, taken in box models and many global circulation models, has been to prescribe either a spatially (and temporally) invariant ratio between $CaCO_3$ and particulate organic carbon ($CaCO_3$:POC) production (Broecker and Peng, 1986; Yamanaka and Tajika, 1996; Archer *et al.*, 1998), or to estimate the $CaCO_3$:POC ratio based on temperature and/or opal production (Archer *et al.*, 2000; Heinze, 2004). However, none of the above methods (ecosystem or alternatives) are capable of predicting a response of calcification and carbonate export to surface ocean acidification. Several recent attempts have been made to address this and incorporate a response of the $CaCO_3$:POC rain ratio to surface ocean carbonate chemistry. These model parameterizations have been based on the deviation from modern surface ocean conditions of either CO_2 partial pressure (Heinze, 2004) or carbonate ion concentrations (Barker *et al.*, 2003).



Example of modeling the combined effects of reduced calcification and reduced $CaCO_3$ ballast on atmospheric pCO_2: (a) reduced calcification acts to lower atmospheric pCO_2, while reduced $CaCO_3$ ballasting of organic carbon acts to increase atmospheric pCO_2; (b) the same calculations but allowing for increased dissolution and remineralization rates (20% shorter remineralization length scales). Reprinted from Barker *et al.* (2003), with permission from the Royal Society of London.

tion. For example, a number of coastal models designed for estuaries can be modified to study coastal calcification processes, but as yet do not include the carbonate system.

Most of the priorities for modeling (**Table 4.5**) parallel concerns noted elsewhere in this document. Workshop participants recommended four main areas of model development needed to tackle these priorities:

1. *Streamlining and standardization:* Develop standard computer codes for addressing specific needs (calcification, dissolution) and make them available to the community;
2. *Hydrodynamics:* Conduct a census of coastal hydrodynamic models that could be adapted for use in coastal carbon cycle modeling;
3. *Ecological modeling:* Conduct a census of ecological models that can be used in carbon cycle modeling. Some of the complex ecosystem models already available for coastal systems could be adapted to examine effects of reduced calcification. This census should be conducted for both benthic and pelagic systems, as well as for models that couple the two; and
4. *Intensive modeling:* Select a high-intensity study area where detailed modeling can be validated and used to examine the most important processes with sufficient modeling complexity.

5. Technology Needs and Standardization of Measurements

5.1 Carbonate Chemistry

5.1.1 Carbonate system measurements

The carbonate chemistry of seawater is so complex that it can be a challenge to accurately measure changes and attribute observed changes to specific mechanisms. One of the key carbon species to quantify for calcification studies is the carbonate ion concentration ($[CO_3^{2-}]$). At this time $[CO_3^{2-}]$ cannot be directly measured. Laboratory studies are underway to develop a method for optically measuring $[CO_3^{2-}]$, but it will be a few years before this is an operational technique. Currently there are four measurable parameters: CO_2 partial pressure (pCO_2), total alkalinity (A_T or TA), total dissolved inorganic carbon (DIC), and pH. Using the thermodynamic dissociation constants and assumptions about the composition of seawater as a function of salinity, the distribution of all the carbonate species can be calculated from the concentrations of any two of these measurable quantities.

The most common measurements for open-ocean discrete water samples are DIC and A_T. DIC is typically measured using a coulometric titration with a semi-automated sample delivery system. The most common system, a single-operator multi-parameter metabolic analyzer (SOMMA), is fitted with a 20- to 30-mL pipette and calibrated by filling a gas loop with a known volume of pure CO_2 gas, then introducing the gas into the carrier gas stream and performing coulometric titration (Johnson *et al.*, 1987; Johnson and Wallace, 1992; Johnson *et al.*, 1993; Johnson *et al.*, 1998). Some systems are calibrated by analyzing sodium carbonate standards. DIC systems that are not coupled with a semi-automated sample analyzer typically introduce the sample manually with a pipette or a syringe. Typical open-ocean accuracy and precision are ±1–2 μmol/kg.

A_T measurements are made by potentiometric titration (using a titrator and a potentiometer). A_T can be determined either by characterizing a full titration curve (Brewer *et al.*, 1986; Millero *et al.*, 1993; DOE, 1994; Ono *et al.*, 1998) or by a single-point titration (Perez and Fraga, 1987). Common analytical differences between systems are in the volume of sample analyzed, the use of either an open or closed titration cell, and the calibration methods. Results can also be obtained from different curve-fitting techniques such as Gran plots, nonlinear fitting, or single-point analysis. Typical open-ocean accuracy and precision are ±2–4 μmol/kg.

Two different types of instruments are typically used to measure discrete pCO_2 samples. The main difference between the systems is the sample size. One system uses ~500 mL samples equilibrated by bubbling a recirculated 50 mL headspace gas through the sample. There is also a small volume technique which equilibrates a 10 mL headspace with a 120 mL sample. With each, an aliquot of seawater is equilibrated at a constant temperature of either 4 or 20°C with a head space of known initial CO_2 content. Subsequently, the head space CO_2 concentration is determined by a nondispersive infrared (NDIR) analyzer or by quantitatively converting the CO_2 to CH_4 and analyzing the concentration using a gas chromatograph (GC) with a flame ionization detector. The initial pCO_2 in the water is determined after correcting for loss (or gain) of CO_2 during the equilibration process. This correction can be significant for large initial pCO_2 differences between the head space and the water, and for systems with a large head-space-to-water volume ratio (Chen *et al.*, 1995). Estimates of precision based on duplicate samples range from 0.1 to 1%,depending on pCO_2 level and the measurement procedure, with higher pCO_2 levels on the small volume system (>700 μatm), being the least reproducible (Chen *et al.*, 1995).

The pH of seawater can be determined using pH electrodes, or more precisely, by a spectrophotometric method (Clayton and Byrne, 1993). The spectrophotometric technique involves adding a pH sensitive indicator (usually m-cresol purple) to a fresh seawater sample and looking at the relative absorbance of the protonated and un-protonated species using either a scanning or diode array spectrophotometer. Variability in the spectrophotometer response is corrected by looking at wavelengths outside of the range of the indicating dye. The results are also a function of the temperature and pressure of the sample at the time of measurement. Seawater pH is not a common open ocean measurement because samples cannot be preserved and must be measured soon after collection, but it does provide a key variable for calcification studies. The estimated accuracy of the spectrophotometric method is ±0.002, although individual precision estimates using this technique may be much better.

Although these techniques are very useful for mesocosm or water column studies from ships, some of the studies outlined in this report require sampling at much higher frequencies or over longer temporal ranges. These measurements can be obtained with autonomous instruments. Carbon researchers have been making high-resolution surface pCO_2 measurements from moving ships for decades using semi-autonomous instruments. These typically use an equilibrator that equilibrates a small, fixed volume of air with essentially an infinite volume of water. The equilibrated air is then analyzed in a manner similar to the discrete pCO_2 measurement using either an infrared detector or a GC (e.g., Wanninkhof and Thoning, 1993; Feely *et al.*, 1998). These systems are regularly calibrated by analyzing gas from a series of known CO_2 concentrations. This technology has also been adapted for use on moorings with a surface buoy.

Underway shipboard pH measurements have also been made using the spectrophotometric method. This technique mixes a colorimetric dye into a flowing seawater stream which is then run through the spectrophotometer. The system is "calibrated" by looking at the wavelengths that are not affected by the dye. This basic principle has also been adapted for a variety of autonomous instruments. The most common instruments determine seawater pCO_2 by taking a dye solution with a known alkalinity and allowing it to equilibrate with ambient seawater conditions. The CO_2 that diffused into the dye solution changes the pH, which is determined with a spectrophotometer. Using the known A_T and measured pH, the pCO_2 of the seawater can be calculated.

Continuous-flow-through analyzers have been developed for DIC (Kimoto *et al.*, 2002) and A_T (Watanabe *et al.*, 2004), for use in shallow-water coastal zones. The continuous DIC analyzer strips CO_2 from an acidified sample, and the CO_2 is then measured with an NDIR analyzer. The flow-through A_T analyzer is based on continuous potentiometric measurements. These systems can measure DIC and A_T at frequencies of 1–5 minutes, with precisions and accuracies of about 2 μmol kg^{-1} in the laboratory (Watanabe *et al.*, 2004). These instruments have been incorporated into an integrated carbonate chemistry monitoring system that additionally measures temperature, pH conductivity, and dissolved oxygen (Kayanne *et al.*, 2002). The integrated system has been used successfully to obtain continuous measurements on reef flats from an anchored boat in Ishigaki and Palau for 6–10 days (Kayanne *et al.*, 2005). The spectrophotometric method has also been adapted for making underway A_T and DIC measurements by comparing acidified water samples to un-acidified samples. Although a few prototype systems have been demonstrated to work, they have not been developed for common oceanographic use.

Moorings and drifting buoys provide another effective way to obtain high temporal resolution data over extended periods, but they have the additional challenge of very limited power and space that typically are not a problem on ships. Variations on the basic principles described for the ship-board systems are also being investigated for the development of autonomous carbon measurements. Two basic types of instruments have been adapted for long-term, truly autonomous deployments in the ocean. One class of instrument uses the spectrophotometric technique to measure pCO_2 in seawater (e.g., Merlivat and Brault, 1995; DeGrandpre *et al.*, 2002). These instruments have been successfully deployed for at least six months in both open-ocean and coastal environments. Although the current commercially available systems are set up to measure pCO_2, they can be easily adapted to measure pH. Another type of instrument that has been successfully deployed in both open-ocean and coastal environments for at least six months is based on the NDIR analyzer (e.g., Friederich *et al.*, 1995). These systems are very similar to the underway ship-board systems in that they equilibrate a large volume of water with a relatively small volume of air and then measure the CO_2 in the equilibrated air.

High resolution data from autonomous systems have been shown to resolve rapid changes in the carbonate system of water overlying the reefs, results which are difficult to obtain through discrete sampling (e.g., `http://www.pmel.noaa.gov/co2/coastal/kbay/`). To fully constrain the carbon system at least two carbon system parameters need to be measured. Although systems are available for pCO_2 and pH, these two parameters co-vary so strongly that they do not make the ideal pair to measure. Several groups are working to develop autonomous DIC and A_T systems that can be deployed on moorings. These systems will allow a more thorough examination of the short-term controls on the carbonate system over extended periods.

5.1.2 Standardization of carbon system measurements

A key to high quality, reproducible carbon measurements is routine analysis of carbon standards. In a recent compilation and quality assessment of global ocean carbon data, the single most useful source of information about data quality was based on the analysis of Certified Reference Materials (CRMs) (Sabine *et al.*, 2005). The mean of a series of CRM analyses conducted over the course of a cruise provides a direct link to the manometric[1] standard for DIC and a critical tool for comparison with data from other cruises where CRMs were also run.

This analysis also provides a useful comparison between multiple instruments being run on a cruise. The standard deviation of the mean CRM results provides an assessment of the long-term stability and precision of the instrument(s). Examination of at least daily CRM analyses can provide a good record of the consistency of the measurements throughout the cruise and can identify when potential offsets might have occurred. The CRMs are intended as a secondary standard to validate the accuracy of the primary calibration, but in the event of a catastrophic failure in the calibration system, the CRMs, together with a good history of CRM analyses on that instrument when the calibration system was working, may provide a way of manually calibrating the instrument. CRMs are currently certified for DIC and A_T and are available at `http://andrew.ucsd.edu/co2qc/`. For this reason, A_T and DIC are the currently preferred measurable carbon system parameters for defining the carbonate system.

5.2 Calcification and Dissolution Rates

5.2.1 Benthic organisms and ecosystems

A wide range of methods to measure calcification rates are available depending on the temporal and spatial scale of the question being asked (**Table 5.1**). Calcification rates in living corals and other benthic organisms are obtained by three basic means: (1) measurement of the uptake of ^{45}Ca into the skeleton; (2) change in the mass of skeleton over time (e.g., buoyant weight technique); and (3) the alkalinity anomaly technique, which estimates calcification rate by tracking changes in alkalinity of some known volume of surrounding seawater. While the ^{45}C methods are thought to yield values closer to the gross rate of calcification (at least when measured over very short time periods), the buoyant weight and alkalinity anomaly methods yield net calcification values; i.e., gross calcification minus dissolution. The buoyant weight and alkalinity anomaly methods have the advantage of being nondestructive.

The most useful unit of calcification rate for ecological and carbon cycle studies is moles of $CaCO_3$ per square meter of planar seafloor per unit time. Calcification rates of organisms are, however, often expressed as or normalized to (a) surface area of the organism being tested, (b) per gram of skeleton, (c) per gram dry weight of tissue, or (d) per gram of protein extracted from the tissue. These normalization methods have the advantage of reducing variability between specimens but make it very difficult to extrapolate the results to the field because statistics on surface area of the organism, grams of skeleton, grams dry weight of tissue, and grams of tissue protein, are generally lacking for natural systems. It is recommended that future studies employ experimental setups such as flumes or mesocosms that permit reporting results in ecologically useful units; i.e., moles $CaCO_3$ per square meter of planar seafloor per unit time. Some intercomparisons have been made between calcification measurements (Smith and Kinsey, 1978; Chisholm and Gattuso, 1991; Tambutté *et al.*, 1995), but many have not and further intercomparisons are recommended to determine their compatibility.

Measurements of coral "growth rates" in the literature usually refer to skeletal extension rates. Although linear extension in the commonly used Indo-Pacific *Porites* spp. is strongly correlated with calcification rate, this correlation does not hold for many other species (Lough and Barnes, 2000; Carricart-Ganivet, 2004) and thus skeletal extension alone is not a reliable proxy for calcification rates. The best records of calcification rates in coral cores or slabs are obtained by combining measurements of both skeletal extension (width) and skeletal density (X-ray radiography, tomography, or gamma densitometry) of annual density bands (e.g., Chalker and Barnes, 1990; Lough and Barnes, 1997). The product of the two measurements yields calcification rates that are typically reported as mass or moles of $CaCO_3$ per square centimeter of coral surface per year.

On geological timescales calcification has been estimated from geometric measurements of reef volume and density of the reef framework. Typically, these entail rather rough estimates based on dated cores, but seismic data can provide 3-dimensional measure-

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[1] A DIC-measuring technique that converts DIC to CO_2 and collects it in a known volume so that the pressure of the CO_2 gas can be measured.

Table 5.1: Methods used to measure calcification rates in benthic and planktonic calcifying organisms, populations, and communities; O = organism, P = population, C = community.

Technique	Applicability	Timescale	Examples	Reference
Radioisotope (incorporation of ^{45}Ca or ^{14}C into skeleton)	O,P	minutes to hours	coccolithophores	Paasche, 1964; Balch and Kilpatrick, 1996; Paasche *et al.*, 1996
			pteropods, heteropods	Fabry, 1989, 1990
			foraminifera	Anderson and Faber, 1984; Lea *et al.*, 1995; Erez, 1983
			corals, calc. algae	Goreau, 1963
ΔA_T	O,P,C	minutes to months	coccolithophores	Sikes *et al.*, 1980
			corals	Chisholm and Gattuso, 1991
			coral reef comm.	Smith, 1973
$\Delta[Ca^{2+}]$	O,P,C	minutes to months	corals	Chisholm and Gattuso, 1991; Al-Horani *et al.*, 2003
			coral reef comm.	Debgoswami *et al.*, 1990
Buoyant weight (increase in skeletal mass)	O,P	days to months	corals	Jokiel *et al.*, 1978
pH-O_2	O,P,C	hours	corals	Jacques and Pilson, 1980
			coral reef comm.	Barnes, 1983
Coral density banding (extension between bands × density)	O	months to 100s of years	corals	Lough and Barnes, 2000
Change in particulate inorganic carbon (PIC)	O,P,C	hours to weeks	coccolithophores	Riebesell *et al.*, 2000; Zondervan *et al.*, 2001; Sciandra *et al.*, 2003; Delille *et al.*, 2005
Change in particulate $[Ca^{2+}]$	O,P,C	hours to weeks	coccolithophores	van Bleijswijk *et al.*, 1994; Paasche, 1999
Change in shell dimensions or mass	O,P	days to years	pteropods	Redfield, 1939; Kobayashi, 1974; Wells, 1974
			foraminifera	Bijma *et al.*, 1999
Secondary production-instantaneous growth rate method (instantaneous growth rate × stocking stock)	P	days to years	pteropods, heteropods	Fabry, 1989, 1990
			ophiuroids	Migné *et al.*, 1998
			benthic invertebrates	Smith, 1972
Sediment trap	P,C	days to years	foraminifera	Deuser and Ross, 1989
			pteropods, heteropods	Betzer *et al.*, 1984; Fabry and Deuser, 1991
			coccolithophores	
Sedimentological	O,P	months	benthic foraminifera	Langer *et al.*, 1997
Geological (thickness × density/time)	O,P,C	1000s of years	corals	Chave *et al.*, 1972

ments of reef volume that better constrain estimates of $CaCO_3$ accumulation (Ryan *et al.*, 2001).

Understandably, these techniques do not necessarily measure the same aspect of calcification rate. Coral calcification rates taken over hours to weeks may not be comparable to calcification rates integrated over an entire year. In some measurements, dissolution and inorganic cementation must also be taken into account. There have been few, if any, studies comparing these different types of measurements.

5.2.2 *Planktonic organisms and systems*

Accurate measurement of calcification in planktonic organisms is challenging, and workers have used a variety of methods (**Table 5.1**). One commonly used method involves addition of radioisotope ($NaH^{14}CO_3$ or $^{45}CaCl$) to seawater samples that are subsequently incubated, and the incorporation of radioisotope into biogenic $CaCO_3$ is measured with a liquid scintillation counter. This method has the advantage of high sensitivity, and therefore can be used in short-term incubations. Calcification rates must be corrected for the passive exchange of radioisotope with stable calcium or carbon in the shell, however, and this can be problematic if the exchange rate is high relative to the calcification rate. In addition, internal pools of carbon or calcium can result in a lag time before the radioisotope appears in the shell, and accurate calcification rates can only be measured after any internal pools have equilibrated with the ambient seawater (Erez, 2003). A range of radioisotope techniques have been used to measure calcification rates in laboratory cultures, mesocosms, and field populations of coccolithophores (e.g., Paasche, 1964; Paasche and Brubak, 1994; van der Wal *et al.*, 1994; Balch and Kilpatrick, 1996; Delille *et al.*, 2005), foraminifera (e.g., Caron *et al.*, 1981; Erez, 1983; Anderson and Faber, 1984; Lea *et al.*, 1995), and pteropods (Fabry, 1989, 1990). Calcification rates determined with radioisotopes are typically recorded as mass or moles of C or $CaCO_3$, per cell or individual organism, per unit time (e.g., pg C $cell^{-1}$ d^{-1} or μmol $CaCO_3$ $individual^{-1}$ h^{-1}). Radioisotope-derived calcification rates are normalized to chlorophyll in coccolithophores and shell mass in foraminifera and pteropods.

Calcification rates in planktonic foraminifera and pteropods have also been reported as a function of shell size or mass versus time in laboratory experiments (Bijma *et al.*, 1999; Erez, 2003) and in field studies (Redfield, 1939; Kobayashi, 1974; Wells, 1976). One advantage of this method is that it is nondestructive. However, shell size may not be a reliable measure because many species increase the thickness of their tests as they grow rather than shell length or diameter. Use of this method in the field is limited to regions where the same population can be repeatedly sampled over time.

The instantaneous growth rate method of measuring secondary production has been used to estimate aragonite production in pteropods and heteropods (Fabry, 1989, 1990). This method combines short-term calcification rates with the standing stocks of pteropod and heteropod aragonite to estimate production in units of mass or moles $CaCO_3$ m^{-2} d^{-1}. Ideally, instantaneous growth rates should be determined over a range of size classes, unless it is known that the organism's calcification rate is constant throughout its life. Because the instantaneous growth rate method assumes a stable population over the time interval of sampling, its use in planktonic organisms may be best suited to estimate daily rates of production.

In coccolithophores, changes in the concentrations of particulate calcium or inorganic carbon have been used to estimate net calcification rates, typically in units of mass or moles C or $CaCO_3$ per cell or unit volume per day. This method has been used most often in cultures or mesocosms where coccolithophore calcite was the only source of $CaCO_3$ (e.g., van Bleijswijk *et al.*, 1994; Paasche, 1999). Recent advances in estimating the standing stocks of particulate inorganic carbon include in situ measurements using a birefringence method (Guay and Bishop, 2002) and the use of algorithms with satellite data (see section 4.1.4).

Sediment traps have been used extensively to estimate $CaCO_3$ export fluxes in many ocean regions (e.g., Betzer *et al.*, 1984; Fabry and Deuser, 1991; Honjo *et al.*, 1995; Wong *et al.*, 1999). As previously discussed, problems with swimmers and dissolution within the trap can confound $CaCO_3$ flux estimates, particularly when sediment traps are located in the upper 1000 m. The export fluxes measured by sediment traps are necessarily less than $CaCO_3$ production rates because they do not include $CaCO_3$ dissolution fluxes within the water column.

5.2.3 *Standardization of calcification measurements*

Given the diverse methods and experimental protocols used to measure calcification rates in planktonic and benthic species and systems, there is a need to standardize calcification rate measurements to allow comparison among data sets. A high priority in advancing research on the impacts of anthropogenic CO_2 on calcifying organisms is the formation of a working group charged with evaluating methods and proposing recommendations for calcification rate measurements of planktonic and benthic organisms in laboratory, mesocosm, and field experiments. The focus of the work group should include evaluating (1) what information each method provides (e.g., gross or net $CaCO_3$ production), and (2) methods for measuring and reporting seawater chemistry and calcification rates. To maximize information exchange, the group should include scientists from both the planktonic and benthic research communities.

5.2.4 *Other measurements*

Many environmental factors including light (Chalker and Taylor, 1975, 1978; Barnes, 1982; Marubini *et al.*, 2001), temperature (Houck *et al.*, 1977; Coles and Jokiel, 1978; Marshall and Clode, 2004), nutrients (Hoegh-Guldberg and Smith, 1989; Stambler *et al.*, 1991; Marubini and Davies, 1996; Marubini and Thake, 1999; Ferrier-Pagés *et al.*, 2000), water motion (Atkinson *et al.*, 1994; Lesser *et al.*, 1994), food availability, and grazing can affect rates of calcification. All must be carefully controlled or monitored in well-designed experiments to avoid a misinterpretation of the results.

Another important issue is the potential effect of changing pH on the speciation of major elements besides inorganic carbon. Changes in pH can generate a cascade of dissolution and precipitation effects on minerals and chemical species that are often not considered. For example, the sensitivity of Mn and Fe minerals and adsorbed ions to small pH changes can alter their availability in the system, and these potential effects on experimental outcomes should be accounted for or considered.

6. Engaging the Scientific Community and Public

DISSEMINATING RESEARCH FINDINGS about the impacts of CO_2 on marine calcifiers to the general research community, the public, and educators is recognized as a growing responsibility of our community. As public awareness about climate change and impacts on marine ecosystems increases, so does demand for up-to-date and clear information. There are several avenues for informing the wider community, including the media, the internet, and published materials. The oceanographic community has typically used all three approaches.

6.1 Media

The media provides the most direct link between scientists and the community, but the effectiveness of how well the media conveys important scientific findings to the public is often no better than how well the scientists communicate with the media. Unfortunately, the topic of ocean acidification and how it affects marine organisms is complex and requires more explanation than, say, the atmospheric greenhouse affect. To improve our communication with the public, we therefore recommend improving media access to this topic, by involving them in scientific meetings and public discussions of our research results. Involving media students in large research projects (internships) would be a particularly effective way of promoting media accuracy, while providing the students with a unique opportunity in scientific reporting.

6.2 Web

Web-based communication of research results and issues of concern to the community is an increasingly popular education-outreach medium. In order to coordinate and streamline outreach activities we recommend support for a community-wide website dedicated to the impacts of CO_2 and climate on marine calcifiers. It should address the broad scientific issues, highlight new research findings, and provide a teaching resource for education, including K-12 educators. These efforts should also be designed within the scope of the larger U.S. Climate Change Science Program to maximize input for K-12 outreach activities, by identifying new ideas that can be developed and incorporated into a community-wide website.

6.3 Data Resources

Several websites disseminate data for studies on ocean acidification and marine calcification, for example: the Carbon Dioxide Information and Analysis Center (CDIAC; `http://cdiac.esd.ornl.gov/`), which provides a wealth of information and data related to the large-scale ocean carbon system; the NOAA Coral Reef Information System, which provides data on calcification rates derived from *Porites* cores (`http://coris.noaa.gov/metadata/records/html/paleoclimatology_masthead_2001.html`); and the USGS South Florida Information Access website, which provides data on air-sea CO_2 fluxes in Florida Bay (`http://sofia.usgs.gov/projects/geo_monitor/maps/carbon-fluxes/`). However, there is no organized effort to assimilate data resources for research on the effects of ocean acidification on marine biota. Indeed, most information derived from past and future studies on marine calcification response to ocean acidification is typically only available on a researcher-by-researcher basis.

The broad range of information that should be assimilated and made available to researchers includes publications, sampling and experimental protocols, standard hydrographic data, data from experimental results, and modeling resources. Establishing these resources is an important recommendation of this research guide, and will require dedicated resources to organize and distribute published information, obtain and quality control data, and disseminate the information via a central website. These issues should be well thought out and planned prior to any significant undertaking of research on ocean acidification and marine calcification. Successful ocean research programs in the past have benefited greatly by addressing the larger scale needs of data collection and dissemination from the outset of a research design. These programs were successful because expert teams were dedicated to ensuring proper data collection (much of which is expensive and irreproducible) and timely dissemination. We therefore recommend that future research projects include an explicit commitment to organize data resources relevant to the ocean acidification and marine calcification issue, and to establish protocols for obtaining high-quality data (e.g., standards for collection, reporting, and quality control of inorganic carbon system measurements; standards of calcification measurements; recommended experimental guidelines; as described in Section 5 of this report).

6.4 Teaching Resources

The topic of ocean acidification and its impacts on marine calcifiers is new and with relatively few specialists, and the science can be confusing. Upcoming research efforts will need to entrain young scientists in this area and to inform the public in ways that are understandable and relevant. We recommend that training of new M.S. and Ph.D. scientists and postdoctoral researchers in carbon cycle and marine ecosystem science be promoted by supporting their participation in nearly every aspect of the program and by reserving a certain percentage of slots at meetings and workshops for young scientists.

Emphasis should also be placed on encouraging constituencies and local communities to better understand the impacts of climate change on marine ecosystems, to promote informed decision making, and to increase stakeholder support for and participation in marine ecosystem conservation. Examples of education and outreach activities include: workshops and training programs with constituents to provide access and orientation to current research findings and data; planned development and distribution of educational materials and displays; fostering community involvement in conservation and restoration projects; and hosting two-way discussions with stakeholders to improve mutual understanding of resource needs and management goals.

Developing partnerships with K-12 schools, Centers for Ocean Science Education Excellence (COSEE), the National Sea Grant Program (Sea Grant) and community organizations can use educational resources and encourage stewardship throughout the community by service learning projects and other initiatives that involve teachers and parents in the process of student learning. Education programs should focus on translating the latest research into activities that help students understand the complex interactions of climate and marine ecosystems and the need for scientists from diverse backgrounds. The training of educators in the use of coral reef science and education materials should also be emphasized to ensure the effectiveness of education programs. This could be coordinated through the proposed National Ocean Education Office as recommended by the U.S. Commission on Ocean Policy (2004).

7. Conclusions and Recommendations

7.1 Impacts of Anthropogenic CO_2 in the Oceans

THE UPTAKE OF ANTHROPOGENIC CO_2 by the ocean changes the seawater chemistry and will significantly impact biological systems in the upper oceans. Estimates of future atmospheric and oceanic CO_2 concentrations, based on the Intergovernmental Panel on Climate Change (IPCC) emission scenarios and general circulation models indicate that atmospheric CO_2 levels could exceed 500 ppmv by the middle of the 21st century, and 800 ppmv by 2100. Corresponding models for the oceans indicate that by 2100, surface water pH will decrease by approximately 0.4 pH units relative to the preindustrial value, lower than it has been for more than 20 My. The carbonate ion concentration will also decrease by almost 50% relative to preindustrial levels. Such changes will significantly lower the ocean's buffering capacity and, therefore, reduce its ability to accept more CO_2 from the atmosphere.

Recent field and laboratory studies reveal that the carbonate chemistry of seawater has a significant effect on the calcification rates of individual species and communities in both planktonic and benthic habitats. The calcification rates of most calcifying organisms studied to date decrease in response to decreased carbonate ion concentration. This response has been observed in multiple taxonomic groups—from reef-building corals to single-celled protists. Experimental evidence points to a 5–50% reduction in calcification rate under a CO_2 level twice that of the preindustrial. The decreased carbonate ion concentration significantly reduces the ability of reef-building corals to produce their $CaCO_3$ skeletons, affecting growth of individual corals and the ability of the larger reef to maintain a positive balance between reef building and reef erosion. Several groups of calcifying plankton—coccolithophorids (single-celled algae), forams, and pteropods (planktonic molluscs)—also exhibit a reduction in their calcium carbonate structures. Many of these organisms are important components of the marine food web.

The effects of reduced calcification on individual organisms and on ecosystems have not been investigated, however, and have only been inferred from knowledge about the role of calcification in organism and ecosystem functioning. This knowledge is limited because calcification rates have only recently been considered vulnerable to increased atmospheric CO_2. Because calcification provides some advantage (or multiple advantages) to calcifying organisms, decreased calcification is likely to compromise the fitness or success of these organisms and could shift the competitive advantage toward non-calcifiers. There is also little information regarding the capacity of calcifying organisms to adapt to changing seawater chemistry. Coral reef organisms have not demonstrated an ability to adapt to decreasing carbonate saturation state, but experiments so far have been relatively short-term (hours to months). Some planktonic organisms, particularly those with rapid generation times, may be able to adapt to lowered saturation state via natural selection. Planktonic calcifiers that cannot adapt to future changes in seawater chemistry are likely to experience reductions in their geographic ranges, or latitudinal shifts. Decreased calcification in marine organisms is likely to impact marine food webs and, combined with other climatic changes in temperature, salinity, and nutrients, could substantially alter the biodiversity and productivity of the ocean.

Seawater pH is a master variable that impacts the speciation of the carbonate system, nutrients, and other major and trace element species in the oceans. It is largely unknown if, or how, various organisms will adapt to the large-scale pH changes that are anticipated over the next two to three centuries. At present, it is not possible to determine how the community structure will change or how these ecosystem changes might influence future climate feedback mechanisms. It is therefore important to develop new research strategies to better understand the long-term vulnerabilities of sensitive marine organisms to these changes. We are just beginning to understand the complex interactions between large-scale changes in ocean chemistry and marine ecological processes. Clearly, seawater carbonate chemistry is changing over decadal and longer timescales and these changes will impact marine biota.

7.2 Research Needs

Data from across the scientific disciplines support the hypothesis that marine calcification and dissolution are largely controlled by carbonate chemistry, elevating the concern that increasing CO_2 poses a considerable threat to the health of our oceans. But these data are sparse, and extrapolating results from controlled experiments to the natural environment is risky. Several workshops and reports have addressed the overall scientific issues of marine calcification under elevated atmospheric CO_2. The St. Petersburg workshop attempted to summarize these issues, identify the most important gaps in our understanding, and provide guidance toward designing research to address them.

Understanding the biological consequences of ocean acidification and placing these changes in a historical context are in the early stages. Now is the time to coordinate scientific research strategies to maximize scientific findings. This is a complex scientific undertaking, and it is essential that new research is well informed by experimentalists and observationalists in marine chemistry, biology/ecology, and geology; and experts in ocean monitoring and technology, paleoreconstructions, and modelers. It is also essential to entrain young scientists into this field, and to provide them with materials that can help guide their research.

Given the broad array of research needs, participants of the St. Petersburg Workshop recommended a research design that could be logically phased based on criteria such as: (a) the most compelling research needs; (b) research that could be done now versus that which requires longer-term planning; (c) research that requires significant technological development; and (d) research that can take advantage of ongoing field activities. **Table 7.1** lists only the most compelling research needs and should not be considered a complete list of necessary research; nonetheless it offers a framework for coordinating an overall research plan to tackle the issue of marine calcification under increasing atmospheric CO_2. Phase I represents high-priority research needs that can be initiated immediately. Phase II represents research that requires additional long-term planning and coordination, and Phase III represents research that requires some additional technological developments for success.

The St. Petersburg participants agreed on several parallel courses of research for the next 5–10 years. First, sustained observations of changes in the ocean carbon system should be continued. Second, additional field and laboratory investigations into the biological and ecological responses of calcifiers to increasing CO_2 should be conducted. Among these, long-term field manipulation experiments present the most compelling and challenging research needs. Third, these observations and experiments should be founded on a strong set of proven standards for chemical and biological measurements, and should be augmented with paleo-records and proxies that can shed light on the natural response of the system over different timescales. Fourth, simultaneous development of ecosystem models is essential if we are to translate future changes in ocean chemistry and calcification/dissolution rates to ecosystem response.

Many researchers have paved the way along these four courses toward tackling the important questions about calcification and dissolution response to increased ocean acidification. We can build on their efforts to understand the capacity for organisms and ecosystems to adapt to carbonate chemistry changes, and to predict the future of marine calcification and its feedback to the marine carbon cycle and global climate.

7.3 Research Collaborations

Collaborative research on the impacts of enhanced atmospheric CO_2 on ocean chemistry and biology needs to be accelerated at the national and international levels. Emphasis should be placed on developing a better understanding of how changes in the metabolic processes at the cellular level will be manifested within the ecosystem or community structure, and how they will influence the climate feedbacks of the future. A fully integrated system of laboratory, mesocosm, field monitoring, and modeling approaches is required to provide policymakers with informed management strategies that address how humans might best mitigate or adapt to these long-term changes.

Such efforts should complement ongoing research programs in marine biogeochemistry and ecology (e.g., OCCC, Ocean Carbon and Climate Change; SOLAS, Surface Ocean-Lower Atmosphere Study; IMBER, Integrated Marine Biogeochemistry and Ecosystem Research; SCOR, Scientific Committee for Ocean Research; etc.). Many of these programs are international. Indeed, the St. Petersburg workshop and the production of this report included substantial input from our non-U.S. partners and we strongly recommend strengthening these partnerships. Advances in carbon system and calcification measurements, in designing experimental mesocosms, in molecular studies, and in modeling, are among expertise seated across a suite of international labs. Most of the important questions outlined in the report are based on international research efforts, and should

Table 7.1: Key research activities, with a general indication of how they could be coordinated within a phased research plan.

Research Area	Activity	Phase I	Phase II	Phase III
Carbonate system monitoring	Identify key areas for monitoring	×		
	Standardize measurements, reporting	×		
	Coordinate carbonate system monitoring with existing observational systems	×		
	Increase monitoring, particularly in regions with high variability	×	×	×
	Develop technology: autonomous sensors for carbonate system and PIC; remote sensing applications		×	×
	Conduct experiments on dissolution and its response to increased CO_2 (including better understanding of thermodynamic constants for high-Mg calcite)	×	×	×
Physiology of calcification	Conduct experiments to determine the various mechanisms of calcification and the photosynthesis/calcification relationship in autotrophs and in heterotrophs with photosynthetic symbionts	×	×	×
Calcification response and organism response	Develop and standardize methods for measuring calcification rates	×		
	Investigate calcification response across multiple taxa: coccolithophorids; planktonic and benthic forams; pteropods; reef-building and deep-sea corals; *Halimeda*; coralline algae; echinoderms; bryozoans; molluscs	×	×	
	Investigate effects of multiple controls on calcification (e.g., pCO_2, T, light, nutrients)	×	×	
	Investigate potential for organisms to adapt	×	×	×
	Investigate multiple life-stages of organisms	×	×	
	Develop field-based experiments to more realistically simulate pCO_2 effects on calcification		×	
	Develop skeletal proxies for paleo-calcification analysis	×	×	
Ecosystem response	Engage benthic and planktonic ecologists and modelers to identify key needs and design research to address ecosystem response	×		
	Develop and begin long-term monitoring and/or long-term experiments on ecological communities; coordinate with existing ecological monitoring		×	×
	Develop appropriate ecosystem models for planktonic and benthic communities	×	×	×
Biogeochemical response	Open ocean—investigate ecosystem shifts and feedbacks on calcification, sedimentation, carbon cycle	×	×	×
	Quantify "reef-building" and $CaCO_3$ budgets of other benthic systems	×	×	×
	Develop technology such as remote-sensing applications		×	×

be approached with a commitment to nurture these partnerships. In addition, many of the key regions for future research are in international waters, and many interdisciplinary efforts demand that expertise be drawn from beyond U.S. borders. Above all, the urgency of understanding the potential consequences of ocean acidification on marine calcifying ecosystems demands that we design future research on this issue as efficiently as possible, which requires ignoring traditional boundaries so that efforts are complementary rather than duplicated.

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8. References

Accornero, A., C. Manno, F. Esposito, and M.C. Gambi (2003) The vertical flux of particulate matter in the polynya of Terra Nova Bay. Part II. Biological components. *Antarctic Sci., 15*(2), 175–188.

Agegian, C.R. (1985) The biogeochemical ecology of *Porolithon gardineri* (Foslie). Ph.D. Dissertation. University of Hawaii.

Al-Horani, F.A. (2005) Effects of changing seawater temperature on photosynthesis and calcification in the scleractinian coral *Galaxea fascicularis*, measured with O_2, Ca^{2+} and pH microsensors. *Sci. Mar., 69*, 347–354.

Al-Horani, F.A., S.M. Al-Moghrabi, and D. De Beer (2003) Microsensor study of photosynthesis and calcification in the scleractinian coral, *Galaxea fascicularis*: active internal carbon cycle. *J. Exper. Mar. Biol. Ecol., 288*, 1–15.

Al-Moghrabi, S., C. Goiran, D. Allemand, N. Speziale, and J. Jaubert (1996) Inorganic carbon uptake for photosynthesis by the symbiotic coral-dinoflagellate association. 2. Mechanisms for bicarbonate uptake. *J. Exper. Mar. Biol. Ecol., 199*, 227–248.

Allemand, D., P. Furla, and S. Bénazet-Tambutté (1998) Mechanisms of carbon acquisition for endosymbiont photosynthesis in Anthozoa. *Can. J. Bot., 76*, 925–941.

Allemand, D. and others (2004) Biomineralisation in reef-building corals: from molecular mechanisms to environmental control. *C.R. Acad. Sc. Paris Palévol., 3*, 453–467.

Anderson, O.R., and W.W. Faber (1984) An estimation of calcium carbonate deposition rate in a planktonic foraminifer *Globigerinoides sacculifer* using ^{45}Ca as a tracer—a recommended procedure for improved accuracy. *J. Foramin. Res., 14*, 303–308.

Andersson, A.J., F.T. Mackenzie, and L.M. Ver (2003) Solution of shallow-water carbonates: An insignificant buffer against rising atmospheric CO_2. *Geology, 31*, 513–516.

Andersson, A.J., F.T. MacKenzie, and A. Lerman (2005) Coastal ocean carbonate ecosystems in the high CO_2 world of the Anthropocene. *Am. J. Sci., 305*, 875–918.

Andersson, A.J., F.T. Mackenzie, and A. Lerman (2006) Coastal ocean CO_2—carbonic acid—carbonate sediment system of the Anthropocene. *Global Biogeochem. Cy., 20*, doi:10.1029/2005GB002506.

Andréfouët , S., and C. Payri (2001) Scaling-up carbon and carbonate metabolism of coral reefs using in-situ data and remote sensing. *Coral Reefs, 19*, 259–269.

Archer, D. (1996) A data-driven model of the global calcite lysocline. *Global Biogeochem. Cy., 10*, 511–526.

Archer, D., and E. Maier-Reimer (1994) Effect of deep-sea sedimentary calcite preservation on atmospheric CO_2 concentration. *Nature, 367*, 260–264.

Archer, D., H. Kheshgi, and E. Maier-Reimer (1998) Dynamics of fossil fuel CO_2 neutralization by marine $CaCO_3$. *Global Biogeochem. Cy., 12*, 259–276.

Archer, D., A. Winguth, D. Lea, and N. Mahowald (2000) What caused the glacial/interglacial atmospheric pCO_2 cycles? *Rev. Geophys., 38*, 159–189.

Armstrong, R.A., C. Lee, J.I. Hedges, S. Honjo, and S.G. Wakeham (2002) A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. *Deep-Sea Res. II, 49*, 219–236.

Atkinson, M.J., E. Kotler, and P. Newton (1994) Effects of water velocity on respiration, calcification, and ammonium uptake of a Porites compressa community. *Pac. Sci., 48*, 296–303.

Augustin, L. and others (2004) Eight glacial cycles from an Antarctic ice core. *Nature, 429*, 623–628.

Aumont, O., and L. Bopp (in press) Globalizing results from ocean in situ iron fertilization studies. *Global Biogeochem. Cy.*

Balch, W.M., and K. Kilpatrick (1996) Calcification rates in the equatorial Pacific along 140°W. *Deep-Sea Res. II, 43*, 971–993.

Balch, W.M., P.M. Holligan, S.G. Ackleson, and K.J. Voss (1991) Biological and optical properties of mesoscale coccolithophore blooms in the Gulf of Maine. *Limnol. Oceanogr., 36*, 629–643.

Balch, W.M., K.A. Kilpatrick, P. Holligan, D. Harbour, and E. Fernandez (1996) The 1991 coccolithophore bloom in the central North Atlantic. 2. Relating optics to coccolith concentration. *Limnol. Oceanogr., 41*, 1684–1696.

Balch, W.M., D.T. Drapeau, T.L. Cucci, R.D. Vaillancourt, K.A. Kilpatrick, and J.J. Fritz (1999) Optical backscattering by calcifying algae: Separating the contribution of particulate inorganic and organic carbon fractions. *J. Geophys. Res., 104*, 1541–1558.

Balch, W.M., D.T. Drapeau, and J.J. Fritz (2000) Monsoonal forcing of calcification in the Arabian Sea. *Deep-Sea Res. II, 47*, 1301–1337.

Balch, W.M., H.R. Gordon, B.C. Bowler, D.T. Drapeau, and E.S. Booth (2005) Calcium carbonate measurements in the surface global ocean based on Moderate-Resolution Imaging Spectroradiometer data. *J. Geophys. Res., 110*, C07001. doi:10.1029/2004JC002560.

Barker, S., J.A. Higgins, and H. Elderfield (2003) The future of the carbon cycle: review, calcification response, ballast and feedback on atmospheric CO_2. *Philos. Trans. Roy. Soc. Lond. A, 361*, 1977–1998.

Barnes, D.J. (1982) Light response curve for calcification in the staghorn coral, *Acropora acuminata*. *Comp. Biochem. Physiol. A, 73*, 41–45.

— (1983) Profiling coral reef productivity and calcification using pH and oxygen electrodes. *J. Exper. Mar. Biol. Ecol., 66,* 149–161.

Barnes, D.J., and M.J. Devereux (1984) Productivity and calcification on a coral reef—A survey using pH and oxygen-electrode techniques. *J. Exper. Mar. Biol. Ecol., 79,* 213–231.

Bates, N.R. (2001) Interannual variability of oceanic CO_2 and biogeochemical properties in the Western North Atlantic subtropical gyre. *Deep-Sea Res. II, 48,* 1507–1528.

— (2002) Seasonal variability of the effect of coral reefs on seawater CO_2 and air-sea CO_2 exchange. *Limnol. Oceanogr., 47,* 43–52.

Bates, N.R., L. Samuels, and L. Merlivat (2001) Biogeochemical and physical factors influencing seawater fCO_2, and air-sea CO_2 exchange on the Bermuda coral reef. *Limnol. Oceanogr., 46,* 833–846.

Bé, A.W.H. (1980) Gametogenic calcification in a spinose planktonic foraminifer, *Globigerinoides sacculifer* (Brady). *Mar. Micropaleontol., 5,* 283–310.

Berelson, W.M. (2002) Particle settling rates increase with depth in the ocean. *Deep-Sea Res. II, 49,* 237–251.

Berelson, W.M., D.E. Hammond, J. McManus, and T.E. Kilgore (1994) Dissolution kinetics of calcium carbonate in equatorial Pacific sediments. *Global Biogeochem. Cy., 8,* 219–235.

Berger, W.H. (1982) Increase of carbon dioxide in the atmosphere during deglaciation: The coral reef hypothesis. *Naturwissenschaften, 69,* 87–88.

Berner, R.A. (1994) GEOCARB-II—A revised model of atmospheric CO_2 over Phanerozoic time. *Am. J. Sci., 294,* 56–91.

— (1997) Paleoclimate—The rise of plants and their effect on weathering and atmospheric CO_2. *Science, 276,* 544–546.

Berner, R.A., and Z. Kothavala (2001) GEOCARB III: A revised model of atmospheric CO_2 over Phanerozoic time. *Am. J. Sci., 301,* 182–204.

Bessat, F., and D. Buigues (2001) Two centuries of variation in coral growth in a massive *Porites* colony from Moorea (French Polynesia): A response of ocean-atmosphere variability from south central Pacific. *Palaeogeogr. Palaeoclimatol. Palaeoecol., 175,* 381–392.

Betzer, P.R., R.H. Byrne, J.G. Acker, C.S. Lewis, R.R. Jolley, and R.A. Feely (1984) The oceanic carbonate system—A reassessment of biogenic control. *Science, 226,* 1074–1077.

Bijma, J. (1991) Lunar pulses of carbonate output by spinose planktonic Foraminifera, p. 353–354. *In* P.C. Reid, C.M. Turley, and P.H. Burkill (eds.), *Protozoa and Their Role in Marine Processes.* NATO ASI Series G: Ecological Sciences, Elsevier.

Bijma, J., and C. Hemleben (1994) Population dynamics of the planktic foraminifer *Globigerinoides-sacculifer* (Brady) from the central Red-Sea. *Deep-Sea Res. I, 41,* 485–510.

Bijma, J., J. Erez, and C. Hemleben (1990) Lunar and semi-lunar reproductive cycles in some spinose planktonic foraminifers. *J. Foramin. Res., 20,* 117–127.

Bijma, J., C. Hemleben, and K. Wellnitz (1994) Lunar-influenced carbonate flux of the planktic foraminifer *Globigerinoides sacculifer* (Brady) from the central Red Sea. *Deep-Sea Res. I, 41,* 511–530.

Bijma, J., H.J. Spero, and D.W. Lea (1999) Reassessing foraminiferal stable isotope geochemistry: Impact of the oceanic carbonate system (experimental results), p. 489–512. *In* G. Fischer, and G. Wefer (eds.), *Use of Proxies in Paleoceanography: Examples from the South Atlantic,* Springer-Verlag.

Bijma, J., B. Honisch, and R.E. Zeebe (2002) The impact of the ocean carbonate chemistry on living foraminiferal shell weight: Comment on "Carbonate ion concentration in glacial-age deep waters of the Caribbean Sea" by W.S. Broecker, and E. Clark. *Geochem. Geophys. Geosyst.,* 3(11), 1064, doi: 10.1029/2002GC000388.

Bishop, J.K.B., R.W. Collier, D.R. Kettens, and J.M. Edmond (1980) The chemistry, biology, and vertical flux of particulate matter from the upper 1500 m of the Panama Basin. *Deep-Sea Res. A, 27,* 615–640.

Böhm, F. and others (2002) Evidence for preindustrial variations in the marine surface water carbonate system from coralline sponges. *Geochem. Geophys. Geosyst.,* 3(3), doi: 10.1029/2001GC000264.

Bopp, L. and others (2001) Potential impact of climate change on marine export production. *Global Biogeochem. Cy., 15,* 81–99.

Bopp, L., K.E. Kohfeld, C. Le Quere, and O. Aumont (2003) Dust impact on marine biota and atmospheric CO_2 during glacial periods. *Paleoceanography, 18*(2), 1046, doi:10.1029/2002PA000810.

Borges, A.V. (2005) Do we have enough pieces of the jigsaw to integrate CO_2 fluxes in the coastal ocean? *Estuaries, 28,* 3–27.

Borowitzka, M.A. (1981) Photosynthesis and calcification in the articulated coralline red algae *Amphiroa anceps* and *Amphiroa foliacea. Mar. Biol., 62,* 17–23.

Boucher, G., J. Clavier, C. Hily, and J.-P. Gattuso (1998) Contribution of soft-bottoms to the community metabolism (primary production and calcification) of a barrier reef flat (Moorea, French Polynesia). *J. Exper. Mar. Biol. Ecol., 225,* 269–283.

Bown, P.R., J.A. Lees, and J.R. Young (2004) Calcareous nannoplankton evolution and diversity through time, p. 481–508. *In* H.R. Thierstein, and J.R. Young (eds.), *From Molecular Processes to Global Impact,* Springer.

Boyd, P.W., and S.C. Doney (2002) Modelling regional responses by marine pelagic ecosystems to global climate change. *Geophys. Res. Lett., 29*(16), 1806, doi: 10.1029/2001GL014130.

Boyd, P.W. and others (2000) A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. *Nature, 407,* 695–702.

Brennan, S.T., T.K. Lowenstein, and J. Horita (2004) Seawater chemistry and the advent of biocalcification. *Geology, 32,* 473–476.

Brewer, P.G., A.L. Bradshaw, and R.T. Williams (1986) Measurements of total carbon dioxide and alkalinity in the North Atlantic Ocean in 1981, p. 358–381. *In* D. Reiche (ed.), *The Global Carbon Cycle: Analysis of the Natural Cycle and Implications of Anthropogenic Alterations for the Next Century*, Springer.

Brewer, P.G., T. Ohsumi, J. Ishizaka, J. Kita, Y. Watanabe (special editors) (2004) Special Section on Ocean Sequestration of Carbon Dioxide. *J. Oceanogr.*, *60*, 691–816.

Brix, H., N. Gruber, and C.D. Keeling (2004) Interannual variability of the upper ocean carbon cycle at station ALOHA near Hawaii. *Global Biogeochem. Cy.*, *18*, GB4019, doi:10.1029/2004GB002245.

Broecker, W.S. (2003) The Ocean $CaCO_3$ Cycle, p. 1–21. *In* H. Elderfield (ed.), *The Oceans and Marine Geochemistry.* Treatise on Geochemistry, Elsevier Pergamon.

Broecker, W., and E. Clark (1999) Re-evaluation of Lohmann's foraminiferal weight dissolution index. *Paleoceanography*, *16*, 531–534.

Broecker, W.S., and E. Clark (2003) $CaCO_3$ dissolution in the deep sea: Paced by insolation cycles. *Geochem. Geophys. Geosyst.*, *4*(7), 1059, doi: 10.1029/2002GC000450.

Broecker, W., C. Langdon, T. Takahashi, T.-S. Peng (2001) Factors controlling the rate of $CaCO_3$ precipitation on Grand Bahama Bank. *Global Biogeochem. Cy.*, *15*, 589–596.

Broecker, W.S., and T.-H. Peng (1982) *Tracers in the Sea.* Eldigio Press, Columbia University.

Broecker, W.S., and T.-H. Peng (1986) Carbon cycle—1985 glacial to interglacial changes in the operation of the global carbon cycle. *Radiocarbon*, *28*, 309–327.

Broecker, W.S., and T. Takahashi (1966) Calcium carbonate precipitation on the Bahama Banks. *J. Geophys. Res.*, *71*, 1575–1602.

Broecker, W.S., T. Takahashi, H.J. Simpson, and T.-H. Peng (1979) Fate of fossil fuel carbon dioxide and the global carbon budget. *Science*, *206*, 409–418.

Broerse, A.T.C., P. Ziveri, J.E. Van Hinte, and S. Honjo (2000) Coccolithophore export production, species composition, and coccolith $CaCO_3$ fluxes in the NE Atlantic (34°N 21°W and 48°N 21°W). *Deep-Sea Res. II*, *47*, 1877–1905.

Brown, C.W., and J.A. Yoder (1994) Coccolithophorid blooms in the global ocean. *J. Geophys. Res.*, *99*, 7467–7482.

Buitenhuis, E., J. van Bleijswijk, D. Bakker, and M.J.W. Veldhuis (1996) Trends in inorganic and organic carbon in a bloom of *Emiliania huxleyi* in the North Sea. *Mar. Ecol.-Prog. Ser.*, *143*, 271–282.

Burdige, D.J., and R.C. Zimmerman (2002) Impact of sea grass density on carbonate dissolution in Bahamian sediments. *Limnol. Oceanogr.*, *47*, 1751–1763.

Burris, J.E., J.W. Porter, and W.A. Laing (1983) Effects of carbon dioxide concentration on coral photosynthesis. *Mar. Biol.*, *75*, 113–116.

Byrne, R.H., J.G. Acker, P.R. Betzer, R.A. Feely, and M.H. Cates (1984) Water column dissolution of aragonite in the Pacific Ocean. *Nature*, *312*, 321–326.

Caldeira, K., and M.E. Wickett (2003) Anthropogenic carbon and ocean pH. *Nature*, *425*, 365.

— (2005) Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean. *J. Geophys. Res.*, *110*, C09S04, doi: 10.1029/2004JC002671.

Campbell, L., L.P. Shapiro, and E. Haugen (1994) Immunochemical characterization of eukaryotic ultraplankton from the Atlantic and Pacific Oceans. *J. Plankton Res.*, *16*, 35–51.

Caron, D.A., A.W.H. Bé, and O.R. Anderson (1981) Effects of variations in light intensity on life processes of the planktonic foraminifer *Globigerinoides sacculifer* in laboratory culture. *J. Mar. Biol. UK*, *62*. 435–451.

Carricart-Ganivet, J.P. (2004) Sea surface temperature and the growth of the West Atlantic reef-building coral *Montastraea annularis*. *J. Exper. Mar. Biol. Ecol.*, *302*, 249–260.

Catubig, N.R., D.E. Archer, R. Francois, P. Demenocal, W. Howard, and E.F. Yu (1998) Global deep-sea burial rate of calcium carbonate during the last glacial maximum. *Paleoceanography*, *13*, 298–310.

Chalker, B.E., and D.J. Barnes (1990) Gamma densitometry for the measurement of coral skeletal density. *Coral Reefs*, *4*, 95–100.

Chalker, B.E., and D.L. Taylor (1975) Light-enhanced calcification, and role of oxidative-phosphorylation in calcification of coral *Acropora cervicornis*. *Proc. Roy. Soc. Lond. B*, *190*, 323–331.

— (1978) Rhythmic variations in calcification and photosynthesis associated with coral *Acropora cervicornis* (Lamarck). *Proc. Roy. Soc. Lond. B*, *201*, 179–189.

Chave, K.E. (1954) Aspects of the biogeochemistry of magnesium. Part 1. Calcareous marine organisms. *J. Geol.*, *62*, 266–283.

Chave, K.E., S.V. Smith, and K.J. Roy (1972) Carbonate production by coral reefs. *Mar. Geol.*, *12*, 123–140.

Chen, C.T.A. (2003) New vs. export production on the continental shelf. *Deep-Sea Res. II*, *50*, 1327–1333.

Chen, C.T.A., K.K. Liu, and R. Macdonald (2003) Continental margin exchanges, p. 53–97. *In* M.J.R. Fasham (ed.), *Ocean Biogeochemistry: a JGOFS Synthesis*, Springer-Verlag.

Chen, C.T.A., A. Andreev, K.R. Kim, and M. Yamamoto (2004) Roles of continental shelves and marginal seas in the biogeochemical cycles of the North Pacific Ocean. *J. Oceanogr.*, *60*, 17–44.

Chen, H.R., R.A. Wanninkhof, R.A. Feely, and D. Greeley (1995) Measurement of fugacity of carbon dioxide in seawater: An evaluation of a method based on infrared analysis, p. 49. *NOAA Data Report ERL AOML-85.*

Chisholm, J.R.M., and J.-P. Gattuso (1991) Validation of the alkalinity anomaly technique for investigating calcification and photosynthesis in coral reef communities. *Limnol. Oceanogr.*, *36*, 1232–1239.

Chung, S.N. and others (2003) Calcium carbonate budget in the Atlantic Ocean based on water column inorganic carbon chemistry. *Global Biogeochem. Cy.*, *17*(4), 1093, doi:10.1029/2002GB002001.

Cicerone, R. and others (2004) The ocean in a high CO_2 World. *Eos Trans. AGU, 85*, 351, 353.

Clayton, T.D., and R.H. Byrne (1993) Spectrophotometric seawater pH measurements—total hydrogen-ion concentration scale calibration of M-cresol purple and at-sea results. *Deep-Sea Res. I, 40*, 2115–2129.

Coale, K.H. and others (1996) A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean. *Nature, 383*, 495–501.

Coale, K.H., X.J. Wang, S.J. Tanner, and K.S. Johnson (2003) Phytoplankton growth and biological response to iron and zinc addition in the Ross Sea and Antarctic Circumpolar Current along 170°W. *Deep-Sea Res. II, 50*, 635–653.

Cohen, A.L. (2004) The skeletal chemistry of scleractinian corals: A window on biomineralization. *Geochim. Cosmochim. Acta, 68*, A205–A205.

Cohen, A.L., and T.A. McConnaughey (2003) Geochemical perspectives on coral mineralization, p. 151–187. *In* P.M. Dove, S. Weiner, and J.J. de Yoreo (eds.), *Biomineralization*. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America.

Cohen, J.E., C. Small, A. Mellinger, J. Gallup, and J. Sachs (1997) Estimates of coastal populations. *Science, 278*, 1211–1212.

Coles, S.L., and P.L. Jokiel (1977) Effects of temperature on photosynthesis and respiration in hermatypic corals. *Mar. Biol., 43*, 209–216.

— (1978) Synergistic effects of temperature, salinity and light on hermatypic coral *Montipora verrucosa*. *Mar. Biol., 49*, 187–195.

Collier, T., J.S. Dymond, S.M Honjo, R. Francois, and R. Dunbar (2000) The vertical flux of biogenic and lithogenic material in the Ross Sea: moored sediment trap observations 1996Ů-1998. *Deep-Sea Res. II, 47*, 3491–3520.

Conand, C., P. Chabenet, P. Cuet, and Y. Letourneur (1997) The carbonate budget of a fringing reef in La Reunion Island (Indian Ocean): Sea urchin and fish bioerosion and net calcification. *Proc. 8th Int. Coral Reef Sym. 1*, 953–958.

Darling, K.F., C.M. Wade, I.A. Stewart, D. Kroon, R. Dingle, and A.J.L. Brown (2000) Molecular evidence for genetic mixing of Arctic and Antarctic subpolar populations of planktonic foraminifers. *Nature, 405*, 43–47.

De la Rocha, C.L., and D.J. DePaolo (2000) Isotopic evidence for variations in the marine calcium cycle over the Cenozoic. *Science, 289*, 1176–1178.

de Vargas, C., R. Nooris, L. Zaninetti, S.W. Gibb, and J. Pawlowski (1999) Molecular evidence of cryptic speciation in planktic foraminifera and their relation to oceanic provinces. *Proc. Nat. Acad. Sci. US, 96*, 2864–2868.

de Villiers, S. (2005) Foraminiferal shell-weight evidence for sedimentary calcite dissolution above the lysocline. *Deep-Sea Res. I, 52*, 671–680.

Debgoswami, A., A. Choudhury, and T.K. Jana (1990) Calcification and organic carbon metabolism in a coral reef at Chidiyatapu in South Andaman. *J. Ecobiol., 2*, 9–14.

DeGrandpre, M.D., G.J. Olbu, C.M. Beatty, and T.R. Hammar (2002) Air-sea CO_2 fluxes on the US Middle Atlantic Bight. *Deep-Sea Res. II, 49*, 4355–4367.

Delille, B. and others (2005) Response of primary production and calcification to changes of pCO_2 during experimental blooms of the coccolithophorid *Emiliania huxleyi*. *Global Biogeochem. Cy., 19*, GB2023 doi: 10.1029/2004GB002318.

Denman, K.E., E. Hoffman, and H. Marchant (1996) Marine biotic responses to environmental change and feedbacks to climate, p. 487–516. *In* J.T. Houghton *et al.* (eds.), *Climate Change 1995*, Cambridge University Press.

Deuser, W.G., and E.H. Ross (1989) Seasonally abundant planktonic foraminifera of the Sargasso Sea—succession, deep-water fluxes, isotopic compositions, and paleoceanographic implications. *J. Foramin. Res., 19*, 268–293.

Dickens, G.R. (2001) On the fate of past gas: What happens to methane released from a bacterially mediated gas hydrate capacitor? *Geochem. Geophys. Geosyst., 2*, doi: 10.1029/2000GC000131.

Dickens, G.R., J.R. Oneil, D.K. Rea, and R.M. Owen (1995) Dissociation of oceanic methane hydrate as a cause of the carbon-isotope excursion at the end of the Paleocene. *Paleoceanography, 10*, 965–971.

Dickson, A.G., and F.J. Millero (1987) A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Res. A, 34*, 1733–1743.

Dodge, R.E. and others (1984) Coral calcification rates by the buoyant weight technique—Effects of alizarin staining *J. Exper. Mar. Biol. Ecol., 75*, 217–232.

DOE (1994) *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water*. Version 2, A.G. Dickson and C. Goyet, eds., ORNL/CDIAC-74.

Doney, S.C. (1999) Major challenges confronting marine biogeochemical modeling. *Global Biogeochem. Cy., 13*, 705–714.

Doney, S.C., and J.L. Sarmiento (1999) Synthesis and Modeling Project; Ocean biogeochemical response to climate change, p. 105 , *U.S. JGOFS Planning Report 22*, U.S. JGOFS Planning Office.

Doney, S.C. and others (2004) Ocean Carbon and Climate Change (OCCC): An Implementation Strategy for U.S. Ocean Carbon Cycle Science, p. 108, UCAR.

Emerson, S., S. Mecking, and J. Abell (2001) The biological pump in the subtropical North Pacific Ocean: Nutrient sources, Redfield ratios, and recent changes. *Global Biogeochem. Cy., 15*, 535–554.

Emerson, S.R., and M. Bender (1981) Carbon fluxes at the sediment-water interface of the deep sea: calcium carbonate preservation. *J. Mar. Res., 39*, 139–162.

Engel, A. and others (2005) Testing the direct effect of CO_2 concentration on a bloom of the coccolithophorid Emiliania huxleyi in mesocosm experiments. *Limnol. Oceanogr., 50*, 493–507.

Erez, J. (1978) Vital effect on stable-isotope composition seen in foraminifera and coral skeletons. *Nature, 273,* 199–202.

— (1983) Calcification rates, photosynthesis and light in planktonic foraminifera, p. 307–312. *In* P. Westbroek, and E. de Jong (eds.), *Biomineralization and Biological Metal Accumulation.* D. Reidel Publishing Company.

— (2003) The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies, p. 115–149. *In* P.M. Dove, J.J. De Yoreo, and S. Weiner (eds.), *Biomineralization,* Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Geochemical Society.

Erez, J., A. Almogi-Labin, and S. Avraham (1991) On the life history of planktonic foraminifera: Lunar reproduction cycle in *Globigerinoides sacculifer* (Brady). *Paleoceanography, 6,* 295–306.

Fabry, V.J. (1989) Aragonite production by pteropod molluscs in the sub-arctic Pacific. *Deep-Sea Res. A, 36,* 1735–1751.

— (1990) Shell growth rates of pteropod and heteropod mollusks and aragonite production in the open ocean—Implications for the marine carbonate system *J. Mar. Res., 48,* 209–222.

Fabry, V.J., and W.G. Deuser (1991) Aragonite and magnesian calcite fluxes to the deep Sargasso Sea. *Deep-Sea Res. A, 38,* 713–728.

Fabry, V.J., and L.L. Robbins (1994) Large scale oceanic production of calcium carbonate: coccolithophorids and cyanobacteria. p. 301–304 *In* Jan Paul and C.-M. Pradier (eds.), *Carbon dioxide chemistry: Environmental Issues,* Royal Society of Chemistry, Cambridge.

Fairhall, A.W. (1973a) Accumulation of fossil CO_2 in atmosphere and sea. *Nature, 245,* 20–23.

— (1973b) Correction. *Nature, 246,* 106–106.

Falkowski, P. and others (2000) The global carbon cycle: A test of our knowledge of earth as a system. *Science, 290,* 291–296.

Feely, R.A., and C.T.A. Chen (1982) The effect of excess CO_2 on the calculated calcite and aragonite saturation horizons in the Northeast Pacific. *Geophys. Res. Lett., 9,* 1294–1297.

Feely, R.A., R.H. Byrne, P.R. Betzer, J.F. Gendron, and J.G. Acker (1984) Factors influencing the degree of saturation of the surface and intermediate waters of the North Pacific Ocean with respect to aragonite. *J. Geophys. Res., 89,* 631–640.

Feely, R.A. and others (1988) Winter-summer variations of calcite and aragonite saturation in the northeast Pacific. *Mar. Chem., 25,* 227–241.

Feely, R.A., R. Wanninkhof, H.B. Milburn, C.E. Cosca, M. Stapp, and P.P. Murphy (1998) A new automated underway system for making high precision pCO_2 measurements onboard research ships. *Anal. Chim. Acta, 377,* 185–191.

Feely, R.A. and others (2002) In situ calcium carbonate dissolution in the Pacific Ocean. *Global Biogeochem. Cy., 16*(4), 1144, doi: 10.1029/2002GB001866.

Feely, R.A., and others (2004) Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. *Science, 305,* 362–366.

Feely, R.A., L.D. Talley, G.C. Johnson, C.L. Sabine, and R. Wanninkhof (2005) Repeat hydrography cruises reveal chemical changes in the North Atlantic. *Eos Trans. AGU, 86,* 399, 404–405.

Feely, R.A., J. Orr, V.J. Fabry, J.A. Kleypas, C.L. Sabine, and C. Langdon (submitted) Present and future changes in seawater chemistry due to ocean acidification. AGU Monograph on "The Science and Technology of Carbon Sequestration."

Fernandez, E., P. Boyd, P.M. Holligan, and D.S. Harbour (1993) Production of organic and inorganic carbon within a large-scale coccolithophore bloom in the Northeast Atlantic Ocean. *Mar. Ecol.-Prog. Ser., 97,* 271–285.

Ferrier-Pagès, C., J.-P. Gattuso, S. Dallot, and J. Jaubert (2000) Effect of nutrient enrichment on growth and photosynthesis of the zooxanthellate coral *Stylophora pistillata. Coral Reefs, 19,* 103–113.

Frankignoulle, M., J.-P. Gattuso, R. Biondo, I. Bourge, G. Copinmontegut, and M. Pichon (1996) Carbon fluxes in coral reefs. 2. Eulerian study of inorganic carbon dynamics and measurement of air-sea CO_2 exchanges. *Mar. Ecol.-Prog. Ser., 145,* 123–132.

Friederich, G.E., P.G. Brewer, R. Herlien, and F.P. Chavez (1995) Measurement of sea surface partial pressure of CO_2 from a moored buoy. *Deep-Sea Res. I, 42,* 1175–1186.

Furla, P., I. Galgani, I. Durand, and D. Allemand (2000) Sources and mechanisms of inorganic carbon transport for coral calcification and photosynthesis. *J. Exp. Biol., 203,* 3445–3457.

Gage, J.D., and P.A. Tyler (1991) *Deep-sea biology: a natural history of organisms at the deep-sea floor.* Cambridge University Press.

Gao, K., Y. Aruga, K. Asada, T. Ishihara, T. Akano, and M. Kiyohara (1993) Calcification in the articulated coralline alga *Corallina pilulifera,* with special reference to the effect of elevated CO_2 concentrations. *Mar. Biol., 117,* 129–132.

Gattuso, J.-P., D. Yellowlees, and M. Lesser (1993a) Depth-dependent and light-dependent variation of carbon partitioning and utilization in the zooxanthellate scleractinian coral *Stylophora pistillata. Mar. Ecol.-Prog. Ser., 92,* 267–276.

Gattuso, J.-P., M. Pichon, B. Delesalle, and M. Frankignoulle (1993b) Community metabolism and air-sea CO_2 fluxes in a coral reef ecosystem (Moorea, French-Polynesia). *Mar. Ecol.-Prog. Ser., 96,* 259–267.

Gattuso, J.-P., M. Pichon, and M. Frankignoulle (1995) Biological control of air-sea CO_2 fluxes: Effect of photosynthetic and calcifying marine organisms and ecosystems. *Mar. Ecol.-Prog. Ser., 129,* 307–312.

Gattuso, J.-P., M. Frankignoulle, S.V. Smith, J.R. Ware, and R. Wollast (1996a) Coral reefs and carbon dioxide. *Science, 271,* 1298.

Gattuso, J.-P., M. Pichon, B. Delesalle, C. Canon, and M. Frankignoulle (1996b) Carbon fluxes in coral reefs. 1. Lagrangian measurement of community metabolism and resulting air-sea CO_2 disequilibrium. *Mar. Ecol.-Prog. Ser.*, *145*, 109–121.

Gattuso, J.-P., C.E. Payri, M. Pichon, B. Delesalle, and M. Frankignoulle (1997) Primary production, calcification, and air-sea CO_2 fluxes of a macroalgal-dominated coral reef community (Moorea, French Polynesia). *J. Phycol.*, *33*, 729–738.

Gattuso, J.-P., M. Frankignoulle, and R. Wollast (1998a) Carbon and carbonate metabolism in coastal aquatic ecosystems. *Ann. Rev. Ecol. Syst.*, *29*, 405–434.

Gattuso, J.-P., M. Frankignoulle, I. Bourge, S. Romaine, and R.W. Buddemeier (1998b) Effect of calcium carbonate saturation of seawater on coral calcification. *Global Planet. Change*, *18*, 37–46.

Gattuso, J.-P., D. Allemand, and M. Frankignoulle (1999a) Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: A review on interactions and control by carbonate chemistry. *Am. Zool.*, *39*, 160–183.

Gattuso, J.-P., M. Frankignoulle, and S.V. Smith (1999b) Measurement of community metabolism and significance in the coral reef CO_2 source-sink debate. *Proc. Nat. Acad. Sci. US*, *96*, 13,017–13,022.

Gattuso, J.-P. and others (2000) Calcification does not stimulate photosynthesis in the zooxanthellate scleractinian coral *Stylophora pistillata*. *Limnol. Oceanogr.*, *45*, 246–250.

Gehlen, M., F.C. Bassinot, L. Chou, and D. McCorkle (2005a) Reassessing the dissolution of marine carbonates: I. Solubility. *Deep-Sea Res. I*, *52*, 1445–1460.

— (2005b) Reassessing the dissolution of marine carbonates: II. Reaction kinetics. *Deep-Sea Res. I*, *52*, 1461–1476.

Goiran, C., S. Almoghrabi, D. Allemand, and J. Jaubert (1996) Inorganic carbon uptake for photosynthesis by the symbiotic coral/dinoflagellate association. 1. Photosynthetic performances of symbionts and dependence on sea water bicarbonate. *J. Exper. Mar. Biol. Ecol.*, *199*, 207–225.

González-Dávila, M., J.M. Santana-Casiano, M.-J. Rueda, O. Llinás, and González-Dávila, E.-F. (2003) Seasonal and interannual variability of sea-surface carbon dioxide species at the European Station for Time Series in the Ocean at the Canary Islands (ESTOC) between 1996 and 2000. *Global Biogeochem. Cy.*, *17*(3), 1076, doi:10.1029/2002GB001993.

Gordon, H.R. and others (1988) A semianalytic radiance model of ocean color. *J. Geophys. Res.*, *93*, 10,909–10,924.

Gordon, H.R., G.C. Boynton, W.M. Balch, S.B. Groom, D.S. Harbour, and T.J. Smyth (2001) Retrieval of coccolithophore calcite concentration from SeaWiFS imagery. *Geophys. Res. Lett.*, *28*, 1587–1590.

Goreau, T.F. (1959) The physiology of skeleton formation in corals. I. A method for measuring the rate of calcium deposition by corals under different light conditions. *Biol. Bull.*, *116*, 59–75.

— (1963) Calcium carbonate deposition by coralline algae and corals in relation to their roles as reef builders. *Ann. NY Acad. Sci.*, *109*, 127–167.

Green, J.C., P.A. Course, and G.A. Tarran (1996) The life cycle of *Emiliania huxleyi*: A brief review and a study of relative ploidy levels analysed by flow cytometry. *J. Mar. Syst.*, *9*, 33–44.

Green, M.A., M.E. Jones, C.L. Boudreau, R.L. Moore, and B.A. Westman (2004) Dissolution mortality of juvenile bivalves in coastal marine deposits. *Limnol. Oceanogr.*, *49*, 727–734.

Gruber, N., C.D. Keeling, and N.R. Bates (2002) Interannual variability in the North Atlantic Ocean carbon sink. *Science*, *298*, 2374–2378.

Gruber, N. and others (2004) The vulnerability of the carbon cycle in the 21st century: an assessment of carbon-climate-human interactions, p. 45–76. *In* C.B. Field and M.R. Raupach (eds.), *The Global Carbon Cycle: Integrating Humans, Climate and the Natural World*, Island Press.

Guay, C.K.H., and J.K.B. Bishop (2002) A rapid birefringence method for measuring suspended $CaCO_3$ concentrations in seawater. *Deep-Sea Res. I*, *49*, 197–210.

Guinotte, J.M., J. Orr, S. Cairns, A. Freiwald, L. Morgan, and R. George (2006) Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? *Front. Ecol. Environ.*, *4*, 141–146.

Hales, B., S. Emerson, and D. Archer (1994) Respiration and dissolution in the sediments of the western North Atlantic: Estimate from models of in situ microelectrode measurements of porewater oxygen and pH. *Deep-Sea Res.*, *41*, 695–719.

Harris, R.P. (1994) Zooplankton grazing on the coccolithophore *Emiliania huxleyi* and its role in inorganic carbon flux. *Mar. Biol.*, *119*, 431–439.

Hautmann, M. (2004) Effect of end-Triassic CO_2 maximum on carbonate sedimentation and marine mass extinction. *Facies*, *50*, 257–261.

Heinze, C. (2004) Simulating oceanic $CaCO_3$ export production in the greenhouse. *Geophys. Res. Lett.*, *31*, L16308, doi: 10.1029/2004GL020613.

Helmle, K.P., K.E. Kohler, and R.E. Dodge (2002) Relative optical densitometry and the coral X-radiograph densitometry system: CoralXDS. *Int. Soc. Reef Studies 2002 European Meeting.*

Hemleben, C., M. Spindler, and O.R. Anderson (1989) *Modern Planktonic Foraminifera*. Springer-Verlag.

Hendrey, G.R., and B.A. Kimball (1994) The FACE Program. *Agr. Forest Meteorol.*, *70*, 3–14.

Herfort, L., B. Thake, and J. Roberts (2002) Acquisition and use of bicarbonate by *Emiliania huxleyi*. *New Phytol.*, *156*, 427–436.

Herfort, L., E. Loste, F. Meldrum, and B. Thake (2004) Structural and physiological effects of calcium and magnesium in *Emiliania huxleyi* (Lohmann) Hay and Mohler. *J. Struct. Biol.*, *148*, 307–314.

Hoegh-Guldberg, O., and G.J. Smith (1989) Influence of the population density of zooxanthellae and supply of ammonium on the biomass and metabolic characteristics of the reef corals *Seriatopora hystrix* and *Stylophora pistillata*. *Mar. Ecol.-Prog. Ser., 57*, 173–186.

Honjo, S., J. Dymond, R. Collier, and S.J. Manganini (1995) Export production of particles to the interior of the Equatorial Pacific Ocean during the 1992 EqPac experiment. *Deep-Sea Res. II, 42*, 831–870.

Honjo, S., R. Francois, S. Managanini, J. Dymond, and R. Collier (2000) Particle fluxes to the interior of the Southern Ocean in the Western Pacific sector along 170°W. *Deep-Sea Res. II, 47*, 3521–3548.

Hossain, M.M.M., and S. Ohde (in press) Calcification of cultured *Porites* and *Fungia* under different aragonite saturation states of seawater at 25°C. *Proc. 10th Int. Coral Reef Sym. 1.* Japanese Coral Reef Society.

Houck, J.E., R.W. Buddemeier, S.V. Smith, and P.L. Jokiel (1977) The response of coral growth and skeletal strontium content to light intensity and water temperature. *Proc. 3rd Int. Coral Reef Sym. 2*, 424–431.

Houdan, A.C. and others (2004) Holococcolithophore-heterococcolithophore (Haptophyta) life cycles: Flow cytometric analysis of relative ploidy levels. *Syst. Biodivers., 1*, 453–465.

Houghton, J.T., Y. Ding, D.J. Griggs, M. Noguer, P. J. van der Linden and D. Xiaosu (2001) *Climate Change 2001: The Scientific Basis.* Cambridge University Press.

Iglesias-Rodriguez, M.D., R. Armstrong, R. Feely, R. Hood, J. Kleypas, J. D. Milliman, C. Sabine, and J. Sarmiento (2002) Progress made in study of ocean's calcium carbonate budget. *Eos Trans. AGU, 83*, 365, 374–375.

IMBER (2005) Science Plan and Implementation Strategy. *IGBP Report No. 52*, IGBP Secretariat, Stockholm, 76 pp.

Invers, O., R.C. Zimmerman, R.S. Alberte, M. Perez, and J. Romero (2001) Inorganic carbon sources for seagrass photosynthesis: an experimental evaluation of bicarbonate use in species inhabiting temperate waters. *J. Exper. Mar. Biol. Ecol., 265*, 203–217.

Invers, O., F. Tomas, M. Perez, and J. Romero (2002) Potential effect of increased global CO_2 availability on the depth distribution of the seagrass *Posidonia oceanica* (L.) Delile: A tentative assessment using a carbon balance model. *Bull. Mar. Sci., 71*, 1191–1198.

Jackson, G.A. (1990) A model of the formation of marine algal flocs by physical coagulation processes. *Deep-Sea Res. A, 37*, 1197–1211.

Jackson, G.A., and A.B. Burd (1998) Aggregation in the marine environment. *Environ. Sci. Technol., 32*, 2805–2814.

Jacques, T.G., and M.E.Q. Pilson (1980) Experimental ecology of the temperate scleractinian coral *Astragia danae.* I. Partition of respiration, photosynthesis and calcification between host and symbionts. *Mar. Biol., 60*, 167–178.

Jahnke, R.A., D.B. Craven, and J.-F. Gaillard (1994) The influence of organic matter diagenesis on $CaCO_3$ dissolution at the deep-sea floor. *Geochim. Cosmochim. Acta, 58*, 2799–2809.

Jansen, H., and M.J. Ahrens (2004) Carbonate dissolution in the guts of benthic deposit feeders: A numerical model. *Geochim. Cosmochim. Acta, 68*, 4077–4092.

Johnson, K.M., and D.W.R. Wallace (1992) The single-operator multiparameter metabolic analyzer for total carbon dioxide with coulometric detection. *DOE Research Summary No. 19*, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory.

Johnson, K.M., J.M. Sieburth, P.J.L. Williams, and L. Brandstrom (1987) Coulometric total carbon-dioxide analysis for marine studies—automation and calibration. *Mar. Chem., 21*, 117–133.

Johnson, K.M., K.D. Wills, D.B. Butler, W.K. Johnson, and C.S. Wong (1993) Coulometric total carbon-dioxide analysis for marine studies—Maximizing the performance of an automated gas extraction system and coulometric detector. *Mar. Chem., 44*, 167–187.

Johnson, K.M. and others (1998) Coulometric total carbon dioxide analysis for marine studies: assessment of the quality of total inorganic carbon measurements made during the US Indian Ocean CO_2 Survey 1994–1996. *Mar. Chem., 63*, 21–37.

Jokiel, P.L., and S.L. Coles (1977) Effects of temperature on mortality and growth of Hawaiian reef corals. *Mar. Biol., 43*, 201–208.

Jokiel, P.L., J.W. Maragos, and L. Franzisket (1978) Coral growth buoyant weight technique, p. 529–542. *In* D.R. Stoddart, and R.E. Johannes (ed.), *Monographs on Oceanographic Methodology*, UNESCO.

Karl, D.M. (1999) A sea of change: Biogeochemical variability in the North Pacific subtropical gyre. *Ecosystems, 2*, 181–214.

Kawahata, H., A. Suzuki, and K. Goto (1997) Coral reef ecosystems as a source of atmospheric CO_2: Evidence from pCO_2 measurements of surface waters. *Coral Reefs, 16*, 261–266.

Kawahata, H., A. Suzuki, T. Ayukai, and K. Goto (2000) Distribution of the fugacity of carbon dioxide in the surface seawater of the Great Barrier Reef. *Mar. Chem., 72*, 257–272.

Kayanne, H., A. Suzuki, and H. Saito (1995) Diurnal changes in the partial pressure of carbon dioxide in coral reef water. *Science, 269*, 214–216.

Kayanne, H. and others (2002) Submergible system to measure seawater pCO_2 on a shallow sea floor. *Mar. Tech. Soc. J., 36*, 23–28.

— (2005) Seasonal and bleaching-induced changes in coral reef metabolism and CO_2 flux. *Global Biogeochem. Cy., 19*, GB3015, doi: 10.1029/2004GB002400.

Kennett, J.P., and L.D. Stott (1991) Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the Paleocene. *Nature, 353*, 225–229.

Kimoto, H., K. Nozaki, S. Kudo, K. Kato, A. Negishi, and H. Kayanne (2002) Achieving high time-resolution with a new flow-through type analyzer for total inorganic carbon in seawater. *Anal. Sci., 18*, 247–253.

Kinsey, D.W. (1978) Alkalinity changes and coral reef calcification. *Limnol. Oceanogr., 23*, 989–991.

Kirkwood, W. and others (2005) Engineering development of the Free Ocean CO_2 Enrichment (FOCE) Experiment. MTS/IEEE Oceans 2005.

Klaas, C., and D.E. Archer (2002) Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio. *Global Biogeochem. Cy., 16*(4), 1116, doi: 10.1029/2001GB001765.

Kleypas, J.A., R.W. Buddemeier, D. Archer, J.-P. Gattuso, C. Langdon, and B.N. Opdyke (1999) Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. *Science, 284,* 118–120.

Kleypas, J.A., R.W. Buddemeier, and J.-P. Gattuso (2001) The future of coral reefs in an age of global change. *Int. J. Earth Sci., 90,* 426–437.

Kleypas, J.A. and others (2005) Comment on "Coral reef calcification and climate change: The effect of ocean warming." *Geophys. Res. Lett., 32,* L08601, doi: 10.1029/2004GL022329.

Kobayashi, H. (1974) Growth cycle and related vertical distribution of thecosomatous pteropod *Spiratella (Limacina) helicina* in the central Arctic Ocean. *Mar. Biol., 26,* 295–301.

Kurihara, H., and Y. Shirayama (2004) Effects of increased atmospheric CO_2 on sea urchin early development. *Mar. Ecol.-Prog. Ser., 274,* 161–169.

Lalli, C.M., and R.W. Gilmer (1989) *Pelagic Snails: The Biology of Holoplanktonic Gastropod Mollusks.* Stanford University Press.

Langdon, C. (2002) Review of experimental evidence for effects of CO_2 on calcification of reef builders. *Proc. 9th Int. Coral Reef Sym. 2,* 1091–1098.

Langdon, C., and M.J. Atkinson (2005) Effect of elevated pCO_2 on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment. *J. Geophys. Res., 110,* C09S07, doi: 10.1029/2004JC002576.

Langdon, C. and others (2000) Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. *Global Biogeochem. Cy., 14,* 639–654.

— (2003) Effect of elevated CO_2 on the community metabolism of an experimental coral reef: *Global Biogeochem. Cy., 17*(1), 1011, doi: 10.1029/2002GB001941.

Langer, G., M. Geisen, and others (in press) Species-specific responses of calcifying algae to changing seawater carbonate chemistry. *Geochem. Geophys. Geosyst.*.

Langer, M.R., M.T. Silk, and J.H. Lipps (1997) Global ocean carbonate and carbon dioxide production: The role of reef foraminifera. *J. Foramin. Res., 27,* 271–277.

Lea, D.W., P.A. Martin, D.A. Chan, and H.J. Spero (1995) Calcium-uptake and calcification rate in the planktonic foraminifer *Orbulina universa. J. Foramin. Res., 25,* 14–23.

Lea, D.W., P.A. Martin, D.K. Pak, and H.J. Spero (2002) Reconstructing a 350 ky history of sea level using planktonic Mg/Ca and oxygen isotope records from a Cocos Ridge core. *Quatern. Sci. Rev., 21,* 283–293.

Leclercq, N., J.-P. Gattuso, and J. Jaubert (2000) CO_2 partial pressure controls the calcification rate of a coral community. *Global Change Biol., 6,* 329–334.

— (2002) Primary production, respiration, and calcification of a coral reef mesocosm under increased CO_2 partial pressure. *Limnol. Oceanogr., 47,* 558–564.

Lee, K. (2001) Global net community production estimated from the annual cycle of surface water total dissolved inorganic carbon. *Limnol. Oceanogr., 46,* 1287–1297.

Lesser, M.P., V.M. Weis, M.R. Patterson, and P.L. Jokiel (1994) Effects of morphology and water motion on carbon delivery and productivity in the reef coral, *Pocillopora damicornis* (Linnaeus)—diffusion barriers, inorganic carbon limitation, and biochemical plasticity. *J. Exper. Mar. Biol. Ecol., 178,* 153–179.

Lirman, D. (2000) Fragmentation in the branching coral *Acropora palmata* (Lamarck): growth, survivorship, and reproduction of colonies and fragments. *J. Exper. Mar. Biol. Ecol., 251,* 41–57.

Lough, J.M., and D.J. Barnes (1997) Several centuries of variation in skeletal extension, density and calcification in massive *Porites* colonies from the Great Barrier Reef: A proxy for seawater temperature and a background of variability against which to identify unnatural change. *J. Exper. Mar. Biol. Ecol., 211,* 29–67.

— (2000) Environmental controls on growth of the massive coral *Porites. J. Exper. Mar. Biol. Ecol., 245,* 225–243.

Lowenstam, H.A., and S. Weiner (1989) *On Biomineralization.* Oxford University Press.

Mackenzie, F.T. (2003) *Our Changing Planet,* 3rd ed. Pearson Education, Inc.

Mackenzie, F.T., A. Lerman, and A.J. Andersson (2004) Past and present of sediment and carbon biogeochemical cycling models. *Biogeosci. Disc., 1,* 27–85.

Marchitto, T.M., W.B. Curry, and D.W. Oppo (2000) Zinc concentrations in benthic foraminifera reflect seawater chemistry. *Paleoceanography, 15,* 299–306.

Marchitto, T.M., J. Lynch-Stieglitz, and S.R. Hemming (2005) Deep Pacific $CaCO_3$ compensation and glacial-interglacial atmospheric CO_2. *Earth Planet. Sci. Lett., 231,* 317–336.

Marshall, A.T., and P.L. Clode (2002) Effect of increased calcium concentration in sea water on calcification and photosynthesis in the scleractinian coral *Galaxea fascicularis. J. Exp. Biol., 205,* 2107–2113.

Marshall, A.T., and P. Clode (2004) Calcification rate and the effect of temperature in a zooxanthellate and an azooxanthellate scleractinian reef coral. *Coral Reefs, 23,* 218–224.

Martin, J.H. and others (1994) Testing the iron hypothesis in ecosystems of the Equatorial Pacific-Ocean. *Nature, 371,* 123–129.

Martin, W.R., and F.L. Sayles (1996) $CaCO_3$ dissolution in sediments of the Ceara Rise, western equatorial Atlantic. *Geochim. Cosmochim. Acta, 60,* 243–264.

Marubini, F., and M.J. Atkinson (1999) Effects of lowered pH and elevated nitrate on coral calcification. *Mar. Ecol.-Prog. Ser., 188,* 117–121.

Marubini, F., and P.S. Davies (1996) Nitrate increases zooxanthellae population density and reduces skeletogenesis in corals. *Mar. Biol., 127,* 319–328.

Marubini, F., and B. Thake (1999) Bicarbonate addition promotes coral growth. *Limnol. Oceanogr., 44,* 716–720.

Marubini, F., H. Barnett, C. Langdon, and M.J. Atkinson (2001) Dependence of calcification on light and carbonate ion concentration for the hermatypic coral *Porites compressa. Mar. Ecol.-Prog. Ser., 220,* 153–162.

Marubini, F., C. Ferrier-Pagés, and J.P. Cuif (2003) Suppression of skeletal growth in scleractinian corals by decreasing ambient carbonate-ion concentration: a cross-family comparison. *Proc. Roy. Soc. Lond. B, 270,* 179–184.

Matear, R.J., and A.C. Hirst (1999) Climate change feedback on the future oceanic CO_2 uptake. *Tellus B, 51,* 722–733.

McConnaughey, T.A. (2003) Sub-equilibrium oxygen-18 and carbon-13 levels in biological carbonates: Carbonate and kinetic models. *Coral Reefs, 22,* 316–327.

McCorkle, D.C., P.A. Martin, D. Lea, and G. Klinkhammer (1995) Evidence of a dissolution effect on benthic foraminiferal shell chemistry: Results from the Ontong-Java Plateau. *Paleoceanography, 10,* 699–714.

McIntyre, A., and A.W.H. Bé (1967) Modern coccolithophoridae of the Atlantic Ocean—I. Placoliths and cyrtoliths. *Deep-Sea Res., 14,* 561–597.

McNeil, B.I., R.J. Matear, and D.J. Barnes (2004) Coral reef calcification and climate change: The effect of ocean warming. *Geophys. Res. Lett., 31,* L22309, doi: 10.1029/2004GL021541.

Mehrbach, C., Ch. Culberso, J.E. Hawley, and Rm. Pytkowic (1973) Measurement of apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr., 18,* 897–907.

Merlivat, L., and P. Brault (1995) CARIOCA Buoy—Carbon-Dioxide Monitor. *Sea Technol., 36,* 23–30.

Michaelidis, B., C. Ouzounis, A. Paleras, and H.O. Pörtner (2005) Effects of long-term moderate hypercapnia on acid-base balance and growth rate in marine mussels *Mytilus galloprovincialis. Mar. Ecol.-Prog. Ser., 293,* 109–118.

Migné, A., D. Davoult, and J.-P. Gattuso (1998) Calcium carbonate production of a dense population of the brittle star *Ophiothrix fragilis* (Echinodermata : Ophiuroidea): Role in the carbon cycle of a temperate coastal ecosystem. *Mar. Ecol.-Prog. Ser., 173,* 305–308.

Millero, F.J., J.Z. Zhang, K. Lee, and D.M. Campbell (1993) Titration alkalinity of seawater. *Mar. Chem., 44,* 153–165.

Millero, F.J., W.S. Yao, K. Lee, J.Z. Zhang, and D.M. Campbell (1998) Carbonate system in the waters near the Galapagos Islands. *Deep-Sea Res. II, 45,* 1115–1134.

Milliman, J.D. (1993) Production and accumulation of calcium carbonate in the ocean—Budget of a nonsteady state. *Global Biogeochem. Cy., 7,* 927–957.

Milliman, J.D., and A.W. Droxler (1996) Neritic and pelagic carbonate sedimentation in the marine environment: Ignorance is not bliss. *Geol. Rundsch., 85,* 496–504.

Milliman, J.D., P.J. Troy, W.M. Balch, A.K. Adams, Y.H. Li, and F.T. Mackenzie (1999) Biologically mediated dissolution of calcium carbonate above the chemical lysocline? *Deep-Sea Res. I, 46,* 1653–1669.

Moore, J.K., S.C. Doney, J.A. Kleypas, D.M. Glover, and I.Y. Fung (2002) An intermediate complexity marine ecosystem model for the global domain. *Deep-Sea Res. II, 49,* 403–462.

Morse, J.W., and R.S. Arvidson (2002) The dissolution kinetics of major sedimentary carbonate minerals. *Earth Sci. Rev., 58,* 51–84.

Morse, J.W., and F.T. Mackenzie (1990) *Geochemistry of Sedimentary Carbonates.* Elsevier.

Muscatine, L. (1990) The role of symbiotic algae in carbon and energy flux in coral reefs, p. 75–87. *In* Z. Dubinsky (ed.), *Coral Reefs,* Elsevier.

Ohde, S., and M.M.M. Hossain (2004) Effect of $CaCO_3$ (aragonite) saturation state of seawater on calcification of *Porites* coral. *Geochem. J., 38,* 613–621.

Ohde, S., and R. Van Woesik (1999) Carbon dioxide flux and metabolic processes of a coral reef, Okinawa. *Bull. Mar. Sci., 65,* 559–576.

Ono, T., S. Watanabe, K. Okuda, and M. Fukasawa (1998) Distribution of total carbonate and related properties in the North Pacific along 30°N. *J. Geophys. Res., 103,* 30,873–30,883.

Opdyke, B.N., and J.C.G. Walker (1992) Return of the coral reef hypothesis: Basin to shelf partitioning of $CaCO_3$ and its effect on atmospheric CO_2. *Geology, 20,* 730–736.

Orr, J.C. and others (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature, 437,* 681–686.

Paasche, E. (1964) A tracer study of the inorganic carbon uptake during coccolith formation and photosynthesis in the coccolithophorid *Coccolithus huxleyi. Physiology Plant Suppl., 3,* 5–81.

— (1999) Reduced coccolith calcite production under light-limited growth: A comparative study of three clones of *Emiliania huxleyi* (Prymnesiophyceae). *Phycologia, 38,* 508–516.

— (2001) A review of the coccolithophorid *Emiliania huxleyi* (Prymnesiophyceae), with particular reference to growth, coccolith formation, and calcification-photosynthesis interactions. *Phycologia, 40,* 503–529.

Paasche, E., and S. Brubak (1994) Enhanced calcification in the coccolithophorid *Emiliania huxleyi* (Haptophyceae) under phosphorus limitation. *Phycologia, 33,* 324–330.

Paasche, E., S. Brubak, S. Skattebøl, J.R. Young, and J.C. Green (1996) Growth and calcification in the coccolithophorid *Emiliania huxleyi* (Haptophyceae) at low salinities. *Phycologia, 35,* 394–403.

Pagani, M. (2002) The alkenone-CO_2 proxy and ancient atmospheric carbon dioxide. *Philos. Trans. Roy. Soc. Lond. A, 360,* 609–632.

Pagani, M., D. Lemarchand, A. Spivack, and J. Gaillardet (2005) A critical evaluation of the boron isotope-pH proxy: The accuracy of ancient ocean pH estimates. *Geochim. Cosmochim. Acta, 69,* 953–961.

Palfy, J. (2003) Volcanism of the Central Atlantic Magmatic Province as a potential driving force in the end-Triassic extinction, p. 255–267. *In* W.E. Hames, J.G. McHone, P.R. Renne, and C. Ruppel (eds.), *The Central Atlantic Magmatic Province: Insights from fragments of Pangea*, Geophysical Monograph Series.

Passow, U. (2002) Transparent exopolymer particles (TEP) in aquatic environments. *Prog. Oceanogr.*, *55*, 287–333.

— (2004) Switching perspectives: Do mineral fluxes determine particulate organic carbon fluxes or vice versa? *Geochem. Geophys. Geosyst.*, *5*, Q04002, doi: 10.1029/2003GC000670.

Pearson, P.N., and M.R. Palmer (2000) Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature*, *406*, 695–699.

Pearson, P.N. and others (2001) Warm tropical sea surface temperatures in the Late Cretaceous and Eocene epochs. *Nature*, *413*, 481–487.

Pelejero, C. and others (2005) Preindustrial to modern interdecadal variability in coral reef pH. *Science*, *309*, 2204–2207.

Pennington, J.T., G.E. Friederich, C.G. Castro, C.A. Collins, W.W. Evans, and F.P. Chavez (in press) California Current System. *In* K.K. Liu, L. Atkinson, R. Quiñones, and L. Talaue-McManus (eds.), *Carbon and Nutrient Fluxes in Continental Margins: A Global Synthesis*, Global Change, The IGBP Series, Springer, Berlin.

Perez, F.F., and F. Fraga (1987) The pH measurements in seawater on the NBS scale. *Mar. Chem.*, *21*, 315–327.

Peterson, M.N.A. (1966) Calcite: Rates of dissolution in a vertical profile in the central Pacific. *Science*, *154*, 1542–1544.

Petit, J.R. and others (1999) Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature*, *399*, 429–436.

Pilskaln, C.H., C. Lehmann, J.B. Paduan, and M.W. Silver (1998) Spatial and temporal dynamics in marine aggregate abundance, sinking rate and flux: Monterey Bay, central California. *Deep-Sea Res. II*, *45*, 1803–1837.

Pond, D.W., R.P. Harris, and C. Brownlee (1995) A microinjection technique using a pH sensitive dye to determine the gut pH of *Calanus helgolandicus*. *Mar. Biol.*, *123*, 75–79.

Prentice, I.C. and others (2001) The carbon cycle and atmospheric CO_2, p. 183–287. *In* J. T. Houghton and D. Yihui (eds.), *Climate Change: The Scientific Basis, Contribution of working group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press.

Puverel, S. and others (2005) Antibodies against the organic matrix in scleractinians: A new tool to study coral biomineralization. *Coral Reefs*, *24*, 149–156.

Quinn, T.M., T.J. Crowley, F.W. Taylor, C. Henin, P. Joannot, and Y. Join (1998) A multicentury stable isotope record from a New Caledonia coral: Interannual and decadal sea surface temperature variability in the southwest Pacific since 1657 AD. *Paleoceanography* *13*(4), 412–426.

Redfield, A. (1939) History of a population of *Limacina retroversa* during the drift across the Gulf of Maine. *Biol. Bull.*, *76*, 26–47.

Renegar, D.A., and B.M. Riegl (2005) Effect of nutrient enrichment and elevated CO_2 partial pressure on growth rate of Atlantic scleractinian coral *Acropora cervicornis*. *Mar. Ecol.-Prog. Ser.*, *293*, 69–76.

Reynaud, S., N.G. Hemming, A. Juillet-Leclerc, and J.-P. Gattuso (2004) Effect of pCO_2 and temperature on the boron isotopic composition of the zooxanthellate coral *Acropora* sp. *Coral Reefs*, *23*, 539–546.

Reynaud, S., N. Leclercq, S. Romaine-Lioud, C. Ferrier-Pagés, J. Jaubert, and J.-P. Gattuso (2003) Interacting effects of CO_2 partial pressure and temperature on photosynthesis and calcification in a scleractinian coral. *Global Change Biol.*, *9*, 1660–1668.

Ridgwell, A., A.J. Watson, M.A. Maslin, and J.O. Kaplan (2003) Implications of coral reef buildup for the controls on atmospheric CO_2 since the Last Glacial Maximum. *Paleoceanography*, *18*, 1083, doi: 10.1029/2003PA000893.

Ridgwell, A., and R.E. Zeebe (2005) The role of the global carbonate cycle in the regulation and evolution of the Earth system. *Earth Planet. Sci. Lett.*, *234*, 299–315.

Riebesell, U. (2004) Effects of CO_2 enrichment on marine phytoplankton. *J. Oceanogr.*, *60*, 719–729.

Riebesell, U., I. Zondervan, B. Rost, P.D. Tortell, R.E. Zeebe, and F.M.M. Morel (2000) Reduced calcification of marine plankton in response to increased atmospheric CO_2. *Nature*, *407*, 364–367.

Rink, S., M. Kühl, J. Bijma, and H. J. Spero (1998) Microsensor studies of photosynthesis and respiration in the symbiotic foraminifer *Orbulina universa*. *Mar. Biol.*, *131*, 583–595.

Robbins, L.L., Y. Tao, and C.A. Evans (1997) Temporal and spatial distribution of whitings on Great Bahama Bank and a new lime mud budget. *Geology*, *25*(10), 947–950.

Rosenheim, B.E., P.K. Swart, S.R. Thorrold, A. Eisenhauer, and P. Willenz (2005) Salinity change in the subtropical Atlantic: Secular increase and teleconnections to the North Atlantic Oscillation. *Geophys. Res. Lett.*, *32*, L02603, doi: 10.1029/2004GL021499.

Rost, B., and U. Riebesell (2004) Coccolithophores and the biological pump: Responses to environmental changes, p. 99–125. *In* H.R. Thierstein, and J.R. Young (eds.), *Coccolithophores: From Molecular Processes to Global Impact*, Springer.

Royal Society (2005) Ocean acidification due to increasing atmospheric carbon dioxide, *Policy Document 12/05*, The Royal Society.

Royer, D.L. and others (2001) Paleobotanical evidence for near present-day levels of atmospheric CO_2 during part of the Tertiary. *Science*, *292*, 2310–2313.

Rundgren, M., and O. Bennike (2002) Century-scale changes of atmospheric CO_2 during the last interglacial. *Geology*, *30*, 187–189.

Ryan, D.A., B.N. Opdyke, and J.S. Jell (2001) Holocene sediments of Wistari Reef: Towards a global quantification of coral reef related neritic sedimentation in the Holocene. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *175*, 173–184.

Sabine, C.L., F.T. Mackenzie, C. Winn, and D.M. Karl (1995) Geochemistry of carbon dioxide in seawater at the

Hawaii Ocean Time-series Station, ALOHA. *Global Biogeochem. Cy., 9*, 637–651.

Sabine, C.L. and others (2002) Distribution of anthropogenic CO_2 in the Pacific Ocean. *Global Biogeochem. Cy., 16*(4), 1083, doi: 10.1029/2001GB001639.

— (2004) The oceanic sink for anthropogenic CO_2. *Science, 305*, 367–371.

— (2005) Global Ocean Data Analysis Project (GLODAP): Results and Data. p. 110. *ORNL/CDIAC-145, NDP-083.* Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy.

Sakai, K. (1998a) Delayed maturation in the colonial coral *Goniastrea aspera* (Scleractinia): Whole-colony mortality, colony growth and polyp egg production. *Res. Popul. Ecol., 40*, 287–292.

— (1998b) Effect of colony size, polyp size, and budding mode on egg production in a colonial coral. *Biol. Bull., 195*, 319–325.

Sakamoto, C.M., F.J. Millero, W.S. Yao, G.E. Friederich, and F.P. Chavez (1998) Surface seawater distributions of inorganic carbon and nutrients around the Galapagos Islands: Results from the PlumEx experiment using automated chemical mapping. *Deep-Sea Res. II, 45*, 1055–1071.

Sanchez Puerta, M.V., T.R. Bachvaroff, and C.F. Delwiche (2004) The complete mitochondrial genome sequence of the haptophyte *Emiliania huxleyi* and its relation to heterokonts. *DNA Res., 29*, 1–10.

Sanyal, A., N.G. Hemming, G.N. Hanson, and W.S. Broecker (1995) Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature, 373*, 234–236.

Sanyal, A., J. Bijma, H. Spero, and D.W. Lea (2001) Empirical relationship between pH and the boron isotopic composition of *Globigerinoides sacculifer*. Implications for the boron isotope paleo-pH proxy. *Paleoceanography, 16*, 515–519.

Sarmiento, J.L., and N. Gruber (2002) Sinks for anthropogenic carbon. *Phys. Today, 55*, 30–36.

Sarmiento, J.L., T.M.C. Hughes, R.J. Stouffer, and S. Manabe (1998) Simulated response of the ocean carbon cycle to anthropogenic climate warming. *Nature, 393*, 245–249.

Schiebel, R. (2002) Planktic foraminiferal sedimentation and the marine calcite budget. *Global Biogeochem. Cy., 16*(4), 1065, doi: 10.1029/2001GB001459.

Schiebel, R., J. Bijma, and C. Hemleben (1997) Population dynamics of the planktic foraminifer *Globigerina bulloides* from the eastern North Atlantic. *Deep-Sea Res. I, 44*, 1701–1713.

Schneider, K., and J. Erez (2006) The effect of carbonate chemistry on calcification and photosynthesis in the hermatypic coral *Acropora eurystoma. Limnol. Oceanogr., 51*(3), 1284–1293.

Schulz, K.G., I. Zondervan, L.J.A. Gerringa, K.R. Timmermans, M.J.W. Veldhuis, and U. Riebesell (2004) Effect of trace metal availability on coccolithophorid calcification. *Nature, 430*, 673–676.

Schuster, F. (2002) Oligocene and Miocene examples of *Acropora* dominated palaeoenvironments: Mesothelenic basin (NW Greece) and northern Gulf of Suez (Egypt). *Proc. 9th Int. Coral Reef Sym. 1*, 199–204.

Sciandra, A. and others (2003) Response of coccolithophorid *Emiliania huxleyi* to elevated partial pressure of CO_2 under nitrogen limitation. *Mar. Ecol.-Prog. Ser., 261*, 111–122.

Seibel, B.A., and V.J. Fabry (2003) Marine biotic response to elevated carbon dioxide, *Advances in Applied Biodiversity Science* 4, 59–67.

Shirayama, Y., and H. Thornton (2005) Effect of increased atmospheric CO_2 on shallow water marine benthos. *J. Geophys. Res., 110*, C09S08, doi: 10.1029/2004JC002618.

Siegenthaler, U., and J.L. Sarmiento (1993) Atmospheric carbon dioxide and the ocean. *Nature, 365*, 119–125.

Siegenthaler, U. and others (2005) Stable carbon cycle-climate relationship during the late Pleistocene. *Science, 310*, 1313–1317.

Sikes, C.S., R.D. Roer, and K.M. Wilber (1980) Photosynthesis and coccolith formation: inorganic carbon sources and net inorganic reaction of deposition. *Limnol. Oceanogr., 25*, 248–261.

Skirrow, G., and M. Whitfield (1975) Effect of increases in atmospheric carbon-dioxide content on carbonate ion concentration of surface ocean water at 25°C. *Limnol. Oceanogr., 20*, 103–108.

Smith, A.D., and A.A. Roth (1979) Effect of carbon dioxide concentration on calcification in the red coralline alga *Bossiella orbigniana. Mar. Biol., 52*, 217–225.

Smith, S.V. (1972) Production of calcium carbonate on mainland shelf of southern California. *Limnol. Oceanogr., 17*, 28–41.

— (1973) Carbon dioxide dynamics: a record of organic carbon production, respiration and calcification in the Eniwetok reef flat community. *Limnol. Oceanogr., 18*, 106–120.

Smith, S.V., and R.W. Buddemeier (1992) Global change and coral reef ecosystems. *Ann. Rev. Ecol. Syst., 23*, 89–118

Smith, S.V., and D.W. Kinsey (1978) Calcification and organic carbon metabolism as indicated by carbon dioxide, p. 469–484. *In* D.R. Stoddart, and R.E. Johannes (eds.), *Coral Reefs: Research Methods*, Unesco.

Smith, S.V., and F. Pesret (1974) Processes of carbon dioxide flux in Fanning Island Lagoon. *Pac. Sci., 28*, 225–245.

Spero, H.J., J. Bijma, D.W. Lea, and B.E. Bemis (1997) Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes. *Nature, 390*, 497–500.

Spindler, M., C. Hemleben, U. Bayer, A.W.H. Bé, and O.R. Anderson (1979) Lunar periodicity of reproduction in the planktonic foraminifer *Hastigerina pelagica. Mar. Ecol.-Prog. Ser., 1*, 61–64.

Stambler, N., N. Popper, Z. Dubinsky, and J. Stimson (1991) Effect of nutrient enrichment and water motion on the coral *Pocillopora damicornis. Pac. Sci., 45*, 299–307.

Stanley, S.M., and L.A. Hardie (1998) Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. *Palaeogeogr. Palaeoclimatol. Palaeoecol., 144*, 3–19.

Stanley, S.M., J.B. Ries, and L.A. Hardie (2002) Low-magnesium calcite produced by coralline algae in seawater of Late Cretaceous composition. *Proc. Nat. Acad. Sci. US*, *99*, 15,323–15,326.

— (2005) Seawater chemistry, coccolithophore population growth, and the origin of Cretaceous chalk. *Geology*, *33*, 593–596.

Suzuki, A., H. Kawahata, T. Ayukai, and K. Goto (2001) The oceanic CO_2 system and carbon budget in the Great Barrier Reef, Australia. *Geophys. Res. Lett.*, *28*, 1243–1246.

Suzuki, A., H. Kawahata, and T. Ayukai (2003) The oceanic CO_2 system and biogeochemical processes in the Great Barrier Reef, Australia. *Geochim. Cosmochim. Acta*, *67*, A458–A458.

Svensen, H. and others (2004) Release of methane from a volcanic basin as a mechanism for initial Eocene global warming. *Nature*, *429*, 542–545.

Takahashi, T. and others (1997) Global air-sea flux of CO_2: An estimate based on measurements of sea-air pCO_2 difference. *Proc. Nat. Acad. Sci. US*, *94*, 8292–8299.

Talley, L.D. (1999) Some aspects of ocean heat transport by the shallow, intermediate and deep overturning circulations, p. 1–22. *In* P.U. Clark, R.S. Webb, and L.D. Keigwin (eds.), *Mechanisms of Global Climate Change at Millennial Time Scales.* Geophysical Monograph Series, American Geophysical Union.

Tambutté, E., D. Allemand, I. Bourge, J.-P. Gattuso, and J. Jaubert (1995) An improved ^{45}Ca protocol for investigating physiological mechanisms in coral calcification. *Mar. Biol.*, *122*, 453–459.

Thierstein, H.R., K.R. Geitzenauer, B. Molfino, and N.J. Shackleton (1977) Global synchroneity of late Quaternary coccolith datum levels: validation by oxygen isotopes. *Geology*, *5*, 400–404.

Tripati, A., and H. Elderfield (2005) Deep-sea temperature and circulation changes at the Paleocene-Eocene thermal maximum. *Science*, *308*, 1894–1898.

Troy, P.J., Y.H. Li, and F.T. Mackenzie (1997) Changes in surface morphology of calcite exposed to the oceanic water column. *Aquat. Geochem.*, *3*, 1–20.

Tsurumi, M., D.L. Mackas, F.A. Whitney, C. Dibacco, M.D. Galbraith, and C.S. Wong (2005) Pteropods, eddies, carbon flux, and climate variability in the Alaska Gyre. *Deep-Sea Res. II*, *52*, 1037–1053.

U.S. Commission on Ocean Policy (2004) An Ocean Blueprint for the 21st Century. Final Report, Washington, DC.

van Bleijswijk, J.D.L., R.S. Kempers, M.J. Velduis, and P. Westbroek (1994) Cell and growth characteristics of types A and B of *Emiliania huxleyi* (Prymnesiophyceae) as determined by flow cytometry and chemical analyses. *J. Phycol.*, *30*, 230–241.

van der Wal, P., J.D.L. van Bleijswijk, and J.K. Egge (1994) Primary productivity and calcification rate in blooms of the coccolithophorid *Emiliania huxleyi* (Lohmann) Hay et Mohler developing in mesocosms. *Sarsia*, *79*, 401–408.

Ver, L.M.B., F.T. Mackenzie, and A. Lerman (1999) Carbon cycle in the coastal zone: Effects of global perturbations and change in the past three centuries. *Chem. Geol.*, *159*, 283–304.

Walsh, I., J. Dymond, and R. Collier (1988) Rates of recycling of biogenic components of settling particles in the ocean derived from sediment trap experiments. *Deep-Sea Res.*, *35*, 43–58.

Walter, L.M., and E.A. Burton (1990) Dissolution of recent platform carbonate sediments in marine pore fluids. *Am. J. Sci.*, *290*, 601–643.

Wanninkhof, R., and K. Thoning (1993) Measurement of fugacity of CO_2 in surface water using continuous and discrete sampling methods. *Mar. Chem.*, *44*, 189–204.

Watanabe, A. and others (2004) A rapid, precise potentiometric determination of total alkalinity in seawater by a newly developed flow-through analyzer designed for coastal regions. *Mar. Chem.*, *85*, 75–87.

Weiner, S., and P.M. Dove (2003) An overview of biomineralization processes and the problem of vital effect, p. 381. *In* P.M. Dove, J.J. De Yoreo, and S. Weiner (eds.), *Biomineralization. Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America and Geochemical Society.

Wells, F.E. (1976) Growth rates of four species of euthecosomatous pteropods occurring off Barbados, West Indies. *The Nautilus*, *90*, 114–116.

Wells, J.M. (1974) The metabolism of tropical benthic communities: In situ determinations and their implications. *M.T.S. Journal*, *8*, 9–11.

Whitfield, M. (1974) Accumulation of fossil CO_2 in atmosphere and in sea. *Nature*, *247*, 523–525.

— (1975) Future impact of fossil CO_2 on sea—Reply. *Nature*, *254*, 274–275.

Wilkinson, C. (ed.). 2004. *Status of Coral Reefs of the World: 2004.* Australian Institute of Marine Science.

Winter, A., and W.G. Siesser (1994) Atlas of living coccolithophores, p. 107–159. *In* A. Winter, and W.G. Siesser (eds.), *Coccolithophores*, Cambridge Univ. Press.

Wolf-Gladrow, D.A., U. Riebesell, S. Burkhardt, and J. Bijma (1999) Direct effects of CO_2 concentration on growth and isotopic composition of marine plankton. *Tellus B*, *51*, 461–476.

Wollast, R. (1998) Evaluation and comparison of the global carbon cycle in the coastal zone and in the open ocean, p. 213–252. *In* K.H. Brink, and A.R. Robinson (eds.), *The Sea: The Global Coastal Ocean Processes and Methods*, John Wiley.

Wong, C.S. and others (1999) Seasonal and interannual variability in particle fluxes of carbon, nitrogen and silicon from time series of sediment traps at Ocean Station P, 1982–1993: Relationship to changes in subarctic primary productivity. *Deep-Sea Res. II*, *46*, 2735–2760.

Yamanaka, Y., and E. Tajika (1996) The role of the vertical fluxes of particulate organic matter and calcite in the oceanic carbon cycle: Studies using an ocean biogeochemical general circulation model. *Global Biogeochem. Cy.*, *10*, 361–382.

Yates, K.K., and R.B. Halley (2003) Measuring coral reef community metabolism using new benthic chamber technology. *Coral Reefs, 22,* 247–255.

— (2006a) CO_3^{2-} concentration and pCO_2 thresholds for calcification and dissolution on the Molokai reef flat, Hawaii. *Biogeosci. Disc., 3,* 123–154.

— (2006b) Diurnal variation in rates of calcification and carbonate sediment dissolution in Florida Bay. *Estuar. Coasts, 29,* 24–39.

Yates, K.K., and L.L. Robbins (1998) Production of carbonate sediments by a unicellular green alga. *American Mineralogist, 83,* 1503–1509, Part 2.

Yates, K.K., and L.L. Robbins (1999) Radioisotope tracer studies of inorganic carbon and Ca in microbially derived $CaCO_3$. *Geochim. Cosmochim. Acta, 63*(1), 129–136.

Yates, K.K., and L.L. Robbins (2001) Microbial lime-mud production and its relation to climate change, p. 267–283. *In* L.C. Gerhard, W.E. Harrison, and B.M. Hanson (eds.), *Geological Perspectives of Global Climate Change,* AAPG Tulsa, OK.

Young, J.R. (1994) Functions of coccoliths, p. 63–82. *In* A. Winter, and W.G. Seisser (eds.), *Coccolithophores,* Cambridge University Press.

Zachos, J.C., K.C. Lohmann, J.C.G. Walker, and S.W. Wise (1993) Abrupt climate change and transient climates during the Paleogene—A marine perspective. *J. Geol., 101,* 191–213.

Zachos, J.C. and others (2003) A transient rise in tropical sea surface temperature during the Paleocene-Eocene thermal maximum. *Science, 302,* 1551–1554.

— (2005) Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. *Science, 308,* 1611–1615.

Zeebe, R. E. and A. Sanyal (2002) Comparison of two potential strategies of planktonic foraminifera for house building: Mg^{2+} or H^+ removal? *Geochim. Cosmochim. Acta, 66*(7), 1159–1169.

Zimen, K.E., and F.K. Altenhein (1973) Future burden of industrial CO_2 on atmosphere and oceans. *Z. Naturforsch. A, 28,* 1747–1752.

Zimmerman, R.C., D.G. Kohrs, D.L. Steller, and R.S. Alberte (1997) Impacts of CO_2 enrichment on productivity and light requirements of eelgrass. *Plant Physiol., 115,* 599–607.

Zondervan, I., R.E. Zeebe, B. Rost, and U. Riebesell (2001) Decreasing marine biogenic calcification: A negative feedback on rising atmospheric pCO_2. *Global Biogeochem. Cy., 15,* 507–516.

Zondervan, I., B. Rost, and U. Riebesell (2002) Effect of CO_2 concentration on the PIC/POC ratio in the coccolithophore *Emiliania huxleyi* grown under light-limiting conditions and different daylengths. *J. Exper. Mar. Biol. Ecol., 272,* 55–70.

9. Acronyms

AIMS	Australian Institute of Marine Science
BATS	Bermuda-Atlantic Time Series
BBSR	Bermuda Biological Station for Research
CACGP	Commission on Atmospheric Chemistry and Global Pollution (IAMAS)
CARIACO	Carbon Retention in A Colored Ocean
CCSP	U.S. Climate Change Science Program (USGCRP)
CDIAC	Carbon Dioxide Information and Analysis Center (Oak Ridge National Laboratory, USA)
CDOM	colored dissolved organic matter; or chromophoric dissolved organic matter
CNRS	Centre National de la Recherche Scientifique (National Center for Scientific Research) (France)
COSEE	Centers for Ocean Science Education Excellence (NSF, Sea Grant, NOAA, ONR)
CRCA	Coral Reef Conservation Act (USA)
CREWS	Coral Reef Early Warning System (NOAA)
CRM	certified reference material
CSUSM	California State University San Marcos
DIC	dissolved inorganic carbon
DOE	Department of Energy (USA)
DYFAMED	Dynamics of Atmospheric Fluxes in the Mediterranean Sea (France)
EPA	Environmental Protection Agency (USA)
EPA-NCER	EPA National Center for Environmental Research
EPA-STAR	EPA Science to Achieve Results program
ESTOC	European Station for Time-series in the Ocean, Canary Islands (Spain and Germany)
FACE	Free Air Carbon Dioxide Enrichment Program (DOE Office of Biological and Environmental Research)
GC	gas chromatograph
GEOCARB	a model for the evolution of the carbon cycle and atmospheric CO_2 over Phanerozoic time
HOT	Hawaiian Ocean Time-Series
IAMAS	International Association of Meteorology and Atmospheric Sciences
ICON	Integrated Coral Observing Network (NOAA)
ICSU	International Council for Science
IGBP	International Geosphere-Biosphere Programme
IKONOS	High-spatial-resolution commercial satellite (based on "eikon," the Greek word for "image")
IMBER	Integrated Marine Biogeochemistry and Ecosystem Research (IGBP-SCOR Project)
IOC	Intergovernmental Oceanographic Commission
IOS	Institute of Ocean Science (Canada)
IPCC	Intergovernmental Panel on Climate Change
IPO	Interdecadal Pacific Oscillation
JGOFS	Joint Global Ocean Flux Survey
KERFIX	Kerguelen Fixed Station; Kerguelen Islands Time-Series Measurement Programme (France-JGOFS); now Climate Océanique à Kerguelen (CLIOKER; component of CLIVAR)
KNOT	Kyodo North Pacific Ocean Time-series (KNOT)
LANDSAT	NASA's Land Remote-Sensing Satellite
LANDSAT ETM	LANDSAT Enhanced Thematic Mapper
MACC	Mainstreaming Adaptation to Climate change (NOAA)
MBARI	Monterey Bay Aquarium Research Institute
NASA	National Aeronautical and Space Administration (USA)
NCAR	National Center for Atmospheric Research (USA)
NCORE	National Center for Caribbean Coral Reef Research (EPA-NCER)
NDIR	nondispersive infrared
NOAA	National Oceanic and Atmospheric Administration (USA)
NOAA-CRED	NOAA, Coral Reef Ecosystem Division

NOAA-NESDIS	NOAA National Environmental, Satellite, and Data Information Service
NOAA-NOS NOAA	NOAA National Ocean Service
NOAA-OAR NOAA	NOAA Office of Oceanic and Atmospheric Research
NOAA-OGP	NOAA Office of Global Programs
NOAA-PMEL	NOAA Pacific Marine Environmental Lab
NSF	National Science Foundation (USA)
NSF-GG	NSF Geobiology and Low-temperature Geochemistry
NSF-LTER	NSF Long-Term Ecological Research
NSF-MGG	NSF Marine Geology and Geophysics
NSF-OCE-BIO	NSF Ocean Sciences, Biological Oceanography Program
NSF-OCE-CHE	NSF Ocean Sciences, Chemical Oceanography Program
OACES	Ocean-Atmosphere Carbon Dioxide Exchange Study (NOAA)
OCCC	Ocean Carbon and Climate Change (USGCRP-CCSP)
ONR	Office of Naval Research (USA)
OSP	Ocean Station Papa (Canada)
OWS	Ocean Weather Station (Canada)
PETM	Paleocene-Eocene Thermal Maximum
PIC	particulate inorganic carbon
POC	particulate organic carbon
RSMAS	Rosenstiel School of Marine and Atmospheric Science (University of Miami, USA)
SCOR	Scientific Committee on Ocean Research (ICSU; non-governmental)
SHARQ	Submersible Habitat for Analyzing Reef Quality (USGS)
SOCM	Shallow Ocean Carbon Model (Mackenzie)
SOIREE	Southern Ocean Iron Enrichment Experiment (multi-national)
SOLAS	Surface Ocean–Lower Atmosphere Study (IGBP, SCOR, WCRP, CACGP)
SOMMA	single-operator multiparameter metabolic analyzer
TAO-TRITON	Tropical Atmosphere Ocean Project (NOAA) and Triangle Trans-Ocean Buoy Network (Japan)
TEP	transparent exopolymer particles
UNESCO	United Nations Educational, Scientific and Cultural Organization
USGCRP	U.S. Global Change Research Program
USGS	U.S. Geological Survey (USA)
USGS-CCWS	USGS Center for Coastal and Watershed Studies
WCRP	World Climate Research Programme
WOCE	World Ocean Circulation Experiment (WCRP)

Participants in the St. Petersburg Workshop

1. Marlin Atkinson
2. Fred Mackenzie
3. Jim Orr
4. Wade Cooper
5. Jean-Pierre Gattuso
6. Frank Millero
7. Bill Kirkwood
8. Linnae De Camp
9. Bob Byrne
10. Tansey Hall
11. Björn Rost
12. Colomban De Vargas
13. Howie Spero
14. Heidi Souder
15. Jelle Bijma
16. Kathy Tedesco
17. Chris Sabine
18. Dan McCorkle
19. Nick Bates
20. Dick Feely
21. Mark Eakin
22. Barney Balch
23. Peter Betzer
24. Eric Sundquist
25. Dwight Gledhill
26. Andy Ridgwell
27. Kevin Wong
28. Bill Fitt
29. Rik Wanninkhof
30. John Guinotte
31. Lisa Robbins
32. Janice Lough
33. Kim Yates
34. Chris Langdon
35. Pamela Hallock
36. Ilsa Kuffner
37. Katie Fagan
38. Hajime Kayanne
39. Rob Van Woesik
40. Will Berelson
41. Jim Hendee
42. Tsung-Hung Peng
43. Vicki Fabry
44. Bob Halley
45. Rebecca Hacker-Santos
46. Joanie Kleypas
47. Lore Ayoub
48. Peter Swart
49. Alexandra Amat

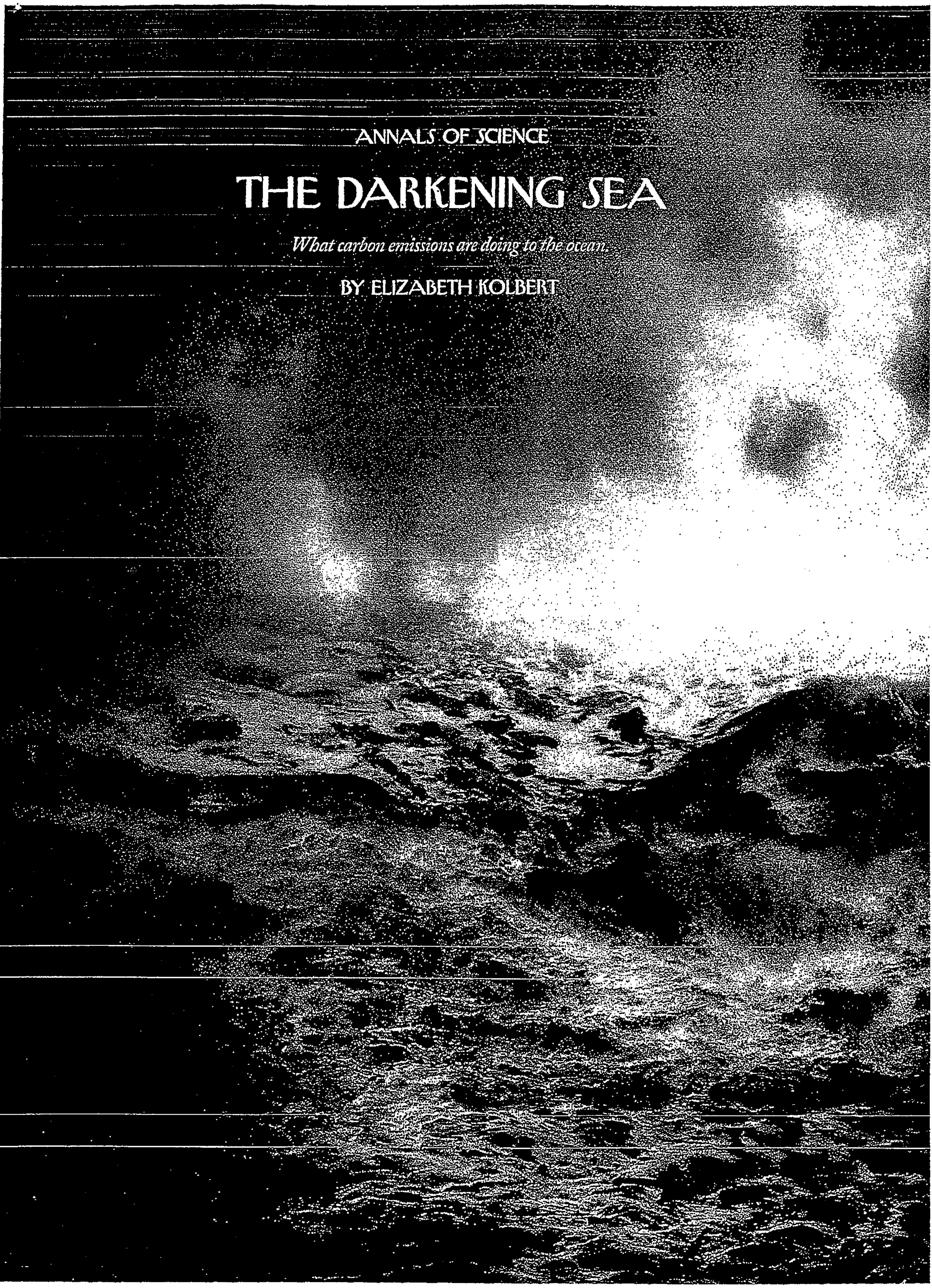
Participants not in photo:
Dick Dodge
Chet Koblinsky

ANNALS OF SCIENCE

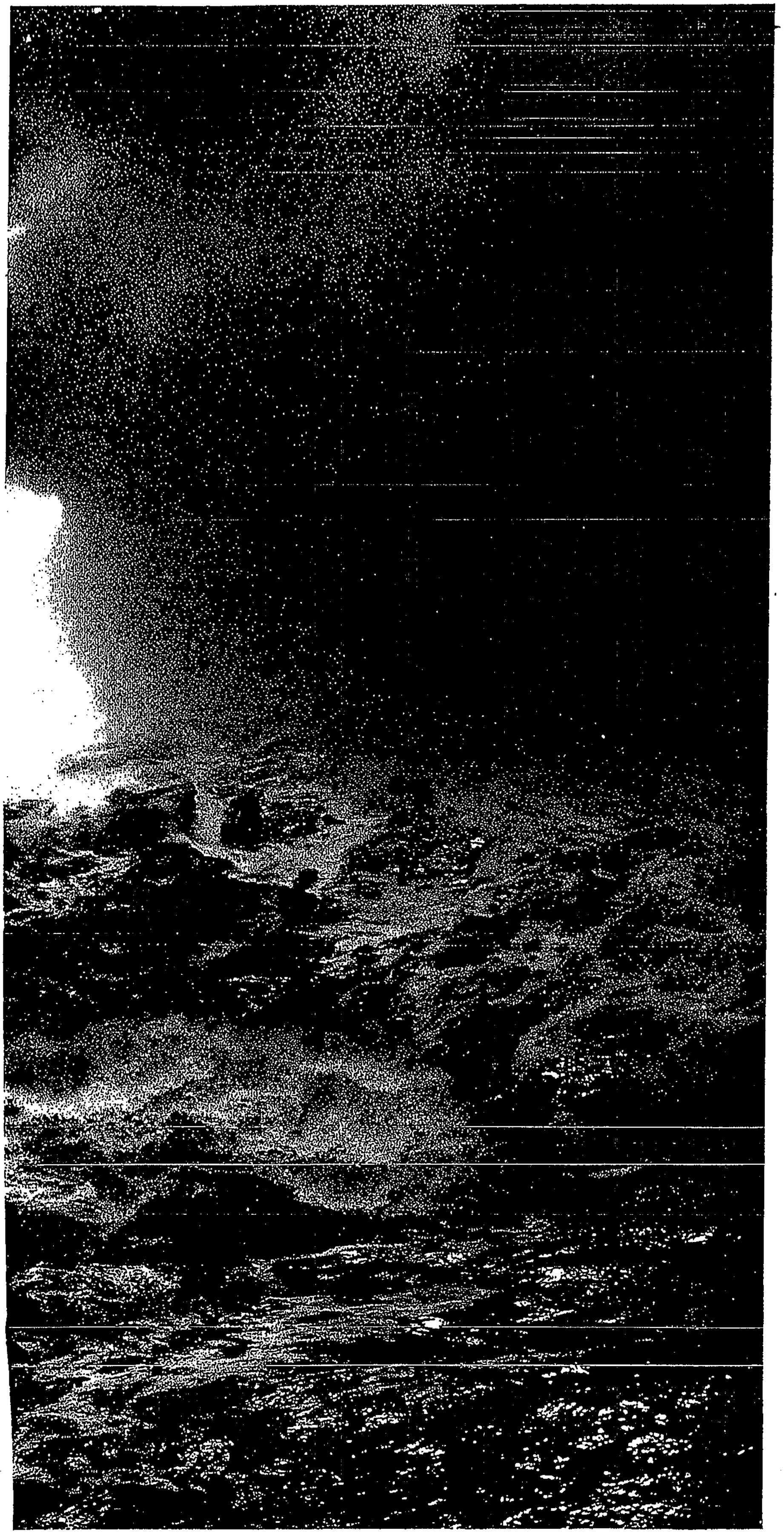
THE DARKENING SEA

What carbon emissions are doing to the ocean.

BY ELIZABETH KOLBERT



DODO JIN MING, "FREE ELEMENT XXXIII" (2003)/LAURENCE MILLER GALLERY



Pteropods are tiny marine organisms that belong to the very broad class known as zooplankton. Related to ,
they swim by means of a pair of winglike gelatinous flaps and feed by entrapping even tinier marine creatures in a bubble of mucus. Many pteropod species—there are nearly a hundred in all—produce shells, apparently for protection; some of their predators, meanwhile, have evolved specialized tentacles that they employ much as diners use forks to spear escargot. Pteropods are first male, but as they grow older they become female.

Victoria Fabry, an oceanographer at California State University at San Marcos, is one of the world's leading experts on pteropods. She is slight and soft-spoken, with wavy black hair and h green eyes. Fabry fell in love with ocean as a teen-ager after visiting the Outer Banks, off North Carolina, and took up pteropods when she was in graduate school, in the early nineteen-eighties. At that point, most basic questions about the animals had yet to be answered, and, for her dissertation, Fabry decided to study their shell growth. Her plan was to raise pteropods in tanks, but she ran into trouble immediately. When distu pteropods tend not to produce the mucus bubbles, and slowly starve. Fabry tried using bigger tanks for her pteropods, but the only correlation, she recalled recently, was that the more time she spent impr ing the tanks "the quicker they di After a while, she resigned herself to constantly collecting new specimens. This, in turn, meant going out on just about any research ship that would have her.

Fabry developed a simple, if brutal, protocol that could be completed at sea. She would catch some pteropods, either by trawling with a net or by scuba diving, and place them in one-litre bottles filled with seawater, to which she had added a small amount of radioactive calcium 45. Forty-eight hours later, she would remove the pteropods from the bottles, dunk them in warm ethanol, and pull their bodies out with a pair of tweezers. Back on land, she would measure how much calcium 45 their shells had taken up during their two days of captivity.

In the summer of 1985, Fabry got a berth on a research vessel sailing f Honolulu to Kodiak Island. Late i trip, near a spot in the Gulf of Alaska known as Station Papa, she came upon a profusion of *Clio pyramidata*, a half-inch-long pteropod with a shell the shape of an unfurled umbrella. In her enthusiasm, Fabry collected too many specimens; instead of putting two or three in a bottle, she had to cram in a dozen. The next day, she noticed that something had gone wrong. "Normally, their shells are transparent," she said. "They look like little gems, little jewels. They're just beautiful. But I could see that, along the edge, they were becoming opaque, chalky."

Like other animals, pteropods take in oxygen and give off carbon dioxide as a waste product. In the open sea, the CO_2 they produce has no effect. Seal them in a small container, however, and the CO_2 starts to build up, changing the water's chemistry. By overcrowding her *Clio pyramidata*, Fabry had demonstrated that the organisms were highly sensitive to such changes. Instead of growing, their shells were dissolving. It stood to reason that other kinds of pteropods—and, indeed, perhaps any number of shell-building species—were similarly vulnerable. This should have represented a major discovery, and a cause for alarm. But, as is so often the case with inadvertent breakthroughs, it went unremarked upon. No one on the boat, including Fabry, appreciated what the pteropods were telling them, because no one, at that point, could imagine the chemistry of an entire ocean changing.

MORE IN DREAMS THAN IN THE FLESH

No wind. No storm.
Just the trees heaving in their own sorrow.
The girl next door who went missing a week ago
Has come back; the faces of her parents stare
Like bare, wounded hills beyond the river.
Often a dream makes one afraid
Of the things one might do. It frightens one
That despair seems to have no boundaries.
The laments for a death are over while death
Is warm and safe and drifts into sleep
In a child's dream.

Some time back I had stumbled
On the decomposing bodies of a young couple
On the hill slope behind the temple. The girl
Couldn't have been more than sixteen years old.
I had made a great effort to defend myself.
Her half-open eyes now wander through
My subdued Sunday mornings as though testing
The courage it took to be a man.

No wind. No storm.
Just the vague light of daybreak
Coming down from the hilltops.
An unknown darkening is in my breath.
And I knew death is born to us in the same way
As when we cast our nets into the night
And draw in the shapes of day.

—*Jayanta Mahapatra*

Since the start of the industrial revolution, humans have burned enough coal, oil, and natural gas to produce some two hundred and fifty billion metric tons of carbon. The result, as is well known, has been a transformation of the earth's atmosphere. The concentration of CO_2 in the air today—three hundred and eighty parts per million—is higher than it has been at any point in the past six hundred and fifty thousand years, and probably much longer. At the current rate of emissions growth, CO_2 concentration will top five hundred parts per million—roughly double pre-industrial levels—by the middle of this century. It is expected that such an increase will produce an eventual global temperature rise of between three and a half and seven degrees Fahrenheit, and that this, in turn, will prompt a string of disasters, including fiercer hurricanes, more deadly droughts, the disappearance of most remaining glaciers, the melting of the Arctic ice cap, and the inundation of many of the world's major coastal cities. But this is only half the story.

Ocean covers seventy per cent of the earth's surface, and everywhere that water and air come into contact there is an exchange. Gases from the atmosphere get absorbed by the ocean and gases dissolved in the water are released into the atmosphere. When the two are in equilibrium, roughly the same quantities are being dissolved as are getting released. But change the composition of the atmosphere, as we have done, and the exchange becomes lopsided: more CO_2 from the air enters the water than comes back out. In the nineteen-nineties, researchers from seven countries conducted nearly a hundred cruises, and collected more than seventy thousand seawater samples from different depths and locations. The analysis of these samples, which was completed in 2004, showed that nearly half of all the carbon dioxide that humans have emitted since the start of the nineteenth century has been absorbed by the sea.

When CO_2 dissolves, it produces carbonic acid, which has the chemical formula H_2CO_3. As acids go, H_2CO_3 is relatively innocuous—we drink it all the time in Coke and other carbonated beverages—but in sufficient quantities it can change the water's pH. Already, humans have pumped enough carbon into the oceans—some hundred and twenty billion tons—to produce a .1 decline in surface pH. Since pH, like the Richter scale, is a logarithmic measure, a .1 drop represents a rise in acidity of about thirty per cent. The process is generally referred to as "ocean acidification," though it might more accurately be described as a decline in ocean alkalinity. This year alone, the seas will absorb an additional two billion tons of carbon, and next year it is expected that they will absorb another two billion tons. Every day, every American, in effect, adds forty pounds of carbon dioxide to the oceans.

Because of the slow pace of deep-ocean circulation and the long life of carbon dioxide in the atmosphere, it is impossible to reverse the acidification that has already taken place. Nor is it possible to prevent still more from occurring. Even if there were some way to halt the emission of CO_2 tomorrow, the oceans would continue to take up carbon until they reached a new equilibrium with the air. As Britain's Royal Society noted in a recent report, it will take "tens of thousands of years for ocean chemistry to return to a condition similar to that occurring at pre-industrial times."

Humans have, in this way, set in motion change on a geologic scale. The question that remains is how marine life will respond. Though oceanographers are just beginning to address the question, their discoveries, at this early stage, are disturbing. A few years ago, Fabry finally pulled her cloudy shells out of storage to examine them with a scanning electron microscope. She found that their surfaces were riddled with pits. In some cases, the pits had grown into gashes, and the upper layer had started to pull away, exposing the layer underneath.

The term "ocean acidification" was coined in 2003 by two climate scientists, Ken Caldeira and Michael Wickett, who were working at the Lawrence Livermore National Laboratory, in Northern California. Caldeira has since moved to the Carnegie Institution, on the campus of Stanford University, and during the summer I went to visit him at his office, which is housed in a "green" building that looks like a barn that has been taken apart and reassembled at odd angles. The building has no air-conditioning; temperature control is provided by a shower of mist that rains down into a tiled chamber in the lobby. At the time of my visit, California was in the midst of a record-breaking heat wave; the system worked well enough that Caldeira's office, if not exactly cool, was at least moderately comfortable.

Caldeira is a trim man with wiry brown hair and a boyish sort of smile. In the nineteen-eighties, he worked as a software developer on Wall Street, and one of his clients was the New York Stock Exchange, for whom he designed computer programs to help detect insider trading. The programs functioned as they were supposed to, but after a while Caldeira came to the conclusion that the N.Y.S.E. wasn't actually interested in catching insider traders, and he decided to switch professions. He went back to school, at N.Y.U., and ended up becoming a climate modeller.

Unlike most modellers, who focus on one particular aspect of the climate system, Caldeira is, at any given moment, working on four or five disparate projects. He particularly likes computations of a provocative or surprising nature; for example, not long ago he calculated that cutting down all the world's forests and replacing them with grasslands would have a slight cooling effect. (Grasslands, which are lighter in color than forests, absorb less sunlight.) Other recent calculations that Caldeira has made show that to keep pace with the present rate of temperature change plants and animals would have to migrate poleward by thirty feet a day, and that a molecule of CO_2 generated by burning fossil fuels will, in the course of its lifetime in the atmosphere, trap a hundred thousand times more heat than was released in producing it.

Caldeira began to model the effects of carbon dioxide on the oceans in 1999, when he did some work for the Department of Energy. The department wanted to know what the environmental consequences would be of capturing CO_2 from smokestacks and injecting it deep into the sea. Caldeira set about calculating how the ocean's pH would change as a result of deep-sea injection, and then compared that result with the current practice of pouring carbon dioxide into the atmosphere and allowing it to be taken up by surface waters. In 2003, he submitted his work to *Nature*. The journal's editors advised him to drop the discussion of deep-ocean injection, he recalled, because the calculations concerning the effects of ordinary atmospheric release were so startling. Caldeira published the first part of his paper under the subheading "The coming centuries may see more [illegible] acidification than the past 300 million years."

Caldeira told me that he had chosen the term "ocean acidification" quite deliberately, for its shock value. Seawater is naturally alkaline, with a pH ranging from 7.8 to 8.5—a pH of 7 is neutral—which means that, for now, at least, the oceans are still a long way from actually turning acidic. Meanwhile, from the perspective of marine life, the drop in pH matters less than the string of chemical reactions that follow.

The main building block of shells is calcium carbonate—$CaCO_3$. (The White Cliffs of Dover are a huge CaCO [illegible] posit, the remains of countless tiny sea creatures that piled up during the Cretaceous—or "chalky"—period.) Calcium carbonate produced by marine organisms comes in two principal forms, aragonite and calcite, which have slightly different crystal structures. How, exactly, different organisms form calcium carbonate remains something of a mystery. Ordinarily in seawater, $CaCO_3$ does not pre[illegible]tate out as a solid. To build their s[illegible] calcifying organisms must, in effect, assemble it. Adding carbonic acid to the water complicates their efforts, because it reduces the number of carbonate ions in circulation. In scientific terms, this i[illegible]ferred to as "lowering the water's sat[illegible]tion state with respect to calcium carbonate." Practically, it means shrinking the supply of material available for shell formation. (Imagine trying to build a house when someone keeps stealing your bricks.) Once the carbonate concentration gets pushed low enough, even existing shells, like those of Fabry's pteropods, begin to dissolve.

To illustrate, in mathematical terms, what the seas of the future will look like, Caldeira pulled out a set of graphs. Plotted on one axis was aragonite saturation levels; on the other, latitude. (Ocean latitude is significant because saturation levels tend naturally to decline toward the poles.) Different colors of lines represented different emissions scenarios. Some scenarios project that the world's economy will continue to grow ra[illegible] and that this growth will be fu[illegible] mostly by oil and coal. Others assume that the economy will grow more slowly,

"I've been researching a little furniture company I'd like to rearrange."

and still others that the energy mix will shift away from fossil fuels. Caldeira considered four much studied scenarios, ranging from one of the most optimistic, known by the shorthand B1, to one of the most pessimistic, A2. The original point of the graphs was to show that each scenario would produce a different ocean. But they turned out to be more similar than Caldeira had expected.

Under all four scenarios, by the end of this century the waters around Antarctica will become undersaturated with respect to aragonite—the form of calcium carbonate produced by pteropods and corals. (When water becomes undersaturated, it is corrosive to shells.) Meanwhile, surface pH will drop by another .2, bringing acidity to roughly double what it was in pre-industrial times. To look still further out into the future, Caldeira modelled what would happen if humans burned through all the world's remaining fossil-fuel resources, a process that would release some eighteen thousand gigatons of carbon dioxide. He found that by 2300 the oceans would become undersaturated from the poles to the equator. Then he modelled what would happen if we pushed still further and burned through unconventional fuels, like low-grade shales. In that case, we would drive the pH down so low that the seas would come very close to being acidic.

"I used to think of B1 as a good scenario, and I used to think of A2 as a terrible scenario," Caldeira told me. "Now I look at them as different flavors of bad scenarios."

He went on, "I think there's a whole category of organisms that have been around for hundreds of millions of years which are at risk of extinction—namely, things that build calcium-carbonate shells or skeletons. To a first approximation, if we cut our emissions in half it will take us twice as long to create the damage. But we'll get to more or less the same place. We really need an order-of-magnitude reduction in order to avoid it."

Caldeira said that he had recently gone to Washington to brief some members of Congress. "I was asked, 'What is the appropriate stabilization target for atmospheric CO_2?' " he recalled. "And I said, 'Well, I think it's inappropriate to think in terms of stabilization targets. I think we should think in terms of emissions targets.' And they said, 'O.K., what's the appropriate emissions target?' And I said, 'Zero.'

"If you're talking about mugging little old ladies, you don't say, 'What's our target for the rate of mugging little old ladies?' You say, 'Mugging little old ladies is bad, and we're going to try to eliminate it.' You recognize you might not be a hundred per cent successful, but your goal is to eliminate the mugging of little old ladies. And I think we need to eventually come around to looking at carbon-dioxide emissions the same way."

Coral reefs grow in a great swath that stretches like a belt around the belly of the earth, from thirty degrees north to thirty degrees south latitude. The world's largest reef is the Great Barrier, off the coast of northeastern Australia, and the second largest is off the coast of Belize. There are extensive coral reefs in the tropical Pacific, in the Indian Ocean, and in the Red Sea, and many smaller ones in the Caribbean. These reefs, home to an estimated twenty-five per cent of all marine fish species, represent some of the most diverse ecosystems on the planet.

Much of what is known about coral reefs and ocean acidification was originally discovered, improbably enough, in Arizona, in the self-enclosed, supposedly self-sufficient world known as Biosphere 2. A three-acre glassed-in structure shaped like a ziggurat, Biosphere 2 was built in the late nineteen-eighties by a private group—a majority of the funding came from the billionaire Edward Bass—and was intended to demonstrate how life on earth (Biosphere 1) could be re-created on, say, Mars. The building contained an artificial "ocean," a "rain forest," a "desert," and an "agricultural zone." The first group of Biosphereans—four men and four women—managed to remain, sealed inside, for two years. They produced all their own food and, for a long stretch, breathed only recycled air, but the project was widely considered a failure. The Biosphereans spent much of the time hungry, and, even more ominously, they lost control of their artificial atmosphere. In the various "ecosystems," decomposition, which takes up oxygen and gives off CO_2, was supposed to be balanced by photosynthesis, which does the reverse. But, for reasons mainly having to do with the richness of the soil that had been used in the "agricultural zone," decomposition won out. Oxygen levels inside the building kept falling, and the Biosphereans developed what amounted to altitude sickness. Carbon-dioxide levels soared, at one point reaching three thousand parts per million, or roughly eight times the levels outside.

When Biosphere 2 officially collapsed, in 1995, Columbia University took over the management of the building. The university's plan was to transform it into a teaching and research facility, and it fell to a scientist named Chris Langdon to figure out something pedagogically useful to do with the "ocean," a tank the size of an Olympic swimming pool. Langdon's specialty was measuring photosynthesis, and he had recently finished a project, financed by the Navy, that involved trying to figure out whether blooms of bioluminescent algae could be used to track enemy submarines. (The answer was no.) Langdon was looking for a new project, but he wasn't sure what the "ocean" was good for. He began by testing various properties of the water. As would be expected in such a high-CO_2 environment, he found that the pH was low.

"The very first thing I did was try to establish normal chemistry," he recalled recently. "So I added chemicals—essentially baking soda and baking powder—to the water to bring the pH back up." Within a week, the alkalinity had dropped again, and he had to add more chemicals. The same thing happened. "Every single time I did it, it went back down, and the rate at which it went down was proportional to the concentration. So, if I added more, it went down faster. So I started thinking, What's going on here? And then it dawned on me."

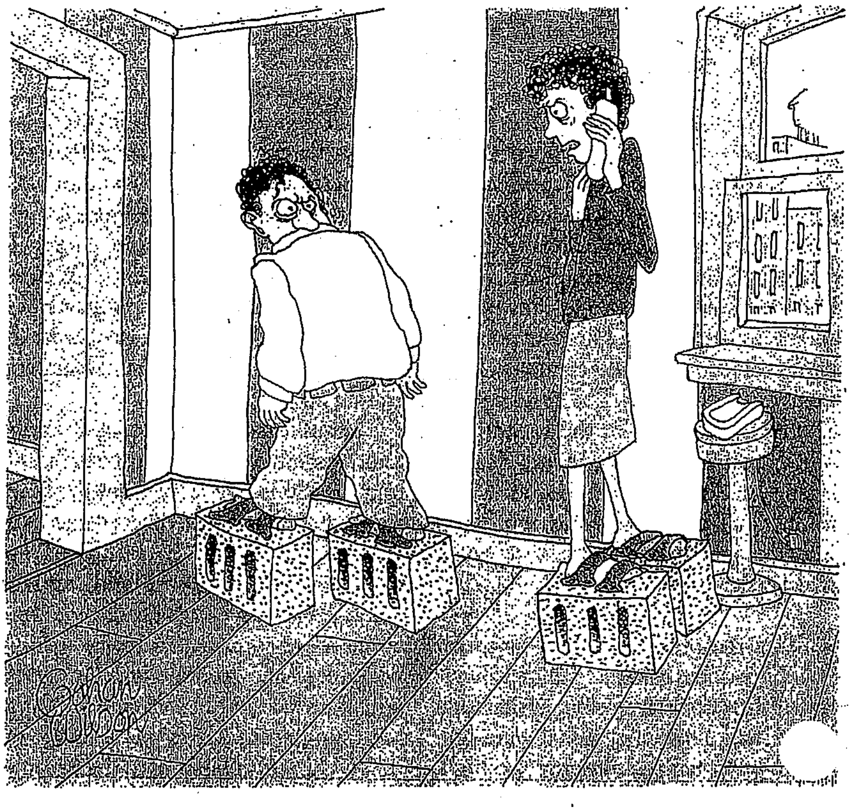
Langdon left Columbia in 2004 and now works at the Rosenstiel School of Marine and Atmospheric Science, at the University of Miami. He is fifty-two, with a high forehead, deep-set blue eyes, and a square chin. When I went to visit him, not long ago, he took me to see his coral samples, which were growing in a sort of aquatic nursery across the street from his office. On the way, we had to pass through a room filled with tanks of purple sea slugs, which were being raised for medical research. In the front row, the youngest sea slugs, about half an inch long, were floating gracefully, as if suspended in gelatine. Toward the back were slugs that had been fed for several months on a lavish experimental diet. These were the size of my forearm and seemed barely able to lift their knobby, purplish heads.

Langdon's corals were attached to tiles arranged at the bottom of long, sinklike tanks. There were hundreds of them, grouped by species: *Acropora cervicornis*, a type of staghorn coral that grows in a classic antler shape; *Montastrea cavernosa*, a coral that looks like a seafaring cactus; and *Porites divaricata*, a branching coral made up of lumpy, putty-colored protuberances. Water was streaming into the tanks, but when Langdon put his hand in front of the faucet to stop the flow, I could see that every lobe of *Porites divaricata* was covered with tiny pink arms and that every arm ended in soft, fingerlike tentacles. The arms were waving in what looked to be a frenzy either of joy or of supplication.

Langdon explained that the arms belonged to separate coral polyps, and that a reef consisted of thousands upon thousands of polyps spread, like a coating of plaster, over a dead calcareous skeleton. Each coral polyp is a distinct individual, with its own tentacles and its own digestive system, and houses its own collection of symbiotic algae, known as zooxanthellae, which provide it with most of its nutrition. At the same time, each polyp is joined to its neighbors through a thin layer of connecting tissue, and all tached to the colony's collective skeleton. Individual polyps constantly add to the group skeleton by combining calcium and carbonate ions in a medium known as the extracytoplasmic calcifying fluid. Meanwhile, other organisms, like parrot fish and sponges, are constantly eating away at the reef in search of food or protection. If a reef were ever to stop calcifying, it would start to shrink and eventually would disappear.

"It's just like a tree with bugs," Langdon explained. "It needs to grow pretty quickly just to stay even."

As Langdon struggled, unsuccessfully, to control the pH in the Biosp "ocean," he started to wonder whether the corals in the tank might be to blame. The Biosphereans had raised twenty different species of coral, and while many of the other creatures, including nearly all the vertebrates selected for the project, had died out, the corals had survived. Langdon wondered whether the chemicals he was adding to raise the pH were, by increasing the saturation state, st ulating their growth. At the ti



"It's the people downstairs complaining about noise again."

seemed an unlikely hypothesis, because the prevailing view among marine biologists was that corals weren't sensitive to changes in saturation. (In many textbooks, the formula for coral calcification is still given incorrectly, which helps explain the prevalence of this view.) Just about everyone, including Langdon's own postdoc, a young woman named Francesca Marubini, thought that his theory was wrong. "It was a total pain in the ass," Langdon recalled.

To test his hypothesis, Langdon employed a straightforward but time-consuming procedure. Conditions in the "ocean" would be systematically varied, and the growth of the coral monitored. The experiment took more than three years to complete, produced more than a thousand measurements, and, in the end, confirmed Langdon's hypothesis. It revealed a more or less linear relationship between how fast the coral grew and how highly saturated the water was. By proving that increased saturation spurs coral growth, Langdon also, of course, demonstrated the reverse: when saturation drops, coral growth slows. In the artificial world of Biosphere 2, the implications of this discovery were interesting; in the real world they were rather more grim. Any drop in the ocean's saturation levels, it seemed, would make coral more vulnerable.

Langdon and Marubini published their findings in the journal *Global Biogeochemical Cycles* in the summer of 2000. Still, many marine biologists remained skeptical, in no small part, it seems, because of the study's association with the discredited Biosphere project. In 2001, Langdon sold his house in New York and moved to Arizona. He spent another two years redoing the experiments, with even stricter controls. The results were essentially identical. In the meantime, other researchers launched similar experiments on different coral species. Their findings were also the same, which, as Langdon put it to me, "is the best way to make believers out of people."

Coral reefs are under threat for a host of reasons: bottom trawling, dynamite fishing, coastal erosion, agricultural runoff, and, nowadays, global warming. When water temperatures rise too high, corals lose—or perhaps expel, no one is quite sure—the algae that nourish them. (The process is called "bleaching," because without their zooxanthellae corals appear white.) For a particular reef, any one of these threats could potentially be fatal. Ocean acidification poses a different kind of threat, one that could preclude the very possibility of a reef.

Saturation levels are determined using a complicated formula that involves multiplying the calcium and carbonate ion concentrations, and then dividing the result by a figure called the stoichiometric solubility product. Prior to the industrial revolution, the world's major reefs were all growing in water whose aragonite saturation level stood between 4 and 5. Today, there is not a single remaining region in the oceans where the saturation level is above 4.5, and there are only a handful of spots—off the northeastern coast of Australia, in the Philippine Sea, and near the Maldives—where it is above 4. Since the takeup of CO_2 by the oceans is a highly predictable physical process, it is possible to map the saturation levels of the future with great precision. Assuming that current emissions trends continue, by 2060 there will be no regions left with a level above 3.5. By 2100, none will remain above 3.

As saturation levels decline, the rate at which reefs add aragonite through calcification and the rate at which they lose it through bioerosion will start to approach each other. At a certain point, the two will cross, and reefs will begin to disappear. Precisely where that point lies is difficult to say, because erosion may well accelerate as ocean pH declines. Langdon estimates that the crossing point will be reached when atmospheric CO_2 levels exceed six hundred and fifty parts per million, which, under a "business as usual" emissions scenario, will occur sometime around 2075.

"I think that this is just an absolute limit, something they can't cope with," he told me. Other researchers put the limit somewhat higher, and others somewhat lower.

Meanwhile, as global temperatures climb, bleaching events are likely to become more common. A major worldwide bleaching event occurred in 1998, and many Caribbean reefs suffered from bleaching again during the summer of 2005. Current conditions in the equatorial Pacific suggest that 2007 is apt to be another bleaching year. Taken together, acidification and rising ocean temperatures represent a kind of double bind for reefs: regions that remain hospitable in terms of temperature are becoming increasingly inhospitable in terms of saturation, and vice versa.

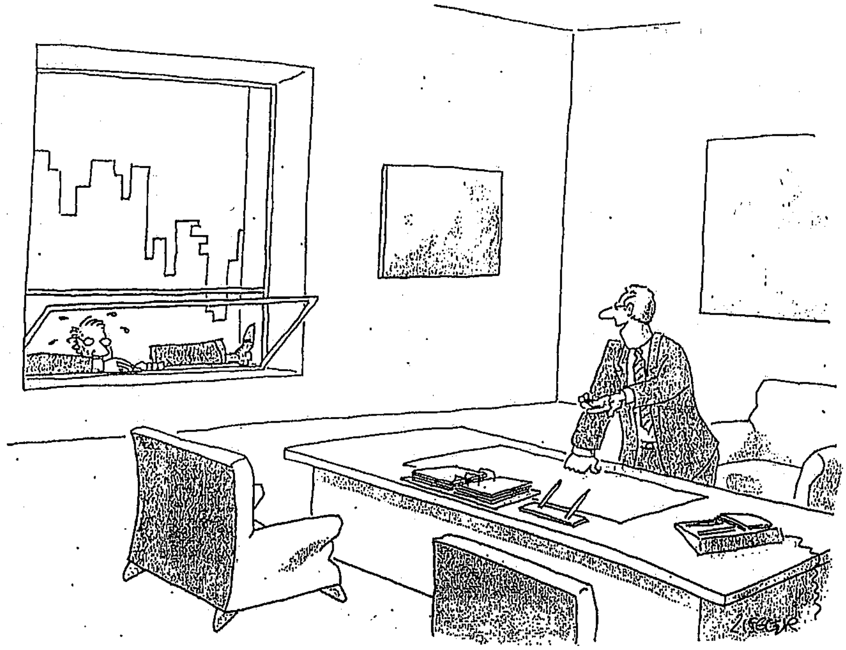
"While one, bleaching, is an acute stress that's killing them off, the other, acidification, is a chronic stress that's preventing them from recovering," Joanie Kleypas, a reef scientist at the National Center for Atmospheric Research, in Boulder, Colorado, told me. Kleypas said she thought that some corals would be able to migrate to higher latitudes as the oceans warm, but that, because of the lower saturation levels, as well as the difference in light regimes, the size of these migrants would be severely limited. "There's a point where you're going to have coral but no reefs," she said.

The tropical oceans are, as a rule, nutrient-poor; they are sometimes called liquid deserts. Reefs are so dense with life that they are often compared to rain forests. This rain-forest-in-the-desert effect is believed to be a function of a highly efficient recycling system, through which nutrients are, in effect, passed from one reef-dwelling organism to another. It is estimated that at least a million, and perhaps as many as nine million, distinct species live on or near reefs.

"Being conservative, let's say it's a million species that live in and around coral," Ove Hoegh-Guldberg, an expert on coral reefs at the University of Queensland, in Australia, told me. "Some of these species that hang around coral reefs can sometimes be found living without coral. But most species are completely dependent on coral—they literally live in, eat, and breed around coral. And, when we see coral get destroyed during bleaching events, those species disappear. The key question is how vulnerable all these various species are. That's a very important question, but at the moment you'd have to say that a million different species are under threat."

He went on, "This is a matter of the utmost importance. I can't really stress it in words strong enough. It's a do-or-die situation."

Around the same time that Langdon was performing his coral experiments at the Biosphere, a German marine biologist named Ulf Riebesell decided to look into the behavior of a class



"I don't see you pencilled in on my calendar, Armstrong. But, as long as you're up here, come on in and have a seat."

of phytoplankton known as coccolithophores. Coccolithophores build plates of calcite—coccoliths—that they arrange around themselves, like armor, in structures known as coccospheres. (Viewed under an electron microscope, they look like balls that have been covered with buttons.) Coccolithophores are very tiny—only a few microns in diameter—and also very common. One of the species that Riebesell studied, *Emiliani huxleyi*, produces blooms that can cover forty thousand square miles, turning vast sections of the ocean an eerie, milky blue.

In his experiments, Riebesell bubbled CO_2 into tanks of coccolithophores to mimic the effects of rising atmospheric concentrations. Both of the species he was studying—*Emiliani huxleyi* and *Gephyrocapsa oceanica*—showed a clear response to the variations. As CO_2 levels rose, not only did the organisms' rate of calcification slow; they also started to produce deformed coccoliths and ill-shaped coccospheres.

"To me, it says that we will have massive changes," Riebesell, who works at the Leibniz Institute of Marine Sciences, in Kiel, told me. "If a whole group of calcifiers drops out, are there other organisms taking their place? What is the rate of evolution to fill those spaces? That's awfully difficult to address in experimental work. These organisms have never, ever seen this in their entire evolutionary history. And if they've never seen it they probably will find it difficult to deal with."

Calcifying organisms come in a fantastic array of shapes, sizes, and taxonomic groups. Echinoderms like starfish are calcifiers. So are mollusks like clams and oysters, and crustaceans like barnacles, and many species of bryozoans, or sea mats, and tiny protists known as foraminifera—the list goes on and on. Without experimental data, it's impossible to know which species will prove to be particularly vulnerable to declining pH and which will not. In the natural world, the pH of the water changes by season, and even time of day, and many species may be able to adapt to new conditions, at least within certain bounds. Obviously, though, it's impractical to run experiments on tens of thousands of different species. (Only a few dozen have been tested so far.) Meanwhile, as the example of coral reefs makes clear, what's more important than how acidification will affect any particular organism is how it will affect entire marine ecosystems—a question that can't be answered by even the most ambitious experimental [illegible] col. The recent report on acidifi[illegible] by Britain's Royal Society noted that it was "not possible to predict" how whole communities would respond, but went on to observe that "without significant action to reduce CO_2 emissions" there may be "no place in the future oceans for many of the species and ecosystems we know today."

Carol Turley is a senior scientist at Plymouth Marine Laboratory, in Plymouth, England, and one of the authors of the Royal Society report. She observed that pH is a critical variable not just in calcification but in other vital marine processes, like the cycling of nutrie[illegible].

"It looks like we'll be changing l[illegible] levels in the food chain," Turley told me. "So we may be affecting the primary producers. We may be affecting larvae of zooplankton and so on. What I think might happen, and it's pure speculation, is that you may get a shortening of the food chain so that only one or two species comes out on top—for instance, we may see massive blooms of jellyfish and things like that, and that's a very [illegible] food chain."

Thomas Lovejoy, who coined the term "biological diversity" in 1980, compared the effects of ocean acidification to "running the course of evolution in reverse."

"For an organism that lives on l[illegible], the two most important factors are temperature and moisture," Lovejoy, who is now the president of the Heinz Center for Science, Economics, and the Environment, in Washington, D.C., told me. "And for an organism that lives in the water the two most important factors are temperature and acidity. So this is just a profound, profound change. It is going to send all kinds of ripples through marine ecosystems, because of the importance of calcium carbonate for so many organisms in the oceans, including those at the base of the food chain. If you back off and look at it, it's as if you or I went to our annual physical and the body chemistry came back and the doctor looked really, really worried. It's a systemic change. You could have food chains collapse, and fish ultimately with them, because mos[illegible] the fish we get from the ocean are at the end of long food chains. You probably will see shifts in favor of invertebrates, or the reign of jellyfish."

Riebesell put it this way: "The risk is that at the end we will have the rise of slime."

Paleooceanographers study the oceans of the geologic past. For the most part, they rely on sediments pulled up from the bottom of the sea, which contain what might be thought of as a vast library written in code. By analyzing the oxygen isotopes of ancient shells, paleooceanographers can, for example, infer the temperature of the oceans going back at least a hundred million years, and also determine how much—or how little—of the planet was covered by ice. By analyzing mineral grains and deposits of "microfossils," they can map archaic currents and wind patterns, and by examining the remains of foraminifera they can re-create the history of ocean pH.

In September, two dozen paleooceanographers met with a roughly equal number of marine biologists at a conference hosted by Columbia University's Lamont-Doherty Earth Observatory. The point of the conference, which was titled "Ocean Acidification—Modern Observations and Past Experiences," was to use the methods of paleooceanography to look into the future. (The ocean-acidification community is still a relatively small one, and at the conference I ran into half the people I had spoken to about the subject, including Victoria Fabry, Ken Caldeira, and Chris Langdon.) Most of the meeting's first day was devoted to a discussion of an ecological crisis known as the Paleocene-Eocene Thermal Maximum, or P.E.T.M.

The P.E.T.M. took place fifty-five million years ago, at the border marking the end of the Paleocene epoch and the beginning of the Eocene, when there was a sudden, enormous release of carbon into the atmosphere. After the release, temperatures around the world soared; the Arctic, for instance, warmed by ten degrees Fahrenheit, and Antarctica became temperate. Presumably because of this, vertebrate evolution veered off in a new direction. Many of the so-called archaic mammals became extinct, and were replaced by entirely new orders: the ancestors of today's deer, horses, and primates all appeared right around the time of the P.E.T.M. The members of these new orders were curiously undersized—the earliest horse was no bigger than a poodle—a function, it is believed, of hot, dry conditions that favored smallness.

In the oceans, temperatures rose dramatically and, because of all the carbon, the water became increasingly acidic. Marine sediments show that many calcifying organisms vanished—more than fifty species of foraminifera, for example, died out—while others that were once rare became dominant. On the seafloor, the usual buildup of empty shells from dead calcifiers ceased. In ocean cores, the P.E.T.M. shows up vividly as a band of reddish clay sandwiched between thick layers of calcium carbonate.

No one is sure exactly where the carbon of the P.E.T.M. came from or what triggered its release. (Deposits of natural gas known as methane hydrates, which sit, frozen, underneath the ocean floor, are one possible source.) In all, the release amounted to about two trillion metric tons, or eight times as much carbon as humans have added to the atmosphere since industrialization began. This is obviously a significant difference in scale, but the consensus at the conference was that if there was any disparity between then and now it was that the impact of the P.E.T.M. was not drastic enough.

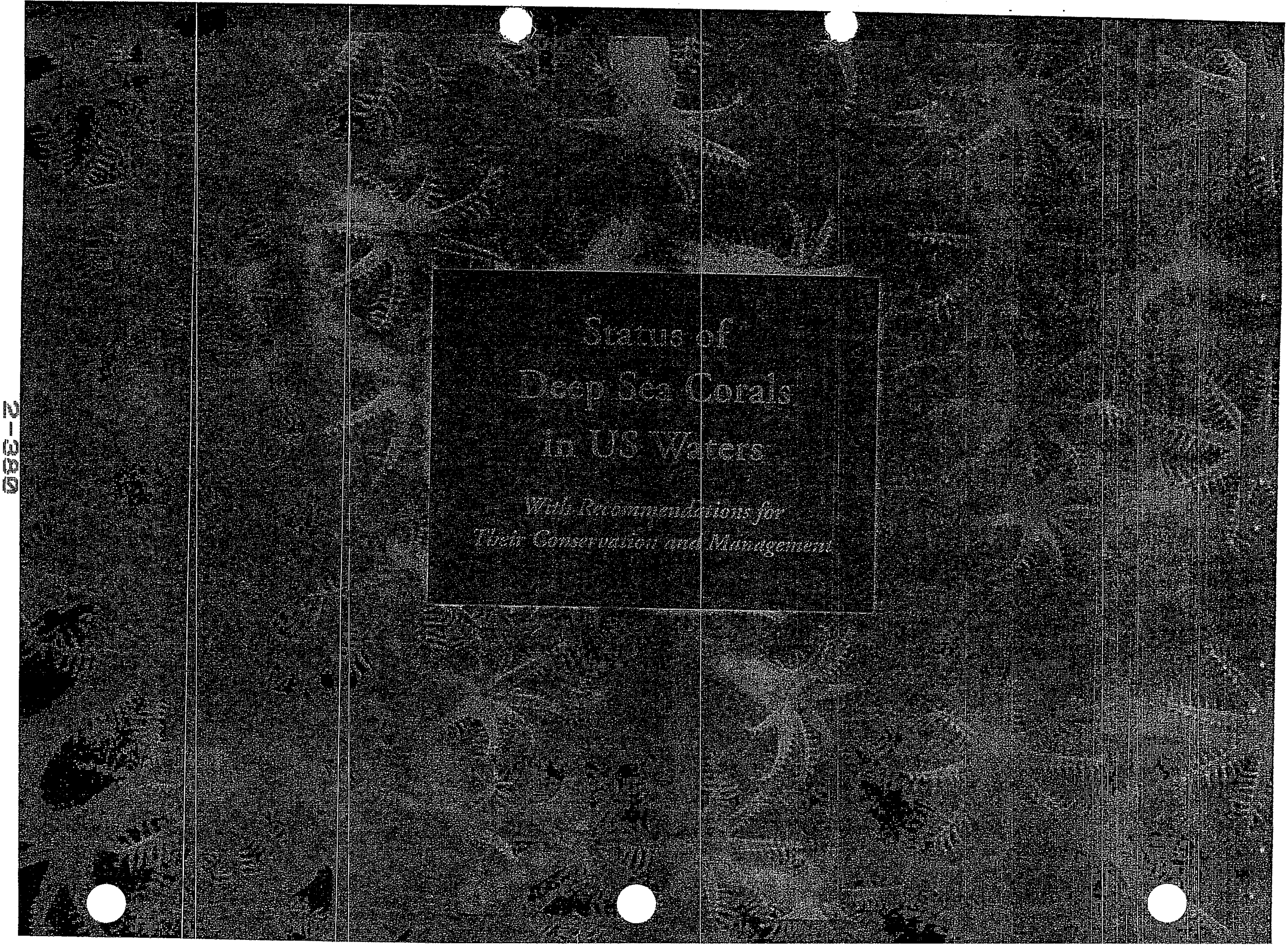
The seas have a built-in buffering capacity: if the water's pH starts to drop, shells and shell fragments that have been deposited on the ocean floor begin to dissolve, pushing the pH back up again. This buffering mechanism is highly effective, provided that acidification takes place on the same timescale as deep-ocean circulation. (One complete exchange of surface and bottom water takes thousands of years.) Paleooceanographers estimate that the release of carbon during the P.E.T.M. took between one and ten thousand years—the record is not detailed enough to be more exact—and thus occurred too rapidly to be completely buffered. Currently, CO_2 is being released into the air at least three times and perhaps as much as thirty times as quickly as during the P.E.T.M. This is so fast that buffering by ocean sediments is not even a factor.

"In our case, the surface layer is bearing all the burden," James Zachos, a paleooceanographer at the University of California at Santa Cruz, told me. "If anything, you can look at the P.E.T.M. as a best-case scenario." Ken Caldeira said that he thought a better analogy for the future would be the so-called K-T, or Cretaceous-Tertiary, boundary event, which occurred sixty-five million years ago, when an asteroid six miles wide hit the earth. In addition to dust storms, fires, and tidal waves, the impact is believed to have generated huge quantities of sulfuric acid.

"The K-T boundary event was more extreme but shorter-lived than what we could do in the coming centuries," Caldeira said. "But by the time we've burned conventional fossil-fuel resources what we've done will be comparable in extremeness, except that it will last millennia instead of years." More than a third of all marine genera disappeared at the K-T boundary. Half of all coral species became extinct, and it took the other half more than two million years to recover.

Ultimately, the seas will absorb most of the CO_2 that humans emit. (Over the very long term, the figure will approach ninety per cent.) From a certain vantage point, this is a lucky break. Were the oceans not providing a vast carbon sink, almost all of the CO_2 that humans have emitted would still be in the air. Atmospheric concentrations would now be nearing five hundred parts per million, and the disasters predicted for the end of the century would already be upon us. That there is still a chance to do something to avert the worst consequences of global warming is thanks largely to the oceans.

But this sort of accounting may be misleading. As the process of ocean acidification demonstrates, life on land and life in the seas can affect each other in unexpected ways. Actions that might appear utterly unrelated—say, driving a car down the New Jersey Turnpike and secreting a shell in the South Pacific—turn out to be connected. To alter the chemistry of the seas is to take a very large risk, and not just with the oceans. ♦

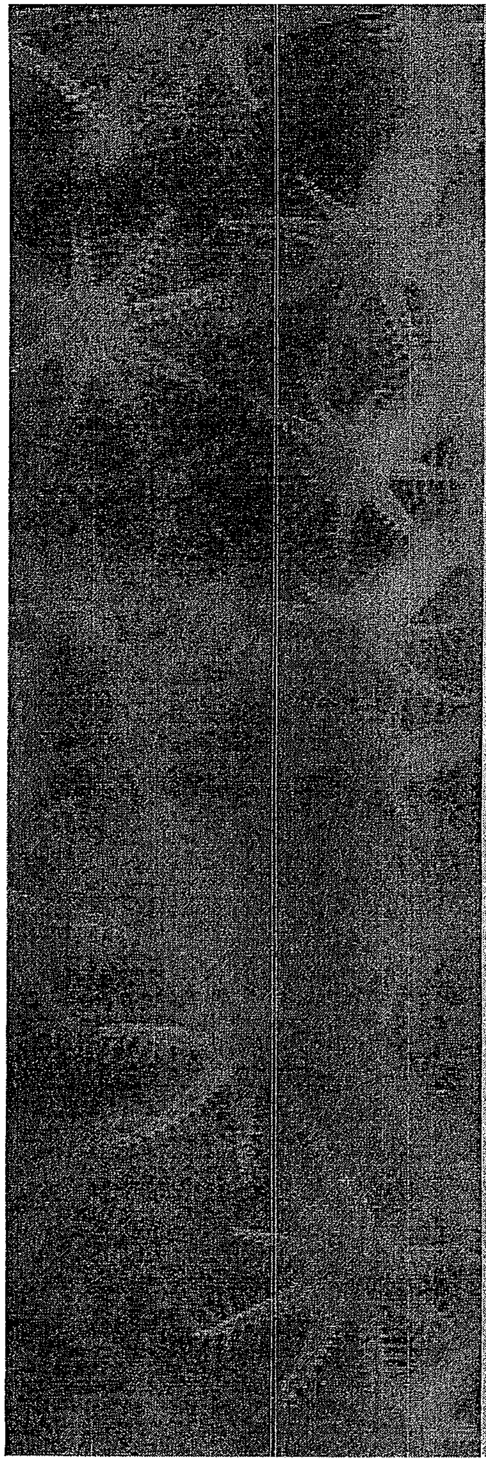


Status of
Deep Sea Corals
in US Waters

With Recommendations for
Their Conservation and Management

"Deep sea ecosystems support bizarre and beautiful life forms,
some of them hundreds or even thousands of years old.
They are being clear-cut by bottom trawl fishing. Today's
fisheries are squandering the riches of the deep sea and
if they are not stopped we will lose them forever. No industry
has the right to destroy the heritage of humanity."

Professor Callum Roberts, professor of marine conservation at the University of York in England and a Pew Fellow in Marine Conservation



Executive Summary

The ocean—especially the deep ocean—is the last frontier of exploration, exploitation and management on our planet. With demand for seafood and petroleum products exacting an ever-increasing toll on the deep sea, damage to deep sea corals is a growing worldwide conservation concern. Recent deep sea exploration has revealed spectacularly diverse seafloor communities. The deep sea corals that structure these communities provide shelter, feeding habitats, and breeding and nursery grounds to many species, including commercially important fishes. Conserving these extremely long-lived animals (some are documented to be over 1,500 years old) is also important because of their potential use in research and medicine. In this report we provide an overview of where these deep sea corals are found in US waters, what activities threaten them, and what current management actions are used to protect them. We conclude with limitations to current management and recommendations for improving deep sea coral conservation.

This report focuses on 5 taxa of deep sea corals found in US waters, stony corals, gold corals, black corals, gorgonian corals and hydrocorals. They come in various shapes and sizes, from massive reefs miles long to single bushy shaped individuals many feet tall. Our understanding of their distribution is expanding, but is currently limited and varies greatly across the different marine waters of the USA. The vast majority of the seafloor has not been surveyed for deep sea corals. What scientists do know suggests that deep sea coral concentrations are very localized, although they are widely distributed throughout the USA. They are commonly found in areas with hard seafloor substrates and appropriate currents, such as the seaward edge of the continental shelf (shelf break), around the edges of submarine canyons, and on banks and seamounts.

A number of human activities pose a threat to deep sea corals. Bottom fishing, especially bottom trawling, threatens the health and survival of deep sea corals, as well as oil and gas exploration and extraction, coral collection and a number of other human activities that contact the seafloor. Impacts from pollution, climate change and invasive species are poorly known but real threats. The effects of most of these activities are relatively unstudied and there is almost no monitoring of seafloor ecosystems anywhere in the USA. Nevertheless, bottom trawling is currently the greatest threat to deep sea corals because it is capable of significant, long-lasting damage in just one pass of the gear, and it takes place over extensive areas where there are corals.

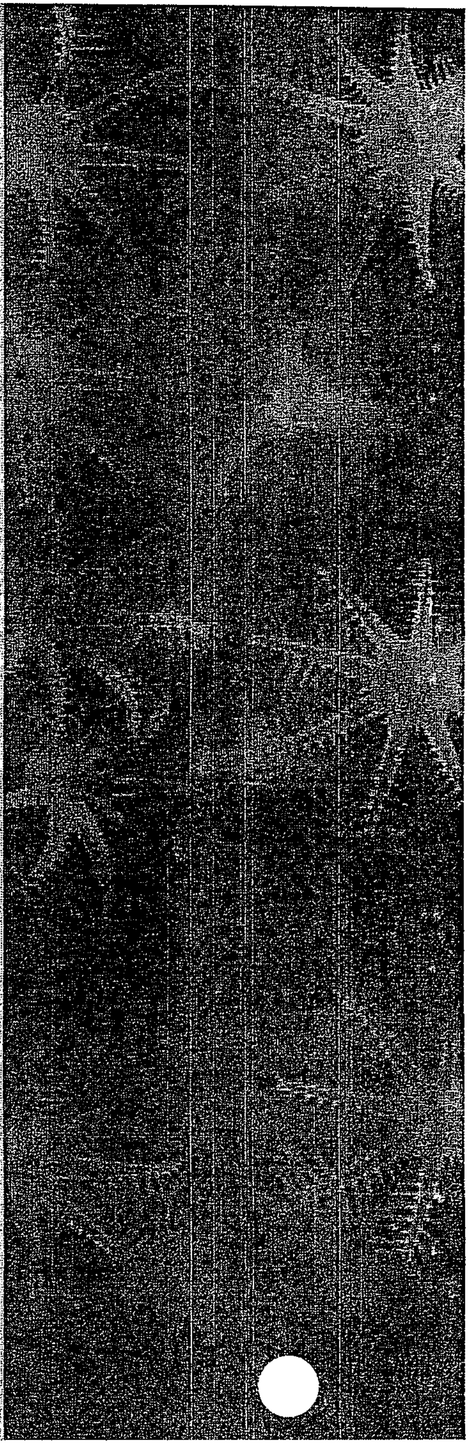
Current ocean management is insufficient to protect these vulnerable and unique deep sea habitats. Fisheries management can provide some protection under existing laws, by either closing areas to fishing or through the designation of essential fish habitat (EFH) for commercially managed species. Several of the fishery management councils have recently designated deep sea corals as EFH and restricted bottom fishing and/or bottom trawling in some cases.

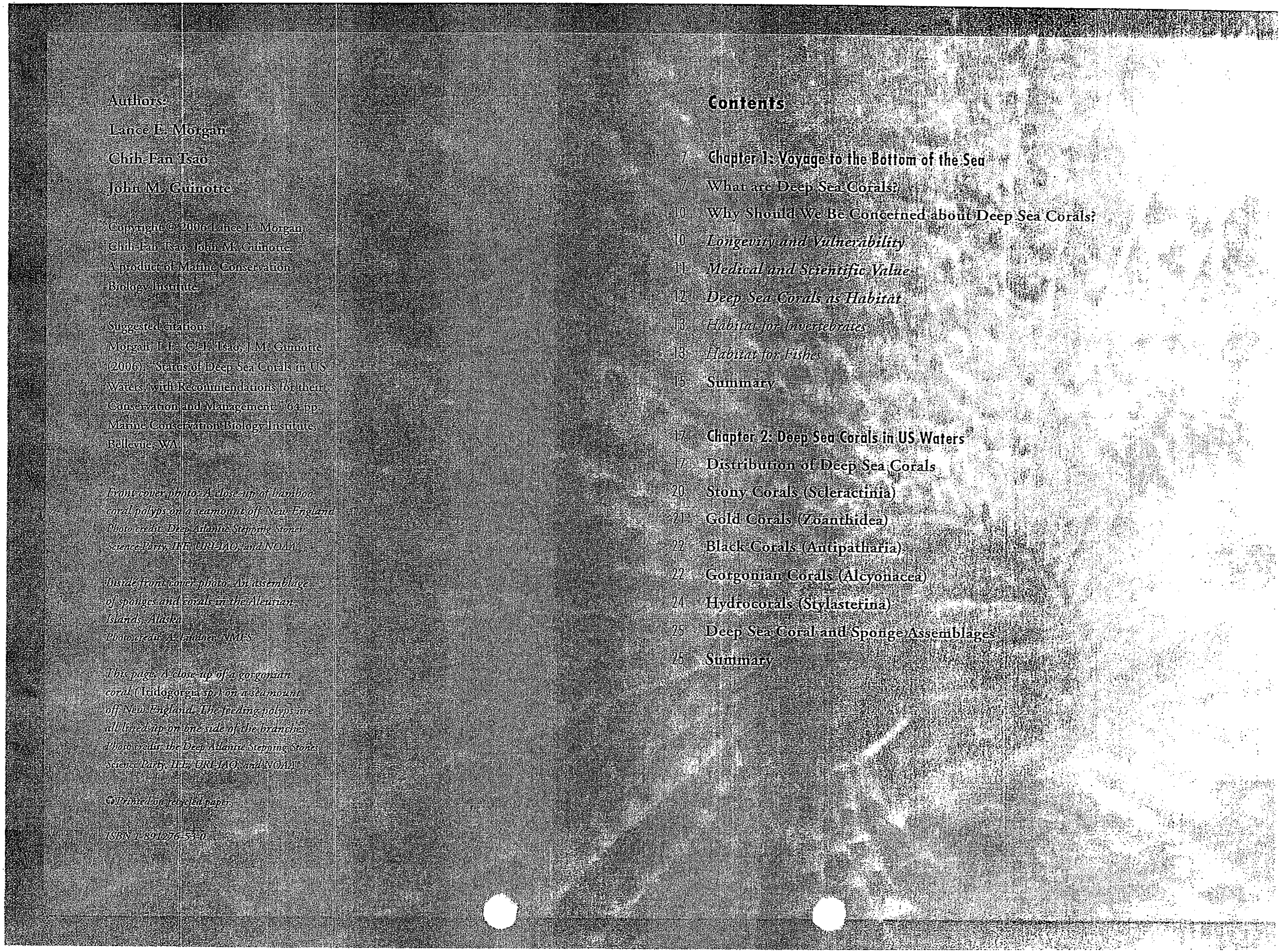
Where areas have been designated, enforcement and monitoring are critically needed. *Oculina* Bank, designated as a Habitat Area of Particular Concern in 1984, in an action years ahead of its time, is now over 90% destroyed because no attention to enforcement followed the designation.

Our National Marine Sanctuary Program, the main federal program charged with protecting ocean ecosystems, does not manage fish and therefore does not regulate the impacts of fishing on deep sea corals or seafloors within its boundaries. The Minerals Management Service, which oversees energy production, can mitigate impacts to deep sea corals by establishing buffer zones around deep sea coral communities, but has yet to do so.

The findings of this report, the first to address the status of deep sea corals in US waters, echo and reinforce recent conclusions by the National Research Council in 2002, the Pew Oceans Commission in 2003, and the US Commission on Ocean Policy in 2004—which find bottom fishing, especially bottom trawling, is a major threat to seafloor communities and deep sea corals. These studies recommend stricter protection of vulnerable deep sea coral habitats. Similarly, the President's 2004 Ocean Action Plan emphasized deep sea coral conservation and called for further identification and protection of deep sea coral areas. Despite these encouraging signs, progress towards increased deep sea coral protection has been slow to occur. Recent actions by fishery management councils to designate essential fish habitat and to freeze the current footprint of bottom trawling are progress for deep sea coral conservation. But those areas that have been comprehensively protected are small in relation to the need.

The recommendations of this report are first, that fishery management councils and national marine sanctuaries must use existing tools to protect deep sea corals, and curtail any further expansion of bottom trawling unless it can be shown that trawling will not damage seafloor habitats. Second, a national mandate to protect deep sea corals is necessary through either amendment to the Magnuson-Stevens Act or new legislation. Third, government should devote substantial resources to achieving a better scientific understanding of where deep sea coral communities are found, their ecological roles and threats to them, especially bottom-contact fishing gears. Last, managers must develop a comprehensive framework to manage all human activities based on their compatibility with different ocean habitats (i.e., ecosystem-based management and ocean zoning). Until we make protecting ecosystems, rather than exploiting resources, the overarching goal of management, we will continue to fall short of protecting deep sea corals, sustaining healthy fisheries, and maintaining the oceans' productivity and biological diversity.





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Bellevue, WA.

Front cover photo: A close-up of bamboo coral polyps on a seamount off New England
Photo credit: Deep Atlantic Stepping Stones Science Party, IFE, URI-IAO, and NOAA

Inside front cover photo: An assemblage of sponges and corals in the Aleutian Islands, Alaska
Photo credit: A. Lindner, NMFS

*This page: A close-up of a gorgonian coral (*Iridogorgia sp.*) on a seamount off New England. The feeding polyps are all lined up on one side of the branches*
Photo credit: the Deep Atlantic Stepping Stones Science Party, IFE, URI-IAO, and NOAA

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Contents

Exploration of deep sea
corals in recent decades provides us
with images and knowledge
of spectacularly diverse seafloor
communities.

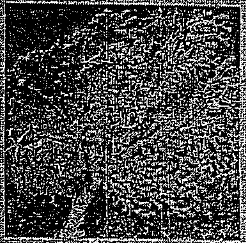
Voyage to the Bottom of the Sea

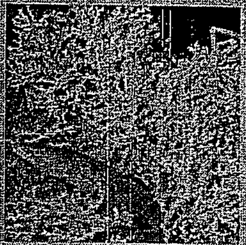
The ocean—especially the deep ocean—is the last frontier we are exploring and exploiting on our planet. As recently as the late 1800s, scientists debated whether or not life existed below the depths to which light penetrates (roughly 660 ft). Today we know that life extends to the deepest ocean depths—below 35,000 ft to the bottom of the Marianas Trench. We are still discovering new deep sea species at a rapid rate. Photographs from research cruises show astoundingly beautiful corals—many new to science—and spectacular, lush coral forests sheltering diverse communities of sea life. Along with these discoveries comes increasing knowledge of the fragility and vulnerability of many species—especially deep sea corals. Recent exploration of the marine realm, aided by remotely operated vehicles (ROVs) and manned submersibles, has provided compelling evidence that our stewardship of the deep sea is insufficient. Images brought back by researchers document deep sea corals damaged or crushed by fishing gears. We are destroying a treasure that we have yet to fully understand. Until we comprehend the complexity and interconnectivity of marine biodiversity, we cannot begin to fathom the impact that the destruction of this diversity will have on our ocean and on us. In the face of our ignorance and the growing threat to deep sea coral habitats, more than 1,400 marine and conservation scientists worldwide have called upon the United Nations and national governments to protect deep sea corals.[1] This report provides a comprehensive overview of the status of and threats to deep sea corals in US waters in the hope that understanding current knowledge of these animals will help us all make the decisions necessary to protect them.

As coastal fish populations decline from overfishing and habitat degradation, commercial fishing fleets are moving further out into deeper waters (Christensen et al. 2003, Roberts 2002). Industrialized fleets are now using advanced technologies (e.g., synthetic fishing gears, larger and more capable ships, satellite navigation systems, computers and electronics) to find and catch fish at ever greater depths. With demand for seafood and petroleum products exacting an ever-increasing toll on the deep sea (Glover and Smith 2003), damage to deep sea corals is a growing worldwide conservation concern (Hain et al. 2004). The significance of this damage is further amplified because deep sea corals are among the longest-lived animals on Earth—hundreds to thousands of years old—and are exceptionally fragile.

What are Deep Sea Corals?

Deep sea corals are not a single taxonomic group of animals; they are a functional group—analogous to the diverse plants included under the descriptors "bushes" or "trees."


Gorgonians in the Gulf of Mexico.
Photo credit: L. Horn, NURC/UNCW


Stony corals off North Carolina.
Photo credit: S.W. Ross et al., UNCW

Opposite page: Deep sea corals at Madison-Swanson protected area in the Gulf of Mexico. Photo credit: L. Horn, NURP/UNCW

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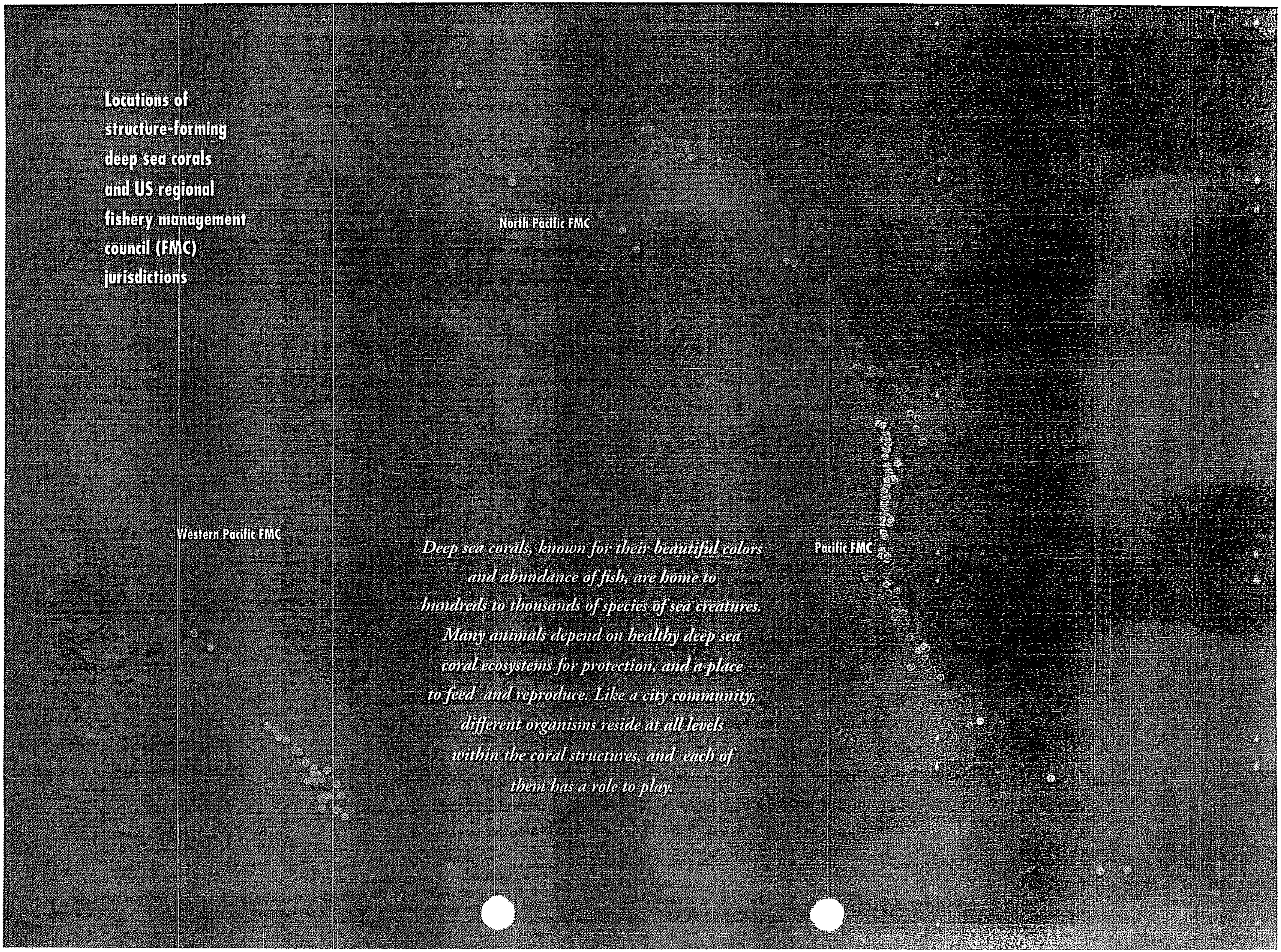
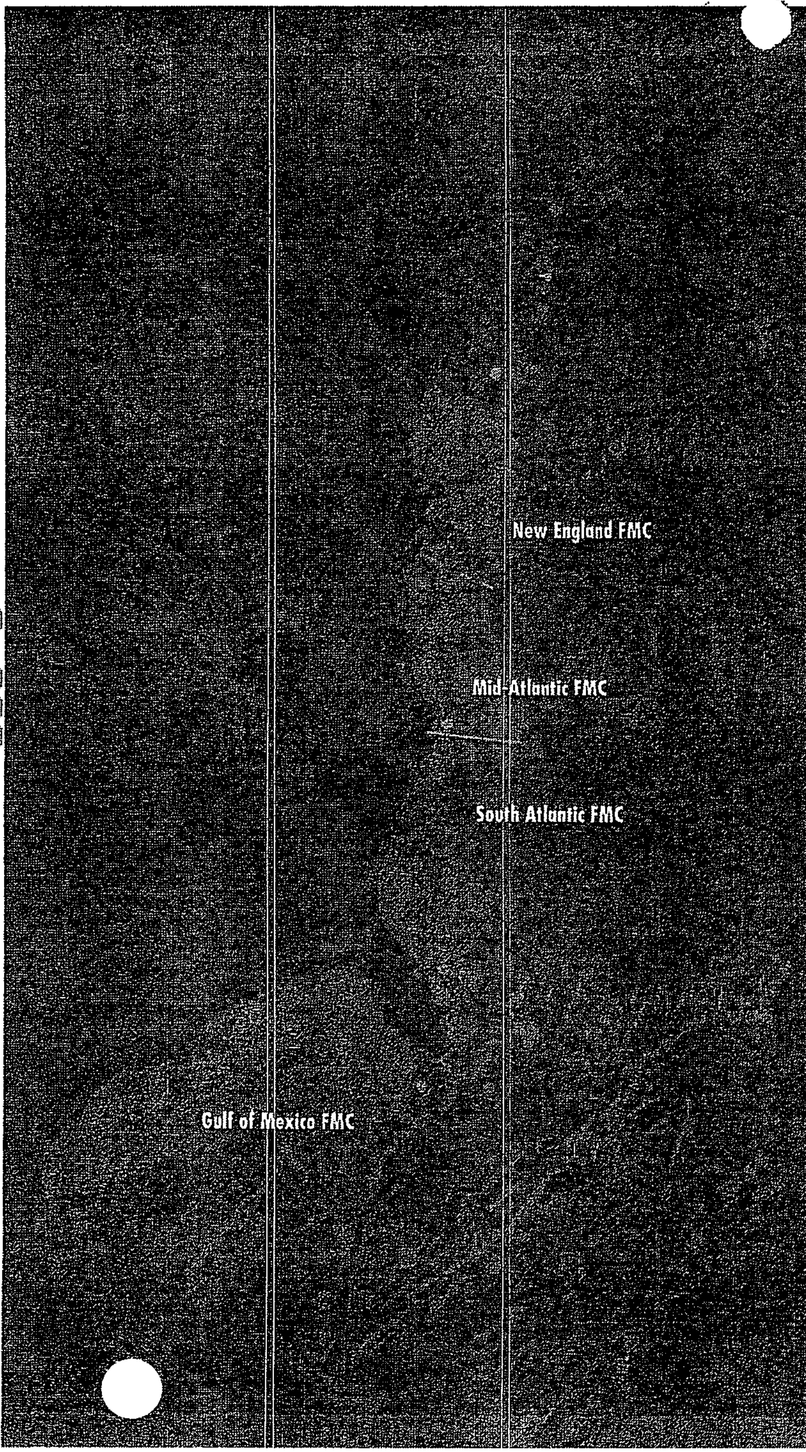
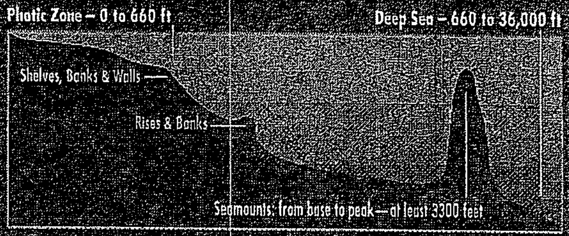
[1] Scientists' Statement on Protecting the World's Deep-sea Coral and Sponge Ecosystems (http://www.mcbi.org/DSC_statement/sign.htm)



Locations of structure-forming deep sea corals and US regional fishery management council (FMC) jurisdictions

Deep sea corals, known for their beautiful colors and abundance of fish, are home to hundreds to thousands of species of sea creatures. Many animals depend on healthy deep sea coral ecosystems for protection, and a place to feed and reproduce. Like a city community, different organisms reside at all levels within the coral structures, and each of them has a role to play.

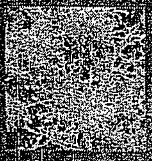




The type of corals that most people are familiar with, such as the stony corals that form the Great Barrier Reef in Australia, are different from corals found in deeper waters in one significant way: shallow-water, reef-building corals contain symbiotic algae which provide the corals with nutrients. Like most plants, algae are able to convert the sun's energy into food through a process called photosynthesis. Corals with symbiotic algae are only found in the upper layers of the sea where sunlight can penetrate (the photic zone), and are usually found near shore in shallow waters adjacent to islands.

By contrast, deep sea corals do not contain symbiotic algae and can thrive at depths below the sun's reach. The deepest known coral came from a depth nearly four miles below the oceans surface! Deep sea corals tend to occur on "hilly" surfaces or where the slope changes abruptly; areas such as the shelf break (the seaward edge of the continental shelf), the continental slope (a much steeper part of the seafloor, seaward of the shelf), and on ridges and seamounts (mountains hundreds or even thousands of feet tall that rise from the seafloor). For example, deep sea stony corals form banks on the continental slope off the southeastern USA, and deep sea gorgonian corals grow on the steep slopes off the Aleutian islands and atop seamounts in waters offshore of California, Hawaii, in the Gulf of Alaska, and throughout the New England Seamount chain.

Not illustrated is the Caribbean FMC including waters surrounding Puerto Rico and the US Virgin Islands. Lightly shaded region denotes US exclusive economic zone. Orange dots represen[illegible]own coral records.



• STONY CORALS

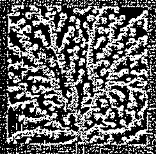
Colonies of stony corals grow together to form large mounds or reefs. They have numerous short, white branches.

• GOLD CORALS

Gold corals are colonies of individuals that grow into branching bush like structures. Growing slowly, some of these corals are estimated at 1,800 years old.

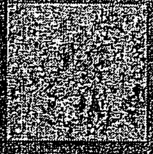
• BLACK CORALS

Black coral colonies have extensive branching patterns which often resemble trees. Though not black while living, the underlying skeleton is black or dark brown.



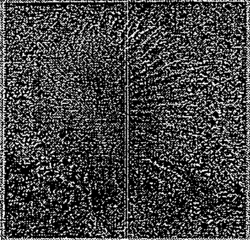
• GORGONIAN CORALS

Gorgonian corals have a flexible internal skeleton that allows them to bend and sway in the currents. They are found on continental shelf breaks, submarine canyons and isolated seamounts.



• HYDROCORALS

Hydrocorals form a rigi[illegible]atively brittle calcium carbonate ske[illegible] numerous pinpoint-sized pores and c[illegible] variety of colors.



An *Iridogorgia* sp. coral growing on a New England seamount

Photo credit: the Deep Atlantic Stepping Stones Science Party, IFE, URI-IAO, and NOAA

"A vast expanse of the planet's unexplored, and potentially most promising, ocean beyond the legal boundaries of nations is being exposed to the reckless plunder of marauding deep sea fishing trawlers."

Jean-Michel Cousteau, Founder and President, Ocean Futures Society

Just as trees include ferns, several families of conifers, and several major groups of flowering plants, deep sea corals include members of a number of different taxonomic groups, including stony corals, gold corals, black corals, gorgonian corals, and hydrocorals. Several things unite the deep sea corals we discuss in this report. They are all members of the phylum Cnidaria, from the Greek word "cnidos" meaning stinging nettle. All cnidarians use modified stinging cells to protect themselves and capture prey. While most tropical coral reefs rely primarily on photosynthesis by symbiotic algae for nourishment, deep sea corals lack symbiotic algae and capture all of their food using stinging cells. Some scientists are investigating whether microbial communities inhabiting deep sea corals may serve functions similar to symbiotic, photosynthetic algae in shallow corals. Where planktonic food particles are available in the deep sea, corals can thrive well beyond the depths to which light penetrates. These corals are variously referred to as deep sea corals, cold water corals, and deep water corals. We use the term "deep sea corals" in this report.

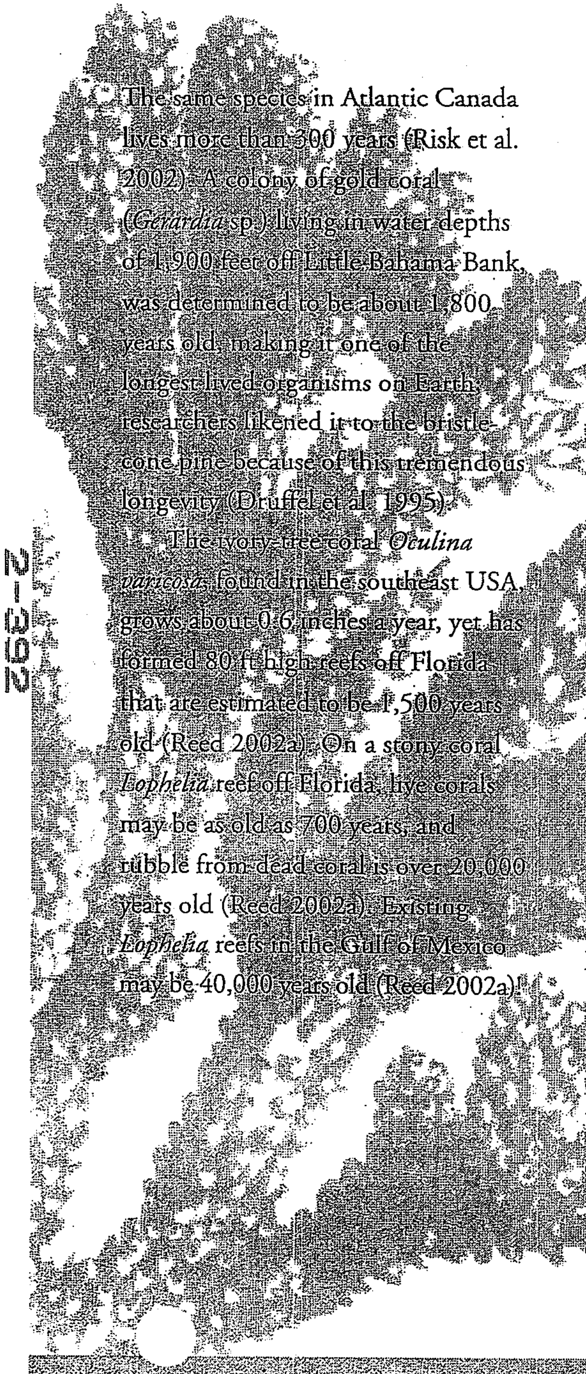
Deep sea corals can grow alone or in colonies, and they come in various colors, shapes, and sizes. Although corals are animals, they are often compared to plants because some (for example black corals, gorgonian corals, and hydrocorals) branch out in bushy or tree-like shapes, resembling forests, groves, and thickets. Additionally, some species of stony corals, including the relatively well-studied species *Lophelia pertusa* and *Oculina varicosa*, develop large reefs. As colonies of these corals increase in size, their complex structure traps sediments at the base. Over time, the dead coral and sediment accumulate, forming a characteristic deep sea coral reef, or "bioherm," with a cap of live coral. Many other types of deep sea coral are relatively small or occur alone. Our focus in this report is on those deep sea corals that grow into "bushes" and "trees," or form reefs.

Why Should We Be Concerned about Deep Sea Corals?

Deep sea corals are long-lived animals that often provide habitat for a diverse array of marine life, including commercially valuable fishery species. They also have untapped potential to produce novel medical compounds and have been valued as jewelry for millennia.

Longevity and Vulnerability

Living in cold water, often at great depths, deep sea corals grow very slowly and have extraordinarily long life spans—up to hundreds or even thousands of years (Figure 1.1). Red-tree corals (*Primnoa resedaeformis*) from southeast Alaska are 100 to 200 years old by the time they reach 6 to 10 ft in height (Andrews et al. 2002).



The same species in Atlantic Canada lives more than 300 years (Risk et al. 2002). A colony of gold coral (*Gerardia* sp.) living in water depths of 1,900 feet off Little Bahama Bank, was determined to be about 1,800 years old, making it one of the longest-lived organisms on Earth; researchers likened it to the bristlecone pine because of this tremendous longevity (Druffel et al. 1995).

The ivory tree coral *Oculina varicosa*, found in the southeast USA, grows about 0.6 inches a year, yet has formed 80 ft-high reefs off Florida that are estimated to be 1,500 years old (Reed 2002a). On a stony coral *Lophelia* reef off Florida, live corals may be as old as 700 years, and rubble from dead coral is over 20,000 years old (Reed 2002a). Existing *Lophelia* reefs in the Gulf of Mexico may be 40,000 years old (Reed 2002a).

Medical and Scientific Value

Because deep sea corals are stationary animals that cannot evade predators by moving away, some species rely on chemical defense mechanisms to protect themselves (Faulkner 2002). These mechanisms generate compounds that exhibit significant bioactivity (effects on living cells or organisms). Some of these compounds show promise as treatments for human ailments. Scientists are studying extracts of deep sea corals, sponges, and other organisms to develop new pharmaceutical products to fight cancer, Alzheimer's disease, asthma, pain, and viral infections (Box 1.1). Some of these compounds are also used in paints and other materials to prevent algae and invertebrates from growing on boat hulls, piers, and bridges.

In addition to their potential value as medical therapies, deep sea corals are also archives of the ocean's history (Box 1.2). Changes in ocean conditions are naturally recorded in the skeletons of corals, and because deep sea corals live a very long time and are distributed across a wide range of depths and latitudes, they provide an excellent window into the ocean's history (Risk et al. 2005, S.W. Ross et al., unpublished data, UNC-Wilmington). As scientists continue to develop techniques to measure the age and growth of deep sea corals and to interpret the changes in these measurements, corals will help reconstruct the history of changes in growth, temperature, and ocean chemistry at great depths beneath the sea.

The tremendous longevity of deep sea corals makes them valuable archives of past conditions on Earth. Furthermore, the erect, branching skeletons of deep sea corals are fragile and easily damaged by disturbances such as mobile bottom fishing gears. Once damaged, these invaluable archives are lost to science, and these seafloor communities may need decades to millennia to recover, if they are able to recover at all.

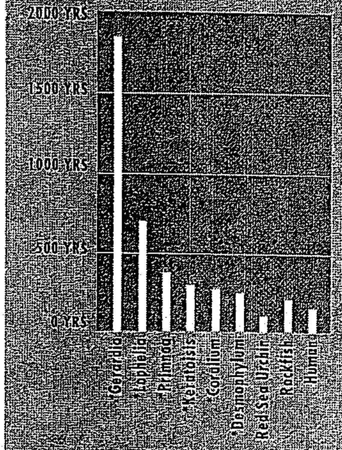


Fig. 1.1: Ages of deep sea corals (*) and other animals from selected studies

Andrews et al. 2002, Andrews et al. 2005, Cailliet et al. 2001, Druffel et al. 1995, Ebert and Southon 2003, Paull et al. 2000, Risk et al. 2002

"The disaster of bottom trawling on the high seas threatens thousands of species and can mean a reversal in evolution of tens of thousands of years."

Mikhail Gorbachev,
Chairman of the Board,
Green Cross International

A stony coral colony (*Enallopsammia* sp.) growing on top of a rock.
Photo credit: the Deep Atlantic Stepping Stones Science Party, IFE, URI-IAO, and NOAA

"About 98 percent of the oceans' species live in, on or just above the seafloor. Many of them including ancient deep sea corals and sponges haven't even been discovered yet."

Dr. Elliott Norse, President of Marine Conservation Biology Institute in Bellevue, WA

Deep Sea Corals as Habitat

As anyone who fishes, snorkels, or dives knows, fish are often encountered in or near places with complex, three-dimensional habitat—for example, kelp forests, coral reefs, and seagrass beds. The amount of three-dimensional habitat on the seafloor generally correlates with the level of biodiversity (Krieger 1993, Love et al. 1991, Risk 1972, Yoklavich et al. 2000). Many deep sea corals form complex, three-dimensional habitats. The spaces and gaps between coral branches serve as shelter and refuge for the eggs, larvae, and juveniles of shrimps, crabs, and fishes, and for many of the adults as well (e.g., Krieger and Wing 2002, Reed 2002b, Reed et al. 2006). A variety of animals forage within deep sea coral areas (Box 1.3), and filter-feeding animals use deep sea corals as a feeding platform that is raised into the higher-current zone above the sea-floor, where more food is available (e.g., Buhl-Mortensen and Mortensen 2005, Krieger and Wing 2002).

Coral ecosystems not only increase local microhabitat, but may also cover vast areas, thus providing resources to uncountable numbers and types of creatures. For example, the Røst Reef located in northern Norway, the largest known deep sea coral reef, is approximately 25 miles long and 1.5 miles wide, covering an area of about 40 mi^2 (Fosså et al. 2005). Those corals that do not create reefs but grow as individual colonies (gold corals, black corals, gorgonian corals, and hydrocorals), also increase structural complexity, particularly if they occur at high densities or are extremely large. Other invertebrates (especially sponges) that co-occur with these corals also contribute to habitat structure (Freese 2001). Studies in the Aleutian Islands suggest that corals and sponges may serve as "keystone structures" that provide

Box 1.1:
Drugs from the Deep Sea

There are currently several drugs in development that are derived from compounds found in deep sea organisms (Maxwell et al. 2005).

Discodermolide. This promising drug recently completed the early stages of clinical trials and is one of the most exciting anticancer compounds to date, because it may treat cancers that are resistant to other drugs. It is isolated from the sponge *Discodermia dissoluta*, found off the coast of the Bahamas in water over 460 ft deep.

E7389. This compound comes from the sponge *Lissodendoryx* sp., which lives in New Zealand waters at depths of 3,330 ft. E7389 is being tested for the treatment of lung and other cancers and is currently undergoing the early stages of clinical trials.

Dictyostatin-1. A sponge from the order Lithistida (family Corallistidae), found at 1,450 ft off the northern coast of Jamaica, yielded Dictyostatin-1, which may be more effective than the very successful anti-cancer drug Taxol®.

Topsentin. Isolated from the sponge *Spongosporites ruetzerli*, which lives at depths of 990 to 1,980 ft, Topsentin shows promise as an anti-inflammatory agent to treat arthritis and skin irritations, as well as for the treatment of Alzheimer's disease and to prevent colon cancer.

Bone Grafts. Scientists are now able to synthesize bone analogs from bamboo corals. Found at depths that can exceed 3,280 ft, these corals have a skeletal structure and dimensions that are almost identical to bone.

Collagen. Bamboo corals also contain gorgonin, which closely resembles collagen, an important component of bone. Collagen can be used for controlled release of medicines, as scaffolding for tissue rebuilding, and for a variety of other applications. Scientists hope that by understanding how corals form gorgonin, they can create a synthetic collagen-like material under the low temperature and high pressure environments that bamboo corals naturally inhabit.

"goods and services" (food resources and shelter) crucial to the survival of associated animals (Heifetz et al. 2005, Tews et al. 2004).

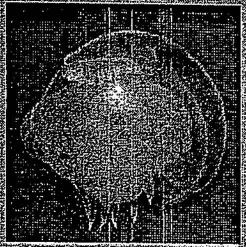
Habitat for Invertebrates

Many studies have found high species diversity where deep sea corals are densely distributed (Roberts et al. 2006). One deep sea coral reef was home to 3 times as many species as the surrounding sandy seafloor (Mortensen et al. 1995). In Atlantic Canada, deep sea gorgonian corals host 114 species—more than some tropical gorgonian coral communities—and support a variety of invertebrates, including crabs, shrimps, clams, snails, and worms (Buhl-Mortensen and Mortensen 2005). In waters off the southeastern USA, a study of *Oculina* colonies found more than 300 species of invertebrates and over 70 species of fish associated with this coral (Reed et al. 1982, Reed 2002b). *Lophelia* reefs in the northeast Atlantic host more than 1,300 species (Roberts et al. 2006) and are home to more animals of more different species than surrounding habitats (Costello et al. 2005).

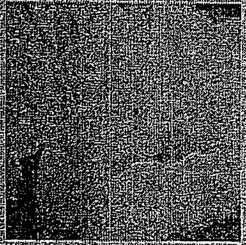
The standing dead portions of large coral colonies are as valuable as, if not more so, than the living portions. A wide range of encrusting and boring organisms use the dead coral skeleton for habitat. For example, dead *Lophelia* colonies in the Florida Straits support sessile organisms such as feather stars and sea anemones that need hard substrate for attachment and are not otherwise found on the surrounding seafloor (Messing et al. 1990). Structure-forming corals are biodiversity hotspots in the deep sea (Jensen and Fredericksen 1992, Raes and Vanreusel 2005).

Habitat for Fishes

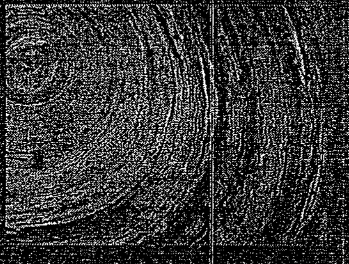
Fish species diversity is directly correlated with three-dimensional habitat on tropical coral reefs (Connell and Jones 1991, Friedlander and Parrish 1998), because complex habitats provide more refuges



Mystery mollusk (Order Nudibranchia) above the Davidson Seamount at 4,943 ft depth. Exploration of the deep sea is discovering many species new to science.
Photo credit: B. Walden, NOAA/MBARI



Yellow sponges surrounding a glass sponge on a seamount off New England.
Photo credit: the Deep Atlantic Stepping Stones Science Party, IFE, URI-IAO, and NOAA



Growth Rings of a Bamboo Coral Skeleton

The width of the cross section is approximately 0.4 in. Formation of these rings is affected by the condition of the seawater around the coral colony.

Photo credit: Courtesy of NIWA and Sanchez et al. 2004

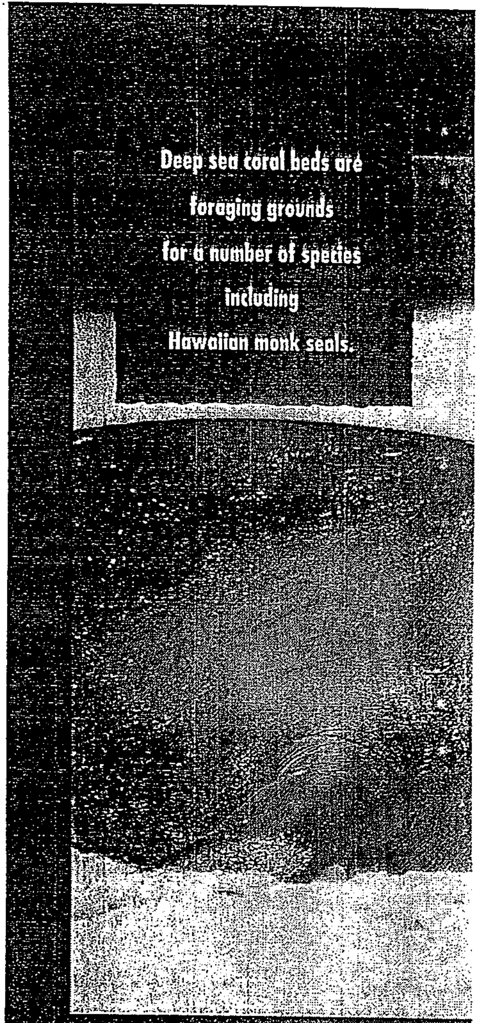
Box 1.2: Climate Information Archived in Deep Sea Corals

Over the long life of a coral, its growth pattern records information on how ocean chemistry and even global climate have changed. Methods to read these archives are still being perfected, but exciting progress has been reported in recent years. Researchers analyzed fossils of the stony coral *Desmophyllum cristagalli* collected off Newfoundland and found a sudden change in one specimen's isotopic composition during its lifetime as well as a major difference between this specimen and other specimens that lived at different times but in the same region. This pattern is a signal of rapid climate change—the Younger Dryas cooling event, a mini ice-age that took place 13,000 years ago (Smith et al. 1997).

from predators than less rugged habitats (Risk 1972). The mortality rates of juvenile fish are greatly reduced when there is abundant refuge from prey (Hixon and Jones 2005, Lindholm et al. 2001), and this may have important population-level effects (Lindholm et al. 1999). The diversity, quality, and extent of seafloor habitats are vital determinants of the diversity, distribution, and abundance of valuable commercial species such as rockfishes (Carr 1991, Nasby-Lucas et al. 2002, O'Connell and Carlisle 1993, Pearcy et al. 1989). The degree to which structure-forming deep sea corals and sponges provide habitat for fish species depends on their size, density, growth form, and the interaction of the fish with the coral structure (Mortensen and Buhl-Mortensen 2006, Pirtle 2005, Tissot et al. 2006).

Surveys of European waters have discovered many different species of fish in *Lophelia* reefs, including cod, saithe, ling, tusk, rabbitfish, redfishes, and others (Costello et al. 2005, Fosså et al. 2002, Husebø et al. 2002). Trawl nets containing large amounts of *Lophelia pertusa* coral material also caught at least 13 species of fish, such as grenadiers, orange roughy, and various sharks (Hall-Spencer et al. 2002). Coral habitats may also be more productive than surrounding areas: fishes found associated with *Lophelia* reefs in Norway were larger than those in non-coral habitats (Husebø et al. 2002). Thus, *Lophelia* reef habitats may be functionally important to deep sea fish species (Costello et al. 2005).

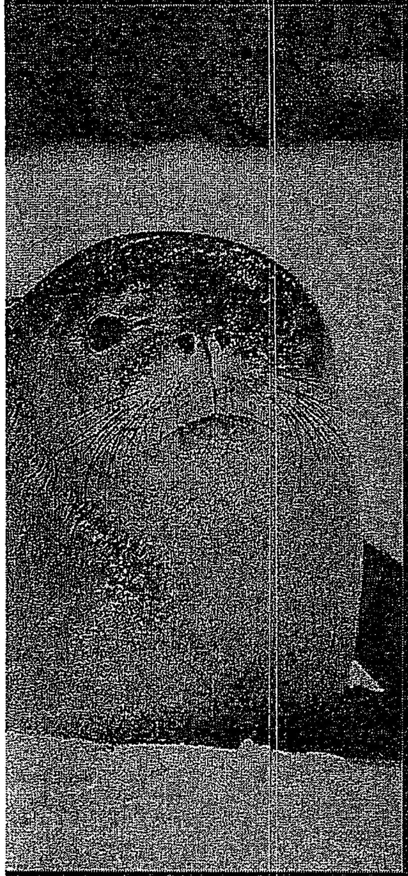
In Alaska, Heifetz (2002) found Atka mackerel and rockfish commonly associated with corals. In a study in southeast Alaska, 85% of the observed large rockfishes were in and around red-tree coral colonies (Krieger and Wing 2002). In the Aleutian Islands, 85% of economically important fishes and crabs and 97% of juvenile rockfishes were observed associated with corals and other structure-forming invertebrates (Stone 2006).



Deep sea coral beds are foraging grounds for a number of species including Hawaiian monk seals.

Box 1.3: Deep Sea Corals as Foraging Grounds

In 2003 researches were fortunate enough to film an endangered Hawaiian monk seal swimming among gold coral colonies at 1,740 ft depth, in the Northwestern Hawaiian Islands. Other research has shown that monk seals also forage



Hawaiian monk seal

Photo credit: J. Palmer, NMFS

in gold, pink and black coral beds feeding on eels and bottomfishes (Parrish et al. 2002).

NOAA Ocean Explorer Northwestern Hawaiian Islands 2003 Expedition: http://oceanexplorer.noaa.gov/explorations/03[illegible]edia/monkseal-video.html

In the southeastern USA, scientists have suggested a strong association between deep sea coral (and other rugged habitats) and certain fish species (Ross and Nizinski in prep.). The *Oculina* reefs off Florida were identified as spawning habitat for various species of grouper, although gag and scamp groupers have undergone severe declines in the last decade (Reed et al. 2005a). Juvenile speckled hind (also a grouper) have been observed in *Oculina* reefs, which suggests that the reefs may be an important nursery habitat for fish (Gilmore and Jones 1992, Koenig et al. 2005). Fish populations from the deep sea coral habitats of the Pourtales Terrace (south Florida Straits) include several important commercial fishes, including snappers, groupers and sharks (Reed et al. 2005b).

In addition to serving as structurally complex habitats for various species of invertebrates, fishes, and mammals, deep sea corals may also be prey for other seafloor animals (Box 1.4). Despite recent progress in deep sea coral research, scientists are still at a very early stage in understanding deep sea coral communities and dynamics, and much has yet to be discovered.

Summary

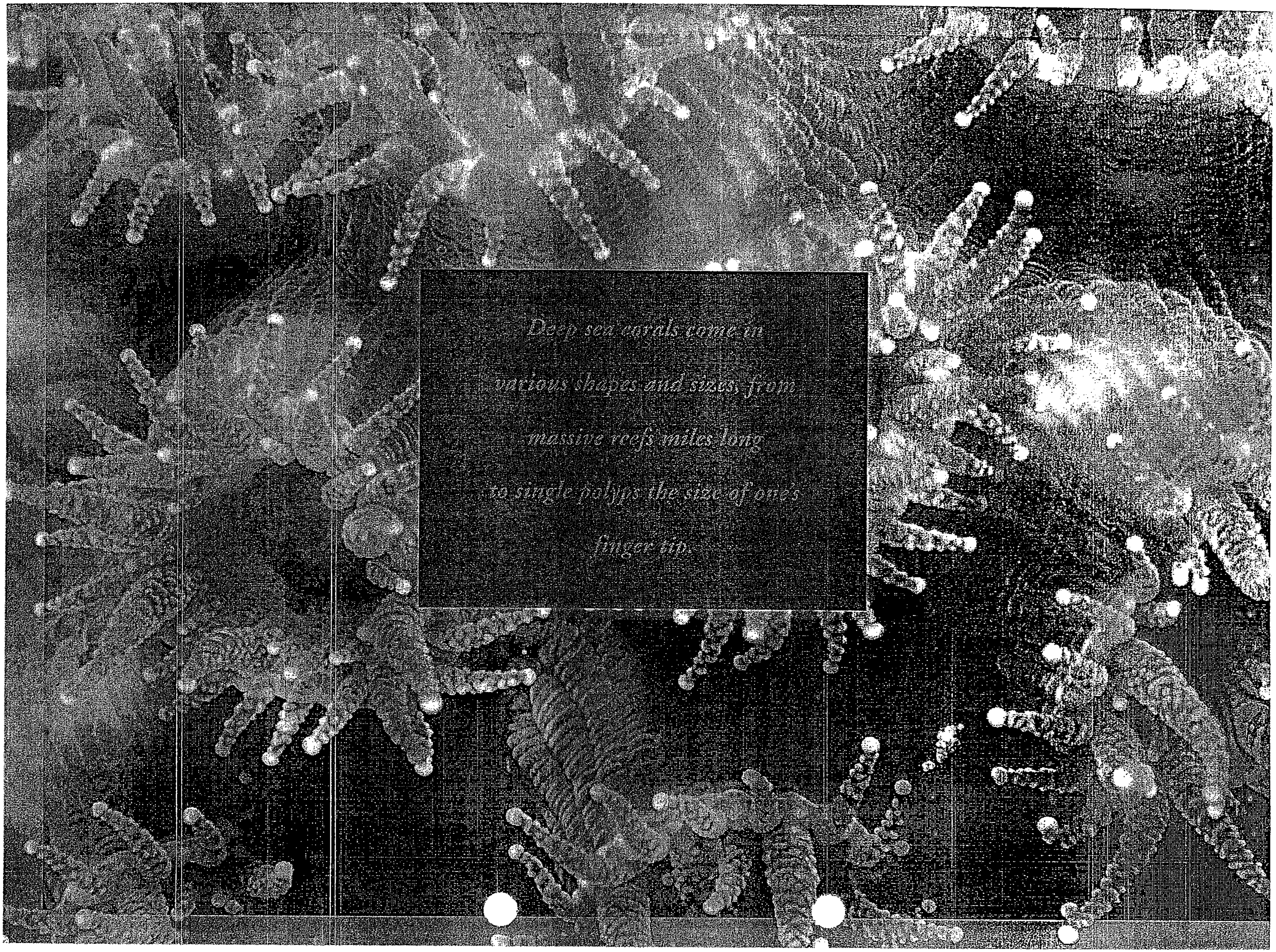
Deep sea exploration is revealing spectacularly diverse seafloor communities. The deep sea corals that structure these communities provide shelter, feeding habitats, and breeding and nursery grounds to many species, including commercially important fishes. Conserving these long-lived animals is also important because of their potential use in climate research and medicine. In this report we provide an overview of where these deep sea corals are found in US waters (Chapter 2), what activities threaten them (Chapter 3), and what current management actions are used to protect them (Chapter 4). We conclude with limitations to current management and recommendations for improving deep sea coral conservation (Chapter 5).

Sea star preying on the live polyps of a bamboo coral colony.

Photo credit: Mountains in the Sea, NOAA

BOX 1.4:
Deep Sea Corals as Prey

Deep sea corals are not only shelters and feeding platforms but also prey. A number of species feed on deep sea coral polyps directly. For example, parasitic copepods, worms, anemones, sea stars, sea slugs, and snails prey on gorgonian corals, such as bamboo corals (e.g., Buhl-Mortensen and Mortensen 2005, Krieger and Wing 2002).



Deep sea corals come in

various shapes and sizes, from

massive reefs miles long

to single polyps the size of ones

finger tip.

Deep Sea Corals in US Waters

Deep sea corals fall within the phylum Cnidaria. Their characteristic trait is the presence of stinging cells, which provide defense against predation and a means of obtaining food. Shallow water corals retain symbiotic algae that use sunlight to produce energy for themselves and their coral hosts. Deep sea corals live beyond the depths at which algae can photosynthesize; therefore, they rely entirely on catching food particles from the water column. Despite these common traits and their sedentary existence, deep sea corals vary widely in morphology, color, size, habitat, life history, and depth range. Some have a cosmopolitan distribution, while others are endemic to a limited area. For the purposes of this review, we examine the distribution of 5 broad taxa of deep sea corals (Figure 2.1) that typically inhabit rocky, hard-bottom areas and provide shelter to other forms of seafloor life:

- Stony corals (Scleractinia)
- Gold corals (Zoanthidea)
- Black corals (Antipatharia)
- Gorgonian corals (Alcyonacea)
- Hydrocorals (Stylasterina)

Distribution of Deep Sea Corals

Deep sea corals are widely distributed throughout US waters (Map 1), but several factors limit where they will thrive: substrate type, current speed, seafloor relief (ruggedness of the seafloor), nutrient availability, and temperature (Freiwald et al. 2004). The deep sea coral species discussed in this report need a hard, rocky substrate on which to attach as larvae. Currents are also important and serve to supply food particles and to prevent sedimentation (deVogeleare et al. 2005, Duineveld et al. 2004, Freiwald 2003, Genin et al. 1986, Roberts et al. 2003). Fan-shaped corals and sponges often orient their broadest profile across the current to maximize their access to food carried in the prevailing current flow. However, currents may also be detrimental to corals, such as during benthic storms when turbulence can resuspend sediments that may bury corals.

Seafloor relief, or topography, influences currents and therefore plays a key role in coral distribution. Both at small and large scales, features that increase vertical relief, and therefore current speeds—such as the shelf breaks, offshore banks, and the slopes and ridges of canyons and seamounts—also increase the suitability of the area for deep sea corals. Map 2 (*next page*) shows a slope gradient analysis which suggests that deep sea corals in the Mid-Atlantic and New England regions are found in greater abundance in areas with the steepest slopes (see Appendix for coral record data sources). Off the southeastern USA, the interaction of the Florida Current and the Gulf Stream with the topography of the seafloor is thought to be an important factor influencing the abundance of corals (Popenoe and Manheim 2001, Reed et al. 2006). Similarly, observations from

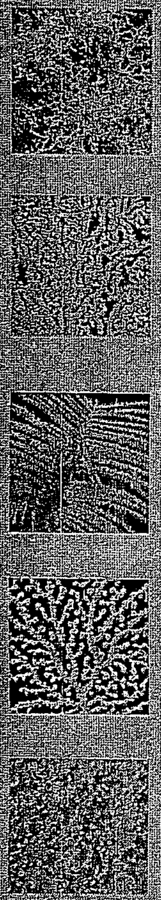
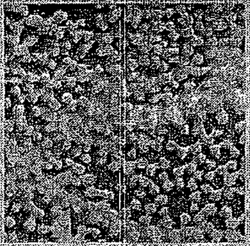


Fig 2.1, From Top: Stony coral, Gold coral, Black coral, Gorgonian coral, and Hydrocoral

Opposite page: Coral polyps on Molasses Reef, Florida Keys National Marine Sanctuary
Photo credit: Brent Deuel

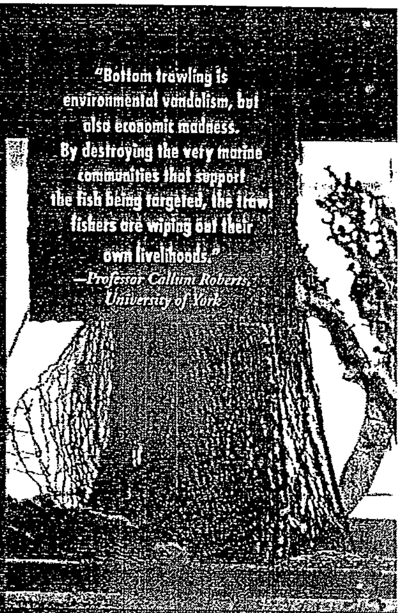


Stony coral (*Enallopsammia* sp.)
Image courtesy of the Deep Atlantic Stepping Stones Science Party IFE, URI-IAO, and NOAA

Map 2: Deep sea corals tend to occur in high-relief areas. This map represents an analysis of steepness (slope) for the Mid-Atlantic and New England regions, overlaid with deep sea coral records. Deep sea corals are abundant in areas with steeper slopes (red color), gentle slopes (blue color). Corals: ● stony corals, ○ gorgonian corals. Black line is US EEZ.

Davidson Seamount off California, suggest that gorgonian and black corals concentrate on ridges where currents are accelerated (Andrews et al. 2005, deVogeleare et al. 2005).

Many corals are observed on rugged surfaces such as ridges and peaks or on boulders, ledges, and rocky outcrops. For example, the walls of sinkholes off southern Florida have high densities of gorgonian corals and hydrocorals (Reed et al. 2005b). On bioherms in the northeastern Straits of Florida, corals are segregated by zone; gold corals on the up-current crest, *Lophelia pertusa* on the up-current slope, and gorgonian corals on the flanks and the downstream crest (Messing et al. 1990). This suggests



"Bottom trawling is environmental vandalism, but also economic madness. By destroying the very marine communities that support the fish being targeted, the trawl fishers are wiping out their own livelihoods."
—*Professor Callum Roberts, University of York*

Box 2.1: Deep Sea Coral Distributions and Shifting Baselines

Historically, deep sea corals were likely present in many areas along the US continental shelf. Since no baseline studies on the distribution of deep sea corals were conducted, it is impossible to determine their former abundance, but reports and anecdotes from fishermen serve as evidence that the seafloor, at least in some areas, has been greatly altered by fishing. One of the first reports of deep sea corals on the West Coast is of a hydrocoral that was hauled up in fishing gear near San Francisco in the late 19th century (Dall 1884). Similar records exist from Georges Bank in New England (Verrill 1878). Canadian fishermen from Nova Scotia were quoted in a 1997 report, "35, 40 years ago, the Stone Fence was full of trees. You couldn't set halibut gear there. They'd haul up

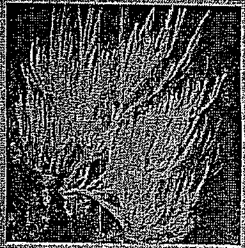
Damage by bottom trawl fisheries is a threat to survival of deep sea corals. The Royal Society of New Zealand's Committee on Biodiversity is petitioning for protection of the world's largest seafloor species, bubblegum coral Paragorgia arborea.
Photo credit: Copyright Greenpeace/Malcom Pullman

big trees, big pieces of trees. They'd be attached to the rocks at the base" (Breeze et al. 1997). The trees in this case were most likely bubblegum corals (*Paragorgia* sp.) or red-tree corals (*Primnoa* sp.). Following the beginning of bottom trawling in this region, fishermen also noted that less and less coral was caught over time. The historical reports of deep sea coral bycatch suggest a need to be cautious when interpreting current deep sea coral distributions, as we have not been witness to changes in the distribution pattern over time from cumulative fishing impacts (i.e., the Shifting Baseline phenomenon, Pa 5).

that different coral species occupy different niches based on preferences for different current flows.

Despite growing knowledge of deep sea coral distributions, the vast majority of the seafloor has not been surveyed for deep sea corals. Thus, an important factor in our current knowledge of deep sea coral distributions is where scientists have conducted research and why. Scientists suggest that the perceived abundance of *L. pertusa* in the northeast Atlantic is partly because of the intense scientific, economic, and military investigations that have occurred there (Freiwald 2003, Roberts et al. 2006). Other examples of activities that have incidentally aided in the collection of deep sea coral distribution data include exploration in Hawaii for precious corals used in jewelry trade, discoveries in the Gulf of Mexico as a byproduct of deep sea research, and bycatch of corals in fisheries. Along the Pacific coast of North America, most deep sea coral records come from research-trawl surveys and bycatch records from fisheries (Etnoyer and Morgan 2003, 2005). Since these early discoveries, many of the same areas have been surveyed by remotely operated vehicles (ROVs) or manned submersibles.

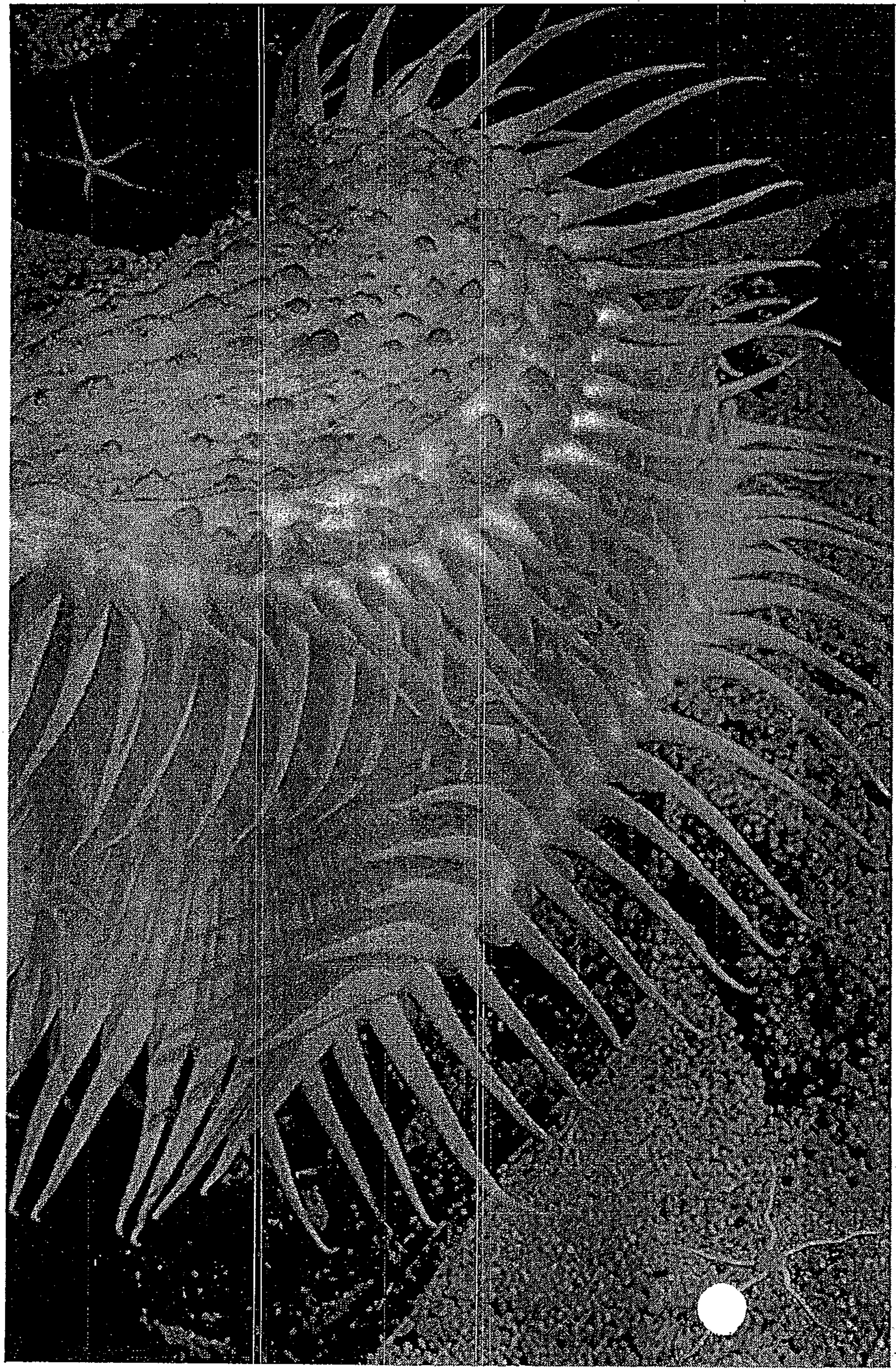
In some cases, however, we should be circumspect about the data we are relying on. Regional knowledge of deep sea coral distributions may vary considerably. For example, fishermen have long known about some deep sea corals from bringing them up in their nets, but scientists have only recently described many others. For those areas that have been historically impacted by fisheries, we will never have baseline information on pre-impact coral distributions (see Box 2.1). Watling and Auster (2005), who produced the most comprehensive review of gorgonian coral records in the New England and Mid-Atlantic regions, state that records have been collected largely opportunistically and sporadically. Etnoyer and Morgan (2003, 2005) classified Pacific deep sea coral records into 4 categories reflecting the degree of expertise associated



The red gorgonian (*Lophogorgia chilensis*)
Photo credit: Shane Anderson

"Bottom trawling is simply not sustainable. The trawl nets are stripping the seabed of life, trashing ancient corals and destroying entire ecosystems. There is much that we are still to learn about life in the oceans. Sadly, much of it will be gone before we get the chance if we don't act now."

Dr. Sylvia Earle,
Executive Director of
Conservation International's
Global Marine Division and
Explorer-in-Residence at the
National Geographic Society



with the coral identifications. Many corals collected from government trawl surveys or recorded on video are difficult to identify beyond the family level, and some survey programs lack the assistance of experts in coral taxonomic identification. The shortage of trained coral taxonomists is a worldwide problem that hinders our understanding of coral distribution (Cairns 2001).

Stony Corals (Scleractinia)

The generic term "coral" is most often applied to stony corals that form hard, calcium-carbonate skeletons. Of the nearly 500 species of stony coral in the deep sea, only 6 or 7 species grow into mounds that resemble the more familiar tropical reefs (Cairns 2001, Freiwald et al. 2004). Although superficially similar to tropical coral reefs, deep sea coral reefs are composed of only 1 or 2 framework species, in contrast to the large diversity of species that comprise tropical reefs. As coral colonies expand, the space between the coral branches is eventually filled with trapped sediments, and the base of the colony becomes a mound of unconsolidated sediment trapped in a dead coral framework, with living corals growing on the outside. While these structures are often described as reefs, scientists refer to them as bioherms. If, over time, the sediment consolidates into a concrete-like crust (a process called lithification) the formation is referred to as a lithoherm (Neumann et al. 1977).

There are 2 major reef-forming species of stony coral in the USA: *Oculina varicosa* and *Lophelia pertusa*. Other stony coral species, such as *Enallopsammia profunda* and *Madrepora oculata*, contribute to the reef framework in some places. *O. varicosa* has slender white branches and can reach up to 7 ft in height. It is often difficult to distinguish individual colonies on mature reefs since they combine over time to form tangled thickets of mixed live and dead coral. *O. varicosa* inhabits relatively shallow coastal waters from

North Carolina to the Caribbean Sea (Reed 2002a), but at deeper depths (230 to 330 ft) off eastern Florida, it forms a nearly contiguous coral bank 103 miles long, with ridges and pinnacles up to 115 ft high (Reed 2002a).

Lophelia pertusa, which is common in the Atlantic and rare in the Pacific, has a similar morphology to *O. varicosa* and also may develop into massive reefs (Figure 2.2). In the US Atlantic *L. pertusa* is distributed from North Carolina to Florida and into the Gulf of Mexico. *Lophelia* reefs rise up nearly 500 ft from the seafloor and live at depths between 1,300 and at least 3,000 ft (Reed 2002a). It has been estimated that the Blake Plateau, especially between southern North Carolina and Cape Canaveral, Florida, contains thousands of coral mounds, most of them unexplored (Paull et al. 2000, Reed 2002a). Significantly, deep sea coral reefs are unknown in the US Pacific, although small specimens of *L. pertusa* have been collected (Etnoyer and Morgan 2003). Recently, a small, isolated patch of *L. pertusa* was discovered by an ROV off the coast of Washington at a depth of 890 ft (Hyland et al. 2005). Scientists speculate that the presence of *L. pertusa*, but the absence of reefs, in the North Pacific may be related to sea water chemistry conditions that are unfavorable for reef building (Guinotte et al. 2006).

E. profunda often co-occurs with *L. pertusa* in waters from South Carolina to Florida (Reed 2002a, S.W. Ross unpublished data). *M. oculata* occurs from North Carolina to Florida and is also found in the northern Gulf of Mexico along the seaward edge of continental shelf (Schroeder et al. 2005). Other stony corals that may form bioherms in US waters include *Solenosmilia variabilis* and *Pourtalosmilia conferta* (Stephen Cairns, National Museum of Natural History, Washington D.C., pers. comm.).

Gold Corals (Zoanthidea)

Members of the order Zoanthidea are colonial, sea-anemone-like organisms. Gold corals are in the genus *Gerardia* and grow rigid branches that form bushy structures. They can grow up to 3.3 ft tall and 5 ft wide on lithoherms in the northeast Straits of Florida at 1800- to 1900-ft depths (Messing et al. 1990). The largest *Gerardia* reported was nearly 7 ft tall (Bell 1891, cited in Druffel et al. 1995). Gold corals are also found throughout the Hawaiian Archipelago, in beds off Oahu and Hawaii, and on the Cross Seamounts, and have been a target for the coral jewelry trade (Grigg 2002).

Gold corals, like other coral species, tend to occur in areas of increased current speed (Figure 2.3). In Hawaii they grow on ridges and walls (Parrish 2005), and off Florida they occur on the up-current portions of the crests of reefs (Messing et al. 1990).

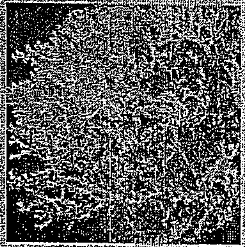


Fig. 2.2: Large *Lophelia pertusa* bush off North Carolina at about 1,200 ft. Note squat lobster and sea urchin near bottom of photo
Photo credit: S.W. Ross et al. UNC-Wilmington

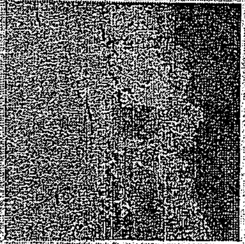


Fig. 2.3: Gold corals growing on a wall in the Northwestern Hawaiian Islands
Source: NOAA

Opposite page: Fly-trap anemone (Family Hormathiidae) on the slope of the Davidson Seamount (6,184 ft depth)
Photo credit: NOAA/MBARI

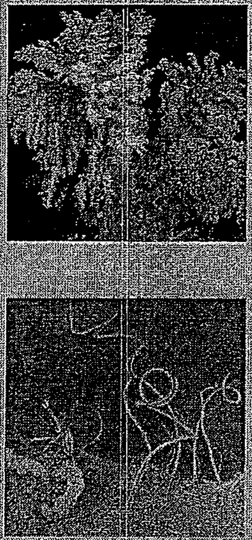


Fig. 2.4. Top: A white Christmas tree coral colony off southern California at 500 ft depth
Photo credit: M. Amend, NMFS

Bottom: Whip-shaped black coral off Florida
Photo credit: J. Reed, HBOI

Black Corals (Antipatharia)

Black corals—members of the order Antipatharia—are, deceivingly, not black in outwards appearance. The underlying skeleton is black or dark brown, but the color of the surrounding tissue varies across species and can be a range of brilliant colors—including red, brown, orange, yellow, green, or white. Black coral polyps are only millimeters wide or even smaller, and they often form colonies in the shape of bushes, trees, or whips up to 8 ft tall (Figure 2.4). The skeletons of black corals are covered in thorn-like spines or knobs, and these corals are sometimes called thorny corals.

Antipathes dichotoma and *A. grandis* are 2 black coral species that have been collected for the jewelry trade off the main Hawaiian Islands at 130- to 250-ft depths (Grigg 2002). Black corals are also found along the Atlantic and Pacific Coasts, in the Gulf of Mexico, and on seamounts. Derickson Seamount (6,562-ft depth) and Denson Seamount (4,593-ft depth) in the Gulf of Alaska (Baco and Cairns 2005)[1] and Manning Seamount (5,577-ft depth) off New England[2] are just a few seamounts where black corals have been found.

Recently, scientists described a new species of black coral—the Christmas tree coral (*Antipathes dendrochristos*) off southern California (Opresko 2005). Despite growing to a height of over 8 ft and living just miles from one of the most densely populated urban centers in the world (Los Angeles), where there are many marine laboratories, this species remained undiscovered until 1995 (Tissot et al. 2006). As their name suggests, these coral colonies resemble Christmas trees, with extensive branching and ornaments of worms, barnacles, shrimps, and crabs. Researchers observed 135 colonies of these pink-, white-, red-, or gold-colored corals distributed at depths of 328–738 ft around the Channel Islands off southern California (Tissot et al. 2006).

Gorgonian Corals (Alcyonacea)

Gorgonian corals, also sometimes referred to as sea fans, have a flexible internal skeleton that allows some species to bend and sway in the currents like the branches of a tree in gusty winds. Gorgonian coral morphology is very diverse; some colonies have dense branches, grow several feet tall, and form groves, while others look like isolated whips or stalks standing upright on the seafloor. All gorgonian corals are members of the group Octocorallia, meaning that each polyp contains 8 tentacles. They are found throughout US waters, from continental shelf breaks and submarine canyons to isolated seamounts. Our focus is on those structure-forming species with erect, bush-like shapes; these species fall predominately into 4 families: red

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[1] NOAA Ocean Explorer Gulf of Alaska 2004 Expedition: http://oceanexplorer.noaa.gov/explorations/04alaska/logs/aug05/media/coral_defense_video.html

[2] NOAA Ocean Explorer Mountains in the Sea 2004 Expedition: http://www.oceanexplorer.noaa.gov/explorations/04mountains/logs/may16/may16.html

or pink corals (Coralliidae), bamboo corals (Isididae), bubblegum corals (Paragorgiidae), and red-tree corals (Primnoidae).

Red or pink corals, belonging to the family Coralliidae, are often referred to as precious corals because they have been used in jewelry since antiquity. Today several species are collected for the jewelry trade (as are some black corals, gold corals, and bamboo corals). Pink coral (*Corallium secundum*) and red coral (*C. lauuense*) are 2 species of Coralliidae found in Hawaii (Grigg 2002, Baco and Shank 2005). Corals in this family also occur on seamounts in the Gulf of Alaska (Baco and Shirley 2005, Heifetz et al. 2005), on Davidson seamount off California (deVogeleare et al. 2005), and on New England seamounts.[3] Their colonies are generally less than 2 ft in height, with a loosely spaced, rigid branching structure.

Bamboo corals in the family Isididae are so named because their skeletons resemble bamboo, with white, bony, calcareous sections separated by black internodes composed of protein (Figure 2.5). However, live colonies with extended feeding tentacles lose their resemblance to bamboo as they take on the red, orange, or white color of the polyps and outer tissue. Bamboo corals can grow in the shape of a branching bush or a single long whip up to 10 ft tall or more.[4] Bamboo corals occur along the East, West, and Gulf Coasts of the USA, in Hawaii, and on seamounts. Some bamboo corals are bioluminescent, emitting blue light when disturbed.[5]

In the family Paragorgiidae, the bubblegum coral (*Paragorgia arborea*) (Figure 2.6) is found primarily in the temperate regions of the USA in both the Atlantic and Pacific Oceans. It is found in submarine canyons and seamounts in the Gulf of Maine (Watling and Auster 2005), on seamounts in the Gulf of Alaska, around the Aleutian Islands in Alaska (Heifetz et al. 2005), in Hawaii, and along the US West Coast (Etnoyer and Morgan 2003). Colonies reaching 33 ft in height have been reported in New Zealand (Smith 2001), whereas in Alaska they seldom grow larger than 7 ft.[6] Bubblegum coral can be white or red, with characteristic round knobs throughout the colony.

Gorgonian corals in the family Primnoidae are usually tree-like or bushy with pinnate branches. Species of this family are found throughout the USA. Colonies of the red-tree coral (*Primnoa resedaeformis*) grow to 10 ft tall and 23 ft wide in Alaska (Krieger and Wing 2002), and have been known to fishermen in the Gulf of Maine since the 1800s (Watling and Auster 2005).

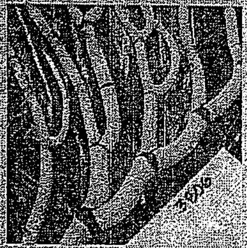

Fig. 2.5: Skeleton of bamboo coral from Warwick Seamount
Photo credit: NOAA OE

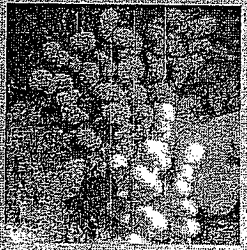

Fig. 2.6: Bubblegum coral in Alaska
Photo credit: A. Lindner, courtesy of NMFS

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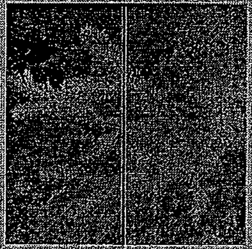
[3] NOAA Ocean Explorer Mountains in the Sea 2003 Expedition: http://oceanexplorer.noaa.gov/explorations/03mountains/logs/jul16/jul16.html

[4] NOAA Ocean Explorer Mountains in the Sea 2004 Expedition: http://www.oceanexplorer.noaa.gov/explorations/04mountains/logs/may12/may12.html

[5] NOAA Ocean Explorer Gulf of Alaska 2004 Expedition http://oceanexplorer.noaa.gov/explorations/04alaska/background/bamboo/bamboo.html

[6] NOAA Ocean Explorer Exploring Alaska's Seamount Expedition: http://www.oceanexplorer.noaa.gov/explorations/02alaska/logs/jul15/media/paragorgia.html



Black coral (Antipatharia) on the Davidson Seamount at 5,016 ft depth.
Photo credit: NOAA/MBARI

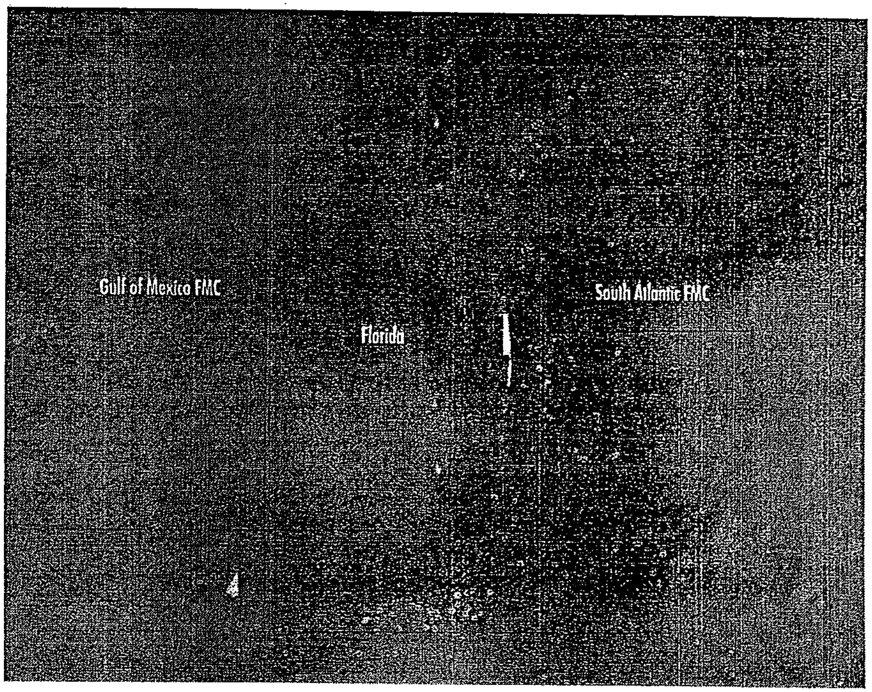
"Today's trawlers are capable of fishing deep sea canyons and rough seafloor that was once avoided for fear of damaging nets. To capture one or two target commercial species, deep-sea bottom trawl fishing vessels drag huge nets armed with steel plates and heavy rollers across the seabed, plowing up and pulverizing everything in their path. For a few commercial target species, thousands of tons of coral are hauled up only to be thrown back dead or dying, along with huge quantities of unwanted bycatch. In a matter of a few weeks or months, bottom trawl fishing can destroy what took many thousands of years to create."
Deepsea Conservation Coalition April 2006

Hydrocorals (Stylasterina)

Hydrocoral is the general term applied to corals in the orders Milleporina (tropical fire corals) and Stylasterina, within the class Hydrozoa. Stylasterines are typically quite delicate, with rigid but brittle calcium carbonate skeletons. As with other cnidarians they contain stinging cells, but the hydrozoan body plan is quite different from that of the other taxa of deep sea corals discussed in this report (which are in the class Anthozoa). Hydrozoan feeding and stinging polyps form groupings called cyclosystems, which are arranged in species-specific patterns over the surface of the skeleton and give hydrocorals a bumpy appearance superficially similar to the polyps of stony corals. There are several genera, but the genus *Stylaster* is one of the most common. Hydrocorals can be a variety of colors, including purple, orange, pink, and white. One of the largest species, *Stylaster cancellatus*, can grow to a height of almost 3.5 ft and is often densely concentrated (Wing and Barnard 2004).

Hydrocorals are distributed throughout the USA. The exceptionally high species diversity of hydrocorals in the Aleutian Islands—20 species or subspecies have been found in the island chain—has led to suggestions that this area may be an evolutionary center of origin for the group (Heifetz et al. 2005). Recent analysis reveals that hydrocorals evolved in the deep sea and later moved into shallow water, a unique pattern not documented in other marine species (Lindner 2005).

Off the east coast of Florida and along the southwest Florida shelf, hydrocorals are common in some locations (Reed et al. 2005b). They are one of the most abundant taxa on lithoherms in the northeast Straits of



Map 3: Waters of the southeastern USA are home to many taxa of deep seal corals. The Oculina *Bank HAPC (white area) off the east coast of Florida is closed to bottom fishing to protect deep sea corals. Corals: ● stony corals, ● gold corals, ● gorgonian corals, ♠ hydrocorals. ▨ HAPC. Black line is US EEZ.*

Florida, occurring at densities of over 8 to 10 colonies per yd^2 (Messing et al. 1990). Further south and west, on the bioherms of the Pourtales Terrace, there are dense fields of hydrocorals, growing to heights of 10 inches, and reaching concentrations of up to 96 colonies per yd^2 (Reed et al. 2005b).

Deep Sea Coral and Sponge Assemblages

Coral colonies of the same species often form nearly exclusive groupings, with representatives of other corals present at lower densities. However, in some cases deep seafloor assemblages can contain a wide diversity and abundance of sponges and deep sea corals. For example, the waters of the southeastern USA, from Georgia to South Carolina, and along the Florida-Hatteras slope, contain many taxa of deep sea corals (Map 3). In many places sponges, gorgonian corals, and black corals are found at high densities within *Lophelia* reefs (Reed 2002a, S.W. Ross et al. unpublished data). Many sponges and gorgonian corals are found within hydrocoral-dominated coral gardens of the Aleutian Islands (Figure 2.7), and black corals are often seen in fields of bamboo coral in the Gulf of Mexico (S. Brooke, U. Oregon, pers. comm.).

Sponges are an important component of most deep sea coral ecosystems and their abundance and diversity can equal or exceed that of the corals. Glass sponges (Hexactinellidae) are a diverse group of sponges found in the deep sea. With the recent expansion of research into deep sea coral habitats, scientists have discovered an astounding variety of sponges, including many new to science (Lehnert et al. 2005). However, we still know virtually nothing about the biology and ecology of these significant components of deep sea coral ecosystems.

Summary

This report focuses on 5 taxa of deep sea corals found in US waters: stony corals, gold corals, black corals, gorgonian corals, and hydrocorals. They come in various shapes and sizes, from massive reefs miles long to single bush-shaped individuals many feet tall. Our understanding of their distribution is currently limited and varies greatly by region. Because of differences in data collection, it is difficult to compare coral distributions from one region to the next. The quantity of data available may be significantly biased toward those geographic areas and depth zones where fishing or oil and gas exploration and development activities occur.

The vast majority of the seafloor has not been surveyed for deep sea coral occurrences. Present data show that deep sea corals are widely distributed, but are often very localized in their concentration. They are generally found in areas with hard seafloor substrates and appropriate currents, such as the seaward edge of the continental shelf (an area also know as the shelf break), around the edges of submarine canyons, and on offshore banks and seamounts.

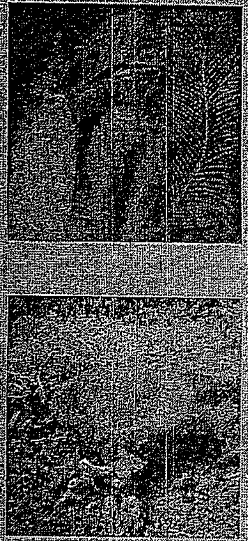
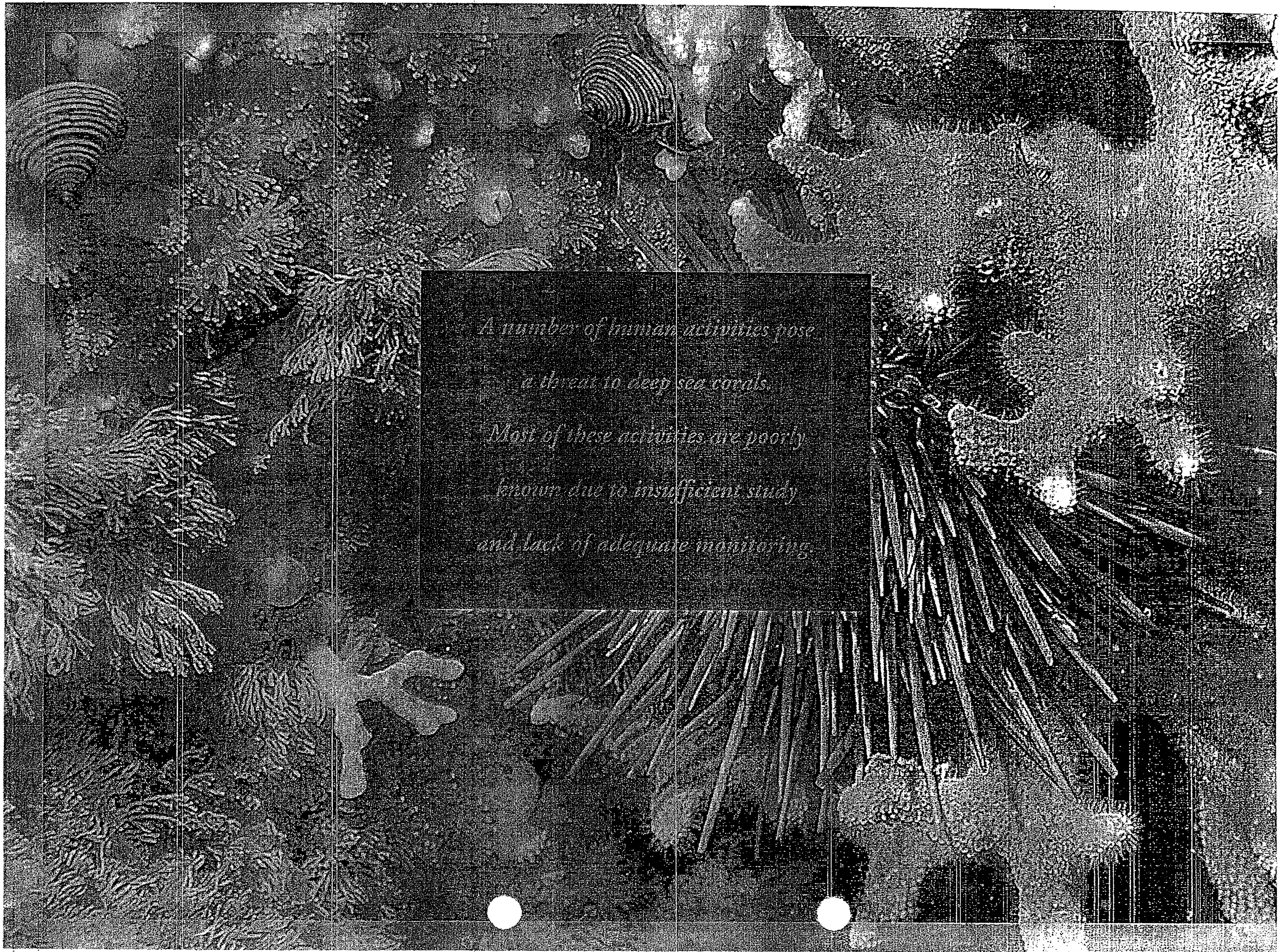


Fig. 2.7 Top: Sponge-gorgonian coral assemblage in Alaska
Photo credit: R. Stone, NMFS

Bottom: Hydrocoral (*Stylaster filogranus*) with Choristida vase sponge in the foreground at a southern Florida bioherm
Photo credit: J. Reed, HBOI

"Sponges are an important component of most deep sea coral ecosystems and their abundance and diversity can equal or exceed that of the corals"



A number of human activities pose
a threat to deep sea corals.
Most of these activities are poorly
known due to insufficient study
and lack of adequate monitoring.

Threats to Deep Sea Corals

Despite their diversity, all deep sea corals share an important characteristic—their vulnerability to human activities that damage the seafloor or alter the deep ocean environment (Freiwald et al. 2004, Guinotte et al. 2006, Kahng and Grigg 2005, Roberts et al. 2006, Rogers 1999). These activities threaten the health and survival of deep sea corals worldwide:

- Fishing, especially bottom trawling
- Oil and gas exploration and extraction
- Coral exploitation and trade
- Introductions of invasive species
- Increasing atmospheric CO_2
- Cable laying
- Waste disposal
- Mineral extraction
- Bioprospecting

Bottom Trawl Fishing

In recent years, many reports have documented the impacts of different fishing methods on seafloor habitats (Barnes and Thomas 2005, Benaka 1999, Kaiser et al. 2006, National Research Council 2002). Bottom trawl fishing gear, which targets fish living on or just above the seafloor, breaks and smashes deep sea corals (Fosså et al. 2002, Hall-Spencer et al. 2002, Puglise et al. 2005). Damaged colonies that do survive bottom trawling may be unable to successfully reproduce (Waller and Tyler 2005). Large bottom trawling gear can weigh several tons (Merrett and Haedrich 1997), and the groundline, which keeps the net in close contact with the seafloor, is often weighted and modified with large, heavy discs, tires, or rollers designed to ride over, or break through obstructions and keep the net from snagging and tearing on the seafloor (Figure 3.1). The damage caused by bottom trawling has been compared to forest clear-cutting (Watling and Norse 1998), and it is considered by scientists, managers, and fishing professionals to be the most ecologically destructive fishing method (Chuenpagdee et al. 2003, Morgan and Chuenpagdee 2003).

Because bottom trawling occurs all over the world, there are many international examples of coral damage caused by this fishing

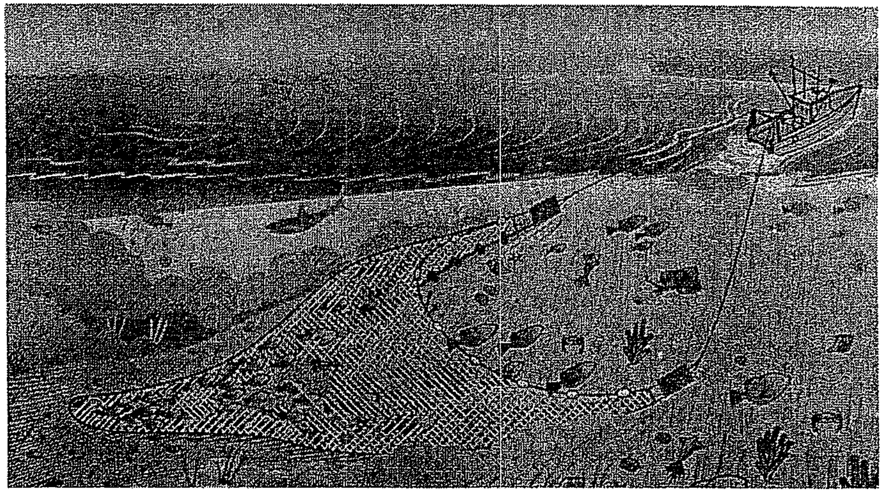
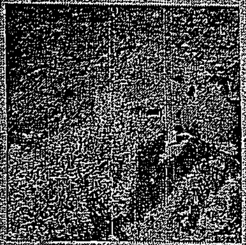


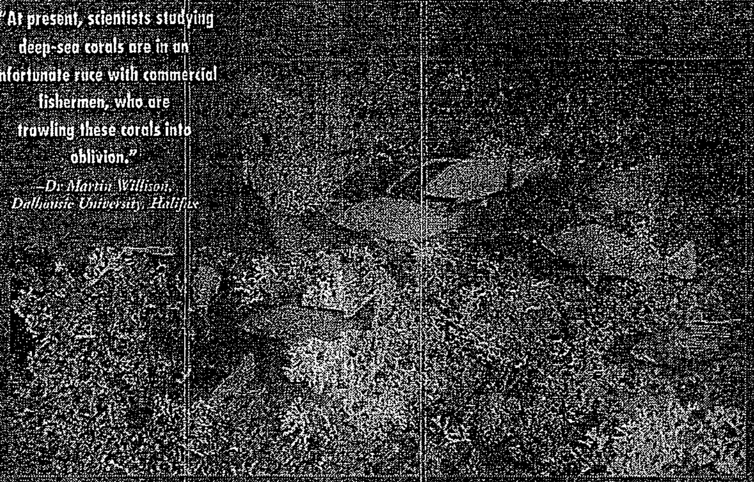
Fig. 3.1: Depiction of bottom trawl gear as it drags along the seafloor damaging everything in its path.


Black coral (*Trissopathes* sp.)
and deep sea octopus
on Davidson Seamount at
6,510 ft depth
Photo: NOAA/MBARI

"The most notorious non-selective equipment includes nets large enough to envelop twelve 747 airliners and capable of catching up to 200,000 pounds of fish at each setting, and lines up to 80 miles long that carry some 3,000 hooks."

United Nations Earth Summit – 5 June 1997

Opposite page: The California hydrocoral (Stylaster californicus) *at Point Lobos often had purple or red sea urchins (shown here* Strongylocentrotus franciscanus) *associated with them.*
Photo credit: Steve Lonhart/MBNMS

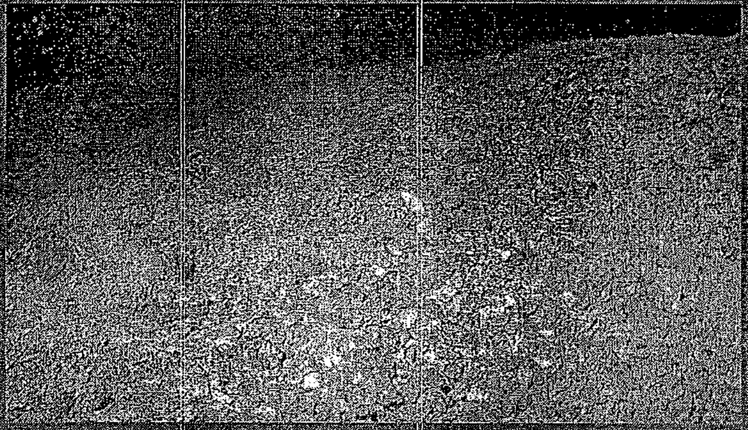


> "At present, scientists studying deep-sea corals are in an unfortunate race with commercial fishermen, who are trawling these corals into oblivion."
>
> —Dr. Martin Willison, Dalhousie University, Halifax

Untrawled

Figure 3.2a: Untrawled *Oculina* reefs.
Groupers were abundant on deep sea *Oculina* reefs off Florida before trawling began; legal and illegal trawling has nearly eliminated the corals and large fishes in this ecosystem

Photo credit: R.G. Gilmore

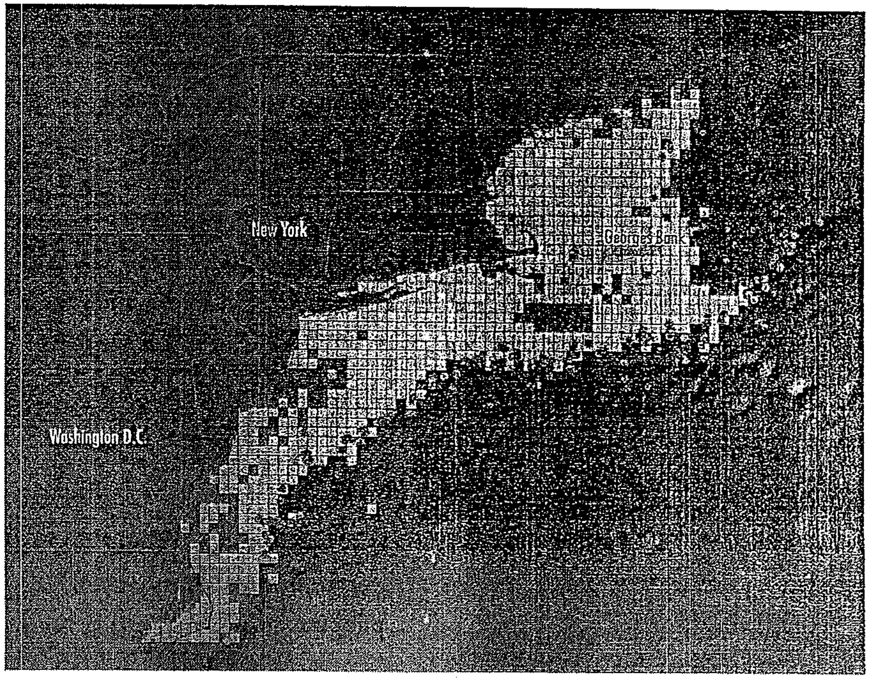


Trawled

Figure 3.2b: Trawled *Oculina* reefs.

Photo credit: L. Horn, NURC/UNCW

method. In Norway, 30 to 50% of pre-existing *Lophelia* reefs have been destroyed by trawling (Fosså et al. 2002). Trawl damage to *Lophelia* reefs in Irish waters has also been documented (Hall-Spencer et al. 2002). Bottom trawling that occurs in Atlantic Canada breaks deep sea corals that inevitably end up in fishing nets (Mortensen et al. 2005). Canadian fishermen have observed a decrease in deep sea corals over time, suggesting that corals have been removed by fishing and are not recovering (Gass and Willison 2005). In the southern hemisphere, trawling has reduced coral coverage on one Tasmanian seamount from 90% to 5% (Koslow et al. 2000). In just a single hour of trawling for orange roughy, trawlers off New Zealand removed 1.6 tons of corals (Anderson and Clark 2003).



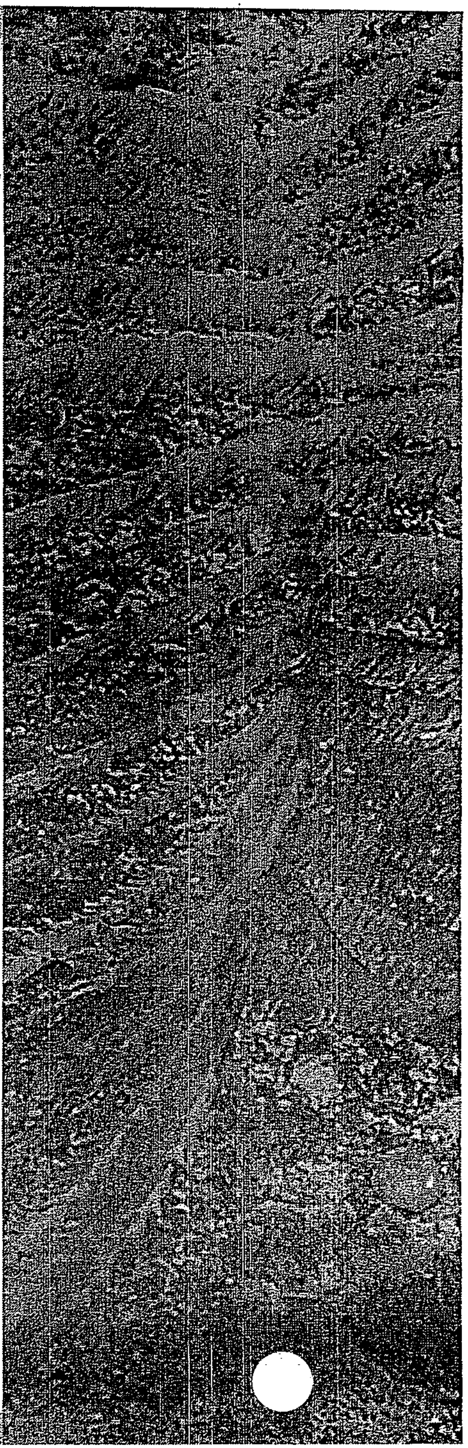
Map 4a: Deep sea corals and fishing intensity by bottom trawl in the New England and Mid-Atlantic fishery management council regions. Total bottom trawl trips for the years 1995–2001: ▨ 51–389, ▨ 390–993, ▨ 994–2045, ▨ 2046–5172 Corals: ● stony corals, ● gorgonian

In the USA, fishing is the most widespread activity directly impacting deep sea corals. In recent years, managers and conservation organizations have begun to analyze the spatial overlap of fishing and deep sea coral distributions (Morgan et al. 2005). However, the detailed data required to conduct these studies are difficult to obtain and are often of insufficient quality for rigorous analyses. One of the largest hurdles in protecting deep sea corals is the incomplete knowledge of their distribution and threats. Here, we review the spatial overlap of available coral distribution and fishing intensity data by region (see Map 1 for the extent of the 8 regions). We obtained fishing data from the National Marine Fisheries Service (NMFS), but in many cases, detailed data on fishing locations were withheld in order to protect the confidentiality of fishermen. Through government and museum efforts and data mining by Etnoyer and Morgan (2003) and Watling and Auster (2005) some regional deep sea coral datasets have been made readily available (see Appendix).

Map 4b: Deep sea corals and fishing intensity by bottom gillnet trips in the New England and Mid-Atlantic fishery manage-m ncil regions. Total bottom gillnet trips for the years 1995–2001: ▨ 1–75, ▨ 26–275, ▨ 276–750, ▨ 751–3831 C tony corals, ● gorgonian corals.

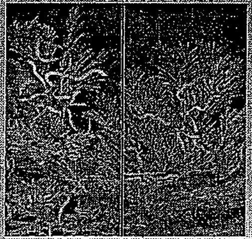
New England and Mid-Atlantic Regions

The fishing grounds in the New England and Mid-Atlantic regions (Map 4a, 4b) have been heavily exploited for centuries, although trawling was not intensive until the last half of the 20th century. Fishing intensity varies throughout this region and across gear types. However, bottom trawling gear is the most widely used fishing gear (Map 4a, previous page). A 1996 study estimated that the entire Georges Bank seafloor is trawled 3–4 times annually (Auster et al. 1996). Georges Bank is the main New England fishing ground, located approximately 60 miles offshore. It is



Black coral on New England seamount
Photo credit: Deep Atlantic Stepping Stones Science Team/ IFE/URI-IAO/NOAA

Rosy rockfish (*Sebastes rosaceus*)
Photo credit: Chad King/MBNMS



Callogorgia americana with a newly discovered species of ophiuroid (*Asteroschema* sp.) in the Gulf of Mexico
Photo credit: S. Brooke et al. courtesy Minerals Management Service

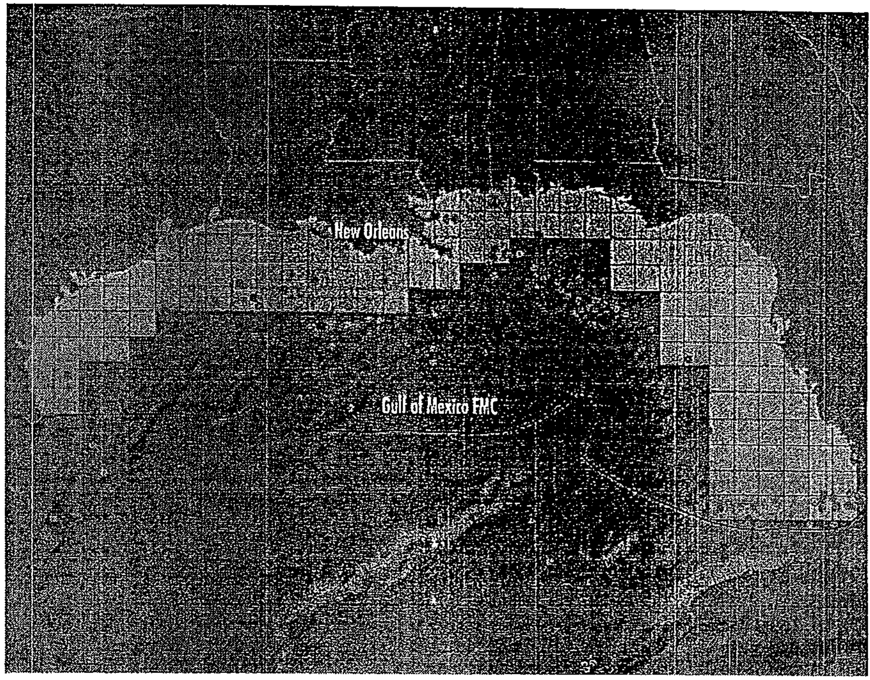
oval in shape, and measures approximately 150 by 75 miles — slightly larger than the state of Massachusetts. Corals have been recorded in this region since 1874 (Watling and Auster 2005, Yale Peabody Museum[1]), but scientists suspect that the distribution of deep sea corals observed today has been altered by bottom fishing, and that many of the corals in historical records have since been destroyed by fishing (Watling and Auster 2005).

South Atlantic Region

In the US South Atlantic region, bottom trawls are widely used in shallow waters along the continental shelf to catch shrimp, but only in Florida does the trawl fishery for rock shrimp significantly interact with deep sea coral reefs. Currently there is little other commercial bottom trawl fishing that could impact corals. The *Oculina* Banks, a series of coral mounds that stretches for some 100 miles along the eastern coast of Florida, is the best known, most significantly degraded deep sea coral habitat in US waters. Since the 1970s, live *Oculina varicosa* coral cover in the 122 mi² Experimental *Oculina* Reseach Reserve has been reduced by over 90%; by far the greatest cause of this devestation has been bottom trawling (Koenig et al. 2005, Reed et al. 2006) (Figures 3.2a and 3.2b, page 28).

Gulf of Mexico Region

In the Gulf of Mexico, there is some cause for concern over bottom trawl fisheries that target shrimp. Bottom trawling for royal red shrimp is potentially problematic because it can occur to depths of 2,400 ft. Though this deep water shrimp fishery is very limited, just one trawl pass can result in decimation of a deep sea *Lophelia* reef. In general,



Map 5: Deep sea coral occurrences and bottom trawl intensity data from NMFS for the Gulf of Mexico. Shrimp (total tons) years 2001–2004: ▨ 320–2500, ▨ 2501–5000, ▨ 5001–30000, ▨ 30001–55862 Corals: ● stony corals, ● gorgonian corals, and ● hydrocorals. Black line is US EEZ.

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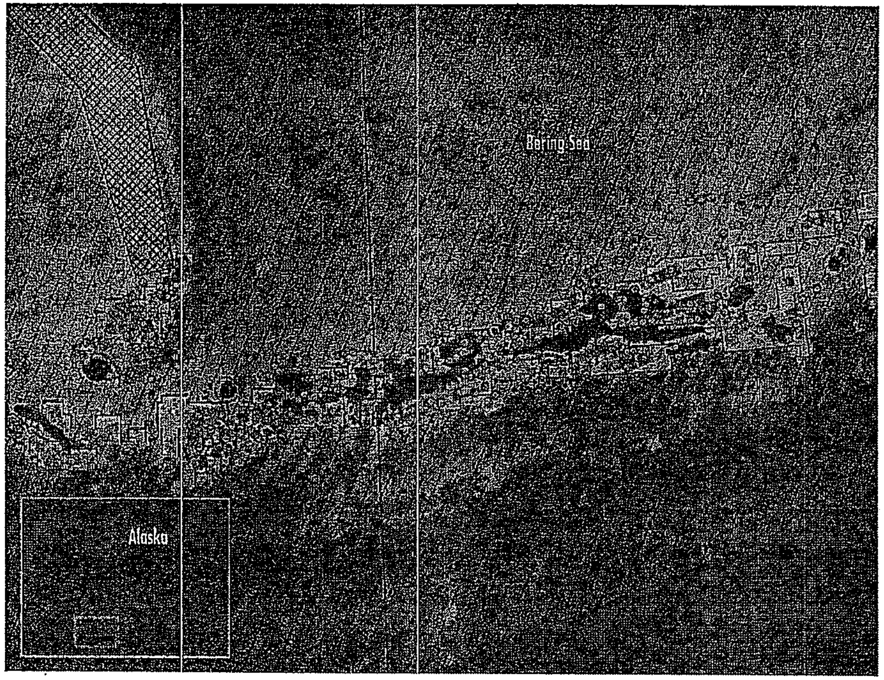
[1] Peabody Museum Invertebrate Zoology Collection: http://www.peabody.yale.edu/collections/iz/

it is difficult to assess the impact of fishing in this region because the NMFS data from the shrimp trawl fishery are summarized into large spatial blocks that are too coarse relative to known deep sea coral locations (Map 5).

Caribbean Region

The Caribbean region includes the EEZ waters of Puerto Rico, US Virgin Islands, and Navassa Island (an uninhabited US territory located between Haiti and Jamaica). No active bottom trawl fisheries occur in this region. Thus far, few occurrences of deep sea corals are known from this region, and therefore no management is in place for their protection. However, several major structure-forming coral species have been observed in the region, including *Enallopsammia rostata*, *Lophelia pertusa*, *Maderopora carolina*, *Madrepora oculata* (Ginsberg and Lutz in prep.), and these observations hint at the presence of deep sea banks or lithoherms.



Map 6: Bottom trawl closures in the Aleutian Islands (hatched areas) prevent the further expansion of the fishing fleet, but intensive trawl fishing continues in areas with deep sea corals (non-hatched areas). Observed bottom trawl trips, 2001–2003: ▨2- ■ 11–50, ■ 51–100, ■ 101–250, ■ 251–682. ▩ Bowers Ridge Habitat Conservation Zone, ▨ Aleutian Islar I Conservation Area, Corals: ● hydrocorals, ● gorgonian corals.

North Pacific Region

In the North Pacific region, bottom trawling is intense in the Bering Sea and Aleutian Islands and to a lesser extent in the Gulf of Alaska. Between 1997 and 2001, an average of 81.5 tons of coral was uprooted every year by commercial fishing in the North Pacific; 97% of this was attributed to bottom trawls (NMFS 2004, North Pacific Fishery Management Council 2003). In the Aleutian Islands, there is an extraordinary diversity of deep sea corals; among the 69 known species and subspecies of corals there, 25 are endemic—found nowhere else in the world (Heifetz et al. 2005). Bottom trawl fishing targeting Atka mackerel and a variety of rockfishes overlaps with deep sea coral occurrences in the Aleutian Islands (Map 6). One cause

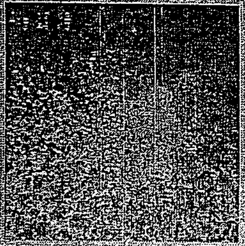
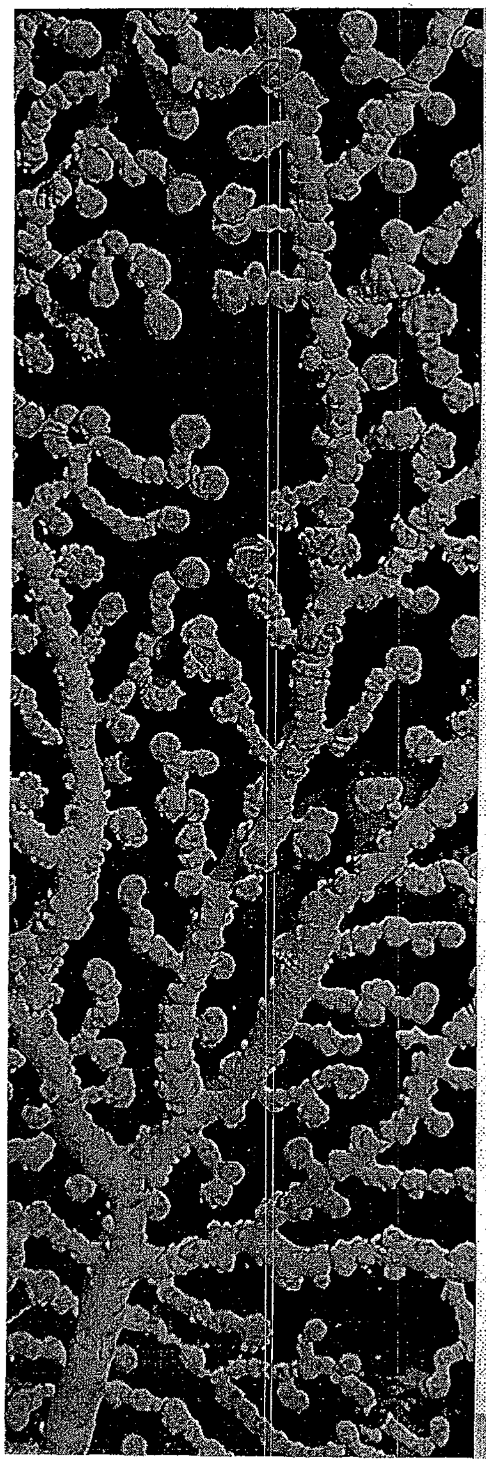


Fig. 3.3a, Top: An intact coral-sponge ecosystem in the Aleutian Islands.
Fig 3.3b, Bottom: An area damaged by traps used for catching gold king crabs.
Photo credit: R. Stone, NMFS



of this overlap is that many deep sea coral records were reported by fishery observers documenting bycatch. Only recently have researchers begun to examine areas outside of historical fishing grounds for the presence of deep sea corals.

Pacific Region

Along the US West Coast from Washington to California, bottom fishing for groundfish species occurs on the continental shelf. While several gear types are used in this fishery, bottom trawling affects the largest area and leaves the largest ecological footprint (Morgan et al. 2005). In Monterey Canyon, the bottom trawl fishery occurs in areas with deep sea corals, but most of the coral records are from the continental shelf break, where fishing intensity is currently low (Morgan et al. 2005). Without historical coral distribution data it is difficult to know whether or not this pattern is the result of decades of fishing pressure on the shelf that may have removed deep sea corals and prevented them from maintaining established colonies.

Western Pacific Region

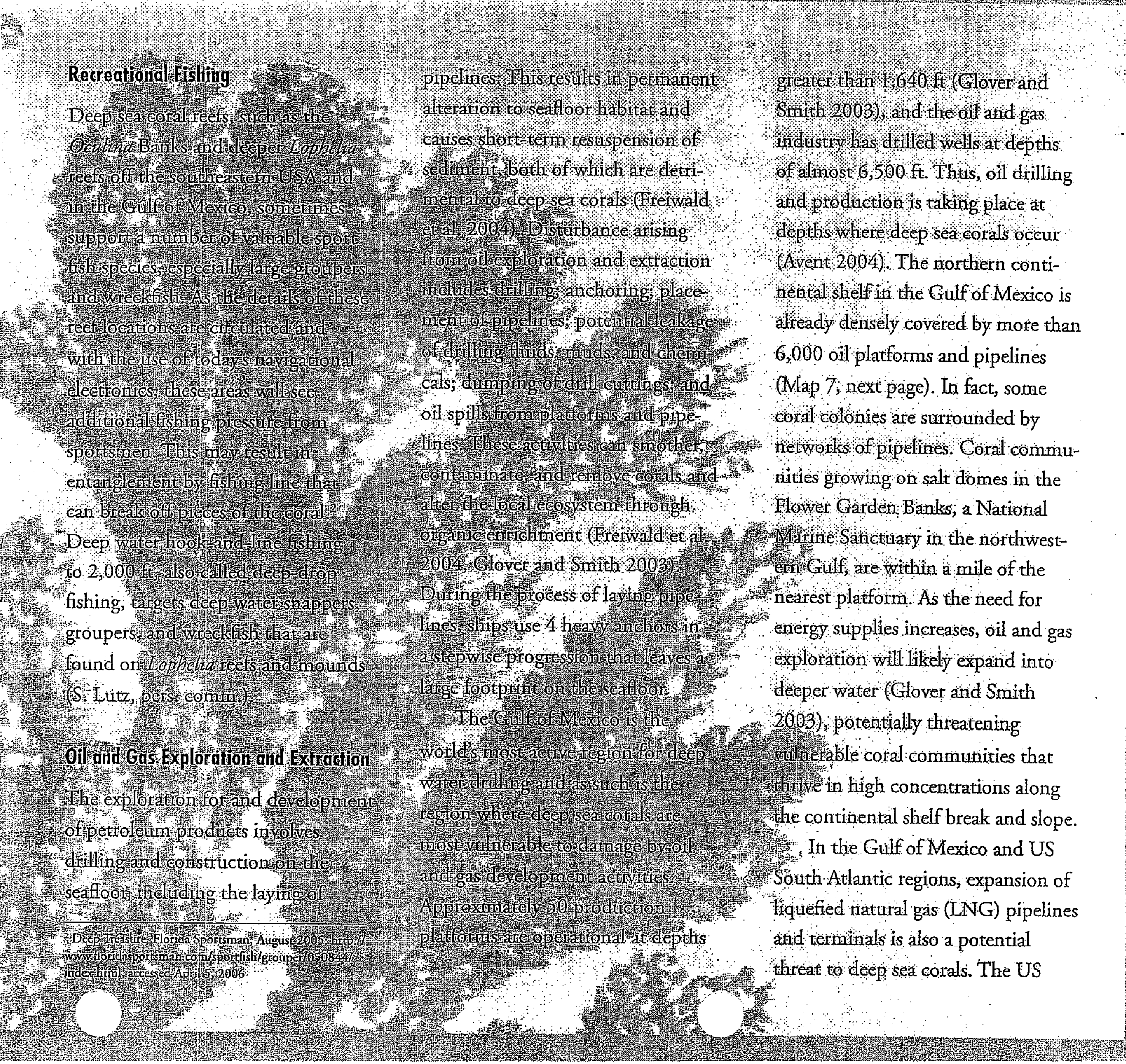
In US waters around Hawaii and other islands of the Pacific (Guam, Marinas, America Samoa and several additional islands) managed by the Western Pacific Fishery Management Council, bottom trawling and dredging are prohibited and therefore do not affect deep sea corals.

Other Commercial Fishing Gears

Other commercial fishing gears also pose a threat to fragile deep sea corals (Morgan and Chuenpagdee 2003, Morgan et al. 2005, Mortensen et al. 2005). All bottom tending gears have the potential to snag or break deep sea corals. In Atlantic Canada, fishing gears such as longlines and gillnets that target demersal fishes (e.g., halibut, cod, and monkfish) entangle and damage delicate deep sea gorgonian corals (Mortensen et al. 2005). These nets and lines are commonly weighted in order to stay on the seafloor, causing damage to corals, and during retrieval they are dragged along the floor, often snagging and breaking corals (Mortensen et al. 2005).

In the North Pacific FMC region, pots for crabs and fishes and longlines for cod may also damage corals (Stone and Wing 2001). Although bycatch from these gears is significantly lower than that from bottom trawls, crab pots are typically deployed on long lines and often snag corals on recovery, significantly damaging them (Figures 3.3a and 3.3b, previous page). Bottom longlines have been documented snagging and knocking over coral colonies in the Gulf of Alaska (Krieger 2001).

Off the east coast of Florida, longline gear was found entangling an *O. varicosa* colony at Sebastian Pinnacles, at a depth of 260 ft (Reed et al. 2005a). In the New England and Mid-Atlantic regions (Map 4b, page 29), bottom gillnet fishing overlaps with known deep sea coral locations (Watling et al. 2003).



Recreational Fishing

Deep sea coral reefs, such as the *Oculina* Banks and deeper *Lophelia* reefs off the southeastern USA and in the Gulf of Mexico, sometimes support a number of valuable sport fish species, especially large groupers and wreckfish. As the details of these reef locations are circulated and with the use of today's navigational electronics, these areas will see additional fishing pressure from sportsmen. This may result in entanglement by fishing line that can break off pieces of the coral.[2] Deep water hook-and-line fishing to 2,000 ft, also called deep-drop fishing, targets deep water snappers, groupers, and wreckfish that are found on *Lophelia* reefs and mounds (S. Lutz, pers. comm.).

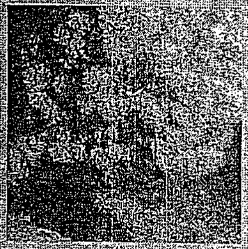
Oil and Gas Exploration and Extraction

The exploration for and development of petroleum products involves drilling and construction on the seafloor, including the laying of pipelines. This results in permanent alteration to seafloor habitat and causes short-term resuspension of sediment, both of which are detrimental to deep sea corals (Freiwald et al. 2004). Disturbance arising from oil exploration and extraction includes drilling; anchoring; placement of pipelines; potential leakage of drilling fluids, muds, and chemicals; dumping of drill cuttings; and oil spills from platforms and pipelines. These activities can smother, contaminate, and remove corals and alter the local ecosystem through organic enrichment (Freiwald et al. 2004, Glover and Smith 2003). During the process of laying pipelines, ships use 4 heavy anchors in a stepwise progression that leaves a large footprint on the seafloor.

The Gulf of Mexico is the world's most active region for deep water drilling and as such is the region where deep sea corals are most vulnerable to damage by oil and gas development activities. Approximately 50 production platforms are operational at depths greater than 1,640 ft (Glover and Smith 2003), and the oil and gas industry has drilled wells at depths of almost 6,500 ft. Thus, oil drilling and production is taking place at depths where deep sea corals occur (Avent 2004). The northern continental shelf in the Gulf of Mexico is already densely covered by more than 6,000 oil platforms and pipelines (Map 7, next page). In fact, some coral colonies are surrounded by networks of pipelines. Coral communities growing on salt domes in the Flower Garden Banks, a National Marine Sanctuary in the northwestern Gulf, are within a mile of the nearest platform. As the need for energy supplies increases, oil and gas exploration will likely expand into deeper water (Glover and Smith 2003), potentially threatening vulnerable coral communities that thrive in high concentrations along the continental shelf break and slope.

In the Gulf of Mexico and US South Atlantic regions, expansion of liquefied natural gas (LNG) pipelines and terminals is also a potential threat to deep sea corals. The US

A brittle star wraps its arms around the branches of a gorgonian coral colony (*Metallogorgia sp*).
Photo credit: the Deep Atlantic Stepping Stones Science Party, IFE, URI-IAO, and NOAA



Bubblegum coral (*Paragorgia sp.*) from Aleutian Islands, AK.
Photo credit: A. Lindner, courtesy of NMFS

Opposite page: Bubblegum coral (Paragorgia arborea) 8 feet in height were not uncommon at the crest of the Davidson Seamount, here shown at 4,150 ft.
Photo credit: NOAA/MBARI

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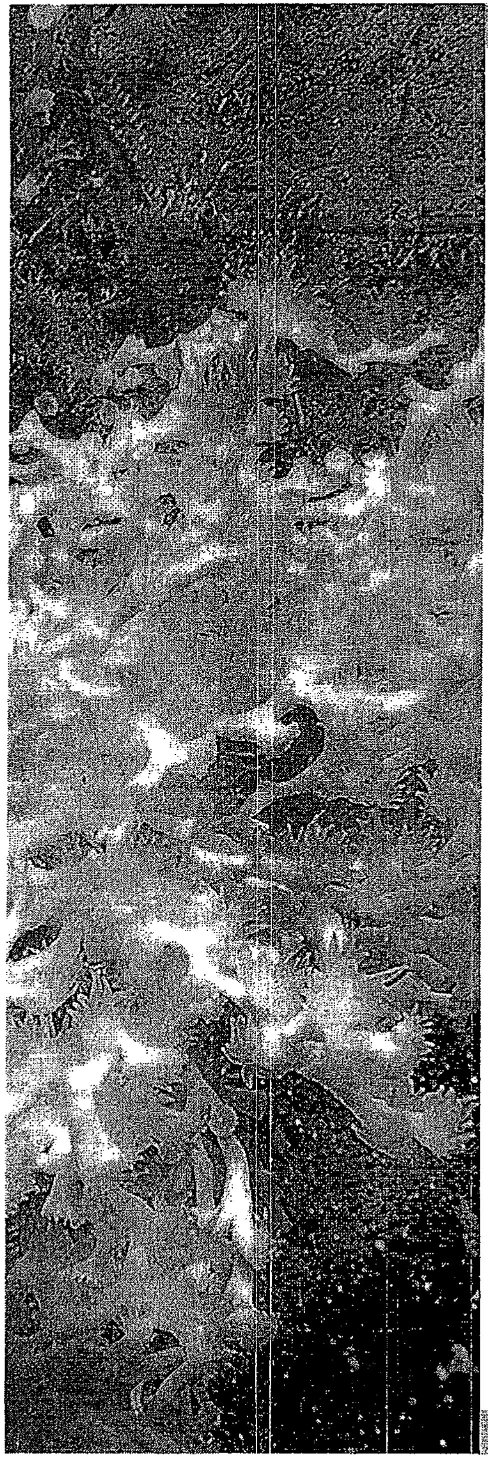
[2] Deep Treasure, Florida Sportsman, August 2005. http://www.floridasportsman.com/sportfish/grouper/050844/index.html, accessed April 5, 2006



Department of Energy forecasts that by 2010, a terminal and pipeline supplying the Florida market will be constructed between the Bahamas and the east coast of Florida, potentially cutting across some important deep sea coral beds (Energy Information Administration 2003).

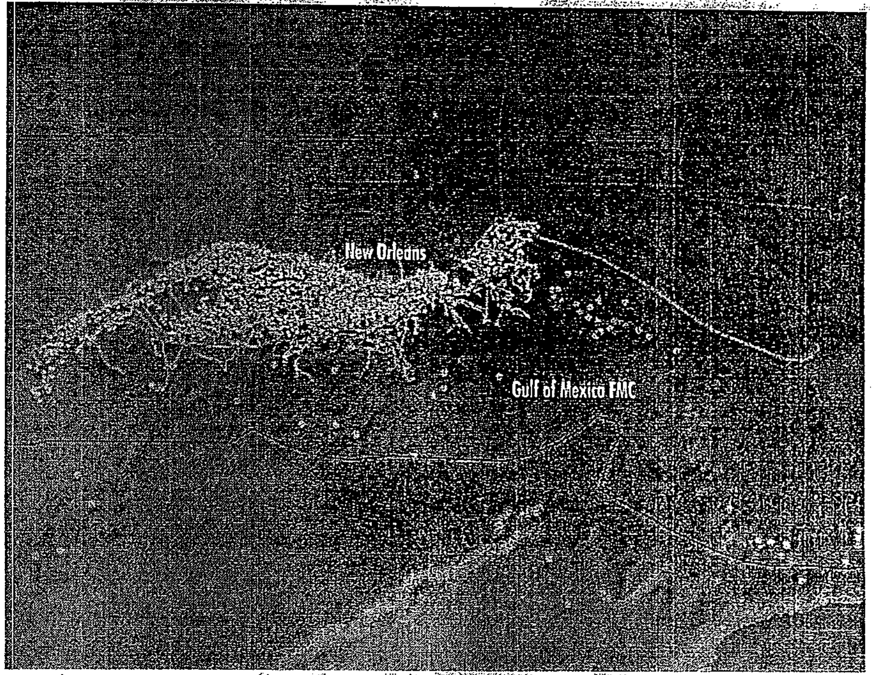
In the Pacific region, smaller-scale oil and gas activities occur off the southern California coast where a new species of deep sea coral — the Christmas tree coral — was recently described (Opresko 2005).

Throughout the waters of the USA, reserves of oil, gas, and minerals exist that may eventually be valuable enough to offset the cost of exploration and extraction. If current trends continue in the global oil and gas markets, other regions may come under pressure as the demand for energy grows and the USA looks to its own waters to supply these needs.

Coral Exploitation and Trade

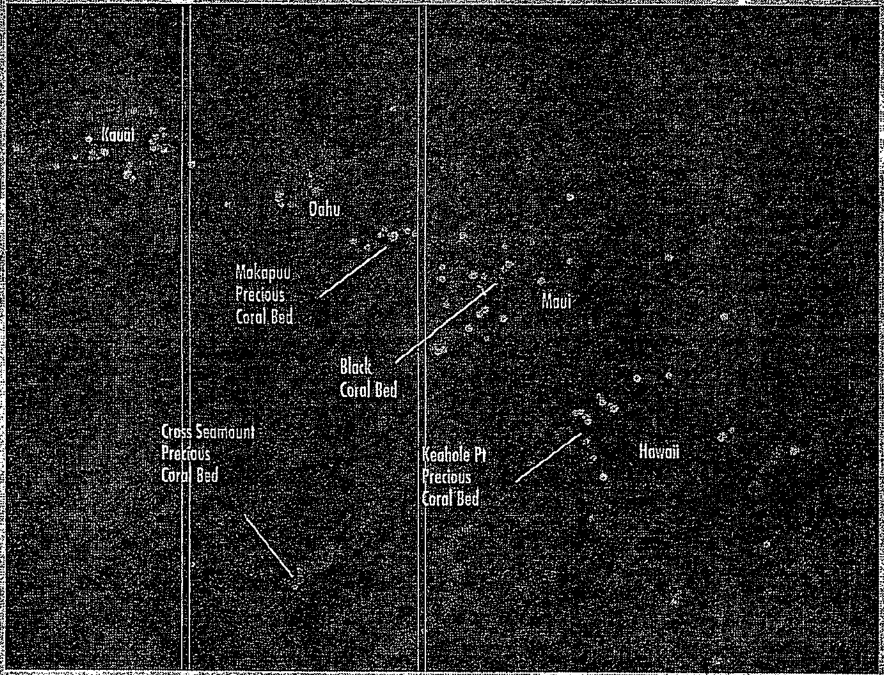
Several species of deep sea corals, including pink, red, bamboo, black, and gold corals, are collected for use in jewelry. These species are often referred to generically as precious corals. In the USA, precious coral collection occurs only in Hawaii (Map 8, Figure 3.4). Precious corals in shallower waters are typically collected by scuba divers, while deeper species are collected by manned submersibles, by remotely operated vehicles (ROVs), or by dragging iron bars and chains across the seafloor to break and ensnare corals. This last practice is highly destructive and unsustainable, and no longer occurs in US waters.

Pink corals were first discovered in Hawaii in 1900, and commercial exploitation began in the 1960s (Grigg 2002). Pink coral beds found on the Emperor Seamount at a depth of 1,312 ft supported a coral fishery for 20 years. During this period, corals were collected by dragging entangling gear along the seafloor, with up to 440,000 lbs of



Map 7: The northern continental shelf in the Gulf of Mexico is densely covered by oil and gas platforms and pipelines. ∗ platforms — pipelines, ● stony corals, ● gorgonian corals. Black line is US EEZ.

corals collected annually by Japanese and Taiwanese fishermen (Grigg 2002). Another pink coral fishery operated in the 1970s off Oahu at a depth of 1,300 ft. Gold and bamboo corals were also discovered in 1970 and collected by manned submersibles and ROVs. Fishing for red, pink, and gold corals has been intermittent since 1999, owing to permit requirements, weather, and high costs. However, in the 1999–2000 season, 2,675 lbs of pink coral, 730 lbs of gold coral, and 134 lbs of red coral were collected in Hawaii (Grigg 2002). Hawaii also supports a fishery for black corals that started in 1958. The main black coral bed is found off Maui at depths of 130 to 250 ft. Between 1981 and 1997, an average of 2,235 lbs of black coral were collected per year. This fishery continues today, primarily conducted by scuba divers (Grigg 2001).



Map 8: Pink, red, bamboo, gold, and black corals have been collected in Hawaii for the jewelry trade. Corals: ● stony corals, ● bl[illegible]orals, ● gorgonian corals, and ● hydrocorals

While there are no large-scale directed coral harvests at present, this may change with market forces. Deep sea corals, including precious corals, are not well studied, and a better assessment of their status is needed to shape collection guidelines. Recently the non-governmental organization SeaWeb petitioned the US Fish and Wildlife Service to request that the United States submit a proposal to include *Corallium* spp. in Appendix II of the Convention of International Trade in Endangered Species of Wild Fauna and Flora (CITES) citing concerns over declining populations (P. Debenham, SeaWeb, pers. comm.).

Invasive Species

Introduced non-native species can invade the habitat of native deep sea corals, greatly reducing populations. Colonies of black corals in the Au'au Channel between the islands of Maui and Lanai are declining because of the invasion of the non-native snowflake coral (*Carijoa riisei*). This species was accidentally introduced to the Hawaiian Islands in

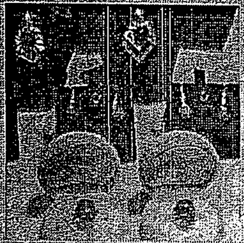


Fig. 3.4: Jewelry made of precious coral.
Photo credit: E. Tsao, MCBI.

"If you wish, you can go to the middle of the ocean and fish on a seamount for any species, and you are accountable to no one—even if that destroys all of the fish and all of the corals and all of the sea life."

Dr. Michael Hirshfield, Oceana's chief scientist and North America vice president for policy

Opposite page: Lophelia pertusa *colony and squat lobster, Gulf of Mexico.*
Photo credit: S. Brook et al., courtesy MMS.

Fig. 3.5: White snowflake coral partially overgrowing an orange-colored black coral colony at a depth of about 311 ft in the Au'au Channel between the islands of Maui and Lanai in Hawaii.
Photo credit: HURL

"Key areas for protection are deep sea coral reefs and seamounts which are being strip-mined by bottom trawl fishing."

Simon Cripps, Director, Global Marine Programme, WWF

1972, probably by boats visiting Pearl Harbor from the Indo-Pacific, and has continued to spread throughout the main islands. It overgrows and smothers black corals in this region, most severely at depths of 260 to 340 ft. In one study, over 60% of all black corals observed were at least partially overgrown (Figure 3.5), and in some areas 90% of black corals had already been killed (Kahng and Grigg 2005).

Increasing Atmospheric CO_2

The oceans are changing both chemically and physically as a result of the carbon dioxide (CO_2) released from the burning of fossil fuels (Kleypas et al. 1999, Feely et al. 2004, Orr et al. 2005). Shallow water and deep sea corals and other marine species that need to build calcium carbonate skeletons will be harmed as oceans become more acidic.

Changing Seawater Chemistry

The influx of CO_2 to the atmosphere and uptake of CO_2 into the world's oceans is causing the sea to become more acidic. Corals and other marine organisms use carbonate ions from the surrounding water to build their skeletons and protective shells. As the oceans become more acidic, the calcification mechanisms of many marine organisms may be impaired, resulting in weaker skeletons (a process similar to osteoporosis in humans), slower growth rates, or both (Buddemeier and Smith 1999, Gattuso et al. 1999, Guinotte et al. 2003, Kleypas et al. 1999). Because deep sea corals also obtain nourishment from capturing plankton, some of which build calcium carbonate shells, these changes in seawater chemistry may also alter the productivity of coral prey (Riebesell 2004, Riebesell et al. 2000, Orr et al. 2005).

Warming Waters

Global temperatures are rising in the deep sea owing to an influx of anthropogenic CO_2 to the atmosphere (Barnett et al. 2005). Rising sea temperatures will probably influence deep sea coral calcification rates, physiology, and biochemistry, even though specific ranges and thresholds are not yet known. Changes in the salinity of the world's oceans as freshwater (ice melt) inputs to high-latitude waters increase may slow down water circulation, reduce upwelling, and alter current patterns (Bryden et al. 2005). These changes will probably alter surface productivity and the delivery of food to the seafloor, which could have a serious impact on the distribution of deep sea corals.

Other Threats

Additional threats to deep sea corals include cable laying, waste dumping and pollution, mineral extraction, and bioprospecting. The effects of these activities on deep sea corals have not been quantitatively studied, but their general impacts on the seafloor are discussed below.

Cable Laying

Installation of telecommunication and electricity cables on the seafloor requires digging a ditch for the cable to be buried in. This procedure and subsequent maintenance repairs will inevitably overturn organisms in the cable's path, resuspend sediment, and disturb the seafloor environment. Cables that are not buried deeply enough, or that are exposed, can be snagged and broken by fishing gears. Broken cables can sway on the seafloor with passing currents, causing continuous disturbance to the local environment (Freiwald et al. 2004).

Waste Disposal and Pollution

Various nations and international bodies have considered the deep sea as a disposal location for waste, including obsolete military ammunition, radioactive waste, sewage sludge, dredge spoil, and CO_2. However, significant waste disposal is not currently underway (Glover and Smith 2003). Leakage of contaminants, toxic substances, and heavy metals can pollute deep sea life. Increases in organic material can also pollute the deep sea and cause localized oxygen depletion that is sometimes fatal to deep sea organisms. CO_2 sequestration, the injection of CO_2 in liquid form to the deep sea, is under experimental study, and may expand in the coming decades to help dispose of greenhouse gases (Glover and Smith 2003). This process acidifies the seawater and alters water pressure at the disposal site, potentially affecting the health and changing the behavior of deep sea species (Glover and Smith 2003).

Mineral Extraction

Extraction of minerals from the deep sea is an expanding industry, targeting several kinds of minerals for multiple purposes. For example, manganese nodules and crusts are extracted for the cobalt, copper, and nickel that they contain, while polymetallic sulfides are taken for their gold and silver components. Methane hydrate extraction from the deep sea is being developed as an energy source. Most of these mineral resources are found in international waters, although further exploration is likely to occur in US waters. Commercial extraction is likely to increase in the next several decades (Glover and Smith 2003); damage to seafloor communities is an expected side effect at any mining site.

Bioprospecting

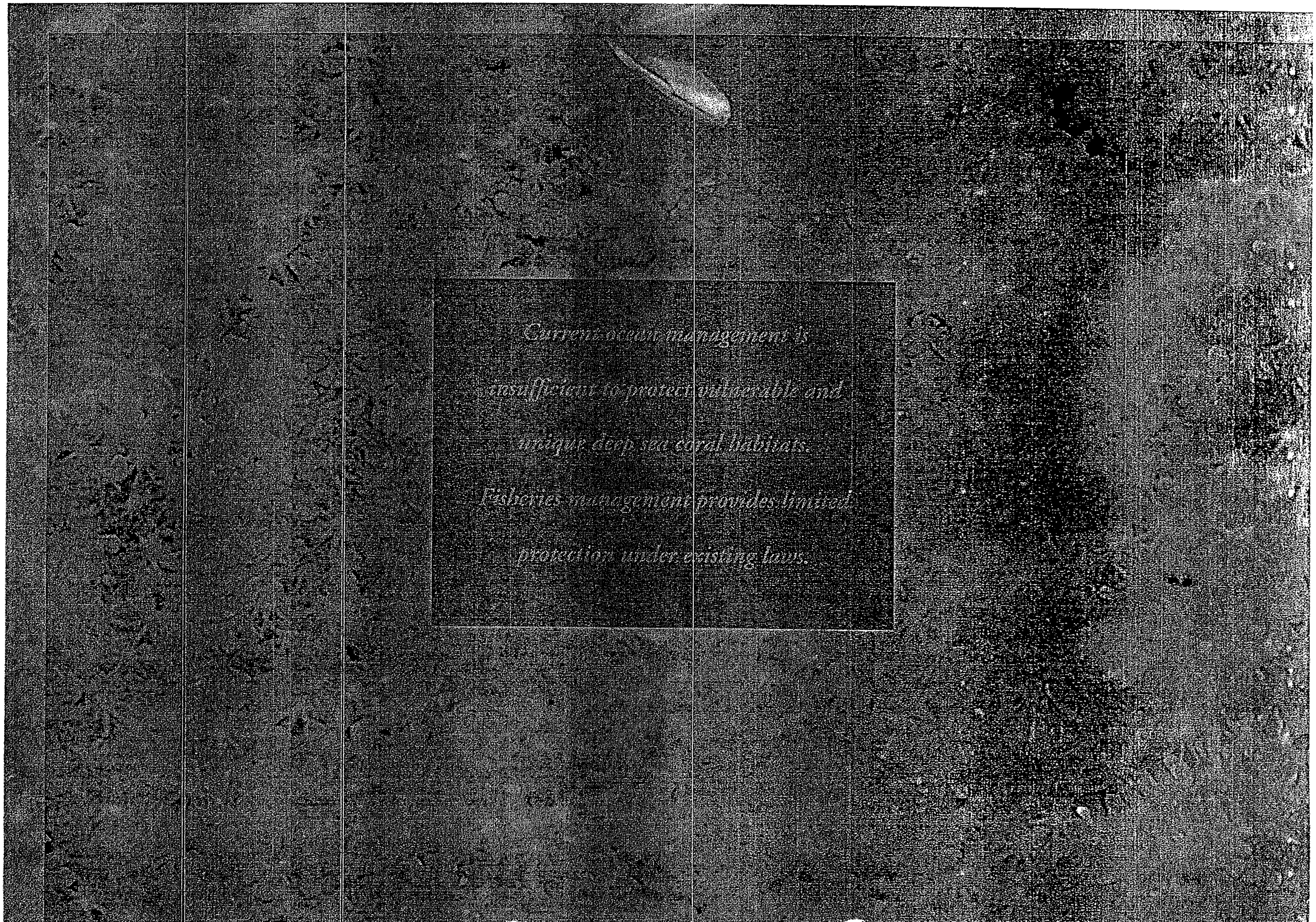
Bioprospecting removes coral colonies from the deep sea for biotechnology and pharmaceutical research and development. Collection of long-lived corals is a concern, but the amounts needed to analyze are usually small (1–2 lbs.). Bioprospecting in US waters currently only takes place in the South Atlantic Bight and Gulf of Mexico. Coral collection in these areas requires a permit and is overseen by the regional fishery management councils. It is unknown how other regions will regulate bioprospecting.

Summary

A number of human activities pose a threat to deep sea corals. Most of these activities are poorly known due to insufficient study and lack of adequate monitoring. Nevertheless, bottom trawling is the greatest current threat posed to deep sea corals because it takes place over extensive areas where corals occur.

Table 3.1: Examples of regional challenges in deep sea coral conservation

Region	Challenges
New England —Mid-Atlantic	Widespread bottom fishing Significant overlaps of trawl fisheries and deep sea corals
South Atlantic	Illegal trawling and poor enforcement of the *Oculina* Bank Continuing development of deep sea fisheries Recreational fishing targeting deep water species Potential LNG pipeline from Bahamas to Florida
Gulf of Mexico	Oil, gas, and LNG development Recreational fishing targeting deep water species
Caribbean	Lack of data
North Pacific	Significant overlaps of trawl fisheries and deep sea corals Other bottom fishing gears
Pacific	Significant overlaps of trawl fisheries and deep sea corals Oil and gas development off California
Western Pacific	Invasive species Precious coral trade
All regions	Baseline lack of scientific understanding Future energy exploration and development Insufficient fishing effort data for coral management Climate change Pollution



Current ocean management is insufficient to protect vulnerable and unique deep sea coral habitats. Fisheries management provides limited protection under existing laws.

Current Management of Deep Sea Corals

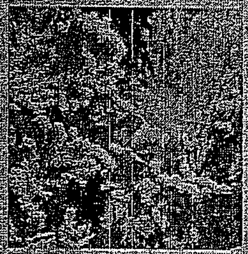
Throughout the world, many nations have recognized the value of deep sea corals and taken steps to provide them with greater protection. The European Union, Norway, Canada, New Zealand, and Australia have all taken steps to prohibit bottom trawling in certain coral areas. These actions range from comprehensive legislation in Norway, which now restricts trawling in known coral areas, to protection of some limited seamount areas in Australia and New Zealand, to fishing closures of relatively small known coral locations in Canada and the European Union. As of 2006, New Zealand is also considering a Benthic Protected Areas proposal that would prohibit bottom trawling and dredging in 31% of its waters, potentially protecting some key coral habitats.[1]

Within the 4.4 million mi^2 of ocean under US jurisdiction there are numerous species of deep sea corals. The US exclusive economic zone (EEZ) covers an area nearly 25% larger than the lands of the USA. The management of the US EEZ falls to multiple government agencies, most of them focused on either extraction or utilization of natural resources. Federal agencies in the USA with the authority to manage deep sea corals include the National Marine Fisheries Service (NMFS), in consultation with 8 regional fishery management councils (FMC); the National Marine Sanctuary Program (NMSP) of the National Ocean Service, both within the Department of Commerce, and the Minerals Management Service (MMS), in the Department of the Interior.

NMFS and the regional fishery management councils can protect corals by adopting regulations that restrict fishing gear types or access to fishing grounds. Until now, national marine sanctuaries have generally been designed to manage designated areas for multiple uses compatible with resource protection, but have in large measure deferred to NMFS and the regional councils in the management of fish and fish habitat within their borders (Chandler and Gillelan 2004). MMS oversees mineral and energy exploration and extraction in federal waters and is responsible for assessing the environmental impacts of these activities on natural resources, including deep sea corals, and limiting or mitigating these impacts. Despite increased research and mapping there is still a lack of dedicated research funding for deep sea corals. Conservation of deep sea corals is hampered by insufficient information, ongoing threats, weak management, insufficient legal mandates for protection, minimal enforcement, and insufficient penalties for resource violations.

NMFS and Regional Fishery Management Councils

Most legal protections for deep sea corals have been adopted in accordance with the Magnuson-Stevens Fishery Conservation and Manage-



Juvenile sharpchin rockfish in a gorgonian red-tree coral community.
Photo credit: V. O'Connell, ADFG

"Everyone must be aware [that] without intact coral reefs, warm and cold water reefs, you will not be able to restore fish stocks fully."

Dr. Klaus Töpfer,
Executive Director,
United Nations Environment Programme (UNEP),
World Oceans Day 2004

Opposite page: A gorgonian coral colony on a seamount off New England.
Photo credit: the Deep Atlantic Stepping Stones Science Party, IFE, URI-IAO, and NOAA

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[1] Deepwater Trawling: Navigating Troubled Waters. Clement and Associates Limited. February 2006: http://www.seafood.co.nz/doclibrary/news/DeepwaterTrawlingSolutions140206.pdf and World's largest EEZ marine conservation measure proposed. New Zealand Government Website. February 14, 2006: http://www.beehive.govt.nz/Vi ument.aspx?DocumentID=24902

Box 4.1: Essential Fish Habitat and Habitat Areas of Particular Concern

The Magnuson-Stevens Fishery Conservation and Management Act (MSA) requires fishery managers to designate essential fish habitat (EFH) in all federal fishery management plans. The MSA defines EFH as "those waters and substrate necessary to fish for spawning, breeding, feeding, or growth to maturity." The purpose of EFH is to identify areas required to support sustainable fisheries and ecosystems and to minimize adverse effects to the extent practicable. Habitat Areas of Particular Concern (HAPC) can also be designated and are defined by their important ecological function, sensitivity to human-induced degradation, degree of stress, and rarity of habitat type (Pautzke 2005). However, the MSA does not require protective regulations for EFH or HAPC, and the HAPC designation only signifies that the HAPC area is a higher priority for conservation.[2]

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[2] NOAA Office of Habitat Conservation: http://www.nmfs.noaa.gov/habitat/habitatprotection/efh/index_b.htm

ment Act (Magnuson-Stevens Act or MSA). Under the MSA, NMFS and the regional fishery management councils (see Map 1 for boundaries) are required to identify and minimize impacts on essential fish habitat (EFH) for each fishery (see Box 4.1 for explanation of EFH). However, the extent to which NMFS and the regional fishery management councils protect deep sea coral areas under the EFH provisions is highly variable. Some councils identify corals as a type of EFH for managed fish species, while others consider deep sea corals themselves to be managed species. Thus, some councils designate EFH specifically for deep sea corals, while others only include deep sea corals as EFH if a federally managed species can be shown to have a strong relationship with the corals. Often deep sea corals are not considered in EFH designations because councils have insufficient data on the location of corals in their regions, or they do not have sufficient information on the nature of the relationship between deep sea corals and managed fish species. Once an area is designated as EFH, the MSA does not require any specific protections to limit damage caused by destructive fishing practices, but NMFS is required to assess the adverse impacts of fishing (or other activities) and adopt protective measures to minimize bycatch of corals or crushing of corals by fishing gear.

National standard 9 of the MSA requires NMFS and the councils to adopt measures that "to the extent practicable, minimize bycatch and to the extent that bycatch cannot be avoided, minimize mortality of such bycatch." This applies to deep sea corals, and is a separate authority from EFH provisions. Below are the highlights of fishery management council actions to protect deep sea corals.

New England and Mid-Atlantic Regions

In the New England and Mid-Atlantic regions, the councils recently declared EFH for groundfish, and amended the fishery management plan to ban monkfish fishing using bottom trawls and bottom gillnets in Oceanographer and Lydonia Canyons on the southern edge of Georges Bank (Map 4). This affords some protection for deep sea corals, however, this ban does not cover bottom gears that target other fish. The monkfish fishery management plan amendment also limits rollers on bottom trawls in the monkfish fishery to a six-inch diameter in the southern half of the region. A pending proposal seeks to protect additional submarine canyons. In the Mid-Atlantic region Hudson Canyon contains deep sea corals, and is included in a habitat area of particular concern (HAPC) for tilefish, but there are no regulations to protect corals.

South Atlantic Region

In the US South Atlantic region, deep sea corals are considered managed species, and their designated EFH is defined as "hard substrate in subtidal to outer shelf depths" throughout the region. As early as 1984, the South Atlantic Fishery Management Council took steps to protect deep sea corals from trawling by establishing the *Oculina* Bank HAPC (Koenig et al. 2005). This 397 mi² HAPC off Florida now prohibits bottom fishing, but enforcement remains weak despite implementation of vessel monitoring in 2002.[3] Trawlers have fished illegally for rock shrimp in the *Oculina* Bank HAPC as recently as 2004,[4] and recreational fishermen frequent the still intact areas of the *Oculina* Bank (S. Brooke, U. Oregon, pers. comm.). Currently under development, the council's draft Comprehensive Fishery Ecosystem Plan Amendment would designate additional HAPCs for known areas of deep sea corals, including the *Lophelia* banks off Cape Lookout, Cape Fear, Stetson Reef, the Savannah and Southwest Florida lithoherms, Miami Terrace, and Pourtales Terrace.

Gulf of Mexico Region

In the Gulf of Mexico, corals are considered a managed species. EFH and HAPCs have been designated for coral areas at shallower depths (< 660 ft.) under the 2005 EFH amendment. Areas designated as HAPCs include Pulley Ridge, McGrail, Stetson, and East and West Flower Garden Banks, in addition to several small hard-bottom areas scattered on the northern shelf of the Gulf, and large hard-bottom areas off the west coast of Florida. Regulations to ban anchoring and the use of bottom trawls, bottom longlines, buoy gear, and traps and pots are being considered for some of the reef HAPCs. These regulations do not cover the known deep sea *Lophelia* reefs in the region. One additional regulation requires a weak link in the tickler chain of bottom trawls on all habitats throughout the Gulf of Mexico EEZ. The weak link is designed to break if the trawl net becomes hung up on uneven seafloor or snags on corals.

Caribbean Region

In this region corals are also a managed species. No active bottom trawl fisheries currently occur in this region. Deep sea corals, such as *Lophelia pertusa* and other stony corals, are known from this region, but no regulations are in place for their protection.

North Pacific Region

In Alaska, deep sea coral areas are considered essential fish habitat for groundfish (Witherell and Coon 2001). Deep sea coral and sponge areas have been designated as HAPCs for groundfish, and fishing is regulated by gear and location in order to protect deep sea corals. Around the Aleutian Islands, the 2005 EFH regulations prohibit bottom trawling in a 366,961 mi² area to address concerns about damage to seafloor habitat, particularly deep sea corals (Box 4.2, Map 9, next page). Additional protections for deep sea corals are in place in the HAPC at Bowers Ridge, where mobile bottom gear is prohibited, and in 6 small Coral Garden

Box 4.2: Freezing the Footprint of Bottom Trawling

In 2005, the North Pacific Fishery Management Council unanimously adopted an EFH amendment to close a 366,961 mi² area to bottom trawling. A similar strategy was also unanimously adopted by the Pacific Fishery Management Council for waters off California, Oregon, and Washington. In both of these cases the closures were put in place to prevent trawling from expanding into waters not yet fished. This has the effect of freezing the footprint of bottom trawling. It also reverses the burden of proof, requiring research to ensure that bottom trawling in an untrawled area is compatible with the habitat found in the area before fishing can be allowed. While preventing the expansion of bottom trawling is an important first step towards protecting deep sea corals, this measure does not protect corals from other fishing gears that can also snag and crush vulnerable coral colonies. Additionally most of the area closed to trawling is far too deep to be fished with current technology.

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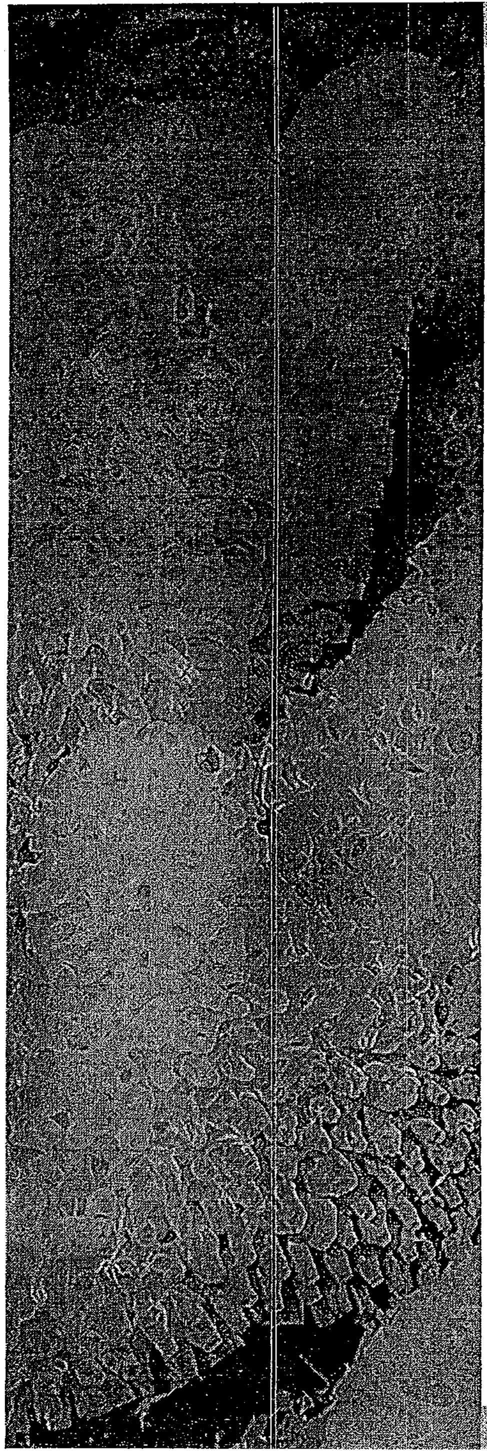
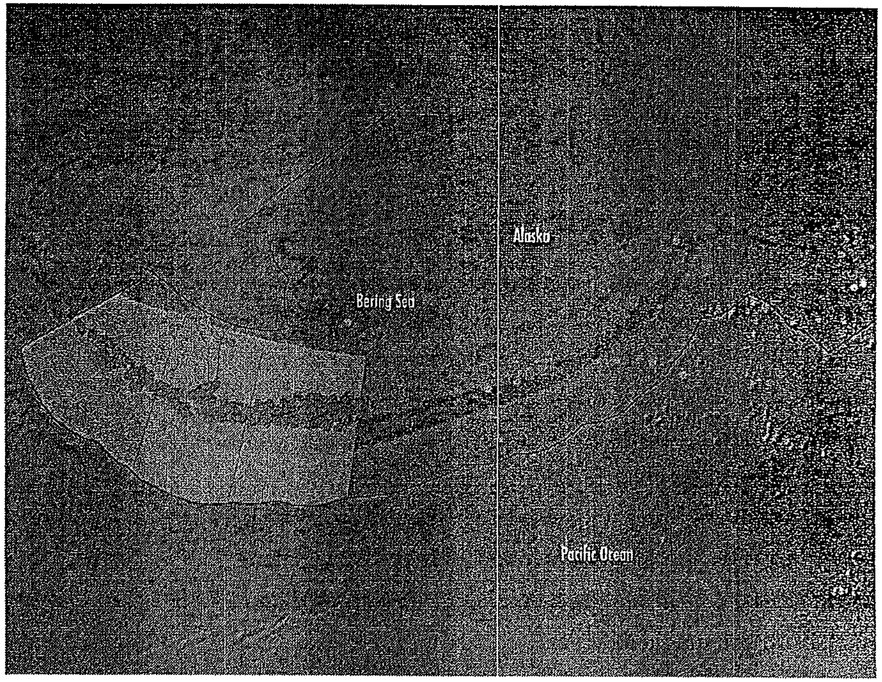
[3] Amendment 5 of the Shrimp Fishery Management Plan. http://www.safmc.net/Library/Shrimp/tabid/413/Default.aspx

[4] Commercial and recreational fishermen fined for Oculina Bank violations. NOAA Fisheries news release, December 8, 2004. http://www.nmfs.noaa.gov/ole/news/news_SED_120804.htm



Marine Reserves (a total of 146 mi^2) closed to all bottom gears. Also, all fishing vessels in the Aleutians with bottom tending gear are required to carry a vessel monitoring system (VMS) device, which allows for better tracking of fishing effort and provides for better monitoring and enforcement of the closed areas.

In the Gulf of Alaska, a total of 20% of the seafloor is closed to bottom gear. The 2005 EFH amendment prohibits bottom trawling for groundfish in 10 areas thought to contain high-relief bottom and coral communities. Bottom gear is prohibited in all of the 16 named seamounts designated as HAPCs. Three areas of red-tree coral off southeast Alaska are also identified as HAPCs. The Southeast Alaska Trawl Closure prohibits bottom trawling, and the small (3.3 mi^2) Sitka Pinnacle Marine Reserve in southeast Alaska prohibits all bottom fishing and anchoring.



Map 9: Recent essential fish habitat designations by the North Pacific Fishery Management Council, including closures to bottom trawling. At this scale Aleutian Island Habitat Conservation Areas are misleading; significant coral areas are subject to bottom trawling in this region. See Map 6 for detailed view. **▨ Aleutian Island Coral Gardens Marine Reserve, ▨ Aleutian Island Habitat Conservation Area, ▨ Alaska Seamounts Marine Preserve, ▨ Bowers Ridge Habitat Conservation Zone, ▨ Gulf of Alaska Habitat Conservation Area. Corals: ● black corals, ● gorgonian corals, and ● hydrocorals. Black line is US EEZ.**

Pacific Region

In 2005, the Pacific Fishery Management Council designated EFH for groundfish species that will restrict bottom trawling in a number of regions including canyons, banks, and seamounts, including Thompson Seamount and Heceta and Daisy Banks. The EFH designation, partially approved by NMFS in 2006, will also place additional restrictions on bottom contact fishing gears in a number of areas, including Davidson Seamount and Cordell Bank. The action also freezes the current bottom trawl fishing footprint in waters between the depths of 4,200 and 11,500 ft (Map 10).

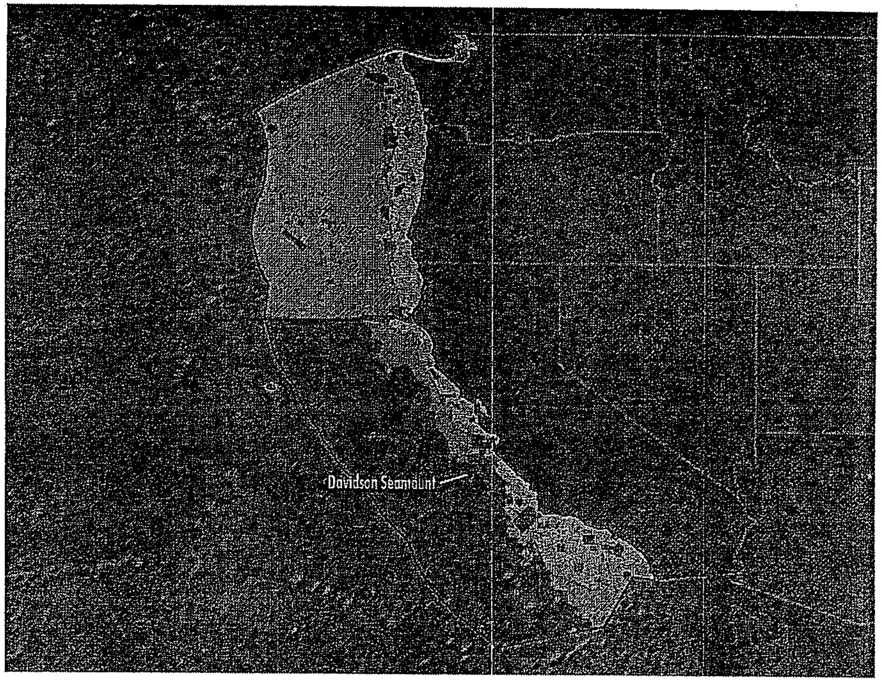
In addition to this management action, which is similar to that instituted by the North Pacific FMC, the Pacific FMC uses time and area closures to restrict fishing for groundfish species and allow them to recover from overfishing. In the Rockfish Conservation Areas, bottom trawling is prohibited; however, the boundaries vary by season and fishery, and are modified based on bycatch data reported by log books and fishery observers. In the 2 Cowcod Conservation Areas off southern California, trawling is prohibited year round. These closures potentially prevent trawl damage to corals, but they could also shift the intensity of trawling effort to coral areas that have not been as intensively fished. The potential of area closures to backfire provides a strong argument for freezing the footprint of bottom trawling as part of a comprehensive EFH plan.

Western Pacific Region

In 1986, bottom trawling and bottom gillnetting were prohibited by the Western Pacific FMC in all US-managed western Pacific waters to protect all types of coral (shallow and deep). Coral fisheries in the region are managed under a Precious Coral Management Plan that restricts non-selective gears such as tangle nets. There is no active fishing for precious corals in federal waters. Fishing for black coral occurs in the state waters of Hawaii. Should precious corals become more valuable in the future, a fishery may resume in federal waters.

National Marine Sanctuary Program

The National Marine Sanctuary Program manages 13 multiple-use sanctuaries (covering a total area less than 0.5% of the US EEZ) and the Northwestern Hawaiian Islands Coral Reef Ecosystem Reserve, which is being considered for sanctuary status. The Northwestern Hawaiian Islands Reserve likely has done the



Map 10: Recent essential fish habitat designations by the Pacific Fishery Management Council
▨ Essential Fish Habitat (< 3,500 m), closed to bottom trawl gear; ■ Closed to all bottom gear; ▨ Open to bottom gear
Black line is US EEZ.

The base of a living bamboo coral, *Isidella* sp., from Warwick Seamount. Notice the long tentacles, referred to as "hula skirts," because scientists don't know exactly what they are. They may be defensive "sweeper" tentacles.
Photo credit: Gulf of Alaska 2004 research team, NOAA OE

> "At present, scientists studying deep-sea corals are in an unfortunate race with commercial fishermen, who are trawling these corals into oblivion."
>
> *Dr Martin Willison, Dalhousie University, Halifax*

*Opposite page: The white ruffle sponge (*Ferrea *sp.) blanketed large areas, at or near the crests, of the Davidson Seamount (shown here at 4,593 feet depth). Several species were often found living on or within the sponge fields, including crabs, basket stars, sea stars, and brittle stars.*
Photo credit: NOAA/MBARI

most to protect corals, as a 2000 Executive Order prohibited taking of deep sea precious corals throughout the area.

Unlike the Northwestern Hawaiian Islands Reserve, several other sanctuaries with known deep sea corals do not protect corals from fishing. A number of sanctuaries contain deep sea corals, but also allow bottom trawling. When scientists found a *L. pertusa* colony in the Olympic Coast Sanctuary, they also observed trawl tracks nearby (Hyland et al. 2005). The Monterey Bay, Cordell Bank and Gulf of the Farallones National Marine Sanctuaries all encompass deep sea coral habitats; portions of these sanctuaries fall within EFH designations. These EFH designations carry varying fishing restrictions, but this protection is implemented under the MSA rather than the Sanctuaries Act. As previously noted, sanctuaries have mostly left fishery regulation within their boundaries to NMFS and the regional fishery management councils. This is not required, but it is current practice. Two exceptions to this are no-fishing marine reserves within the Florida Keys National Marine Sanctuary and the Channel Islands National Marine Sanctuary. None of these reserves extend into significant deep sea coral habitats. For the most part, sanctuaries are in shallower coastal waters, and because they do not use their legal authority to regulate incompatible fishing practices, sanctuaries are not currently an effective mechanism for protecting deep sea corals.

Minerals Management Service

The Minerals Management Service (MMS), within the US Department of the Interior, manages the nation's energy and mineral resources in federal offshore waters of the US EEZ. Currently these activities primarily occur in 3 regions of the USA— the Gulf of Mexico, southern California, and Alaska—but may expand under current pressure to develop more oil and gas reserves and explore ways to harness energy from wind and waves. MMS is responsible for providing scientific and technical information to support decisions on the offshore energy and hard minerals programs; the extraction of which has the potential to damage the seafloor. Following the sale of lease blocks, MMS monitors resource development to determine the extent and duration of environmental effects and to identify potential mitigation measures. MMS is also required to collect and make available to the public any information needed to analyze, discuss, and guide future decisions on exploration, development, production, and proposed lease sales.

A number of MMS research programs are underway to study deep sea communities in the Gulf of Mexico, the primary region of oil and gas development in the USA. One mechanism used by MMS to mitigate impacts is to send a Notice to Lessees (NTL), that requires a minimum separation distance between the biological feature such as a deep sea coral reef and proposed seafloor disturbances. This has been used to protect deepwater chemosynthetic communities (NTL 88-11) in the Gulf of Mexico from oil explorations activities. MMS is also considering an NTL to protect *Lophelia* reefs in the Gulf (T. Ahlfeld, MMS, pers. comm.). Deep sea coral research programs are especially important because the expansion of oil and gas into deep water suggests the potential for greater conflicts with deep sea corals in the future (see Chapter 3 and Map 7).

Undetermined Habitat Value of Corals Limits Protection

Although EFH is currently the main mechanism used to provide protection for deep sea corals, it has significant limitations. In many coral areas, a dependence on coral habitats by commercial fish species or their prey has not yet been scientifically documented; therefore, these areas may not qualify as essential fish habitat. Bob Stone, Jon Heifetz and colleagues at NMFS have documented this dependence in the waters off Alaska (Heifetz 2002, Krieger and Wing 2002, Stone 2006). Grant Gilmore, Christopher Koenig, John Reed and others have shown similar associations between fish and *Oculina* coral off Florida (Gilmore and Jones 1992, Koenig et al. 2005, Reed et al. 2005a). However, other studies have been less conclusive.

Many fish and fisheries co-occur with deep sea coral habitats, but the precise nature of the association is unclear. The standard of scientific proof required by scientists and managers to designate deep sea coral habitats as EFH is unclear and appears to vary by region. In a few cases, fish appear to prefer three-dimensional structures, but do not differentiate between corals and other living or nonliving structures (Auster 2005, Tissot et al. 2006). Furthermore, fish of different sizes, ages and species behave differently, and may respond to an ROV by swimming away or hiding, making them difficult to observe. These factors complicate scientists' observations of how fishes use coral habitats and whether they depend on them. What scientists do know is that changes in habitat resulting from coral removal likely have influenced the survival and behavior of fishes (Sainsbury et al. 1997). Thus, current research on fish-habitat associations in these altered ecosystems may not accurately reflect the nature of these associations in an intact deep sea coral community.

In the Gulf of Maine, the density of fish does not seem to be affected by the presence of corals. Thus far, the only fish in the Gulf of Maine known to demonstrate a preference for coral areas over other structures for shelter and feeding grounds is the oreo, *Neocyttus helgae* (Auster 2005, Auster et al. 2005). However, since it is almost certain that fishing has altered deep sea corals in this region, the correlation between fish and corals may also have been changed (Watling and Auster 2005).

Within and surrounding the Christmas tree coral colonies off southern California (Figure 4.1), scientists observed large invertebrates and fishes, but the abundance of

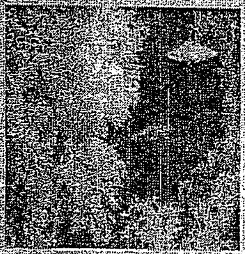
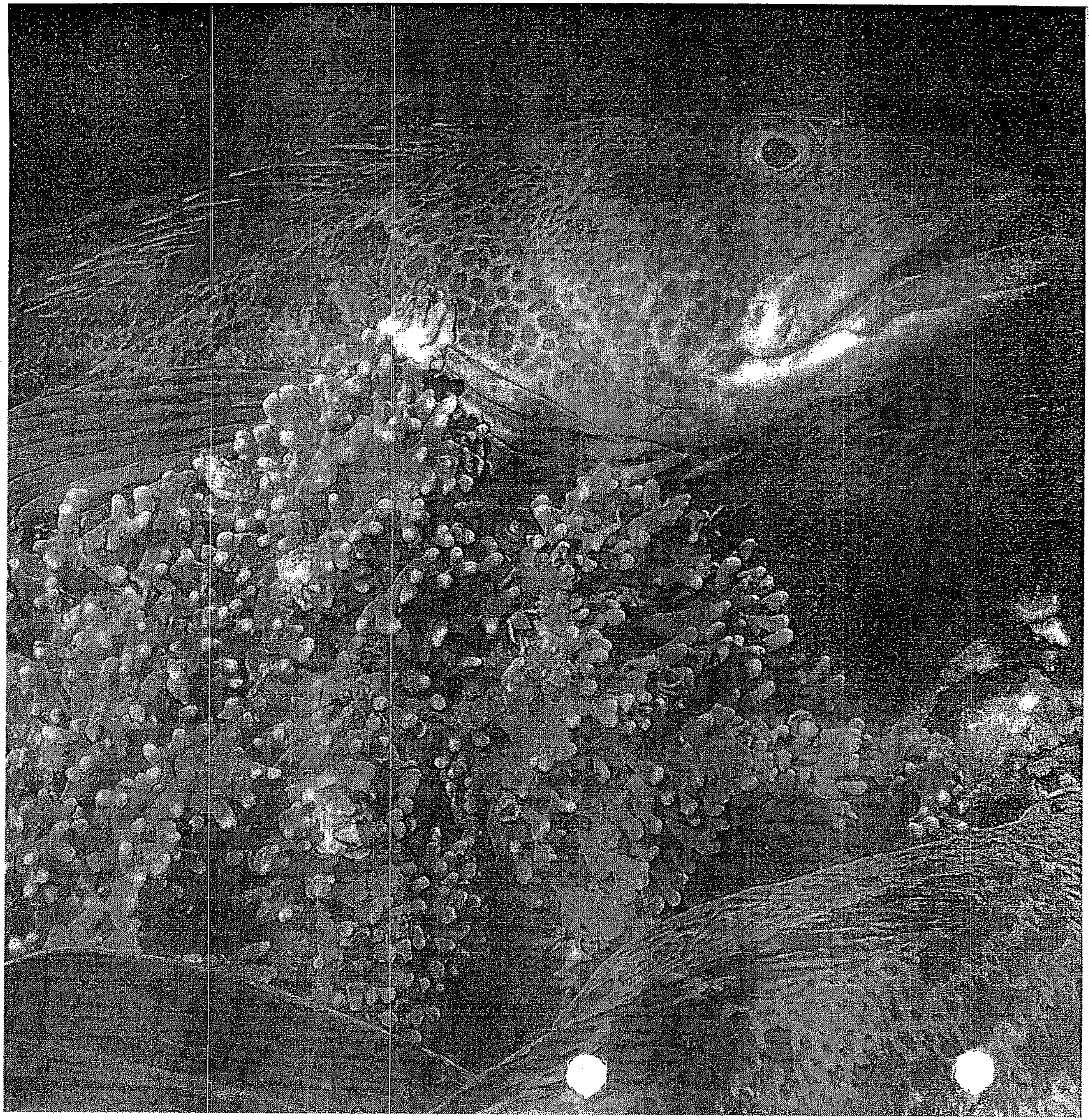


Fig. 4.1 Rockfish intermingled with Christmas tree corals near Santa Cruz Island, CA.
Photo credit: L. Snook

"A vast expanse of the planet's unexplored, and potentially most promising, ocean beyond the legal boundaries of nations is being exposed to the reckless plunder of marauding deep sea fishing trawlers."

Jean-Michel Cousteau,
Founder and President,
Ocean Futures Society

Opposite page: A white gorgonian coral tree (Paragorgia sp.) with a large brisingid star on a seamount off New England.
Photo credit: the Deep Atlantic Stepping Stones Science Party, IFE, URI-IAO, and NOAA



these animals was low (Tissot et al. 2006). Only 8 of the 106 observed fish species showed higher concentrations inside the coral area as opposed to outside (Tissot et al. 2006). Possible explanations for the lack of a fish-coral association include the relatively small size (< 20 in.), low number or sparse density of observed corals, all factors which may alter the abundance of associated animals.

In and around black coral beds in the Main Hawaiian Islands (164–240 ft depths), researchers observed 40 fish taxa, suggesting that the tree-shaped corals (approximately 30 in high) may be an important fish habitat. One fish species (*Oxycirrhites typus*) was found exclusively in the coral beds, and 4 others used the corals as shelter to evade human divers (Boland and Parrish 2005). Some fish species use the corals more at night than during the day (Boland and Parrish 2005).

The necessity to prove functional relationships between fish and deep sea corals prior to EFH designation is squarely at odds with official assertions that require managers to manage in a precautionary manner and on an ecosystem basis. Until this issue is clarified, it will present a barrier to EFH designation and protective regulation in some council regions, and a hindrance to the conservation of deep sea corals under US jurisdiction.

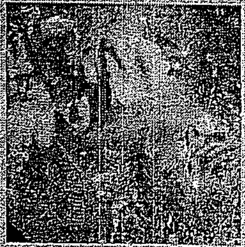
Current Protection for Deep Sea Coral is Inadequate

Deep sea coral protection must not be solely predicated on their value to commercial fisheries, but current ocean management, policies and practices limit comprehensive protection for deep sea coral habitats and ecosystems. Steps have been taken to protect deep sea corals under the existing authorities of the MSA, but most management actions are neither comprehensive nor focused on deep sea corals. In most cases, EFH designations and closures are gear or species specific. For example, although trawling and gillnetting for monkfish are prohibited in 2 submarine canyons in New England, other bottom-tending gears and bottom trawls not targeting monkfish can still be used to catch other species in those same canyons, potentially damaging deep sea corals. Seasonal rockfish closures along the US West Coast are only designed to reduce bycatch of certain depleted fishes, so while the closures temporarily restrict trawling, they cannot be expected to protect deep sea corals because trawling occurs during other seasons.

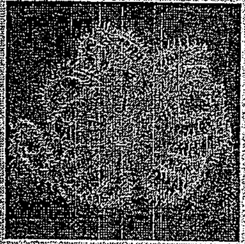
Bottom trawling must be properly managed in order to deal with the immediate and widespread threat to deep sea corals. However, even where areas are closed to bottom trawling with the clear purpose of protecting corals, the protection is limited if other fishing gears continue to be used. Many of the complete gear closures designated for deep sea corals are small, piecemeal, and opportunistic. Freezing the trawl footprint may close vast areas, but these areas may not contain the most important coral habitats. In addition, experience shows that enforcement of closures is generally inadequate. Expansion of vessel monitoring systems like those currently used in the North Pacific region would likely strengthen enforcement in other regions.

Summary

Current ocean management is insufficient to protect vulnerable and unique deep sea coral habitats. Fisheries management provides limited protection under existing laws, primarily through the designation of essential fish habitat (EFH) for federally managed species. Deep sea corals can be protected if the designation of EFH includes restrictions on fishing, but such provisions are not a requirement. The National Marine Sanctuary Program, the main program charged with protecting special ocean ecosystems, has the legal ability to regulate seafloor damaging fishing practices, but rarely uses it. Minerals Management Service can mitigate impacts of energy production by establishing buffer zones around deep sea coral communities, but has yet to do so.

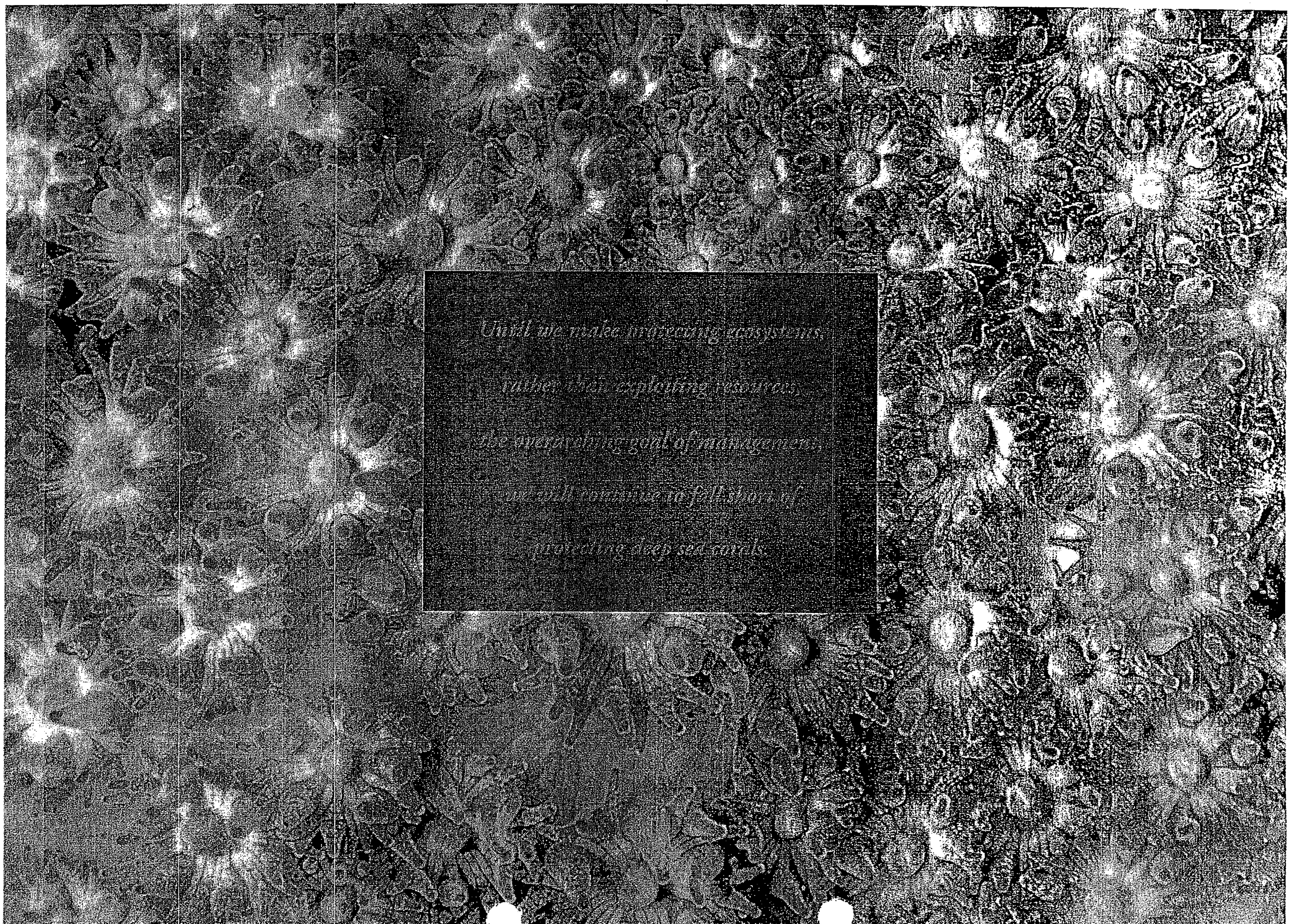


Rockfish in deep sea sponge and coral community
Photo credit: R. Stone, NMFS



A large brisingid sea star from Manning Seamount
Photo credit: Jon Moore

Opposite page: Lingcod in hydrocoral bed in SE Alaska
Photo credit: V. O'Connell, ADFG



Until we make protecting ecosystems,

rather than exploiting resources,

the overarching goal of management,

we will continue to fall short of

protecting deep sea corals.

Status and Recommendations for Deep Sea Coral Protection

Deep sea corals are widespread in US waters, but threats to these organisms are also widespread, especially the dominant threat of bottom trawl fishing. Current management has limited ability to protect deep sea corals because it focuses on commercially important fish rather than on protecting habitats. Where deep sea corals are protected, regulations are seldom comprehensive, or if comprehensive, do not extend over large areas. Given that deep sea corals are extremely long-lived, are important habitats for other species, and are valuable in their own right, the protection of deep sea corals is an under-appreciated but key component of sustainable fisheries and healthy ecosystems.

In this chapter we summarize the status of deep sea corals, taking into account the spatial proximity of corals and threats and the quality of information available. We conclude with recommendations to improve deep sea coral management in the USA.

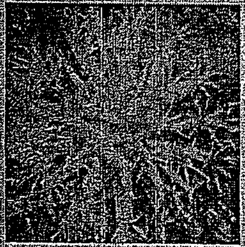
Current Status of Deep Sea Corals

Ideally, a status assessment would be based on a comprehensive examination of coral distributions, the health of coral populations, and the activities threatening them. The information that has been gathered in recent years by a variety of government, academic, and conservation organizations provides us with the first opportunity to examine the distribution of and threats to deep sea corals. However, significant data gaps still exist.

It is no coincidence that the deep sea coral area that is thought to be the most damaged and threatened, the *Oculina* Bank off Florida, is at relatively shallow depths—roughly 150 to 300 ft—and is relatively close to shore. Its proximity to humans makes it both vulnerable to fishing activities and relatively easy to study. It is one of the few places about which we have extensive information, yet the prognosis for corals in this area is relatively bleak. Within the Experimental *Oculina* Research Reserve over 90% has been destroyed by fishing (Box 5.1), despite awareness for over 20 years of this area and the impact of bottom trawl fishing.

In almost every other location in the USA, specific assessments are difficult to make. The detailed studies needed to document impacts are few and far between and are often focused on narrow transects (< 25 ft in width) across banks or ridges. Although the level of our understanding at present does not allow us to examine many areas or species in detail, general trends regarding the impact of human activities on deep sea corals can be identified.

It is clear from videotape footage and photographs that fishing gears that contact the seafloor are currently the greatest immediate threat to corals and that focus on limiting bottom trawling is the correct first step. Damage to corals from fishing has been shown to occur in multiple locations throughout the USA—from the Aleutian Islands to the banks of Florida. We know that bottom trawl-

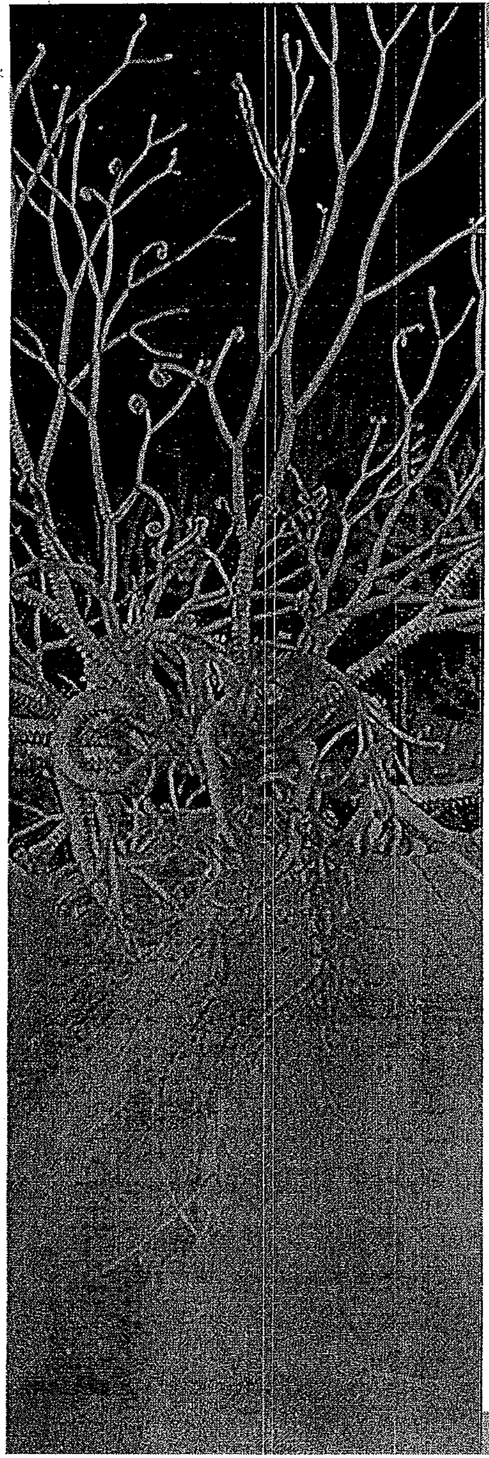


Mushroom soft coral (*Anthomastus* sp.) on Davidson Seamount at 4,823 ft depth.
Photo credit: NOAA/MBARI

"Towing a heavy trawl net through a cold-water coral reef is a bit like driving a bulldozer through a nature reserve. The only practical way of protecting these reefs is therefore to find out where they are and then prevent boats from trawling over them. We know that most fishing boat skippers would rather steer clear of coral reefs, as the reefs can damage their gear, so producing accurate maps will actually help them to avoid these areas."

David Griffith, General Secretary of ICES (International Council for the Exploration of the Sea)

Opposite page: Live coral polyps in colonial coral.
Photo credit: Collection of Dr. James P. McVey, NOAA Sea Grant Program



ing and other fishing activities destroy corals and that these activities are widespread along the continental shelves of the USA. Only in the island regions of the Caribbean and Hawaii, therefore areas without continental shelves, is bottom trawling not an immediate threat to deep sea corals. Fishing activity and deep sea coral distributions substantially overlap in many regions, especially in the waters off Alaska, the US West Coast, and New England. There are also significant data gaps regarding the location and intensity of fishing. Without more detailed recording of fishing effort, bycatch, and landings, it is very difficult to determine the exact nature of the threat.

With the current trend towards fishing in deeper waters as coastal fisheries are depleted, there is a need to stem the expansion of fishing into the deep sea. The first step, to freeze the footprint of trawling, has been taken by the North Pacific and Pacific fishery management councils. The next step is to limit fishery impacts in other regions, such as the still intact *Lophelia* reefs of the southeastern USA. Steps are underway by the South Atlantic FMC to protect some of these known habitats.

As we gain greater knowledge of coral locations, protecting coral habitats within currently fished grounds will be a challenge for managers. Future protections for deep sea corals will need to be comprehensive, protecting them not only from bottom trawls, but from entanglement in bottom longlines or gillnets and from being crushed under crab or fish pots. Despite regulations that freeze the footprint of bottom trawling in the Pacific Ocean, the amount of known deep sea coral habitat that is entirely off limits to all types of bottom fishing is relatively small.

Finally, fishing is not the only human activity affecting the deep sea. Other activities undoubtedly have impacts; however, many of these are restricted to much smaller areas, are limited in scale, or, like climate change and increasing ocean acidification, are the result of widespread activities that are global in scale and hence exceedingly difficult to manage. One thing is clear—management can address the impacts of fishing, the most well recognized and certain threat to deep sea corals.

Recommendations to Improve Deep Sea Coral Conservation

It is clear that we should protect deep sea corals from further destruction. In this report we have identified key threats and obstacles affecting the conservation and management of deep sea corals, including: widespread bottom fishing in areas with deep sea corals; an institutionally constrained management focus on commercially important species (rather than habitat protection); a lack of data on deep sea coral distribution, ecology, and biology; gaps in monitoring and analysis of current and potential threats, especially fishing; insufficient use of closed area management (marine protected areas); and weak enforcement of regulations. To remedy

Box 5.1: Last Corals Standing — Protection of the *Oculina* Banks

The *Oculina varicosa* banks off central Florida are one of the relatively well-studied coral ecosystems in US waters. These reefs were first documented in 1963 based on commercial fishermen's reports, and scientists have surveyed the area multiple times since the 1970s. The area was listed as a candidate site by the National Marine Sanctuary Program in 1983, but never designated. However in the following year *Oculina* Bank Habitat Area of Particular Concern (HAPC) was created by the SAFMC, and closed to bottom trawl and dredge fishing gear. In 1994, the *Oculina* Bank HAPC was closed to all bottom fishing gear. In 2000, the HAPC boundaries were expanded to 397 mi² in order to protect a large portion of the remaining *Oculina* reefs. In 2003 the closure and its regulations were extended indefinitely.

Despite the attention of management for nearly a quarter century, protections have proven to be ineffective. A survey in 2001 found 90% of the areas designated in 1984 contained only coral rubble, and only 0.3 mi² (or 9.5 baseball fields) of intact deep sea coral reefs remain. Nearly all the corals had been demolished by trawl gears. Furthermore, *Oculina* reefs outside the HAPC are being demolished; a mound off Cape Canaveral that was 100% covered by live *O. varicosa* colonies in 1976 retained only a few scattered colonies in 2001, a year after it became part of the *Oculina* HAPC.

Bottom trawling for rock shrimp is the primary threat to the *Oculina* reefs, and illegal trawling has occurred in the *Oculina* HAPC as recently as 2004. Abandoned longlines and trawl nets that entangle corals, trawl tracks on the seafloor, and sightings of trawlers in the protected area are evidence that fishing activities are destroying the fragile *Oculina* reefs. Obviously enforcement has been poor.

Through the last 3 decades of research on the *Oculina* reefs, scientists have demonstrated that the reefs are breeding and feeding grounds for groupers and snappers; measured the reefs' slow growth rate (0.6 in per year); discovered reefs that are 1,500 years old; and identified many locations of *Oculina* occurrences. Our understanding of *O. varicosa* far exceeds that of other deep sea coral species. However, none of this has prevented the devastation of the *Oculina* reefs. Immediate action to make deep sea coral protection a national priority, coupled with strict enforcement, heavy penalties, and further research, monitoring, outreach and education, is the remaining corals' only hope for survival.

Source: [illegible] et al. 2005a, Koenig et al. 2005

Table 5.1: Current deep sea coral management actions and their limitations.

Current Management Action	Limitations	Remedy
Designating selected coral areas as EFH for commercial fish species (e.g., Oceanographer Canyon in the New England region)	EFH designation is subject to interpretation by councils. Definitions vary by region.	A national mandate to define and protect deep sea corals comprehensively through ecosystem-based management (EBM).
	EFH is not required to have conservation regulations.	A national mandate to define and protect deep sea corals comprehensively through EBM.
	Where fish dependence on corals has not been established, deep sea corals are not protected.	Research and mapping, precautionary approach to management that will protect all deep sea coral concentrations.
Freezing the footprint of bottom trawling (e.g., around the Aleutian Islands in the North Pacific region)	Areas closed to bottom trawling may encompass fewer deep sea corals or corals that are not currently threatened.	Increase research efforts to map known coral concentrations in areas open to trawling.
Setting up protected areas specifically for deep sea corals (e.g., *Oculina* Bank in the South Atlantic region)	Enforcement and monitoring of closure in offshore areas is challenging.	Increase the use of vessel monitoring systems (VMS) and onboard observers.
Prohibiting bottom fishing to restore depleted fish populations with incidental effect of protecting deep sea corals (e.g., Rockfish Conservation Area in the Pacific region)	Could push fishing effort from low coral abundance areas to high coral abundance areas.	A national mandate to define and protect deep sea corals comprehensively through EBM.
National Marine Sanctuary Program (e.g., Olympic Coast National Marine Sanctuary in the Pacific region)	The Sanctuaries Act allows multiple uses to occur in a sanctuary, many of which are incompatible with coral conservation.	A national mandate to define and protect deep sea corals comprehensively through EBM. Better use of existing authority to regulate bottom contact gear damage to corals.

"We are protecting less than one percent of our oceans. If we are to protect this priceless natural heritage for future generations, we must learn to value marine life less as commodities and more as part of the natural world on which we too depend."

Dr Sylvia Earle,
Executive Director of Conservation International's Global Marine Division and Explorer-in-Residence at the National Geographic Society

Opposite page: Basket star (Gorgonocephalus eucnemis) *perched atop a yellow sponge* (Staurocalyptus *sp.) on the Davidson Seamount (4,469 ft depth).*
Photo credit: NOAA/MBARI

Box 5.2: Bottom Trawl and Deep Sea Coral Habitat Act of 2005

As proposed, the Bottom Trawl and Deep Sea Coral Habitat Act would provide significant protection for fragile and ecologically significant ocean habitats by changing the way deep sea coral habitats are managed. Specifically, the Act would allow bottom trawls to be used in almost all areas where the gear has been used in the past 7 years for which records are available, while establishing a national mandate for deep sea coral protection. The Act contains the following provisions:

- Temporarily bans the use of bottom trawl gear in unstudied areas (any area in which records indicate that mobile bottom tending fishing gears have not been used) until research determines whether deep sea coral ecosystems are present. If no deep sea coral ecosystems are found in an area, that area could be opened for the use of bottom trawls and designated a Bottom Trawl Zone.
- Permanently bans bottom trawling in Coral Habitat Conservation Zones where deep sea coral ecosystems are known to exist.
- Requires monitoring of coral bycatch. High bycatch levels are an indicator of the presence of deep sea coral ecosystems. Areas that produce high bycatch levels would be studied for potential designation as Coral Habitat Conservation Zones under the authority of the Secretary of Commerce.
- Requires all bottom trawl vessels fishing in waters deeper than 50 m (~165 ft) to carry a vessel monitoring system (VMS) device.
- Provides for penalties and enforcement of the Act.
- Authorizes $15,000,000 a year to carry out the provisions of the Act.

these problems we provide the following recommendations for deep sea coral protection:

Recommendation 1: Use and enforce existing laws to protect deep sea corals.

Recommendation 2: Establish a national mandate to protect deep sea corals.

Recommendation 3: Expand scientific research (basic and applied) of deep sea corals.

Recommendation 4: Implement ecosystem-based management.

RECOMMENDATION 1:
Use and Enforce Existing Laws

Current laws and federal fishing regulations allow fishery management councils to enact spatial closures (marine protected areas) to protect deep sea corals from trawling and other potentially damaging fishing gears, including longlines, dredges, fish traps, crab pots, and bottom gillnets. Essential Fish Habitat and Habitat Areas of Particular Concern designations must be accompanied by restrictions on all fishing gears that affect seafloor habitats and deep sea corals. Closed areas should also be surrounded by a buffer zone that prevents inadvertent damage from fishing activity, and fishing permits must require vessel monitoring systems (VMS). In addition, deep sea coral closures should be accompanied by research and monitoring plans as well as education and outreach activities.

As noted for *Oculina* Bank HAPC (Box 5.1), enforcement of existing regulations remains a challenge. Authorities should examine additional means of enforcement, including event data recorders, vessel monitoring, and at-sea surveillance. We recommend that all fishery management councils adopt a precautionary approach to management that will restrict expansion of fisheries until they demonstrate that the gear used is compatible with sustainable fishing, habitat protection, and maintenance of healthy ecosystems.

The National Marine Sanctuaries Program should re-examine and use its mandate to manage all habitats within sanctuary boundaries, and regulate uses incompatible with resource protection.

The Minerals Management Service should act on existing information on the locations of deep sea coral and provide suitably sized buffers between deep sea coral areas and exploration, drilling, and other extraction and energy production activities.

RECOMMENDATION 2:

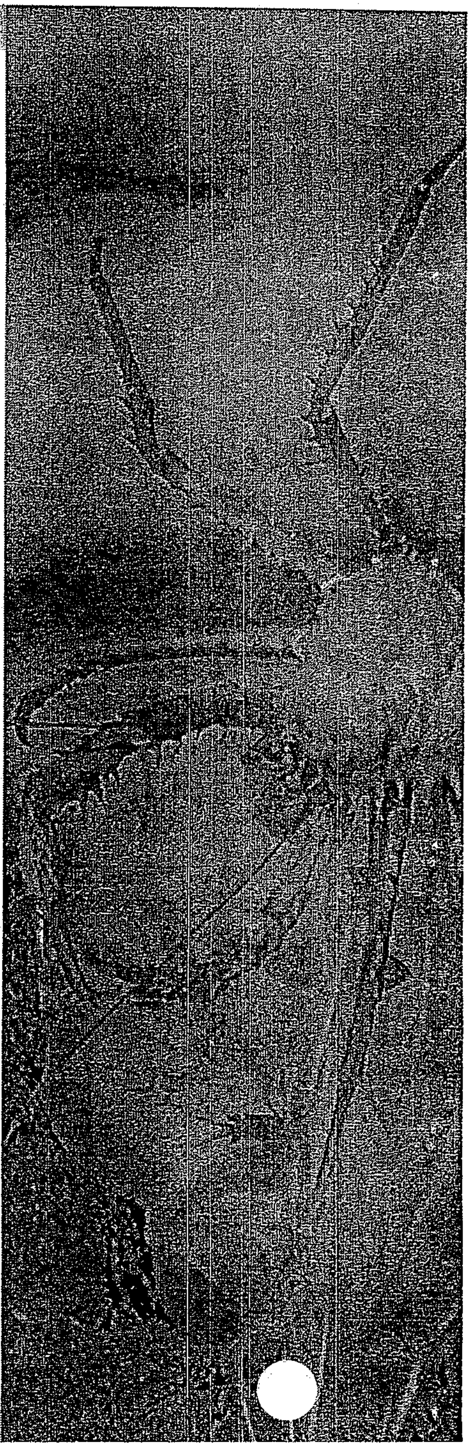
Establish a National Mandate to Protect Deep Sea Corals

Limitations to current laws, including the Magnuson-Stevens Act (MSA) and the National Marine Sanctuaries Act, prevent comprehensive protection of deep sea coral ecosystems. This suggests that a new mandate from Congress is needed. At this time the MSA is undergoing reauthorization by Congress, and the Bottom Trawl and Deep Sea Coral Habitat Act of 2005 (introduced in the House and Senate as H.R. 3778 and S. 1635) could be used as an amendment to the MSA or as new legislation. Modeled on the actions taken in the Pacific and North Pacific FMC regions, the bill would freeze the footprint of bottom trawlers and protect deep sea corals that have not yet been demolished, while allowing bottom trawlers to continue to fish in areas where they have historically fished. The bill would also provide for the implementation of vessel monitoring and for increased coral research efforts in the deep sea. The provisions of the bill are summarized in Box 5.2.

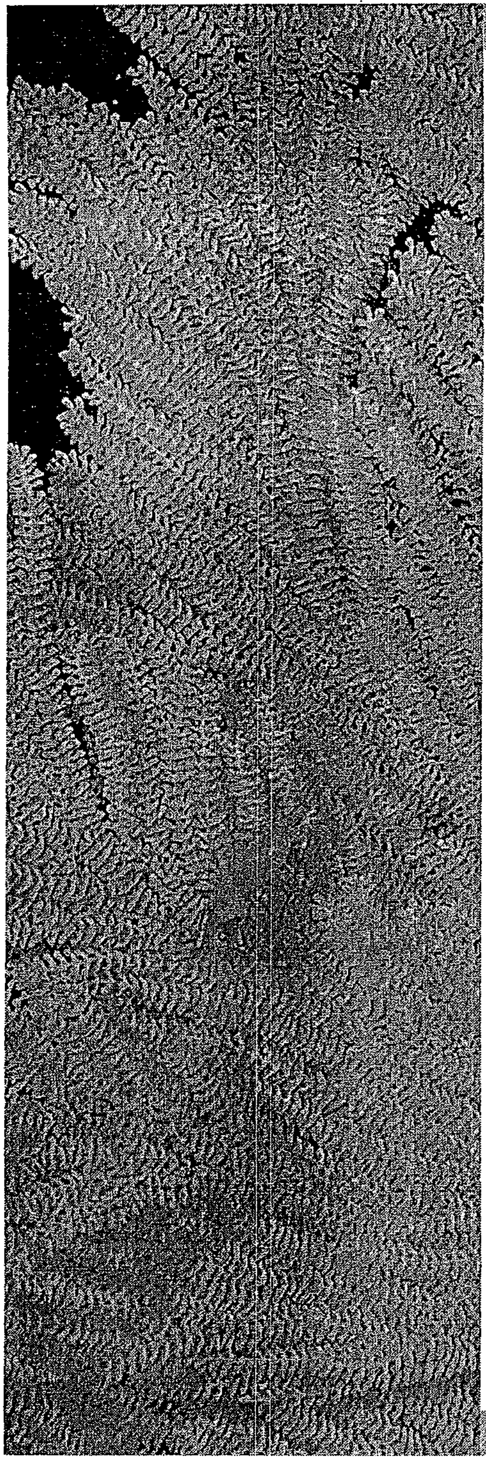
RECOMMENDATION 3:

Expand Science and Research

Continued research is critical to furthering our understanding of deep sea corals and improving their management. The quality of information on the distribution of deep sea corals varies from one region to another because of different research methods and priorities. NMFS and its regional science centers have undertaken excellent small-scale studies of coral and fish habitats. The National Undersea Research Centers and other academic centers have also provided valuable research. NOAA's Office of Ocean Exploration has sponsored a series of research cruises in recent years to better understand deep sea coral distribution and ecology. These cruises explored seamounts off California, New England and the Gulf of Alaska, as well as the *Lophelia* and *Oculina* reefs of the southeastern USA, the coral gardens of the Aleutian Islands, and several other areas. On these explorations, manned submersibles and ROVs captured images of deep sea corals and collected samples for further analyses. This provided a detailed look at selected deep sea coral communities and documented the locations of corals. However, each study covered only a small area or a few narrow transects.



*Red vermillion crab (*Paralomis verrilli*) dangling off a yellow sponge (*Staurocalyptus *sp.); amidst a white ruffle sponge (*Farrea *sp.); white branched sponges (*Asbestopluma *sp.); shrimp; brittle stars; and an isopod on the Davidson Seamount (4,462 ft depth).*
Photo credit: NOAA/MBARI



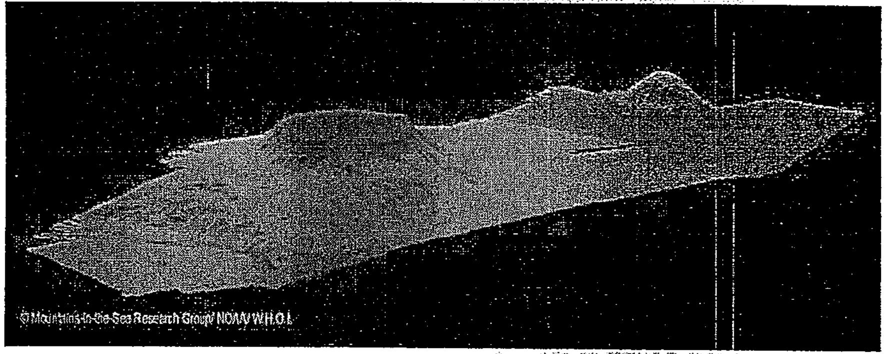


Fig. 5.1: Map of Bear Seamount (foreground) and Physalia Seamount (background) in the New England seamount chain, produced with multi-beam sonar shows detailed bathymetry
Image credit: Mountains in the Sea research group/NOAA/WHOI

Greater use of multibeam sonar mapping of the seafloor will facilitate scientific exploration (Figure 5.1). Unlike trawl surveys, seafloor mapping will provide much greater spatial resolution of potential coral locations. When paired with ground-truthing efforts using ROVs or manned submersibles to confirm the presence of deep sea corals, this technique will offer a much more precise and accurate understanding of coral distribution (Schroeder et al. 2005).

Future research should continue to identify coral communities for protection. A comprehensive research program for deep sea corals needs to:

1. Fund further exploration work to identify coral concentrations;

2. Develop high-resolution multi-beam mapping of continental shelves and slopes with ground truthing from ROVs or manned submersibles;

3. Develop and fund new tools such as autonomous underwater vehicles (AUVs) for sampling and mapping environmental factors;

4. Develop models to predict deep sea coral distribution based on hydrography and geology;

5. Produce higher resolution, spatially explicit maps of fishing effort and landings to facilitate the assessment of the threat of fishing to deep sea corals;

6. Research impacts of all fishing gears on seafloor habitats, as well as the recovery of these areas from fishing;

7. Fund research in basic taxonomy of deep sea corals;

8. Substantially improve deep sea coral identification training for fishery observers;

9. Use fishermen's knowledge to augment data on deep sea coral occurrences.

RECOMMENDATION 4:

Implement Ecosystem-Based Management

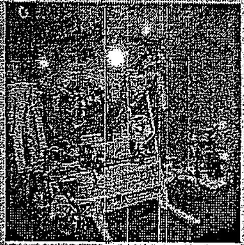
The challenges of deep sea coral conservation exemplify the multiple conflicting uses of marine resources, from fishing and petroleum activities to harbor dredging and anchoring. Management cannot succeed when multiple agencies operate under different, often conflicting mandates that only address individual pieces of a larger ecosystem. Habitat conservation will not occur without a coherent approach to management that focuses on maintaining the structure and function of the ecosystem.

Implementation of ecosystem-based management (EBM) for an entire region will markedly improve the conservation and management of deep sea corals for 3 reasons. First, EBM addresses more than commercially valuable species and seeks to maintain habitats and ecosystem function (Pikitch et al. 2004, Murawski 2005). In EBM, deep sea corals do not have to be proven essential for commercial fishes before receiving protection. The habitat complexity that deep sea corals contribute to the seafloor is enjoyed by commercial and noncommercial fishes alike, and EBM lends itself to protecting all parts of the ecosystem regardless of their commercial value. EBM departs from the single-species approach to fisheries management and limits collateral damage of fishing on the ecosystem. Deep sea corals will thus gain comprehensive protection from fishing as opposed to the haphazard, piecemeal case-by-case and gear-by-gear management actions that have taken place so far. EBM would also benefit other cnidarians and sponges, which play important roles in structuring the seafloor.

Second, EBM integrates the management not only of fishing activities but also of other human impacts on the ecosystem (Rosenberg and McLeod 2005). It provides a framework for assessing the consequences for deep sea corals of energy development, waste dumping, cable laying, climate change, and other activities. More important, EBM allows us to evaluate and manage the synergistic impacts of all these threats combined.

Third, EBM bases adaptive management on the precautionary principle. EBM places the burden of proof on those whose activities affect the ecosystem (Murawski 2005, Pikitch et al. 2004). Under EBM, the fishing industry would be required to prove that fishing does not result in detrimental effects on the habitat of a particular area before fishing is allowed there. As scientific understanding progresses and ecosystem components and their functions are better understood, management can adapt and regulate activities that are either compatible or incompatible with specific ecosystem properties. Given that new locations and species of deep sea coral are discovered every year and deep sea coral research is expanding at a fast pace, adaptive management is a suitable approach for integrating new research findings into the crafting of protection measures.

In recent years, managers of commercial fisheries in the USA have begun to recognize the interconnectedness of exploited species and their supporting ecosystems. NMFS appears to be committed to viewing fishery management as more than the sum of multiple fishery stock assessments (Murawski 2005). This is very good news to those concerned with biodiversity conservation, but current laws continue to do a

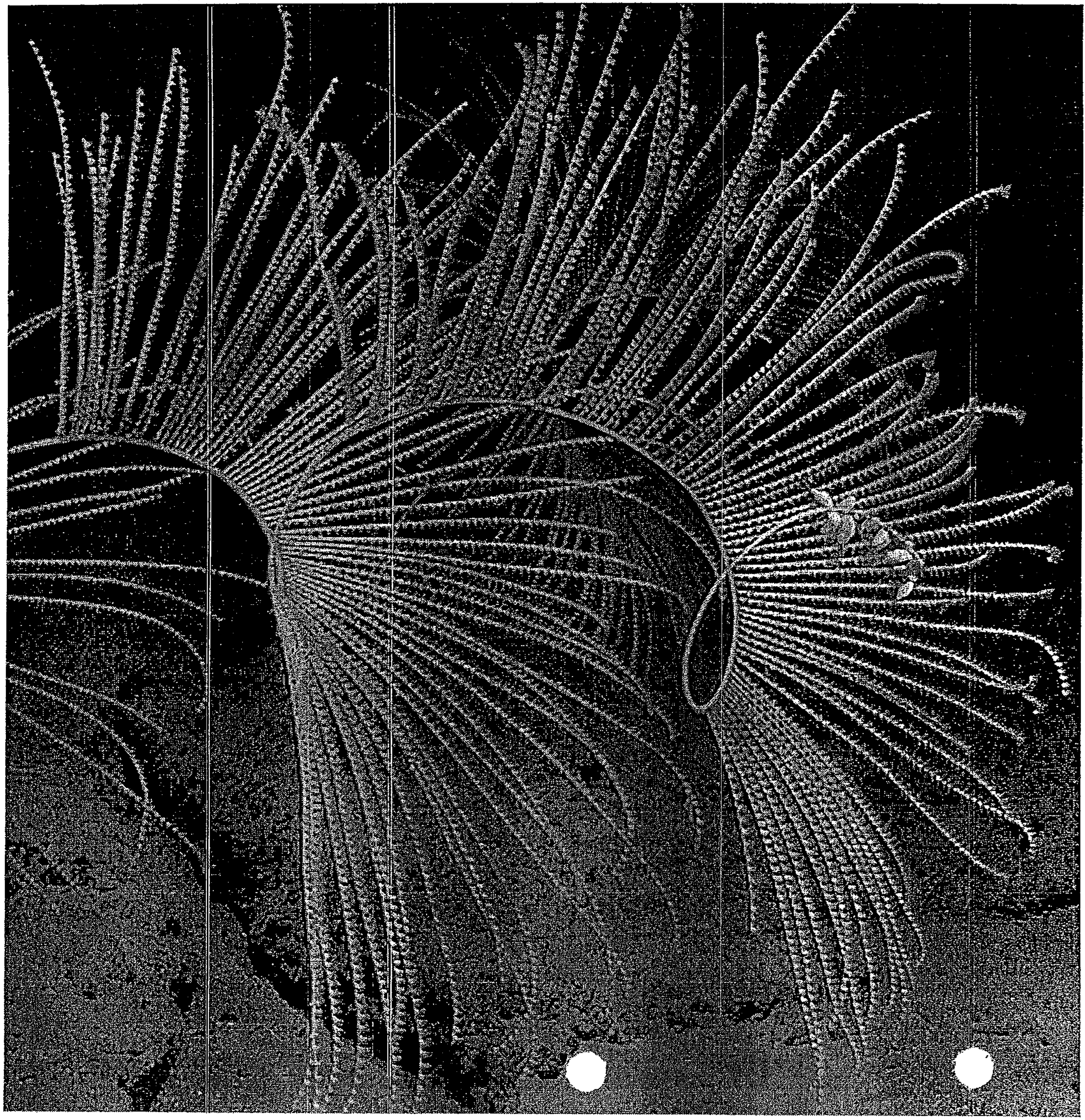


The manned submersible Johnson Sea-Link contributed greatly to our understanding of the *Oculina* Banks and *Lophelia* deep sea coral reefs.
Photo credit: HBOI

"The deep ocean, ranging in depths up to 10,000 meters, is an amazing cradle for an estimated 500,000 to 10 million species, many of them still undiscovered."

Jean-Michel Cousteau,
Founder and President,
Ocean Futures Society

Opposite page: Big white coral (Family Primnoidae)
Photo credit: NOAA/MBARI



disservice to marine organisms that are not "proven" contributors to commercial fisheries.

Comprehensive ocean zoning offers a means of implementing EBM that will help manage multiple uses (Norse 2003, 2005, Pew Oceans Commission 2003, Pikitch et al. 2004). Ocean zoning provides for multiple uses within a defined area, combining compatible activities and avoiding overlap of incompatible ones. In order to protect deep sea corals, zoning must start with the clear conservation goal of allowing activities compatible with the maintenance of ecosystem structure and function, but severely restricting activities that harm the seafloor. Of course, for zoning to prove effective it will need to address all human

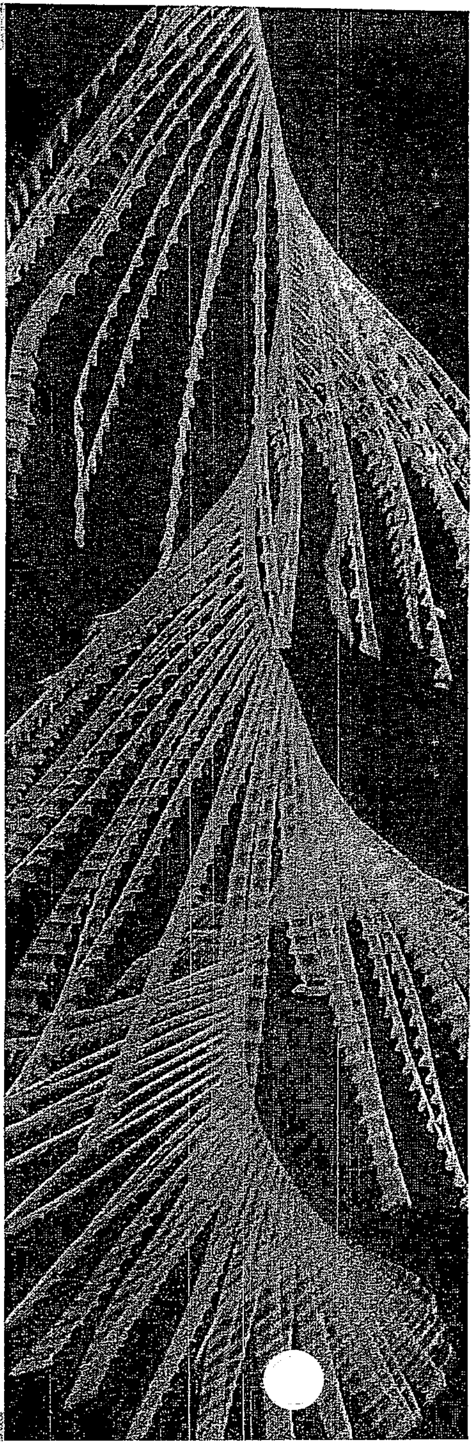
*Left: An eight foot tall spiraling colony of gorgonian coral (*Iridogorgia *sp.). Scientists using a remotely operated vehicle (ROV) to study seamounts off New England in 2005 captured this image with a high-definition video camera. Scientists visited 10 seamounts in the northwest Atlantic with the ROV; mapped the seafloor with multibeam sonar; collected over 537 samples of corals, sponges and associated fauna; identified and documented the habitat and foraging behavior of dozens of fish species; and took thousands of digital still images and frame captures of seamount landscapes.*

Photo credit: Deep Atlantic Stepping Stones Science Party, IFE, URI-IAO, and NOAA activities. This will require an extensive commitment to research and mapping as well as discussion and negotiations about the best uses of particular marine habitats. One opportunity on the horizon is the idea of designating allowable fishing zones. This would be in line with a precautionary approach to management, whereby selected areas would be open to fishing based on the compatibility of gears with particular habitat types. Because the future will undoubtedly see greater human activity at sea, it is time to bring ecosystem and zoning concepts into ocean management.

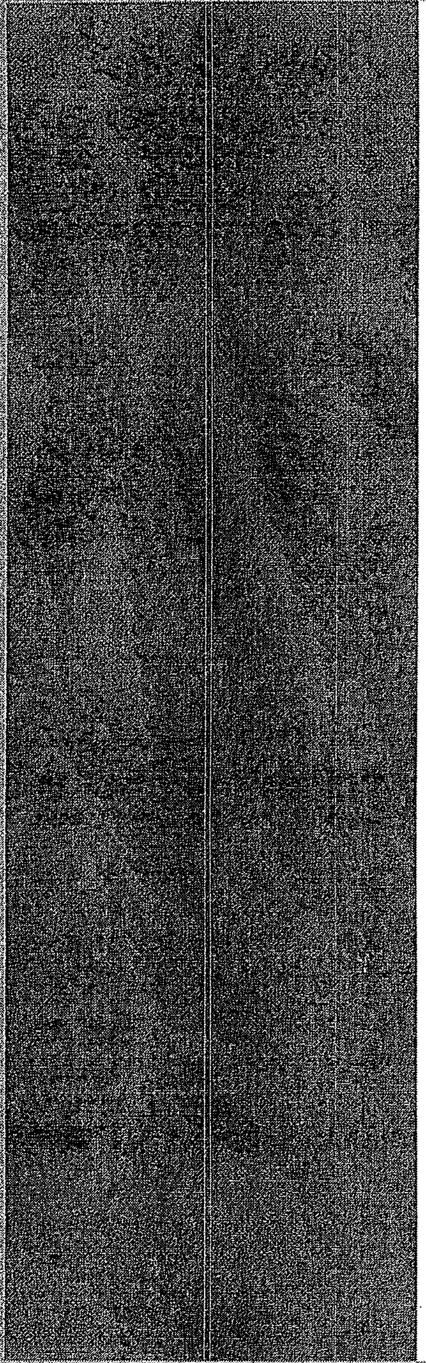
Conclusions

Deep sea corals are threatened by a number of human activities, but the largest and most immediate threat comes from bottom trawl fishing. This conclusion echoes recent findings by the National Research Council in 2002, the Pew Oceans Commission in 2003, and the US Commission on Ocean Policy in 2004 that bottom fishing, especially bottom trawling, is a major threat to deep sea corals. These bodies recommend stricter protection of vulnerable coral habitats. Similarly, the President's 2004 Ocean Action Plan emphasized deep sea coral conservation and called for further identification and protection of deep sea coral areas. Despite these encouraging signs, progress towards increased deep sea coral protection has been slow. Freezing the footprint of bottom trawling under fishery management council regulations limits the expansion of fishing fleets, but does not protect known coral locations in currently fished areas. The deep sea coral areas that have been comprehensively protected are small in relation to the overall need.

The recommendations of this report seek primarily to address the most significant threat to deep sea corals—bottom trawling—and to address additional impacts in a stepwise manner. First, fishery management councils and national marine sanctuaries must use existing tools to protect deep sea corals and curtail any further expansion of bottom trawling unless it can be shown that trawling will not damage seafloor habitats. Second, a national mandate to protect deep sea corals is necessary. Third, government-funded research should devote resources to achieving a better scientific understanding of where deep sea coral communities are found and of their ecological roles. Last, managers must develop a comprehensive framework to manage all human activities based on their compatibility with different ocean habitats (i.e., ecosystem-based management and ocean zoning). Until we make protecting ecosystems, rather than exploiting resources, the overarching goal of management, we will continue to fall short of protecting deep sea corals, sustaining healthy fisheries, and maintaining the oceans' productivity and biological diversity.



Right: Iridigorgia *sp. collected at Kelvin Seamount. Photo courtesy of M. Grady.*



Literature Cited

Anderson, O.F. and M.R. Clark. 2003. Analysis of bycatch in the fishery for orange roughy, *Hoplostethus atlanticus*, on the South Tasman Rise. Mar. Freshw. Res. 54:643-652.

Andrews, A.H., G.M. Cailliet, *et al.* 2005. Investigations of age and growth for three deep-sea corals from the Davidson Seamount off central California. pp. 1021-1038 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems*. Springer-Verlag, Berlin.

Andrews, A.H., E.E. Cordes, *et al.* 2002. Age, growth and radiometric age validation of a deep-sea, habitat-forming gorgonian (*Primnoa resedaeformis*) from the Gulf of Alaska. Hydrobiol. 471:101-110.

Auster, P., R. Malatesta, *et al.* 1996. The impacts of mobile fishing gear on seafloor habitats in the Gulf of Maine (Northwest Atlantic): Implications for conservation of fish populations. Rev. Fish. Sci. 4:185-202.

Auster, P.J. 2005. Are deep-water corals important habitats for fishes? pp. 747-760 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems*. Springer-Verlag, Berlin.

Auster, P. J., J. Moore, *et al.* 2005. A habitat classification scheme for seamount landscapes: assessing the functional role of deep-water corals as fish habitat. pp. 761-769 *in* A. Freiwald and J. M. Roberts, eds. *Cold-Water Corals and Ecosystems*. Springer-Verlag, Berlin.

Avent, R. 2004. Mineral Management Service Environmental Studies Program: A History of Biological Investigations in the Gulf of Mexico, 1973-2000. US DOI, Minerals Management Service, New Orleans.

Baco, A. and S. D. Cairns. 2005. Distribution of corals on Derickson Seamount, a deep seamount near the Aleutian chain of Alaska. Third Inter. Symp. on Deep-sea Corals Science and Management, Miami (abstract).

Baco, A. and T. Shirley. 2005. Distribution of deep-sea corals on the northern chain of seamounts in the Gulf of Alaska. Third Inter. Symp. on Deep-sea Corals Science and Management, Miami (abstract).

Baco, A.R., and T.M. Shank. 2005. Population genetic structure of the Hawaiian precious coral *Corallium lauuense* (Octocorallia: Coralliidae) using microsatellites. pp. 663-678 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems*. Springer-Verlag, Berlin.

Barnes, P.W. and J.P. Thomas. 2005. *Benthic Habitats and the Effects of Fishing*: AFS Symposium 41. American Fisheries Society, Bethesda.

Barnett, T. P., D. W. Pierce, *et al.* 2005. Penetration of human-induced warming into the world's oceans. Science 309:284-287.

Benaka, L. R., ed. 1999. *Fish Habitat: Essential Fish Habitat and Rehabilitation*: AFS Symposium 22. American Fisheries Society, Bethesda.

Boland, R.C. and F.A. Parrish. 2005. A description of fish assemblages in the black coral beds off Lahaina, Maui, Hawai'i. Pac. Sci. 59:411-420.

Breeze, H., D.S. Davis and M. Butler. 1997. *Distribution and Status of Deep Sea Corals Off Nova Scotia*. Ecology Action Centre, Marine Issues Spec. Pub.1, Halifax.

Bryden, H.L., H.R. Longworth, et al. 2005. Slowing of the Atlantic meridional overturning circulation at 25°N. Nature 438:655-657.

Buddemeier, R.W. and S.V. Smith. 1999. Coral adaptation and acclimatization: a most ingenious paradox. Amer. Zool. 39:1-9.

Buhl-Mortensen, L. and P. Mortensen. 2005. Distribution and diversity of species associated with deep-sea gorgonian corals off Atlantic Canada. pp. 849-879 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems*. Springer-Verlag, Berlin.

Cailliet, G.M., A.H. Andrews, *et al.* 2001. Age determination and validation studies of marine fishes: do deep-dwellers live longer? Exper. Geront. 36: 739–764.

Cairns, S.D. 2001. A brief history of taxonomic research on azooxanthellate Scleractinia (Cnidaria: Anthozoa). Bull. Biol. Soc. Wash. 10:191-203.

Carr, M. H. 1991. Habitat selection and recruitment of an assemblage of temperate marine reef fishes. J. Exper. Mar. Biol. Ecol. 146:113-137.

Chandler, W. J. and H. Gillelan. 2004. The history and evolution of the National Marine Sanctuaries Act. Environ. Law Rev. News Anal. 34:10505-10565.

Christensen, V., S. Guenette, *et al.* 2003. Hundred-year decline of North Atlantic predatory fishes. Fish and Fish. 4:1-24.

Chuenpagdee, R., L.E. Morgan, *et al.* 2003. Shifting gears: Assessing collateral impacts of fishing methods in US waters. Front. Ecol. Environ. 1:517-524.

Connell, J. and G.P. Jones. 1991. The influence of habitat complexity on post-recruitment processes in a temperate reef fish population. J. Exper. Mar. Biol. Ecol. **151**:271-294.

Costello, M.J., M. McCrea, *et al.* 2005. Role of cold-water *Lophelia pertusa* coral reefs as habitat in the NE Atlantic. pp. 771-805 *in* A. Freiwald and J. M. Roberts, editors. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Dall, W.A. 1884. On some hydrocorallinae from Alaska and California. Proc. Biol. Soc. Washington 2:111-115.

DeVogelaere, A.P., E.J. Burton, *et al.* 2005. Deep-sea corals and resource protection at the Davidson Seamount, California, U.S.A. pp. 1189-1198 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Druffel, E.R.M., S. Griffin, *et al.* 1995. *Gerardia*: Bristlecone pine of the deep-sea? Geoch. Cosmo. Acta. **59**:5031-5036.

Duineveld, G., M. Lavaleye, and E. Berghuis. 2004. Particle flux and food supply to a seamount cold-water coral community (Galicia Bank, NW Spain). Mar. Ecol. Prog. Ser. **272**:13-23.

Ebert, T.A. and J.R. Southon. 2003. Red sea urchins (*Strongylocentrotus franciscanus*) can live over 100 years: confirmation with A-bomb ^{14}carbon. Fish. Bull. **101**, 915–922.

Energy Information Administration. 2003. The Global Liquefied Natural Gas Market: Status and Outlook. DOE/EIA-0637, US Department of Energy, Energy Information Administration, Washington DC.

Etnoyer, P. and L. Morgan. 2003. *Occurrences of Habitat-forming Deep Sea Corals in the Northeast Pacific Ocean.* Marine Conservation Biology Institute, Redmond, and National Oceanic and Atmospheric Administration, Silver Spring.

Etnoyer, P. and L.E. Morgan. 2005. Habitat-forming deep-sea corals in the Northeast Pacific Ocean. pp. 331-343 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Faulkner, J.D. 2002. Marine natural products. Nat. Prod. Rev. **19**:1-48.

Feely, R., C. Sabine, *et al.* 2004. Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. Science **305**:362-366.

Fosså, J. H., B. Lindberg, et al. 2005. Mapping of *Lophelia* reefs in Norway: experiences and survey methods. pp. 359-391 in A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Fosså, J. H., P. B. Mortensen and D.M. Furevik. 2002. The deep water coral *Lophelia pertusa* in Norwegian waters: distribution and fishery impacts. Hydrobiol. **471**:1-12.

Freese, J. L. 2001. Trawl-induced damage to sponges observed from a research submersible. Mar. Fish. Review **63**:7-13.

Freiwald, A. 2003. Reef-forming cold-water corals. pp. 365-385 *in* G. Wefer, D. Billett, *et al.*, eds. *Ocean Margin Systems.* Springer-Verlag, Heidelberg.

Freiwald, A., J. H. Fosså, *et al.* 2004. *Cold Water Coral Reefs: Out of Sight—No Longer Out of Mind.* UNEP World Conservation Monitoring Center, Cambridge.

Friedlander, A.M. and J.D. Parrish. 1998. Habitat characteristics affecting fish assemblages on a Hawaiian coral reef. J. Exper. Mar. Biol. Ecol. **224**:1-30.

Gass, S.E., and J.H.M. Willison. 2005. An assessment of the distribution of deep-sea corals in Atlantic Canada by using both scientific and local forms of knowledge. pp. 223-245 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Gattuso, J., D. Allemand and M. Frankignoulle. 1999. Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: a review on interactions and control by carbonate chemistry. Amer. Zool. **39**:160-183.

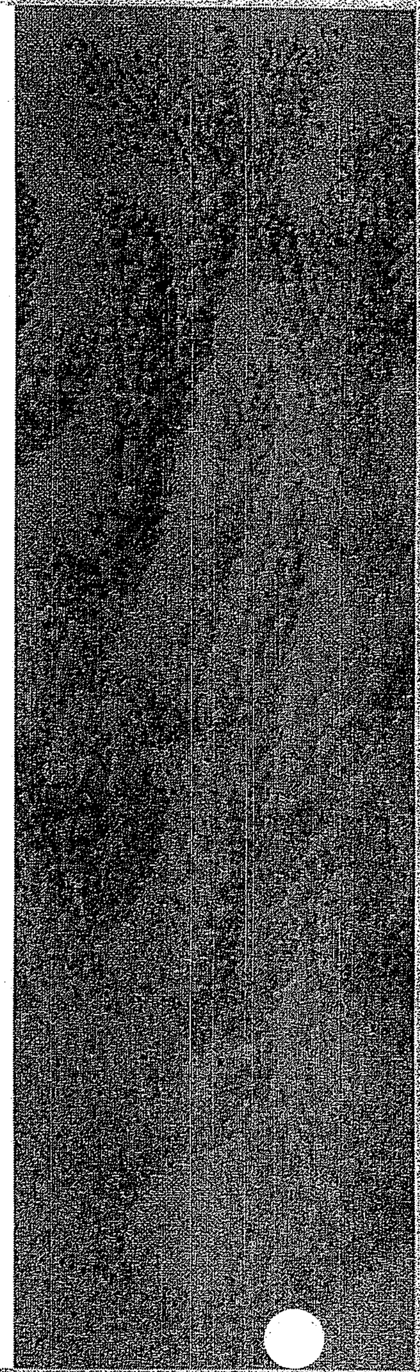
Genin, A., P.K. Dayton, *et al.* 1986. Corals on seamount peaks provide evidence of current acceleration over deep-sea topography. Nature **322**:59-61.

Gilmore, R.G. and R. Jones. 1992. Color variation and associated behavior in the epihepheline groupers, *Mycteroperca microlepis* (Goode and Bean) and *M. phenax* (Jordan and Swain). Bull. Mar. Sci. **51**:83-103.

Ginsberg, R.N. and S.J. Lutz (in prep.) Structure-forming cold-water corals of the Caribbean. NOAA Technical Report.

Glover, A.G. and C.R. Smith. 2003. The deep-sea floor ecosystem: current status and prospects of anthropogenic change by the year 2025. Environ. Cons. **30**:219-241.

Grigg, R. 2001. Black coral: history of a sustainable fishery in Hawai'i. Pac. Sci. **55**:291-299.



Grigg, R. 2002. Precious corals in Hawaii: discovery of a new bed and revised management measures for existing beds. Mar. Fish. Rev. 64:13-20.

Guinotte, J. M. R. W. Buddemeier and J. A. Kleypas. 2003. Future coral reef habitat marginality: temporal and spatial effects of climate change in the Pacific basin. Coral Reefs 22:551-558.

Guinotte, J., J. Orr, *et al.* 2006. Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? Front. Ecol. Environ. 4:141-146.

Hain, S., E. Corcoran *et al.* 2004. The status of the cold-water corals reefs of the world. pp. 115-135 *in* C. Wilkinson, ed. *Status of Coral Reefs of the World*: 2004, vol. 1. Australian Institute of Marine Science, Townsville.

Hall-Spencer, J., V. Allain and J.H. Fosså. 2002. Trawling damage to Northeast Atlantic ancient coral reefs. Proc. Royal Soc. London Ser. B 269:507-511.

Heifetz, J. 2002. Coral in Alaska: distribution, abundance, and species associations. Hydrobiol. 471:19-28.

Heifetz, J., B.L. Wing, *et al.* 2005. Corals of the Aleutian Islands. Fish. Ocean. **14** (s1):131-138.

Hixon, M.A., and G.P. Jones. 2005. Competition, predation, and density-dependent mortality in demersal marine fishes. Ecology 86:2847-2859.

Husebø, A., L. Nottestad, *et al.* 2002. Distribution and abundance of fish in deep-sea coral habitats. Hydrobiol. 471:91-99.

Hyland, J., C. Cooksey, *et al.* 2005. A pilot survey of deepwater coral/sponge assemblages and their susceptibility to fishing/harvest impacts at the Olympic Coast NMS, cruise report for NOAA Ship McArthur II. NOAA Technical Memo NOS NCCOS 15, Charleston.

Jensen, A. and R. Frederiksen. 1992. The fauna associated with the bank-forming deepwater coral *Lophelia pertusa* (Scleractinaria) on the Faroe shelf. Sarsia 77:53-69.

Kahng, S. and R. Grigg. 2005. Impact of alien octocoral, *Carijoa riisei*, on black corals in Hawaii. Coral Reefs 24:556-562.

Kaiser, M.J., K.R. Clarke, et al. 2006. Global analysis of response and recovery of benthic biota to fishing. Mar. Ecol. Prog. Ser. 311:1-14.

Kleypas, J.A., R.W. Buddemeier, *et al.* 1999. Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. Science 284:118-120.

Koenig, C.C., A.N. Shepard, *et al.* 2005. Habitat and fish populations in the deep-sea *Oculina* coral ecosystem of the Western Atlantic. pp. 795-805 *in* P.W. Barnes and J.P. Thomas, eds. *Benthic Habitats and the Effects of Fishing*, AFS Symposium 41, American Fisheries Society, Bethesda.

Koslow, J.A., G.W. Boehlert, *et al.* 2000. Continental slope and deep-sea fisheries: implications for a fragile ecosystem. Ices J. Mar. Sci. 57:548-557.

Krieger, K.J. 1993. Distribution and abundance of rockfish determined from a submersible and by bottom trawling. Fish. Bull. 91:87-96.

Krieger, K.J. 2001. Coral (*Primnoa*) impacted by fishing gear in the Gulf of Alaska. pp. 106-116 *in* J. H. M. Willison, ed. Proc. First Inter. Symp. Deep-Sea Corals. Ecology Action Centre and Nova Scotia Museum, Halifax.

Krieger, K.J. and B.L. Wing. 2002. Megafauna associations with deepwater corals (*Primnoa* spp.) in the Gulf of Alaska. Hydrobiol. 471:83-90.

Lehnert, H., L. Watling and R. Stone. 2005. *Cladorhiza corona* sp. nov. (Porifera: Demospongiae: Cladorhizidae) from the Aleutian Islands (Alaska). J. Mar. Biol. Assoc. U.K. 85:1359-1366.

Lindholm, J.B., P.J. Auster and L.S. Kaufman. 1999. Habitat-mediated survivorship of juvenile (0-year) Atlantic cod *Gadus morhua*. Mar. Ecol. Prog. Ser. 180:247-255.

Lindholm, J.B., P.J. Auster, *et al.* 2001. Modeling the effects of fishing and implications for the design of marine protected areas: juvenile fish responses to variations in seafloor habitat. Cons. Biol. 15:424-437.

Lindner, A. 2005. Evolution and Taxonomy of Stylasterid Corals. PhD dissertation. Duke University, Durham.

Love, M.S., M.H. Carr and L.J. Haldorson. 1991. The ecology of substrate-associated juveniles of the genus *Sebastes*. Environ. Biol. Fish. 30:225-243.

Maxwell, S., H. Ehrlich, *et al.* 2005. Medicines from the Deep: the Importance of Protecting High Seas from Bottom Trawling. Natural Resource Defense Council, New York.

Merrett, N., and R. Haedrich. 1997. *Deep-Sea Demersal Fish and Fisheries.* Chapman and Hall, London.

Messing, C.G., A.C. Neuman, and J.C. Lang. 1990. Biozonation of deep-water lithoherms and associated hardgrounds in the northeastern Straits of Florida. Palaios 5:15-33.

Morgan, L.E., and R. Chuenpagdee. 2003. *Shifting Gears: Addressing the Collateral Impacts of Fishing Methods in U.S. Waters.* Island Press, Washington, DC.

Morgan, L.E., P. Etnoyer, *et al.* 2005. Conservation and management implications of deep-sea coral and fishing effort distributions in the NE Pacific Ocean. pp. 1171-1187 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Mortensen, P., and L. Buhl-Mortensen. 2005. Deep-water corals and their habitats in The Gully, a submarine canyon off Atlantic Canada. pp. 247-277 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Mortensen, P. B., L. Buhl-Mortensen, *et al.* 2005. Effects of fisheries on deepwater gorgonian corals in the Northeast Channel, Nova Scotia. pp. 369-382 *in* P. W. Barnes and J. P. Thomas, eds. *Benthic Habitats and the Effects of Fishing,* AFS Symp. 41, AFS, Bethesda.

Mortensen, P. B., M. Hovland, *et al.* 1995. Deep-water bioherms of the scleractinian coral *Lophelia pertusa* (L) at 64-degrees-N on the Norwegian shelf—structure and associated megafauna. Sarsia **80**:145-158.

Murawski, S. 2005. Strategies for incorporating ecosystem considerations in fisheries management. pp. 163-171 *in* D. Witherell, ed. *Managing Our Nation's Fisheries II: Focus on the Future.* North Pacific Fishery Management Council, Anchorage.

Nasby-Lucas, N. M., B. W. Embley, *et al.* 2002. Integration of submersible transect data and high-resolution multibeam sonar imagery for a habitat-based groundfish assessment of Heceta Bank, Oregon. Fish. Bull. **100**:739-751.

National Research Council. 2002. *Effects of Trawling and Dredging on Seafloor Habitat.* National Academies Press, Washington DC.

Neumann, A.C., J.W. Kofoed and G.H. Keller. 1977. Lithoherms in the Straits of Florida. Geology 5:4-10.

NMFS. 2004. *Final Programmatic Supplemental Groundfish Environmental Impact Statement for Alaska Groundfish Fisheries.* NOAA, NMFS, Juneau.

Norse, E. 2003. A zoning approach to managing marine ecosystems. pp. 53-57 *in* B. Cicin-Sain, C. Ehler, and K. Goldstein, eds. *Workshop on Improving Regional Ocean Governance in the U.S.* Center for the Study of Marine Policy, Newark.

Norse, E.A. 2005. Ending the range wars on the last frontier: zoning the sea. pp. 422-443 *in* E.A. Norse and L.B. Crowder, eds. *Marine Conservation Biology: the Science of Maintaining the Sea's Biodiversity.* Island Press, Washington DC.

North Pacific Fishery Management Council. 2003. Stock Assessment and Fishery Evaluation Report for the Groundfish Resources of the Bering Sea/ Aleutian Islands Region, pp. 662-678. North Pacific Fishery Management Council, Anchorage.

O'Connell, V.M. and C.W. Carlisle. 1993. Habitat-specific density of adult yelloweye rockfish *Sebastes ruberrimus* in the eastern Gulf of Alaska. Fish. Bull. **91**:304-309.

Opresko, D.M. 2005. A new species of antipatharian coral (Cnidaria: Anthozoa: Antipatharia) from the southern California Bight. Zootaxa **852**:1-10.

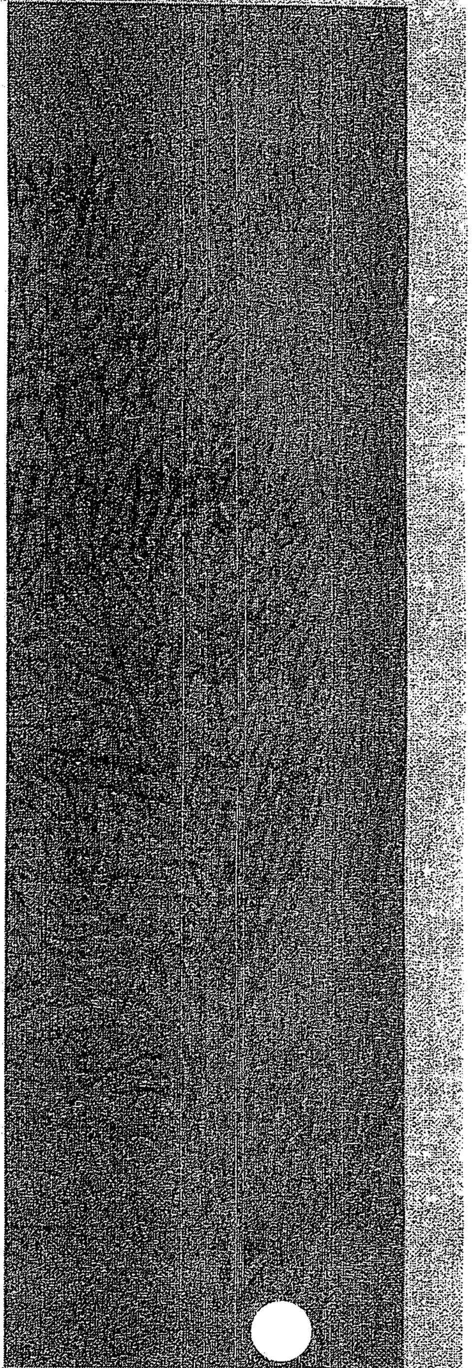
Orr, J.C., V.J. Fabry, *et al.* 2005. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature **437**:681-686.

Parrish, F.A. 2005. Habitat and fish assemblages of three deep-sea corals in Hawaii. Third Inter. Symp. on Deep-sea Corals Science and Management, Miami (abstract):108.

Paull, C.K., A.C. Neumann, *et al.* 2000. Lithoherms on the Florida-Hatteras slope. Mar. Geol. **166**:83-101.

Pauly, D. 1995. Anecdotes and the shifting baseline syndrome of fisheries. Trends Ecol. & Evol. **10**:430.

Pautzke, C. 2005. The challenge of protecting fish habitat through the Magnuson-Stevens Fishery Conservation and Management Act. pp. 19-40 in P.W. Barnes and J.P. Thomas,



eds. *Benthic Habitats and the Effects of Fishing.* AFS Symp. 41. American Fisheries Society, Bethesda.

Pearcy, W.G., D.L. Stein, *et al.* 1989. Submersible observations of deep-reef fishes of Heceta Bank, OR. Fish. Bull. 87:955-965.

Pew Oceans Commission. 2003. *America's Living Oceans: Charting a Course for Sea Change. A Report to the Nation.* Pew Oceans Commission, Arlington.

Pikitch, E.K., C. Santora, *et al.* 2004. Ecosystem-based fishery management. Science 305:346-347.

Pirtle, J.L 2005. Habitat-based Assessment of Structure Forming Megafaunal Invertebrates and Fishes on Cordell Bank, California. Master's Thesis, Washington State University, Vancouver.

Popenoe, P. and F.T. Manheim. 2001. Origin and history of the Charleston Bump—geological formations, currents, bottom conditions, and their relationship to wreckfish habitats on the Blake Plateau. pp. 43-93 *in* G.R. Sedberry, ed. *Island in the Stream: Oceanography and Fisheries of the Charleston Bump*: AFS Symposium 25. American Fisheries Society, Bethesda.

Puglise, K.A., R.J. Brock and J.J. McDonough. 2005. Identifying critical information needs and developing institutional partnerships to further the understanding of Atlantic deep-sea coral ecosystems. pp. 1129-1140 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Raes, M. and A. Vanreusel. 2005. The metazoan meiofauna associated with a cold-water coral degradation zone in the Porcupine Seabight (NE Atlantic). pp. 821-847 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Reed, J.K. 2002a. Deep-water *Oculina* coral reefs of Florida: biology, impacts, and management. Hydrobiol. 471:43-55.

Reed, J.K. 2002b. Comparison of deep-water coral reefs and lithoherms off southeastern USA. Hydrobiol. 471:57-69.

Reed, J.K., R.H. Gore, *et al.* 1982. Community composition, structure, areal and trophic relationships of decapods associated with shallow-water and deep-water *Oculina varicosa* coral reefs. Bull. Mar. Sci. 32:761-786.

Reed, J.K., A.N. Shepard, *et al.* 2005a. Mapping, habitat characterization and fish surveys of the deep-water *Oculina* coral reef marine protected area: a review of historical and current research. pp. 443-465 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Reed, J., S.A. Pomponi, *et al.* 2005b. Deep-water sinkholes and bioherms of south Florida and the Pourtales Terrace- habitat and fauna. Bull. Mar. Sci. 77:267-296.

Reed, J.K., D.C. Weaver, and S.A. Pomponi. 2006. Habitat and fauna of deep-water *Lophelia pertusa* coral reefs off the southeastern U.S.: Blake Plateau, Straits of Florida, and Gulf of Mexico. Bull Mar. Sci. 78: 343-375.

Riebesell, U. 2004. Effects of CO_2 enrichment on marine phytoplankton. J. Oceanogr. 60:719-729.

Riebesell, U., I. Zondervan, *et al.* 2000. Reduced calcification of marine plankton in response to increased atmospheric CO_2. Nature 407:364-367.

Risk, M.J. 1972. Fish diversity on a coral reef in the Virgin Islands. Atoll Research Bulletin 153:1-6.

Risk, M.J., J. Hall-Spencer and B. Williams. 2005. Climate records from the Faroe-Shetland Channel using *Lophelia pertusa* (Linnaeus, 1758). pp. 1097-1108 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Risk, M.J., J.M. Heikoop, *et al.* 2002. Lifespans and growth patterns of two deep-sea corals: *Primnoa resedaeformis* and *Desmophyllum cristagalli.* Hydrobiol. 471:125-131.

Roberts, C.M. 2002. Deep impact: the rising toll of fishing in the deep sea. Trends Ecol. & Evol. 17:242-245.

Roberts, J.M., D. Long, *et al.* 2003. The cold-water coral *Lophelia pertusa* (Scleractinia) and enigmatic seabed mounds along the north-east Atlantic margin: are they related? Mar. Poll. Bull. 46:7-20.

Roberts, J.M., A.J. Wheeler and A. Freiwald. 2006. Reefs of the deep: the biology and geology of cold-water coral ecosystems. Science. 312:543-547.

Rogers, A.D. 1999. The biology of *Lophelia pertusa* (Linnaeus 1758) and other deep-water reef-forming corals and impacts from human activities. Internat. Rev. Hydrobiol. 84:315-406.

Rosenberg, A.A., and K.L. McLeod. 2005. Implementing ecosystem-based approaches to management for the conservation of ecosystem services. Mar. Ecol. Prog. Ser. 241:270-274.

Ross, S.W. and Nizinski, M.S. in prep. State of the deep sea coral ecosystems in the United States: regional chapter for the southeastern United States (Cape Hatteras to southeastern Florida). NOAA, Silver Spring.

Sainsbury, K.J. and R.A. Campbell. 1997. Experimental management of an Australian multispecies fishery: Examining the possibility of trawl induced habitat modifications. pp. 107-112 *in* E.K. Pikitch, D.D. Huppert, and M.P. Sissenwine, eds. *Global Trends: Fisheries Management.* AFS, Bethesda.

Sanchez, J., D. Tracey, *et al.* 2004. Coral rings in the deep ocean: using SEM to date New Zealand's bamboo corals. Water & Atmosphere. 12:22-23.

Schroeder, W.W., S.D. Brooke, *et al.* 2005. Occurrence of deep-water *Lophelia pertusa* and *Madrepora oculata* in the Gulf of Mexico. pp. 297-307 *in* A. Freiwald and J.M. Roberts, eds. *Cold-Water Corals and Ecosystems.* Springer-Verlag, Berlin.

Smith, J.E., M.J. Risk, *et al.* 1997. Rapid climate change in the North Atlantic during the Younger Dryas recorded by deep-sea corals. Nature 386:818-820.

Smith, P.J. 2001. Managing biodiversity: Invertebrate by-catch in seamount fisheries in the New Zealand Exclusive Economic Zone (a case study). UNEP Workshop on Managing Global Fisheries for Biodiversity, Victoria.

Stone, R. 2006. Coral habitat in the Aleutian Islands of Alaska: depth distribution, fine-scale species associations, and fisheries interactions. Coral Reefs 25:229-238.

Stone, R. and B. Wing. 2001. Growth and recruitment of an Alaskan shallow-water gorgonian. pp. 88-94 *in* J.H.M. Willison, ed. Proc. First Inter. Symp. Deep-Sea Corals. Ecology Action Centre and Nova Scotia Museum, Halifax.

Tews, J., U. Brose, *et al.* 2004. Animal species diversity driven by habitat heterogeneity/diversity: the importance of keystone structures. J. Biogeo. 31:79-92.

Tissot, B. N., M. M. Yoklavich, *et al.* 2006. Structure-forming invertebrates as components on benthic habitat on deep banks off Southern California with special reference to deep sea corals. Fish. Bull. 104:167-181.

US Commission on Ocean Policy. 2004. An Ocean Blueprint for the 21st Century—Final Report U.S. Commission on Ocean Policy. Washington DC.

Waller, R.G. and P.A. Tyler. 2005. The reproductive biology of two deep water, reef-building scleractinians from the NE Atlantic Ocean. Coral Reefs 24: 514–522

Watling, L. and P.J. Auster. 2005. Distribution of deep-water Alcyonacea off the northeast coast of the United States. pp. 279-296 *in* A. Freiwald and J.M. Roberts, eds. *Cold-water Corals and Ecosystems.* Springer-Verlag, Berlin.

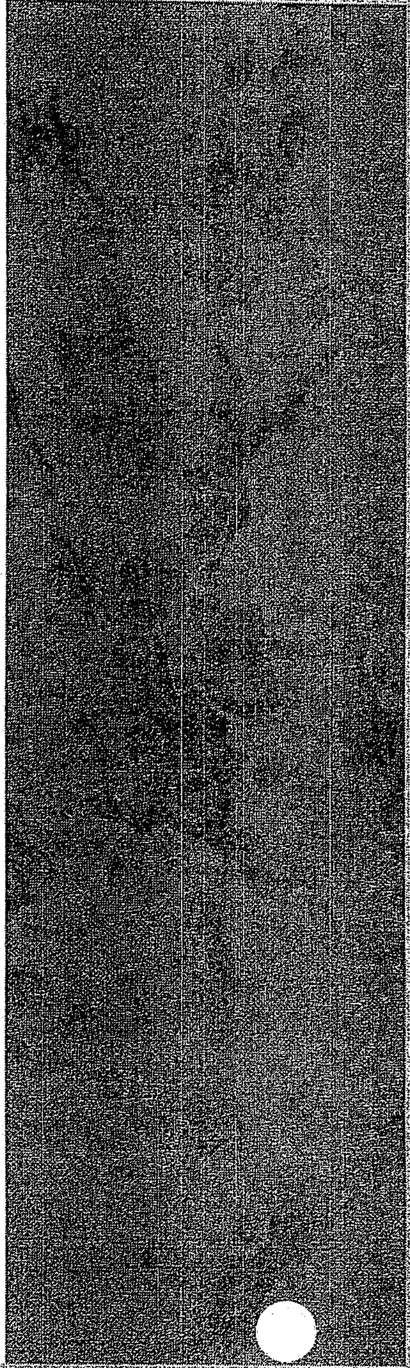
Watling, L., P.J. Auster, *et al.* 2003. A geographic database of deepwater alcyonaceans of the Northeastern US continental shelf and slope, version 1.0 CD-ROM. NURC/Univ. Conn., Groton.

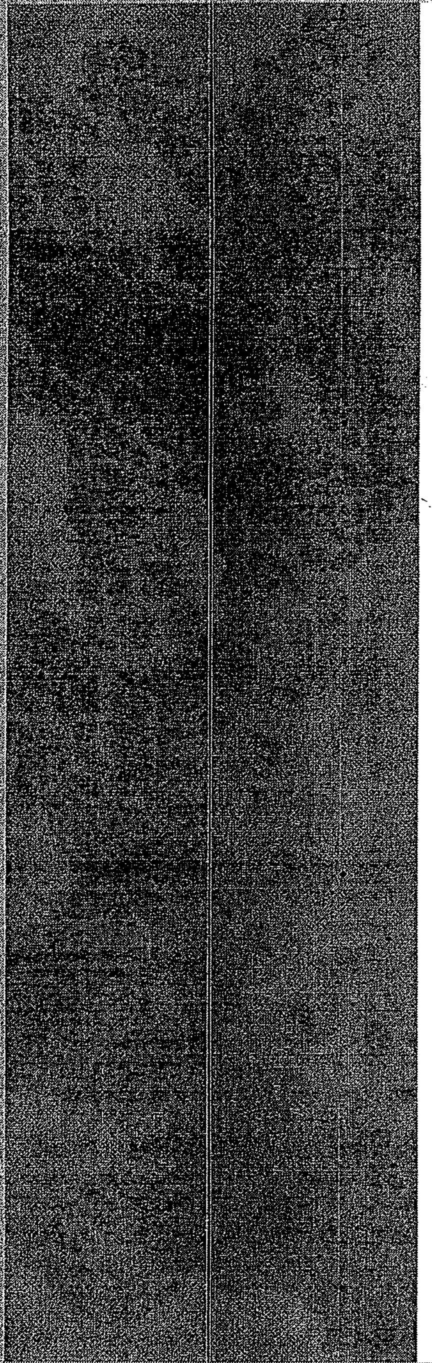
Watling, L. and E.A. Norse. 1998. Disturbance of the seabed by mobile fishing gear: a comparison with forest clear-cutting. Cons. Biol. 12:1189-1197.

Wing, B.L. and D.R. Barnard. 2004. A Field Guide to Alaskan Corals, NMFS-AFSC-146. Juneau.

Witherell, D. and C. Coon. 2001. Protecting gorgonian corals off Alaska from fishing impacts. pp. 117-125 *in* J.H.M. Willison, ed. Proc. First Inter. Symp. on Deep Sea Corals. Ecology Action Centre and Nova Scotia Museum, Halifax.

Yoklavich, M.M., H.G. Greene, *et al.* 2000. Habitat associations of deep-water rockfishes in a submarine canyon: an example of a natural refuge. Fish. Bull. 98:625-641.





Appendix: Data Sources for Maps

Bathymetry:

ETOPO-2 — seafloor data between latitudes 64° North and 72° South. These data were derived from satellite altimetry observations and shipboard echo-sounding measurements. For more information see Smith, W.H.F. and D.T. Sandwell, 1997. Global sea floor topography from satellite altimetry and ship depth soundings. Science 277 (5334): 1956–1962.

Deep Sea Coral Records:

Etnoyer and Morgan 2003
Grigg 2001 and 2002
Schroeder et al. 2005
Tissot et al. 2006
Watling et al. 2003
Stephen Cairns, Smithsonian Institution
Peter Etnoyer, Aquanautix Consulting
André Freiwald, University of Erlangen
Jon Heifetz, NMFS (RACEBase)
John Reed, Harbor Branch
  Oceanographic Institutión
John Warrenchuk, Oceana
California Academy of Sciences
Hawaii Undersea Research Laboratory
Monterey Bay Aquarium Research Institute
Monterey Bay National Marine Sanctuary
Smithsonian Institution
Scripps Institution of Oceanography

Fishing Catch and Effort data:

Tom Hourigan, NMFS
John Olson, NMFS
David Stevenson, NMFS

EEZ Boundaries:

General Dynamics Global Maritime
  Boundaries Database

Gulf of Mexico Oil Platform and Pipelines:

US Minerals Management Service

Essential Fish Habitat Boundaries:

North Pacific Fishery Management Council
Pacific Fishery Management Council
South Atlantic Fishery Management Council

Data sets used with permission.
Available from MCBI by request.

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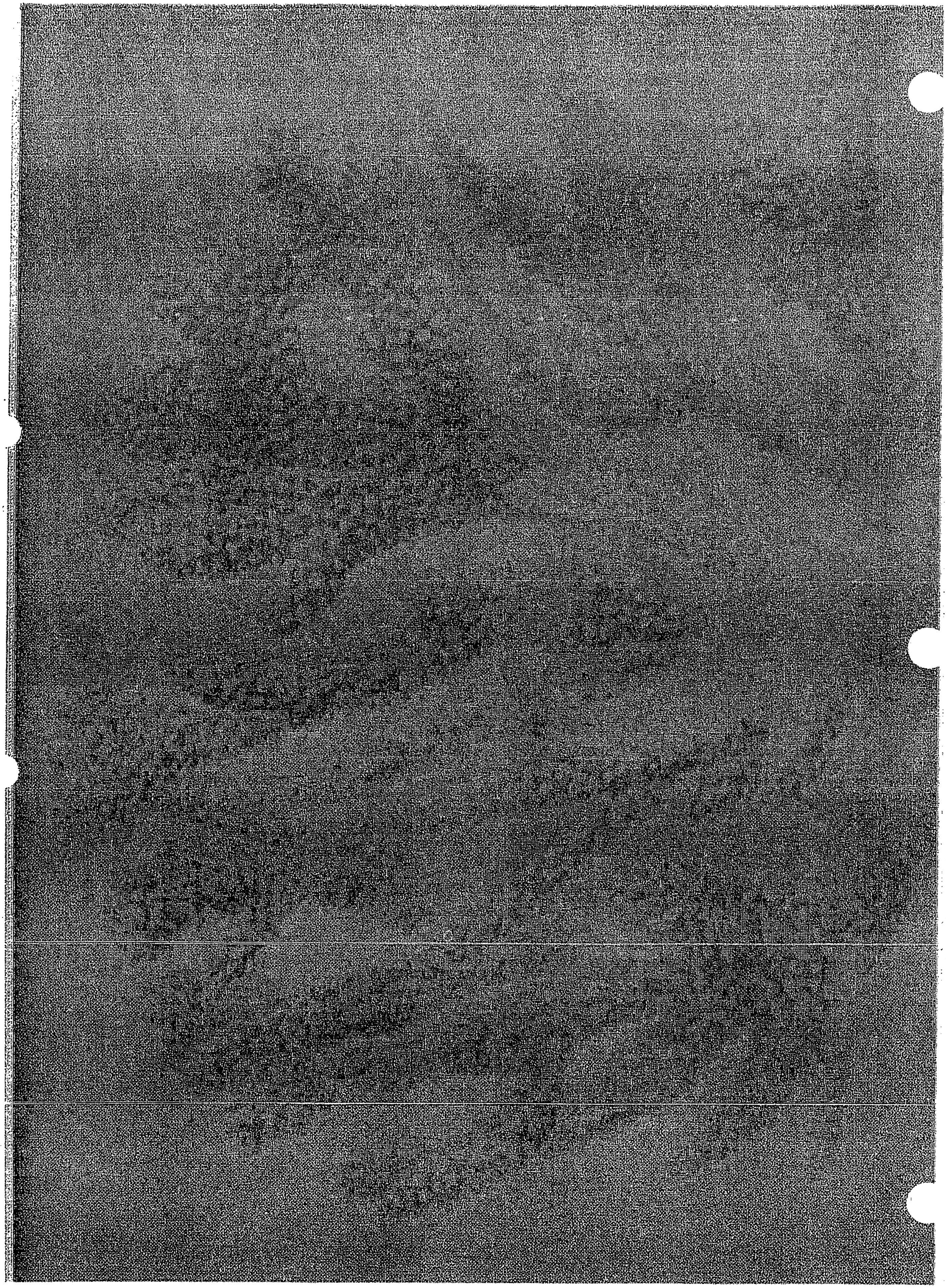

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Reefs of the Deep: The Biology and Geology of Cold-Water Coral Ecosystems

J. Murray Roberts,[1] Andrew J. Wheeler,[2] André Freiwald[3]

Coral reefs are generally associated with shallow tropical seas; however, recent deep-ocean exploration using advanced acoustics and submersibles has revealed unexpectedly widespread and diverse coral ecosystems in deep waters on continental shelves, slopes, seamounts, and ridge systems around the world. Advances reviewed here include the use of corals as paleoclimatic archives and their biogeological functioning, biodiversity, and biogeography. Threats to these fragile, long-lived, and rich ecosystems are mounting: The impacts of deep-water trawling are already widespread, and effects of ocean acidification are potentially devastating.

Cold-water corals have been known since the 18th century. Only recently, as fishery and oil exploration activities in deeper waters have increased, have developments in acoustic survey techniques and access to submersibles revealed the scale and abundance of cold-water coral ecosystems (*1*, *2*). Corals occur individually, as isolated colonies, in small patch reefs several meters across, or they form large reefs and giant carbonate mounds up to 300 m high and several kilometers in diameter over many thousands to millions of years. Because of their age and growth rates, reefs contain high-resolution records of long-term climate change and may also be important speciation centers in the deep sea. Recent research suggests a coupling between the reef fauna and surface productivity, with reef development controlled by the interplay of local hydrography and sedimentary dynamics.

Corals, Reefs, and Carbonate Mounds

Cold-water corals are cnidarians encompassing stony corals (Scleractinia), soft corals (Octocorallia, including "precious" corals, gorgonian sea fans, and bamboo corals), black corals (Antipatharia), and hydrocorals (Stylasteridae) (Fig.1). They are azooxanthellate (i.e., lacking symbiotic dinoflagellates) and often form colonies supported by a common skeleton, providing structural habitat for other species. Here we focus on scleractinian reef framework–forming species. Gorgonian and antipatharian corals, although not reef-forming, can develop dense assemblages that form important structural habitats (Fig. 1). These are mostly outside the scope of this review, although their value as paleoclimatic archives is discussed below.

Species, habitats, and ecosystems discussed here are distinct from those of tropical coral reefs and are specifically associated with colder conditions, often in deep offshore waters (*3*). Reefs and mounds tend to cluster in "provinces," where specific hydrodynamic and food supply conditions favor coral growth. Some provinces are characterized by small mound features; e.g., the Darwin Mounds in the northern Rockall Trough (*4*, *5*), or giant bonate mounds where reefs have bee repeatedly established since the Late Pliocene/Pleistocene; e.g., in the Porcupine Seabight, NE Atlantic (*6*, *7*).

Reef Distribution, Genesis, and Development

Cold-water corals are largely restricted to oceanic waters and temperatures between 4° and 12°C. These conditions are generally found in relatively shallow waters (~50 to 1000 m) at high latitudes, and at great depths (up to 4000 m) beneath warm water masses at low latitudes. Approximately 800 species of reef-building scleractinians are described in shallow waters, yet fewer than 10 are known to make substantial deep-water reef frameworks (*1*, *8*). Of these, we have an incomplete view of their global distribution (Fig. 2), which remains skewed by the geographically varied levels of research activity and the bias of deep-water mapping initiatives to the developed world. Despite this, some intriguing patterns in their global biogeography are becoming evident. Cold-water scleractinian species diversity is highest around the Philippines, with global distribution influ-

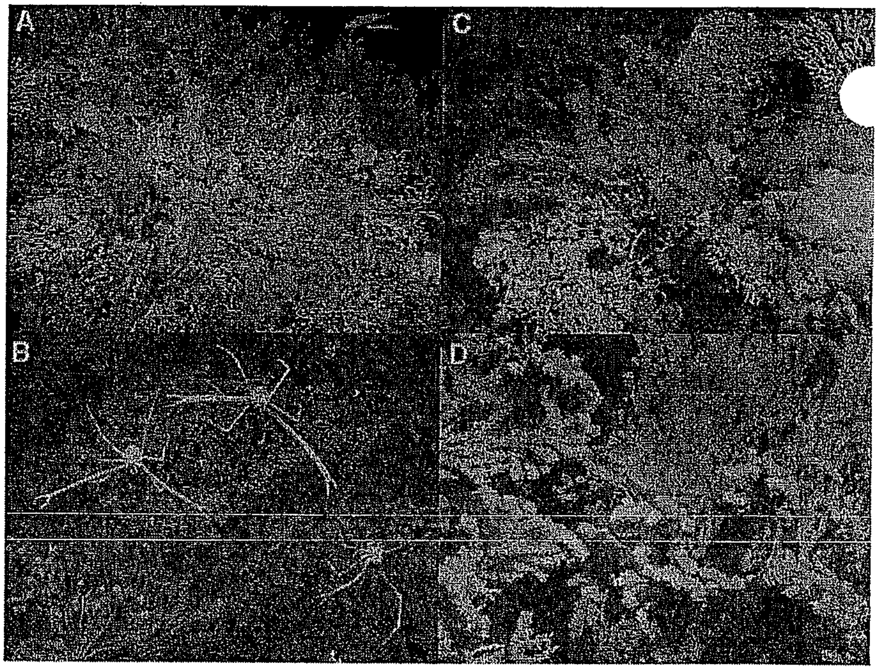

Fig. 1. Cold-water coral reef fauna. (**A**) Sloping flank of the Galway carbonate mound colonized by scleractinian and gorgonian corals and glass sponges. (**B**) Currently undescribed antipatharian coral (*Leiopathes* sp., pers. comm. D. Opresko) and associated anomuran crustaceans from the Twin Mounds, Porcupine Bank (NE Atlantic). [Images courtesy Alfred-Wegener-Institut für Polar und Meeresforschung and Institut Français de Recherche pour l'Exploitation de la Mer] (**C**) Diverse coral and sponge fauna recently discovered off the Aleutian Islands. [Image courtesy of A. Lindner, National Oceanic and Atmospheric Administration (NOAA) Fisheries] (**D**) Sharpchin rockfish (*Sebastes* sp.) among gorgonian corals (*Primnoa* sp.) in the Gulf of Alaska (N Pacific). [Image courtesy of V. O'Connell, Alaska Department of Fish and Game]

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enced by seawater carbonate chemistry (*9*). Recent work shows a striking relationship between the number of cold-water scleractinian occurrences and the depth of the aragonite saturation horizon (ASH). This may help explain the abundance of coral records in the NE Atlantic, where the ASH is >2000 m deep, compared with the paucity of records from the N Pacific, where the ASH is as shallow as 50 to 600 m and the coral fauna is dominated by octocorals and stylasterids (*9*, *10*).

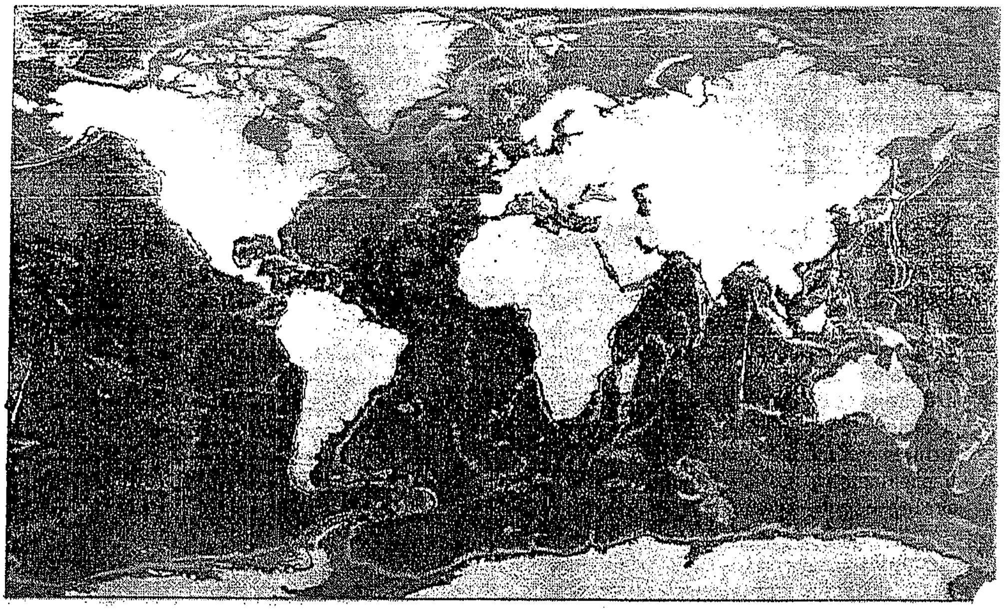

Fig. 2. Current global distribution of reef framework–forming cold-water corals [modified from (*1*)].

Reefs develop after an initial settlement of a coral larva to a hard substratum. As a coral grows, polyps in older portions die, and the skeleton becomes increasingly vulnerable to bioeroders (notably, clionid sponges) and mechanical breakage. Bioeroded skeletons may break, fall to the seabed, and extend the perimeter of the reef patch. These processes are fundamental in creating the reef framework that, over time, baffles and traps mobile sediment. Provided that coral growth keeps pace with sediment infill, localized mound formation is initiated (*11*, *12*). The development of deep-water reef mounds and their colonization can be thought of in a cyclical sense, with the associated community predicted to vary with the stage of reef development and available microhabitats (Fig. 3).

Lophelia pertusa reefs on the Norwegian shelf and carbonate mounds in the Porcupine Seabight were thought to be related to light hydrocarbon seepage, a concept later developed into a hydraulic theory of cold-water coral reef development (*13*). However, isotopic compositions of coral skeleton and tissue are not compatible with a seepage-based food chain (*14*), and although some reefs are reported close to seeps and pockmarks, many, if not most, are not. In May 2005, the International Ocean Drilling Program (IODP) Expedition 307 drilled to the base of the Challenger Mound in the Porcupine Seabight and found no gas accumulation beneath or within the mound and no evidence that mound growth was initiated by hydrocarbon seepage (*7*). Conversely, mound growth appears to be initiated at several sites over a wide area upon an unconformity followed by a rapid period of mound growth and coalescence. We believe this may indicate that clusters of small mounds may, over time and under favorable environmental conditions, form giant carbonate mounds.

Trophic Dynamics

Unlike the predictions of the hydraulic theory, recent research shows that cold-water corals are fueled by primary productivity in surface waters and subsequent food transport to the sea floor (*14*). Corals are frequently reported from sites with locally accelerated currents, or from areas of the continental slope where internal tidal waves enhance seabed food supply. Around topographic highs, such as the Porcupine Bank in the NE Atlantic, currents trap nutrient-rich waters above the bank that, under certain conditions of bottom slope and density stratification, may drain slowly off-slope through the benthic boundary layer (Ekman drainage) and supply food to the coral reefs associated with large carbonate mounds on its slopes (*15*). Recent studies in the Darwin Mounds found fresh labile material, including lipids and polyunsaturated fatty acids, present at depths of almost 1 km (*16*). Coral lipid and nitrogen isotope compositional analysis suggests that *L. pertusa* and *Madrepora oculata* rely predominantly on a zooplankton diet; but compared with *M. oculata*, *L. pertusa* is enriched in monounsaturated fatty acids and $\delta^{15}N$, has far larger polyps, and has been seen capturing live zooplankton in the field. It is therefore possible that these two species adopt different feeding strategies, although species-specific metabolic differences cannot be ruled out (*17*). Recent work on shallow-water scleractinians reinforces the view that corals are cosmopolitan consumers able to feed from suspended sediments, dissolved organic matter, bacteria, protozoans, and both zoo- and phytoplankton (*18*). Detrital and resuspended materials are likely to be important food sources for corals in deep waters. Sediment-trap studies show that phytodetritus, fecal pellets, and zooplankton were the most substantial sources of particulate carbon available to cold-water coral communities on Galicia Bank in the NE Atlantic (*14*). Although currently unquantified, diurnally migrating zooplankton and over-wintering populations of calanoid copepods are likely to be ecologically important prey items.

Reproductive Ecology and Population Genetics

Little is known about the reproduction of cold-water corals, despite its fundamental importance. Most shallow-water scleractinians are hermaphrodites, but the majority of cold-water corals studied to date are gonochoristic (have separate sexes). Seasonally enhanced food flux associated with spring phytoplankton blooms greatly influences benthic carbon flux and reproductive periodicity in deep-sea fauna. In the NE Atlantic, it seems that gamete production in *L. pertusa* follows phytodetrital food fall, and this species is likely to spawn before the following spring (*19*).

The application of molecular tools to cold-water coral populations is a powerful approach to elucidate taxonomic and systematic relationships. For example, ribosomal RNA (rRNA) sequencing suggests that *M. oculata* may have been historically misclassified (*20*). The degree of reef connectivity can also be examined by using a molecular approach. Microsatellite and ribosomal internal transcribed spacer (ITS) sequence analyses indicate that *L. pertusa* is not a panmictic population in the NE Atlantic but seems to form discrete fjord and shelf populations (*21*). In the Darwin Mounds, microsatellite analysis shows that the coral population is clonal (*21*), and a histological study found no reproductive corals (*22*). In the Pacific Ocean, microsatellite studies suggest that the precious gorgonian coral *Corallium* *lauuense* is suffering inbreeding depression on Hawaiian seamounts, perhaps because of fishing pressure for its skeleton, which is used in jewelry making (*23*). Such information is vital to develop conservation policies, and we anticipate major advances in this area in the coming years as more genetic markers are developed and applied.

Biodiversity and Endemism

Cold-water corals are arguably the most three-dimensionally complex habitats in the deep ocean, providing niches for many species. For example, we know that over 1300 species have been found living on *L. pertusa* reefs in the NE Atlantic (*24*). Their biodiversity may be comparable to that found on tropical coral reefs, but few quantitative studies allowing regional comparisons have been made. We understand little of the functional relationships between species on cold-water coral reefs, and the reefs' importance as a fish habitat is unclear (*8*).

We also understand little of the connectivity between reef provinces. Seamounts trap ocean currents producing localized circulation patterns. Under these conditions, larvae could be retained, which would limit species' dispersal, promote local adaptation, and potentially enhance rates of speciation (*25*). Although very few of the estimated 30,000 to 50,000 seamounts have been studied, species endemism appears to be high. For example, up to 34% of species on SW Pacific seamounts were newly discovered and potentially endemic. Because there were few common species between seamounts in this region, it is possible that, especially along ridge systems, seamounts may be analogous to island groups (*26*). Cold-water coral reefs are frequently reported from seamounts; therefore, given their species diversity, propensity to localized circulation patterns, and longevity, cold-water coral reefs may be major speciation centers.

Longevity and Paleoclimatic Archives

Cold-water coral reef and mound development in the NE Atlantic reflect environmental change over geological time scales corresponding to recurrent glacial cycles. In northern Europe, Scandinavian reefs date from the Holocene after the retreat of the Pleistocene ice sheet ~10,000 to 14,000 years ago. Stratigraphic studies from the giant carbonate mounds off Ireland show pronounced depositional cycles of coral-rich and hemipelagic sedimentation associated with glacial-interglacial periods extending back to at least the early Pleistocene, albeit with substantial hiatuses (*7*, *12*). In the Mediterranean Sea, off NW Africa, and on the mid-Atlantic ridge beyond the southern limit of the ice sheets, U/Th dating suggests continuous cold-water coral growth over the last 50,000 years (*27*). Given that reef framework–forming corals such as *L. pertusa* cannot survive in water masses <4°C but can rapidly colonize new anthropogenic substrata (*28*), it seems likely that high-latitude reefs have repeatedly diminished during glacial periods and flourished during interglacial periods. This would limit their potential role as speciation centers. Conversely, we suggest that coral ecosystems at lower latitudes, especially those on seamounts where biodiversity and endemism are known to be high, are likely to be important speciation centers and glacial refugia in the deep sea.

Given their longevity over geological time scales, cosmopolitan distributions, and banded skeletal structure, cold-water corals are important paleo-environmental archives. There are two broad categories of studies: (i) those that estimate past seawater temperatures from skeletal chemistry and (ii) those that follow the ventilation history of the ocean by dating skeletal material. Both are fundamental in reconstructing climate history.

Stable oxygen isotopes from biogenic carbonates have been used for many years to estimate paleo-seawater temperatures and salinities. However, scleractinian coral skeletons do not form in isotopic equilibrium with seawater, and in azooxanthellate corals, stable isotopes of oxygen and carbon are strongly correlated. These kinetic effects may relate to the rate of coral calcificat that is probably driven by seasonal fac notably, annual phytodetrital deposition ([illegible]). Despite this, stable isotopes from cold-water corals have been used to derive seawater temperatures (*30*). Interpreting chronologies from scleractinian framework-forming species like *L. pertusa* is complicated by cryptic banding patterns and complex skeletal morphologies, even though they are widespread and well-preserved in the fossil record. Recent work on *Enallopsammia rostrata* shows that even though the banding pattern is not annual, it may be possible to interpret annual chronology using ^{210}Pb as a time proxy (*31*). There is now good evidence that the tree-like stems of cold-water octocorals are annually banded (*32*), unlike *E. rostrata*, and Mg/Ca ratio analysis of gorgonian and bamboo corals has yielded convincing paleo-temperatures (*33*, *34*).

Shifts in deep-ocean circulation patterns profoundly affect global climate, and there is now

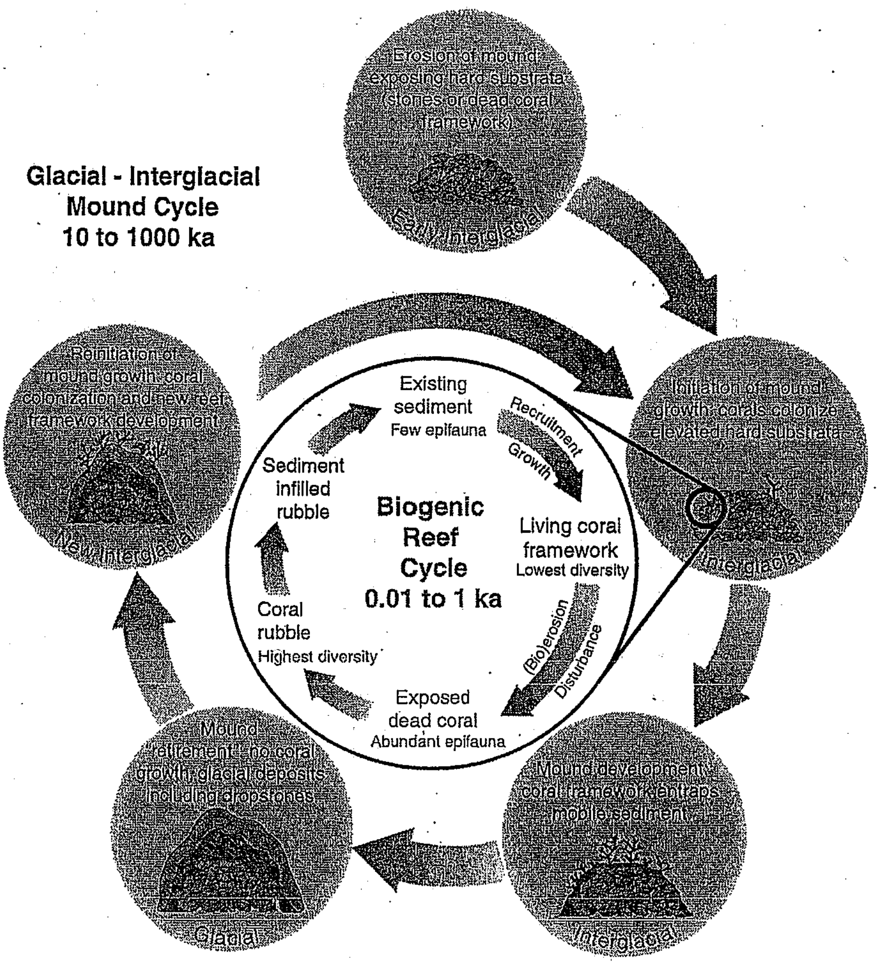

Fig. 3. Schematic illustration showing the following: **(Outer circle)** Cyclic stages of carbonate mound growth from initiation, development, retirement, and recolonization. **(Inner circle)** Smaller scale cycle of reef microhabitats, succession, and faunal diversity.

evidence that cold-water corals have recorded these oceanic shifts in their skeletons. Because U/Th dating yields coral age and ^{14}C dating provides coral age plus the age of the inorganic carbon in seawater, complementary U/Th and ^{14}C studies infer the age of the seawater in which the coral grew (*35*). Adkins *et al.* (*36*) suggest that the solitary coral *Desmophyllum cristagalli* experienced shoaling of "young," low-nutrient North Atlantic deep water and replacement with "old," high-nutrient southern source water. Shoaling of more than 200 m occurred very rapidly, i.e., during the coral's 160-year lifetime, and coincided with the transition to the Bølling-Allerød warming period. This approach has now been used to study ventilation histories in the Southern Ocean (*37*) and North Atlantic (*38*).

Threats

Although we are only now starting to realize the ubiquity of cold-water coral reefs, their biodiversity, and value as paleoclimatic resources, human activities threaten these ecosystems in three ways: (i) bottom trawling causes damage, (ii) hydrocarbon drilling and seabed mining have potential impacts, and (iii) ocean acidification has potentially severe effects on calcifying reef fauna.

There is global evidence that these habitats have been damaged by trawling for deep-water fish, causing severe physical damage from which recovery to former reef status will take several hundreds or thousands of years, if at all (Fig. 4) (*1*, *39*–*41*). Several nations, including Canada, Norway, UK, and USA, have responded by closing cold-water coral habitats to bottom fishing. Beyond territorial waters on the High Seas, no individual nation has jurisdiction, and any conservation measures would need to be developed using the United Nations Convention on the Law of the Sea (*1*).

Compared with widespread evidence for physical damage to reef structures from bottom trawling, there is little evidence that hydrocarbon exploitation substantially threatens cold-water coral ecosystems. *L. pertusa* colonizes North Sea oil platforms and seems to have formed a self-seeding population, despite proximity to drilling discharges (*42*). Greatest concern is over the potential for drill cuttings to smother reef fauna (*43*), but such effects would be highly localized when compared with the extent of seabed affected by bottom trawling. To date, there has been little interest in mining the rich mineral deposits found in some seamounts and along oceanic ridge systems. However, mining activities risk causing local extinctions on seamounts supporting endemic species.

Perhaps the most insidious threat to cold-water coral reef ecosystems is from ocean acidification. There is general consensus that atmospheric carbon dioxide levels are rising sharply, and modeled scenarios suggest that this could cause the greatest increase in ocean acidification over the last 300 million years (*44*). Current research predicts that tropical coral calcification would be reduced by up to 54% if atmospheric carbon dioxide doubled (*45*). There have been no studies to examine these effects on cold-water corals, but given the lowered carbonate saturation state at higher latitudes and deeper waters, these species may be even more vulnerable. In addition to the effect acidification could have on coral calcification, modeling studies predict that the depth at which aragonite dissolves could shallow by several hundred meters, thereby raising the prospect that areas once suitable for cold-water coral growth will become inhospitable (*10*, *45*, *46*).

Conclusions

This Review highlights recent major advances in our understanding of cold-water coral ecosystems after intensified research efforts across the biological and geological sciences. Of particular importance are studies into paleoclimatic archives, biodiversity, and habitat destruction. Emerging concepts are the importance of cold-water coral reefs as speciation centers and deep-water glacial refugia, major threats posed by the impacts of ocean acidification, and evidence confirming hydrodynamic biogeological carbonate mound growth processes. We expect to see continued advances in many areas, particularly reproductive and genetic studies, biodiversity, biogeography, species interaction, and ecological studies where time series of data are required. Sea floor observatories are anticipated to play an important future role (*47*).

Despite the inherent difficulties of studying these habitats, there is an urgent need for sound information on which to base long-term management plans. Bottom trawling, often on the High Seas, has damaged cold-water coral ecosystems, and we do not understand the long-term implications of ocean acidification. The vast majority of cold-water coral reef studies so far are from the developed world; therefore, a need exists to transfer expertise in deep-water surveys to the developing world and to begin unified ocean basin–scale comparisons if we are to appreciate the global connectivity and importance of these reefs of the deep.

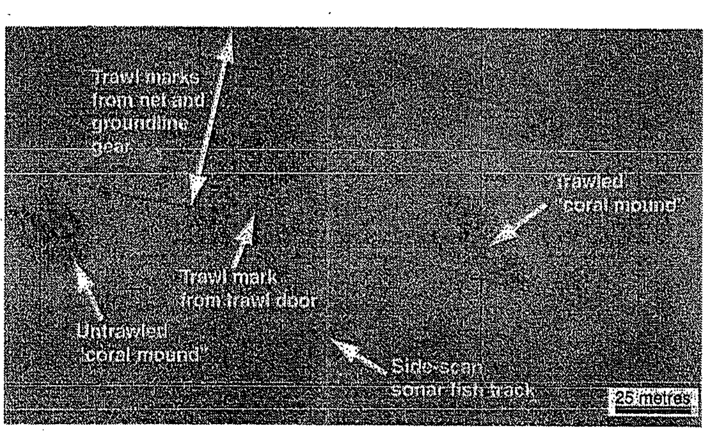

Fig. 4. Side-scan sonograph showing trawl damage to the Darwin Mounds at almost 1-km water depth in the Rockall Trough (NE Atlantic). Reduced backscatter (lighter tones) from the trawl-damaged mound strongly suggests decreased coral abundance [modified from (*5*)].

References and Notes

1. A. Freiwald, J. H. Fosså, A. Grehan, T. Koslow, J. M. Roberts, *Cold-Water Coral Reefs* (United Nations Environment Programme–World Conservation Monitoring Centre, Cambridge, 2004).
2. J. M. Roberts, C. J. Brown, D. Long, C. R. Bates, *Coral Reefs* 24, 654 (2005).
3. The terms "cold water," "deep water," or "deep sea" have all been used to discriminate these corals from shallow, warm-water tropical species. Depth-based definitions are inadequate, because cold-water corals have wide depth distributions, e.g., *L. pertusa* occurs at depths of 40 m in fjords to over 3000 m in the open ocean. Confusion exists over whether cold-water corals form reefs. Biogenic cold-water coral reefs are frameworks produced by scleractinian corals that alter sediment deposition, provide structural habitat, and are subject to dynamic processes of growth and (bio)erosion. Cold-water coral carbonate mounds are larger structures formed by successive periods of coral reef development, sedimentation, and (bio)erosion. They may or may not support contemporary reefs and are referred to as active or retired mounds, respectively (*11*).
4. D. G. Masson *et al.*, *Mar. Geol.* 194, 159 (2003).
5. A. J. Wheeler, B. J. Bett, D. S. M. Billett, D. G. Masson, D. Mayor, in *Benthic Habitats and the Effects of Fishing*, P. W. Barnes, J. P. Thomas, Eds. (American Fisheries Society, Maryland, 2005), pp. 807–817.
6. N. H. Kenyon *et al.*, *Mar. Geol.* 195, 5 (2003).
7. Expedition Scientists, *Tech. Rep. IODP Prel. Rept.* 307, 10.2204/iodp.pr.307.2005 (2005).
8. Additional information is available as supporting material on *Science* Online.
9. S. D. Cairns, unpublished data.
10. J. M. Guinotte *et al.*, *Front. Ecol. Environ.* 4, 141 (2006).
11. V. A. I. Huvenne *et al.*, in *Cold-Water Corals and Ecosystems*, A. Freiwald, J. M. Roberts, Eds. (Springer, Berlin, 2005), pp. 535–569.
12. B. Dorschel, D. Hebbeln, A. Rüggeberg, W.-C. Dullo, A. Freiwald, *Earth Planet. Sci. Lett.* 233, 33 (2005).
13. M. Hovland, M. Risk, *Mar. Geol.* 198, 83 (2003).
14. G. C. A. Duineveld, M. S. S. Lavaleye, E. M. Berghuis, *Mar. Ecol. Prog. Ser.* 277, 13 (2004).
15. M. White, C. Mohn, H. de Stigter, G. Mottram, in *Cold-Water Corals and Ecosystems*, A. Freiwald, J. M. Roberts, Eds. (Springer, Berlin, 2005), pp. 503–514.
16. K. Kiriakoulakis, B. J. Bett, M. White, G. A. Wolff, *Deep Sea Res.* 51, 1937 (2004).
17. K. Kiriakoulakis *et al.*, in *Cold-Water Corals and Ecosystems*, A. Freiwald, J. M. Roberts, Eds. (Springer, Berlin, 2005), pp. 715–729.
18. K. R. N. Anthony, K. E. Fabricius, *J. Exp. Mar. Biol. Ecol.* 252, 221 (2000).
19. R. G. Waller, in *Cold-Water Corals and Ecosystems*, A. Freiwald, J. M. Roberts, Eds. (Springer, Berlin, 2005), pp. 691–700.

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20. M. C. Le Goff-Vitry, A. D. Rogers, D. Baglow, *Mol. Phylogenet. Evol.* 30, 167 (2004).
21. M. C. Le Goff-Vitry, O. G. Pybus, A. D. Rogers, *Mol. Ecol.* 13, 537 (2004).
22. R. G. Waller, P. A. Tyler, *Coral Reefs* 24, 514 (2005).
23. A. R. Baco, T. M. Shank, in *Cold-Water Corals and Ecosystems*, A. Freiwald, J. M. Roberts, Eds. (Springer, Berlin, 2005), pp. 663–678.
24. Species lists from cold-water reefs along the NW European margin studied during the European Atlantic Coral Ecosystem Study (ACES) were compiled from Galicia Bank, the Porcupine Seabight, Darwin Mounds, Kosterfjord, and the Sula Ridge. In total, 1317 species were listed. The lists reflected differing sampling methodology and taxonomic expertise, and further work to characterize the high faunal diversity of NE Atlantic cold-water coral reefs is on-going (www.eu-hermes.net) (*8*).
25. A. D. Rogers, *Adv. Mar. Biol.* 30, 305 (1994).
26. B. Richer de Forges, J. A. Koslow, G. C. B. Poore, *Nature* 405, 944 (2000).
27. A. Schröder-Ritzrau, A. Freiwald, A. Mangini, in *Cold-Water Corals and Ecosystems*, A. Freiwald, J. M. Roberts, Eds. (Springer, Berlin, 2005), pp. 157–172.
28. J. M. Roberts, D. Long, J. B. Wilson, P. B. Mortensen, J. D. Gage, *Mar. Pollut. Bull.* 46, 7 (2003).
29. B. Spiro, M. Roberts, J. Gage, S. Chenery, *Rapid Commun. Mass Spectrom.* 14, 1332 (2000).
30. J. E. Smith, H. P. Schwarcz, M. J. Risk, T. A. McConnaughey, N. Keller, *Palaios* 15, 25 (2000).
31. J. F. Adkins, G. M. Henderson, S.-L. Wang, S. O'Shea, F. Mokadem, *Earth Planet. Sci. Lett.* 227, 481 (2004).
32. O. A. Sherwood, D. B. Scott, M. J. Risk, T. P. Guilderson, *Mar. Ecol. Prog. Ser.* 301, 129 (2005).
33. O. A. Sherwood *et al.*, in *Cold-Water Corals and Ecosystems*, A. Freiwald, J. M. Roberts, Eds. (Springer, Berlin, 2005), pp. 1061–1079.
34. R. Thresher *et al.*, *Geophys. Res. Lett.* 31, L07212 (2004).
35. A. Mangini, M. Lomitschka, R. Eichstädter, N. Frank, S. Vogler, *Nature* 392, 347 (1998).
36. J. F. Adkins, H. Cheng, E. A. Boyle, E. R. M. Druffel, R. L. Edwards, *Science* 280, 725 (1998).
37. S. J. Goldstein, D. W. Lea, S. Chakraborty, M. Kashgarian, M. T. Murrell, *Earth Planet. Sci. Lett.* 193, 167 (2001).
38. A. Schröder-Ritzrau, A. Mangini, M. Lomitschka, *Earth Planet. Sci. Lett.* 216, 399 (2003).
39. J. H. Fosså, P. B. Mortensen, D. M. Furevik, *Hydrobiologia* 471, 1 (2002).
40. J. M. Hall-Spencer, V. Allain, J. H. Fosså, *Proc. R. Soc. London Ser. B* 269, 507 (2002).
41. J. A. Koslow *et al.*, *Mar. Ecol. Prog. Ser.* 213, 111 (2001).
42. S. E. Gass, J. M. Roberts, *Mar. Pollut. Bull.*, in press (10.1016/j.marpolbul.2005.10.002).
43. A. D. Rogers, *Int. Rev. Hydrobiol.* 84, 315 (1999).
44. K. Caldeira, M. E. Wickett, *Nature* 425, 365 (2003).
45. The Royal Society, "Ocean Acidification due to Increasing Atmospheric Carbon Dioxide" (Policy document 12/05, ISBN 0 85403 617 2, London, 2005).
46. J. C. Orr *et al.*, *Nature* 437, 681 (2005).
47. J. M. Roberts *et al.*, in *Cold-Water Corals and Ecosys* A. Freiwald, J. M. Roberts, Eds. (Springer, Berlin, 20), pp. 483–502.
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Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms

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Today's surface ocean is saturated with respect to calcium carbonate, but increasing atmospheric carbon dioxide concentrations are reducing ocean pH and carbonate ion concentrations, and thus the level of calcium carbonate saturation. Experimental evidence suggests that if these trends continue, key marine organisms—such as corals and some plankton—will have difficulty maintaining their external calcium carbonate skeletons. Here we use 13 models of the ocean-carbon cycle to assess calcium carbonate saturation under the IS92a 'business-as-usual' scenario for future emissions of anthropogenic carbon dioxide. In our projections, Southern Ocean surface waters will begin to become undersaturated with respect to aragonite, a metastable form of calcium carbonate, by the year 2050. By 2100, this undersaturation could extend throughout the entire Southern Ocean and into the subarctic Pacific Ocean. When live pteropods were exposed to our predicted level of undersaturation during a two-day shipboard experiment, their aragonite shells showed notable dissolution. Our findings indicate that conditions detrimental to high-latitude ecosystems could develop within decades, not centuries as suggested previously.

Ocean uptake of CO_2 will help moderate future climate change, but the associated chemistry, namely hydrolysis of CO_2 in seawater, increases the hydrogen ion concentration $[H^+]$. Surface ocean pH is already 0.1 unit lower than preindustrial values. By the end of the century, it will become another 0.3–0.4 units lower[1,2] under the IS92a scenario, which translates to a 100–150% increase in $[H^+]$. Simultaneously, aqueous CO_2 concentrations $[CO_2(aq)]$ will increase and carbonate ion concentrations $[CO_3^{2-}]$ will decrease, making it more difficult for marine calcifying organisms to form biogenic calcium carbonate ($CaCO_3$). Substantial experimental evidence indicates that calcification rates will decrease in low-latitude corals[3–5], which form reefs out of aragonite, and in phytoplankton that form their tests (shells) out of calcite[6,7], the stable form of $CaCO_3$. Calcification rates will decline along with $[CO_3^{2-}]$ owing to its reaction with increasing concentrations of anthropogenic CO_2 according to the following reaction:

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^- \qquad (1)$$

These rates decline even when surface waters remain supersaturated with respect to $CaCO_3$, a condition that previous studies have predicted will persist for hundreds of years[4,8,9].

Recent predictions of future changes in surface ocean pH and carbonate chemistry have primarily focused on global average conditions[1,2,10] or on low latitude regions[4], where reef-building corals are abundant. Here we focus on future surface and subsurface changes in high latitude regions where planktonic shelled pteropods are prominent components of the upper-ocean biota in the Southern Ocean, Arctic Ocean and subarctic Pacific Ocean[11–15]. Recently, it has been suggested that the cold surface waters in such regions will begin to become undersaturated with respect to aragonite only when atmospheric CO_2 reaches 1,200 p.p.m.v., more than four times the preindustrial level ($4 \times CO_2$) of 280 p.p.m.v. (ref. 9). In contrast, our results suggest that some polar and subpolar surface waters will become undersaturated at $\sim 2 \times CO_2$, probably within the next 50 years.

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Changes in carbonate

We have computed modern-day ocean carbonate chemistry from observed alkalinity and dissolved inorganic carbon (DIC), relying on data collected during the CO_2 Survey of the World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Study (JGOFS). These observations are centred around the year 1994, and have recently been provided as a global-scale, gridded data product GLODAP (ref. 16; see Supplementary Information). Modern-day surface $[CO_3^{2-}]$ varies meridionally by more than a factor of two, from average concentrations in the Southern Ocean of 105 μmol kg^{-1} to average concentrations in tropical waters of 240 μmol kg^{-1} (Fig. 1). Low $[CO_3^{2-}]$ in the Southern Ocean is due to (1) low surface temperatures and CO_2-system thermodynamics, and (2) large amounts of upwelled deep water, which contain high $[CO_2(aq)]$ from organic matter remineralization. These two effects reinforce one another, yielding a high positive correlation of present-day $[CO_3^{2-}]$ with temperature (for example, $R^2 = 0.92$ for annual mean surface maps). Changes in $[CO_3^{2-}]$ and $[CO_2(aq)]$ are also inextricably linked to changes in other carbonate chemistry variables (Supplementary Fig. S1).

We also estimated preindustrial $[CO_3^{2-}]$ from the same data, after subtracting data-based estimates of anthropogenic DIC (ref. 17) from the modern DIC observations and assuming that preindustrial and modern alkalinity fields were identical (see Supplementary Information). Relative to preindustrial conditions, invasion of anthropogenic CO_2 has already reduced modern surface $[CO_3^{2-}]$ by more than 10%, that is, a reduction of 29 μmol kg^{-1} in the tropics and 18 μmol kg^{-1} in the Southern Ocean. Nearly identical results were found when, instead of the data-based anthropogenic CO_2 estimates, we used simulated anthropogenic CO_2, namely the median from 13 models that participated in the second phase of the Ocean Carbon-Cycle Model Intercomparison Project, or OCMIP-2 (Fig. 1c).

To quantify future changes in carbonate chemistry, we used simulated DIC from ocean models that were forced by two atmospheric CO_2 scenarios: the Intergovernmental Panel on Climate Change (IPCC) IS92a 'continually increasing' scenario (788 p.p.m.v. in the year 2100) and the IPCC S650 'stabilization' scenario (563 p.p.m.v. in the year 2100) (Fig. 1). Simulated perturbations in DIC relative to 1994 (the GLODAP reference year) were added to the modern DIC data; again, alkalinity was assumed to be constant. To provide a measure of uncertainty, we report model results as the OCMIP median ± 2σ. The median generally outperformed

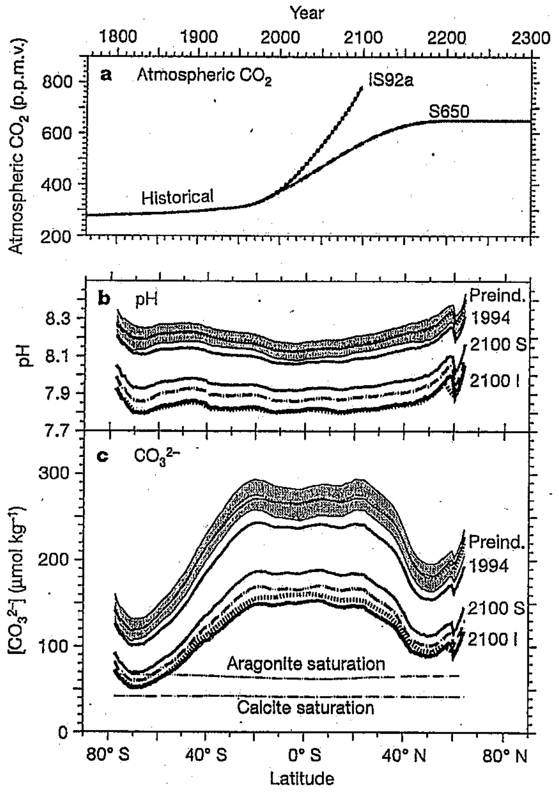

Figure 1 | Increasing atmospheric CO_2 and decreasing surface ocean pH and $[CO_3^{2-}]$. **a**, Atmospheric CO_2 used to force 13 OCMIP models over the industrial period ('Historical') and for two future scenarios: IS92a ('I' in **b** and **c**) and S650 ('S' in **b** and **c**). **b**, **c**, Increases in atmospheric CO_2 lead to reductions in surface ocean pH (**b**) and surface ocean $[CO_3^{2-}]$ (**c**). Results are given as global zonal averages for the 1994 data and the preindustrial ('Preind.') ocean. The latter were obtained by subtracting data-based anthropogenic DIC (ref. 17) (solid line in grey-shaded area), as well as by subtracting model-based anthropogenic DIC (OCMIP median, dotted line in grey-shaded area; OCMIP range, grey shading). Future results for the year 2100 come from the 1994 data plus the simulated DIC perturbations for the two scenarios; results are also shown for the year 2300 with S650 (thick dashed line). The small effect of future climate change simulated by the IPSL climate–carbon model is added as a perturbation to IS92a in the year 2100 (thick dotted line); two other climate–carbon models, PIUB-Bern and Commonwealth Scientific and Industrial Research Organisation (CSIRO), show similar results (Fig. 3a). The thin dashed lines indicating the $[CO_3^{2-}]$ for sea water in equilibrium with aragonite and calcite are nearly flat, revealing weak temperature sensitivity.

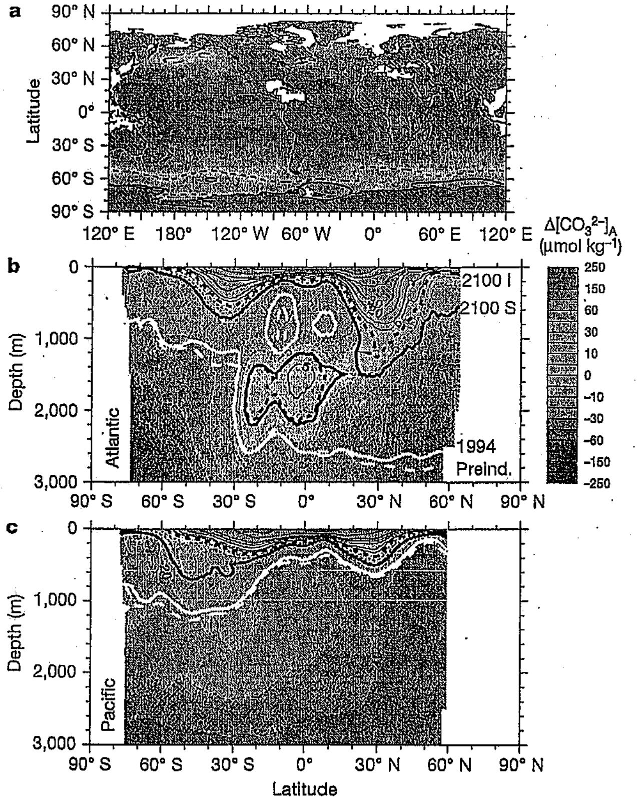

Figure 2 | The aragonite saturation state in the year 2100 as indicated by $\Delta[CO_3^{2-}]_A$. The $\Delta[CO_3^{2-}]_A$ is the *in situ* $[CO_3^{2-}]$ minus that for aragonite-equilibrated sea water at the same salinity, temperature and pressure. Shown are the OCMIP-2 median concentrations in the year 2100 under scenario IS92a: **a**, surface map; **b**, Atlantic; and **c**, Pacific zonal averages. Thick lines indicate the aragonite saturation horizon in 1765 (Preind.; white dashed line), 1994 (white solid line) and 2100 (black solid line for S650; black dashed line for IS92a). Positive $\Delta[CO_3^{2-}]_A$ indicates supersaturation; negative $\Delta[CO_3^{2-}]_A$ indicates undersaturation.

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individual models in OCMIP model–data comparison (Supplementary Fig. S2). By the year 2100, as atmospheric CO_2 reaches 788 p.p.m.v. under the IS92a scenario, average tropical surface $[CO_3^{2-}]$ declines to $149 \pm 14\,\mu mol\,kg^{-1}$. This is a 45% reduction relative to preindustrial levels, in agreement with previous predictions[4,8]. In the Southern Ocean (all waters south of 60° S), surface concentrations dip to $55 \pm 5\,\mu mol\,kg^{-1}$, which is 18% below the threshold where aragonite becomes undersaturated ($66\,\mu mol\,kg^{-1}$).

These changes extend well below the sea surface. Throughout the Southern Ocean, the entire water column becomes undersaturated with respect to aragonite. During the twenty-first century, under the IS92a scenario, the Southern Ocean's aragonite saturation horizon (the limit between undersaturation and supersaturation) shoals from its present average depth of 730 m (Supplementary Fig. S3) all the way to the surface (Fig. 2). Simultaneously, in a portion of the subarctic Pacific, the aragonite saturation horizon shoals from depths of about 120 m to the surface. In the North Atlantic, surface waters remain saturated with respect to aragonite, but the aragonite saturation horizon shoals dramatically; for example, north of 50° N it shoals from 2,600 m to 115 m. The greater erosion in the North Atlantic is due to deeper penetration and higher concentrations of anthropogenic CO_2, a tendency that is already evident in present-day data-based estimates[17,18] and in models[19,20] (Supplementary Figs S4 and S5). Less pronounced changes were found for the calcite saturation horizon. For example, in the year 2100 the average calcite saturation horizon in the Southern Ocean stays below 2,200 m. Nonetheless, in 2100 surface waters of the Weddell Sea become slightly undersaturated with respect to calcite.

In the more conservative S650 scenario, the atmosphere reaches $2 \times CO_2$ in the year 2100, 50 years later than with the IS92a scenario. In 2100, Southern Ocean surface waters generally remain slightly supersaturated with respect to aragonite. However, the models also simulate that the Southern Ocean's average aragonite saturation horizon will have shoaled from 730 m to 60 m, and that the entire water column in the Weddell Sea will have become undersaturated (Fig. 2). In the north, all surface waters remain saturated under the S650 scenario. North of 50° N, the annual average aragonite saturation horizon shoals from 140 m to 70 m in the Pacific, whereas it shoals by 2,000 m to 610 m in the North Atlantic. Therefore, under either scenario the OCMIP models simulated large changes in surface and subsurface $[CO_3^{2-}]$. Yet these models account for only the direct geochemical effect of increasing atmospheric CO_2 because they were all forced with prescribed modern-day climate conditions.

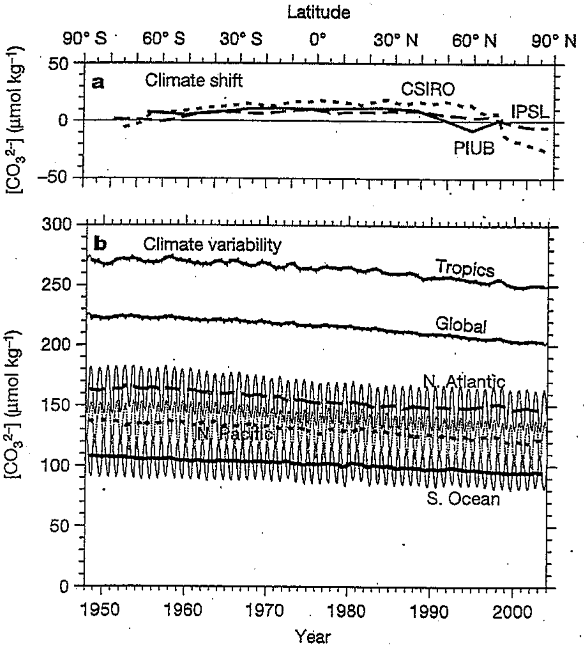

Figure 3 | Climate-induced changes in surface $[CO_3^{2-}]$. **a**, The twenty-first century shift in zonal mean surface ocean $[CO_3^{2-}]$ due to climate change alone, from three atmosphere–ocean climate models—CSIRO-Hobart (short dashed line), IPSL-Paris (long dashed line) and PIUB-Bern (solid line)—that each include an ocean carbon-cycle component (see Supplementary Information). **b**, The regional-scale seasonal and interannual variability is simulated by an ocean carbon-cycle model forced with reanalysed climate forcing.

In addition to this direct geochemical effect, ocean $[CO_3^{2-}]$ is also altered by climate variability and climate change. To quantify the added effect of future climate change, we analysed results from three atmosphere–ocean climate models that each included an ocean carbon-cycle component (see Supplementary Information). These three models agree that twenty-first century climate change will cause a general increase in surface ocean $[CO_3^{2-}]$ (Fig. 3), mainly because most surface waters will be warmer. However, the models also agree that the magnitude of this increase in $[CO_3^{2-}]$ is small, typically counteracting less than 10% of the decrease due to the geochemical effect. High-latitude surface waters show the smallest increases in $[CO_3^{2-}]$, and even small reductions in some cases. Therefore, our analysis suggests that physical climate change alone will not substantially alter high-latitude surface $[CO_3^{2-}]$ during the twenty-first century.

Climate also varies seasonally and interannually, whereas our previous focus has been on annual changes. To illustrate how climate variability affects surface $[CO_3^{2-}]$, we used results from an ocean carbon-cycle model forced with the daily National Centers for Environmental Prediction (NCEP) reanalysis fields[21] over 1948–2003 (see Supplementary Information). These fields are observationally based and vary on seasonal and interannual timescales. Simulated interannual variability in surface ocean $[CO_3^{2-}]$ is negligible when compared with the magnitude of the anthropogenic decline (Fig. 3b). Seasonal variability is also negligible except in the high latitudes, where surface $[CO_3^{2-}]$ varies by about $\pm 15\,\mu mol\,kg^{-1}$

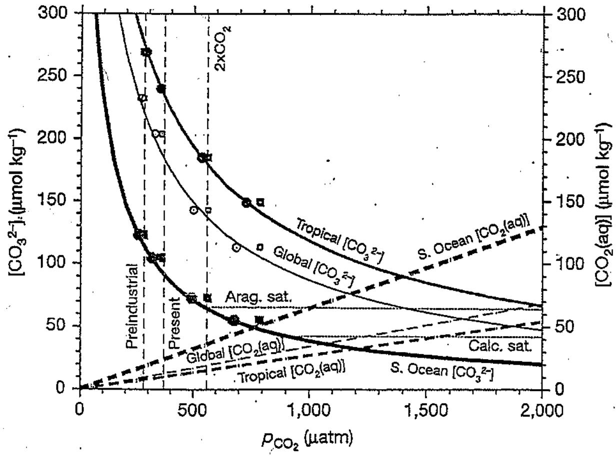

Figure 4 | Key surface carbonate chemistry variables as a function of p_{CO_2}. Shown are both $[CO_3^{2-}]$ (solid lines) and $[CO_2(aq)]$ (dashed lines) for average surface waters in the tropical ocean (thick lines), the Southern Ocean (thickest lines) and the global ocean (thin lines). Solid and dashed lines are calculated from the thermodynamic equilibrium approach. For comparison, open symbols are for $[CO_3^{2-}]$ from our non-equilibrium, model-data approach versus seawater p_{CO_2} (open circles) and atmospheric p_{CO_2} (open squares); symbol thickness corresponds with line thickness, which indicates the regions for area-weighted averages. The nearly flat, thin dotted lines indicate the $[CO_3^{2-}]$ for seawater in equilibrium with aragonite ('Arag. sat.') and calcite ('Calc. sat.').

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when averaged over large regions. This is smaller than the twenty-first-century's transient change (for example, ~50 μmol kg^{-1} in the Southern Ocean). However, high-latitude surface waters do become substantially less saturated during winter, because of cooling (resulting in higher [CO_2(aq)]) and greater upwelling of DIC-enriched deep water, in agreement with previous observations in the North Pacific[22]. Thus, high-latitude undersaturation will be first reached during winter.

Our predicted changes may be compared to those found in earlier studies, which focused on surface waters in the tropics[8] and in the subarctic Pacific[22,23]. These studies assumed thermodynamic equilibrium between CO_2 in the atmosphere and the surface waters at their *in situ* alkalinity, temperature and salinity. If, in the equilibrium approach, the p_{CO_2} is taken only to represent seawater p_{CO_2}, then the results agree with our non-equilibrium approach when the sets of carbonate chemistry constants are identical (Fig. 4). However, assuming equilibrium with the atmosphere leads to the prediction that future undersaturation will occur too soon (at lower atmospheric CO_2 levels), mainly because the anthropogenic transient in the ocean actually lags that in the atmosphere. For example, with the equilibrium approach, we predict that average surface waters in the Southern Ocean become undersaturated when atmospheric CO_2 is 550 p.p.m.v. (in the year 2050 under IS92a), whereas our non-equilibrium approach, which uses models and data, indicates that undersaturation will occur at 635 p.p.m.v. (in the year 2070). Despite these differences, both approaches indicate that the Southern Ocean surface waters will probably become undersaturated with respect to aragonite during this century. Conversely, both of these approaches disagree with a recent assessment[9] that used a variant of the standard thermodynamic equilibrium approach, where an incorrect input temperature was used inadvertently.

Uncertainties

The three coupled climate–carbon models show little effect of climate change on surface [CO_3^{2-}] (compare Fig. 3a to Fig. 1) partly because air–sea CO_2 exchange mostly compensates for the changes in surface DIC caused by changes in marine productivity and circulation. In subsurface waters where such compensation is lacking, these models could under- or over-predict how much [CO_3^{2-}] will change as a result of changes in overlying marine productivity. However, the models project a consistent trend, which only worsens the decline in subsurface [CO_3^{2-}]; that is, all coupled climate models predict increased evaporation in the tropics and increased precipitation in the high latitudes[24]. This leads to greater upper ocean stratification in the high latitudes, which in turn decreases nutrients (but not to zero) and increases light availability (owing to more shallow mixed layers). Thus, at 2 × CO_2 there is a 10% local increase in surface-to-deep export of particulate organic carbon (POC) in the Southern Ocean using the Institut Pierre Simon Laplace (IPSL)-Paris model[25]. Subsequent remineralization of this exported POC within the thermocline would increase DIC, which would only exacerbate the decrease in high-latitude subsurface [CO_3^{2-}]. For the twenty-first century, these uncertainties appear small next to the anthropogenic DIC invasion (see Supplementary Information).

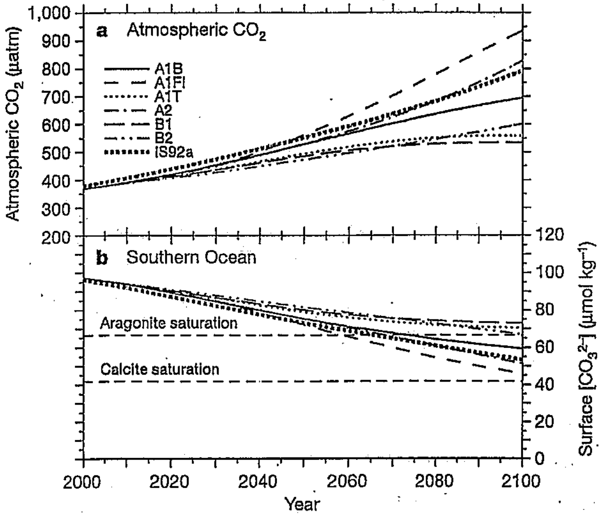

Figure 5 | Average surface [CO_3^{2-}] in the Southern Ocean under various scenarios. Time series of average surface [CO_3^{2-}] in the Southern Ocean for the PIUB-Bern reduced complexity model (see Fig. 3 and Supplementary Information) under the six illustrative IPCC SRES scenarios. The results for the SRES scenarios A1T and A2 are similar to those for the non-SRES scenarios S650 and IS92a, respectively.

The largest uncertainty by far, and the only means to limit the future decline in ocean [CO_3^{2-}], is the atmospheric CO_2 trajectory. To better characterize uncertainty due to CO_2 emissions, we compared the six illustrative IPCC Special Reports on Emission Scenarios (SRES) in the reduced complexity, Physics Institute University of Bern (PIUB)-Bern model. Under the moderate SRES B2 scenario, average Southern Ocean surface waters in that model become undersaturated with respect to aragonite when atmospheric CO_2 reaches 600 p.p.m.v. in the year 2100 (Fig. 5). For the three higher-emission SRES scenarios (A1FI, A2 and A1B), these waters become undersaturated sooner (between the years 2058 and 2073); for the two lower-emission scenarios (A1T and B1), these waters remain slightly supersaturated in 2100. Thus, if atmospheric CO_2 rises above 600 p.p.m.v., most Southern Ocean surface waters will become undersaturated with respect to aragonite. Yet, even below this level, the Southern Ocean's aragonite saturation horizon will shoal substantially (Fig. 2). For a given atmospheric CO_2 scenario, predicted changes in surface ocean [CO_3^{2-}] are much more certain than the related changes in climate. The latter depend not only on the model response to CO_2 forcing, but also on poorly constrained physical processes, such as those associated with clouds.

Ocean CO_2 uptake

With higher levels of anthropogenic CO_2 and lower surface [CO_3^{2-}], the change in surface ocean DIC per unit change in atmospheric CO_2 (μmol kg^{-1} per p.p.m.v.) will be about 60% lower in the year 2100 (under IS92a) than it is today. Simultaneously, the CO_3^{2-}/CO2(aq) ratio will decrease from 4:1 to 1:1 in the Southern Ocean (Fig. 4). These decreases are due to the well-understood anthropogenic reduction in buffer capacity[26], already accounted for in ocean carbon-cycle models.

On the other hand, reduced export of $CaCO_3$ from the high latitudes would increase surface [CO_3^{2-}], thereby increasing ocean CO_2 uptake and decreasing atmospheric CO_2. Owing to this effect, ocean CO_2 uptake could increase by 6–13 petagrams (Pg) C over the twenty-first century, based on one recent model study[27] that incorporated an empirical, CO_2-dependant relationship for calcification[7]. Rates of calcification could decline even further, to zero, if waters actually became undersaturated with respect to both aragonite and calcite. We estimate that the total shutdown of high-latitude aragonite production would lead to, at most, a 0.25 Pg C yr^{-1} increase in ocean CO_2 uptake, assuming that 1 Pg C yr^{-1} of $CaCO_3$ is exported globally[28], that up to half of that is aragonite[9,29], and that perhaps half of all aragonite is exported from the high latitudes. The actual increase in ocean CO_2 uptake could be much lower because the aragonite fraction of the $CaCO_3$ may be only 0.1 based on low-latitude sediment traps[30], and the latitudinal distribution of aragonite export is uncertain. Thus, increased CO_2 uptake from reduced export of aragonite will provide little compensation for decreases in ocean CO_2 uptake due to reductions in buffer capacity. Of greater concern are potential biological impacts due to future undersaturation.

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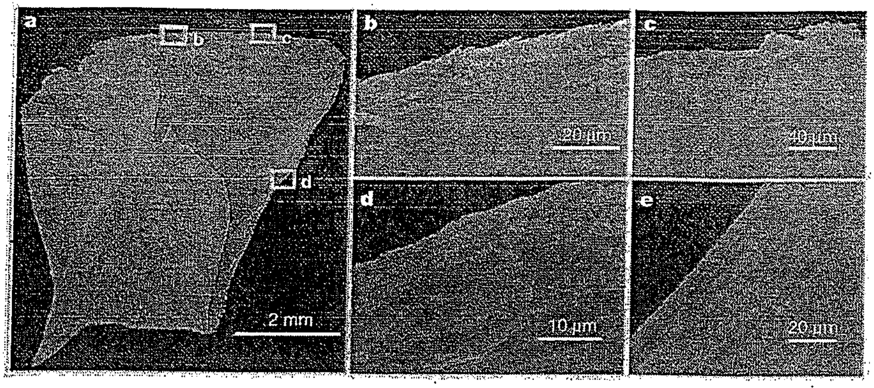

Figure 6 | Shell dissolution in a live pteropod. **a–d**, Shell from a live pteropod, *Clio pyramidata*, collected from the subarctic Pacific and kept in water undersaturated with respect to aragonite for 48 h. The whole shell (**a**) has superimposed white rectangles that indicate three magnified areas: the shell surface (**b**), which reveals etch pits from dissolution and resulting exposure of aragonitic rods; the prismatic layer (**c**), which has begun to peel back, increasing the surface area over which dissolution occurs; and the aperture region (**d**), which reveals advanced shell dissolution when compared to a typical *C. pyramidata* shell not exposed to undersaturated conditions (**e**).

Biological impacts

The changes in seawater chemistry that we project to occur during this century could have severe consequences for calcifying organisms, particularly shelled pteropods: the major planktonic producers of aragonite. Pteropod population densities are high in polar and subpolar waters. Yet only five species typically occur in such cold water regions and, of these, only one or two species are common at the highest latitudes[31]. High-latitude pteropods have one or two generations per year[12,15,32], form integral components of food webs, and are typically found in the upper 300 m where they may reach densities of hundreds to thousands of individuals per m^3 (refs 11, 13–15). In the Ross Sea, for example, the prominent subpolar–polar pteropod *Limacina helicina* sometimes replaces krill as the dominant zooplankton, and is considered an overall indicator of ecosystem health[33]. In the strongly seasonal high latitudes, sedimentation pulses of pteropods frequently occur just after summer[15,34]. In the Ross Sea, pteropods account for the majority of the annual export flux of both carbonate and organic carbon[34,35]. South of the Antarctic Polar Front, pteropods also dominate the export flux of $CaCO_3$ (ref. 36).

Pteropods may be unable to maintain shells in waters that are undersaturated with respect to aragonite. Data from sediment traps indicate that empty pteropod shells exhibit pitting and partial dissolution as soon as they fall below the aragonite saturation horizon[22,36,37]. *In vitro* measurements confirm such rapid pteropod shell dissolution rates[38]. New experimental evidence suggests that even the shells of live pteropods dissolve rapidly once surface waters become undersaturated with respect to aragonite[9]. Here we show that when the live subarctic pteropod *Clio pyramidata* is subjected to a level of undersaturation similar to what we predict for Southern Ocean surface waters in the year 2100 under IS92a, a marked dissolution occurs at the growing edge of the shell aperture within 48 h (Fig. 6). Etch pits formed on the shell surface at the apertural margin (which is typically ~7-µm-thick) as the <1-µm exterior (prismatic layer) peeled back (Fig. 6c), exposing the underlying aragonitic rods to dissolution. Fourteen individuals were tested. All of them showed similar dissolution along their growing edge, even though they all remained alive. If *C. pyramidata* cannot grow its protective shell, we would not expect it to survive in waters that become undersaturated with respect to aragonite.

If the response of other high-latitude pteropod species to aragonite undersaturation is similar to that of *C. pyramidata*, we hypothesize that these pteropods will not be able to adapt quickly enough to live in the undersaturated conditions that will occur over much of the high-latitude surface ocean during the twenty-first century. Their distributional ranges would then be reduced both within the water column, disrupting vertical migration patterns, and latitudinally, imposing a shift towards lower-latitude surface waters that remain supersaturated with respect to aragonite. At present, we do not know if pteropod species endemic to polar regions could disappear altogether, or if they can make the transition to live in warmer, carbonate-rich waters at lower latitudes under a different ecosystem. If pteropods are excluded from polar and subpolar regions, their predators will be affected immediately. For instance, gymnosomes are zooplankton that feed exclusively on shelled pteropods[33,39]. Pteropods also contribute to the diet of diverse carnivorous zooplankton, myctophid and nototheniid fishes[40–42], North Pacific salmon[43,44], mackerel, herring, cod and baleen whales[45].

Surface dwelling calcitic plankton, such as foraminifera and coccolithophorids, may fare better in the short term. However, the beginnings of high-latitude calcite undersaturation will only lag that for aragonite by 50–100 years. The diverse benthic calcareous organisms in high-latitude regions may also be threatened, including cold-water corals which provide essential fish habitat[46]. Cold-water corals seem much less abundant in the North Pacific than in the North Atlantic[46], where the aragonite saturation horizon is much deeper (Fig. 2). Moreover, some important taxa in Arctic and Antarctic benthic communities secrete magnesian calcite, which can be more soluble than aragonite. These include gorgonians[46], coralline red algae and echinoderms (sea urchins)[47]. At $2 \times CO_2$, juvenile echinoderms stopped growing and produced more brittle and fragile exoskeletons in a subtropical six-month manipulative experiment[48]. However, the responses of high-latitude calcifiers to reduced $[CO_3^{2-}]$ have generally not been studied. Yet experimental evidence from many lower-latitude, shallow-dwelling calcifiers reveals a reduced ability to calcify with a decreasing carbonate saturation state[9]. Given that at $2 \times CO_2$, calcification rates in some shallow-dwelling calcareous organisms may decline by up to 50% (ref. 9), some calcifiers could have difficulty surviving long enough even to experience undersaturation. Certainly, they have not experienced undersaturation for at least the last 400,000 years[49], and probably much longer[50].

Changes in high-latitude seawater chemistry that will occur by the end of the century could well alter the structure and biodiversity of polar ecosystems, with impacts on multiple trophic levels. Assessing these impacts is impeded by the scarcity of relevant data.

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1. Haugan, P. M. & Drange, H. Effects of CO_2 on the ocean environment. *Energy Convers. Mgmt* 37, 1019–1022 (1996).

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2. Brewer, P. G. Ocean chemistry of the fossil fuel CO_2 signal: the haline signal of "business as usual". *Geophys. Res. Lett.* 24, 1367–1369 (1997).
3. Gattuso, J.-P., Frankignoulle, M., Bourge, I., Romaine, S. & Buddemeier, R. W. Effect of calcium carbonate saturation of seawater on coral calcification. *Glob. Planet. Change* 18, 37–46 (1998).
4. Kleypas, J. A. *et al.* Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. *Science* 284, 118–120 (1999).
5. Langdon, C. *et al.* Effect of elevated CO_2 on the community metabolism of an experimental coral reef. *Glob. Biogeochem. Cycles* 17, 1011, doi:10.1029/2002GB001941 (2003).
6. Riebesell, U. *et al.* Reduced calcification of marine plankton in response to increased atmospheric CO_2. *Nature* 407, 364–367 (2000).
7. Zondervan, I., Zeebe, R., Rost, B. & Riebesell, U. Decreasing marine biogenic calcification: A negative feedback on rising atmospheric p_{CO_2}. *Glob. Biogeochem. Cycles* 15, 507–516 (2001).
8. Broecker, W. S. & Peng, T.-H. Fate of fossil fuel carbon dioxide and the global carbon budget. *Science* 206, 409–418 (1979).
9. Feely, R. A. *et al.* The impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. *Science* 305, 362–366 (2004).
10. Caldeira, K. & Wickett, M. E. Anthropogenic carbon and ocean pH. *Nature* 425, 365 (2003).
11. Urban-Rich, J., Dagg, M. & Peterson, J. Copepod grazing on phytoplankton in the Pacific sector of the Antarctic Polar Front. *Deep-Sea Res. II* 48, 4223–4246 (2001).
12. Kobayashi, H. A. Growth cycle and related vertical distribution of the thecosomatous pteropod *Spiratella "Limacina" helicina* in the central Arctic Ocean. *Mar. Biol.* 26, 295–301 (1974).
13. Pakhomov, E. A., Verheye, H. M., Atkinson, A., Laubscher, R. K. & Taunton-Clark, J. Structure and grazing impact of the mesozooplankton community during late summer 1994 near South Georgia, Antarctica. *Polar Biol.* 18, 180–192 (1997).
14. Fabry, V. J. Aragonite production by pteropod molluscs in the subarctic Pacific. *Deep-Sea Res. I* 36, 1735–1751 (1989).
15. Bathmann, U., Noji, T. T. & von Bodungen, B. Sedimentation of pteropods in the Norwegian Sea in autumn. *Deep-Sea Res.* 38, 1341–1360 (1991).
16. Key, R. M. *et al.* A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP). *Glob. Biogeochem. Cycles* 18, 4031, doi:10.1029/2004GB002247 (2004).
17. Sabine, C. L. *et al.* The ocean sink for anthropogenic CO_2. *Science* 305, 367–370 (2004).
18. Gruber, N. Anthropogenic CO_2 in the Atlantic Ocean. *Glob. Biogeochem. Cycles* 12, 165–191 (1998).
19. Sarmiento, J. L., Orr, J. C. & Siegenthaler, U. A perturbation simulation of CO_2 uptake in an ocean general circulation model. *J. Geophys. Res.* 97, 3621–3645 (1992).
20. Orr, J. C. *et al.* Estimates of anthropogenic carbon uptake from four three-dimensional global ocean models. *Glob. Biogeochem. Cycles* 15, 43–60 (2001).
21. Kalnay, E. *et al.* The NCEP/NCAR 40-year reanalysis project. *Bull. Am. Meteorol. Soc.* 77, 437–471 (1996).
22. Feely, R. A. *et al.* Winter–summer variations of calcite and aragonite saturation in the northeast Pacific. *Mar. Chem.* 25, 227–241 (1988).
23. Feely, R. A., Byrne, R. H., Betzer, P. R., Gendron, J. F. & Acker, J. G. Factors influencing the degree of saturation of the surface and intermediate waters of the North Pacific Ocean with respect to aragonite. *J. Geophys. Res.* 89, 10631–10640 (1984).
24. Sarmiento, J. L. *et al.* Response of ocean ecosystems to climate warming. *Glob. Biogeochem. Cycles* 18, 3003, doi:10.1029/2003GB002134 (2004).
25. Bopp, L. *et al.* Potential impact of climate change of marine export production. *Glob. Biogeochem. Cycles* 15, 81–99 (2001).
26. Sarmiento, J. L., Le Quéré, C. & Pacala, S. Limiting future atmospheric carbon dioxide. *Glob. Biogeochem. Cycles* 9, 121–137 (1995).
27. Heinze, C. Simulating oceanic $CaCO_3$ export production in the greenhouse. *Geophys. Res. Lett.* 31, L16308, doi:10.1029/2004GL020613 (2004).
28. Iglesias-Rodriguez, M. D. *et al.* Representing key phytoplankton functional groups in ocean carbon cycle models: Coccolithophorids. *Glob. Biogeochem. Cycles* 16, 1100, doi:10.1029/2001GB001454 (2002).
29. Berner, R. A. in *The Fate of Fossil Fuel CO_2 in the Oceans* (eds Andersen, N. R. & Malahoff, A.) 243–260 (Plenum, New York, 1977).
30. Fabry, V. J. Shell growth rates of pteropod and heteropod molluscs and aragonite production in the open ocean: Implications for the marine carbonate system. *J. Mar. Res.* 48, 209–222 (1990).
31. Bé, A. W. H. & Gilmer, R. W. *Oceanic Micropaleontology* Vol. 1 (ed. Ramsey, A.) 733–808 (Academic, London, 1977).
32. Dadon, J. R. & de Cidre, L. L. The reproductive cycle of the Thecosomatous pteropod *Limacina retroversa* in the western South Atlantic. *Mar. Biol.* 114, 439–442 (1992).
33. Seibel, B. A. & Dierssen, H. M. Cascading trophic impacts of reduced biomass in the Ross Sea, Antarctica: Just the tip of the iceberg? *Biol. Bull.* 205, 93–97 (2003).
34. Accornero, A., Manno, C., Esposito, F. & Gambi, M. C. The vertical flux of particulate matter in the polyna of Terra Nova Bay. Part II. Biological components. *Antarct. Sci.* 15, 175–188 (2003).
35. Collier, R., Dymond, J., Susumu Honjo, S. M., Francois, R. & Dunbar, R. The vertical flux of biogenic and lithogenic material in the Ross Sea: moored sediment trap observations 1996–1998. *Deep-Sea Res. II* 47, 3491–3520 (2000).
36. Honjo, S., Francois, R., Manganini, S., Dymond, J. & Collier, R. Particle fluxes to the interior of the Southern Ocean in the western Pacific sector along 170° W. *Deep-Sea Res. II* 47, 3521–3548 (2000).
37. Betzer, P. R., Byrne, R., Acker, J., Lewis, C. S. & Jolley, R. R. The oceanic carbonate system: a reassessment of biogenic controls. *Science* 226, 1074–1077 (1984).
38. Byrne, R. H., Acker, J. G., Betzer, P. R., Feely, R. A. & Cates, M. H. Water column dissolution of aragonite in the Pacific Ocean. *Nature* 312, 321–326 (1984).
39. Lalli, C. M. Structure and function of the buccal apparatus of *Clione limacina* (Phipps) with a review of feeding in gymnosomatous pteropods. *J. Exp. Mar. Biol. Ecol.* 4, 101–118 (1970).
40. Foster, B. A. & Montgomery, J. C. Planktivory in benthic nototheniid fish in McMurdo Sound, Antarctica. *Environ. Biol. Fish.* 36, 313–318 (1993).
41. Pakhomov, E., Perissinotto, A. & McQuaid, C. D. Prey composition and daily rations of myctophid fishes in the Southern Ocean. *Mar. Ecol. Prog. Ser.* 134, 1–14 (1996).
42. La Mesa, M., Vacchi, M. & Sertorio, T. Z. Feeding plasticity of *Trematomus newnesi* (Pisces, Nototheniidae) in Terra Nova Bay, Ross Sea, in relation to environmental conditions. *Polar Biol.* 23, 38–45 (2000).
43. Willette, T. M. *et al.* Ecological processes influencing mortality of juvenile pink salmon (*Oncorhynchus gorbuscha*) in Prince William Sound, Alaska. *Fish. Oceanogr.* 10, 14–41 (2001).
44. Boldt, J. L. & Haldorson, L. J. Seasonal and geographical variation in juvenile pink salmon diets in the Northern Gulf of Alaska and Prince William Sound. *Trans. Am. Fisheries Soc.* 132, 1035–1052 (2003).
45. Lalli, C. M. & Gilmer, R. *Pelagic Snails* (Stanford Univ. Press, Stanford, 1989).
46. Freiwald, A., Fosså, J. H., Grehan, A., Koslow, T. & Roberts, J. M. *Cold-water Coral Reefs: Out of Sight—No Longer Out of Mind* (No. 22 in Biodiversity Series, UNEP-WCMC, Cambridge, UK, 2004).
47. Dayton, P. K. in *Polar Oceanography, Part B: Chemistry, Biology and Geology* (ed. Smith, W. O.) 631–685 (Academic, San Diego, 1990).
48. Shirayama, Y. & Thornton, H. Effect of increased atmospheric CO_2 on shallow-water marine benthos. *J. Geophys. Res.* 110, C09S09, doi:10.1029/2004JC002561 (2005).
49. Petit, J. R. *et al.* Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* 399, 429–436 (1999).
50. Pearson, P. N. & Palmer, M. R. Middle Eocene seawater pH and atmospheric carbon dioxide concentrations. *Science* 284, 1824–1826 (1999).

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Review

Biological Impact of Elevated Ocean CO_2 Concentrations: Lessons from Animal Physiology and Earth History

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CO_2 currently accumulating in the atmosphere permeates into ocean surface layers, where it may impact on marine animals in addition to effects caused by global warming. At the same time, several countries are developing scenarios for the disposal of anthropogenic CO_2 in the worlds' oceans, especially the deep sea. Elevated CO_2 partial pressures (hypercapnia) will affect the physiology of water breathing animals, a phenomenon also considered in recent discussions of a role for CO_2 in mass extinction events in earth history. Our current knowledge of CO_2 effects ranges from effects of hypercapnia on acid-base regulation, calcification and growth to influences on respiration, energy turnover and mode of metabolism. The present paper attempts to evaluate critical processes and the thresholds beyond which these effects may become detrimental. CO_2 elicits acidosis not only in the water, but also in tissues and body fluids. Despite compensatory accumulation of bicarbonate, acid-base parameters (pH, bicarbonate and CO_2 levels) and ion levels reach new steady-state values, with specific, long-term effects on metabolic functions. Even though such processes may not be detrimental, they are expected to affect long-term growth and reproduction and may thus be harmful at population and species levels. Sensitivity is maximal in ommastrephid squid, which are characterized by a high metabolic rate and extremely pH-sensitive blood oxygen transport. Acute sensitivity is interpreted to be less in fish with intracellular blood pigments and higher capacities to compensate for CO_2 induced acid-base disturbances than invertebrates. Virtually nothing is known about the degree to which deep-sea fishes are affected by short or long term hypercapnia. Sensitivity to CO_2 is hypothesized to be related to the organizational level of an animal, its energy requirements and mode of life. Long-term effects expected at population and species levels are in line with recent considerations of a detrimental role of CO_2 during mass extinctions in the earth's history. Future research is needed in this area to evaluate critical effects of the various CO_2 disposal scenarios.

Keywords:
- Rising tropospheric CO_2 concentrations,
- ocean disposal of CO_2,
- critical CO_2 thresholds in marine animals,
- physiological effects of hypercapnia,
- acid-base disturbances,
- CO_2 in marine ecosystems,
- mass extinction events.

1. Introduction

Anthropogenic CO_2 production and the direct and indirect effects of accumulating CO_2 on marine ecosystems have come increasingly into focus in recent years. The current trend of accumulating CO_2 goes hand in hand with regional trends in other climate factors, especially increasing temperatures and increasing temperature variability (IPCC 2001). Global warming in itself threatens to change the geographical distribution of marine and terrestrial animals with the potential consequence of local extinction of previously common species (Parmesan and Yohe, 2003; Thomas *et al.*, 2004). The CO_2 emitted by human activities may also play a role in this context as it already permeates into ocean surface layers, where it may impact on marine organisms combined with effects exerted by current trends of warming and eutrophication. Whereas the rise in atmospheric CO_2 and its equilibration with the surface waters of the world's oceans is expected to fertilize marine phytoplankton depending on the

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availability of other nutrients (e.g. Riebesell *et al.*, 1993; Wolf-Gladrow *et al.*, 1999) and to affect calcification processes in phytoplankton, other effects of CO_2 on the physiology of marine organisms, especially animals, are not very well understood. In 1996, the observed accumulation of CO_2 in surface water had already caused a decrease in water pH by 0.1 pH units (Haugan and Drange, 1996) and a detectable impact on planktonic algae was observed (Riebesell *et al.*, 2000).

Additional interest in such effects has arisen from recent plans to dispose of anthropogenic CO_2 by introducing it into the ocean, especially the deep sea (an idea originally proposed by Marchetti, 1977, 1979) where it would affect particularly animals living in the aphotic zone. The basic idea is to accelerate the equilibration of rising atmospheric CO_2 with the deep sea, which would otherwise be delayed for centuries, and to reduce the transient atmospheric CO_2 peak otherwise expected to rise from 370 ppm ($PCO_2 = 370$ μatm) up to more than 1500 ppm ($PCO_2 = 1{,}500$ μatm) between the years 2100 and 2200, unless CO_2 emissions can be reduced (e.g. Wigley *et al.*, 1996). Under all the different disposal scenarios, organisms will have to tolerate high local CO_2 concentrations at the site of disposal (Shirayama, 1995), the actual magnitude depending upon the strategy applied. Liquid and gaseous CO_2 would be brought into the deep sea by pipeline from land or even a travelling ship. It may be stored in the form of CO_2 lakes filling local basins on the sea floor, or may be more evenly distributed in deep water layers (e.g. Ohsumi, 1995).

The relevance of potential CO_2 effects on animals is emphasized by the present discussion of aquatic CO_2 oscillations, which played a key role in the Perm Trias mass extinction events (Knoll *et al.*, 1996; Bambach *et al.*, 2002; Berner, 2002). Moreover, the evolution of high performance life forms in the sea may have depended on the reduction of atmospheric CO_2 levels during early metazoan evolution. Cambrian CO_2 levels reached as high as 0.5% (PCO_2 around 0.5 kPa or 5,000 μatm) and mean values decreased progressively thereafter (cf. Dudley, 1998). Recently, Cornette *et al.* (2002) suggested a relationship between atmospheric CO_2 levels and the rate of species diversification in the marine realm, while the mechanisms and time scales involved are presently unclear.

Under present conditions, CO_2 represents an abiotic factor that remains more or less constant in most of the pelagic zones of the sea. CO_2 levels will fluctuate where volcanic emissions occur in the sea and where excessive respiration occurs in confined areas filled with plant and animal life, e.g. in rockpools of the intertidal zone at night. It also fluctuates in marine sediments or hypoxic bottom waters as it depends on the oxidation of organic matter, rates of oxygen consumption and anaerobic metabolism of bacteria, meio- and macrofauna in an environment where mixing with the surface water is poor. PCO_2 values as high as 1.60 kPa (16,000 μatm) are conceivable in anoxic environments (Knoll *et al.*, 1996) and levels of up to 8.00 kPa (80,000 μatm) have been recorded close to deep sea hydrothermal vents where some hydrothermal vent fauna, like the vestimentifera, may make use of the high CO_2 levels for CO_2 fixation by symbiontic bacteria (Childress *et al.*, 1993).

Accordingly, some animals appear to be characterized by the development of specialized metabolic features to tolerate CO_2 or may be exposed to hypercapnia only periodically. This includes those pre-adapted to the accumulation of internal CO_2 (during exercise). Such animal models can be used to study hypercapnic effects and the underlying mechanisms.

All of these observations lead us to ask about both the general and the specific effects of CO_2 on various animal groups, from molecular and cellular to whole animal levels. The results presented in this paper originate from a field (physiological ecology) which aims at a deeper understanding of the effects of environmental variables on the physiology and biochemistry of organisms. Investigations also address how marine organisms adapt to a changing environment and what the tradeoffs and constraints in this adaptability are. Species living in the pelagic zone are adapted to constantly low CO_2 levels and may be more sensitive, whereas species dwelling in sediments may tolerate CO_2 fluctuations to some extent, especially in the intertidal zone. It is the latter species that permit the general and long-term effects of CO_2 and the underlying mechanisms to be studied in more detail. It should be emphasized that the investigation of sublethal effects appears crucial in terms of the evaluation of long-term effects of CO_2 in those species which survive acute CO_2 exposure. These long-term effects, for intervals greater than the duration of the reproduction cycle or the life span of an individual, may be overlooked but may nevertheless drastically change an ecosystem.

In general, the present paper is intended to assess criteria for an evaluation of maximum CO_2 concentrations tolerated by different marine animals from a physiological point of view. It draws on research that addresses the physiological and biochemical processes affected by CO_2 in shallow water animals, since few comparable data are currently available for deep-sea species. However, most mechanisms affected by CO_2 should be similar in all animals and, wherever adequate, extrapolations to the deep-sea situation will be included, with adequate precaution. For a more unifying picture, we are also drawing on information available for some freshwater animals as well as for CO_2 effects on such long-term processes as growth and reproduction and on various life stages, such as eggs, sperm, larvae and juveniles.

2. Physiology of CO_2 Effects: Molecular to Organismic Levels

When atmospheric CO_2 partial pressures rise, the quantities of CO_2 dissolved in water increase in accordance with Henry's law, leading to levels similar to those in air due to the great physical solubility of the gas in water. CO_2 enters the organism by diffusion, equilibrates between all body compartments and acts predominantly through its acidifying effect on acid-base balance. With an elevation in PCO_2, pH drops and bicarbonate levels rise, depending on the effect of buffers other than bicarbonate (non-bicarbonate buffers), which are titrated by the rise in carbonic acid concentration. The drop in pH is higher and the rise in bicarbonate is less in those fluids with lower buffer capacity. Accordingly, the passive rise in bicarbonate caused by increasing water PCO_2 is much less in sea water than in extracellular fluids, and here again, much less than in intracellular compartments. In contrast, the largest pH drop can be observed in sea water due to the small amounts of non-bicarbonate buffers, and the smallest pH drop occurs intracellularly owing to high levels of non-bicarbonate buffering, which is five times higher than in extracellular compartments. In most animals, invertebrates and vertebrates, extracellular pH is set to values 0.5–0.8 pH-units above intracellular pH. In consequence, bicarbonate levels are higher in extracellular than in intracellular fluids.

The analysis of effects of external CO_2 on acid-base regulation in water breathing animals (investigated in numerous species) follows the same lines as the analysis of respiratory influences. Respiratory changes titrate non-bicarbonate buffer values with changing PCO_2 and lead to pH decreases and an accumulation of bicarbonate. In only a few species has this approach been combined with an analysis of CO_2 effects on metabolism, not only when hypoxia and anaerobic metabolism occur (Reipschläger *et al.*, 1997) but also in the sense that CO_2 may affect overall metabolic rate and the partitioning of energy between individual metabolic processes by changes in either one or a combination of the different acid-base parameters in the water or in body compartments (Pörtner and Reipschläger, 1996; Pörtner *et al.*, 2000; Langenbuch and Pörtner, 2002).

The present paper focuses on ectothermic, water breathing animals whose body fluid CO_2 tension is much lower than in air breathers. Ventilation is driven largely by the limiting factor of water oxygenation (e.g. Jouve-Duhamel and Truchot, 1983) but there is growing evidence for a direct ventilatory sensitivity to CO_2, e.g. in teleosts and elasmobranchs (Burleson and Smatresk, 2000; McKendry *et al.*, 2001). Thus, an acute stimulatory effect of hypercapnia on ventilation was demonstrated in European eel (McKenzie *et al.*, 2002). However, the capacity for ventilatory compensation of the effect of hypercapnia on acid-base status is very limited in water breathers due to the small diffusion gradient of CO_2 between the organism and the water (Scheid *et al.*, 1989). Water breathers therefore rely almost exclusively on ion exchange mechanisms for a compensation of hypercapnic disturbances in acid-base status.

The processes of membrane-bound ion regulation will respond to respiratory or metabolic acid loads as well as to changes in water acid-base parameters and will strive to re-establish original or new acid-base equilibria in the body fluids. The carriers involved transport H^+ and/or bicarbonate, leading to an accumulation of bicarbonate and to a partial or complete compensation of the pH drop. Exchange processes will occur in epithelial membranes between animal and water and in membranes separating intra- and extracellular compartments. Ion transport depends on the sodium gradient built by ATP consuming Na^+/K^+-ATPase or consumes energy (ATP) directly in the case of the H^+-ATPase (Heisler, 1993). Research has as yet given us a far from complete understanding of the regulatory integration of these proton equivalent ion transport mechanisms, but phenomenological descriptions exist for fish and marine invertebrates and some carriers have been identified (cf. Heisler, 1986b, 1993; Pörtner and Reipschläger, 1996; Ishimatsu and Kita, 1999; Pörtner *et al.*, 2000; Claiborne *et al.*, 2002).

Following Heisler (1986b), the principle response to hypercapnia in fish is similar in freshwater and marine teleosts and elasmobranchs. Environmental hypercapnia causes an almost immediate reduction of plasma pH induced by elevated plasma PCO_2. In fish, more than 90% of all acid-base equivalent ion transport processes occur across the branchial epithelium (Heisler, 1986a), nevertheless intestine (Grosell *et al.*, 2001) and kidney (Wood *et al.*, 1999) are involved to a minor degree. One has to bear in mind that acid-base relevant transfer is always coupled with the problem of osmoregulation due to the required uptake of appropriate counter ions, which lead to an additional NaCl load of up to 10% in marine fish (Evans, 1984). Therefore, freshwater adapted fish species mainly rely on apical H^+-ATPase for the electrogenic transfer of H^+ to the ambient water; a process that also drives the uptake of external Na^+ into gill cells via Na^+ channels (Lin *et al.*, 1994). In contrast, different isoforms of Na^+/H^+ exchangers (NHE) are thought to be the main component responsible for acid-base transfer in seawater adapted fishes. At high external $[Na^+]$, thermodynamic considerations favour Na^+/H^+ exchange for acid-base regulation (Potts, 1994) and functional studies confirmed the role of apical NHE for H^+ extrusion from gill cells (Edwards *et al.*, 2001).

Among marine invertebrates, the system of membrane proteins responsible for intracellular pH homeostasis comprises v-type H^+-ATPase as well as Na^+/

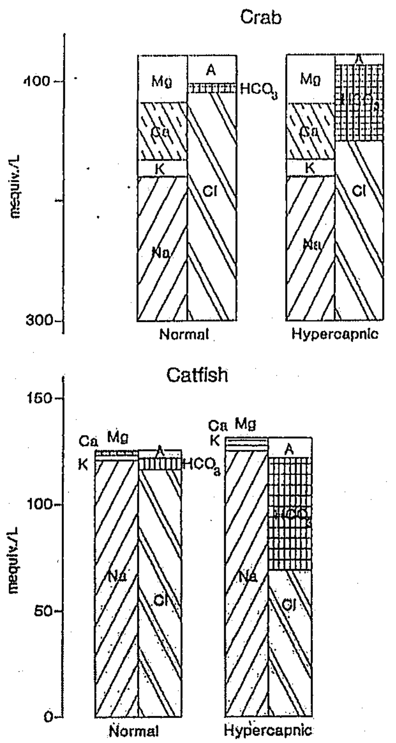

Fig. 1. Gamblegrams depicting the ionic composition of extracellular fluids in blue crabs and catfish (plasma) under control conditions and during environmental hypercapnia at a PCO_2 of 45 mm Hg (crab) and 56 mm Hg (catfish). A = unaccounted-for anion, probably mostly protein (adopted from Cameron and Iwama, 1989). Note the accumulation of bicarbonate under hypercapnia.

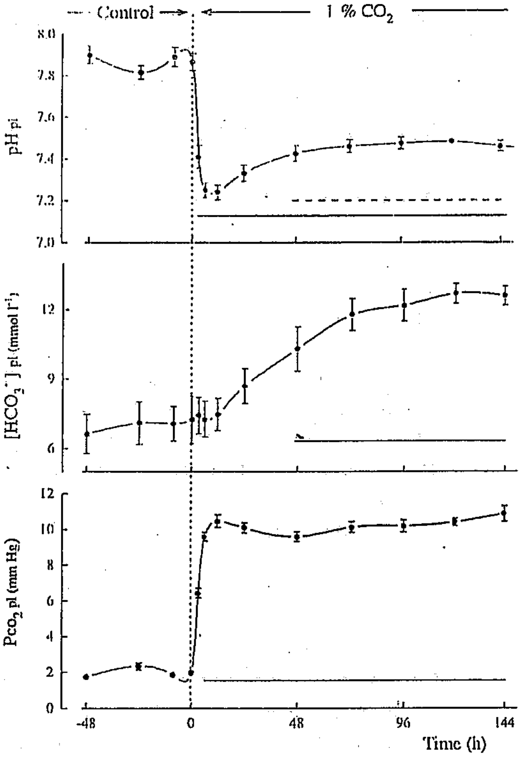

Fig. 2. Acid-base variables (pH, "$[HCO_3^-]$", PCO_2) in the coelomic plasma (extracellular fluid) of *Sipunculus nudus* under control conditions and subsequent hypercapnia (modified after Pörtner *et al.*, 1998). Note the incomplete compensation of the acidosis in the extracellular space.

H^+- and Na^+-dependent Cl^-/HCO_3^- exchange, as seen in the benthic sipunculid worm *Sipunculus nudus* (Pörtner *et al.*, 2000). The mechanisms of acid-base regulation operative at the organism water interface remain unidentified in this species.

In decapod crustaceans, HCO_3^- anion exchange plays an important role in the restoration of acid-base status after acid-base imbalance. The strongly euryhaline crab *Callinectes sapidus*, for example, uses the uptake of HCO_3^-, associated with an efflux of Cl^-, to compensate for hypercapnic acidosis (Truchot, 1979). Similar to fishes, a strong relationship between acid-base status and ion regulation has been found in decapod crustaceans. Compensation of the acidosis causes large and perhaps unfavorable changes in the ionic composition of plasma and other body fluids (see Fig. 1; Cameron and Iwama, 1989). Interestingly, changes in haemolymph acid-base status were only secondary to ion regulation and cell volume control in *Eriocheir sinensis* (Whiteley *et al.*, 2001).

In all organisms studied so far, acid-base disturbances elicited by hypercapnia are compensated for by an accumulation of bicarbonate anions (Heisler, 1986b; Wheatly, 1989; Pörtner *et al.*, 1998), a process that is most effective in the intracellular but not the extracellular compartment. In Atlantic cod, for instance, Larsen *et al.* (1997) observed a complete compensation of hypercapnia-induced acidosis in both extra- and intracellular compartments. However, while this process was rapid in the intracellular space of muscle tissue, extracellular pH reached control values only after 24 h via an increase in extracellular bicarbonate concentration paralleled by a reduction in chloride levels. Nevertheless, extracellular pH may not always return to the original value and the degree of compensation is lower, especially in marine invertebrates (e.g. 30% in a marine worm, see Fig. 2; Pörtner *et al.*, 1998), than in freshwater as well as marine teleost and elasmobranch fish under the same conditions. In the fish, extracellular pH also rarely reaches the original value (Heisler, 1986a). One limiting factor for the degree of compensation may be the extent to which bicarbonate is available from the ambient water for extracellular compensation, or from the extracellular fluid (blood, haemolymph) for intracellular compensation (Heisler, 1993; Pörtner *et al.*, 1998). However, in fish these relationships are also influenced by the level of sodium, which is used to extrude H^+ from the organism (Iwama and Heisler, 1991).

An assessment of the adaptive and ecophysiological importance of these patterns gives rise to the questions of what are the benefits of acid-base regulation for the organism? And what is the effect of changes in acid-base parameters under conditions of environmental stress, like elevated concentrations of ambient CO_2? To start with, work on two invertebrate species of completely different mode of life may illustrate the levels at which CO_2 exerts its specific effects. The level of organization of the organism, its activity level, mobility and reactivity are likely to be correlated with the sensitivity level. The organisms chosen are at the two extreme ends of the spectrum, one relatively tolerant to CO_2 and the other one of the most sensitive species known so far. One of them is *Sipunculus nudus*, a protostome invertebrate (body weight up to 80 g and body length up to 30 cm) living in marine sediments where fluctuations of environmental parameters like oxygen and CO_2 are regular. The species range extends from the intertidal zone up to water depths of 2300 m, making it a suitable model organism for studying principal CO_2 effects. The overall physiological characters of this animal comprise a low metabolic rate, slow body movements, oxyconformity of oxygen consumption, biochemical characteristics of a facultative anaerobe, and the abilities to reduce metabolic rate under extreme conditions and to undergo long-term starvation (Pörtner and Grieshaber, 1993).

The second model organism is the squid *Illex illecebrosus*, which lives in the pelagic zone of the open ocean and displays a level of activity which is comparable to, or even exceeds that of similar sized fish (O'Dor and Webber, 1986). Squids are invertebrates with high metabolic power compared to fish and must therefore be considered even more sensitive to fluctuations in environmental parameters than highly active fish (cf. Pörtner, 1994). Finally, the literature available on fishes indicates that their sensitivity to CO_2 is intermediate (see below).

2.1 CO_2 effects on apparently tolerant species

In many animal groups tolerant to CO_2 oscillations, CO_2 has long been known to cause a drop in metabolic rate and even anaesthesia, especially in insects. A narcotic effect of high, non-determined CO_2 levels was also observed in deep-sea hagfish after CO_2 disposal in situ, possibly as the result of respiratory distress (reduced O_2 carrying capacity of the blood, Tamburri *et al.*, 2000). *Sipunculus nudus* experiences a long-term depressing effect of CO_2 on aerobic energy metabolism which is related to the level of hypercapnia (depression by 35% at 20000 μatm PCO_2, water pH ≈ 6.6). Further study revealed that under both normo- and hypercapnia, acidosis elicits a drop in metabolic rate which can only be explained by the decrease in extracellular pH (see Fig. 3; Reipschläger and Pörtner, 1996). Neither intracellular pH nor intra- or extracellular bicarbonate levels or PCO_2 were involved in eliciting metabolic depression under hypercapnia. These relationships have not yet been investigated in fish.

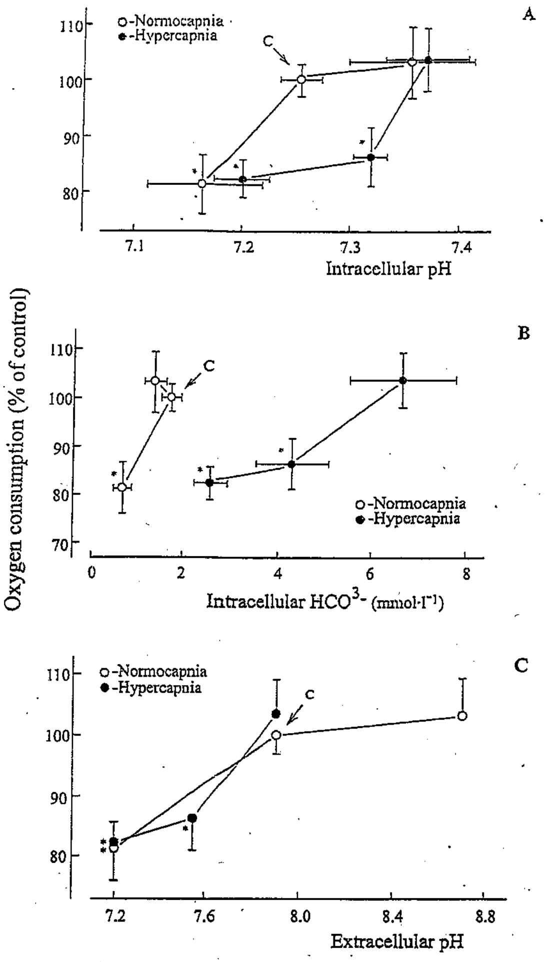

Fig. 3. Oxygen consumption rates of isolated body wall musculature of *Sipunculus nudus* during normocapnia and during hypercapnia depicted as a function of intracellular pH values (A), intracellular bicarbonate concentrations (B), and values of extracellular pH (C). Only plot C is consistent for both normo- and hypercapnic data and demonstrates that oxygen consumption is significantly depressed below a threshold value of extracellular pH (modified after Reipschläger and Pörtner, 1996).

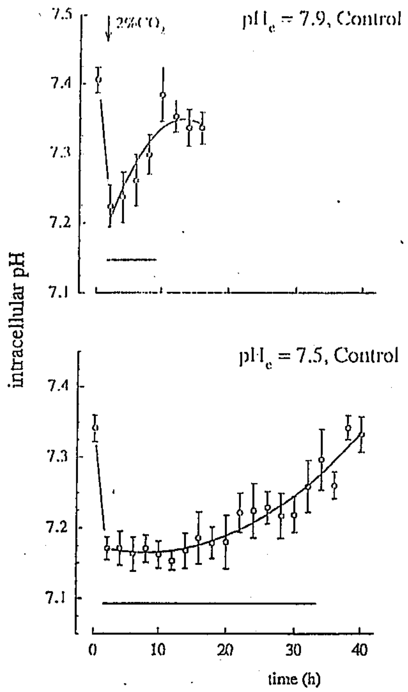

Fig. 4. Time course of pHi recovery in isolated body wall musculature of *S. nudus* during acute hypercapnia under 2% CO_2 at high and low extracellular pH. Recovery of intracellular pH takes longer during acidosis due to the specific effect of low extracellular pH on transmemembrane ion exchange (see text and Pörtner *et al.*, 2000).

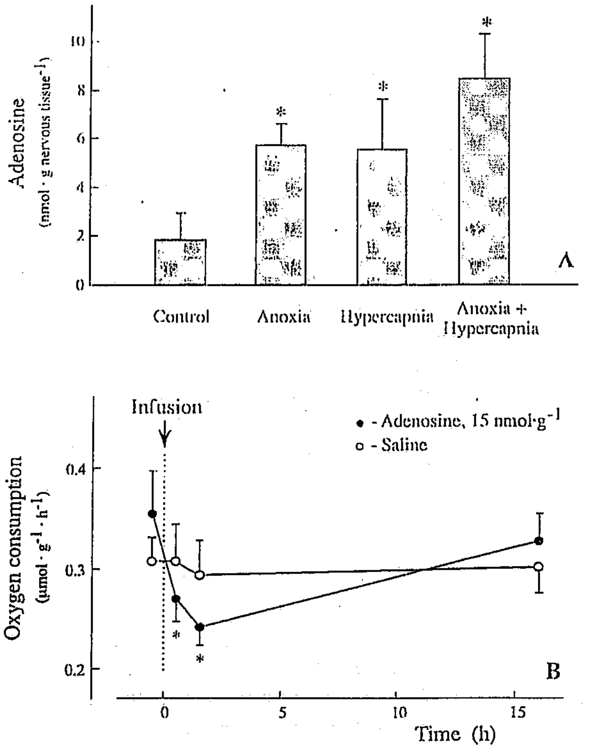

Fig. 5. (A) Adenosine levels in the nervous tissue of *Sipunculus nudus* after 24h of exposure to hypercapnia, anoxia and anoxic hypercapnia. (B) Effect of adenosine infusion on the oxygen consumption rate of *Sipunculus nudus*. Adenosine solution or saline were infused into the coelomic fluid via an indwelling catheter (after Reipschläger *et al.*, 1997).

Decreasing extracellular pH slows down the rate of H^+ equivalent ion exchange by both Na^+/H^+- and Na^+-dependent Cl^-/HCO_3^--transporters which are responsible for the regulation of the intracellular acid-base status. Therefore, less sodium needs to be pumped by the Na^+/K^+-ATPase, thus diminishing the energy requirements of acid-base regulation (see Fig. 4; Pörtner *et al.*, 2000). The general relevance of these relationships among water breathing animals is confirmed by data collected on tilapia from alkaline Lake Magadi, which indicate that the cost of acid-base regulation can even range above 50% of baseline metabolism under extreme environmental conditions (Wood *et al.*, 2002).

Further investigation at the whole animal (systemic) level revealed that a modulation in the cost of acid-base regulation cannot fully explain metabolic depression since ventilatory activity was reduced under hypercapnia, suggesting a contribution from a central nervous mechanism (Pörtner *et al.*, 1998). Among neurotransmitters, adenosine accumulated in the nervous tissue of *S. nudus* during hypercapnia, hypoxia, and even more so during combined hypoxia and hypercapnia (Fig. 5). Infusion of adenosine caused metabolic depression (Reipschläger *et al.*, 1997). A similar role for adenosine is also known for some vertebrates (e.g. freshwater fish and turtles) subjected to anoxic conditions (Hylland *et al.*, 1997; for review see Lutz and Nilsson, 1997). No studies addressing the specific role of adenosine or other neurotransmitters in marine fish during hypercapnia are available as yet.

Most importantly, not only metabolic depression but also metabolic imbalance may arise under hypercapnia, depending on the degree of compensation in acid-base status. Under conditions of extreme acidosis (metabolic depression by up to 45% of control values), Langenbuch and Pörtner (2002) found lowered atomic ratios of oxygen consumed (O) to nitrogen produced (N) in muscle tissue of *S. nudus*, despite a concomitant drop in oxygen consumption and ammonia excretion rates (Fig. 6). On the one hand, these results indicate a shift in N metabolism with a preferred degradation of amino acids like asparagine, glutamine or their dicarboxylic acids, which yields low O/N ratios. This results in an increased pro-

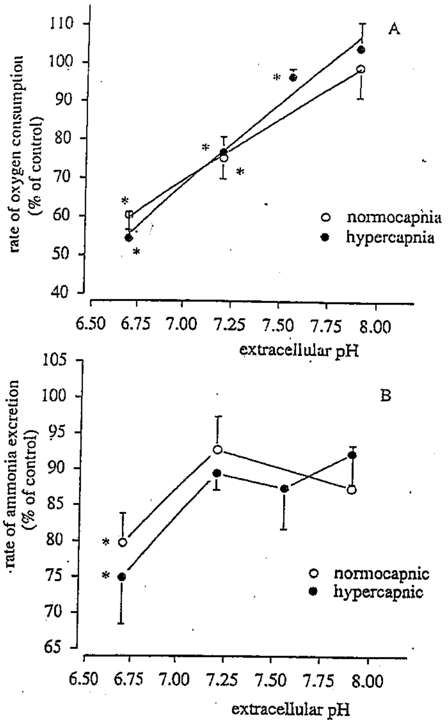

Fig. 6. Rates of oxygen consumption (A) and ammonia excretion (B) at different values of extracellular pH under normocapnic and hypercapnic conditions in *Sipunculus nudus* isolated muscle tissue. Note the progressive drop in oxygen consumption with falling extracellular pH and the delayed decrease in the rate of ammonia excretion under conditions of severe acidosis (after Langenbuch and Pörtner, 2002).

duction of bicarbonate, which supports the regulation of intracellular pH. On the other hand, the decrease in O/N ratios suggests that hypercapnia may cause a long-term drop in protein synthesis, possibly induced by the drop in intracellular pH (Langenbuch and Pörtner, 2002). This context remains largely uninvestigated for other organisms but it can be postulated to affect the long-term physiology of the animals: a reduction in growth and reproduction is expected, processes which largely depend on protein synthesis and which support the maintenance of a population. Reduced growth rates under hypercapnia were found in marine penaeid prawns (Wickins, 1984) and in juvenile white sturgeon, with reductions in foraging activity being involved in the latter (Crocker and Cech, 1996).

Much work has focused on pH as a stress factor affecting reproduction and associated processes in fresh water and marine species. Low water pH decreases the size of the eggs and delays hatching in perch, *Perca fluviatilis* (Vinogradov and Komov, 1985). In clams (*Tivela stultorum*) fertilization was most successful at slightly alkaline sea water pH (Alvarado-Alvarez *et al.*, 1996), suggesting that even small reductions of pH may reduce reproductive success in some species (see also Desrosiers *et al.*, 1996). Thus, in white sturgeon (*Acipenser transmontanus*), sperm motility was shown to be affected by low pH or increased PCO_2 (Ingermann *et al.*, 2002).

One additional aspect not yet considered is that elevated CO_2 levels cause a disturbance of calcification processes in organisms relying on shells or other calcified structures (Wickins, 1984). Barker and Elderfield (2002) demonstrated that glacial-interglacial changes in the shell weights of several species of planktonic foraminifera are, in a negative feedback mechanism, related to changes in ambient carbonate ion concentrations over time in response to changing atmospheric PCO_2. Thus, marine calcification seems to be directly affected by elevated atmospheric carbon dioxide. There will even be a dissolution of calcified structures that are already present (e.g. Bamber, 1987; Shirayama, 1995). These disturbances will contribute to the predicted reduction in growth and reproduction as seen at low pH in molluscs (Bamber, 1987, 1990). There may also be differences between animal groups in this respect: if CO_2 was a key factor in late Permian mass extinctions it affected corals, articulate brachiopods, bryozoans and echinoderms to a greater extent than molluscs, arthropods and chordates, which may partly be due to the greater reliance of the former groups on heavily calcified skeletons (Knoll *et al.*, 1996).

In general, the tolerance limits to CO_2 have been seen as related to the acidifying action (cf. Shirayama, 1995; Auerbach *et al.*, 1997); however, specific effects exerted by CO_2 and bicarbonate have to be included in a complete consideration of CO_2 effects (Pörtner and Reipschläger, 1996). Recent studies confirmed this hypothesis, providing evidence for different sensitivities to CO_2- versus HCl (fixed acid)-induced water acidification. Higher mortalities resulted in all CO_2 exposed groups of tested fish larvae compared to groups exposed to the same water pH set by fixed acid (Ishimatsu *et al.*, 2004). Observed differences may partly result from the more rapid entry of highly diffusive CO_2 into body fluids, whereas disturbances may take longer to develop in HCl^-acidified seawater. Overall, CO_2-related water pH values as low as 7 and 6.5 may be tolerated, at least temporarily, by individual animals, but it is reasonable to predict that CO_2 will cause a change in the mode of metabolism. Reduced growth and reproduction may result, with long term effects at the population level. These effects may set in rather early. According to recent data reported by Shirayama (2002), even very moderate increases in CO_2 (200 μatm above control levels) are able to cause a reduction in growth rate and even survival of shelled animals like echinoderms and gastropods. Accordingly, many species would tolerate transient CO_2 fluctuations but may not be able to settle and thrive in areas where CO_2 remains permanently elevated (with the potential exception of hydrothermal vent fauna). For an estimation of true critical thresholds in tolerant species, long-term exposures are required as well as studies of growth and reproduction. No such comprehensive studies are available as yet.

2.2 *CO_2 effects on acutely "intolerant" species*

The number of species acutely sensitive to even small changes in CO_2 levels may be rather small but among them are the most fascinating and powerful invertebrate species, squid. A look at the special metabolic and respiratory design of squid explains why these creatures are so sensitive to ambient CO_2 fluctuations (Pörtner and Zielinski, 1998). In contrast to the low metabolic rate associated with undulatory swimming in fish, the squid's oxygen demand is much higher due to their less efficient mode of swimming by jet propulsion (O'Dor and Webber, 1986). The high metabolic rate of these animals needs to be supported by blood oxygen transport which occurs by use of an extracellular pigment, the haemocyanin (Fig. 7). The pigment concentration determines the capacity of the blood to bind and transport oxygen. However, there is a limit to the concentration of pigment, since soluble protein binds water (colloidal osmotic pressure) and can remove it from the tissues. High protein concentrations also increase the viscosity of the blood. Nonetheless, oxygen transport by the haemocyanin needs fine tuning to allow efficient oxygen transport. This occurs by pH, seen as a large Bohr effect, which causes a reduced binding affinity for oxygen with falling pH. Therefore, control of arterial pH as well as pH changes between arterial and venous blood are very important for oxygen transport. This conclusion is supported by the existence of large, pH-dependent cooperativity (i.e. interaction between haemocyanin subunits) which enhances the level of coordination between pH and oxygen binding. The high metabolic rate of the mantle causes haemocyanin to fully release its load in the tissue even under resting conditions, and not just during active periods. In contrast to the situation in fish, there is no venous oxygen reserve (Pörtner, 1990).

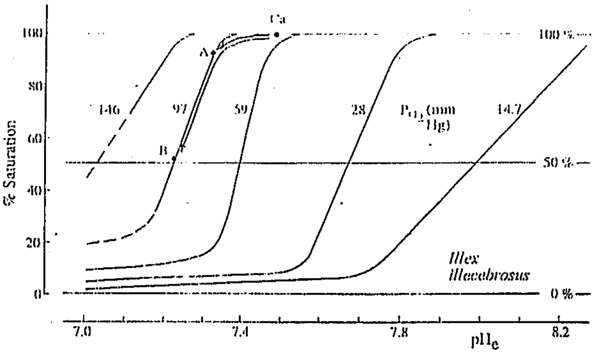

Fig. 7. Oxygen saturation of the blood of *Illex illecebrosus* depicted in a pH/saturation diagram (modified after Pörtner, 1990, 1994). The oxygen isobars show the change in hemocyanin bound oxygen levels with extracellular pH at constant PO_2. The acid-base and gas status of arterial blood under control resting conditions is depicted by C_a, changing into A during moderate (1.5 mm Hg) and into B during slightly more severe hypercapnia (5 mm Hg), thus reflecting the drop in arterial oxygenation with pH.

The relationship between O_2 binding, oxygen partial pressure (PO_2) and pH is clearly illustrated by pH saturation analysis (see Fig. 7). The oxygen isobars (lines of constant PO_2) show which pH changes in the blood enable the pigment to buffer dissolved oxygen or PO_2, as it unloads and saturation drops from 100% in the artery to the venous level. In accordance with a maximum cooperativity, the slope of oxygen isobars is steepest where pH is close to that of *in vivo* blood (about 7.4). This shows that extracellular pH must be closely controlled and protected against fluctuations. While a moderate decrease in pH (by 0.15 pH-units) caused by a rise in water PCO_2 above 2,000 μatm would decrease the aerobic scope for activity, a larger rise in PCO_2 (up to 6,700 μatm) would cause blood pH to fall by about 0.25 pH units, reduce oxygen capacity by about 50%, and most likely induce lethal effects in the ommastrephid, open ocean squid *Illex illecebrosus* (Pörtner and Reipschläger, 1996). Squid of lower activity levels appear to be less sensitive. For example, Redfield and Goodkind, as early as 1929, demonstrated in the coastal squid *Loligo pealei* that CO_2 partial pressures of about 26,500 μatm would be acutely lethal, associated with a similar drop in blood oxygenation (Redfield and Goodkind, 1929). Acute critical CO_2 thresholds may be alleviated to some extent by long-term adjustments to rising ambient CO_2, allowing for some compensatory acid-base regulation.

2.3 *CO_2 sensitivity in fish*

In comparison to squid, fish are much better protected from CO_2 effects since they have a lower metabolic rate and some venous oxygen reserve. Their hemoglobin is located in erythryocytes, where it is being protected from extracellular pH disturbances by the great capacity for intracellular acid-base regulation. This will reduce acute sensitivity to elevated CO_2 as opposed to squid, and critical levels may not be reached even at CO_2 partial pressures of 4 kPa or more (40,000 μatm, e.g. Crocker and Cech, 1996). Nevertheless, the question of pH sensitivity of the oxygen-transport system in fishes, especially concerning deep sea animals, remains controversial, because available data are very sparse. As some deep sea animals display relatively large pH sensitivities of respiratory pigments at high oxygen affinities, similar to deep water Antarctic species (e.g. among octopods; Zielinski *et al.*, 2001), Seibel and Walsh (2001) postulated that deep sea animals would experience serious problems in oxygen supply under conditions of increased environmental CO_2 concentrations. They refer to midwater organisms which possess pigments with large Bohr effects and high O_2 affinities, like the mysid crustacean *Gnathophausia ingens* and some fish species (Childress and Seibel, 1998; Sanders and Childress, 1990). However, it remains unclear whether these animals are representative of the deep sea fauna because they are residents of so called "oxygen minimum layers" at intermediate depths with special adaptations for the efficient extraction of oxygen from hypoxic waters. For a definite evaluation of CO_2 sensitivity under these conditions, combined hypoxia and CO_2 exposure scenarios would have to be considered. In contrast, Graham *et al.* (1985) found very low hemoglobin levels in the blood of three deep sea fishes, comparable to those of a number of Antarctic fishes (Wells *et al.*, 1980). The hemoglobins of these fish species displayed hyperbolic oxygen dissociation curves, low Hill constants and small Bohr effects, associated with their low activity habits and a reduced importance of blood oxygen transport.

Moreover, fish (and squid) lead a sluggish life at depths below 300 to 400 m. A decline in metabolic activity of pelagic animals, including fishes and cephalopods, with increasing minimum depth of occurrence has been reported in several studies (Childress, 1995; Seibel *et al.*, 1997). A comparative study of Antarctic stenothermal and eurythermal temperate cephalopods showed that the magnitude of the Bohr effect also depends upon the level of activity. Furthermore, the Bohr effect was decreased and the pH-insensitive oxygen reserve increased during cooling, suggesting that the relevance of pH sensitivity is reduced in the cold (Zielinski *et al.*, 2001). In addition, the hemoglobins of Antarctic notothenioids like *Trematomus newnesi*, *Artedidraco orianae* and *Pogonophryne scotti* are characterized by a modest Bohr effect, very weak or no Root effect, and very low cooperativity of oxygen binding, features most likely related to their low resting metabolic rate (Tamburrini *et al.*, 1998; D'Avino and DeLuca, 2000). Similar trends may be found in deep sea fishes below the oxygen minimum layer.

Once again, it may not be the acute toxic effects of hypercapnia but the long-term sublethal effects on deep sea fauna which are more detrimental to population structure and species distribution. Due to their low metabolic activity, the efficiency of cellular and tissue acid-base regulation is likely to be greatly diminished in deep sea fishes compared to their shallow-living counterparts (Seibel and Walsh, 2001). A lower intracellular non-bicarbonate buffering capacity (Seibel *et al.*, 1997) and reduced rates of active ion exchange in the gills (Goffredi and Childress, 2001) may be typical of deep sea fauna. In consequence, the capacity to fully compensate systemic acid-base disturbances may be limited, suggesting shifting acid-base and ion equilibria and associated metabolic consequences (see above). This may in fact lead to constantly depressed energy turnover rates and subsequent constraints in growth and reproduction processes as outlined above.

3. Conclusions and Perspectives

The number of species suffering from acute CO_2 toxicity will be limited. In general, long-term steady-state elevations in CO_2 levels may be tolerated by animals with a low activity mode of life or pre-adapted to large fluctuations in environmental parameters. Tolerance also depends upon the capacity to compensate for associated acid-base disturbances. However, this refers only to short to medium term survival of the individuals of a population. At present it is difficult, if not impossible, to give numbers for a critical threshold and to really qualify animal species as being permanently tolerant to elevations in ambient CO_2 since long-term effects have not yet been sufficiently investigated. The data reported by Shirayama (2002) indicate that shallow water calcifying species may respond rather early with reduced growth and survival (see above).

Figure 8 summarizes our knowledge of carbon dioxide effects at different organisational levels. Analogous to a recent treatment of thermal sensitivities (Pörtner, 2002), an ecosystem to molecular hierarchy of CO_2 tolerance is proposed on the basis of current physiological data. The data given above give rise to the general prediction that CO_2 will cause a change in the mode of metabolism. Reduced growth and reproduction may result in apparently tolerant species and populations, contributing to a long-term decrease of population density or even local extinction of species. However, such effects have yet to be demonstrated in long term field investigations.

Nevertheless, such effects are in accordance with CO_2 effects that have been supposed to contribute to the extinction of species during the Perm/Trias mass extinction event (cf. Knoll *et al.*, 1996). In the mass extinction scenario, PCO_2 levels were reached in surface waters that are in the low range of those expected in CO_2 disposal scenarios. The notion by Knoll *et al.*, that animals without gills, with a weak internal circulation and low metabolic rate are more sensitive to hypercapnia is not supported by the data compiled in this review. Ventilatory compensation of hypercapnia does not represent a possi-

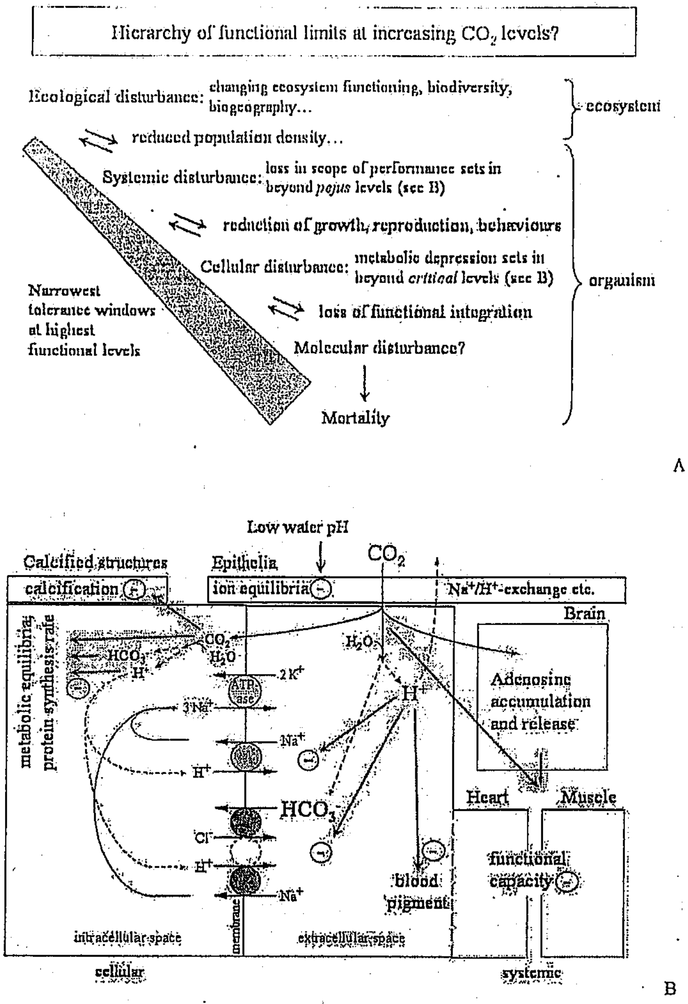

Fig. 8. Overview of effects of elevated ocean CO_2 levels on marine animal organisms and ecosystems. (A) Application of Shelford's law of tolerance and of the concept of a systemic to molecular hierarchy of tolerance limits, as recently elaborated in thermal physiology, supports a categorization of CO_2 dependent phenomena. The integrated concert of different functional levels leads to narrowest tolerance windows at high hierarchical levels which shape ecological functions and their shift under elevated CO_2 concentrations. Note that tolerance thresholds (pejus and critical levels) likely vary between species and phyla, partly depending on the level of energy turnover (see text). Long-term tolerance limits (pejus levels), which define the onset of performance limitations, still await quantification. (B) Summary of physiological functions and their changes and interactions under the effect of CO_2 in a generalized marine water breathing animal. The processes depicted here are hypothesized to elicit the patterns depicted in (A). Note that this picture is incomplete and hypothetical with respect to some details and ignores the specific phylogenetic constraints characterizing individual phyla and species (see text). The generalized cellular processes depicted on the left probably have their specific functional consequences in tissues like brain, heart or muscle depicted on the right (experimental results and concepts adopted from Pörtner and Reipschläger, 1996; Reipschläger and Pörtner, 1996; Reipschläger *et al.*, 1997; Larsen *et al.*, 1997; Pörtner *et al.*, 2000; Langenbuch and Pörtner, 2002, 2003; Pörtner, 2002; Shirayama, 2002; Ishimatsu *et al.*, 2004; Kurihara *et al.*, 2004).

ble advantage for the more active water breathers since PCO_2 gradients between water and blood are too low. Rather, the much greater reliance on calcified structures may have defined the limits in those groups of articulates, echinoderms, bryozoans and cnidarians which were severely affected by mass extinction. Calcification is usually less expressed in the more active animal groups since this will hamper mobility.

However, although CO_2 may have been one of the effective parameters, the relevant analysis by Knoll *et al.* neglects the role of temperature oscillations, which most probably contributed to mass extinction events through the long term effects of repeated exposure to extreme climate oscillations and associated cooling events (Pörtner, 2001, 2004). These considerations indicate that current trends of warming and CO_2 accumulation in marine surface waters may exert synergistic effects on marine fauna. According to a recently proposed principle, thermal tolerance windows of animals are set by limitations of the integrated capacities of ventilation and cardio-circulation for oxygen uptake and distribution in the organism (Pörtner, 2001, 2002). Warming and anthropogenic eutrophication will cause falling oxygen levels in marine environments and thereby a reduction of tolerance to thermal extremes, finding reflection in a narrowing of thermal windows. This trend is likely to be exacerbated by accumulating CO_2 since it reduces animal performance, as outlined above and will probably act in the same way as hypoxia. Synergistic effects of warming and CO_2 accumulation will probably be harmful to animal populations, especially at the borders of their biogeographical range.

As a corollary, future research is required to study the long-term effects of elevated CO_2 levels and evaluate critical threshold levels for a detrimental effect of CO_2 in both apparently tolerant and acutely intolerant species. This research should consider the physiological importance of each individual CO_2 species in addition to pH effects. Furthermore, and on a long-term basis, combined effects of CO_2 accumulation and global warming should be studied to develop our understanding of potential synergistic effects.

It seems to be important to find a model organism to represent the large group of deep sea fishes which are barely accessible *in vivo* for laboratory work. Their metabolic requirements are on the low side among fishes, even lower than in polar fish (Torres and Somero, 1988). Those species uniquely adapted to little or no light, low temperatures (below 5°C) and huge hydrostatic pressures show a great diversity, are endemic to these extreme environments, and are characterized by slow growth and reproduction (Gage and Tyler, 1991). This picture already suggests that deep sea fauna is sensitive to any change that may occur suddenly and is well beyond the range of conditions under which this fauna has evolved (Hädrich, 1996). Due to the difficulties in the collection and handling of live deep sea animals, we have started to work on benthic Antarctic eelpout *Pachycara brachycephalum* (Zoarcidae). In particular, the physiological characteristics of benthic Antarctic fauna should be close to those of deep sea fish. These zoarcids are also highly adapted to constantly low temperatures (around 0°C) and their sluggish benthic lifestyle contributes to an exceptionally low metabolic rate (Anderson, 1990, 1994; van Dijk *et al.*, 1999). In the future, results obtained in studies on the physiological tolerance of *P. brachycephalum* to hypercapnia should yield valuable information which should be applicable to deep sea fish species.

Present data indicate that relatively moderate CO_2 increases of 200 μatm may have significant long term effects. This already casts doubt on whether CO_2 should be disposed by even distribution in the sea, although this would possibly keep levels below those which elicit acute lethal effects on the most active organisms of the pelagic. Due to the danger of long term detrimental effects, and if CO_2 disposal strategies to the ocean cannot be avoided, CO_2 should be pH neutralized and converted to bicarbonates or rather be trapped in confined stable areas like bottom depressions (canyons) where virtually no life will continue under those anoxic and hypercapnic conditions. These sites in the deep sea filled by CO_2 lakes could be looked at in the same way as landfills. If they were to use only a minor percentage of the total surface area of the deep-sea floor, such strategies should leave a large fraction of the marine environment unaffected so that the net damage to marine ecosystems should be less than with an even distribution of CO_2.

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References

Alvarado-Alvarez, R., M. C. Gould and I. L. Stephano (1996): Spawning, in vitro maturation and changes in oocyte electrophysiology induced by serotonin in *Tivela stultorum*. *Biol. Bull.*, **190**, 322–328.

Anderson, M. E. (1990): Zoarcidae. p. 256–276. In *Fishes of the Southern Ocean*, ed. by O. Gon, P. C. Heemstra and J. L. B. Smith, Institute of Ichthyology, Grahamstown.

Anderson, M. E. (1994): Systematics and Osteology of the Zoarcidae (Teleostei: Perdiformes). *Ichthyol. Bull.*, **60**, 120.

Auerbach, D., J. A. Caulfield, E. E. Adams and H. J. Herzog (1997): Impacts of ocean CO_2 disposal on marine life: I. A toxicological assessment integrating constant-concentration laboratory assay data with variable-concentration field exposure. *Env. Model. Assessment*, **2**, 333–343.

Bambach, R. K., A. H. Knoll and J. J. Sepkowski, Jr. (2002): Anatomical and ecological constraints on Phanerozoic animal diversity in the marine realm. *PNAS*, **99**, 6845–6859.

Bamber, R. N. (1987): The effects of acidic sea water in young carpet-shell clams, *Venerupis decussata* (L.) (Mollusca: Venracea). *J. Exp. Mar. Biol. Ecol.*, **108**, 241–260.

Bamber, R. N. (1990): The effects of acidic sea water on three species of lamellibranch molluscs. *J. Exp. Mar. Biol. Ecol.*, **143**, 181–191.

Barker, S. and H. Elderfield (2002): Foraminiferal calcification response to glacial-interglacial changes in atmospheric CO_2. *Science*, 297, 833–836.

Berner, R. A. (2002): Examination of hypotheses for the Permo-Triassic boundary extinction by carbon cycle modeling. *PNAS*, 99, 4172–4177.

Burleson, M. L. and N. J. Smatresk (2000): Branchial chemoreceptors mediate ventilatory response to hypercapnic acidosis in channel catfish. *Comp. Biochem. Physiol. A*, **125**, 403–414.

Cameron, J. N. and G. K. Iwama (1989): Compromises between ionic regulation and acid-base regulation in aquatic animals. *Can. J. Zool.*, 67, 3078–3084.

Childress, J. J. (1995): Are there physiological and biochemical adaptations of metabolism in deep-sea animals? *Trends Ecol. Evolut.*, **10**, 30–36.

Childress J. J. and B. A. Seibel (1998): Life at stable low oxygen levels: adaptations of animals to oceanic oxygen minimum layers. *J. Exp. Biol.*, **201**, 1223–1232.

Childress, J. J., R. Lee, N. K. Sanders, H. Felbeck, D. Oros, A. Toulmond, M. C. K. Desbruyeres and J. Brooks (1993): Inorganic carbon uptake in hydrothermal vent tubeworms facilitated by high environmental PCO_2. *Nature*, **362**, 147–149.

Claiborne, J. B., S. L. Edwards and A. I. Morrison-Shetlar (2002): Acid-base regulation in fishes: cellular and molecular mechanisms. *J. Exp. Biol.*, 293(3), 302–319.

Cornette, J. L., B. S. Lieberman and R. H. Goldstein (2002): Documenting a significant relationship between macroevolutionary origination rates and Phanerozoic pCO_2 levels. *PNAS*, **99**, 7832–7835.

Crocker, C. E. and J. J. Cech (1996): The effects of hypercapnia on the growth of juvenile white sturgeon, *Acipenser transmontanus*. *Aquaculture*, **147**, 293–299.

D'Avino, R. and R. DeLuca (2000): Molecular modelling of *Trematomus newnesi* Hb1: insights for a lowered oxygen affinity and lack of Root effect. *Proteins*, 39(2), 155–165.

Desrosiers, R. R., J. Desilets and F. Dube (1996): Early developmental events following fertilization in the giant scallop, *Placopecten magellanicus*. *Can. J. Fish. Aquat. Sci.*, 53, 1382–1392.

Dudley, R. (1998): Atmospheric oxygen, giant Palaeozoic insects and the evolution of aerial locomotor performance. *J. Exp. Biol.*, **201**, 1043–1050.

Edwards, S. L., J. B. Claiborne, A. I. Morrison-Shetlar and T. Toop (2001): Expression of Na^+/H^+ exchanger mRNA in the gills of the Atlantic hagfish (*Myxine glutinosa*) in response to metabolic acidosis. *Comp. Biochem. Physiol.*, **130**, 81–91.

Evans, D. H. (1984): The roles of gill permeability and transport mechanisms in euryhalinity. p. 239–283. In *Fish Physiology*, Vol. XA, ed. by W. S. Haar and D. J. Randall, Academic Press, New York.

Gage, J. D. and P. A. Tyler (1991): *Deep Sea Biology*. Cambridge University Press, New York.

Goffredi, S. K. and J. J. Childress (2001): Activity and inhibitor sensitivity of ATPases in the hydrothermal vent tubeworm *Riftia pachyptila*: a comparative approach. *Mar. Biol.*, 138(2), 259–265.

Graham, M. S., R. L. Hädrich and G. L. Fletcher (1985): Hematology of three deep-sea fishes: a reflection of low metabolic rates. *Comp. Biochem. Physiol. A*, **80**, 79–84.

Grosell, M., C. N. Laliberte, S. Wood, F. B. Jensen and C. M. Wood (2001): Intestinal HCO_3^- secretion in marine teleost fish: evidence for an apical rather than basolateral Cl^-/HCO_3^- exchanger. *Fish Physiol. Biochem.*, 24, 81–95.

Hädrich, R. L. (1996): Perspective on deep sea fishes. p. 121–131. In *Ocean Storage of Carbon Dioxide. Workshop 2-Environmental Impact*, ed. by B. Ormerod and M. V. Angel, International Energy Agency Greenhouse Gas R&D Programm, Cheltenham, U.K.

Haugan, P. M. and H. Drange (1996): Effects of CO_2 on the ocean environment. *Energ. Convers. Manage.*, 37, 1019–1022.

Heisler, N. (1986a): Acid-base regulation in fishes. p. 309–356. In *Acid-base Regulation in Animals*, ed. by N. Heisler, Elsevier Biomedical Press, Amsterdam.

Heisler, N. (1986b): Comparative aspects of acid-base regulation. P. 397–450. In *Acid-base Regulation in Animals*, ed. by N. Heisler, Elsevier Biomedical Press, Amsterdam.

Heisler, N. (1993): Acid-base regulation. p. 343–377. In *The Physiology of Fishes*, ed. by D. H. Evans, CRC Press Inc., Boca Raton (FL), U.S.A.

Hylland, P., S. Milton, M. Pek, G. E. Nilsson and P. L. Lutz (1997): Brain Na^+/K^+-ATPase activity in two anoxia tolerant vertebrates: Crucian carp and freshwater turtle. *Neurosci. Lett.*, 235(1–2), 89–92.

Ingermann, R. L., M. Holcomb, M. L. Robinson and J. G. Cloud (2002): Carbon dioxide and pH affect sperm motility of white sturgeon (*Acipenser transmontanus*). *J. Exp. Biol.*, **205**, 2885–2890.

Ishimatsu, A. and J. Kita (1999): Effects of environmental hypercapnia on fish. *Jap. J. Ichthyol.*, **46**, 1–13.

Ishimatsu, A., T. Kikkawa, M. Hayashi, K.-S. Lee and J. Kita (2004): Effects of CO_2 on marine fish: larvae and adults. *J. Oceanogr.*, **60**, this issue, 731–741.

Iwama, G. K. and N. Heisler (1991): Effect of environmental water salinity on acid-base regulation during environmental hypercapnia in the rainbow trout (*Oncorhynchus mykiss*). *J. Exp. Biol.*, **158**, 1–18.

Jouve-Duhamel, A. and J. P. Truchot (1983): Ventilation on the shore crab *Carcinus maenas* as a function of ambient oxygen and carbon dioxide: Field and laboratory studies. *J. Exp. Mar. Biol. Ecol.*, **70**, 281–296.

Knoll, A. K., R. K. Bambach, D. E. Canfield and J. P. Grotzinger (1996): Comparative earth history and late Permian mass extinction. *Science*, **273**, 452–457.

Kurihara, H., S. Shimode and Y. Shirayama (2004): Sub-lethal effects of elevated concentration of CO_2 on planktonic copepods and sea urchins. *J. Oceanogr.*, **60**, this issue, 743–750.

Langenbuch, M. and H. O. Pörtner (2002): Changes in metabolic rate and N-excretion in the marine invertebrate *Sipunculus nudus* under conditions of environmental hypercapnia: identifying effective acid-base parameters. *J. Exp. Biol.*, **205**, 1153–1160.

Langenbuch, M. and H. O. Pörtner (2003): Energy budget of Antarctic fish hepatocytes (*Pachycara brachycephalum* and *Lepidonotothen kempi*) as a function of ambient CO_2: pH dependent limitations of cellular protein biosynthesis? *J. Exp. Biol.*, **206**, 3895–3903.

Larsen, B. K., H. O. Pörtner and F. B. Jensen (1997): Extra- and intracellular acid-base balance and ionic regulation in cod (*Gadus morhua*) during combined and isolated exposures to hypercapnia and copper. *Mar. Biol.*, **128**, 337–346.

Lin, H., D. C. Pfeiffer, A. W. Vogl, J. Pau and D. J. Randall (1994): Immunolocalization of proton ATP-ase in the gill epithelia of rainbow trout. *J. Exp. Biol.*, **195**, 169–183.

Lutz, P. L. and G. E. Nilsson (1997): Contrasting strategies for anoxic brain survival—glycolysis up or down. *J. Exp. Biol.*, **200**, 411–419.

Marchetti, C. (1977): On geoengineering and the CO_2 problem. *Climatic Change*, **1**, 59–68.

Marchetti, C. (1979): Constructive solutions to the CO_2 problem. p. 299–311. In *Man's Impact on Climate*, ed. by W. Bach, J. Pankrath and W. Kellogg, Elsevier Science Publ., Amsterdam.

McKendry, J. E., W. K. Milsom and S. F. Perry (2001): Branchial CO_2 receptors and cardiorespiratory adjustments during hypercarbia in Pacific spiny dogfish (*Squalus acanthias*). *J. Exp. Biol.*, **204**, 1519–1527.

McKenzie, D. J., E. W. Taylor, A. Z. Dalla Valle and J. F. Steffensen (2002): Tolerance of acute hypercapnic acidosis by the European eel (*Anguilla anguilla*). *J. Comp. Physiol. B*, **172**, 339–346.

O'Dor, R. K. and D. M. Webber (1986): The constraints on cephalopods: why squid aren't fish. *Can. J. Zool.*, **64**, 1591–1605.

Ohsumi, T. (1995): CO_2 storage options in the deep sea. *Mar. Technol. Soc. J.*, **29**, 58–66.

Parmesan, C. and G. Yohe (2003): A globally coherent fingerprint of climate change impacts across natural systems. *Nature*, **421**, 37–42.

Pörtner, H. O. (1990): An analysis of the effects of pH on oxygen binding by squid (*Illex illecebrosus*, *Loligo pealei*) haemocyanin. *J. Exp. Biol.*, **150**, 407–424.

Pörtner, H. O. (1994): Coordination of metabolism, acid-base regulation and haemocyanin function in cephalopods. *Mar. Freshw. Behav. Phy.*, **25**, 131–148.

Pörtner, H. O. (2001): Climate change and temperature dependent biogeography: oxygen limitation of thermal tolerance in animals. *Naturwissenschaften*, **88**, 137–146.

Pörtner, H. O. (2002): Climate change and temperature dependent biogeography: systemic to molecular hierarchies of thermal tolerance in animals. *Comp. Biochem. Physiol.*, **132**, A739–761.

Pörtner, H. O. (2004): Climate variability and the energetic pathways of evolution: the origin of endothermy in mammals and birds. *Physiol. Biochem. Zool.* (in press).

Pörtner, H. O. and M. K. Grieshaber (1993): Characteristics of the critical PO_2(s): gas exchange, metabolic rate and the mode of energy production. p. 330–357. In *The Vertebrate Gas Transport Cascade: Adaptations to Environment and Mode of Life*, ed. by J. E. P. W. Bicudo, CRC Press Inc., Boca Raton (FL), U.S.A.

Pörtner, H. O. and A. Reipschläger (1996): Ocean disposal of anthropogenic CO_2: physiological effects on tolerant and intolerant animals. p. 57–81. In *Ocean Storage of CO_2. Environmental Impact*, ed. by B. Ormerod and M. Angel, Massachusetts Institute of Technology and International Energy Agency, Greenhouse Gas R&D Programme, Cheltenham/Boston.

Pörtner, H. O. and S. Zielinski (1998): Environmental constraints and the physiology of performance in squids. p. 207–221. In *Cephalopod Biodiversity, Ecology and Evolution*, ed. by A. I. L. Payne, M. R. Lipinski, M. R. Clarke and M. A. C. Roeleveld, South African Journal of Marine Science, 20.

Pörtner, H. O., A. Reipschläger and N. Heisler (1998): Metabolism and acid-base regulation in *Sipunculus nudus* as a function of ambient carbon dioxide. *J. Exp. Biol.*, **201**, 43–55.

Pörtner, H. O., C. Bock and A. Reipschläger (2000): Modulation of the cost of pHi regulation during metabolic depression: a 31P-NMR study in invertebrate (*Sipunculus nudus*) isolated muscle. *J. Exp. Biol.* **203**, 2417–2428.

Potts, W. T. W. (1994): Kinetics of sodium uptake in freshwater animals—a comparison of ion-exchange and proton pump hypotheses. *Am. J. Physiol.*, **266**, R315–R320.

Redfield, A. C. and R. Goodkind (1929): The significance of the Bohr effect on the respiration and asphyxiation of the squid, *Loligo pealei*. *J. Exp. Biol.*, **6**, 340–349.

Reipschläger, A. and H. O. Pörtner (1996): Metabolic depression during environmental stress: the role of extra- versus intracellular pH in *Sipunculus nudus*. *J. Exp. Biol.*, **199**, 1801–1807.

Reipschläger, A., G. E. Nilsson and H. O. Pörtner (1997): Adenosine is a mediator of metabolic depression in the marine worm *Sipunculus nudus*. *Am. J. Physiol.*, **272**, R350–R356.

Riebesell, U., D. A. Wolf-Gladrow and V. Smetacek (1993): Carbon dioxide limitation of marine phytoplankton growth rates. *Nature*, **361**, 249–251.

Riebesell, U., I. Zondervan, B. Rost, P. D. Tortell, R. E. Zeebe and F. M. Morel (2000): Reduced calcification of marine Plankton in response to increased atmospheric CO_2. *Nature*, **407**, 364–367.

Sanders, N. K. and J. J. Childress (1990): A comparison of the respiratory function of the hemocyanins of vertically migrating and non-migrating oplophorid shrimps. *J. Exp. Biol.*, **152**, 167–187.

Scheid, P., H. Shams and J. Piper (1989): Gas exchange in vertebrates. *Verh. Dtsch. Zool. Ges.*, **82**, 57–68.

Seibel, B. A. and P. J. Walsh (2001): Potential impacts of CO_2 injections on deep-sea biota. *Science*, **294**, 319–320.

Seibel, B. A., E. V. Thuesen, J. J. Childress and L. A. Gorodezky (1997): Decline in pelagic cephalopod metabolism with habitat depth reflects differences in locomotory efficiency. *Biol. Bull.*, **192**, 262–278.

Shirayama, Y. (1995): Current status of deep-sea biology in relation to the CO_2 disposal. p. 253–264. In *Direct Ocean Disposal of Carbon Dioxide*, ed. by N. Handa and T. Oshumi, TERRAPUB, Tokyo.

Shirayama, Y. (2002): Towards comprehensive understanding of impacts on marine organisms due to raised CO_2 concentration. In *Proceedings of the 5th International Symposium on CO_2 Fixation and Efficient Utilization of Energy*, Tokyo Institute of Technology, Tokyo.

Tamburri, M. N., E. T. Peltzer, G. E. Friedrich, I. Aya, K. Yamane and P. G. Brewer (2000): A field study of the effects of CO_2 ocean disposal on mobile deep-sea animals. *Mar. Chem.*, 72, 95–101.

Tamburrini, M., M. Romano, V. Carratore, A. Kunzmann, M. Coletta and G. diPrisco (1998): The hemoglobins of the Antarctic fishes *Artedidraco orianae* and *Pogonophryne scotti*. *J. Biol. Chem.*, 273(49), 32452–32459.

Thomas, C. D.; A. Cameron, R. E. Green, M. Bakkenes, L. J. Beaumont, Y. C. Collingham, B. F. N. Erasmus, M. Ferreira de Siqueira, A. Grainger, L. Havannah, L. Hughes, B. Huntley, A. S. van Jaarsveld, G. F. Midgley, L. Miles, M. A. Ortega-Huerta, A. Townsend Peterson, O. L. Phillips and S. E. Williams (2004): Extinction risk from climate change. *Nature*, **427**, 145–148.

Torres, J. J. and G. N. Somero (1988): Vertical distribution and metabolism in Antarctic mesopelagic fishes. *Comp. Biochem. Physiol.*, **90B**, 521–528.

Truchot, J. P. (1979) Mechanisms of compensation of blood respiratory acid-base disturbances in the shore crab *Carcinus maenas* (L.). *J. Exp. Zool.*, **210**, 407–416.

van Dijk, P. L. M., C. Tesch, I. Hardewig and H. O. Pörtner (1999): Physiological disturbances at critically high temperatures. A comparison between stenothermal Antarctic, and eurythermal temperate eelpouts (Zoarcidae). *J. Exp. Biol.*, **202**, 3611–3621.

Vinogradov, G. A. and V. T. Komov (1985): Ion regulation in the perch, *Perca fluviatilis*, in connection with the problem of acidification of water bodies. *J. Ichthyol.*, **25**, 53–61.

Wells, R. M. G., M. D. Ashby, S. J. Duncan and J. A. Macdonald (1980): Comparative study of the erythrocytes and haemoglobins of nototheniid fishes from Antarctica. *J. Fish Biol.*, **17**, 517–527.

Wheatly, M. G. (1989): Physiological response of the crayfish *Pacifasticus leniusculus* (Dana) to environmental hypoxia. I. Extracellular acid-base and electrolyte status and transbranchial exchange. *J. Exp. Biol.*, 57, 673–680.

Whiteley, N. M., J. L. Scott, S. J. Breeze and L. McCann (2001): Effects of water salinity on acid-base balance in decapod crustaceans. *J. Exp. Biol.*, **204**, 1003–1011.

Wickins, J. F. (1984): The effect of hypercapnic sea water on growth and mineralization in penaeid prawns. *Aquaculture*, **41**, 37–48.

Wigley, T. M. L., R. Richels and J. A. Edmonds (1996): Economic and environmental choices in the stabilization of atmospheric CO_2 concentrations. *Nature*, **379**, 240–243.

Wolf-Gladrow, D. A., U. Riebesell, S. Burkhardt and J. Bijma (1999): Direct effects of CO_2 concentration on growth and isotopic composition of marine plankton. *Tellus*, **51B**, 461–476.

Wood, C. M., C. L. Milligan and P. J. Walsh (1999): Renal responses of trout to chronic respiratory and metabolic acidosis and metabolic alkalosis. *Am. J. Physiol.*, **46**, R482–R492.

Wood, C. M., B. Wilson, H. L. Bergman, A. N. Berman, P. Laurent, G. Otiang'a-Owite and P. J. Walsh (2002): Obligatory urea production and the cost of living in the Magadi tilapia revealed by acclimation to reduced salinity and alkalinity. *Physiol. Biochem. Zool.*, **75**(2), 111–122.

Zielinski, S., F. J. Sartoris and H. O. Pörtner (2001): Temperature effects on hemocyanin oxygen binding in an Antarctic cephalopod. *Biol. Bull.*, **200**, 67–76.

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Synergistic effects of temperature extremes, hypoxia, and increases in CO_2 on marine animals: From Earth history to global change

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[1] Currently rising CO_2 levels in atmosphere and marine surface waters as well as projected scenarios of CO_2 disposal in the ocean emphasize that CO_2 sensitivities need to be investigated in aquatic organisms, especially in animals which may well be the most sensitive. Moreover, to understand causes and effects, we need to identify the physiological processes that are sensitive to CO_2 beyond the current emphasis on calcification. Few animals may be acutely sensitive to moderate CO_2 increases, but subtle changes due to long-term exposure may already have started to be felt in a wide range of species. CO_2 effects identified in invertebrate fauna from habitats characterized by oscillating CO_2 levels include depressed metabolic rates and reduced ion exchange and protein synthesis rates. These result in shifts in metabolic equilibria and slowed growth. Long-term moderate hypercapnia has been observed to produce enhanced mortality with as yet unidentified cause and effect relationships. During future climate change, simultaneous shifts in temperature, CO_2, and hypoxia levels will enhance sensitivity to environmental extremes relative to a change in just one of these variables. Some interactions between these variables result from joint effects on the same physiological mechanisms. Such interactions need to be considered in terms of future increases in atmospheric CO_2 and its uptake by the ocean as well as in terms of currently proposed mitigation scenarios. These include purposeful injection of CO_2 in the deep ocean or Fe fertilization of the surface ocean, which reduces subsurface O_2 levels. The resulting ecosystem shifts could develop progressively, rather than beyond specific thresholds, such that effects parallel CO_2 oscillations. It is unsure to what extent and how quickly species may adapt to permanently elevated CO_2 levels by microevolutionary compensatory processes.

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1. Introduction

[2] Global climate change includes the ongoing accumulation of CO_2 in the atmosphere as well as regional trends in other climate factors, due to increases in average temperatures and temperature variability [*Intergovernmental Panel on Climate Change* (*IPCC*), 2001]. Global warming threatens to change species specific geographical distributions, including local extinction of previously common species [*Parmesan and Yohe*, 2003; *Thomas et al.*, 2004]. In this context, the CO_2 emitted by human activities (anthropogenic CO_2) will also play a role as it permeates into ocean surface layers. There it will affect marine organisms in combination with current trends of warming and eutrophication, which also involve a reduction of oxygen levels.

[3] Various strategies of reducing greenhouse gas emissions or of carbon sequestration have been discussed during recent years to mitigate effects of climate change [*Lackner*, 2003]. Such strategies would reduce the degree of CO_2 accumulation in surface waters; however, they would also transfer CO_2 effects expected from accumulation in the upper ocean to the deeper ocean. Direct ocean disposal scenarios include injecting CO_2 into the deep ocean, with some dispersal over part of the water column or in the form of concentrated lakes of liquid CO_2 [*Ohsumi*, 1993]. It has also been proposed to neutralize added CO_2 by adding limestone [*Kheshgi*, 1995; *Caldeira and Rau*, 2000; *Lackner*, 2003] as a means to extend storage time and minimize pH changes. Alternatively, iron fertilization of surface waters has been proposed as an indirect means of ocean disposal. Thus atmospheric CO_2 is bound up by organic matter production, which is exported to the deep ocean and released as dissolved inorganic

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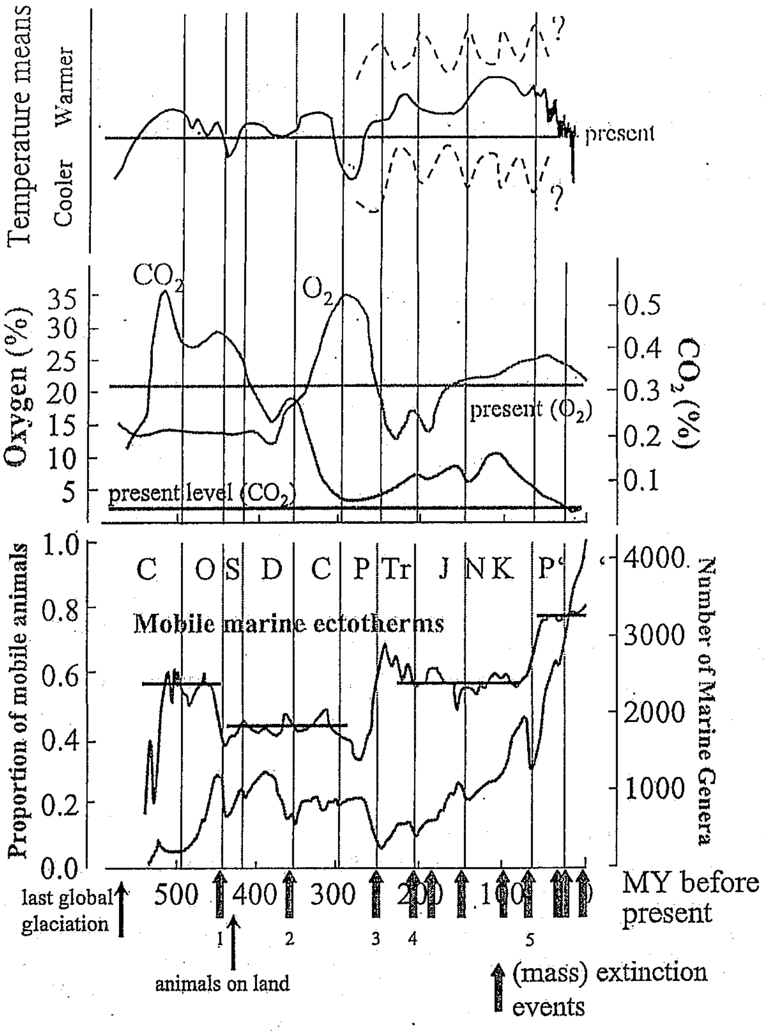

Figure 1. Changes in mean global temperatures, atmospheric oxygen, and CO_2 levels in Earth history compared to present atmospheric levels and the evolution of marine fauna (figure modified after *Dudley* [1998], *Berner and Kothalova* [2001], *Huch et al.* [2001], and *Bambach et al.* [2002]). High CO_2 and low oxygen levels are interpreted to favor hypometabolic life forms. Once ambient O_2 levels were high and CO_2 levels low, a stepwise evolutionary shift to more mobile animal forms starting with the Perm Trias mass extinction events appear as a consequence of (climate-induced) evolutionary crises. Such shifts are consistent with the "cost of eurythermy" hypothesis [*Pörtner*, 2004]. Survival of high-energy turnover lifestyles and elevated capacities of circulatory and ventilatory structures was favored by cold exposures during excessive climate oscillations. During more stable climate periods the upward shift of performance levels and energy turnover likely supported the exponential rise in the number of marine genera over the last 55–65 million years, when atmospheric CO_2 levels were low (see text). See color version of this figure in the HTML.

carbon (DIC) through bacterial activity [*Gribbin*, 1988]. In this case, the detour used to bind CO_2 first into organic matter by biological activity causes an increase in the complexity of environmental impacts, ranging from a large-scale loss of surface macronutrients to enhanced rates of oxygen consumption in the deep sea. The latter could reduce oxygen availability for higher life to the point that deep sea fauna could suffer from combined effects of hypercapnia and hypoxia. Such proposals need to be examined not only in terms of feasibility or cost, but also with respect to potential environmental impacts. Benefits and risks must be weighed carefully before such proposals are implemented.

[4] Clearly, future scenarios not only involve changes in oceanic CO_2 inventories and associated effects on marine organisms. Business-as-usual scenarios lead to continued CO_2 enrichment along with warming and eutrophication trends which cause a decrease in dissolved oxygen in

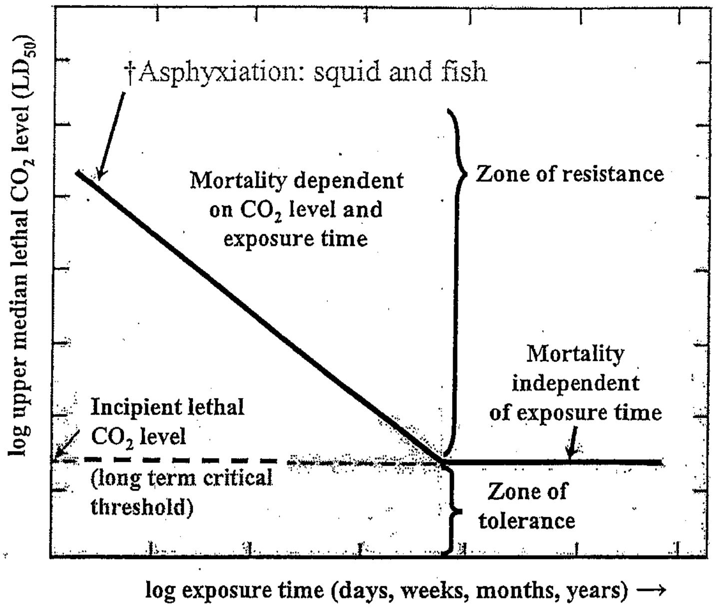

Figure 2. Roles of timescale and CO_2 concentration in causing time- and concentration-dependent mortality in animals (conceptual considerations). Long-term critical thresholds(= incipient lethal CO_2 levels) may exist at the species level. However, the onset of long-term effects in individual species at low levels of CO_2 accumulation (see text) and the likelihood of differences between sensitivities of species suggest that ecosystem shifts may develop progressively rather than suddenly beyond thresholds. In consequence, effects may parallel environmental CO_2 oscillations. Acute effects involve asphyxiation as seen (for different reasons and at different concentrations) in squid and fish (see text). Note that the depiction is hypothetical as such data and graphs have not been generated for any organism under CO_2. Long-term critical levels and the underlying physiological mechanisms are unknown (figure developed based on studies of thermal stress in fish by *Doudoroff* [1945], after *Cossins and Bowler* [1987]).

surface waters. Indirect disposal during iron fertilization would be associated with eutrophication and oxygen depletion in the deep sea. Temperature and oxygen will thus change in parallel with CO_2 levels. Increased CO_2 could affect the sensitivity of organisms to other environmental factors and vice versa. Thus the combined effects of these variables must also be considered. Here we aim to provide a conceptual analysis of how effects from these factors may be intertwined and to identify gaps in our knowledge. Our goal is to develop a mechanistic cause-and-effect understanding and to explore possibly relevant tolerance windows or thresholds which are set by the integrated changes in all of these factors. Sensitivities of different life stages also require consideration. Here we rely on Shelford's law of tolerance, which has been used in thermal physiology to identify ecologically relevant thermal limitation thresholds in marine ectothermal animals [*Frederich and Pörtner*, 2000; *Pörtner*, 2001, 2002a, 2002b].

2. CO_2 Effects: Timescales and Tolerance Limits

[5] Extant animal life, especially that with high levels of performance, evolved when atmospheric CO_2 had fallen far below the Cambrian levels of 5000 ppm (see Figure 1; in this paper the partial pressure of CO_2, pCO_2, is expressed as a ppm fraction of atmospheric pressure). Oscillating CO_2 levels may have been relevant in animal evolutionary history. For example, a detrimental role of elevated aquatic CO_2 levels has been suggested to contribute to the Permian/Triassic mass extinction events in Earth history [*Knoll et al.*, 1996]. In present day marine ecosystems, CO_2 partial pressures may be elevated (hypercapnia) periodically or permanently due to natural phenomena in sediments of the intertidal zone, in estuaries [*Diaz and Rosenburg*, 1995] or in hypoxic bottom waters [*Knoll et al.*, 1996]. In most of the pelagic zones of the sea, however, CO_2 levels remain relatively constant. Physiological and ecological studies of CO_2 effects should support an evaluation of the relevance of CO_2 as an evolutionary factor and as a potential stress factor in extant marine environments.

[6] Effects of elevated CO_2 levels on marine animals have recently been reviewed [*Pörtner et al.*, 2004a]. Here, after summarizing and updating this work, we emphasize the need for further study from a conceptual point of view. Studies of CO_2 effects have distinguished acute from chronic, and lethal from sublethal effects. However, the continuum between time- and concentration-dependent effects has not been clearly elaborated for any species studied (Figure 2), especially with respect to the existence of critical thresholds limiting long-term survival. The physiological mechanisms underlying long-term critical levels are also unknown although individual physiological mechanisms that respond to CO_2 have been identified. The integration of individual effects into a whole animal or

even whole ecosystem scenario is still in its infancy. The early onset of long-term effects in individual species and the likelihood of different sensitivity levels in various species would suggest that ecosystem shifts develop progressively rather than simply at given thresholds, and thus they may follow environmental CO_2 oscillations.

2.1. Mechanisms of Short-Term Sensitivity to CO_2

[7] Available studies indicate that physiological CO_2 effects are mediated through low pH in acidified water as well as through diffusive CO_2 entry into the organism. Elevated CO_2 elicits an acidosis in tissues and body fluids. Acute effects may occur because plasma pH is lowered rapidly and oxygen transport by pH sensitive blood pigments is disrupted. For example, in cephalopods, a limited concentration of pigment (haemocyanin) is dissolved extracellularly in the plasma. Efficient oxygen transport by haemocyanin strongly depends on pH. This dependence may be what defines critical CO_2 levels for short-term exposure (min to hours). Critical CO_2 levels can be as low as about 3 kPa (30,000 ppm) in the coastal squid *Loligo pealei* [*Redfield and Goodkind*, 1929] or less than 1 kPa (10,000 ppm) in the more active open ocean squid *Illex illecebrosus* [*Pörtner*, 1990].

[8] In fish, *Ishimatsu et al.* [2004] consider cardiac failure as the main physiological perturbation responsible for acutely limited tolerance to high CO_2 levels. In yellowtail tuna (*Seriola quinqueradiata*), they found a dramatic drop in cardiac output at 5% CO_2. As a result, there was severely limited oxygen delivery to tissues even though oxygen concentrations in arterial blood remained nearly constant [see also *Lee et al.*, 2003]. Thus under hypercapnia in fish, circulation rather than ventilation is limiting, similar to recent findings for fish under thermal stress (reviewed by *Pörtner et al.* [2004b]).

[9] Susceptibility to elevated CO_2 levels is higher for early developmental stages (eggs, sperm, larvae, juveniles) than for adults [*Crocker and Cech*, 1996; *Ingermann et al.*, 2002; *Kikkawa et al.*, 2003; *Ishimatsu et al.*, 2004]. In adult fish, mortality due to elevated pCO_2/and thus lower pH sets in when pCO_2 goes beyond 30,000 to 50,000 ppm (for incubation periods up to 72 hours) [*Takeda and Itazawa*, 1983; *Grottum and Sigholt*, 1996; *Ishimatsu et al.*, 2004], whereas the equivalent limit is 13,000 to 28,000 ppm in fish larvae.

[10] These studies generally indicate, that the sensitivity to acutely elevated CO_2 levels is lower in fish than in most invertebrates, especially those having high performance levels, e.g., the coleoid cephalopods (see above). Fish may be less sensitive to acute effects because they use intracellular haemoglobin in oxygen transport as opposed to the extracellular haemocyanin used by cephalopods. Furthermore, vertebrates have a higher regulatory capacity of ion exchange and they have epithelia, which limit diffusive ion losses. Such may promote higher short-term as well as long-term CO_2 tolerance in vertebrates relative to invertebrates.

[11] The trend to accumulate CO_2 and to lose the capacity to transport oxygen in the blood because of lowered pH might be counteracted by enhanced ventilation, as observed repeatedly in fish [e.g., *McKenzie et al.*, 2002]. This would cause enhanced CO_2 release and an alleviation of the pH disturbance. Yet, ventilatory capacity to enhance CO_2 release is extremely limited in water breathers because of the close to equilibrium distribution of CO_2 between the organism and the water [*Scheid et al.*, 1989]. Water breathers must therefore rely nearly exclusively on transepithelial ion exchange mechanisms to compensate for the disturbance of pH by high CO_2. With elevated PCO_2, pH drops and bicarbonate levels rise depending on the amount of non-bicarbonate buffers [*Heisler*, 1986a]. Bicarbonate is observed to increase in all animals studied so far, e.g., fish [*Heisler*, 1986b; *Larsen et al.*, 1997; *Ishimatsu et al.*, 2004], crustaceans [*Wheatly*, 1989] and other invertebrates (*Sipunculus nudus* [*Pörtner et al.*, 1998]). Hence acid-base and ion equilibria reach new steady state values, associated with specific, long-term shifts in metabolic equilibria. In most cases such processes may not be acutely life threatening for the individual; nevertheless, they are still expected to hamper slow processes like growth and reproduction. Thus they are potentially harmful on longer timescales and at the population, species, and ecosystem levels.

[12] Many studies have identified detrimental effects of low ambient pH on reproductive success, growth and survival of marine animals [e.g., *Wickins*, 1984; *Vinogradov and Komov*, 1985; *Crocker and Cech*, 1996; *Desrosiers et al.*, 1996; *Alvarado-Alvarez et al.*, 1996; *Kurihara et al.*, 2004]. In adult organisms, tolerance to pH excursions varies greatly, ranging from 50% mortality observed in mesopelagic copepods after 6 days of exposure to waters with a pH level 0.2 units below the control [*Yamada and Ikeda*, 1999] to the same level of mortality reached after a 60 day exposure to a pH of 6.90 in *Ostrea edulis* [*Bamber*, 1990]. Adverse effects increase with the intensity of the pH disturbance and the duration of exposure [*Bamber*, 1987, 1990; *Grottum and Sigholt*, 1996; *Adams et al.*, 1997] (see Figure 2). In addition to the effects due to changes in pH, we also need to reconsider those due to increased CO_2 and bicarbonate [*Pörtner and Reipschläger*, 1996]. *Ishimatsu et al.* [2004] found that at the same pH, seawater with CO_2 had higher acute toxicity than that acidified with HCl. Hence CO_2 acts more quickly than fixed acid, probably because of its rapid diffusive entry into the organism.

2.2. Mechanisms of Long-Term Sensitivity to CO_2

[13] Overall, the critical thresholds for the onset of detrimental effects during long-term CO_2 exposures (see Figure 2) are not yet available, with most studies only analyzing LC_{50} values for short to medium exposure periods (hours to a couple of weeks). Long-term critical thresholds (Figure 2) are likely to be found at unexpectedly low levels of CO_2 for many animals. *Shirayama* [2002] and *Shirayama and Thornton* [2005] demonstrated that a reduction in growth rate and survival of echinoderms and gastropods sets in long term at CO_2 concentrations only 200 ppm (0.02 kPa PCO_2) above extant levels. High sensitivity to long-term exposure is emphasized by recent data obtained in the marine mussel *Mytilus galloprovincialis* grown during a 3 month hypercapnic incubation in water at pH 7.3. This pH is close to that expected in marine surface waters around 2300 [*Caldeira and Wickett*, 2003]. Under these conditions, the mussels displayed a 55% reduction in shell growth rate and soft body growth (Figure 3), combined with a 65% reduction in metabolic rate [*Michaelidis et al.*, 2005]. Thus we suspect substantial effects in marine surface waters

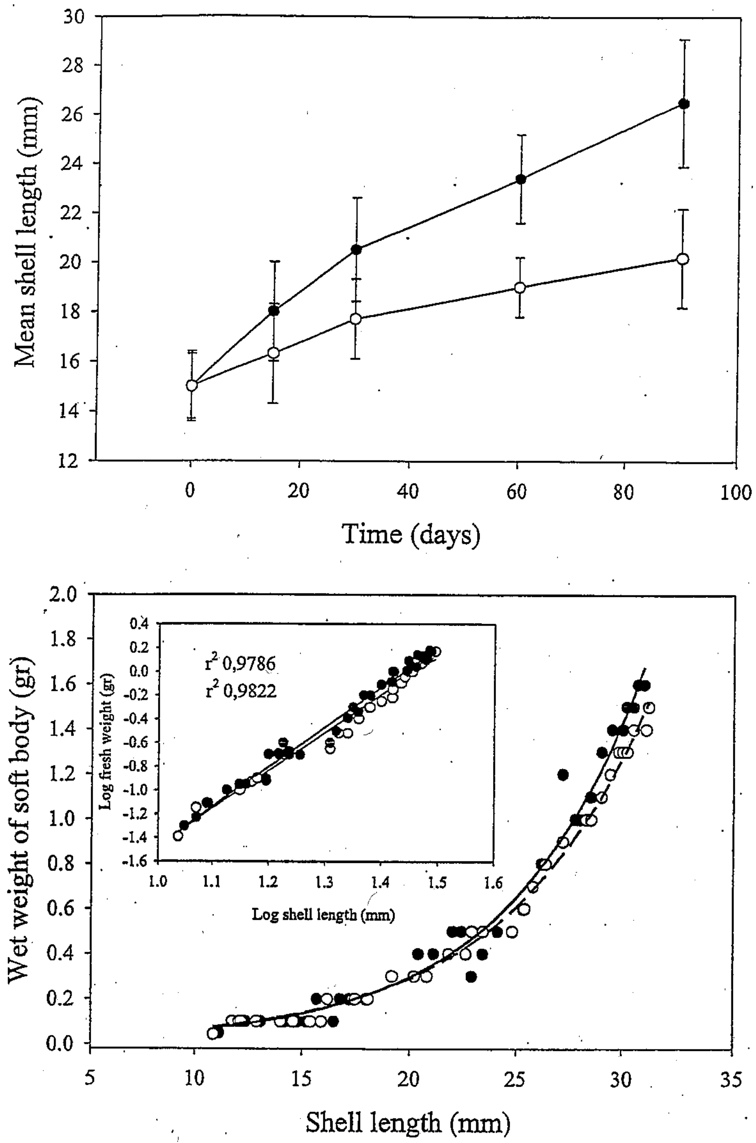

Figure 3. (top) Mean rate of shell growth of normocapnic (closed cycles) and hypercapnic (open cycles) mussels *Mytilus galloprovincialis* at 18°C. (bottom) Fresh weight was closely related to shell length in growing mussels under both normocapnia (solid line, closed cycles) and hypercapnia (dashed line, open circles) (data by *Michaelidis et al.* [2005]). Hypercapnic mussels kept at sea water pH 7.3 as set by controlled additions of gaseous CO_2 displayed a 55% reduction in growth rate. The chosen water pH value is close to that expected from business-as-usual scenarios of anthropogenic CO_2 production and release into the atmosphere by year 2300 [*Caldeira and Wickett*, 2003].

from CO_2 levels reached during business-as-usual scenarios of anthropogenic CO_2 production and release.

[14] Considering the spectrum of species-specific findings and sensitivities, we will be able to assess the patterns of sensitivity and the capacities for adaptation only if we can identify the unifying principles of the underlying physiological mechanisms that limit long-term performance and fitness under hypercapnia. Within an organism, changes in CO_2, pH and bicarbonate affect molecular, cellular, tissue, and whole organism functions. Similar to effects of temperature [*Pörtner*, 2002a], effects of CO_2 at lower levels of organization (e.g., on various molecular functions) likely integrate into functional changes at higher levels of biological organization. These higher-level functions may result more sensitive than each individual molecular function. The first sign of sensitivity would be a decrease in functional capacity [*Pörtner et al.*, 2004a] (see Figure 5).

[15] Existing information on physiological effects in marine animals originates mostly from studies of invertebrates adapted to frequent CO_2 oscillations within their natural habitat. The most prominent adaptive strategy of these invertebrates is their ability to suppress aerobic energy turnover rates ("metabolic depression") in response to environmental stress such as hypercapnia [*Barnhart and McMahon*, 1988; *Barnhart*, 1989; *Rees and Hand*, 1990; *Pörtner et al.*, 1998] (for a review, see *Guppy and Withers*

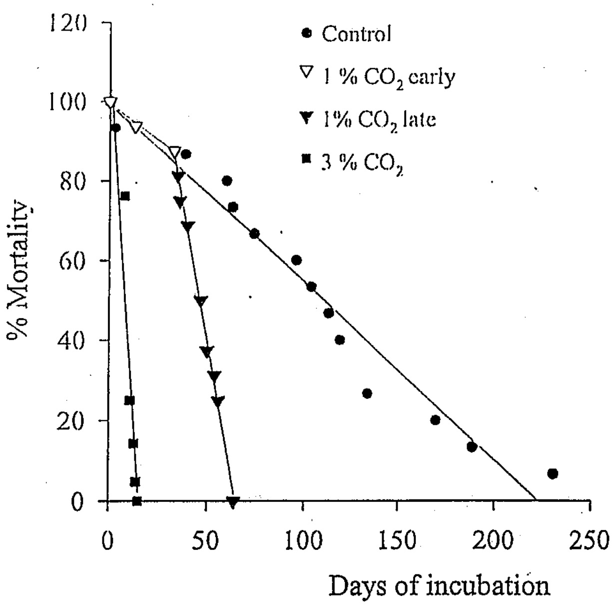

Figure 4. Limited tolerance of the eurybathic noncalcifying sipunculid *S. nudus* (L.) to long-term "disturbed" maintenance under control conditions and at elevated CO_2. Animals were stimulated to repeatedly rebury into sediment. Note the delayed onset of enhanced mortality under 1% CO_2. Under these conditions, no decrease in body energy stores occurred; however, animals were unable to continue repeated reburying (data by *Langenbuch and Pörtner* [2004]).

[1999]). Under hypercapnia, this suppression is mediated by the incomplete compensation of disturbances in intra- and/or extracellular pH levels (pHi/pHe). In brine shrimp embryos, this suppression is mainly attributed to an acidotic shift in pHi, whereas in *Sipunculus nudus*, a reduction in pHe contributes to a depression of aerobic energy turnover [*Reipschläger and Pörtner*, 1996].

[16] Mechanisms contributing to hypercapnia-induced metabolic depression have been extensively investigated in the sipunculid *S. nudus*, a marine eurybathic worm from intertidal and subtidal sediments. Under conditions of severe respiratory acidosis (PCO_2 = 10,000 ppm), the oxygen consumption of whole animals is reduced [*Pörtner et al.*, 1998]. This reduction involves a 45% drop in the metabolic rate of (isolated) muscle tissue [*Langenbuch and Pörtner*, 2002]. During this metabolic depression less ATP is consumed because of the lower cost of net H^+ excretion from the muscle tissue at a decreased rate of intracellular acid-base regulation [*Pörtner et al.*, 2000]. In addition to metabolic depression, a metabolic imbalance may arise from acidosis. *Langenbuch and Pörtner* [2002] found lowered ratios of oxygen consumed (O) to nitrogen produced (N) in muscle tissue of *S. nudus* despite simultaneous declines in ammonia excretion and oxygen consumption rates. Probably this implies a change in the use of amino acid substrates in catabolism, namely a preferred degradation of low O/N amino acids like asparagine or glutamine, or of their dicarboxylic acids. As a result, there is increased production of bicarbonate, which may partially compensate for the intracellular acidosis [*Langenbuch and Pörtner*, 2002]. Moreover, the decrease in O/N ratios as well as a drop in phenylalanine incorporation rates into muscle protein that has been determined under severe acidosis suggests that hypercapnia-induced acidosis leads to long-term reduction in protein biosynthesis rates [*Langenbuch and Pörtner*, 2002; M. Langenbuch et al., manuscript in preparation, 2005]. Eventually this could enhance mortality (Figure 4) [*Langenbuch and Pörtner*, 2004]. These findings may explain the permanent decrease in growth found during long-term uncompensated extracellular acidosis induced by hypercapnia in the mussel, *Mytilus galloprovincialis* [*Michaelidis et al.*, 2005] (see Figure 3). This growth reduction is likely to be due to the pH-dependent reduction in the rates of both calcification and protein synthesis. In extreme cases, hypercapnia and anoxia-induced hypometabolism is associated with a global arrest of cellular transcription and translation, as found with *Artemia franciscana* embryos [*Hofmann and Hand*, 1994; *van Breukelen et al.*, 2000]. All these data suggest a progressive limitation of essential cellular functions under elevated CO_2 concentrations. Dose-response analyses of expected anthropogenic CO_2 accumulation and pH reduction scenarios are urgently needed to provide a quantitative understanding of CO_2 effects. They are also needed to determine whether shifts develop progressively rather than beyond thresholds (Figure 2).

[17] Further whole animal investigations of *S. nudus* revealed that metabolic depression under hypercapnia goes beyond just modulating the cost of cellular acid-base regulation. Oxygen consumption and associated ventilatory activity were also reduced in response to an accumulation of the neuromodulator adenosine, which suggests that a central nervous mechanism also contributes [*Reipschläger et al.*, 1997; *Pörtner et al.*, 1998]. In vertebrates, adenosine has been shown to depress neuronal excitability (e.g., in the brains of mammals) [*Rudolphi et al.*, 1992] as well as the excitability at neuromuscular endplates [*Robitaille et al.*, 1999; *Thomas and Robitaille*, 2001; *Schwartz et al.*, 2003]. Infusion of adenosine causes metabolic depression in *S. nudus*, suggesting a beneficial metabolic response to temporary CO_2 accumulation [*Reipschläger et al.*, 1997]. This short-term benefit may switch to being harmful under long-term exposure due to depression of whole organism functions which would reduce fitness for survival. Yet, we understand neither the CO_2-dependent mechanism of adenosine production and release nor the extent to which the substance remains accumulated under chronic CO_2 stress. In conclusion, available data for *S. nudus* shows that CO_2 fluctuations are felt at all levels of organization: from specific cellular metabolic pathways to, ultimately, the functional integration of different tissue types into whole organism functioning and its control by the central nervous system (see Figure 5). Studies addressing how hypercapnia affects the role of adenosine or other neurotransmitters in marine fish are not yet available. It remains to be seen if the key physiological process ultimately limiting CO_2 tolerance may be located at a higher, i.e., systemic or central nervous, level of the organism.

[18] At the ambient CO_2 levels that elicit metabolic depression in invertebrates, such depression is not visible at the whole animal level in most fish. Probably there is

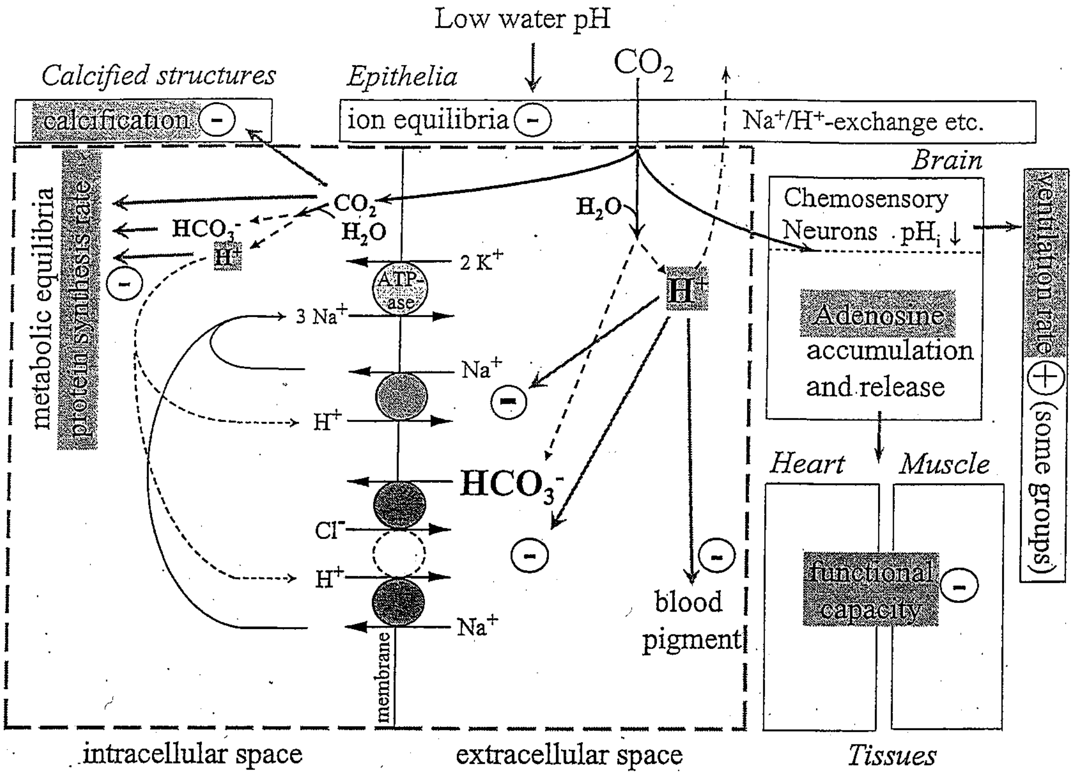

Figure 5. Processes relevant for growth and energy budget (shaded areas) in a concert of molecular to organismic CO_2 effects depicted for a generalized marine water breathing animal (updated from *Pörtner et al.* [2004a] (for further explanations see text)). Sublethal effects on short to medium timescales include the modulation of cellular processes, functional capacity of tissues, shifts in energy budget due to changing energy demand of individual processes, and of behavorial aspects, including the functional capacity for food uptake and consumption. An increase in ventilation rate under elevated CO_2 levels was observed in fish (see text) and in cephalopods (*Sepia officinalis* (S. Schmidt et al., unpublished manuscript, 2005)). Several of these processes are also affected by temperature (due to temperature-induced hypoxia) and by ambient hypoxia itself (e.g., acid-base regulation, functional capacity and aerobic scope, protein synthesis rate, and adenosine formation and release (see text and Figure 6)). See color version of this figure in the HTML.

complete compensation of extracellular and intracellular acidosis (in inner organs and musculature) (e.g., in eelpout, *Pachycara brachycephalum*, or Atlantic cod, *Gadus morhua*) [*Heisler*, 1986a, 1986b; *Larsen et al.*, 1997; *Ishimatsu et al.*, 2004; C. Burghard et al., unpublished manuscript, 2005]. Metabolism may even be stimulated by hypercapnia. However, at the cellular level, mechanisms leading to a marked reduction in energy turnover seem to be similar in fish and marine invertebrates (see above). Similar to *S. nudus* muscle tissue, hepatocytes of two species of Antarctic fish also showed a decrease of oxygen consumption rates under high CO_2 stress; simultaneously there was an almost complete shut down of cellular protein biosynthesis [*Langenbuch and Pörtner*, 2003].

[19] In contrast to observations in *S. nudus*, ventilatory frequency and effort increase under hypercapnia in teleosts and elasmobranchs [*Burleson and Smatresk*, 2000; *McKendry et al.*, 2001; *McKenzie et al.*, 2002] and also in cephalopods (S. Schmidt et al., unpublished manuscript, 2005). Such increase may require enhanced metabolic costs. Unfortunately no comprehensive data are available to quantify the contribution of elevated ventilatory activity to CO_2-induced increases in energy turnover. We also do not know the consequences of elevated ventilation for energy reallocation in an animal's overall energy budget (e.g., at the expense of growth, under long-term hypercapnic exposure in vivo).

[20] Such enhanced ventilation under high CO_2 in fish is similar to that observed in mammals. For mammals, enhanced respiratory drive under hypercapnia (observed at 5–10% CO_2 in air) has been attributed to the uncompensated intracellular acidosis in chemosensitive neurons causing an increased firing rate [*Filosa et al.*, 2002; *Wang et al.*, 2002]. Simultaneously, elevated ambient CO_2 causes bradycardia, i.e., a slowing of heart rate [e.g., *Brevard et al.*, 2003]. Elevated CO_2 also causes vasodilation of cerebral blood vessels due to combined effects of adenosine, NO, and low plasma pH, which affect ATP-sensitive K^+ channels and cause enhanced potassium ion conductance across vascular smooth muscle [*Nakahata et al.*, 2003; *Brevard et al.*, 2003]. Finally, very high CO_2 levels result in respiratory depression and anaesthesia in humans [*Dean et al.*, 2003].

[21] Given these findings for mammals, the responses of ventilation (enhanced frequency) and circulation (bradycardia) to hypercapnia also need to be studied in terms of their CO_2-dependent regulation in fish, particularly regarding their influence on the central nervous system. *Söderström and Nilsson* [2000], for instance, reported that the hypercapnia-induced increase in cerebral blood flow velocity in rainbow trout is independent of NO production. Thus mediating mechanisms may be different in lower vertebrates and must be carefully analyzed. Neurotransmitter or hormonal activity may also change. For example, environmental CO_2 stress is known to induce secretion of catecholamines into the circulation of fish [*Perry et al.*, 1989; *Aota et al.*, 1990]. There is also a clear influence of catecholamines on cardiovascular function in trout [*Bernier and Perry*, 1996]. Catecholamine secretion from chromaffine kidney cells is controlled by cholinergic nerve fibers of the sympathetic nervous system [*Bernier and Perry*, 1996]. In contrast, in more "primitive" organisms like hagfish or lampreys, adenosine may play a role in the control of hormone release [*Reid et al.*, 1998].

[22] Comparing the patterns seen in mammals and fish with those found in invertebrates suggests once again that the effect of metabolic suppression due to CO_2 sets in with lower CO_2 increments in invertebrates. The uncompensated acidosis found in some invertebrates, e.g., *Sipunculus nudus*, *Mytilus galloprovincialis*, and *Sepia officinalis* [*Pörtner et al.*, 1998; *Michaelidis et al.*, 2005; S. Schmidt et al., unpublished manuscript, 2005], may contribute to their lower resistance and enhanced mortality under long-term moderate hypercapnia, particularly if there is also metabolic depression. In contrast, acidosis under the same degree of hypercapnia in fish is nearly fully compensated. This reflects the enhanced capacity of the vertebrates to avoid early metabolic depression, and their comparatively high resistance to long-term elevated CO_2 levels. Available observations indicate a complex interaction of cellular, neural, and humoral factors in the control of essential systemic functions under hypercapnia (Figure 5). These observations also reflect changes in energy use and allocation at the cellular and organismic levels, with potential consequences for long-term survival.

3. Sensitivities to Temperature, Hypoxia, and CO_2

[23] The increasing importance of CO_2 as a general stress factor opens the question as to what extent CO_2 will interfere or combine with other factors shaping marine environments. Meridional temperature gradients and global climate patterns are seen as the most important factors governing large-scale biogeography of marine ectothermic animals [*Angel*, 1991]. Oscillations of ambient CO_2 and temperature may naturally parallel the concomitant development of ambient hypoxia, which occurs, for example in oxygen minimum layers at intermediate depths, in isolated bottom waters [*Knoll et al.*, 1996], in tide pools at night [*Bridges*, 1993], and in marine sediments (for a review, see *Grieshaber et al.* [1994]). These patterns may involve excessive respiration by macroalgae and metazoa (in tide pools) or by microbial life (in the sediment or bottom waters or oxygen minimum layers) which contribute to enhanced CO_2 accumulation via the oxidation of organic matter. Climate fluctuations and corresponding changes in ocean circulation (slowing of the thermohaline circulation) are seen as key processes that affect the oxygen budget of the ocean [*Matear et al.*, 2000; *Plattner et al.*, 2002; *Joos et al.*, 2003]. Concurrent changes in temperature (due to global warming), oxygen (due to eutrophication and less oxygen export to the deep due to increased stratification), and anthropogenic CO_2 accumulation could interact in terms of their combined effect on marine ecosystems. Although studies have investigated the relevance of each of these factors, no experimental studies have focused on their combined effects. Thus we provide here a conceptual analysis of whether and how these factors may exert synergistic effects on marine fauna.

3.1. Temperature

[24] Compared with terrestrial fauna, marine organisms cover larger ranges of geographical distribution and exhibit latitudinal zonation which is more distinct than that of terrestrial animals [*Pielou*, 1979; *Rapoport*, 1994]. Temperature is a key factor in these patterns. Therefore the identification of mechanisms of thermal limitation and adaptation [e.g., *Johnston and Bennett*, 1996] is important, particularly in the light of future shifts in the geographical distribution and in the physiological performance of ectothermic animals due to global warming [e.g., *Wood and MacDonald*, 1997; *Pörtner et al.*, 2001].

[25] In various phyla of marine invertebrates and in fish, the transition to internal (systemic) hypoxia was found to characterize the borders of the thermal tolerance window, in fully oxygenated waters. Finally, anaerobic metabolism sets in at both cold and warm temperature extremes. These observations led to the development of the concept that animals have an oxygen-limited thermal tolerance [*Pörtner et al.*, 2000, 2004b; *Pörtner*, 2001, 2002a, 2002b] (see Figure 6). This concept suggests that the first level of thermal intolerance at low and high temperature extremes in animals is due to a loss in whole organism aerobic scope when near the low and high edges of the thermal envelope, i.e., the so-called pejus thresholds. This loss is not caused by reduced concentrations of ambient oxygen, but by the limited capacity of oxygen supply mechanisms (ventilation, circulation) to cover an animal's temperature-dependent oxygen demand. With continued cooling or warming, aerobic scope finally disappears at low or high critical threshold temperatures (T_c), where there occurs a transition to anaerobic mitochondrial metabolism and cellular energy levels become progressively insufficient. Anaerobic metabolism, combined with molecular protection mechanisms, thus enable the animal to survive temporary periods of exposures to temperature extremes.

[26] The growing inability of oxygen supply to match demand thus represents the first line of sensitivity to both cold and warm temperature extremes. This mismatch will affect all higher organismic functions beyond those relevant for basic maintenance. Such higher functions include motor activity, behavior, feeding, digestion, growth, and reproduction. Thus inadequate O_2 supply will affect the long-term fate of organisms, populations, and species in various climates. Only when an organism is within the optimum range of the window, where maximum aerobic

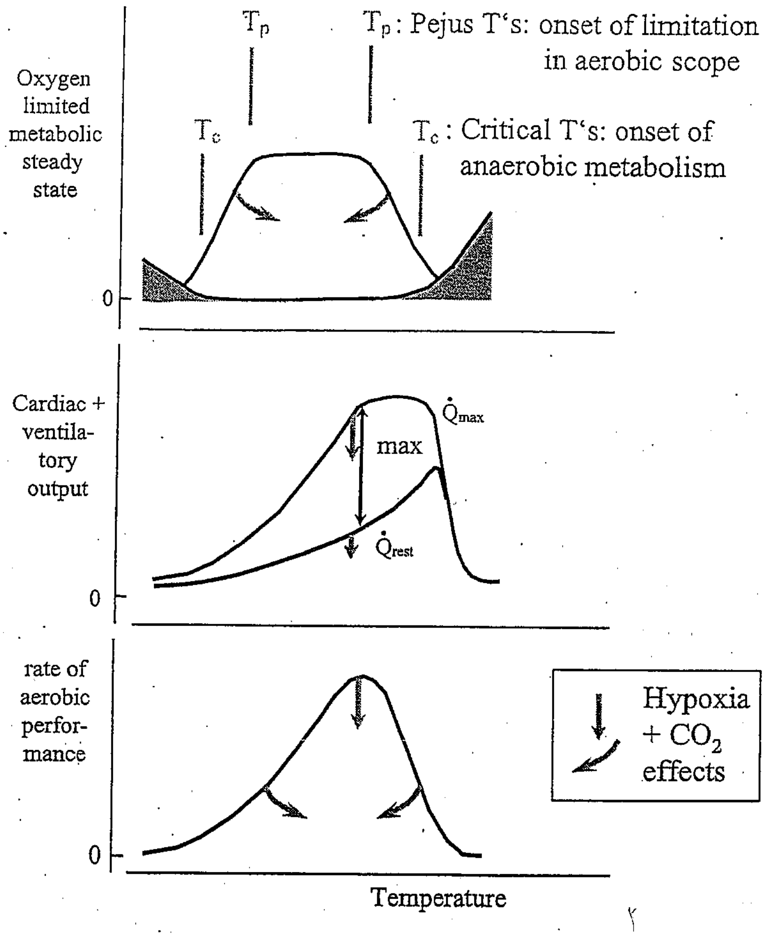

Figure 6. Schematic of oxygen-limited thermal tolerance and performance capacity in fish and other metazoa, set by the capacity of oxygen supply mechanisms (after *Pörtner* [2001, 2002a, 2002b] and *Pörtner et al.* [2004b]). (top) First limitation at thermal extremes is the onset of a loss in aerobic scope, i.e., the flexibility of the organism to respond to changing energy demand. This loss becomes severe at critical temperatures, when anaerobic metabolism sets in due to temperature-induced hypoxia. (center) Maximum scope (Δmax) between resting and maximum rate of oxygen supply through ventilatory and cardiac activity results at the upper pejus temperature T_p, before aerobic scope becomes thermally limited. (bottom) This supports an asymmetric performance curve of the whole organism. Arrows indicate how the thermal tolerance window is narrowed under the effects of enhanced CO_2 and hypoxia levels because several physiological processes respond unidirectionally under the effects of CO_2 as well as temperature-induced and ambient hypoxia (Figure 5). While CO_2 will support passive but time-limited survival of hypoxia and thermal extremes, it will at the same time cause a decrease in aerobic scope, with prospected decrements in long-term aerobic performance and growth functions as a result as well as a narrowing of thermal windows. For further explanations, see text. See color version of this figure in the HTML.

scope is reached, is there adequate flexibility of aerobic metabolic rate.

[27] The high and low limits of thermal tolerance are interdependent. Such has been interpreted to result from tradeoffs between optimized tissue functional capacity, and baseline oxygen and energy demand. The biochemical factors that are involved and modified during thermal adaptation, are common properties of all eukaryotes. They relate to primary, energy producing metabolism and to energy consuming functions and have whole organism implications. These functions include the glycolytic pathway and mitochondrial metabolism such as respiratory chain and the Krebs cycle, as well as interactions of membrane bound and catabolic processes. The thermal responses of such fundamental biochemical mechanisms contribute to defining performance levels including the overall capacity of oxygen supply and delivery (ventilation and circulation), which is optimal only within a limited window of thermal tolerance.

[28] Hence there are links between the different levels of functional hierarchy from molecules to the whole animal. For example, temperature-induced hypoxia from thermal extremes in an intact animal elicits limitations in tissue functional capacity due to insufficient aerobic energy. That is followed by a transition to anaerobic metabolism, associated metabolic depression, and ultimately disturbance of

tissue as well as cellular and molecular functions. Consequently, the earliest limits of thermal tolerance are set at the highest level of organizational complexity, i.e., the functional coordination of molecular, cellular, and tissue components works toward the larger unit and toward the resulting whole organism functional capacity. This functional capacity defines how animals exert their ecological functions through their mode of life and behavioral traits [e.g., *Pörtner*, 2002b]. It is likely that there is a systemic to molecular hierarchy of thermal limitations (for a review, see *Pörtner* [2002a]). A similar hierarchy may also exist with respect to the tolerance to elevated CO_2 [*Pörtner et al.*, 2004a].

3.2. Temperature and Hypoxia Interactions

[29] Adaptations and limitations associated with hypoxia have been studied in animals from various marine environments. Studies have focused on the mechanisms that allow animals to extract oxygen from the environment down to the lowest possible level of ambient oxygen while they remain fully aerobic. At this low level, termed the critical PO_2 (for a review, see *Pörtner and Grieshaber* [1993]), anaerobic metabolism sets in, being associated with disturbances of acid-base status and metabolic equilibria (for a review, see *Grieshaber et al.* [1994]). An organism responds to oxygen deficiency by metabolic down-regulation that is elicited by a wide range of organismal and cellular mechanisms [*Hand and Hardewig*, 1996; *Guppy and Withers*, 1999]. These include intra- and extracellular acidosis as well as central nervous mechanisms, e.g., via adenosine accumulation. Such a role for adenosine is not only found among marine invertebrates [*Reipschläger et al.*, 1997] but also in lower vertebrates (e.g., freshwater fish and turtles) that have been subjected to anoxic conditions [*Hylland et al.*, 1997] (for a review, see *Lutz and Nielsson* [1997]).

[30] Heat- or cold-induced hypoxia is also likely to elicit such responses that appear beneficial. At least, heat-induced hypoxia could counteract the warm-induced acceleration of baseline metabolic costs. The interdependence of thermal tolerance and aerobic scope has only recently been introduced as a unifying principle in animals [*Pörtner*, 2001]. Therefore the effect of temperature-induced hypoxia on metabolic regulation has not been widely investigated. There is evidence from invertebrates in the intertidal zone that supports a role for hypoxic adaptations in the survival of thermal extremes. When these organisms are exposed to both low tide and midday heat they experience both, extreme temperatures and hypoxia from lack of respiratory water [*Sokolova and Pörtner*, 2003]. Under such conditions, they switch to an anaerobic metabolism and undergo metabolic depression which contributes to energy savings during low tide. Metabolic depression likely occurs throughout the period when temperatures go beyond the maximum (or minimum) critical or even pejus temperatures.

[31] The combined response to hypoxia and temperature is elucidated by the observation that ectotherms exposed to hypoxia also decrease their preferred body temperature. More specifically, hypoxia-induced behavioral hypothermia is provoked by the onset of oxygen limitation at the critical oxygen tension of amphibians [*Wood and Malvin*, 1991; *Pörtner et al.*, 1994], reptiles [*Branco et al.*, 1993], fish [*Schurmann and Steffensen*, 1992], and crustaceans [*Robertson et al.*, 2002]. The onset of anaerobic metabolism linked to succinate and lactate accumulation characterizes the critical PO_2 in similar ways as it typifies the critical temperature [*Frederich and Pörtner*, 2000]. Lactate may well be involved in eliciting the downward shift of preferred body temperature in ectotherms [*Pörtner et al.*, 1994; *de Wachter et al.*, 1997; *Branco and Steiner*, 1999]. These findings underscore the close relationships between aerobic scope, thermal preferences and the range of thermal tolerance. They also emphasize the relevance of hypoxia-temperature interactions in setting tolerance to environmental extremes.

3.3. Integrated Effects of Temperature, Hypoxia, and CO_2

[32] We hypothesize that CO_2 affects several mechanisms that are also affected by oxygen deficiency and thermal extremes. Exposure to reduced ambient oxygen levels or to thermal extremes associated with increased ambient CO_2 would thus imply integrated effects of hypoxia and CO_2. Moreover, once animals respond to environmental extremes (e.g., hypoxia, thermal extremes) by metabolic depression, the rate of gas exchange across respiratory epithelia is reduced, internal oxygen stores are depleted, and respiratory CO_2 usually accumulates. Systemic hypoxia combined with hypercapnia will thus emphasize metabolic depression. This extends the period an organism is able to passively withstand environmental extremes, particularly in species preadapted to hypoxic environments.

[33] All individual mechanisms affected by CO_2, temperature, or hypoxic extremes (see Figure 5) result in reduced metabolism and functional flexibility or are otherwise protective during passive tolerance of adverse environmental conditions. This tolerance is time limited. Similar to hypoxia, high CO_2 affects the metabolic rate by shifting the steady state acid-base equilibria [e.g., *Pörtner*, 1993; *Pörtner et al.*, 1998], and by reducing the rates of relevant transmembrane ion exchange [*Pörtner et al.*, 2000]. Shifted steady state acid-base equilibria also limit the rate of protein synthesis with long-term consequences for growth and reproduction. Another similarity is that protective behavioral hypothermia is not only elicited by hypoxia (and the transition to anaerobic metabolism) but also by environmental hypercapnia [*Riedel and Wood*, 1988], possibly mediated by NO [*Barros and Branco*, 1998]. Combining high CO_2 and anoxia causes a synergistic metabolic depression via the effect of adenosine on central nervous functions [e.g., *Reipschläger et al.*, 1997]. Adenosine which accumulates during both hypercapnia and anoxia acts as a central mediator of behavioral hypothermia [*Branco et al.*, 2000]. Thus high CO_2 probably affects the metabolism of neurotransmitters and it may be involved in dampening the functional capacity of neuromuscular junctions, e.g., in response to hypercapnia-induced adenosine accumulation. On short to medium timescales, CO_2 accumulation may well be protective in terms of reducing metabolic energy turnover, and in doing so it may also minimize oxidative damage [*Vesela and Wilhelm*, 2002].

[34] However, all of these findings imply that high CO_2-induced shifts in cellular and organismic equilibria synergistically reduce the functional capacity of the whole organism with consequences on behavior, growth, repro-

duction, and thus long-term survival in a changing ecosystem. Several physiological processes (e.g., regulation of acid-base or ionic equilibria, aerobic energy turnover, and protein synthesis) are depressed due to the effects of CO_2 and temperature-induced or ambient hypoxia. While the consecutive depression of aerobic metabolic rate under CO_2 will support extended survival of hypoxia and thermal extremes, it will simultaneously cause a decrease in the capacity of an animal to increase its rate of aerobic energy turnover, even at temperatures that remain within the optimal range of thermal tolerance. Thus transgression to pejus (worse) conditions occurs more rapidly, resulting in limited performance and growth functions. Thus high CO_2 likely narrows the thermal window of an animal by enforcing such limitations in aerobic scope (see Figure 6).

[35] Such effects and interactions may well have been important during mass extinction events in Earth history. They may explain the role of CO_2 in the Permian-Triassic extinctions as previously suggested [*Knoll et al.*, 1996]. Temperature oscillations most probably contributed repeatedly to mass extinction events via the long-term effects of repeated exposure to extreme climate oscillations and associated cooling events [*Pörtner*, 2001, 2004]. The narrowing of thermal windows caused by both the transient CO_2 accumulation and hypoxia would have enhanced the detrimental effect of large-scale temperature fluctuations on marine ecosystems. Only the most extreme eurytherms, which were also the more active life forms, survived these events. This survival of active eurytherms could explain the stepwise increase in the fraction of more active marine species in evolution depicted in Figure 1 [*Pörtner*, 2004].

[36] These considerations suggest that current trends of warming, of CO_2 increase, and of oxygen reduction in marine waters may exert synergistic effects on marine fauna. These factors may be protective early on by extending the period of passive tolerance to environmental extremes, but they will become harmful as these conditions persist and worsen.

4. Comparison of Scenarios

[37] Such integrated effects of temperature, hypoxia, and CO_2 must be considered in the analysis of environmental impacts of climate change scenarios. Moreover, they will need to be considered in regard to various proposed scenarios of anthropogenic CO_2 accumulation and disposal. These include an uncompensated rise in the release of fossil fuel derived CO_2 to the atmosphere and upper ocean, or various strategies of direct sequestration of CO_2 into the deep ocean as well as enhanced CO_2 uptake through iron fertilization. All of these strategies involve specific tradeoffs where the degree of harm to the natural environment must be considered before any implementation.

4.1. Business as Usual

[38] The ongoing combustion of fossil fuels has led to a progressive rise in surface ocean CO_2 concentration and a drop in seawater pH that is already detectable today [*Haugan and Drange*, 1996; *Brewer*, 1997; *Wolf-Gladrow et al.*, 1999]. Atmospheric CO_2 levels could reach 970 ppm by the end of this century [*IPCC*, 2001]. During the next 300 years, there could be a further increase to 1900 ppm, which is unprecedented probably for at least the last 300 million years; with that surface ocean pH would decrease by 0.77 units [*Caldeira and Wickett*, 2003]. Continued uptake of anthropogenic CO_2 by the ocean indicates that this abiotic factor will progressively become a general stress factor in aquatic environments. The first studies to focus on related biotic impacts have considered a potential CO_2 fertilization of marine phytoplankton growth [e.g., *Riebesell et al.*, 1993; *Wolf-Gladrow et al.*, 1999] as well as the disturbance of biogenic calcification [*Done*, 1999; *Marubini and Atkinson*, 1999; *Riebesell et al.*, 2000]. More recently, there is evidence (see above) that indicates that CO_2 effects will progressively compromise marine water breathing macrofauna, including calcifying invertebrates but also noncalcifying species.

[39] The progressive increase in marine surface water CO_2 content will most certainly not reach thresholds of acute effects among animals (e.g., via disturbance of pH-dependent oxygen transport in high performance invertebrates like squid). However, long-term moderate effects are likely. These will begin at relatively low CO_2 levels and will first result in decreased calcification rates in sessile animals, most visibly among corals. On a continuum between low CO_2 levels and the highest levels expected, the ratio of noncalcified over calcified organisms may increase progressively. Additionally and unless compensated for during microevolutionary adaptation, a progressively enhanced reduction in organismic energy turnover will likely affect marine animals more widely, especially invertebrates. These limitations may be less severe or may set in later in fish, if they occur at all, because of the greater capacity of fish to compensate acid-base disturbances. Metabolic depression involves a reduction in metabolism associated with a reduction in physical activity as well as in growth and reproduction. While transient exposure allows survival by metabolic depression, such depression probably becomes detrimental during long-term exposure. Both calcified and noncalcified organisms likely experience decreases in population densities once growth and reproduction rates begin to be affected. Furthermore, elements higher in the food chain, e.g., vertebrates, will also be affected because of reduced food availability.

[40] The principle interactions between hypoxia, temperature, and CO_2 along with the available evidence that indicates significant animal responses to CO_2 increases of just 200 ppm [*Shirayama*, 2002], suggest that effects of rising CO_2 levels on animal performance likely set in early on (see above). Thus they will aggravate current ecosystem responses to enhanced levels of environmental hypoxia and temperature extremes. The expected narrowing of the thermal window (see Figure 6) is likely to affect those animals living at the edge of their temperature-dependent (northern or southern) distribution, thereby also causing a narrowing of geographical distribution windows. Consequently, progressive shifts in marine and terrestrial ecosystems should be analyzed in terms of whether they are caused by the synergistic action of global warming and CO_2 accumulation. As the availability of ambient oxygen and the thermal sensitivity of animal organisms are closely intertwined, trends of global warming, associated decrements in oxygen availability despite increasing demand, as well as thermal and CO_2 sensitivities may closely interact to cause large-

and small-scale shifts in geographical distribution as well as ecosystem composition and functioning.

4.2. Ocean Disposal: Direct Injection

[41] The proposed dumping of anthropogenic CO_2 into the deep sea [*Marchetti*, 1977, 1979] will cause immediate increments in CO_2 levels with the highest CO_2 concentrations and largest pH excursions directly at the site of injection. Minimum levels of pH 4.0- 5.0 are expected to occur depending on the sequestration technique [*Auerbach et al.*, 1996, 1997; *Adams et al.*, 1997]. Formation of CO_2 lakes would leave no benthic animal life in the chosen area. Large-scale mitigation options (e.g., towed pipe scenario) would reduce the degree of local impacts; however, they would still include significant increases in CO_2 partial pressure and lowering of pH in the entire affected ocean. These changes would probably affect deep sea biology. As a major benefit, direct CO_2 injection would introduce one individual stress factor only. That is, it would not substantially alter deep sea O_2 and temperature. Deep sea disposal would occur in a natural environment characterized by stable temperatures mostly between 1° and 4°C (with the exception of the Mediterranean, 11°–12°C, and the Red Sea, 21°C). This would exclude a role for a change in thermal sensitivity as a result of CO_2 effects unless CO_2 not only elicits a narrowing but also a shift of the thermal tolerance window by depressing aerobic scope.

[42] However, deep sea animals depend on oxygen supply by the thermohaline ocean circulation which is seen as the major process shaping the deep sea oxygen inventory. Deep water oxygen levels remaining somewhat below air saturation indicate that oxygen supply may be limited. Deep sea oxygen demand due to oxidation of organic matter is apparently in a sensitive equilibrium with lateral oxygen import from high latitudes, reflected by reduced steady state oxygen levels in the deep ocean. In line with a synergistic effect of hypoxia and CO_2 on metazoan physiology, CO_2 effects will be exacerbated if animals experience concomitant exposure to more severe hypoxia in response to global warming.

[43] Initial field experiments in the deep [*Tamburri et al.*, 2000] have not determined the tolerable limits for pH and CO_2 fluctuations over long timescales. Acute lethal effects were seen during experimental CO_2 exposure in some deep sea animals [see *Barry et al.*, 2005]. However, dose-response relationships remain again obscure. Generally it is thought that deep sea ecosystems may experience significant shifts in composition from even moderate pH changes of ~0.1–0.3 such as might be caused by long-term repeated large-scale CO_2 injection. These changes would drive shifts in population dynamics due to initially sublethal impacts that involve reduced rates of growth and reproduction. Effects would be more detrimental under long-term exposure.

[44] Onset of CO_2-related effects due to long-term exposure at low levels of CO_2 already casts doubt on whether large-scale strategies of CO_2 disposal should be implemented. Although this would possibly keep levels below those which elicit acute lethal effects on the most active pelagic organisms, there is considerable danger for long-term detrimental effects, and associated risks have not been properly quantified. Nevertheless, if ocean disposal were to be implemented, strategies would have to be developed to leave a large fraction of the marine environment unaffected, i.e., so that the net long-term damage to marine ecosystems should be less than with a large-scale distribution of CO_2. The degree of pH reduction and of PCO_2 increase as well as harmful effects could be limited by carbonate neutralization strategies [*Kheshgi*, 1995; *Caldeira and Rau*, 2000] which would also extend the ocean's retention time of disposed CO_2 to several thousand years [*Lackner*, 2003]. Still such would need to be found practicable in terms of its environmental impact.

4.3. Ocean Disposal: Iron Fertilization

[45] Concerns about large-scale ecosystem effects have also arisen in response to proposals to fertilize the ocean with iron [*Chisholm et al.*, 2001]. The goal of iron fertilization is to stimulate phytoplankton growth by alleviating the limiting availability of iron in ocean waters, thereby increasing the export of organic carbon to the deep sea, which would increase some air-sea CO_2 flux [*Gribbin*, 1988]. Increased degradation of organic matter in the deep ocean would progressively enhance CO_2 levels, but probably much more slowly and moderately than with direct injection. However, the efficiency of this process, i.e., the degree of net export of organic material to the deep ocean is likely to be rather low [*Buesseler and Boyd*, 2003; see *Baar*, 2005]. Moreover, the export of carbon and its subsequent oxidation along the way and after sedimentation will lead to deep sea eutrophication with enhanced oxygen consumption in those areas used for iron fertilization. Thus depending on where iron fertilization is carried out, oxygen minimum layers found at 500–1500 m depths in low latitudes will be more intense.

[46] The deep sea below these layers is more oxygenated due to lateral import of cold oxygenated water from polar areas, but steady state oxygen levels still remain below air saturation. These observations emphasize that the deep sea represents an oxygen limited environment with a steady state equilibrium of limited supply vs. moderate demand. Most parts of the extant deep are permanently oxygenated because oxygen demand is low due to low nutrient content, scarcity of food, low density of oxygen demanding organisms and their low metabolic rates. Furthermore, oxygen gradients exist, especially close to the sediment, depending on the density of O_2 consuming organisms present. This present situation has not persisted throughout Earth history and may thus not be well stabilized. On evolutionary timescales, large-scale oscillations in oxygen content and associated increments in CO_2 levels have likely influenced evolutionary patterns (see Figure 1 and above). Repeated extinctions due to oxygen deficiency suggest a relatively recent recruitment of deep sea faunas [*Jacobs and Lindberg*, 1998].

[47] In conclusion, the oxygen inventory of the deep ocean could be most sensitive to human interference. In a deep ocean limited by oxygen supply, the equilibrium between oxygen supply and demand would be shifted to lower oxygen levels by the increased import and subsequent oxidation of organic matter [*Sarmiento and Orr*, 1991; *Chisholm et al.*, 2001]. The aerobic or anaerobic degradation of organic matter in bottom layers would

cause net accumulation of CO_2. Animals would be exposed to combined hypoxia and hypercapnia at rather stable temperatures. In response to iron fertilization, integrated effects of hypoxia and CO_2 on higher organisms would thus cause and exacerbate detrimental long-term ecosystem consequences.

5. Synopsis

[48] Available evidence suggests that the long-term consequences of anthropogenic CO_2 accumulation have already begun in surface waters. When combined with effects of global warming and enhanced hypoxia, this will cause and exacerbate shifts in ecosystem equilibria which affect higher marine organisms, i.e., the metazoa. Yet, ocean biota will also be affected by all mitigation scenarios which involve ocean CO_2 disposal. Direct storage in the deep ocean would reduce effects in surface waters from the passive invasion of anthropogenic CO_2 at the expense of similar overall effects in the deep ocean. Direct injection would also avoid the combined effects of eutrophication, oxygen depletion, and CO_2 accumulation that would come with an iron fertilization strategy. If ocean disposal were deemed necessary (e.g., due to limited capacities of geological storage), a scenario with little large-scale impact should be chosen. To avoid or minimize large-scale impacts, pH neutralization strategies combined with localized CO_2 disposal in stable deep sea dump sites (lake option) have been suggested [*Pörtner et al.*, 2004a]. Thus higher priority should be given to evaluating those options with less severe overall impact.

[49] We conclude from the results of available physiological studies, that the mechanistic understanding of CO_2 effects on animals is still incomplete, as are potential synergistic effects with increasing temperature and hypoxia. No simple cause-and-effect relationship of CO_2 effects was found. Rather there may exist a complex hierarchy of CO_2 sensitivities, ranging from systemic functions and their central nervous control down to the tissue, cellular, and molecular levels [*Pörtner et al.*, 2004a]. Whereas cellular processes display high flexibility in response to acute hypercapnia, in terms of acid-base regulation [*Pörtner et al.*, 2000], and protein synthesis [*Langenbuch and Pörtner*, 2003; M. Langenbuch et al., manuscript in preparation, 2005], little is known about the limiting physiological processes effective on extended timescales for higher organizational levels. Such mechanisms, including neural or hormonal control, may partly determine the time-dependent onset of mortality that was observed under long-term exposure to moderate CO_2 levels. In the future, these mechanisms need to be identified.

[50] Furthermore, for a clear assessment and comparison of environmental impacts of any ocean CO_2 enrichment scenario CO_2-dependent effects in relation to those of temperature and hypoxia need to be understood and quantified at the whole organism and ecosystem levels. Knowledge of CO_2-dependent mechanisms, their role in ecosystem structure, and functioning and their "titration" by increasing CO_2 (lower pH), at various temperatures and oxygen levels, are crucial to understand cause-and-effect relationships. Field observations of ecosystem trends and fluctuations need to be carried out at the same time.

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References

Adams, E. E., A. J. Caulfield, H. J. Herzog, and D. I. Auerbach (1997), Impacts of reduced pH from ocean CO_2 disposal: Sensitivity of zooplankton mortality to model parameters, *Waste Manage.*, *17*, 375–380.

Alvarado-Alvarez, R., M. C. Gould, and I. L. Stephano (1996), Spawning, in vitro maturation and changes in oocyte electrophysiology induced by serotonin in *Tivela stultorum*, *Biol. Bull.*, *190*, 322–328.

Angel, M. V. (1991), Variations in time and space: Is biogeography relevant to studies of long-time scale change?, *J. Mar. Biol. Assoc. U. K.*, *71*, 191–206.

Aota, S., K. D. Holmgren, P. Gallaugher, and D. J. Randall (1990), A possible role for catecholamines in the ventilatory responses associated with internal acidosis or external hypoxia in rainbow trout *Oncorhynchus mykiss*, *J. Exper. Biol.*, *151*, 57–70.

Auerbach, D., H. Herzog, E. Adams, and J. Caulfield (1996), Environmental impacts of CO_2 release into the ocean, topical report, Mass. Inst. of Technol., Cambridge.

Auerbach, D., J. A. Caulfield, E. E. Adams, and H. J. Herzog (1997), Impacts of ocean CO_2 disposal on marine life: I. A toxicological assessment integrating constant-concentration laboratory assay data with variable-concentration field exposure, *Environ. Modell. Assess.*, *2*, 333–343.

Bambach, R. K., A. H. Knoll, and J. J. Sepkowski Jr. (2002), Anatomical and ecological constraints on Phanerozoic animal diversity in the marine realm, *Proc. Natl. Acad. Sci.*, *99*, 6845–6859.

Bamber, R. N. (1987), The effects of acidic sea water in young carpet-shell clams, *Venerupis decussata* (L.) (Mollusca: Venracea), *J. Exper. Mar. Biol. Ecol.*, *108*, 241–260.

Bamber, R. N. (1990), The effects of acidic sea water on three species of lamellibranch molluscs, *J. Exper. Mar. Biol. Ecol.*, *143*, 181–191.

Barnhart, M. C. (1989), Respiratory acidosis and metabolic depression in dormant invertebrates, in *Living in the Cold*, edited by A. Malan and B. Canguilhem, pp. 315–401, Colloque INSERM/John Libbey Eurotext Ltd., London.

Barnhart, M. C., and B. R. McMahon (1988), Depression of aerobic metabolism and intracellular pH by hypercapnia in land snails *Otala lactea*, *J. Exper. Biol.*, *138*, 289–299.

Barros, R. C., and L. G. S. Branco (1998), Effect of nitric oxide synthase inhibition on hypercapnia-induced hypothermia and hyperventilation, *J. Appl. Physiol.*, *85*, 967–972.

Barry, J. P., K. R. Buck, C. Lovera, L. Kuhnz, and P. J. Whaling (2005), Utility of deep sea CO_2 release experiments in understanding the biology of a high-CO_2 ocean: Effects of hypercapnia on deep sea meiofauna, *J. Geophys. Res.*, *110*, C09S12, doi:10.1029/2004JC002629.

Berner, R. A., and Z. Kothalova (2001), Geocarb III: A revised model of atmospheric CO_2 over phanerozoic time, *Am. J. Sci.*, *301*, 182–204.

Bernier, N. J., and S. F. Perry (1996), Control of catecholamine and serotonin release from the chromaffin tissue of the Atlantic hagfish, *J. Exper. Biol.*, *199*, 2485–2497.

Branco, L. G. S., and A. A. Steiner (1999), Central thermoregulatory effects of lactate in the toad *Bufo paracnemis*, *Comput. Biochem. Physiol. A*, *122*, 457–461.

Branco, L. G. S., H. O. Pörtner, and S. C. Wood (1993), Interaction between temperature and hypoxia in the alligator, *Am. J. Physiol.*, *265*, 1339–1343.

Branco, L. G. S., A. A. Steiner, G. J. Tattersall, and S. C. Wood (2000), Role of adenosine in the hypoxia-induced hypothermia of toads, *Am. J. Physiol.*, *279*, 196–201.

Brevard, M. E., T. Q. Duong, J. A. King, and C. F. Ferris (2003), Changes in MRI signal intensity during hypercapnic challenge under conscious and anesthetized conditions, *Magn. Res. Imag.*, *21*, 995–1001.

Brewer, P. G. (1997), Ocean chemistry of the fossil fuel CO_2 signal: The haline signal of "business as usual,", *Geophys. Res. Lett.*, *24*, 1367–1369.

Bridges, C. R. (1993), Adaptation of vertebrates to the intertidal environment, in *The Vertebrate Gas Transport Cascade: Adaptations to Environment and Mode of Life*, edited by J. E. P. W. Bicudo, pp. 12–22, CRC Press, Boca Raton, Fla.

Buesseler, K. O., and P. W. Boyd (2003), Will ocean fertilization work?, *Science*, *300*, 67–68.

Burleson, M. L., and N. J. Smatresk (2000), Branchial chemoreceptors mediate ventilatory response to hypercapnic acidosis in channel catfish, *Comput. Biochem. Physiol. A*, *125*, 403–414.

Caldeira, K., and G. H. Rau (2000), Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: Geochemical implications, *Geophys. Res. Lett.*, *27*, 225–228.

Caldeira, K., and M. E. Wickett (2003), Anthropogenic carbon and ocean pH, *Nature*, *425*, 365.

Chisholm, S. W., P. G. Falkowski, and J. J. Cullen (2001), OCEANS: Discrediting ocean fertilization, *Science*, *294*, 309–310.

Cossins, A. R., and K. Bowler (1987), *Temperature Biology of Animals*, 339 pp., CRC Press, Boca Raton, Fla.

Crocker, C. E., and J. J. Cech (1996), The effects of hypercapnia on the growth of juvenile white sturgeon, *Acipenser transmontanus*, *Aquaculture*, *147*, 293–299.

Dean, J. B., D. K. Mulkey, A. J. Garcia III, R. W. Putnam, and R. A. Henderson III (2003), Neuronal sensitivity to hyperoxia, hypercapnia, and inert gases at hyperbaric pressures, *J. Appl. Physiol.*, *95*, 883–909.

Desrosiers, R. R., J. Desilets, and F. Dube (1996), Early developmental events following fertilization in the giant scallop, *Placopecten magellanicus*, *Can. J. Fish. Aquat. Sci.*, *53*, 1382–1392.

De Wachter, B., F.-J. Sartoris, and H.-O. Pörtner (1997), The anaerobic endproduct lactate has a behavioural and metabolic signalling function in the shore crab *Carcinus maenas*, *J. Exper. Biol.*, *200*, 1015–1024.

Diaz, R. J., and R. Rosenburg (1995), Marine benthic hypoxia: A review of its ecological effects and the behavioural responses of benthic macrofauna, *Oceanogr. Mar. Biol. Annu. Rev.*, *33*, 245–303.

Done, T. J. (1999), Coral community adaptability to environmental change at the scales of regions, reefs and reef zones, *Am. Zool.*, *39*, 66–79.

Doudoroff, P. (1945), The resistance and acclimatization of marine fishes to temperature changes. II. Experiments with *Fundulus* and *Atherinops*, *Biol. Bull.*, *88*, 194–206.

Dudley, R. (1998), Atmospheric oxygen, giant Palaeozoic insects and the evolution of aerial locomotor performance, *J. Exper. Biol.*, *201*, 1043–1050.

Filosa, J. A., J. B. Dean, and R. W. Putnam (2002), Role of intracellular and extracellular pH in the chemosensitive response of rat locus coeruleus neurones, *J. Physiol.*, *541*, 493–509.

Frederich, M., and H. O. Pörtner (2000), Oxygen limitation of thermal tolerance defined by cardiac and ventilatory performance in the spider crab *Maja squinado*, *Am. J. Physiol.*, *279*, 1531–1538.

Gribbin, J. (1988), Any old iron?, *Nature*, *331*, 570.

Grieshaber, M. K., I. Hardewig, U. Kreutzer, and H. O. Pörtner (1994), Physiological and metabolic responses to hypoxia in invertebrates, *Rev. Physiol. Biochem. Pharmacol.*, *125*, 43–147.

Grottum, I. A., and T. Sigholt (1996), Acute toxicity of carbon dioxide on European seabass (*Dicentrarchus labrax*): Mortality and effects on plasma ions, *Comput. Biochem. Physiol. A*, *116*, 323–327.

Guppy, M., and P. Withers (1999), Metabolic depression in animals: Physiological perspectives and biochemical generalizations, *Biol. Rev.*, *74*, 1–40.

Hand, S. C., and I. Hardewig (1996), Downregulation of cellular metabolism during environmental stress: Mechanisms and implications, *Annu. Rev. Physiol.*, *58*, 539–563.

Haugan, P. M., and H. Drange (1996), Effects of CO_2 on the ocean environment, *Energy Convers. Manage.*, *37*, 1019–1022.

Heisler, N. (1986a), Buffering and transmembrane ion transfer processes, in *Acid-Base Regulation in Animals*, edited by N. Heisler, pp. 3–47, Elsevier, New York.

Heisler, N. (1986b), Acid-base regulation in fishes, in *Acid-Base Regulation in Animals*, edited by N. Heisler, pp. 309–356, Elsevier, New York.

Hofmann, G. E., and S. C. Hand (1994), Global arrest of translation during invertebrate quiescence, *Proc. Natl. Acad. Sci. U. S. A.*, *91*, 8492–8496.

Huch, M., G. Warnecke, and K. Germann (Eds.) (2001), *Klimazeugnisse der Erdgeschichte: Perspektiven für die Zukunft*, 229 pp., Springer, New York.

Hylland, P., S. Milton, M. Pek, G. E. Nilsson, and P. L. Lutz (1997), Brain Na^+/K^+-ATPase activity in two anoxia tolerant vertebrates: Crucian carp and freshwater turtle, *Neurosci. Lett.*, *235*, 89–92.

Intergovernmental Panel on Climate Change (IPCC) (2001), *Climate Change 2001: Impacts, Adaptations and Vulnerability*, Cambridge Univ. Press, New York.

Ingermann, R. L., M. Holcomb, M. L. Robinson, and J. G. Cloud (2002), Carbon dioxide and pH affect sperm motility of white sturgeon (*Acipenser transmontanus*), *J. Exper. Biol.*, *205*, 2885–2890.

Ishimatsu, A., T. Kikkawa, M. Hayashi, K.-S. Lee, and J. Kita (2004), Effects of CO_2 on marine fish: Larvae and adults, *J. Oceanogr.*, *60*, 731–741.

Jacobs, D. K., and D. R. Lindberg (1998), Oxygen and evolutionary patterns in the sea: Onshore/offshore trends and recent recruitment of deep-sea faunas, *Proc. Natl. Acad. Sci.*, *95*, 9396–9401.

Johnston, I. A., and A. F. Bennett (Eds.) (1996), *Animals and Temperature: Phenotypic and Evolutionary Adaptation*, Cambridge Univ. Press, New York.

Joos, F., G. K. Plattner, T. F. Stocker, A. Körtzinger, and D. W. R. Wallace (2003), Trends in marine dissolved oxygen: Implications for ocean circulation changes and the carbon budget, *Eos Trans. AGU*, *84*, 197,201.

Kheshgi, H. S. (1995), Sequestering atmospheric carbon dioxide by increasing ocean alkalinity, *Energy Int. J.*, *20*, 915–922.

Kikkawa, T., A. Ishimatsu, and J. Kita (2003), Acute CO_2 tolerance during the early developmental stages of four marine teleosts, *Environ. Toxicol.*, *18*, 375–382.

Knoll, A. K., R. K. Bambach, D. E. Canfield, and J. P. Grotzinger (1996), Comparative Earth history and late Permian mass extinction, *Science*, *273*, 452–457.

Kurihara, H., S. Shimode, and Y. Shirayama (2004), Effects of raised concentration of CO_2 on the life histories of marine organisms, *J. Oceanogr.*, *60*, 743–750.

Lackner, K. S. A. (2003), A guide to CO_2 sequestration, *Science*, *300*, 1677–1678.

Langenbuch, M., and H. O. Pörtner (2002), Changes in metabolic rate and N-excretion in the marine invertebrate *Sipunculus nudus* under conditions of environmental hypercapnia: Identifying effective acid-base parameters, *J. Exper. Biol.*, *205*, 1153–1160.

Langenbuch, M., and H. O. Pörtner (2003), Energy budget of Antarctic fish hepatocytes (*Pachycara brachycephalum* and *Lepidonotothen kempi*) as a function of ambient CO_2: pH dependent limitations of cellular protein biosynthesis?, *J. Exper. Biol.*, *206*, 3895–3903.

Langenbuch, M., and H. O. Pörtner (2004), High sensitivity to chronically elevated CO_2 in marine invertebrates, *Aquat. Toxicol.*, *70*, 55–61.

Larsen, B. K., H. O. Pörtner, and F. B. Jensen (1997), Extra- and intracellular acid-base balance and ionic regulation in cod (*Gadus morhua*) during combined and isolated exposures to hypercapnia and copper, *Mar. Biol.*, *128*, 337–346.

Lee, K.-S., J. Kita, and A. Ishimatsu (2003), Effects of lethal levels of environmental hypercapnia on cardiovascular and blood-gas status in yellowtail *Seriola quinqueradiata*, *Zool. Sci.*, *20*, 417–422.

Lutz, P. L., and G. E. Nielsson (1997), Contrasting strategies for anoxic brain survival—Glycolysis up or down, *J. Exper. Biol.*, *200*, 411–419.

Marchetti, C. (1977), On geoengineering and the CO_2 problem, *Clim. Change*, *1*, 59–68.

Marchetti, C. (1979), Constructive solutions to the CO_2 problem, in *Man's Impact on Climate*, edited by W. Bach, J. Pankrath, and W. Kellogg, pp. 299–311, Elsevier, New York.

Marubini, F., and M. J. Atkinson (1999), Effects of lowered pH and elevated nitrate on coral calcification, *Mar. Ecol. Prog. Ser.*, *188*, 117–121.

Matear, R. J., A. C. Hirts, and B. I. McNeil (2000), Changes in dissolved oxygen in the Southern Ocean with climate change, *Geochem. Geophys. Geosyst.*, *1*, doi:10.1029/2000GC000086.

McKendry, J. E., W. K. Milsom, and S. F. Perry (2001), Branchial CO_2 receptors and cardiorespiratory adjustments during hypercarbia in Pacific spiny dogfish (*Squalus acanthias*), *J. Exper. Biol.*, *204*, 1519–1527.

McKenzie, D. J., E. W. Taylor, A. Z. Dalla Valle, and J. F. Steffensen (2002), Tolerance of acute hypercapnic acidosis by the European eel (*Anguilla anguilla*), *J. Comput. Physiol.*, *172*, 339–346.

Michaelidis, B., C. Ouzounis, A. Paleras, and H. O. Pörtner (2005), Effects of long-term moderate hypercapnia on acid-base balance and growth rate in marine mussels (*Mytilus galloprovincialis*), *Mar. Ecol. Prog. Ser.*, *293*, 109–118.

Nakahata, K., H. Kinoshita, Y. Hirano, Y. Kimoto, H. Iranami, and Y. Hatano (2003), Mild hypercapnia induces vasodilation via adenosine triphosphate-sensitive K^+ channels in parenchymal microvessels of the rat cerebral cortex, *Anaesthesiology*, *99*, 1333–1339.

Ohsumi, T. (1993), Prediction of solute carbon dioxide behaviour around a liquid carbon dioxide pool on deep ocean basin, *Energy Convers. Manage.*, *33*, 685–690.

Parmesan, C., and G. Yohe (2003), A globally coherent fingerprint of climate change impacts across natural systems, *Nature*, *421*, 37–42.

Perry, S. F., R. Kinkead, P. Gallaugher, and D. J. Randall (1989), Evidence that hypoxemia promotes catecholamine release during hypercapnic acidosis in rainbow trout (*Salmo gairdneri*), *Respir. Physiol.*, *77*, 351–364.

Pielou, E. C. (1979), A quick method of determining the diversity of foraminiferal assemblages, *J. Paleontol.*, *53*, 1237–1242.

Plattner, G.-K., F. Joos, and T. F. Stocker (2002), Revision of the global carbon budget due to changing air-sea oxygen fluxes, *Global Biogeochem. Cycles*, *16*(4), 1096, doi:10.1029/2001GB001746.

Pörtner, H. O. (1990), An analysis of the effects of pH on oxygen binding by squid (*Illex illecebrosus*, *Loligo pealei*) haemocyanin, *J. Exper. Biol.*, *150*, 407–424.

Pörtner, H. O. (1993), Multicompartmental analyses of acid-base and metabolic homeostasis during anaerobiosis: Invertebrate and lower vertebrate examples, in *Surviving Hypoxia: Mechanisms of Control and Adaptation*, edited by P. W. Hochachka et al., pp. 139–156, CRC Press, Boca Raton, Fla.

Pörtner, H. O. (2001), Climate change and temperature dependent biogeography: Oxygen limitation of thermal tolerance in animals, *Naturwissenschaften*, *88*, 137–146.

Pörtner, H. O. (2002a), Climate change and temperature dependent biogeography: Systemic to molecular hierarchies of thermal tolerance in animals, *Comput. Biochem. Physiol. A*, *132*, 739–761.

Pörtner, H. O. (2002b), Physiological basis of temperature dependent biogeography: Tradeoffs in muscle design and performance in polar ectotherms, *J. Exper. Biol.*, *205*, 2217–2230.

Pörtner, H. O. (2004), Climate variability and the energetic pathways of evolution: The origin of endothermy in mammals and birds, *Physiol. Biochem. Zool.*, *77*, 959–981.

Pörtner, H. O., and M. K. Grieshaber (1993), Critical PO_2(s) in oxyconforming and oxyregulating animals: Gas exchange, metabolic rate and the mode of energy production, in *The Vertebrate Gas Transport Cascade: Adaptations to Environment and Mode of Life*, edited by J. E. P. W. Bicudo, pp. 330–357, CRC Press, Boca Raton, Fla.

Pörtner, H. O., and A. Reipschläger (1996), Ocean disposal of anthropogenic CO_2: Physiological effects on tolerant and intolerant animals, in *Ocean Storage of CO_2: Environmental Impact*, pp. 57–81, Mass. Inst. of Technol., Int. Energy Agency, Cambridge.

Pörtner, H. O., L. G. S. Branco, G. M. Malvin, and S. C. Wood (1994), A new function for lactate in the toad *Bufo marinus*, *J. Appl. Physiol.*, *76*, 2405–2410.

Pörtner, H. O., A. Reipschläger, and N. Heisler (1998), Metabolism and acid-base regulation in *Sipunculus nudus* as a function of ambient carbon dioxide, *J. Exper. Biol.*, *201*, 43–55.

Pörtner, H. O., C. Bock, and A. Reipschläger (2000), Modulation of the cost of pHi regulation during metabolic depression: A ^{31}P-NMR study in invertebrate (*Sipunculus nudus*) isolated muscle, *J. Exper. Biol.*, *203*, 2417–2428.

Pörtner, H. O., et al. (2001), Climate induced temperature effects on growth performance, fecundity and recruitment in marine fish: Developing a hypothesis for cause and effect relationships in Atlantic cod (*Gadus morhua*) and common eelpout (*Zoarces viviparus*), *Cont. Shelf Res.*, *21*, 1975–1997.

Pörtner, H. O., M. Langenbuch, and A. Reipschläger (2004a), Biological impact of elevated ocean CO_2 concentrations: Lessons from animal physiology and Earth history?, *J. Oceanogr.*, *60*, 705–718.

Pörtner, H. O., F. C. Mark, and C. Bock (2004b), Oxygen limited thermal tolerance in fish? Answers obtained by Nuclear Magnetic Resonance techniques, *Respir. Physiol. Neurobiol.*, *141*, 243–260.

Rapoport, E. H. (1994), Remarks on marine and continental biogeography: An aerographical viewpoint, *Philos. Trans. R. Soc. London, Ser. B*, *343*, 71–78.

Redfield, A. C., and R. Goodkind (1929), The significance of the Bohr effect on the respiration and asphyxiation of the squid, *Loligo pealei*, *J. Exper. Biol.*, *6*, 340–349.

Rees, B. B., and S. C. Hand (1990), Heat dissipation, gas exchange and acid-base status in the land snail *Oreohelix* during short-term estivation, *J. Exper. Biol.*, *152*, 77–92.

Reid, S. G., N. J. Bernier, and S. F. Perry (1998), The adrenergic response in fish: Control of catecholamine storage and release, *Comput. Biochem. Physiol. A*, *120*, 1–27.

Reipschläger, A., and H. O. Pörtner (1996), Metabolic depression during environmental stress: The role of extra- versus intracellular pH in *Sipunculus nudus*, *J. Exper. Biol.*, *199*, 1801–1807.

Reipschläger, A., G. E. Nilsson, and H. O. Pörtner (1997), A role for adenosine in metabolic depression in the marine invertebrate *Sipunculus nudus*, *Am. J. Physiol.*, *272*, 350–356.

Riebesell, U., D. A. Wolf-Gladrow, and V. Smetacek (1993), Carbon dioxide limitation of marine phytoplankton growth rates, *Nature*, *361*, 249–251.

Riebesell, U., I. Zondervan, B. Rost, P. D. Tortell, R. E. Zeebe, and F. M. M. Morel (2000), Reduced calcification in marine plankton in response to increased atmospheric CO_2, *Nature*, *407*, 634–637.

Riedel, C., and S. C. Wood (1988), Effects of hypercapnia and hypoxia on temperature selection on temperature selection of the toad, *Bufo marinus*, *Fed. Proc.*, *2*, A500.

Robertson, R. F., J. Meagor, and E. W. Taylor (2002), Specific dynamic action in the shore crab, *Carcinus maenas* (L.), in relation to acclimation temperature and to the onset of the emersion response, *Physiol. Biochem. Zool.*, *75*, 350–359.

Robitaille, S., S. Thomas, and M. P. Charlton (1999), Effects of adenosine and Ca^{2+} entry in the nerve terminal of the frog neuromuscular junction, *Can. J. Phyisol. Pharmacol.*, *77*, 707–714.

Rudolphi, K. A., P. Schubert, F. E. Parkinson, and B. B. Fredholm (1992), Adenosine and brain ischemia, *Cerebrovascular Brain Metabolism Rev.*, *4*, 346–369.

Sarmiento, J. L., and J. C. Orr (1991), Three-dimensional simulations of the impact of the Southern Ocean nutrients depletion on atmospheric CO_2 and ocean chemistry, *Limnol. Oceanogr.*, *36*, 1928–1950.

Scheid, P., H. Shams, and J. Piiper (1989), Gas exchange in vertebrates, *Verh. Dtsch. Zool. Ges.*, *82*, 57–68.

Schurmann, H., and J. F. Steffensen (1992), Lethal oxygen levels at different temperatures and the preferred temperature during hypoxia of the Atlantic cod, *Gadus morhua*, *J. Fish Biol.*, *41*, 927–934.

Schwartz, A. D., C. L. Whitacre, Y. Lin, and D. F. Wilson (2003), Adenosine inhibits N-type calcium channels at the rat neuromuscular junctions, *Clin. Exper. Pharmacol. Physiol.*, *30*, 174–177.

Shirayama, Y. (2002), Towards comprehensive understanding of impacts on marine organisms due to raised CO_2 concentration, in *Proceedings of the 5th International Symposium on CO_2 Fixation and Efficient Utilization of Energy*, pp. 177–181, Tokyo Inst. of Technol, Tokyo.

Shirayama, Y., and H. Thornton (2005), Effect of increased atmospheric CO_2 on shallow-water marine benthos, *J. Geophys. Res.*, *110*, C09S08, doi:10.1029/2004JC002618.

Söderström, V., and G. E. Nilsson (2000), Brain blood flow during hypercapnia in fish: No role of nitric oxide, *Brain Res.*, *857*, 207–211.

Sokolova, I. M., and H. O. Pörtner (2003), Metabolic plasticity and critical temperatures for aerobic scope in a eurythermal marine invertebrate (*Littorina saxatilis*, Gastropoda: Littorinidae) from different latitudes, *J. Exper. Biol.*, *206*, 195–207.

Takeda, T., and Y. Itazawa (1983), Possibility of applying anesthesia by carbon dioxide in the transportation of live fish, *Bull. Jpn. Soc. Sci. Fish.*, *49*, 725–731.

Tamburri, M. N., E. T. Peltzer, G. E. Friederich, I. Aya, K. Yamane, and P. G. Brewer (2000), A field study of the effects of CO_2 ocean disposal on mobile deep-sea animals, *Mar. Chem.*, *72*, 2–4.

Thomas, C. D., et al. (2004), Extinction risk from climate change, *Nature*, *427*, 145–148.

Thomas, S., and S. Robitaille (2001), Differential frequency-dependent regulation of transmitter release by endogenous nitric oxide at the amphibian neuromuscular synapse, *J. Neurosci.*, *21*, 1087–1095.

van Breukelen, F., R. Maier, and S. C. Hand (2000), Depression of nuclear transcription and extension of mRNA half life under anoxia in *Artemia franciscana* embryos, *J. Exper. Biol.*, *203*, 1123–1130.

Vesela, A., and J. Wilhelm (2002), The role of carbon dioxide in free radical reactions of the organism, *Physiol. Res.*, *51*, 335–339.

Vinogradov, G. A., and V. T. Komov (1985), Ion regulation in the perch, *Perca fluviatilis*, in connection with the problem of acidification of water bodies, *J. Ichthyol.*, *25*, 53–61.

Wang, W., S. R. Bradley, and G. B. Richerson (2002), Quantification of the response of rat medullary raphe neurons to independent changes in pH_o and P_{CO_2}, *J. Physiol.*, *540*, 951–970.

Wheatly, M. G. (1989), Physiological response of the crayfish *Pacifasticus leniusculus* (Dana) to environmental hypoxia. I. Extracellular acid-base and electrolyte status and trans-branchial exchange, *J. Exper. Biol.*, *57*, 673–680.

Wickins, J. F. (1984), The effect of hypercapnic sea water on growth and mineralization in penaeid prawns, *Aquaculture*, *41*, 37–48.

Wolf-Gladrow, D. A., U. Riebesell, S. Burkhardt, and J. Bijma (1999), Direct effects of CO_2 concentrations on growth and isotopic composition of marine plankton, *Tellus, Ser. B*, *51*, 461–476.

Wood, C. M., and D. G. MacDonald (Eds.) (1997), *Global Warming: Implications for Freshwater and Marine Fish*, 425 pp., Cambridge Univ. Press, New York.

Wood, S. C., and G. M. Malvin (1991), Physiological significance of behavioral hypothermia in hypoxic toads, *Bufo marinus*, *J. Exper. Biol.*, *159*, 203–215.

Yamada, Y., and T. Ikeda (1999), Acute toxicity of lowered pH to some oceanic zooplankton, *Plankton Biol. Ecol.*, *46*, 62–67.

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Reduced calcification of marine plankton in response to increased atmospheric CO_2

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The formation of calcareous skeletons by marine planktonic organisms and their subsequent sinking to depth generates a continuous rain of calcium carbonate to the deep ocean and underlying sediments[1]. This is important in regulating marine carbon cycling and ocean–atmosphere CO_2 exchange[2]. The present rise in atmospheric CO_2 levels[3] causes significant changes in surface ocean pH and carbonate chemistry[4]. Such changes have been shown to slow down calcification in corals and coralline macroalgae[5,6], but the majority of marine calcification occurs in planktonic organisms. Here we report reduced calcite production at increased CO_2 concentrations in monospecific cultures of two dominant marine calcifying phytoplankton species, the coccolithophorids *Emiliania huxleyi* and *Gephyrocapsa oceanica*. This was accompanied by an increased proportion of malformed coccoliths and incomplete coccospheres. Diminished calcification led to a reduction in the ratio of calcite precipitation to organic matter production. Similar results were obtained in incubations of natural plankton assemblages from the north Pacific ocean when exposed to experimentally elevated CO_2 levels. We suggest that the progressive increase in atmospheric CO_2 concentrations may therefore slow down the production of calcium carbonate in the surface ocean. As the process of calcification releases CO_2 to the atmosphere, the response observed here could potentially act as a negative feedback on atmospheric CO_2 levels.

By the end of the next century, the expected increase in atmospheric CO_2 (ref. 3) will give rise to an almost threefold increase in surface ocean CO_2 concentrations relative to pre-industrial values. This will cause CO_3^{2-} concentrations and surface water pH to drop by about 50% and 0.35 units, respectively[4]. Changes of this magnitude have been shown to significantly slow down calcification of temperate and tropical corals and coralline macroalgae[5,6]. Although coral reefs are the most conspicuous life-supporting calcareous structures, the majority of biogenic carbonate precipitation (>80%) is carried out by planktonic microorganisms[1], particularly coccolithophorids[7]. These unicellular microalgae are major contributors to marine primary production and an important component of open ocean and coastal marine ecosystems[8]. Two prominent representatives of the coccolithophorids, *Emiliania huxleyi* and *Gephyrocapsa oceanica*, are both bloom-forming and have a world-wide distribution. *G. oceanica* is the dominant coccolithophorid in neritic environments of tropical waters[9], whereas *E. huxleyi*, one of the most prominent producers of calcium carbonate in the world ocean[10], forms extensive blooms covering large areas in temperate and subpolar latitudes[9,11].

The response of these two species to CO_2-related changes in seawater carbonate chemistry was examined under controlled

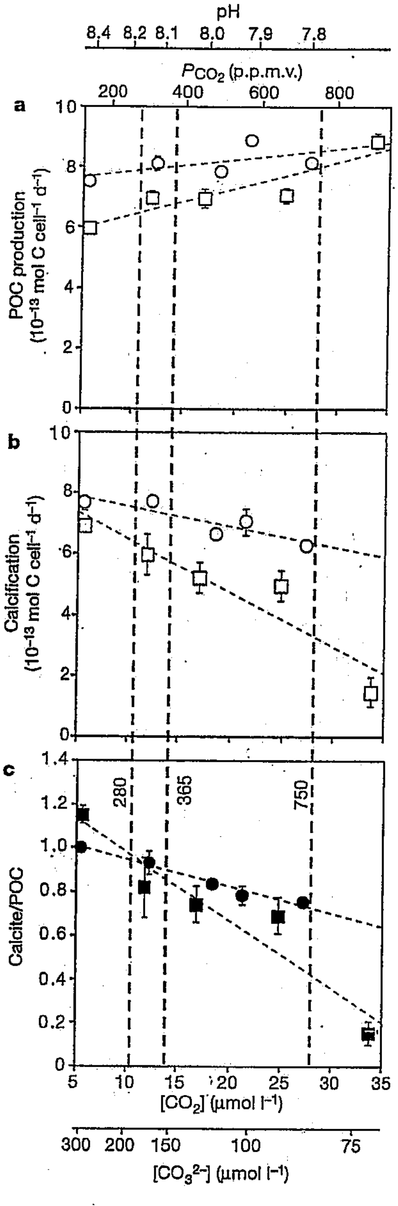

Figure 1 Response of organic and inorganic carbon production to CO_2 concentration in laboratory-cultured coccolithophorids. **a**, Particulate organic carbon (POC) production; **b**, calcification; and **c**, the ratio of calcification to POC production (calcite/POC) of the coccolithophorids *Emiliania huxleyi* (circles) and *Gephyrocapsa oceanica* (squares) as a function of CO_2 concentration, $[CO_2]$. Bars denote ±1 s.d. ($n = 3$); dotted lines represent linear regressions. Also indicated are corresponding ranges of pH, p_{CO_2}, and $[CO_3^{2-}]$. We note that DIC and total alkalinity differed slightly between experimental sets for the two species; values for pH, p_{CO_2} and $[CO_3^{2-}]$, therefore, are only approximations. Vertical lines indicate p_{CO_2} values of 280, 365 and 750 p.p.m.v., representing pre-industrial, present day and future concentrations.

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laboratory conditions. The carbonate system of the growth medium was manipulated by adding acid or base to cover a range from pre-industrial CO_2 levels (280 p.p.m.v.) to approximately triple pre-industrial values (about 750 p.p.m.v.). Over this range, *E. huxleyi* and *G. oceanica* experience a slight increase in photosynthetic carbon fixation of 8.5% and 18.6%, respectively (Fig. 1a), and a comparatively larger decrease in the rate of calcification of 15.7% and 44.7%, respectively (Fig. 1b). The ratio of calcite to organic matter production (calcite/POC) for the two species decreased by 21.0% and 52.5%, respectively, between 280 and 750 p.p.m.v. (Fig. 1c). Since calcite production has been shown to vary with ambient light conditions[12], we have grown *E. huxleyi* under different light/dark cycles and photon flux densities. A similar decrease in the calcite/POC ratio in response to CO_2-related changes in carbonate chemistry was obtained over a fivefold range in photon flux densities (Fig. 2).

Scanning electron microscopy indicated that malformed coccoliths and incomplete coccospheres increased in relative numbers with increasing CO_2 concentrations (Fig. 3). Coccolith under-calcification and malformation is a common phenomenon frequently observed both in natural environments and under laboratory conditions[13]. The systematic trend in the relative abundance of malformed coccoliths and coccospheres observed here, however, suggests a direct effect of seawater carbonate chemistry on the regulatory mechanisms controlling coccolith production inside the cell. Based on light microscopic analysis, no consistent trend was obtained in the number of attached or free coccoliths per coccosphere.

Our laboratory results are consistent with CO_2-related responses of natural plankton assemblages collected in the subarctic north Pacific, a region where coccolithophorids are major contributors to primary production[14]. After incubation of replicate samples at p_{CO_2} levels of about 250 p.p.m.v. and about 800 p.p.m.v. for 1.5 to 9 days, the rate of calcification was reduced by 36% to 83% in high-CO_2 relative to low-CO_2 treatments in four independent experiments (Fig. 4). A similar CO_2-dependent response was obtained under

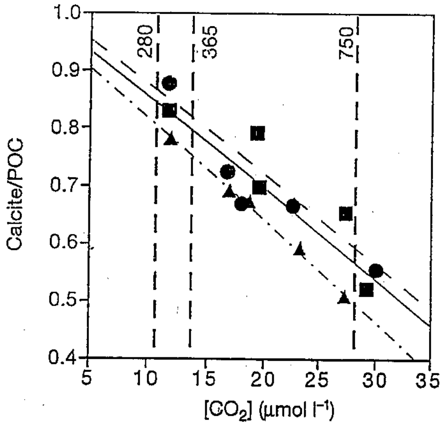

Figure 2 Ratio of calcification to POC production (calcite/POC) of *Emiliania huxleyi* as a function of CO_2 concentration, $[CO_2]$. Cells were incubated at photon flux densities of 30, 80 and 150 μmol m^{-2} s^{-1} (denoted by circles, squares and triangles and corresponding solid, dashed, dash-dotted regression lines, respectively). Bars denote ±1 s.d. ($n = 3$); lines represent linear regressions. Vertical lines indicate p_{CO_2} values of 280, 365 and 750 p.p.m.v.

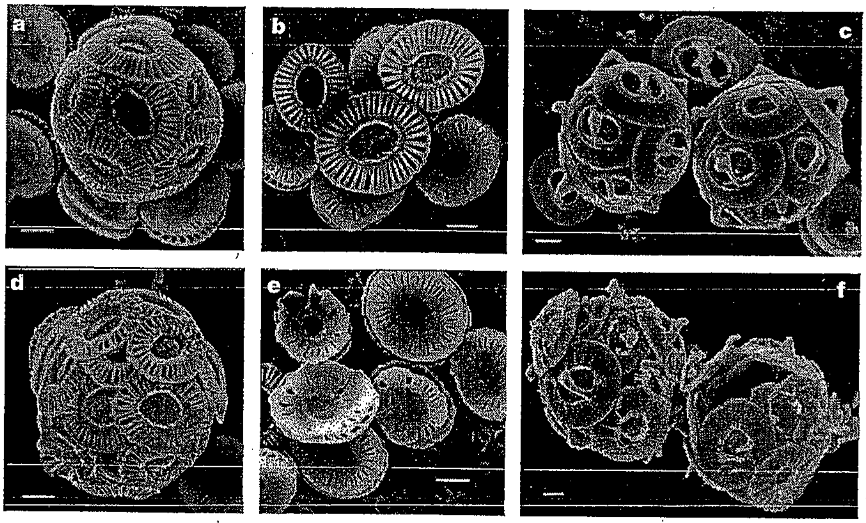

Figure 3 Scanning electron microscopy (SEM) photographs of coccolithophorids under different CO_2 concentrations. **a**, **b**, **d**, **e**, *Emiliania huxleyi*, and **c**, **f**, *Gephyrocapsa oceanica* collected from cultures incubated at $[CO_2] \approx 12$ μmol l^{-1} (**a–c**) and at $[CO_2] \approx 30$–33 μmol l^{-1} (**d–f**), corresponding to p_{CO_2} levels of about 300 p.p.m.v. and 780–850 p.p.m.v., respectively. Scale bars represent 1 μm. Note the difference in the coccolith structure (including distinct malformations) and in the degree of calcification of cells grown at normal and elevated CO_2 levels. Pictures are selected from a large set of SEM photographs to depict the general trend in coccolith calcification. As the culture medium was super-saturated with respect to calcium carbonate under all experimental conditions, post-formation calcite dissolution is not expected to have occurred.

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reduced light intensities (10% surface irradiance, data not shown). No significant differences were obtained between short and longer-term incubations of the natural assemblages. As short-term incubations are not likely to experience large changes in species composition, the observed response most probably reflects a reduction in carbonate precipitation of the calcifying organisms in the plankton assemblage.

The observed decrease in calcification with increasing p_{CO_2}, if representative of biogenic calcification in the world's ocean, has significant implications for the marine carbon cycle. Owing to its effect on carbonate system equilibria, calcification is a source of CO_2 to the surrounding water[15], whereby the increase in CO_2 concentration, due to calcification is a function of the buffer capacity of sea water. Theoretically, the buffer state of pre-industrial sea water resulted in 0.63 mole CO_2 released per mole $CaCO_3$ precipitated[16] (assuming temperature $T = 15$ °C, and salinity $S = 35$). Followin' the predictions of future atmospheric CO_2 rise, this value w. increase to 0.79 in 2100 (assuming Intergovernmental Panel on Climate Change (IPCC) scenario IS92a, ref. 3). At constant global ocean calcification this results in an additional source of CO_2 to the atmosphere. In the case of reduced calcification, this positive feedback is reversed. Assuming a pre-industrial pelagic inorganic carbon production of 0.86 Gt C y^{-1} (ref. 17) and a CO_2-related decrease in planktonic calcification as observed in our laboratory and field experiments (ranging between 16% and 83%), model calculations yield an additional storage capacity of the surface ocean for CO_2 between 6.2 Gt C and 32.3 Gt C for the period of 1950 to 2100.

Our results indicate that the ratio of calcite to organic matter production in cultured coccolithophorids and in oceanic phytoplankton assemblages is highly sensitive to the seawater p_{CO_2}. Although it is presently not clear what the physiological and ecological role of coccolith formation is[18], we propose that CO_2-dependent changes in calcification may affect cellular processes such as acquisition of inorganic carbon[19] and nutrients[20] as well as trophic interactions, and particle sinking rate[21,22]. These, in turn, may influence the structure and regulation of marine ecosystems in which coccolithophorids are dominant. From a geochemical viewpoint, a decrease in global ocean calcification would enhance CO_2 storage in the upper ocean[3,15,23], thus providing a negative feedback for changes in atmospheric p_{CO_2}. Such a feedback should be taken into account when predicting the role of the ocean in mitigating future anthropogenic CO_2 increases or in reconstructing the relation between ocean productivity and glacial–interglacial variations in p_{CO_2}. □

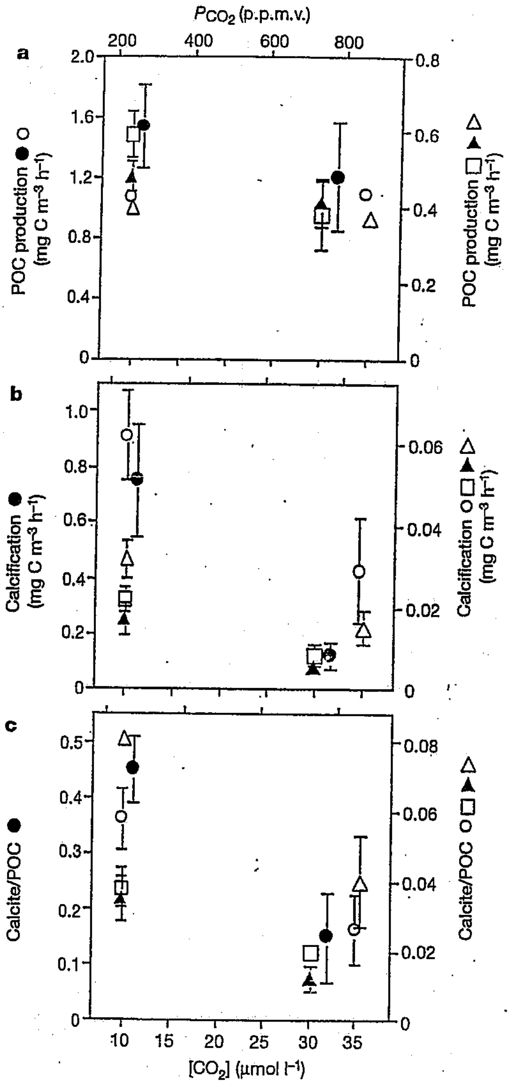

Figure 4 Effects of CO_2 manipulations on POC production, calcification and the ratio of calcification to POC production (calcite/POC) in subarctic North Pacific phytoplankton assemblages. **a**, POC production; **b**, calcification; and **c**, the calcite/POC ratio. Station P26 (50 °N, 145 °W) 1998, 6.8-day CO_2 pre-conditioning (filled circles). Station P26 1999, 2-day CO_2 pre-conditioning (squares). Station P26 1999, 9-day CO_2 pre-conditioning (filled triangles). Station P20 (43° 30′ N, 138° 40′ W) 1999, 1.5-day CO_2 pre-conditioning (open triangles). Station Z9 (55° N, 145° W) 1999, 1.5-day pre-conditioning (open circles). In all five experiments, POC production did not differ significantly between CO_2 treatments (t-test, $p \geq 0.4$). The statistical significance of calcification rate differences (t-test) is as follows: P26, all experiments and measurements ($p < 0.05$); P20, calcification ($p = 0.056$); calcite/POC ($p = 0.074$); Z9, calcification ($p = 0.135$); calcite/POC ($p = 0.11$). Error bars represent standard errors of means.

Methods

Laboratory

Monospecific cultures of the coccolithophorids *Emiliania huxleyi* (strain PML B92/11A) and *Gephyrocapsa oceanica* (strain PC7/1) were grown in dilute batch cultures at 15 °C in filtered (0.2 µm) sea water enriched with nitrate and phosphate to concentrations of 100 and 6.25 µmol l^{-1}, respectively, and with metals and vitamins according to the *f*/2 culture medium (ref. 24). The carbonate system was adjusted through addition of 1 N HCl or 1 N NaOH to the medium. Cells were acclimated to the experimental conditions for 7–9 generations and allowed to grow for about 8 cell divisions during experiments. Cultures were incubated in triplicate at photon flux densities of 150 µmol $m^{-2} s^{-1}$, light/dark (L/D) cycle = 16/8 h (Fig. 1) and of 150, 80 and 30 µmol $m^{-2} s^{-1}$, L/D = 24/0 (Fig. 2). Dissolved inorganic carbon (DIC) was measured coulometrically in duplicate (UIC model 5012)[25]. Alkalinity was determined in duplicate through potentiometric titration[26]. pH, CO_2 and CO_3^{2-} concentrations were calculated from alkalinity, DIC and phosphate concentrations ($T = 15$ °C; $S = 31$) using the dissociation constants of ref. 27. Subsamples for total particulate carbon (TPC) and particulate organic carbon (POC), which in L/D = 16/8 were taken at the end of the dark phase, were filtered onto pre-combusted (12 h, 500 °C) QM-A filters (pore width is about 0.6 µm) and stored at −25 °C. Before analysis, POC filters were fumed for 2 h with saturated HCl solution in order to remove all inorganic carbon. TPC and POC were subsequently measured on a mass spectrometer (ANCA-SL 20-20 Europa Scientific). Particulate inorganic carbon (PIC) was calculated as the difference between TPC and POC. Cell counts obtained with a Coulter Multisizer at the beginning and the end of incubations were used to calculate specific growth rates. PIC and POC production rates were calculated from cellular inorganic and organic carbon contents and specific growth rates.

Field

Ship-board productivity and calcification experiments were conducted at three stations in the subarctic North Pacific Ocean in June of 1998 (one experiment) and September of 1999 (four experiments). Station locations are given in the legend of Fig. 4. Surface seawater (10–20 m) was collected using a trace-metal-clean *in situ* pumping system and dispensed into acid-soaked polycarbonate bottles (3–4 replicate bottles per treatment). Samples were incubated on deck at about 30% surface irradiance levels in a flow-through incubator at *in situ* temperatures (13 ± 1 °C). CO_2 concentrations in samples were manipulated by either bubbling with commercially prepared CO_2/air mixtures (Station P26, 1998/1999) or by the addition of high-purity (trace-metal-clean) HCl/NaOH. Low CO_2 samples contained about 10 µM CO_2 (~250 p.p.m.v.) with a pH of about 8.20 while high CO_2 treatments contained approximately 33 µM CO_2 (~800 p.p.m.v.) with a pH of about 7.75. Total alkalinity (~2180 µEq l^{-1}) was unaffected by CO_2 bubbling while HCl and NaOH additions changed alkalinity by −6.4% and +3.4%, respectively. CO_2

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concentrations in samples were calculated from measurements of pH and alkalinity using the algorithm developed by ref. 28. After a pre-conditioning period ranging from 1.5–9 days, samples were incubated with 40 μCi ^{14}C (50 mCi mmol^{-1}) for 6–9 hours, harvested onto 0.4-μm polycarbonate filters, and immediately frozen in scintillation vials at −20 °C. In the laboratory, filter samples were acidified with either 10% HCl or H_3PO_4 to measure acid-stable (organic) carbon. The liberated acid-labile (particulate inorganic) carbon was trapped in NaOH solution contained either in small vials suspended in the primary vials or soaked into small GF/D glass fibre filters stuck onto the caps of the primary vials. Samples were measured on a liquid scintillation counter and corrected for ^{14}C uptake in dark control bottles as well as filtered seawater blanks.

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1. Milliman, J. D. Production and accumulation of calcium carbonate in the ocean: budget of a nonsteady state. *Glob. Biogeochem. Cycles* 7, 927–957 (1993).
2. Holligan, P. M. & Robertson, J. E. Significance of ocean carbonate budgets for the global carbon cycle. *Glob. Change Biol.* 2, 85–95 (1996).
3. Houghton, J. T. *et al.* (eds) *Climate Change 1994: Radiative Forcing of Climate Change and an Evaluation of the IS92 Emission Scenario* (Cambridge Univ. Press, Cambridge, 1995).
4. Wolf-Gladrow, D. A., Riebesell, U., Burkhardt, S. & Bijma, J. Direct effects of CO_2 concentration on growth and isotopic composition of marine plankton. *Tellus* 51B, 461–476 (1999).
5. Gattuso, J.-P., Frankignoulle, M., Bourge, I., Romaine, S. & Buddemeier, R. W. Effect of calcium carbonate saturation of seawater on coral calcification. *Glob. Planet. Change* 18, 37–46 (1998).
6. Langdon, C., Takahashi, T., Sweeney, C., Chipman, D., Goddard, J., Marubini, F., Aceves, H., Barnett, H. & Atkinson, M. Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. *Global Biogeochem. Cycles* 14, 639–654 (2000).
7. Westbroek, P., Young, J. R. & Linschooten, K. Coccolith production (biomineralisation) in the marine alga *Emiliania huxleyi*. *J. Protozool.* 36, 368–373 (1989).
8. Westbroek, P. *et al.* A model system approach to biological climate forcing. The example of *Emiliania huxleyi*. *Glob. Planet. Change* 8, 27–46 (1993).
9. Winter, A., Jordan, R. W. & Roth, P. H. in *Coccolithophores* (eds Winter, A. & Siesser, W. G.) 161–179 (Cambridge Univ. Press, Cambridge, 1994).
10. Westbroek, P. *et al.* Strategies for the study of climate forcing by calcification. *Bull. Inst. Oceanogr. Monaco* (Spec. Issue) 13, 37–60 (1994).
11. Holligan, P. M. *et al.* A biogeochemical study of the coccolithophore, *Emiliania huxleyi*, in the North Atlantic. *Glob. Biogeochem. Cycles* 7, 879–900 (1993).
12. Nielsen, M. V. Growth, dark respiration and photosynthetic parameters of the coccolithophorid *Emiliania huxleyi* (Prymnesiophyceae) acclimated to different day length-irradiance combinations. *J. Phycol.* 33, 818–822 (1997).
13. Young, J. R. Variation in *Emiliania huxleyi* coccolith morphology in samples from the Norwegian EHUX Experiment, 1992. *Sarsia* 79, 417–425 (1994).
14. Booth, B. C., Lewin, J. & Postel, J. R. Temporal variation in the structure of autotrophic and heterotrophic communities in the subarctic Pacific. *Prog. Oceanogr.* 32, 57–99 (1993).
15. Purdie, D. A. & Finch, M. S. Impact of a coccolithophorid bloom on dissolved carbon dioxide in sea water enclosures in a Norwegian fjord. *Sarsia* 79, 379–387 (1994).
16. Frankignoulle, M., Canon, C. & Gattuso, J.-P. Marine calcification as a source of carbon dioxide: Positive feedback of increasing atmospheric CO_2. *Limnol. Oceanogr.* 39, 458–462 (1994).
17. Morse, J. W. & Mackenzie, F. T. in *Developments in Sedimentology 48: Geochemistry of Sedimentary Carbonates* (Elsevier, Amsterdam, 1990).
18. Young, J. R. in *Coccolithophores.* (eds Winter, A. & Siesser, W. G.) 63–82 (Cambridge Univ. Press, Cambridge, 1994).
19. McConnaughey, T. A. Calcification, photosynthesis, and global cycles. *Bull. Inst. Océanogr. Monaco* (Spec. Issue) 13, 137–161 (1994).
20. McConnaughey, T. A. & Whelan, J. F. Calcification generates protons for nutrient and bicarbonate uptake. *Earth Sci. Rev.* 42, 95–117 (1997).
21. Harris, R. P. Zooplankton grazing on the coccolithophorid *Emiliania huxleyi* and its role in inorganic carbon flux. *Mar. Biol.* 119, 431–439 (1994).
22. Fritz, J. J. & Balch, W. M. A light-limited continuous culture study of *Emiliania huxleyi*: determination of coccolith detachment and its relevance to cell sinking. *J. Exp. Mar. Biol. Ecol.* 207, 127–147 (1996).
23. Kheshgi, H. S., Flannery, B. P. & Hoffert, M. I. Marine biota effects on the compositional structure of the world oceans. *J. Geophys. Res.* 96, 4957–4969 (1991).
24. Guillard, R. R. L. & Ryther, J. H. Studies of marine planktonic diatoms. I. *Cyclothella nana* (Hustedt) and *Detonula confervacea* (Cleve). *Can. J. Microbiol.* 8, 229–239 (1962).
25. Johnson, K. M., Wills, K. D., Butler, D. B., Johnson, W. K. & Wong, C. S. Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector. *Mar. Chem.* 44, 167–187 (1993).
26. Bradshaw, A. L., Brewer, P. G., Shafer, D. K. & Williams, R. T. Measurements of total carbon dioxide and alkalinity by potentiometric titration in the GEOSECS program. *Earth Planet. Sci. Lett.* 55, 99–115 (1981).
27. Goyet, C. & Poisson, A. New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. *Deep-Sea Res.* 36, 1635–1654 (1989).
28. Lewis, E. & Wallace, D. W. R. Program Developed for CO_2 System Calculations. ORNL/CDIAC-105. (Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, 1998).

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Increased dissolved oxygen in Pacific intermediate waters due to lower rates of carbon oxidation in sediments

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Concentrations of dissolved oxygen in the ocean seem to correlate well with climate instabilities over the past 100,000 years. For example, the concentration of dissolved oxygen in Pacific intermediate waters was considerably higher during Pleistocene glacial periods than it is today[1–4]. This has been inferred from the presence of bioturbated sediments, implying that oxygen levels were sufficient for burrowing organisms to live. Today, basins in the northeastern Pacific Ocean are floored by laminated sediments implying lower oxygen levels, which may be explained by reduced ventilation[2–4]. Here we report a recent return to bioturbated sediments in the northeastern Pacific Ocean since the late 1970s. From the carbon isotope composition of benthic foraminifers living in the sediment, we infer a twofold decrease in the carbon oxidation rate occurring within sediments, equivalent to an increase in dissolved oxygen concentration of 15–20 micromoles per litre. These changes, at the edges of the Santa Barbara, Santa Monica and Alfonso basins, are coincident with a change in North Pacific climate which has reduced upwelling by 20–30% and increased sea surface temperatures by 1.5–3 °C. This suggests that climate effects on surface productivity, reducing the supply organic matter to sediments, may have had a greater effect on benthic oxygen levels than changes in ocean circulation patterns.

Laminated sediments have been accumulating in the Santa Barbara and Santa Monica basins, and basins within the Gulf of California, for the past few centuries. However, the spatial extent of laminated sediments within these basins has been changing[5]. In Santa Monica basin, a study of Holocene sediment patterns revealed that between AD 1600 and the 1970s, laminated sediments spread systematically outwards and upwards into shallower waters from the centre of the basin, so as to encompass the entire basin floor by the 1970s (ref. 5). During this same period, laminated sediments were also forming in Santa Barbara basin and in the basins along the margins of the Gulf of California[6–11]. The temporal record of expanding laminated sediments in Santa Monica basin suggests that there are factors operating on centennial timescales that affect bottom-water oxygen levels, which probably control the distribution of bioturbating organisms. It is also now clear that there are shorter-timescale environmental changes that also affect the North Pacific marine environment, and that these are superimposed on the longer-scale patterns of variability. In particular, the mean climate state of the North Pacific, as measured by a number of different variables, has varied between a warm and a cold phase with a quasi-regular decadal oscillation[12–19]. This decadal pattern has been referred to as the Pacific Decadal Oscillation[19] (PDO). In the ocean, the PDO is characterized by a shift in the bifurcation point of the Sub-arctic Current as it approaches North America. This point of bifurcation strongly influences oceanographic, as well as weather patterns along the coast of the western USA[15–18]. The last clear PDO shift was coincident with a 1976–77 El Niño event. Since that time, the average sea surface temperatures within the southern California Current during the months of upwelling (spring/summer) have increased by 1.5–3 °C (Fig. 1). Upwelling along the coast at the latitude of Santa Monica basin during the spring has also decreased (Fig. 1). The result of these changes has been a systematic decline in marine fisheries in the southern California Current,

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Ocean acidification due to increasing atmospheric carbon dioxide

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Annexes

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The oceans cover over two-thirds of the Earth's surface. They play a vital role in global biogeochemical cycles, contribute enormously to the planet's biodiversity and provide a livelihood for millions of people.

The oceans are absorbing carbon dioxide (CO_2) from the atmosphere and this is causing chemical changes by making them more acidic (that is, decreasing the pH of the oceans). In the past 200 years the oceans have absorbed approximately half of the CO_2 produced by fossil fuel burning and cement production. Calculations based on measurements of the surface oceans and our knowledge of ocean chemistry indicate that this uptake of CO_2 has led to a reduction of the pH of surface seawater of 0.1 units, equivalent to a 30% increase in the concentration of hydrogen ions.

If global emissions of CO_2 from human activities continue to rise on current trends then the average pH of the oceans could fall by 0.5 units (equivalent to a three fold increase in the concentration of hydrogen ions) by the year 2100. This pH is probably lower than has been experienced for hundreds of millennia and, critically, this rate of change is probably one hundred times greater than at any time over this period. The scale of the changes may vary regionally, which will affect the magnitude of the biological effects.

Ocean acidification is essentially irreversible during our lifetimes. It will take tens of thousands of years for ocean chemistry to return to a condition similar to that occurring at pre-industrial times (about 200 years ago). Our ability to reduce ocean acidification through artificial methods such as the addition of chemicals is unproven. These techniques will at best be effective only at a very local scale, and could also cause damage to the marine environment. **Reducing CO_2 emissions to the atmosphere appears to be the only practical way to minimise the risk of large-scale and long-term changes to the oceans.**

All the evidence collected and modelled to date indicates that acidification of the oceans, and the changes in ocean chemistry that accompany it, are being caused by emissions of CO_2 into the atmosphere from human activities. The magnitude of ocean acidification can be predicted with a high level of confidence. The impacts of ocean acidification on marine organisms and their ecosystems are much less certain but it is likely that, because of their particular physiological attributes, some organisms will be more affected than others.

Predicting the direction and magnitude of changes in a complex and poorly studied system such as the oceans is very difficult. However, there is convincing evidence to suggest that acidification will affect the process of calcification, by which animals such as corals and molluscs make shells and plates from calcium carbonate. The tropical and subtropical corals are expected to be among the worst affected, with implications for the stability and longevity of the reefs that they build and the organisms that depend on them. Cold-water coral reefs are also likely to be adversely affected, before they have been fully explored.

Other calcifying organisms that may be affected are components of the phytoplankton and the zooplankton, and are a major food source for fish and other animals. Regional variations in pH will mean that by 2100 the process of calcification may have become extremely difficult for these groups of organisms particularly in the Southern Ocean. Some shallow water animals, which play a vital role in releasing nutrients from sediments, also calcify, and may be affected by changes in the chemistry of the oceans. Some studies suggest that growth and reproduction in some calcifying and non-calcifying marine species could be reduced due to the projected changes in ocean chemistry.

From the evidence available it is not certain whether marine species, communities and ecosystems will be able to acclimate or evolve in response to changes in ocean chemistry, or whether ultimately the services that the ocean's ecosystems provide will be affected. **Research into the impacts of high concentrations of CO_2 in the oceans is in its infancy and needs to be developed rapidly. We recommend that a major, internationally coordinated effort be launched to include global monitoring, experimental, mesocosm and field studies. Models that include the effects of pH at the scale of the organism and the ecosystem are also necessary. The impacts of ocean acidification are additional to, and may exacerbate, the effects of climate change. For this reason, the necessary funding should be additional and must not be diverted from research into climate change.**

Oceans play a very important role in the global carbon cycle and Earth's climate system. There are potentially important interactions and feedbacks between changes in the state of the oceans (including their pH) and changes in the global climate and atmospheric chemistry. Changes in the chemistry of the oceans will reduce their ability to absorb additional CO_2 from the atmosphere, which will in turn affect the rate and scale of global warming. The knowledge of these impacts and effects is currently poor and requires urgent consideration. **The understanding of ocean acidification and its impacts needs to be taken into account by the Intergovernmental Panel on Climate Change and kept under review by international scientific bodies such as the Intergovernmental Oceanographic Commission, the Scientific Committee on Oceanic Research and the International Geosphere-Biosphere Programme.**

The socio-economic effects of ocean acidification could be substantial. Damage to coral reef ecosystems and the fisheries and recreation industries that depend on them could amount to economic losses of many billions of dollars per year. In the longer term, changes to the stability of coastal reefs may reduce the protection they offer to coasts. There may also be direct and indirect effects on commercially important fish and shellfish species.

Marine ecosystems are likely to become less robust as a result of the changes to the ocean chemistry and these will be more vulnerable to other environmental impacts (such as climate change, water quality, coastal deforestation, fisheries and pollution). **The increased fragility and sensitivity of marine ecosystems needs to be taken into consideration during the development of any policies that relate to their conservation, sustainable use and exploitation, or the communities that depend on them.**

If the risk of irreversible damage arising from ocean acidification is to be avoided, particularly to the Southern Ocean, the cumulative future human derived emissions of CO_2 to the atmosphere must be considerably less than 900 Gt C (gigatonnes of carbon) by 2100.

In setting targets for reductions in CO_2 emissions, world leaders should take account of the impact of CO_2 on ocean chemistry, as well as on climate change. These targets must be informed by sound science.

Ocean acidification is a powerful reason, in addition to that of climate change, for reducing global CO_2 emissions. Action needs to be taken now to reduce global emissions of CO_2 to the atmosphere to avoid the risk of irreversible damage to the oceans. We recommend that all possible approaches be considered to prevent CO_2 reaching the atmosphere. No option that can make a significant contribution should be dismissed.

1 Introduction

1.1 *Background to the report*

Covering around 70% of the planet, the oceans play a central role in the Earth's major processes. They are host to thousands of species of organisms, which live in a variety of habitats and ecosystems. Carbon dioxide (CO_2) emitted to the atmosphere by human activities is absorbed by the oceans, making them more acidic (lowering the pH—the measure of acidity). Initial evidence shows that the surface waters of the oceans, which are slightly alkaline, are already becoming more acidic: we refer to this process as ocean acidification. There is growing concern that as atmospheric concentrations of CO_2 continue to rise, the increasing acidity will have significant effects on the marine system.

In recent years global warming and the resulting climate changes, has received considerable global attention. There is now a clear scientific consensus that increasing atmospheric levels of CO_2 (one of the major greenhouse gases), resulting mainly from human activities, are causing global mean surface temperatures to rise (IPCC 2001).

Ocean acidification is an additional concern to that of climate change, but the threat it poses to the marine environment has only recently been recognised. Parts of the international scientific community are beginning to take this issue seriously, for example the 2004 UNESCO symposium on the Oceans in a High-CO_2 World. An understanding of the chemical processes involved when CO_2 is absorbed from the atmosphere and dissolves in seawater is fairly well established. However, much less is known about the oceans and the biological and chemical processes of the life within them. Therefore predicting the impacts of ocean acidification is a complex and significant challenge.

For this reason the Royal Society has undertaken this study to provide a concise overview of the present state of scientific knowledge of ocean acidification and its likely impacts on marine organisms. This report will be of interest to those taking decisions and making policies on climate change, energy policy and environmental protection; for scientists studying the oceans, atmosphere and climate; and for anyone who is interested in the impact of human activities on the natural processes of our planet.

1.2 *The oceans and carbon dioxide: acidification*

Carbon dioxide is being produced in substantial quantities mainly through the combustion of fossil fuels, cement production, agriculture and deforestation. The concentration of CO_2 in the atmosphere has been increasing from its recent pre-industrial level of about 280 parts per million (ppm) to about 380 ppm today. What is significant for biological systems is that the rate of this increase is unprecedented since the peak of the last Ice Age—for at least 20 000 years (IPCC 2001). Atmospheric CO_2 levels are predicted to continue to increase for at least the next century and probably longer, and unless emissions are substantially reduced, may well reach levels exceeding 1 000 ppm by 2100, higher than anything experienced on Earth for several million years.

Oceans play a fundamental role in the exchange of CO_2 with the atmosphere. Over the past 200 years, since pre-industrial times, the oceans have absorbed about a half of the CO_2 emissions produced from burning fossil fuels and cement manufacture. This demonstrates the integral role that oceans play within the natural processes of cycling carbon on a global scale—the so-called carbon cycle.

The oceans and the organisms they support contain about 38 000 Gt C (gigatonnes of carbon; 1 Gt C = 10^{15} grams) (Figure 1). This accounts for about 95% of all the carbon that is in the oceans, atmosphere and terrestrial system, constituting a substantial reservoir of carbon. As we explain in Section 2, the chemical properties of the dissolved carbon in this system enable the oceans to buffer, or neutralise, changes in acidity due to the uptake of CO_2 emissions. However, as absorption of the CO_2 emissions from human activities increases (currently about 2 Gt C per year), this reduces the efficiency of the oceans to take up carbon. Carbon dioxide exchange is a two-way process, with the oceans and atmosphere absorbing and releasing CO_2. A decrease in the amount of CO_2 absorbed by the oceans will mean that relatively more CO_2 will stay in the atmosphere. This will make global efforts to reduce atmospheric concentrations of CO_2 and the associated climate change more difficult.

The surface waters of the oceans are slightly alkaline, with an average pH of about 8.2, although this varies across the oceans by ±0.3 units because of local, regional and seasonal variations. Carbon dioxide plays an important natural role in defining the pH of seawater (a brief account of measures of acidity such as pH, and the acid–base chemistry of the CO_2–carbonate system in the oceans, is given in Annex 1). When CO_2 dissolves in seawater it forms a weak acid, called carbonic acid. Part of this acidity is neutralised by the buffering effect of seawater, but the overall impact is to increase the acidity. This dissolution of CO_2 has lowered the average pH of the oceans by about 0.1 units from pre-industrial levels (Caldeira & Wickett 2003). Such a value may seem small but because of the way pH is measured, as we explain in Section 2, this change represents about a 30% increase in the concentration of hydrogen ions, which is a considerable acidification of the oceans. Increasing atmospheric concentration of CO_2 will lead to further acidification of the oceans.

In Section 2 we outline the main chemical reactions associated with ocean acidification. We look at the effects that CO_2 emissions from human activities have already caused and consider how the chemistry, nutrients and trace metals of the oceans may change with future emissions. These changes will affect the many important natural processes that are affected by its acidity/alkalinity (pH).

1.3 *Acidification and the surface oceans*

In this report we use the term 'surface oceans' to describe the near-surface waters where exchange of CO_2 occurs. Only the near-surface waters, or surface layers, of the oceans (down to about 100 m on average) are well mixed and so in close contact with the atmosphere. Carbon dioxide in the atmosphere dissolves in the surface waters of the oceans and establishes a concentration in equilibrium with that of the atmosphere. Molecules of CO_2 exchange readily with the atmosphere and on average only remain in the surface waters for about 6 years. However mixing and advection (vertical motions, sinking and upwelling) with the intermediate and deep waters of the oceans (down to about 1 000 m and 4 000 m respectively) is much slower, and takes place on timescales of several hundred years or more. Over time this mixing will spread the increased atmospheric uptake of CO_2 to the deeper oceans. Owing to this slow mixing process most of the carbon stored in the upper waters of the oceans will be retained there for a long time. This makes the impacts in the surface waters greater than if the CO_2 absorbed from the atmosphere was spread uniformly to all depths of the oceans.

1.4 *Ocean life and acidification*

Most of the biological activity in the oceans (and all of the photosynthesis) takes place in the near-surface waters through which sunlight penetrates; the so-called photic zone.

Marine organisms are, by definition, adapted to their environment. However, changes in ocean chemistry, especially rapid modifications such as ocean acidification, could have substantial direct and indirect effects on these organisms and upon the habitats in which they live. Direct effects include the impact of increasing CO_2 concentration and acidity, which may affect all stages of the life cycle. Indirect effects include the impact on organisms arising from changes in availability or composition of nutrients as a result of increased acidity.

One of the most important implications of the changing acidity of the oceans relates to the fact that many marine photosynthetic organisms and animals, such as corals, make shells and plates out of calcium carbonate ($CaCO_3$). This process of 'calcification', which for some marine organisms is important to their biology and survival, is impeded progressively as the water becomes acidified (less alkaline). This adverse effect on calcification is one of the most obvious and possibly most serious of the likely environmental impacts of ocean acidification.

Any changes in the biological processes in the surface ocean waters will also affect the deeper water of the oceans. This is because organisms and habitats living at the lower levels of the oceans — far from the sunlight — rely mainly on the products created by life in the surface waters. On a longer timescale, these organisms may also be vulnerable to acidification and changes in ocean chemistry as higher levels of CO_2 mix throughout the oceans.

In Section 3 of the report we explore the biological systems of the oceans and highlight processes and groups of species that may be vulnerable to changes in ocean chemistry. We examine how effects on organisms may affect populations of species; how these will affect interactions between species; and finally we consider whether species will acclimatise or evolve in response to ocean acidification. Section 4 looks at how these changes will affect ecosystems most likely to be at risk, such as coral reefs. Coral structures provide a valuable habitat for many other species, but being composed of $CaCO_3$ could be most at risk from increasing surface ocean CO_2 concentrations.

1.5 *Interaction with the Earth systems*

Ocean acidification will not occur in isolation from the rest of the Earth systems. Oceans play a significant role in the regulation of global temperature and so affect a range of climatic conditions and other natural processes. The Earth's climate is currently undergoing changes as a result of global warming, which is having an impact across many chemical and biological processes. Considerable interactions may exist between all these processes, which may have beneficial or adverse impacts, alongside those of ocean acidification. In Section 5 we identify the important interactions and consider the possible impacts of changes in ocean chemistry on other global processes.

1.6 *Adaptation to and mitigation of ocean acidification*

Any changes in natural resources as a result of ocean acidification could impact upon the livelihoods of people who rely on them. In Section 6 we look at the areas where there could be large socio-economic effects and evaluate the potential costs of these impacts.

Apart from reducing emissions to the atmosphere, engineering approaches (such as adding limestone, a carbonate material) have been suggested for tackling ocean acidification. These approaches aim to reduce some of the chemical effects of increased CO_2 through the addition of an alkali to the oceans. In Section 6 we briefly evaluate the potential of some of these methods to mitigate ocean acidification.

1.7 Artificial deep ocean storage of carbon dioxide

Our report focuses on ocean acidification as a result of increasing CO_2 being absorbed from the atmosphere. We do not directly address the issue of the release and storage of CO_2 on the ocean floor and in the deep oceans as part of a carbon capture and storage (CCS) programme. As the report does address the possible effects of increased CO_2 on organisms and ocean chemistry, some of our findings will be relevant to those interested in CCS. The concept of CCS is to capture emissions of CO_2 from power generation for example, and to store them, for thousands of years, in places that are isolated from the atmosphere, such as in liquid form on the seabed in the deep oceans and in underground geological structures. This subject is part of a forthcoming special report on carbon capture and storage by the Intergovernmental Panel on Climate Change (IPCC), due in late 2005.

1.8 Conduct of the study

The Royal Society convened a working group of international experts across several scientific disciplines to write this report. The Council of the Royal Society has endorsed its findings. We are very grateful to those individuals and organisations (listed in Annex 2) who responded to our call for evidence to inform this study. These have been valuable contributions, and in many cases have been reflected in our report.

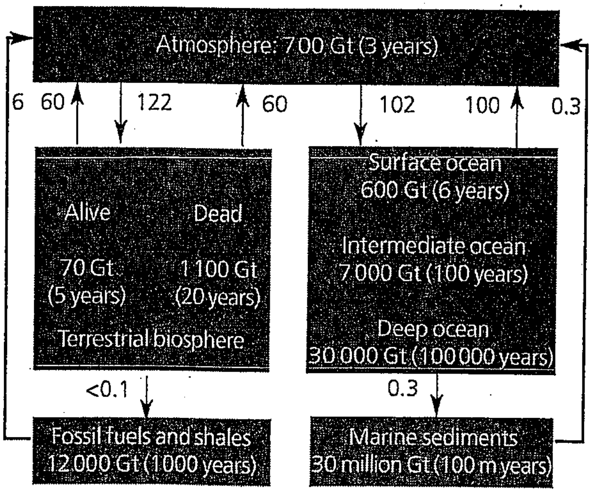
2 Effects of atmospheric CO_2 enhancement on ocean chemistry

2.1 Introduction

The oceans are a significant store of carbon within the Earth systems. They readily exchange carbon in the form of CO_2 with the atmosphere and provide an important sink for CO_2. Human activities are releasing CO_2 that would otherwise be locked away from the atmosphere in geological reservoirs. Because of these changes, atmospheric concentrations of CO_2 are higher today than for at least 420 000 years (IPCC 2001).

Approximately one-half of the CO_2 produced by fossil fuel burning and cement production as a result of human activities in the past 200 years is being taken up by the oceans. This absorption process is chemically changing the oceans, in particular increasing its acidity. In this section we consider the evidence of increased uptake of CO_2 by the oceans over the past century and how this reflects changes in atmospheric CO_2 levels and ocean acidity. We provide an overview of the chemical processes involved as CO_2 dissolves in the oceans; how ocean chemistry responds to changes in CO_2 levels; and an introduction to how these changes may affect the biological systems, which are considered further in Sections 3 and 4.

Figure 1. Diagram of the global carbon cycle showing sizes of carbon reservoirs (units are Gt (gigatonnes): 1 Gt = 10^{15} grams) and exchange rates ('fluxes') between reservoirs (units are gigatonnes per year) in the terrestrial (green) and the oceanic (dark blue) parts of the Earth system. Also shown are 'residence times' (in years) of carbon in each reservoir: however, some mixing between the deep oceans and marine sediments does occur on shorter timescales. Carbon exchanges readily between the atmosphere, the surface oceans and terrestrial biosphere. However, the residence time of carbon in the atmosphere, oceans and biosphere combined, relative to exchange with the solid Earth, is about 100 000 years. (Reprinted and redrawn from Holmen (2000) with permission from Elsevier.)



2.2 The impact of increasing CO_2 on the chemistry of ocean waters

2.2.1 The oceans and the carbon cycle

Carbon exists throughout the planet in several 'reservoirs' and in a variety of forms (Figure 1). The exchange of carbon between the important reservoirs of the biosphere, atmosphere and oceans is known as the carbon cycle. One of the more commonly known exchanges of carbon in this cycle is its absorption, in the form of CO_2, by trees and herbaceous plants on land during photosynthesis, also known as primary production (the production of organic from inorganic carbon), and subsequent release back into the atmosphere by respiration. Carbon dioxide also dissolves in the oceans and can be released back into the atmosphere, making the oceans a considerable point of exchange in the carbon cycle. Organisms within the surface ocean exchange CO_2 in much the same way as the biological processes on land. Although the biological uptake of CO_2 per unit area of the surface oceans is lower than that in most terrestrial systems, the overall biological absorption is almost as large as that in terrestrial environment. This is because the surface area of the oceans is so much larger (Field et al 1998).

The oceans are a substantial carbon reservoir. When measured on short timescales of hundreds of years, their greatest exchanges of carbon are with the atmosphere. The pre-industrial oceanic carbon reservoir has been estimated at about 38 000 Gt, compared with about 700 Gt in the atmosphere and somewhat less than 2 000 Gt in the terrestrial biosphere (approximately 700 Gt as biomass and 1 100 Gt as soil) (Brovkin et al 2002). These reservoirs exchange quantities of carbon each year that are large relative to the amount of carbon stored within them. Figure 1 illustrates that the oceans are acting as an important carbon sink, absorbing 2 Gt C per year more CO_2 than they are releasing into the atmosphere. This is small in comparison to the amount of carbon that is cycled between the different reservoirs but is a significant proportion of the 6 Gt C per year released into the atmosphere from human activity (Figure 1).

The carbon buried in some reservoirs, such as rocks and organic-rich shale, exchanges with the other reservoirs on geologically long timescales. As a result, carbon in these reservoirs will not affect the atmosphere or oceans on short timescales (up to about 10^3 years) unless exchange rates are artificially increased by human activity such as limestone mining, oil, gas and coal production. It is the carbon released by human activities that has produced increased atmospheric concentrations of CO_2 to levels unprecedented for at least 420 000 years and possibly for the past tens of millions of years (IPCC 2001).

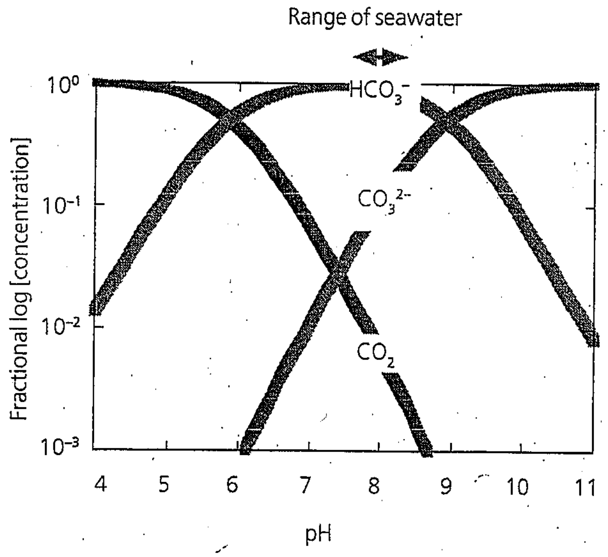
Carbon dioxide, like other gases, obeys Henry's law, which means that an increase in the atmospheric level of CO_2 increases the concentration of CO_2 in the surface oceans.

Carbon dioxide in the atmosphere is a chemically unreactive gas but, when dissolved in seawater, becomes more reactive and takes part in several chemical, physical, biological and geological reactions, many of which are complex (Annex 1).

One of the overall effects of CO_2 dissolving in seawater is to increase the concentration of hydrogen ions, ([H^+]), within it. This is the result of an initial reaction between water (H_2O) and CO_2 to form carbonic acid (H_2CO_3). This weak acid readily releases the hydrogen ions to form the other types of dissolved inorganic carbon (Annex 1). As we explain in Annex 1, acidity is determined by the concentration of hydrogen ions. This is measured on the pH scale, with an acid having a pH of less than 7 and alkali having a pH of greater than 7 units. The more acidic a solution, the more hydrogen ions are present and the lower the pH. Therefore the amount of CO_2 that dissolves in seawater has a strong influence on the resultant acidity/alkalinity and pH of the oceans.

In the oceans, CO_2 dissolved in seawater exists in three main inorganic forms collectively known as dissolved inorganic carbon (DIC). These are: (i) aqueous CO_2 (about 1% of the total); in this report this term also includes carbonic acid (H_2CO_3), (as aqueous CO_2 can be in either form), and two electrically charged forms, (ii) bicarbonate 8%). Thus under current ocean conditions, bicarbonate is the most abundant form of CO_2 dissolved in seawater followed by carbonate and then aqueous CO_2 (Figure 2). There is approximately an order of magnitude difference in abundance between each of the three forms; however, amounts vary somewhat with seawater temperature, salinity and pressure.

Figure 2. Relative proportions of the three inorganic forms of CO_2 dissolved in seawater. The green arrows at the top indicate the narrow range of pH (7.5–8.5) that is likely to be found in the oceans now and in the future. Note the ordinate scale (vertical axis) is plotted logarithmically (see Table 1 for numeric details and Annex 1 for further explanation).



All three forms of dissolved CO_2 are important for the biological processes of marine organisms. These processes include photosynthesis by marine algae (mostly phytoplankton), the production of complex organic carbon molecules from sunlight, and calcification, providing structures such as $CaCO_3$ shells. When these organisms die or are consumed, most of the carbon either stays in the surface waters or is released back into the atmosphere. However, some of this $CaCO_3$ and organic material falls as particle sediments to the deep oceans (Figure 3). The process whereby carbon is transferred from the atmosphere to the deep ocean waters and sediments is referred to as the 'biological pump'. By removing carbon from the surface waters and taking it to greater depths, the pump increases the capacity for the oceans to act as a sink for atmospheric CO_2. Any changes in the strength of this pump would have significant consequences on the amount of carbon being sequestered to the deep ocean environments and therefore removed from the atmosphere.

2.2.3 *The oceans as a carbonate buffer*

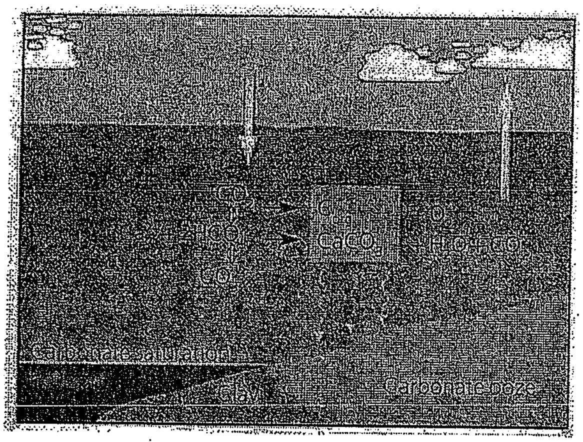
The relative proportion of the three forms of DIC (CO_2, HCO_3^- and CO_3^{2-}) reflects the pH of seawater and maintains it within relatively narrow limits. This DIC operates as a natural buffer to the addition of hydrogen ions—this is called the 'carbonate buffer'. If an acid (such as CO_2) is added to seawater, the additional hydrogen ions react with carbonate (CO_3^{2-}) ions and convert them to bicarbonate (HCO_3^-). This reduces the concentration of hydrogen ions (the acidity) such that the change in pH is much less than would otherwise be expected (Annex 1). When atmospheric CO_2 dissolves in seawater, the oceans increase in acidity but, because of the carbonate buffer, the resultant solution is still slightly alkaline.

The capacity of the buffer to restrict pH changes diminishes as increased amounts of CO_2 are absorbed by the oceans. This is because when CO_2 dissolves, the chemical processes that take place reduces some carbonate ions, which are required for the ocean pH buffer (Annex 1).

2.3 *Natural variation in pH of the oceans*

Surface oceans have an average pH globally of about 8.2 units. However, pH can vary by ±0.3 units due to local, regional and seasonal factors. The two primary factors

Figure 3. Diagram of the carbonate buffer and biological pump in the surface oceans. After absorption of CO_2 into the oceans it is converted by the carbonate buffer. Calcification in the oceans also releases CO_2, some of which is returned to the atmosphere. The biological pump (represented as descending wiggly arrows) converts CO_2 from the atmosphere into organic carbon (C_{org}) and $CaCO_3$ and transfers it to the deep ocean waters and sediments. The vertical scale is compressed: the process depicted by the equations and the 'box' occur within the surface oceans (top few hundred metres). This is far above the carbonate saturation horizon (Section 2.7.1), which for the calcite form, occurs at depths in the range of about 1.5 to 5 km and for the aragonite form, at depths in the range of about 0.5 to 2.5 km. (Reprinted with permission from Elderfield (2000); copyright ASSA).



governing the spatial distribution (Figure 4) of ocean pH are (i) temperature of the surface oceans and (ii) upwelling of CO_2-rich deep water into the surface waters. Lower surface water temperatures tend to increase CO_2 uptake, whilst surface warming drives its release. When CO_2 is released from the oceans, at constant temperatures, pH increases. In the deep oceans, the CO_2 concentration increases as sinking organic matter from biological production (which varies seasonally) is decomposed. These additions of CO_2 to the deep oceans cause its pH to decrease as the deep waters transit from the North Atlantic to the Pacific Ocean. When this CO_2-rich deep water upwells to the surface, it creates regions with lower-pH in the surface waters.

Seasonal changes such as those in temperature and in bio-productivity, including variations in photosynthesis and respiration, contribute to fluctuations in ocean pH (Gonzalez-Davila et al 2003). Coastal waters are more likely to be affected by the terrestrial system, such as run off from rivers, leading to wider variations in ocean pH in these areas (Hinga 2002).

Geographic pH variation for the global surface oceans (50 m) for the year 1994 is shown in Figure 4. The pH values are calculated using data from the Global Data Analysis Project (GLODAP). Surface values range from 7.9 to 8.25 with a mean value of 8.08 (Sabine personal communication). The lowest values are observed in upwelling regions (eg Equatorial Pacific, Arabian Sea) where subsurface waters with lower pH values are brought to the surface. The highest values are observed in regions of high biological production and export. In these regions DIC is converted into organic carbon by phytoplankton and exported by the biological pump into the deeper oceans resulting in higher pH values in the surface waters.

In Sections 2.5 and 2.6 we evaluate the affect of increased atmospheric CO_2 from human activities on surface ocean chemistry and pH, and compare these changes to natural and historical variations.

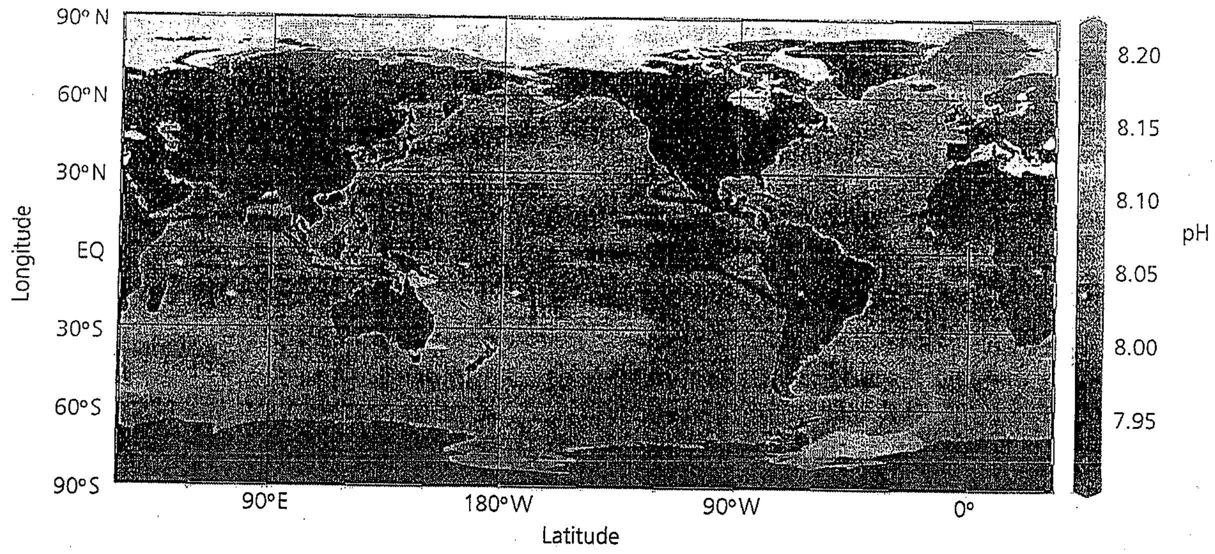
2.4 Factors affecting CO_2 uptake by the oceans

Several chemical, physical and biological factors have the potential to affect the uptake of CO_2 by the oceans (Houghton et al 2001). Chemical processes that may affect CO_2 uptake include changes to the CO_2 buffering capacity (Sarmiento et al 1995) and the effects of temperature on CO_2 solubility. Physical factors that affect uptake include increased ocean stratification due to increasing global temperatures. Warming of the oceans leads to increased vertical stratification (decreased mixing between the different levels in the oceans), which would reduce CO_2 uptake, in effect, reducing the oceanic volume available to CO_2 absorption from the atmosphere. Stratification will reduce the return flow of both carbon and nutrients from the deep oceans to the surface. Biologically linked processes, discussed in greater detail below and in Section 3, are perhaps the most difficult to evaluate; however, the removal of nutrients from the upper oceans with a slower return flow from the deep oceans could have negative impact on life in the surface oceans.

In addition to its effects upon CO_2 uptake and ocean chemistry, any acidification of marine surface waters may influence parts of the Earth systems through the emission of gases to the atmosphere. These broader factors are considered in more detail in Section 5.

2.5 How oceans have responded to changes in atmospheric CO_2 in the past

We are only certain of the atmospheric CO_2 concentrations over the past 420 000 years, the time for which we have an archive of ancient air trapped in bubbles of Antarctic ice (IPCC 2001). During this period the atmospheric concentrations have always been lower than today. With less certainty, we can reconstruct CO_2 concentrations much further back in time. To do this we can use inferred reconstructions from 'proxy' data as diverse as boron isotopes in carbonates (Pearson and Palmer 2000), rocks derived from ancient soils (Cerling 1991), the stomata on fossil leaves, and models of the processes we believe (upper 50 m) pH values in the global oceans for the nominal year 1994. The lowest *values are observed in upwelling regions (eg Equatorial Pacific, Arabian Sea) where subsurface waters with lower pH values are brought to the surface. The highest values are observed in regions of high biological production and export. In these regions DIC is fixed by phytoplankton and exported by the biological pump into the deeper layers resulting in higher pH values in the surface waters. Values are calculated from the GLODAP DIC and total alkalinity dataset (Key et al 2004) using the Dickson & Millero refit of the Merbach carbonate dissociation constants (Dickson and Millero 1987). Physical oceanographic modelling is based on Bryan (1969) and Cox (1984).*



control atmospheric CO_2 (Berner 1994; Bergman et al 2004). Such studies agree that atmospheric CO_2 has probably been relatively low for the past few million years, but that in the more distant past it was much higher than it is today. In the warm world of the Cretaceous for example (100 million years ago), concentrations were between three and ten times higher than present. Four hundred million years ago, before the land was colonised by forests, they were probably 20 times higher.

As we outlined in Section 2.2.2, as atmospheric CO_2 levels increase so does the concentration of CO_2 in the surface oceans. However it is unlikely that the past atmospheric concentrations would have led to a significantly lower pH in the oceans, as the rate at which atmospheric CO_2 changed in the past was much slower compared with the modern day. The fastest natural changes that we are sure about are those occurring at the ends of the recent ice ages, when CO_2 rose about 80 ppm in the space of 6 000 years (IPCC 2001). This rate is about one-hundredth that of the changes currently occurring. During slow natural changes, the carbon system in the oceans has time to interact with sediments and stays therefore approximately in steady state with them. For example if the deep oceans starts to become more acidic, some carbonate will be dissolved from sediments. This process tends to buffer the chemistry of the seawater so that pH changes are lessened (see section 2.2.3 and Annex 1 for a more detailed review).

Data from the air trapped in Antarctic ice (IPCC 2001) show a variation of atmospheric concentration of CO_2 from about 190 ppm to 300 ppm over the past 420 000 years. At constant temperature and alkalinity, this would represent a pH variation in the oceans of about 0.16 units, with the highest pH values when the atmospheric CO_2 values are lowest at glacial maxima (the value was derived using the procedures employed in constructing Table 1). At constant concentration of CO_2, temperature influence on pH is minor. However, this figure is likely to be upper bound because interactions with carbonate sediments would diminish this pH variation. This carbonate-sediment buffering occurs on a time scale of less than 10 000 years, whereas the full range of glacial-interglacial change occurs on this time scale or longer. Estimates of glacial–interglacial deep-ocean pH changes of 0.12 (Ridgwell 2001) are consistent with these model calculations.

Proxy estimates from a study based on boron isotopes suggest that 50 million years ago, ocean pH was as much as 0.6 pH units lower than today (Pearson and Palmer 2000), though the interpretation of these data in terms of pH change is open to question (Pagani et al 2005). Models suggest that dissolution of $CaCO_3$ sediments would have had sufficient time to buffer the change in pH in the past, even when the CO_2 concentration of the atmosphere was high.

Other proxy estimates have been made for pH at the peak of the more recent Ice Age, about 20 000 years ago, when atmospheric CO_2 concentrations were 190 ppm compared with today's value of about 380 ppm. One estimate, also based on boron isotopes (Sanyal et al 1995), suggests that the pH of the oceans was 0.3 units higher than today (that is, more alkaline). This implies that doubling of CO_2 decreases pH by 0.3 units. However, another estimate, based on the preservation of marine calcifying organisms (Anderson & Archer 2002), suggests that there was no such whole-ocean pH change.

We caution, therefore, that there is substantial uncertainty in both proxy and model reconstructions, and that these uncertainties increase as one goes back from centuries to millennia and to millions of years in time.

2.6 Change in ocean chemistry due to increases in atmospheric CO_2 from human activities

Based upon current measurements of ocean pH, analysis of CO_2 concentration in ice cores, our understanding of the rate of CO_2 absorption and retention in the surface oceans, and knowledge of the $CaCO_3$ buffer (Section 2.2.2), it is possible to calculate that the pH of the surface oceans was 0.1 units higher in pre-industrial times (Caldeira & Wickett 2003; Key et al 2004). This 0.1 pH change over about the past 200 years corresponds to about a 30% increase in the concentration of hydrogen ions.

It is also possible to make projections of likely further pH reductions in seawater over the next centuries as a result of additional atmospheric CO_2 emissions. These projections of future pH change (Table 1; Caldeira & Wickett in press) show that if CO_2 from human activities is allowed to continue on present trends this will lead to a decrease in pH of up to 0.5 units by the year 2100 in the surface oceans. This corresponds to a three fold increase in the concentration of hydrogen ions from pre-industrial times, which is an increase in ocean pH outside the range of natural variation and probably to a level not experienced for at least hundreds of thousands of years and possibly much longer (Sections 2.3 and 2.5). Critically, the rate of change is also probably at least 100 times higher than the maximum rate during this time period.

2.6.1 Change to the oceans due to CO_2 enhancement in recent centuries

It is possible to measure the amount of carbon added to seawater over the past two centuries as a result of human activities. This information has been developed using a substantial database taken through the global oceans observing programmes of the World Ocean Circulation Experiment and the Joint Global Ocean Flux Study in the 1990s. In these programmes data were collected from around 10 000 monitoring stations. This data set provides the most accurate and comprehensive overview of the past and current distribution of DIC in the oceans.

Ocean observations indicate increases in DIC as a result of additional CO_2 being absorbed from the atmosphere. Using a sophisticated tracer technique (Gruber et al 1996), this DIC can be separated into naturally occurring dissolved carbon in seawater and that added to the oceans by human activity. This is estimated using the relationship between the variables in seawater (nutrients, DIC, alkalinity etc) that are assumed to be free of excess CO_2, and by then subtracting this inferred natural DIC concentration from the observed increased seawater concentration.

Using this approach, it can be estimated that between 1800 and 1994 the oceans have absorbed about 48% of the total CO_2 emitted by human activities, mainly by fossil fuel burning and cement manufacturing. This has been deduced from the measurement of total DIC (106 ± 17 Gt C) and extrapolating for the regions of oceans not surveyed, leading to a sum of 118 ± 19 Gt C over this period. A continuation of trends inferred for the 1980s and 1990s from ocean models and atmospheric observations would indicate that over 140 Gt C (over 500 Gt CO_2) resulting from human activities reside in the oceans today. Even though uncertainties exist due to the estimates in the amount of CO_2 from human activities and errors in mapping, this number is probably accurate better than 20%. Analysis of this data shows that the uptake and redistribution of CO_2 varies geographically due to temperature and ocean circulation currents (Section 2.3) (Sabine et al 2004).

Given that CO_2 enters the oceans by exchange across the air–sea interface, it follows that analysis of the distribution of CO_2 uptake show highest values (and therefore the greatest pH change), in near-surface waters. As it takes many centuries for the downward mixing of CO_2, little of the CO_2 derived from human activities has yet reached the deep oceans. When averaged for the oceans globally, about 30% of the anthropogenic CO_2 is found at depths shallower than 200 m, with 50% at depths less than 400 m, leading to the conclusion that most of the CO_2 that has entered the oceans as a result of human activity still resides in relatively shallow waters.

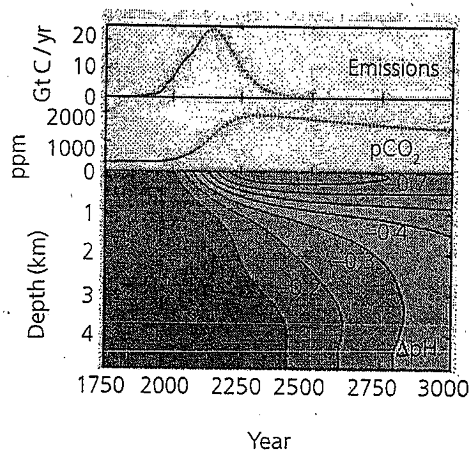
2.6.2 How oceanic pH will change in the future

As we have shown in the previous section, it is possible to make projections of the extent to which oceanic pH will fall as a consequence of increases in CO_2 from human activities. The simplest estimate, takes a situation where human CO_2 emissions continue to be released on current trends; considers the surface oceans as a single 'box' at a constant temperature (25 °C) and salinity with an initial (pre-industrial) pH of 8.2 units, and assumes no mixing with the deeper oceans. Under these circumstances it is predicted that pH will fall to below 7.9 by 2100 (Zeebe and Wolf-Gladrow 2001).

A more detailed analysis of projected pH changes has been done using an ocean general-circulation model with observed atmospheric CO_2 from 1975 to 2000 and a projected mid-range CO_2 emission scenario (IPCC IS92a scenario (Houghton et al 2001)) for 2000–2100 (Caldeira & Wickett 2003). The results are shown in Figure 5 where, assuming that after 2100 emissions follow a logistic resources, emissions of CO_2 from human activities have peaked around 2 150. However, the CO_2 remains in the atmosphere at a high concentration for several thousand years, before it is absorbed by the oceans or the terrestrial biosphere. The initial changes in the surface ocean pH are rapid, but as CO_2 continues to be absorbed from the atmosphere it is slowly transferred to the deep oceans (including ocean sediments) by mixing and through the biological pump, with subsequent changes in pH.

The study predicts a possible decrease in pH of 0.5 units by the year 2100 in the surface oceans, which, as stated earlier, corresponds to a three fold increase in the concentration of hydrogen ions from pre industrial times. The simulated atmospheric CO_2 exceeds 1 900 ppm at around 2300, and the maximum reduction in pH in the oceans' surface would be 0.77 units (Figure 6). The lowering of pH would be moderated slightly by factors such as changes in temperature, but by less than 10%. Taking this example, even at high CO_2 concentrations, with a significant lowering of ocean pH, the carbonate buffer means that the oceans are still slightly alkaline (ie a pH of less than 7). These changes in ocean pH are outside the range of natural variability and, as we evaluate in Sections 3 and 4, could have a substantial affect on and biological processes in the surface oceans.

Figure 5. Projected change in pH of the oceans due to release of CO_2 from human activities. The top layer of the diagram shows past and projected emissions of CO_2 to the atmosphere in Gt C per year. Carbon dioxide emission trends are based on mid-range CO_2 emission scenario (IPCC IS92a scenario (Houghton et al 2001)). The decrease in emissions after 2150 assumes that human activities will continue at levels until the eventual burning of the remaining fossil fuel resources. The second layer shows historical atmospheric CO_2 levels to 1975, observed atmospheric CO_2 concentrations from 1975 to 2000 and predicted concentrations to year 3000. The decrease in atmospheric CO_2 levels after 2400 reflects the excess of uptake of CO_2 by the oceans and sequestered down to the oceans' sediments. The coloured sections at the bottom of the figure show the projected average change in ocean pH with depth. The Figure assumes the chemistry and pH is uniform on the horizontal plane throughout the oceans. The maximum reduction in the surface oceans shown is 0.77 units. The vertical variations relate to mixing over time of the surface waters with deeper parts of the oceans and chemical reactions in the deep oceans. These CO_2 effects were estimated using the Lawrence Livermore National Laboratory (LLNL) ocean general-circulation model. Physical oceanographic modelling is based on Bryan (1969) and Cox (1984). (Reprinted with permission from Nature in Caldeira & Wickett Anthropogenic carbon and ocean pH. Copyright 2003, Macmillan Publishers Ltd. http://www.nature.com).



Even the current level of ocean acidification is essentially irreversible during our lifetimes. It will take tens of thousands of years for ocean chemistry to return to a condition similar to that occurring at pre-industrial times, about 200 years ago.

The delay arises because it takes tens of thousands of years for mixing to take place throughout the oceans. This mixing is required to bring up compounds from the oceans' sediments to buffer the changes as a result of increased CO_2 on ocean surface chemistry. As we have highlighted above, the oceans have in the past been able to adapt to increased atmospheric CO_2 levels because the rate of change took place over time periods that enabled sufficient mixing with deeper waters..

Warming of the oceans, as a result of global warming, may also reduce the rate of mixing with deeper waters and this would further delay recovery.

2.7 The role of carbon chemistry in ocean systems

Below we provide an introduction to the important chemical changes that are predicted to affect marine biological processes.

2.7.1 Effects on calcium carbonate and saturation horizons

Marine organisms that construct $CaCO_3$ structures, such as shells, are dependent on the presence of bicarbonate and carbonate forms of dissolved inorganic carbon in seawater. Once formed, $CaCO_3$ will dissolve back into the water unless the surrounding seawater contains sufficiently high concentrations of carbonate ions (CO_3^{2-}) (ie it is saturated) (Annex 1). Calcium carbonate also becomes more soluble with decreasing temperature and increasing pressure, and hence with ocean depth. It is also affected by the flow of CO_2-rich deep waters between ocean basins (Section 2.3). A natural boundary develops in seawater as a result of these different variables. This is known as the 'saturation horizon' and it identifies a clear depth of seawater above which $CaCO_3$ can form, but below it dissolves.

The marine organisms that produce $CaCO_3$ shells live above the saturation horizon, where $CaCO_3$ does not readily dissolve. Increasing CO_2 levels and the resultant lower pH of seawater decreases the saturation state of $CaCO_3$ and raises the saturation horizon closer to the surface. Therefore increases in surface ocean CO_2 levels could have severe consequences for organisms that make external $CaCO_3$ shells and plates.

Calcium carbonate exists in two commonly occurring forms: aragonite and calcite (Box 1). Because the aragonite form of $CaCO_3$ is more soluble than calcite, the aragonite saturation horizon is always nearer the surface of the oceans than the calcite saturation horizon. Therefore calcifying organisms that produce the calcite form of $CaCO_3$ (coccolithophores and foraminifera) are possibly less vulnerable to changes in ocean acidity than those that construct aragonite structures (corals and pteropods) (see Figure 7 and Table 2 for a description of the key groups of relevant marine life within the oceans). Projected changes in pH and the calcite and aragonite saturation state in the surface oceans in 2100 under a range of possibilities for future CO_2 emissions are shown in Figure 6 (based on IPCC 2000). When modelled under one of the more modest emission scenarios (B1), which projects cumulative CO_2 emissions to be about 900 Gt C by 2100, the Southern Ocean is already undersaturated with respect to aragonite. This would mean that any aragonite $CaCO_3$ structure produced by organisms in this environment would dissolve. The cold Southern Ocean is particularly vulnerable to changes in saturation levels because it currently has very low saturation levels. The impacts of changing carbonate saturation on ecosystems, particularly for coral reefs, and the Southern Ocean are examined in greater detail in Sections 4.2.1 and 4.2.2.

Box 1 Forms of calcium carbonate

Calcium carbonate ($CaCO_3$) exists in two main structures. These are (i) aragonite, which has orthorhombic symmetry in its structure, and (ii) calcite, which is trigonal. Both aragonite and calcite are abundant in organisms. However, because of its structure, calcite is less soluble.

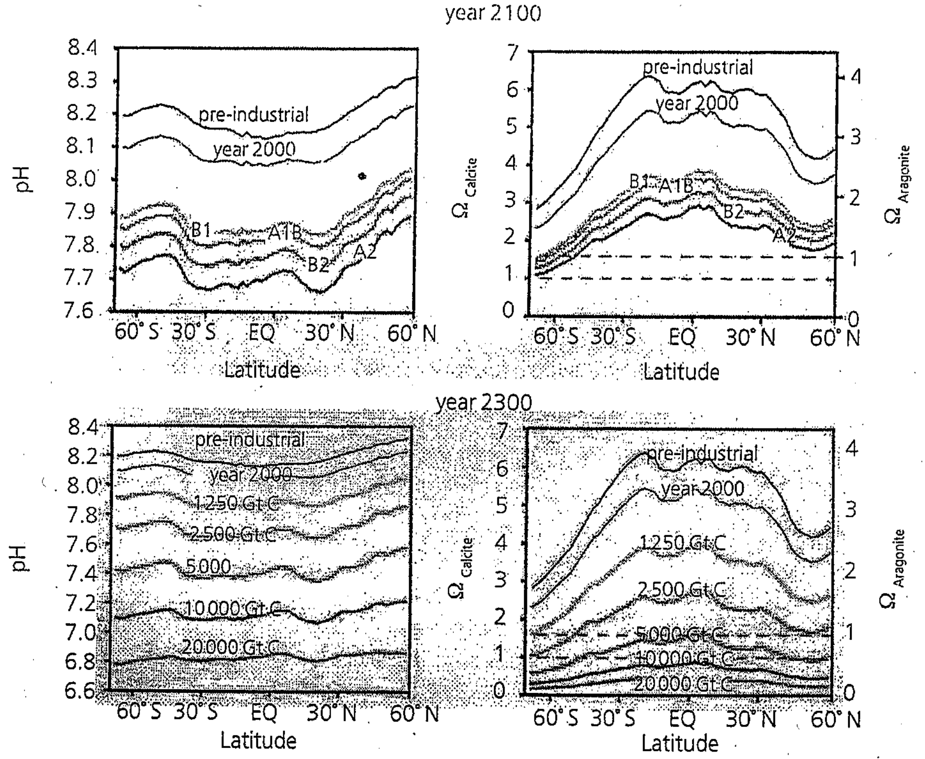
As we describe in Sections 3 and 4, these $CaCO_3$ structures are widespread and integral to the biology of key species in the marine ecosystem, including primary producers and herbivores.

Throughout the report the phrase undersaturated with respect to $CaCO_3$ (aragonite, calcite or both) refers to the situation where there is insufficient $CaCO_3^{2-}$ available to prevent $CaCO_3$ dissolving in sea water. In practice this also means there is insufficient CO_3^{2-} available for organisms to make $CaCO_3$ structures. This results from factors, such as ocean acidification, changing ocean chemistry.

The saturation level of the calcite and aragonite horizons can be mapped, and the changes can be shown between the present and pre-industrial locations of the horizons resulting from penetration of CO_2 into seawater from human activities (Feely et al 2004). Lower seawater temperature towards the poles means that the saturation levels are lower at higher latitudes (Figure 5). Across most of the oceans the saturation horizon, for the calcite form, occurs at depths between 1.5 to 5 km and, for the aragonite form, at depths between 0.5 to 2.5 km below the surface of the oceans.

The production of $CaCO_3$ by free-floating organisms plays a key role in the biological pump (Figure 3). Once the organism dies, the $CaCO_3$ causes it to sink, thereby taking its carbon content to the deeper waters. If the saturation horizon moves closer to the surface, this would lead to both a reduced production of $CaCO_3$ by organisms and an increased dissolution of calcified structures. These effects may have serious consequences for the amount of carbon that is produced in the near-surface waters and sequestered into the deeper oceans. However effects of this kind may be offset by an increase in the production of other organic carbon compounds by surface marine organisms. The biological role of $CaCO_3$ and organic carbon is discussed in more detail in Section 3.5.

The formation of $CaCO_3$ leads to an increased CO_2 concentration in the water. This apparently counterintuitive behaviour arises because two ions of bicarbonate (HCO_3^-) react with one ion of doubly charged calcium (Ca^{2+}) to form one molecule of $CaCO_3$, which leads to the release of one molecule of CO_2. Some of this released CO_2 is converted to bicarbonate by the buffering process, outlined above and in Annex 1. Under current conditions, for each molecule of CO_2 produced during calcification about 0.6 molecules are released, potentially to the atmosphere, while the rest is taken up by the bicarbonate-carbonate buffer (Ware et al 1992). As the capacity of the oceans to buffer CO_2 decreases with increasing acidity, this ratio is expected to increase. Specifically, if CO_2 emissions continue at their present rate, atmospheric concentration is estimated to reach about 700 ppm by 2100 (IPCC 2001). It is then estimated that, by 2150, for each CO_2 molecule produced from calcification 0.79 molecules would be potentially released to the atmosphere (Zondervan et al 2001). This would increase the total emission of CO_2 from the oceans as a result of the calcification process by about 0.22 Gt C per year, and this would lead to a change in CO_2 emissions from about 0.63 Gt C per year in 1850 to about 0.85 Gt C per year in 2150 (Zondervan et al 2001). However, it is important to stress that this calculation assumes that the rate of calcification would remain constant, at about 1 Gt C per year, and not be affected by changes in the acidity. A decrease in calcification resulting from increased acidity would counteract this increase and according to some estimates, would decrease the total emission from the oceans, providing a *variations in pH and calcite ($\Omega_{Calcite}$) and aragonite ($\Omega_{Aragonite}$) saturation state in the surface oceans modelled for a range possibilities for future CO_2 emissions in 2100 (top panels). The bottom panels show the total amount of carbon projected to be emitted by 2300 (based on IPCC 2000). B1 represents the most benign scenario with lowest CO_2 emissions, whereas A2 and B2 could be regarded as the changes predicted to occur if CO_2 emissions continue at current levels. Pre-industrial and year 2000 values shown at the top are calculated from Key et al (2004). Dashed lines show calcite and aragonite saturation horizons where a saturation state of less than 1 is undersaturated. The Southern Ocean is regarded as the area below latitude 50° S. As the graphs on the right indicate the Southern Ocean will be undersaturated for aragonite by 2100 under the A2 scenario. By 2300 even ambitious targets for emissions will lead to undersaturation across large parts of the oceans. Chemistry changes are computed from zonal mean average concentrations in the three-dimensional ocean model. (Caldeira & Wickett in press). Copyright 2005, American Geophysical Union. (Physical oceanographic modelling is based on Bryan (1969) and Cox (1984)).*



negative feedback on increasing atmospheric CO_2 concentrations (Zondervan et al 2001). Essentially this is an area of great uncertainty. This example is provided, in part to highlight the complexity of the interactions between the chemical and biological processes in the oceans.

2.7.2 Impacts of acidification on the chemistry of nutrients and toxins

Substances in seawater other than the components of the CO_2–bicarbonate–carbonate system are significant for life in the oceans as nutrients or as toxins. Nutrients are essential for life, whereas toxins are damaging. In some cases essential nutrients act as toxins when present at high concentrations; examples are the trace elements copper and zinc. In addition to changes in the carbonate system, ocean acidification is expected to produce changes in ocean chemistry that may affect the availability of nutrients and toxins to marine organisms.

The chemical form of an element in seawater (its speciation) is affected by the presence of other chemical 'species' with which it may interact. Among these is the hydrogen ion concentration. Metals exist in two forms in seawater; complex and free dissolved. The main concern about changes in metal speciation is that it is generally the free dissolved form that is most toxic. A decrease in pH generally increases the proportion of free dissolved forms of toxic metals.

However, the impact (deleterious or advantageous) of pH-induced changes in seawater speciation is difficult to determine. The role of trace elements in the biochemistry, and of trace element availability on the growth of marine micro-organisms are topics of active research. Phytoplankton growth rates are known to be limited by iron

Table 1. Changes to ocean chemistry and pH estimated using the OCMIP3 models calculated from surface ocean measurements and our understanding of ocean chemistry. Note that the concentration of bicarbonate ion (HCO_3^-) and carbonic acid (H_2CO_3) increase with rising atmospheric concentration of CO_2 while carbonate ion (CO_3^{2-}) decreases. The average pH of the surface ocean waters decreases with increasing atmospheric CO_2 concentration. (Assumptions used in model: Total alkalinity = 2324 mol/kg, temperature = 18° C. All other assumptions as per OCMIP3 (Institut Pierre Simon Laplace 2005). Aragonite and calcite saturation calculated as per Mucci & Morse (1990). Physical oceanographic modelling is based on Bryan (1969) and Cox (1984).

	Pre-industrial	Today	2 × pre-industrial	3 × pre-industrial	4 × pre-industrial	5 × pre-industrial	6 × pre-industrial
Atmospheric concentration of CO_2	280 ppm	380 ppm	560 ppm	840 ppm	1120 ppm	1400 ppm	1680 ppm
H_2CO_3 (mol/kg)	9	13	19	28	38	47	56
HCO_3^- (mol/kg)	1768	1867	1976	2070	2123	2160	2183
CO_3^{2-} (mol/kg)	225	185	141	103	81	67	57
Total dissolved inorganic carbon (mol/kg)	2003	2065	2136	2201	2242	2272	2296
Average pH of surface oceans	8.18	8.07	7.92	7.77	7.65	7.56	7.49
Calcite saturation	5.3	4.4	3.3	2.4	1.9	1.6	1.3
Aragonite saturation	3.4	2.8	2.1	1.6	1.2	1.0	0.9

availability over at least 10% of the oceans' surface (Boyd et al 2000). Therefore any effect of pH on iron speciation may be important in these areas and reduce the iron limitation, as one effect of reduced pH would be to increase the proportion of soluble to insoluble iron (Morel et al 2003).

A decrease in pH will also probably change the nature and form of particle surfaces in seawater and hence have an additional indirect effect on the speciation of trace metals (Mouvet & Bourg 1983). Indeed, the main impact of change in pH on speciation of trace metals may be to release previously bound metals from the sediment to the water column. This could be of particular importance in shallow seas.

There appear to have been no studies of the impact of change in pH on nutrient speciation. It therefore remains unclear whether such changes would significantly affect biological systems. However, theoretical speciation diagrams allow a qualitative prediction of the effect of pH on nutrient speciation (Zeebe & Wolf-Gladrow 2001). These show significant changes in speciation of phosphate, silicate, iron and ammonia within the range of decrease in pH considered in this report. Reduced pH would, for example, lower the concentrations of ammonia (NH_3) in seawater in preference to ammonium (NH_4^+). In mesotrophic coastal waters with frequently high nutrient concentrations, a change of pH from 8.1 to 7.8 halves the fraction of NH_3 in the ratio of NH_4^+:NH_3 (Raven 1986). Further quantitative research is required on the impacts of pH on nutrient speciation, concentration and availability and their non-equilibrium behaviour that is typical of natural systems.

The biological implications of these changes in chemical speciation are considered in Section 3.

2.8 Conclusions

The chemical changes in the oceans caused by increases in the concentration of CO_2 in the atmosphere will include a lowering of the pH, an increase in dissolved CO_2, a reduction in the concentration of carbonate ions and an increase in bicarbonate ions.

The oceans are currently taking up about one tonne of CO_2 associated with human activities per year for each person on the planet (IPCC 2001). Almost half of the CO_2 produced in the past 200 years by burning fossil fuels and cement manufacture has been absorbed by the oceans. This has already resulted in a change to ocean chemistry, reducing surface seawater pH by about 0.1 units, which corresponds to an increase of about 30% in the concentration of hydrogen ions.

The affects of possible impacts of future cumulative CO_2 emissions by 2100 have been modelled for the oceans. These models, including analyses from the GLODAP, International Carbon-cycle Model Intercomparison Project Phase 3 (OCMIP3) and the LLNL presented in this Section, rely on the same basic modelling approaches (Bryan 1969; Cox 1984). These studies show that even at a modest future projection of CO_2 emissions, of about 900 Gt C, direct impact of ocean acidification is very likely to cause the Southern Ocean to become undersaturated with respect to aragonite. This would lead to severe consequences for organisms that make the aragonite form of $CaCO_3$ shells and plates.

enters the atmosphere from human activity, more will be taken up by the oceans (Table 1). If CO_2 emissions continue on current trends, this could result in the average pH of the surface oceans decreasing by 0.5 units below the level in pre-industrial times, by 2100. This is beyond the range of natural variability and represents a level probably not experienced for at least hundreds of thousands of years and possibly much longer (Caldeira & Wickett 2003). Critically, the rate of change is also at least 100 times higher than the maximum rate observed during this time period. These changes are so rapid that they will significantly reduce the buffering capacity of the natural processes that have moderated changes in ocean chemistry over most of geological time.

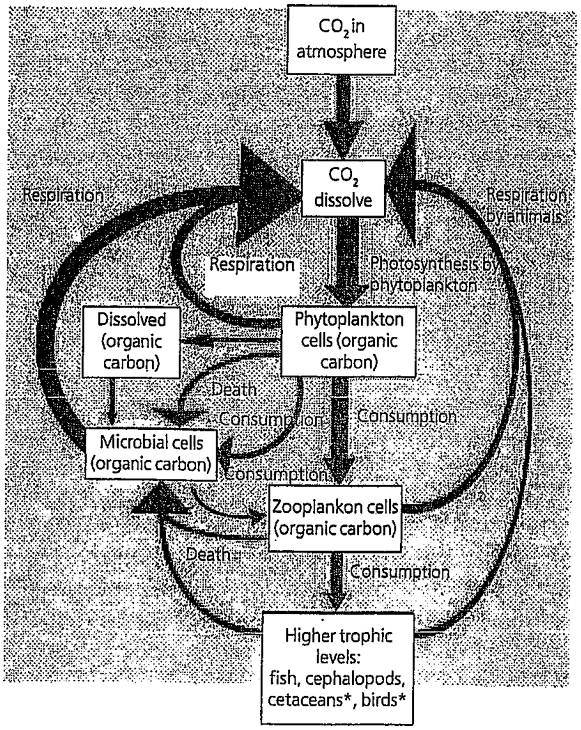
In Sections 3 and 4 we consider the biology of the marine system and examine the implications of the projected changes in ocean chemistry. We then examine the species, populations and ecosystems that may be vulnerable to changes in ocean chemistry.

3 Biological impacts: effects of changing ocean chemistry on organisms and populations

3.1 Introduction

The increase in surface ocean CO_2 and the corresponding decrease in pH predicted for 2100 represent an extent of change in sea surface chemistry that has not been experienced for at least the past 420 000 years and possibly much longer (Section 2.5). As significant is the rate of this change, which is at least 100 times the maximum rate observed during this time period (Section 2.5). Such extents, and rates, of change will inevitably have effects on organisms in the oceans. Here we discuss the effects these changes in ocean chemistry have on present-day marine organisms (Figure 7; Table 2). We also consider the possibilities of acclimation or adaptation of organisms to the changing environment within the constraints of their current genetic composition, as well as the potential for evolution (genetic changes selected in relation to the changed ocean chemistry).

*Figure 7. Importance of micro-organisms (phytoplankton and non-photosynthetic zooplankton and microbial cells) and of larger animals in the marine carbon cycle. The thickness of the lines indicates relative carbon flow through the pathway. *Cetaceans (whales and dolphins) and birds release CO_2 to the atmosphere, not to water, but this is a minor pathway. The cycle assumes no net input of carbon or loss from the oceans. A similar diagram showing CO_2 flow patterns could also be produced for benthic primary producers, bringing in, for example echinoderms (such as starfish and sea urchins) among the larger animals, but with a similar major role for micro-organisms.*



Photosynthetic marine organisms play a major ecological role, providing more than 99% of the organic matter used by marine food webs. Converting dissolved CO_2 to organic carbon, they account for just under half of the total primary productivity on Earth (Field et al 1998). The vast majority occur as free-floating microscopic phytoplankton, over the whole of the surface oceans. They fix about 50 Gt of carbon per year into their bodies (Field et al 1998), with significant additional extracellular dissolved organic carbon (Engel et al 2004). Most of the organic matter produced by these photosynthetic organisms is immediately or ultimately consumed by other micro-organisms (Figure 7).

The other major primary producers in the oceans are the benthic (bottom-dwelling) photosynthetic organisms, such as seaweed, sea grasses and corals. Limited to shallower waters, they have a net primary productivity of about 1 Gt of carbon per year (Field et al 1998). Despite their limited role in global primary productivity, these benthic primary producers are crucial components of coastal ecosystems, providing, for example, habitats and breeding grounds for other species, as well as recycling nutrients and reducing coastal erosion by reducing the power of waves.

Higher up the marine food webs are the multicellular animals. Although these are dependent on the availability of the micro-organisms for food, and are therefore affected indirectly by changes in ocean carbon chemistry, the physiology of these complex organisms may also be affected directly by changes in ocean chemistry. For animals, such as fish, these direct effects of ocean acidification on their physiology, with other pressures such as fishing, are additional to any changes in the availability of their food species caused by changes in ocean chemistry.

Of all the organisms in the surface oceans the impacts are very likely to be most severe for the calcifying species (Table 2), such as molluscs, crustaceans, echinoderms, corals, large calcareous algae, foraminifera and some phytoplankton. This will occur principally because of a reduction in the availability of the chemical constituents needed for calcified shells and plates, although their physiology may also be affected.

In this section we outline what is known about these organisms and, starting at the base of the food chain, consider how they are likely to be affected by acidification. We consider the direct effect of CO_2 and pH changes on the organisms and the indirect effects *deposited and their habitat. Aragonite dissolves more rapidly at low carbonate concentrations than calcite. Photosynthesis in foraminifera and warm-water corals depends on symbiosis with algae (Lowenstam (1981), Berner & Berner (1996) and references in Section 3.5).*

Organisms		Photosynthetic or non-photosynthetic	Form of calcium carbonate	Habitat
Foraminifera		Some photosynthetic	Calcite	Benthic
		Non-photosynthetic	Calcite	Planktonic
Coccolithophores		Photosynthetic	Calcite	Planktonic
Macroalgae*		Photosynthetic	Aragonite or calcite	Benthic
Corals:	warm water	Photosynthetic	Aragonite	Benthic
	cold water	Non-photosynthetic	Aragonite	Benthic
Pteropod molluscs		Non-photosynthetic	Aragonite	Benthic
Non-pteropod molluscs*		Non-photosynthetic	Aragonite + calcite	Benthic or Planktonic
Crustaceans*		Non-photosynthetic	Calcite	Benthic or Planktonic
Echinoderms		Non-photosynthetic	Calcite	Benthic

**Not all members of the group are calcified.*

through changes in other resources on which they depend. In many cases there are few data, so for example we are generally unable to say whether organisms will be able to adapt to the changing environment in the short term, or evolve in the long term.

3.2 Effects of ocean acidification on photosynthetic and non-photosynthetic micro-organisms

This section looks at the some of the possible major effects of increased CO_2 and the associated change in ocean pH on micro-organisms. As we discussed in Section 2.7, calcifying organisms could be particularly affected by changes in ocean pH. We therefore look at calcification in detail in Section 3.5. The discussion below considers the other possible effects, aside from calcification, from changes to ocean chemistry on marine organisms.

On land, plants take up CO_2 primarily by diffusion, although some have mechanisms that actively take up CO_2. As a result, increasing atmospheric CO_2 generally has a positive effect on photosynthesis, productivity and growth (Ainsworth & Long 2005). In contrast, most marine phytoplankton have concentrating mechanisms that actively take up inorganic carbon; either as CO_2 or bicarbonate ions (HCO_3^-) or both. Because they actively concentrate CO_2, changes in the pH and CO_2 content of the water have less effect on their photosynthesis (Giordano et al 2005). Carbon-concentrating mechanisms are thought to be less widespread in benthic photosynthetic organisms (Giordano et al 2005).

Variation in the availability of nutrients caused by increasing CO_2 concentration and pH change may also have an indirect effect on the growth of photosynthetic organisms. In particular, changes in pH, as discussed in Section 2.7.2, will affect the availability of nutrients. This may alter rates of growth and photosynthesis. Changes may also occur in the cell composition, which could affect the nutritional value of the micro-organisms to the animals that feed on them.

3.2.1 Effects on phytoplankton: photosynthetic organisms

Photosynthesis

As we underline throughout the report, a reduction in ocean pH (acidification), is one of a number of changes to the oceans that results from increased atmospheric CO_2 levels. It is impossible to differentiate unequivocally between the effects of increased CO_2 and those of decreased pH in experiments on marine organisms, since there is significant co-variance of these environmental factors (see Annex 1). In almost all of the phytoplankton species examined to date, it has been found that doubling the present atmospheric CO_2 concentration has only a small direct effect, 10% or less, on the rate of photosynthesis (Beardall & Raven 2004; Schippers et al 2004; Giordano et al 2005; Figure 8). This conclusion comes from experiments performed on several species to examine their photosynthetic response to altered atmospheric CO_2 concentrations. In some experiments, algae were grown at present-day concentrations, and then exposed to varying CO_2 levels for measurement of their photosynthetic rate. In other experiments, species have also been grown for several generations at altered CO_2 concentrations before having their photosynthetic rates measured (Burkhardt et al 2001; Rost et al 2003; Beardall & Raven 2004). Generally, both types of experiment gave similar results, namely relatively small increases in photosynthesis. This lack of response is primarily due to the presence of carbon-concentrating mechanisms, which mean that even at today's CO_2 concentration photosynthesis is saturated with inorganic carbon.

An important exception to this has been found in the case of the globally very abundant calcifying phytoplankton *Emiliania huxleyi* (Figure 8). This organism exhibits a greater increase in photosynthetic rate in response to elevated CO_2. It might be expected to benefit from elevated CO_2 as a result of this photosynthetic response. However, it is also observed to decrease calcification at elevated CO_2, which might offset any beneficial effect due to increased photosynthesis in terms of the growth and competitiveness of the organism (Section 3.5). A complete inhibition of photosynthesis (and growth) was found in two species of marine planktonic dinoflagellate 24 hours after exposure to high CO_2 (Dason & Colman 2004), although the CO_2 increase and corresponding pH decrease in those experiments was much greater than those considered likely by this report.

The evidence for the general lack of effect on photosynthesis due to changes in inorganic carbon concentrations resulting from increased atmospheric CO_2 has been derived mainly from laboratory studies. Many laboratory experiments have involved artificially altering the total inorganic carbon concentrations, the pH value, or both. As a result, the ratios of CO_2 and HCO_3^- do not mimic the change that would be found if atmospheric CO_2 was increased (Giordano et al 2005). Some experiments that change the gas phase of CO_2, to mimic the situation in the real world, have been carried out in the laboratory and in mesocosms. The results are similar to those from the other types of manipulation of the inorganic carbon system (Burkhardt et al 2001; Rost et al 2003).

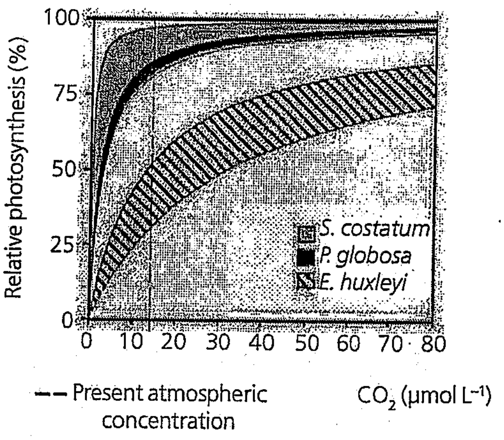
Most of the experiments conducted on marine phytoplankton have been short term and did not provide sufficient time for any genetic modifications that might allow them to adapt to the change in conditions. Further long-term experiments are required to determine if the organisms will evolve to take advantage of the increased CO_2. This is discussed further in Section 3.6.

Growth and composition

Experiments carried out so far show that increased (even double) atmospheric CO_2 concentrations have relatively little direct effect on the growth rate and the elemental composition of marine phytoplankton (Burkhardt et al 1999; Gervais & Riebesell 2001). There is also the possibility of indirect effects through changes in nutrient availability and in the toxic substances, resulting from the decreased pH (Section 2.7.2).

In recent mesocosm studies (Riebesell personal communication) there was an increase in inorganic carbon assimilation, and also in the ratios of carbon to nitrogen and carbon to phosphorus in phytoplankton, at 750 ppm CO_2 compared with the present day (380 ppm) CO_2 levels. Other studies showed little effect of such changes in CO_2 on the productivity of a natural assemblage of phytoplankton species (Hein & Sand-Jensen 1997; Tortell et al 2002).

Figure 8. Photosynthesis of phytoplankton species differ in sensitivity to CO_2 concentrations. Although most species (here Skeletonema costatum and Phaeocystis globosa) reach their maximum photosynthetic rate under present-day ambient CO_2 levels (14.7 μmol per litre), some species, such as the coccolithophore Emiliania huxleyi show increased rates of photosynthesis when CO_2 is increased above present levels. This raises the possibility that coccolithophores may benefit directly from the current increase in atmospheric CO_2. The range in photosynthetic rates for each organism reflects the extent of which the physiology of the organism changes as a function of the concentration of CO_2 at which they are grown. (Reprinted from Rost & Riebesell (2004) with permission of Springer Science and Business Media).



The effect that increasing CO_2 has on growth rate and cell composition needs to be superimposed on the availability of other resources. Some of these resources can be limiting: for example, nitrogen for much of the world's oceans; and for parts of the oceans or at particular times, iron and phosphorus. Climate change may alter this availability, with rising temperatures tending to increase stratification and reduce mixing with nutrient-enriched deeper waters. In areas when there is deep mixing (tens of metres or more) of the surface oceans, light can become a limiting factor for phytoplankton growth. It is known that, measured over short periods, the dependence of photosynthesis on the CO_2 concentration during growth is affected by the availability of these resources (Giordano et al 2005).

Many of the data on growth and composition have come from laboratory experiments. However, these experiments have not always been performed under the nutrient-limiting conditions that may occur in the oceans. Further experiments are needed to show the effects of total nutrient concentrations and ratios of nutrient species, such as nitrogen, phosphate, iron and (for diatoms) silicic acid.

the impacts that increasing CO_2 might have on the growth and composition of marine phytoplankton. In addition, experiments so far have not been long enough to indicate if existing species will be able to evolve to changing conditions. However, any reduction in the total biomass production by phytoplankton, either through reduced photosynthesis or from greater energy demand to obtain nutrients, could have significant implications for marine food webs. In addition, these effects of increasing CO_2 concentrations need to be considered in relation to other environmental changes. Further experiments are needed on the effect of changes in pH on phytoplankton nutrition for nutrients supplied as solutes whose extent of ionisation varies with pH in the relevant range of pH values; such experiments should use both growth-limiting and growth-saturating concentrations of the nutrients.

Extracellular polysaccharides

For phytoplankton, a significant component of the organic carbon produced by photosynthesis is dissolved extracellular organic carbon, of which much is polysaccharide. Production of extracellular dissolved organic carbon is a rather variable fraction of photosynthesis, with 3–40% found for different natural marine planktonic systems. This provides an important food source for non-photosynthetic micro-organisms in the surface oceans. The proportion of the total organic carbon produced by cells that appears as extracellular polysaccharides is increased by higher CO_2 concentrations, but additional photosynthesis (for example in *E. huxleyi*: Figure 8) with increased CO_2 could increase the rate of extracellular organic carbon production (Engel 2002; Engel et al 2004, 2005).

These polysaccharides are also important in the aggregation and then sedimentation of phytoplankton cells and other particles (Engel et al 2004). This means that increased CO_2 could potentially increase particle sedimentation in the 'biological pump' (Section 2.2.2). However, this needs to be balanced against reductions in calcification by coccolithophores caused by increased CO_2 levels (Riebesell et al 2000; Section 2.7.1), reducing the input of mineral ballast and hence decreasing the rate of sinking of the aggregates (Section 5.2).

Further work is needed to understand how increases in CO_2 affect organic carbon sedimentation, and the consequences for feedback effects on surface CO_2 concentrations and on the absorption of CO_2 from the atmosphere, and hence to the global carbon cycle.

3.2.2 Effects on non-photosynthetic micro-organisms

Non-photosynthetic micro-organisms in the oceans include archaea, bacteria, fungi and a range of protists including flagellates and ciliates. They feed on organic

nutrients, producing CO_2 and other gases such as halocarbons (Section 5). These organisms play major roles in the marine carbon cycle, because they are the main means by which primary productivity in the oceans is recycled to CO_2 (del Giorgio & Williams 2005; Figure 7). They are abundant in the open oceans as well as in muddy and sandy benthic habitats (Section 3.3). Although their physiology suggests that they will respond to increased CO_2 in the surface oceans and to decreased pH, there are few data available to demonstrate any responses and therefore impact that this might have on the functioning of the organisms in their natural environment.

Like photosynthetic micro-organisms, non-photosynthetic micro-organisms are affected by changes in the concentration and speciation of nutrients as a result of changes in pH (Section 2.7.2). Seawater pH also affects the mechanisms that transport these solutes into the cells. Apart from depending on photosynthetic micro-organisms for food, the non-photosynthetic micro-organisms that grow in the illuminated surface oceans are in direct competition with them for inorganic nutrients, but not for CO_2. Any changes in this nutrient supply may alter the productivity of either group.

Compared with marine photosynthetic phytoplankton, non-photosynthetic micro-organisms have a greater metabolic diversity. One example of a metabolic process is nitrification (conversion of ammonia (NH_3) and ammonium (NH_4^+) to nitrate), which occurs mainly in the non-illuminated part of the oceans. The organisms responsible for this part of nitrification can only use ammonia as their substrate. In experiments simulating the pH decrease likely to occur in very high CO_2 concentrations, Heusemann et al (2002) found a drastic reduction in the rate of nitrification. If this concentration was reached in surface waters it could lead to accumulation of ammonium instead of nitrate. However, these experiments were done at significantly greater concentrations of CO_2 than is likely to occur as a result of human-produced emissions of CO_2 to the atmosphere.

Micro-organisms and dead organic particles provide a valuable food supply for benthic invertebrate detrital and suspension feeders, again producing CO_2 and inorganic nutrients. The micro-organisms living deeper in muddy and sandy sediments are less exposed to the direct influence of increases in surface ocean CO_2 than are those living nearer the sediment surface or in the plankton (Section 4.2.3).

3.3 Effects of ocean acidification on photosynthesis in benthic organisms

The dominant primary producers growing on the sea bed, in areas where the oceans are shallow enough to allow photosynthesis to occur, are large algae (seaweeds), marine flowering plants (seagrasses) and, in some warmer waters, photosynthetic coral reefs. The seagrasses mainly grow rooted in mud or sand, whereas most seaweed and all corals are attached to solid, rocky substrata.

Compared with the work on phytoplankton, fewer data are available on the effects of increased concentration of CO_2 on photosynthetic rate and especially on growth rate and composition of seaweeds, seagrasses and the alga–invertebrate and alga-protist symbioses, such as corals and benthic foraminifera (Beer et al 2002; Giordano et al 2005). However, compared with marine phytoplankton, there seems to be a larger fraction of the species of benthic macro-organisms studied that show increased rates of photosynthesis as CO_2 is increased above the present atmospheric level (Giordano et al 2005). Experiments conducted on a species of red seaweed, that are believed to rely on CO_2 entry by diffusion, found that CO_2 at twice the present atmospheric level increased the growth rate very significantly (Kübler et al 1999). It is difficult to draw conclusions about whether benthic plants rely more on CO_2 diffusion than phytoplankton as there is insufficient information about the use of carbon-concentrating mechanisms.

It would be unwise to generalise from these very limited data. More work is needed to establish how the production of organic material by these benthic organisms responds to increased CO_2 in the surface oceans. However, this community of primary producers plays an important ecological and economical role; any change in their productivity could have significant implications.

3.4 Effects of ocean acidification on multicellular animals

3.4.1 Changes to physiology of larger animals

The larger marine animals that live in the oceans and do not breathe air, such as fish and the larger invertebrates including some zooplankton, take up oxygen and lose respired CO_2 through their gills. Increased CO_2 and decreased pH could have a major effect on this respiratory gas exchange system. This is because oxygen is much harder to obtain from surface seawater than it is from air, mainly due to the lower oxygen concentration in water. The processes involved in supplying oxygen to the gills means that more CO_2 is removed from these aquatic animals than is removed from air breathing animals of a similar size. This more ready removal of CO_2 from body fluids means that the level and range of CO_2 concentration in the bodies of water-breathing animals are much lower than is the case for air-breathing animals. As a result, large water breathing marine animals are more sensitive to changes in the CO_2 concentration in the surrounding seawater than are large air-breathing animals. This has important implications as increased CO_2 will acidify the body tissues and fluids and affects the ability of blood to carry oxygen.

Known as hypercapnia, acidification of body fluids of marine animals as a result of increasing external CO_2 occurs rapidly, in a matter of hours. In addition to reducing the pH, increased CO_2 concentration also changes the levels of bicarbonate and other ions. Small changes can be buffered within the cell, but larger changes require the active secretion of ions out of the body through specialised cells. In fish, the structure and activity of some of these secretion cells changes after 24 hours of hypercapnia. Some fish can change the density of these cells in a matter of hours or days, giving them greater tolerance to acidification (Ishimatsu et al 2004).

There is strong experimental evidence that acidosis of tissues will decrease cellular energy use and lower respiratory activity (Pörtner et al 2000, 2004). Evidence is also increasing of lower rates of protein synthesis, under these conditions, with impacts on almost all aspects of the functioning of larger animals including growth and reproduction (Langenbuch & Pörtner 2002, 2003). Experiments have shown that rising external atmospheric CO_2 will increase mortality, in some cases quite significantly (Kikkawa et al 2004). However, these experiments correspond to higher seawater CO_2 concentrations than are expected up to 2100, and more research is needed to understand if large mortality events, such as fish kills, will result from even the extreme projections of future atmospheric CO_2 concentrations.

Some animals, particularly deep sea fish and Cephalopods such as squid, are very sensitive to increases in external CO_2 (Ishimatsu et al 2004). Squid are particularly sensitive because of their highly muscular and energy-demanding way of movement (jet propulsion), which is fundamentally different from the lower-energy demands of undulatory swimming seen in fish (Pörtner and Zielinski 1998). This high-energy use requires a good supply of oxygen from the blood. However, this can be severely compromised by increasing CO_2 concentration, as it lowers the pH of the blood thereby reducing its ability to carry oxygen. However, the experiments (Pörtner and Reipschläger 1996) showing large effects involve CO_2 concentrations higher than those considered reasonable given projected future CO_2 concentrations, and further work is needed to explore the effects of smaller increases in seawater CO_2 concentrations.

3.4.2 Changes to reproduction in larger animals

The effects of increasing CO_2 on multicellular animals appear to vary throughout the lifecycle. In freshwater fish, pH is known to affect the physiology and activation of sperm. In steelhead trout (*Oncorhynchus mykiss*), for example, decreasing pH from 8.5 to 7.5 units by increasing the partial pressure of CO_2 resulted in a 40% reduction in respiration rate (Ingermann et al 2003). It is not known whether marine fin-fish are equally sensitive, oysters (*Crassostrea gigas*) has been shown in much larger changes in pH from 8 to 6 units (Dong et al 2002); however, this is beyond any expected changes in the oceans due to increases in atmospheric CO_2 concentration up to the year 2300. Experiments have also demonstrated significant decreases in egg production by copepods, but no effect on survival of adults, over the 8 days tested using CO_2 values well in excess of what is expected in future oceans (Kurihara et al 2004a, 2004b). In another experiment, lower pH decreased hatching of the egg sacs of a gastropod mollusc (*Babylonia areolata*) farmed in the Far East (Luo et al 2004). Other studies using very high concentrations of CO_2, beyond what is expected in the future oceans, have also shown effects on the embryos and larvae of silver sea bream (*Pagrus major*) (Ishimatsu et al 2004) and on the reproductive success of sea urchins (Kurihara et al 2004a). These experiments suggest that the early stages of the life cycle may show the greatest sensitivities to increased CO_2 concentrations, with potentially widespread implications for population size, community structure and biodiversity. However, as with effects on other life-cycle stages, the CO_2 concentrations used in these were greater than those considered likely in the future oceans. There is an urgent requirement for experiments addressing the effects of smaller increases in CO_2 on the reproduction of marine animals.

3.5 Effects of ocean acidification on calcifying organisms

3.5.1 Introduction

The formation of shells or plates of $CaCO_3$, by calcification, is a widespread phenomenon among marine organisms, such as most molluscs, corals, echinoderms, foraminifera and calcareous algae. Although it is not always clear what function this calcification has, it seems integral to their biology; so any decrease in calcification, as a result of increased CO_2, is therefore likely to have significant consequences such as the weakening of coral skeletons and reef structures generally.

Calcification is a tightly controlled process and generally requires biological initiation even in the present day surface seawater which is super-saturated with respect to $CaCO_3$. However, the mechanism of calcification is currently poorly understood. It can be intracellular, in specific calcifying compartments, or on external surfaces, which suggests that large differences exist in the mechanisms and transport routes leading up to the precipitation reaction. The various groups of calcifying organisms also differ in the crystal structure and chemical composition of their carbonate skeletons (Section 2.7.1; Table 2). Whereas corals and a group of molluscs called pteropods precipitate aragonite, coccolithophores (calcifying phytoplankton) and foraminifera (protist plankton) produce the less soluble calcite, generally in internal compartments. Mollusc shells consist of layers of either all aragonite or inter-layered aragonite and calcite. Echinoderms, which include sea urchins, sea stars and brittle stars, form calcite structures that are high in magnesium and have a very high porosity often exceeding 50%. Calcareous benthic algae precipitate either high-magnesium calcite or aragonite and perform the important function of 'gluing' the skeletons of corals together to create reefs. Despite this variation the principal steps of calcification are likely to be similar in each case.

To make these calcareous structures, seawater has to be supersaturated with calcium (Ca^{2+}) and carbonate (CO_3^{2-}) ions to ensure that once formed the $CaCO_3$ does not dissolve. Lower pH reduces the carbonate saturation of the seawater, making calcification harder and also weakening any structures that have been formed. Although calcite is less soluble than aragonite, making it less susceptible to pH changes, the incorporation of magnesium into either form increases their solubility.

3.5.2 Calcified protists and algae

Foraminifera are important in global ocean calcification in both the plankton and in bottom-dwelling environments. They are thought to form high-magnesium calcite during the initial stages of calcification, but without going though a step involving an amorphous precursor of high solubility (Erez 2003). This is in contrast with the echinoderms considered below (Section 3.5.3). The encapsulation of seawater has been proposed as the starting point for calcification for some calcifying organisms such as foraminifera (Erez 2003). During the calcification process the alkalinity of the captured water is lowered (the pH decreases). To compensate for this the organism is thought to actively raise the pH, which immediately increases the carbonate ion (CO_3^{2-}) concentration. If the pH of the ambient water is already decreased, this process will therefore require more energy, which may explain the decrease in calcification with decreasing pH. Allocating more energy to calcification to counteract the effect of decreasing pH could mean that less is available for other vital metabolic processes, which may reduce the growth and fitness of the organism.

In laboratory experiments on the symbiont-bearing foraminiferans, the shell weights of *Orbulina universa* and *Globigerinoides sacculifer* varied with the carbonate ion concentration of the seawater (Bijma et al 1999, 2002). Similar results were obtained for the foraminifera *Amphistegina lobifera* and *A. hemprichii* (Erez 2003). A strong reduction in the calcification rate occurred as pH decreased from 9 to 7. The trend reverses above pH 9, with calcification rate decreasing as pH increases. A positive correlation between foraminiferal shell weight and the carbonate ion concentration (and the carbonate saturation state) is also observed in the palaeoceanographic record as a response to known glacial–interglacial changes in atmospheric CO_2 of the past 50 000 years (Barker & Elderfield 2002). Plotting calcification rate versus the carbonate ion concentration reveals a similar slope, with a two- to threefold increase in calcification rate with CO_3^{2-} increasing from 100 to 400 μM (Erez 2003).

Coccolithophores are planktonic algae whose photosynthesis, in the species investigated, is not saturated at present levels of CO_2 (Section 3.2.1). The coccolithophores are considered to be the most productive calcifying organisms on Earth. They are covered with one to several layers of minute calcite platelets, the coccoliths. The coccoliths are produced inside the coccolithophore cells, and do not involve the internalisation of seawater (Berry et al 2002). Benthic macroalgae deposit either calcite or aragonite externally.

3.5.3 *Calcified larger animals*

Corals, crustaceans, echinoderms and molluscs are important calcified benthic animals, and calcified crustaceans and molluscs are significant members of many pelagic marine communities. As we show in Sections 3.5.4 and 4.2.1, the mechanical function of calcification is obvious in these calcified animals.

Echinoderms are among several groups that may be especially sensitive to ocean acidification. The larvae of sea urchins and also of molluscs have been shown to form skeletal parts consisting of magnesium-bearing calcite that form through an amorphous precursor phase, which is 30 times more soluble than calcite without magnesium (Politi et al 2004). The same type of skeletal material is used by most adult echinoderms. Lower pH in the oceans may inhibit the formation of these highly soluble amorphous calcite precursors, which echinoderms need in the construction of their shells. Further work is needed on the mechanism of calcification in echinoderms, in view of their importance in many coastal ecosystems: in some cases they are keystone predators (sea stars) or very important grazers (urchins). This is also true of coastal molluscs and arthropods, which in addition are also of great economic importance. Crustacea may be a particularly vulnerable group because of their dependence on the availability of calcium and bicarbonate ions for the mineralization of their exoskeleton after moulting. In freshwater species this mineralization the animals' ability to control blood pH is affected by changes in water composition in intensive culture, particularly in recirculation systems (Brown et al 1991). Similar effects may occur in marine species, although further work is needed to establish the significance of effects within the range of seawater CO_2 concentrations considered in this report.

3.5.4 *Functions of calcification and effects of decreased calcification*

Decreased calcification may equally influence the organism's competitive fitness, but this ultimately depends on the functional role of the calcareous structures or the metabolic function of the calcification process. The function of calcareous structures is obvious in some groups of organisms, such as for the structural frameworks of corals or the exoskeletons serving as mechanical protection in pteropods and foraminifera. Reduced calcification in corals can translate into declining coral cover and reduced, possibly disappearing, reef frameworks (Gattuso et al 1999; Kleypas et al 2001). A decrease in carbonate supersaturation may also weaken carbonate skeletal structures, making them more susceptible to erosion (both physical and biological) and dissolution. This effect, which will be most pronounced in aragonitic groups such as the pteropods, would presumably compromise the fitness of these organisms and could shift the ecological and evolutionary competitive advantage to non-calcifying organisms.

The function of calcification is less clear in other groups such as the coralline algae and coccolithophores. A variety of protective, metabolic and adaptive functions have been proposed for calcification in coccolithophores (Brownlee & Taylor 2004), but the evidence remains for the most part inconclusive.

In addition to structural roles for calcification, calcium carbonate deposits can also influence the acid-base balance in anoxia (absence of oxygen) (Booth et al 1984; Lindinger et al 1984). Anoxia occurs, counter-intuitively, when intertidal organisms are exposed to air at low tide and seal themselves off from exposure to the air in limiting water loss at the expense of preventing entry of oxygen.

As calcium carbonate structures make organisms denser, increased sinking rate is therefore an unavoidable consequence of calcification in planktonic organisms that are unable to swim. This includes the most abundant, non-flagellated (flagellates are used in propulsion) stages of coccolithophores, and planktonic foraminifera, because calcite is denser than other components of the organisms. This argument also applies to the aragonite-depositing pteropods after they have died and can no longer swim. It is not clear what competitive advantage this increased sinking caused by calcification might offer and therefore it is difficult to conclude how it might have evolved (Raven and Waite 2004). However, regardless of the evolutionary basis for calcification, a reduction in calcification decreases the amount of ballast available for the sedimentation of organic matter and $CaCO_3$, which has implications for the operation of the biological pump (Sections 2.2.2 and 5.2).

Since the functions of calcification are not fully understood, the long-term implications of reduced calcification on the physiological and ecological fitness of calcifying organisms are unknown.

3.5.5 *Influence of increased CO_2 on calcification*

Because of the dissimilarities in the calcification process, it is surprising to find a rather narrow range of laboratory and field studies reveal that the degree of carbonate supersaturation has a profound effect on the calcification rates of individual species and communities in both planktonic and benthic habitats. Published data on corals, coccolithophores and foraminifera all suggest a reduction in calcification by 5–25% in response to a doubling of atmospheric CO_2 from pre-industrial values (from 280 to 560 ppm CO_2) (Feely et al 2004). This reduced calcification rate also occurs even when the carbonate saturation level was well above one (at values below one, $CaCO_3$ dissolves) (Section 2). This response holds for intracellular as well as extracellular calcification and across both aragonite and calcite forms.

However, it should be noted that research on the sensitivity of calcifying organisms to CO_2-related changes in seawater chemistry have so far been limited mostly to short-term studies with single strains of organism. It is unknown whether the observed responses can be extrapolated to the genetically diverse populations that prevail in the natural environment and to what extent calcifying organisms can acclimatise or adapt to these changes. The rather uniform sensitivity to CO_2 and pH may also be biased by selective testing of species and clones dominant under (and therefore best adapted to) present-day CO_2 levels. In a recent study, calcification in a clone of the coccolithophore, *Coccolithus pelagicus*, proved to be insensitive to increased CO_2 (decreased pH) in the growth medium (Langer personal communication). Another species, *Calcidiscus leptoporus*, showed a decline in calcification rate and an increase in coccolith malformations at CO_2 concentrations above *and* below present-day levels (Langer personal communication). These results suggest that the previously derived simple relationship between pH and calcification may become more complex as new species and clones are tested.

It is currently unknown to what extent calcifying organisms are able to adapt to decreasing carbonate saturation states. Thus the extent to which physiological or genetic diversity may contribute to the resistance to the acidification process is unknown.

3.6 Potential adaptation and evolution resulting from the surface ocean CO_2 increase and acidification

As described in Section 2 the high rate of increase in CO_2 concentration means that organisms are being exposed to changes that are faster than they have encountered in their recent evolutionary past. Few experiments have so far been conducted for long enough to indicate whether organisms will be able to genetically adapt to these changes.

Most of our evidence comes from short-term exposures, within the lifetime of the organism or, for more rapidly generations. Few experiments have gone on long enough for genotype selection to be significant (Burkhardt et al 1999; Gervais & Riebesell 2001; Collins & Bell 2004). The only published work for longer-term experiments was carried out on the freshwater microscopic alga *Chlamydomonas* (Collins & Bell 2004). Grown at almost three times the present atmospheric CO_2 concentration, the cells acclimatised to the change but did not show any genetic mutations that could be described as adaptation. However, several mutants were obtained which grew very poorly when returned to CO_2 at just above the present atmospheric level. Work of the type carried out on *Chlamydomonas* is needed for marine phytoplankton species to determine if they show 'adaptation' to growth at higher CO_2.

Although the work on *Chlamydomonas* represents a very promising start, much more work is needed on a range of marine organisms representing different trophic levels, with different generation times and breeding systems, to provide information on the possibilities of long-term evolutionary adaptations. Ideally, such work would also consider the effects on particularly sensitive stages in the life cycle. Investigations should also include inter-species interactions, such as the effect of any changes in the chemical composition of primary producers (Section 3.2.1) on consumer organisms, such as grazers.

There is a very limited database from which to draw conclusions about the possibility of adaptation of organisms to the present rapid change in ocean surface CO_2. Further investigation of this topic is very important. However, this could be particularly time consuming if organisms with long generation times are studied.

3.7 Possible impact of ocean acidification on the structure of marine communities

With or without genetic change in relation to increased CO_2 at the species level, there is clearly also the possibility of changes in the relative abundance of species as CO_2 increases in the oceans. This is not an easy topic to address on the basis of available data from the oceans, because the effects are nonlinear and complex. But such changes of species composition are likely as CO_2 increases, given the growing evidence of potential effects of increased CO_2 on growth and reproduction differing among organisms (Denmen et al 1996; Boyd & Doney 2003).

Contradictory results have been obtained for the effect of CO_2 on species representation in phytoplankton communities. Experiments on samples of surface seawater on ship-borne microcosms in the tropical Pacific and mesocosms in Norwegian coastal waters showed a shift towards calcifying coccolithophores (such as *Emiliania huxleyi*) at low or present-day CO_2, and towards diatoms at high CO_2 (Tortell et al 2002; Martin-Jézéquel et al 2004). However, a decrease in diatoms and an increase in other phytoplankton organisms were observed at increased CO_2 and temperature in ship-borne microcosm incubations carried out in the Bering Sea (Hutchins personal communication). These contradictory results indicate that the impact of rising CO_2 on phytoplankton species composition may be community- or regime specific and is hence likely to differ seasonally and geographically.

For many ecosystems the impact that such changes in species composition would have on their productivity and the services that they provide is unclear. It is possible that different species may dominate and fill the gap in the food web left by those that are adversely affected by ocean acidification.

3.8 *Conclusions*

Effects of ocean acidification on micro-organisms

The evidence considered in Section 3.2 suggests that the increase of CO_2 in the surface oceans expected by 2100 is unlikely to have any significant direct effect on photosynthesis or growth of most micro-organisms in the oceans. Changes in elemental composition of the cells also appear to be small and variable. More work is needed before these negligible, or small, effects of increased CO_2 can be generalised and applied with confidence to the oceans as an indication of future trends. Moreover, much of the work that has been done relates to the acclimatisation of cells to increased CO_2 and has not been conducted for long enough to determine whether the organisms will be able to evolve, through natural selection, to the changed environment.

Changes in CO_2 concentrations and pH will lead to changes in nutrient concentrations and speciation. Insufficient data is currently available to identify the indirect impacts these changes might have.

A substantial increase in information is required if we are to arrive at widely applicable conclusions on the effect of increased surface ocean CO_2 on the functioning of non-photosynthetic micro-organisms in the oceans.

Effects of ocean acidification on multicellular animals

In the short term (20–40 years), projected increases in atmospheric CO_2 will produce minor impacts on multicellular marine animals. Climate change scenarios that involve three- to fourfold increases in atmospheric CO_2 are more likely to stress their physiology and may reduce their growth. Increased CO_2 in the seawater may also increase mortality, particularly for organisms with high metabolic rates such as squid. Reproduction of multicellular animals is strongly influenced by CO_2 at the very high concentrations tested. However, much more work is needed to establish the effects of the changes in surface ocean CO_2 concentrations expected over the next century. In particular, we need to examine the effects of increased CO_2 on the complete life cycle of multicellular animals to determine the validity of the suggestion that the gametes and juvenile (larval) stages are more sensitive to high CO_2 and low pH than is the adult stage.

The influence of ocean acidification on marine organisms other than those exerted through calcification, could include decreased reproductive potential, slower growth or increased susceptibility to disease. These responses could have cascading effects through food webs, with possible consequences for ecosystem structure and elemental cycling.

Effects of ocean acidification on calcification

From our understanding of ocean chemistry and available evidence, it is clear that increasing the acidity of the oceans will reduce the concentration and therefore the availability of carbonate ions. It is expected that calcifying organisms will find it more difficult to produce and maintain their shells and hard structures. However, the lack of a clear understanding of the mechanisms of calcification and its metabolic or structural function means that it is difficult, at present, to reliably predict the full consequences of CO_2-induced ocean acidification on the physiological and ecological fitness of calcifying organisms. What is clear is that any decrease in calcification, as a result of increased CO_2, is likely to have significant consequences such as the weakening of coral skeletons and reef structures generally (Section 4.2). The widespread use of calcification in the oceans suggests that it is an essential aspect of the biology and ecology of many calcifying organisms. As outlined in Section 2, any changes in calcification will also have important implications for the global carbon cycle.

Organisms will continue to live in the oceans wherever nutrients and light are available, even under conditions arising from ocean acidification. However, from the data available, it is not known if organisms at the various levels in the food web will be able to adapt or if one species will replace another. It is also not possible to predict what impacts this will have on the community structure and ultimately if it will affect the services that the ecosystems provide. Without significant action to reduce CO_2 emissions into the atmosphere, this may mean that there will be no place in the future oceans for many of the species and ecosystems that we know today. This is especially likely for some calcifying organisms.

It is unclear how direct effects of increasing CO_2 interact with those of other environmental changes occurring simultaneously, such as those of climate and nutrient supply, the extent of oxygenation of sediments, surface ocean mixing and stratification. Independent of these that that various groups of marine organisms will experience significant alterations in their geographical ranges (Boyd & Doney 2003).

acidification on species and communities of organisms, in the following section we look at the wider picture and consider which marine ecosystems may be most vulnerable to the projected changes in ocean chemistry.

ocean chemistry

4.1 Introduction

Section 2 shows that ocean chemistry is being, and will increasingly be, altered by rising atmospheric CO_2 levels. As the CO_2 concentration in the surface oceans increases, this raises their acidity (reduces their pH), and importantly for organisms that calcify, lowers the carbonate saturation status of the surface oceans. The extent and rate of change to ocean chemistry that is predicted to occur by 2100 has no precedent for at least hundreds of thousands of years and possibly much longer. Section 3 demonstrates that, while the effects of these changes in ocean chemistry on marine organisms are not well understood, significant effects are expected, especially for some calcifying organisms. Based on the conclusions in Section 3, here we examine the likely impacts of these changes in ocean chemistry on the ecosystems that are most likely to be at risk.

4.2 Impact of ocean acidification on benthic systems

4.2.1 Coral reefs

Photosynthetic coral reefs require calcified structures to survive. Considerations of changes in ocean chemistry in the tropics and subtropics suggest that these systems are liable to significantly decline as a result of surface ocean acidification.

Coral reefs cover an estimated 1.28 million square kilometres of the world's tropical and subtropical oceans (Spalding et al 2001). They occur primarily in well-lit and shallow waters, characterised by low water-column turbidity (Spalding et al 2001). In contrast to cold-water corals, warm-water reef-building corals are symbiotic with single-celled dinoflagellate algae (Table 2). High rates of calcification allow the building of a scaffolding or framework, which becomes home to hundreds of thousands of other species that dwell in coral reefs (Reaka-Kudla 1996). Without the presence and activities of reef-building corals, coral reefs would be vastly different from the diverse and productive ecosystems that typify shallow tropical and subtropical oceans today. Despite representing less than 1.2% of the world's continental shelf area, coral reefs are critical resources to people and industries in many countries (Spalding et al 2001). The socio-economic value of coral reefs is considered in Section 6.

Warm-water coral reefs generally exist within a narrow environmental envelope defined largely by sea temperature, light and the aragonite saturation state (Kleypas et al 1999a). The growth of coral reefs is minimal outside this envelope. Climate change, through its effect on ocean temperature and aragonite saturation state (Section 2.7.1), has already had an impact on the world's coral reefs (Hoegh-Guldberg 1999). Almost 30% of warm-water corals have disappeared since the beginning of the 1980s, a change largely due to increasingly frequent and intense periods of warm sea temperatures. High ocean temperatures cause corals to bleach (ie lose their pigmented dinoflagellate symbionts and, if conditions are warm enough for long enough, die). The increase in atmospheric CO_2 is compounding this effect, by lowering the aragonite saturation state of seawater, making carbonate ions less available for calcification (Section 2.7). Gattuso et al (1999) and Kleypas et al (1999b) have proposed that the calcification rates of corals would decrease by 10–30% under a doubling of atmospheric CO_2 concentrations. Ample evidence now indicates that coral calcification is directly proportional to the aragonite saturation (Gattuso et al 1999; Marubini & Atkinson 1999; Langdon et al 2000, 2003; Leclercq et al 2000, 2002; Marubini et al 2001, 2002). These studies, done in laboratory or mesocosm settings, reveal that doubling atmospheric CO_2 causes a 3–54% decrease in carbonate production.

Some studies have suggested that the decrease due to declining concentrations of carbonate ions will be more than offset by increases in calcification due to the increase in ocean temperature (Lough & Barnes 2000; McNeil et al 2004). These assessments are based on the assumption that calcification increases in direct proportion to temperature, despite the fact that all studies so far have shown that coral calcification reaches a maximum at or just below current-day temperatures. For this and other reasons, these theoretical counter-perspectives have been regarded as 'seriously flawed' (Kleypas et al 2005). Other suggestions that coral reefs may expand significantly to higher latitudes as seas warm have been countered by the observation that carbonate ion concentrations decrease towards the poles and will reach even lower values at high latitudes than is the case now as atmospheric CO_2 increases (Kleypas et al 2001). This, and the fact that light for photosynthesis also decreases at higher latitudes, suggests that the latitudinal limit for coral reefs will remain within a few hundred kilometres of where it is today.

The synergistic interaction of elevated sea temperature and atmospheric CO_2 is likely to produce major changes to coral reefs over the next few decades and centuries. Under most IPCC emission scenarios (IPCC 2000), corals are unlikely to remain abundant on reefs and could be rare on tropical and subtropical reefs by the middle of this century if CO_2 doubles or triples above present levels. Over longer timescales, reef frameworks that are critical for the protection of coastlines across tropical and subtropical regions may start to disappear as the rate of erosion starts to exceed calcification rates (Burke 2004).

reducing the energy of wave impacts during the Southeast Asian tsunami (in December 2004). In this case coastlines that did not have well-developed coral reefs suffered greater damage to infrastructure and saw greater loss of life as waves battered the coastal towns and cities (Brown 2004).

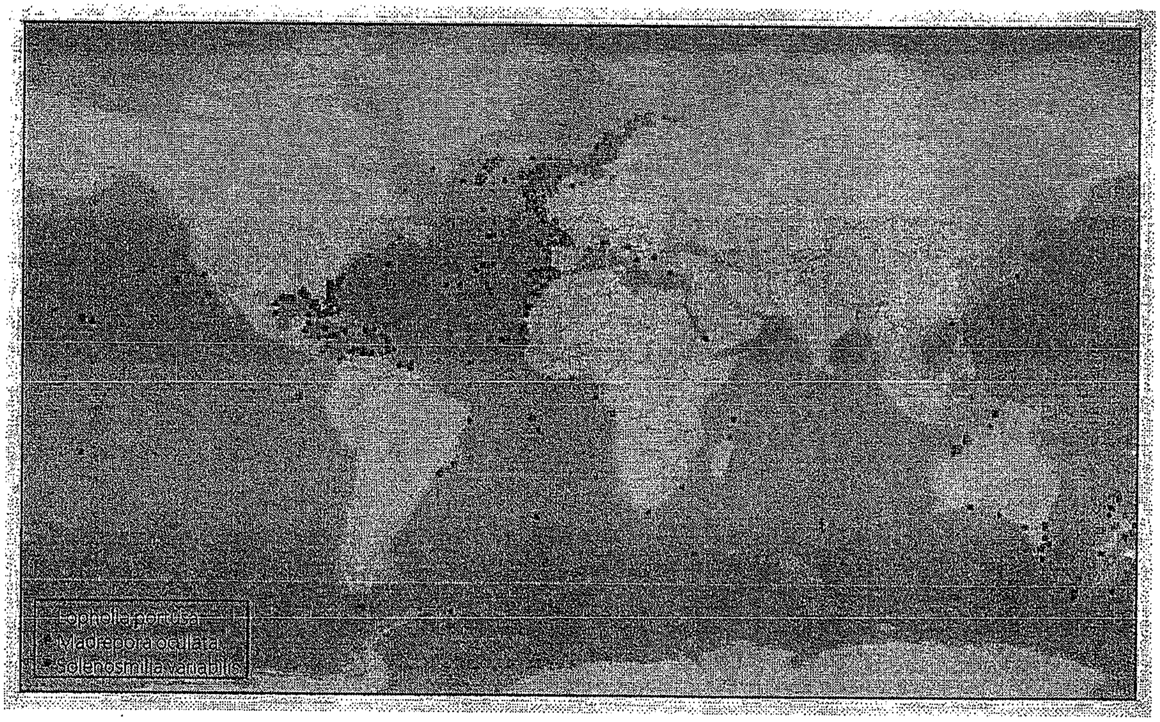
The changes projected for coral reefs are likely to have major ramifications for their biodiversity and function and those of associated ecosystems (sea grass, mangrove). The implications of these changes for people and industries that depend on coral reefs are likely to be significant (Section 6).

4.2.2 Cold-water coral reefs

Non-symbiotic cold-water coral reefs have only been studied intensively for about a decade, when scientists gained access to increasingly sophisticated instrumentation to explore deep-water environments. The use of advanced technology has challenged conventional wisdom that coral reefs are confined to shallow and warm tropical and subtropical regions. Our knowledge of the biology and ecology of cold-water corals, their geographical distribution and spatial coverage, and their role in the marine ecosystem is still rudimentary. Decreasing surface ocean pH may have a significant impact on these systems before they have been fully explored.

the world's oceans and seas: in fjords, along the edge of the continental shelf, and around offshore submarine banks and seamounts (Freiwald et al 2004). Although frequently referred to as 'deep water' corals, they occur over a wide depth range, from a few tens of metres to over 1 000 m. Their distribution is probably mainly determined by temperature, as is reflected by some occurrences in shallow water at high latitudes and exclusively deep-water occurrences in tropical and subtropical waters. The full extent of the area covered by cold-water coral ecosystems is unknown, but recent studies indicate that it could equal, or even exceed, that of warm-water reefs (Freiwald et al 2004). Numerous new species were recently discovered in cold-water coral ecosystems; others found in association with them were previously thought to be extinct (Freiwald personal communication). Living primarily in dark, deep waters, cold-water coral ecosystems have no light-dependent symbiotic algae but depend on organic matter supplied from above. They are long lived, slow growing and fragile. Radioactive dating techniques have shown cold-water coral banks and reefs to be up to 8 000 years old. Geological records show that they have existed for millions of years. Cold-water reefs are derived from several systematic groups, with colonial stony corals (order Scleractinia), true soft corals (subclass Octocoralia), black corals (order Antipatharia) and calcifying lace corals (class Hydrozoa) being the most important taxonomic

Figure 9. Global distribution of cold-water coral reefs: points on the map indicate observed reefs, but not the actual area covered. The three most common cold-water corals are identified: Lophelia pertusa, Madrepora oculata and Solenosmilia variabilis. The high density of reefs shown in the North Atlantic most probably reflects the intensity of research in this region. Further discoveries are expected worldwide, particularly in the deeper waters of subtropical regions. (Reprinted from Freiwald et al (2004) with permission from UNEP-WCMC.)



cosmopolitan stony coral *Lophelia pertusa*, a habitat-forming, reef-building species which occurs in dense girdles stretching from the southwestern Barents Sea along the eastern Atlantic continental margin down to West Africa. Evidence is emerging of a similar belt along the western margin of the Atlantic off Nova Scotia to the Florida Straits and into the Gulf of Mexico. Other groups with global distribution include the genera *Madrepora* and *Solenosmilia* (Figure 9). Cold-water reefs and structures harbour a distinct and rich ecosystem, providing niches and nursery grounds for a variety of species, including commercial fish species.

So far, there are no studies on the sensitivity of cold-water corals to CO_2-related changes in seawater chemistry. However, because of the comparatively uniform response of all calcifying organisms tested so far, it is reasonable to expect that calcification of cold-water corals will also be reduced as carbonate supersaturation declines. Because the carbonate saturation state generally decreases with latitude and water depth, the conditions in waters typically inhabited by cold-water corals are less favourable for calcification to start with. This may cause cold-water corals to be affected earlier and more strongly by CO_2-related ocean acidification than their warm-water counterparts. Model calculations, based on a situation where CO_2 emissions continue on current trends, indicate that the aragonite saturation horizon (the depth below which aragonite dissolves) will rise closer to the oceans' surface) by several hundred metres for most of the ocean, and may reach the surface in the Southern Ocean by 2100 (Caldeira & Wickett in press). Thus, not only is the ocean-wide decrease in the aragonite saturation level likely to decrease cold-water coral calcification, large areas of the oceans may also become completely uninhabitable for cold-water corals as the impacts of increased CO_2 are greater at higher latitudes.

If CO_2 emissions continue on current trends, ocean acidification will threaten the existence of cold-water corals before we have even started to understand and appreciate their biological richness and importance for the marine ecosystem.

4.2.3 Shallow sediments and benthic organisms

Sediment-dominated habitats, which occupy a large fraction of the area of the oceans, play a crucial role in several key ecosystem functions and processes in shelf sea environments. For example, in shallow (less than 50 m) coastal areas productivity in the overlying water column relies on the sediment system, with up to 80% of the nitrogen required by phytoplankton coming from the bacterial regeneration of organic matter within the seabed (Dale & Prego 2002). Phytoplankton are the main marine primary producers upon which the whole marine food chain depends, so the supply of nutrients for their growth from the sediment is essential for sea shelf productivity. This benthic–pelagic (bottom dwelling –

receiving the 'fall-out' of organic matter from the overlying primary production, by the biological pump (Section 2.2.3). This material acts as the primary food resource for benthic organisms, which in turn support a benthic food web with demersal fish (such as cod and plaice) being at the top. Hence both bottom dwelling and pelagic fisheries in shelf seas are dependent on a healthy sediment ecosystem and on benthic–pelagic coupling. Changes to the biological pump, and therefore the supply of food to the sediment-dwelling organisms, will affect the benthic food web and the benthic–pelagic coupling.

Ocean acidification has many potential implications for benthic organisms and their ecosystems. This section focuses on benthic systems, particularly those concerning animals living in soft mud or on the sandy floor. This excludes temperate and tropical reefs (considered benthic) which are considered above (Section 4.2); and muddy or sandy bottoms occupied by seagrass beds, which have been mentioned in Section 3.3.

Sediments in unmixed settings are characterised by strong geochemical gradients. For example, the pH at depths of 30 cm or so can be as much as one unit lower than the pH of the sediment surface and overlying water (Fenchel & Riedl 1970). In the face of such geochemical variability it is difficult to conceive how benthic sediment systems could be affected by the relatively small pH changes expected from surface ocean acidification. A number of processes in the surface layers of sediments (typified by pH values that are closer to overlying seawater) may be affected by changes expected under ocean acidification. By considering some of the potential changes to the distribution and activities of sediment-dwelling organisms, it is possible to identify areas where these small changes could have potentially large consequences for sediment communities and biogeochemical processes.

The communities of benthic sediments are strongly stratified, with different species characteristically occupying different depths (Barnes & Hughes 1988). The surface layer is the most densely inhabited and is home to most of the animals, whereas only those species capable of oxygenating their immediate environment are able to dwell below the depth where the rate at which oxygen diffusion from overlying water is inadequate to supply the respiratory requirements of organisms (Furukawa 2001). Microbial communities and the functions they perform (for example nitrification and denitrification) also differ considerably in their ability to tolerate oxygen and hence in where they are situated between the surface sediments and the deeper layers devoid of oxygen. The presence of these depth-constrained niches means that although benthic systems as a whole are already subject to a relatively large range in pH, many of the organisms and processes that exist within them are not. Although most larger animal species are restricted to the upper oxic (oxygen-containing) layers, others are able to inhabit the permanent burrows through which they are able to draw down oxygenated water from above. The burrows created by these larger animals experience significant oscillation in pH (as much as two pH units) and dissolved oxygen concentration (between saturation and near anoxia (absence of oxygen)), generated by the periodic ventilation of burrows (Furukawa 2001). Such oscillation is absent at the water–sediment interface. Consequently, animals that inhabit permanent burrows may have a greater tolerance to changes in pH than those that do not build burrows. This potential difference in pH tolerance between benthic species could lead to the selection of more tolerant species and thereby substantial changes in the structure and function of sediment communities in the face of changing levels of pH. Recent work has already identified significant variability in pH sensitivity for several different benthic groups (Shirayama et al 2004). Even among organisms that depend on $CaCO_3$ structures, variability in tolerance has been observed with echinoderms showing less tolerance to pH change than molluscs (Shirayama et al 2004). Such variability in sensitivity could have considerable implications for the diversity and functioning of sediment communities in shallow seas with declining pH.

It has long been recognised that organisms living within the sediment have the ability to alter the physical and chemical characteristics of their immediate environment, contributing significantly to the rate of nutrient fluxes at the sediment–water interface (Banta et al 1995; Nedwell & Walker 1995; Widdicombe & Austen 1998) and the maintenance of biodiversity (Widdicombe & Austen 1998; Widdicombe et al 2000). In soft sediment habitats the single most important mechanism by which nutrients are exchanged with and released from the sediments is bioturbation: the disturbance and mixing of the sediments by animals as they go through them (Rhoads & Young 1970). Any factor that alters the rate of bioturbation will have considerable implications for the functioning of marine ecosystems and, as some bioturbating species rely on calcareous structures, an increase in the acidity of coastal seas would be such a factor. Two of the most important groups of bioturbating organisms are the burrow-forming thalassinidean crustaceans (such as some shrimps) and the highly mobile subsurface echinoderms. Although both groups actively bioturbate the sediment, the mechanisms by which they do this are very different, which has important implications for their impact on the sediment environment. Burrowing shrimps create a permanent system of tunnels which enables oxygen and other water-borne substances to penetrate deep into the sediment. This has been shown to significantly increase the uptake of nitrate and the release of ammonium, as well as stimulating the process of denitrification by microorganisms (Howe et al 2004). Conversely, burrowing urchins 'bulldoze' through the surface sediment, creating a deep, uniform oxic layer which decreases the flux of nitrate into the sediment permanent burrows (for example thalassinidean shrimps) are already exposed to low and variable levels of pH whereas those species that inhabit the upper few centimetres of the sediment and do not create permanent burrows are not (for example burrowing urchins). In addition, the body structure of echinoderms would seem to make them particularly susceptible to changes in pH as they rely on a calcareous skeleton and have more ready exchange of CO_2 between ambient seawater and the internal body cavities than is the case for other marine animals of a similar size. This potential vulnerability of echinoderms to changes in pH is supported by the small amount of evidence currently available, which indicates that echinoderms are significantly impacted by a pH decrease of as little as 0.3 units (Shirayama et al 2004).

Most benthic animals have a pelagic larval stage to enhance their distribution. Bivalve larvae that are settling from the pelagic to the benthic phase have an extremely high mortality (greater than 98%) in the first days and weeks. This has been linked to undersaturation of carbonates which makes calcification difficult and weakens the shells (Green et al 2004).

Such major differences in the potential response of organisms from different taxa and functional groups to reduced pH could have a considerable impact on the functioning of marine sediments and the 'goods and services' they provide. Consequently, whilst changes in seawater pH may have a direct effect on sediment and seawater chemistry through changes in nutrient speciation, this effect may be exacerbated by changes in the type and intensity of megafaunal bioturbation.

4.3 Impact of ocean acidification on pelagic systems

4.3.1 Coastal and open ocean pelagic ecosystems

Calcified organisms are very significant components of pelagic ecosystems and any changes in the functioning of these calcified components in response to surface ocean acidification would have large implications on the functioning of the ecosystem. Pelagic ecosystems supply the organic carbon used by organisms deeper in the oceans and are important in the interactions of the surface oceans with the atmosphere, such as in the exchange of CO_2.

A diverse and often abundant community of coccolithophores, foraminifera and pteropods inhabits the sunlit (euphotic) zone of all open and coastal ocean areas, with the exception of the Southern Ocean (Section 4.3.2) (south of the polar front) and the Arctic Ocean. Massive blooms of coccolithophores, which can cover hundreds of thousands of square kilometres of surface oceans and can each produce up to one million tonnes of calcite (Holligan et al 1993), are seen from satellites in

2002). However, even outside these blooms, which are predominantly formed by only one species, *Emiliania huxleyi*, coccolithophores are a common and often dominant component of the phytoplankton community (for example in subtropical circulation currents). Although the spatial and temporal distributions of coccolithophores are consistent with a requirement for high-calcite saturation states (Tyrrell and Merico 2004), which is also reflected by their absence in low calcite saturation areas as such as the polar oceans, it is not clear what role this factor plays for the occurrence of this group. Laboratory and field experiments show that calcification of coccolithophores decreases with decreasing saturation state (Riebesell et al 2000; Zondervan et al 2001).

Ocean acidification is likely to also affect calcification of foraminifera, a group of calcite-producing protists. As with other calcifying organisms, changes to the distribution and abundance of these protists could have significant effects on the global carbon cycle.

As saturation states decline globally, it might be expected that calcifying organisms in near-polar areas, where saturation state is the lowest, will be affected first. Owing to the higher solubility of aragonite, pteropods, that produce $CaCO_3$ in its aragonite form, will be more strongly affected than the coccolithophores and foraminifera which produce the calcite form. If CO_2 emissions continue on current trends the aragonite saturation horizon will rise to the surface of the oceans before the end of this century, making aragonite skeletons unstable throughout the water column over the entire Southern Ocean (Section 4.2.1). The highest-latitude coccolithophore blooms are currently in the Barents Sea at more than 70° N. Satellite images suggests that these blooms are probably more, rather than less, numerous today than during the 1980s and early 1990s (Smyth et al 2004). Changes other than ocean acidification, such as global warming and related enhanced stratification at these high latitudes, may have favoured the northward extension of coccolithophore blooms in recent years.

The shift from coccolithophore to a diatom-dominated phytoplankton community, or *vice versa*, can have strong impacts on the entire ecosystem of the region where it occurs. In the eastern Bering Sea such a regime shift occurred in the late 1990s. Although previously dominated by diatoms, extensive blooms of *Emiliania huxleyi* have occurred throughout the eastern Bering Sea between 1996 and 2000 (Merico et al 2003). This change in the dominant primary producer was correlated with a restructuring of the region's ecosystem at all trophic levels. One of the results of this was a strong decline in salmon catches during these years.

The finding that coccolithophore blooms are now occurring at high latitudes shows that there are significant factors determining the abundance of coccolithophores other than the calcite saturation state.

organisms, including coccolithophores, will decline as CO_2 in the surface oceans increases, with important implications for trophic interactions and ecosystem function (Section 5). It is important to note that we have much less understanding of the factors determining the occurrence of coccolithophore blooms than of the determinants of diatom blooms (Flynn 2001).

4.3.2 Southern Ocean food webs

Southern Ocean food webs are of particular concern (Section 2.7.1). Calcifying organisms in the Southern Ocean will be among the first to be affected from ocean acidification. Aragonite-producing pteropods are the dominant calcifiers in the Southern Ocean. These pelagic molluscs account for a significant proportion of the biological pump of the Antarctic polar front, and in the Ross Sea (Section 2.2.2, Gardener et al 2000; Seibel & Dierssen 2003). Pteropods have a global distribution, but reach their highest abundances (up to 1 000 individuals per cubic metre) in polar and subpolar waters. These pelagic molluscs are an important food source for marine predators in the Antarctic food web and sometimes replace krill as the dominant zooplankton group in parts of the Southern Ocean. The response of pteropods to increased CO_2 has not yet been tested. However, it is likely to be consistent with the other biogenic carbonate producers (Seibel & Fabry 2003). If pteropods are restricted to aragonite-saturated waters, then their habitat will become increasingly limited latitudinally and vertically as the aragonite saturation horizon moves closer to the oceans' surface.

In the event that pteropods were eliminated from the Southern Ocean, there would be a reduction in the biological pump to the deeper oceans of particulate inorganic and organic carbon in the region. Although pteropods contribute to the diet of carnivorous zooplankton, North Pacific salmon, mackerel, herring, cod and baleen whales (LeBrasseur 1966; Takeuchi 1972), most of these would probably be able to switch to other prey types. However, this could result in greater predation pressure on juvenile fishes. Gymnosomes, the shell-less planktonic molluscs that are believed to prey exclusively on pteropods, would probably shift their geographical distribution with that of their pteropod prey (Lalli and Gilmer 1989). Decreasing carbonate saturation state will impact the depth ranges of pteropods in several other regions of the world's oceans, such as the subarctic Pacific, where saturation levels are already low, as well as upwelling areas associated with the Benguela Current, the western Arabian Sea and the Peru Current, where pteropod abundances can be high (Fabry 1990; Hitchcock et al 2002).

Over the next few centuries, as the aragonite saturation horizon moves progressively closer to the surface of the oceans in these regions, and the calcite saturation state of the euphotic zone decreases, the trophic dynamics and

and organic matter will be affected (Feely et al 2004).

4.4 *Conclusions*

According to the evidence available, changes in ocean chemistry will present severe challenges to some of the components of these vast and important ecosystems ecosystems such as coral reefs, to the carbon cycle of the Southern Ocean and to deep-water reef ecosystems will have large-scale ramifications for this and other interconnected ecosystems. That said, we recognise that there are large gaps in our knowledge of how these processes might be affected and the outcome of the changes being exerted on them.

5.1 Introduction

Modelling of aspects of the effect of future climate change on the oceans has incorporated physical and biological processes. Such studies have considered the ability of the oceans to absorb CO_2 (see, for example, Sarmiento et al 1998; Sarmiento & LeQuere 1996) and on the emission of gases, such as dimethyl sulphide (DMS), from the ocean (Bopp et al 2003). However, these studies have generally not addressed the role of pH change.

In this section, we address the possible direct effects of enhanced ocean acidification by CO_2 on the Earth systems. In particular we look at the exchange of gases between the oceans and atmosphere, which is important for the chemistry of the atmosphere and which might affect global climate change. The processes behind each of these feedback effects are very complex, understanding the overall impact on the Earth systems is a significant challenge.

5.2 Feedback effects of reduced calcification

One can expect that the effect of lowered pH on the amount of CO_2 absorbed by the oceans will be very dependent on any changes that may occur in the composition of species within surface ocean communities. For example, if the amount of calcification is reduced by the lower pH (as discussed in Sections 3 and 4), there will be a net increase in CO_2 uptake as a result of a reduced return flux of the gas released from the calcification reaction (as discussed in Section 2). Model calculations indicate that if CO_2 concentrations continue to increase at current levels, the projected decrease in calcification would lead to a reduction in atmospheric CO_2 of 4–10 ppm by 2100 (Zondervan et al 2000; Heinze 2004). Making global ocean calcification proportional to the declining calcite saturation state causes a reduction of 19 ppm in atmospheric CO_2 by 2100 (Klepper & de Haan 1995).

A reduction and possibly regional cessation of calcification by organisms in the oceans would strongly affect ecosystem regulation and the flow of organic material to the seafloor. As discussed in Section 2, the biological pump removes carbon from the surface waters. It has been suggested that $CaCO_3$ acts as a mineral ballast for the export of organic carbon, such as plankton cells and other particulate matter, in the biological pump (Section 3.2.1) (Klaas & Archer 2002). Any reduction in $CaCO_3$ production will reduce the amount of ballast available to the biological pump and may therefore diminish the flow of carbon to the deep oceans. However, because any link between the flow of this mineral 'ballast' and the flow of organic matter is unknown, the significance of this effect remains uncertain (Passow 2004).

Another potential effect of ocean acidification may be the disappearance of coccolithophore blooms (Section 4.3.1). These massive blooms add to the albedo affect of the Earth. This means that they quantifiably increase the amount of sunlight that is reflected back into space, which cannot then contribute to global warming. It has been projected that the loss of these blooms could reduce the global albedo by up to 0.13%, and could therefore enhance global warming (Tyrrell et al 1999).

5.3 Other feedbacks within the Earth systems

As discussed in Section 3, it is unclear what impact rising atmospheric CO_2 will have on the physiology of phytoplankton (such as diatoms and flagellates). As a result it is uncertain whether it will lead to greater productivity and therefore draw down more CO_2 or reduce productivity thus absorbing less.

Apart from the CO_2, the climate is affected by a number of other gases that are produced by marine organisms, including the greenhouse gases nitrous oxide (N_2O) and methane (CH_4). In addition, some groups of plankton produce DMS, a gas that when oxidised in the atmosphere produces cloud-forming particles which can lead to climatic cooling. Changes in DMS production under elevated CO_2 conditions, as with the preceding discussion on calcification, will be very dependent on which plankton species are most affected by the changed conditions. For example, it is well established that there is wide variation in the ability of different groups of phytoplankton to produce DMS from its biochemical precursor, dimethylsulphoniopropionate (DMSP). For example in the phytoplankton, diatoms form little DMSP whereas the alga *Phaeocystis* and coccolithophores are prolific producers (Liss et al 1994). Changes in the abundance of these groups would affect the size of the feedback.

Notwithstanding this uncertainty, a recent modelling study (Gunson, personal communication) suggests a considerable climatic sensitivity to changes in DMS emissions from the oceans. These models indicate that a relatively small (two-fold) increase in DMS emission, if occurring globally, would produce an atmospheric temperature decrease in the order of 1-2°C. Such a cooling would clearly be significant and changes in DMS emissions of this size are certainly possible. However, it should be stressed that there are considerable uncertainties in the modelling, including the mechanisms of particle and cloud formation on oxidation of DMS in the atmosphere, as well as in the representation in models of the variations in DMS production by different plankton species.

In this context it is important to note that organisms forming $CaCO_3$ plates, such as the coccolithophores, are major producers of DMS. This means that a decline in related cloud formation (Malin & Steinke 2004) and so have a feedback effect on climate. In some recent laboratory and mesocosm studies it was found that under elevated CO_2 conditions the amounts of DMS and DMSP produced by the phytoplankton were halved (Avgoustidi personal communication). However, it needs to be stressed that such studies are very short-term (days to weeks in duration) and that the organisms are subject to rapid change in CO_2 level compared with what will happen in the real-world situation of relatively slow pH change.

Other gases formed by marine organisms can affect air quality; these include organo-halogens, non-methane hydrocarbons and oxygenated organics. Once released from the oceans into the troposphere (lower atmosphere), these gases can affect the formation of particles and destroy oxidants in the atmosphere. These oxidants, such as ozone, are important for improving air quality by breaking down organic pollutants.

of atmospheric particles and precipitation; these include ammonia, sulphur dioxide, and other products of DMS oxidation.

5.4 Conclusions

In the case of the gases N_2O, CH_4 and DMS, which can affect atmospheric chemistry, there is not enough information about how their emission to the atmosphere might change as the ocean pH decreases. This uncertainty is increased by the current lack of understanding of the processes controlling their production in marine surface waters.

There are potentially important interactions between changes in the state of the oceans (including their pH) and changes in the global climate and atmospheric chemistry. Our knowledge of these impacts and effects is currently poor and requires urgent consideration as part of the broader drive to understand Earth Systems processes.

6 Socio-economic effects of ocean acidification

6.1 Introduction

It is clear that the full range and magnitude of the biological and biogeochemical effects of acidification of the surface oceans are still so uncertain that a reliable and quantitative estimate of the likely socio-economic effects is not yet possible. However, some general indications of the possible size of such effects can be obtained for at least some of the aspects discussed above, and a preliminary attempt to set such effects in context, by estimating at least the economic value of the resources at risk, even if the extent of damage is uncertain, is given below.

6.2 Effects on coral reefs

The likely effects of ocean acidification on coral reefs (Section 4.2.1) are probably the best understood and documented of those considered in this report. These alone are sufficient to give rise to serious concern. Coral reefs support many millions of people globally through subsistence food gathering. Many more people are supported through industries, such as tourism and fisheries that bring in billions of dollars annually (Hoegh-Guldberg & Hoegh-Guldberg 2004). The projected impacts and the implications for the ecosystems associated with the coral reefs (sea grass, mangrove) are likely to have adverse effects on tourism and fisheries, both of which are extremely important for the economic welfare of local populations, particularly in areas where alternative economic opportunities are scarce.

Research into the socio-economic effects of coral reef degradation has focused on damage to corals as a result of global warming. Studies in this area have not yet included the effects of ocean acidification on corals, such as declining calcification rates. However, they provide indicative values on socio-economic impacts of the loss of coral reefs from adverse environmental changes. As ocean acidification has not been included, these studies have to be considered conservative in terms of potential global impacts.

Potential socio-economic impacts of reef health have been explored for the world's largest coral reef ecosystem, the Great Barrier Reef. Hoegh-Guldberg & Hoegh-Guldberg (2004) assessed how climate-driven changes on the mortality of coral reefs would affect the industries of local coastal Queensland. The study developed a new measure of the importance of 'reef-interested' tourism for the five regions of coastal Queensland – a measure that considerably increases previous estimates. In terms of contribution to the regional economies (gross regional product, GRP), the estimated reef-interested component accounts for 68% of the total – AU$1.4 billion (about £58 000 million, using the exchange rate in May 2005). The reef-interested proportion of the interested component is highest in Far North Queensland (AU$800 million of a total tourism GRP of AU$900 million in 1999). The authors then calculate the diminishing effect of the tourist appeal of the Great Barrier Reef as the bleaching and mortality of corals (and the associated organisms) changes with increases in temperature. This effect was calculated using the possible future greenhouse gas emission scenarios developed by the IPCC (2000). Even under a modest emission scenario, leading to an atmospheric concentration of CO_2 of about 600 ppm by 2100, climate change is predicted to cost local economies substantially—a minimum of AU$2.5 billion over 19 years to 2020. Under scenarios in which global greenhouse emissions continue to grow rapidly (IPCC 2000), leading to an atmospheric concentration CO_2 of over 800 ppm by 2100, losses for the coastal economies of Queensland rise to over AU$14 billion.

The World Resources Institute (Burke et al 2004) has estimated that in 2000, Caribbean coral reefs alone 'provided annual net benefits in terms of fisheries, dive tourism, and shoreline protection services with an estimated value between US$3.1 billion and US$4.6 billion' (about £2 000 million and £3 000 million, using the exchange rate in May 2005); and that the loss of income by 2015 from these degraded reefs may be several hundred million dollars per annum. As pointed out by several authors (see, for example, Hoegh-Guldberg & Hoegh-Guldberg 2004), these baseline estimates are minimal estimates of the economic value of coral reefs because they do not value indirect contributions that coral reefs make such as the stabilisation of coastlines and their role in creating the circumstances for other ecosystems such as mangroves and sea grasses to flourish. These, when considered with the future accumulated benefits, make the value of coral reefs significantly higher than those associated with the direct benefits to industry.

Coastal reefs in Hawaii have been estimated to generate almost US$364 million each year in added value (Cesar et al 2002). Here 'added value' is the net business revenues (ie income minus costs), directly and indirectly from residents and tourists going snorkelling and diving on Hawaii's reefs. About 84% of this added value (US$304 million) is generated from snorkelling and diving on reefs and emerges from US$700–$800 million in gross sales per year. Added value from property generates another US$40 million each year. This number reflects the higher prices for homes and higher occupancy and room rates for commercial properties adjacent to healthy coral reefs. In addition, there is a 'non-use value' (US$7 million), which estimates the amount of money residents, visitors and non-visitors are willing to pay to ensure active management of a healthy reef. Finally, the annual added value for near-shore fisheries within the main Hawaiian islands' coastal reefs is about US$2.5 million per annum.

their costs.

It is clear that globally the economic value of coral reefs is many billions of dollars per annum, and that the likelihood of significant degradation of reefs would be a sufficient cause for action to protect them.

6.3 *Effects on marine fisheries*

Revenue from global capture fisheries in 2002 was around US$78 billion, with marine capture fisheries accounting for about 90% of this (FAO 2004). Although the major adverse effect on marine fisheries at present is that of the mortality generated by large-scale fishing (Pauly et al 1998), any further adverse effect on their productivity would nevertheless lead to very substantial social and economic losses.

Direct effects on marine fish include physiological effects such as hypercapnia, which has been studied on some species of fish in elevated CO_2 levels (Section 3.4.1). There is insufficient information to predict whether future high levels of CO_2 will lead to significant adult fish mortality. Similarly, it is not possible to predict if there will be any changes in the reproductive success of marine organisms (Section 3.4.2), which would have wide-ranging impacts on marine fisheries.

One of the major indirect impacts on tropical coastal fisheries may be associated with the loss of coral. In addition to the effect on tourism of rising acidity on coral growth, the potential loss of coral-dominated reef systems in the tropics may lead to large-scale changes to the critical habitats of many commercial fish species. These organisms, many of which are completely dependent on coral for food and shelter, would be expected to undergo a major contraction as coral populations dwindle. Organisms that are associated with coral but not as dependent may be expected to be relatively unaffected. Several studies already support this proposal. The orange-spotted filefish (*Oxymonacanthus longirostris*), which is unable to survive without coral, rapidly disappeared from Okinawan reefs after the 1998 bleaching event (Kokita & Nakazono 2001). This particular species, like many others such as butterflyfish and angelfish, requires coral for food, larval settlement and shelter. Although this species is not of great commercial concern, it illustrates the likely impacts of large-scale changes to the habitat of tropical coastal fishes. Other fish associated with coral reefs may stand to benefit from reefs that change from coral domination to reefs that are mostly dominated by algal species. Herbivorous fish populations appear to have increased after the 1998 mass bleaching event on Tanzanian reef systems (Lindahl et al 2001). Similar conclusions have been seen at other sites by Chabanet (2002). Our understanding of the relationships between organisms on coral reefs is relatively scant; hence our ability to project diversity and community structure on coral reefs is limited. However, the impact of the loss of carbonate structures along tropical coastal areas, and therefore this important habitat, could be substantial.

These considerations show that there could be very significant effects of increased ocean surface CO_2 on fisheries.

6.4 *More general ecosystem effects*

As noted in previous sections, pH is such a fundamental variable for marine biogeochemical processes that pervasive effects on ecosystem structure and function are possible. The widespread effects on the ecosystem of the eastern Bering Sea caused by the coccolithophorid blooms (Section 4.3.1) in 1997 may serve as an example of the significant impacts on an ecosystem that can result from small changes in the Earth systems. In this case it was a change in temperature (Pitcher & Calder 2000), which caused an opposite effect on coccolithophores than would be expected with ocean acidification. Observations of the coccolithophorid blooms in 1997 showed a detrimental affect on the mortality of diving seabirds and the migration of sockeye salmon. The number of sockeye salmon migrating in Bristol Bay was so low – an estimated 5 million to 12 million animals failed to appear – that the fishery was declared a 'commercial failure' (Fisheries 1998).

6.5 *Ecosystem services and vulnerability*

The oceans provide numerous ecosystem services that benefit human-kind (Millennium Ecosystem Assessment 2005). These services, such as fisheries contribute significantly to global employment and economic activity. Other services provided by the oceans, for example providing a site for the release of wastes and pollutants, and protection of coastal area by coral from wave energy, are not sufficiently accounted for by standard economic measures. Attempts to quantify some of these services have produced estimates of many billons of dollars (Millennium Ecosystem Assessment 2005). Therefore any significant degradation (even by a few per cent) of these services could have a considerable impact on the global economy.

The Millennium Ecosystem Assessment report highlights established but incomplete, evidence that changes made to an ecosystem increase the likelihood of further nonlinear changes to that ecosystem (Millennium Ecosystem Assessment 2005). These may include accelerated, abrupt and potentially irreversible changes to ecosystem structure which would have significant consequences for human well-being. Owing to projected changes in ocean chemistry, marine ecosystems are likely to become less resilient to further change and more impacts (for example climate change, coastal deforestation, large-scale fishing and pollution).

6.6 Corrosion

Corrosion of metals in seawater is a major economic issue for industries involved in shipping and fixed marine structures. Increase in water acidity has the potential to increase rates of metal corrosion. However, the pH decreases discussed in previous sections (a decrease of 0.5 pH units by the year 2100) are unlikely to be sufficient to lead to a significant direct increase in corrosion rate. This is because the rate of corrosion at pH values around those found in the oceans (about pH 8.2) is largely unaffected by small changes in pH. Corrosion is also likely to be limited by the rate of diffusion of oxygen to the metal surface. A further possible effect arises because metal surfaces in seawater tend to acquire an inorganic coating of which the major component is $CaCO_3$ (Laque 1975). The formation of these coatings is enhanced where the metal surface has been treated with another metal to form cathodic protection; which induces a small protective electric current between the two metals in seawater to inhibit the rate of corrosion. Such inorganic coatings have a beneficial effect in slowing corrosion, but if they are subject to dissolution due to decreased pH then this might increase the rate of corrosion. However, we have been unable to find quantitative information on this effect and how significant a pH decrease of 0.5 units might be; it would appear to be a suitable topic for future study.

6.7 Conclusions

The likely adverse effects of ocean acidification on coral reef ecosystems projected in this report would have significant consequences for the human livelihoods, such as tourism, that are based on them. This may lead to economic losses of many billions of dollars per year, and major socio-economic impacts on the vulnerable societies that depend upon them. In addition, changes to the stability of coastal reefs in tropical and subtropical parts of the globe may lead to serious decreases in coastal protection over longer timescales. These changes could fundamentally change the nature of entire coastlines and the resources available to human societies that depend on them. Future planning, especially in vulnerable coastal societies in developing countries, should include strategies that incorporate these potentially damaging effects of ocean acidification.

Ocean acidification may have significant impacts on the life cycles (including the reproductive success) of some marine fish and shellfish species, putting at risk some unknown fraction of the global economic value of these resources (about $100 billion). It may well cause a significant perturbation of the whole marine biogeochemical system and the ecosystem services (valued at billions of dollars per year) which it provides, to an extent and in ways that at present cannot be foreseen.

However, estimates of the economic consequences of ocean acidification are uncertain, as they do not take into account large non-monetary effects that are outside the scope of formal economic assessments. Some off-setting beneficial effects may also occur to some components of the ecosystem, although there are invariably significant costs involved in adapting to change of any sort. Moreover, as future ocean acidification may involve a significant rate of change of pH, and the oceans and organisms in the past have evolved with much slower rates of change, it would be prudent to expect that the greater the rate and scale of change due to the present ocean acidification, the more adverse the impacts will be on the marine ecosystem.

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This section considers the practicality of some of the engineering approaches that have been suggested as ways to mitigate the chemical effects on the oceans of increased atmospheric CO_2 concentrations.

There are many approaches to preventing the emissions of CO_2 to the atmosphere (for example improved efficiency, renewable energy, carbon sequestration). A discussion of these approaches is beyond the scope of this report; however, the Royal Society has commented in detail on the national and international implementation of these methods in previous reports (for example, Royal Society & Royal Academy of Engineering 1999; Royal Society 2002, 2003, 2005).

Some of the approaches to reduce the accumulation of CO_2 emissions to the atmosphere, for example direct injection of CO_2 into the deep oceans or fertilization of the upper oceans with iron (Coale 1996; Boyd et al 2000), have the potential to exacerbate chemical changes to the oceans. These chemical changes may have a range of important biological consequences, including some potentially negative impacts, and require further consideration.

It has been suggested that some of the chemical effects of CO_2 addition could be mitigated with the addition of alkalinity to the oceans (Kheshgi 1995; Rau & Caldeira 1999). However, this mitigation would be at best partial. If enough alkalinity were added to restore the mineral saturation state of ocean carbonate, only half of the pH change would be mitigated (Annex 1). If enough alkalinity were added to restore ocean pH, the oceans would become more saturated with carbonate minerals (Caldeira & Wickett in press). This in itself could potentially lead to ecosystem level changes. A major concern relating to this approach is the ecological damage from the amount of limestone mining that would be required (see below).

The challenges in achieving mitigation at a global scale, or even a local scale are formidable. Alkalinity could be provided by highly soluble minerals such as magnesium hydroxide, $Mg(OH)_2$ (Kheshgi 1995). Unfortunately, such minerals are relatively rare and probably could not be obtained at the required scale. Thus, most attention has focused on carbonate minerals (for example limestone). The scale of the mining and transportation operation that would be required for a global effort appears to be prohibitively large and would also require a great deal of energy. This energy is likely to come from fossil fuel sources and would increase rates of greenhouse gas emissions. To counteract the changes in acidity caused by today's ocean uptake of roughly 2 Gt C per year (IPCC 2001) would require roughly 20 Gt $CaCO_3$ per year (Caldeira & Rau 2000), which, for a limestone layer 100 m thick, would require the removal of roughly 60 km^2 each year. This limestone would need to be coastally located, or transportation costs would likely be prohibitive (Rau & Caldeira 1999). Thus, features such as the white cliffs of Dover could be rapidly consumed. Therefore the introduction of limestone to offset ocean acidification would raise a host of additional environmental problems. Furthermore, limestone does not dissolve in surface waters, so additional processing, and energy, would be needed (Kheshgi 1995; Rau & Caldeira 1999).

Although the vast amounts of carbonate minerals needed may make this approach infeasible at the scale required to mitigate global changes in ocean chemistry, this approach is widely used by salt-water aquarists to promote coral growth in fish tanks. Thus, it might be possible to use alkalinity addition to save specific coral reefs (Rau & Caldeira 2002), but such ideas have never been tested *in situ* and therefore must be regarded as speculative.

Reducing the scale of future changes to the chemistry and acidity of the oceans is only possible by preventing the accumulation of CO_2 in the atmosphere. Alternative solutions, such as adding chemicals to counter the effects of acidification, are likely to be only partly effective and only at a very local scale.

8.1 Conclusions

1 **The oceans are absorbing CO_2 produced from human activities from the atmosphere and this is causing chemical changes which make them more acidic (ie there is a decrease in the pH of the oceans).**

a **Ocean acidification, like global warming, is a predictable response to those human activities that increase the atmospheric concentration of CO_2. The magnitude and rate of the acidification of the oceans can be predicted with more confidence than the rise in temperature due to global warming, as they are less dependent on climate-system feedbacks.**

b Predictions of the consequences of CO_2 emissions must take into consideration the close chemical and physical coupling between the oceans and the atmosphere. For example, changes in the chemistry of the oceans will affect its ability to absorb additional CO_2, which will in turn affect the rate and scale of global warming. Rising sea temperatures caused by global warming also affect ocean chemistry, as well as other physical and biological processes.

c The oceans are currently taking up about one tonne of human-derived CO_2 per year for each person on the planet. Almost a half of the CO_2 produced in the past 200 years from burning fossil fuels and cement manufacture has been absorbed by the oceans. Calculations based on measurements of the surface oceans and our understanding of ocean chemistry indicate that this uptake of CO_2 has already reduced surface seawater pH by about 0.1 units, which corresponds to an increase of about 30% in the concentration of hydrogen ions.

d As CO_2 continues to enter the atmosphere from human activity, a proportion will be taken up by the oceans. If CO_2 emissions are not regulated, this could result in the pH decreasing by 0.5 units by the year 2100. This is beyond the range of current natural variability and probably to a level not experienced for at least hundreds of thousands of years and possibly much longer. Critically, the rate of change is also probably at least 100 times higher than the maximum rate during this time period. These changes are so rapid that they will significantly reduce the buffering capacity of the natural processes that have moderated changes in ocean chemistry over most of geological time.

e The chemical changes in the oceans caused by increases in the concentration of CO_2 in the atmosphere will include a lowering of the pH, an increase in dissolved CO_2, a reduction in the concentration of carbonate ions, and an increase in bicarbonate ions. All of these will affect the organisms and processes in the oceans.

f **There appears to be no practical way to remove this additional CO_2 from the oceans after it has been absorbed, nor any realistic way to reverse its widespread chemical and probable biological effects.** It will take many thousands of years for natural processes to remove this excess CO_2 and return the oceans to a level close to their pre-industrial state. Thus, it appears that the only practical way to minimise long-term consequences for the oceans is to reduce CO_2 emissions to the atmosphere.

2 **These changes in ocean chemistry will impact on marine organisms and ecosystems.**

a Seawater pH is a critical variable in marine systems; even small changes will have a large impact on ocean chemistry. These changes are likely to alter the biodiversity of marine ecosystems, and may affect the total productivity of the oceans. The impacts will be greater for some regions and ecosystems. However, apart from a few ecosystems such as coral reefs and the Southern Ocean, the direction and magnitude of these impacts are very uncertain. Most of the available evidence suggests that these changes are likely to reduce the resilience of marine ecosystems.

b The best scientific information currently available suggests that these changes in ocean chemistry will almost certainly have major adverse effects on corals and the reefs they build in tropical and subtropical waters. This will affect the stability and longevity of the structures supporting these ecosystems with implications for the biodiversity and their ecological sustainability. Cold-water coral reefs are also likely to be adversely affected, before they have been fully explored.

c Future changes in ocean chemistry, resulting from enhanced atmospheric CO_2, specifically the likely reduction in the concentration of carbonate ions, will make it more difficult for animals to produce hard structures such as carbonate skeletons and shells. The evidence available suggests that this will probably adversely affect most of these organisms. For groups of phytoplankton and zooplankton will be affected.

d Increased CO_2 and the associated reduction in seawater pH may be particularly stressful for organisms with a high metabolism such as squid. Some studies indicate that the physiology of other large marine animals may also be affected, possibly restricting their growth, reproduction or both.

e Ecosystems near the ocean floor, especially on the seabed of shallow waters, provide an essential service for other organisms in the surface oceans: receiving food from the sunlit waters above in the form of sinking particles, they also recycle nutrients from the sediments, which are required for the growth of other organisms. Differences in the response of these diverse organisms to reduced pH could have a considerable impact on the functioning of marine sediments and the 'ecosystem goods and services' they provide.

f Organisms will continue to live in the oceans wherever nutrients and light are available, even with ocean acidification. However, from the data available, it is not known if organisms at the various levels in the food web will be able to adapt or if one species will replace another. It is also not possible to predict what impacts this will have on the community structure and ultimately if it will affect the services that the ecosystems provide. Without significant action to reduce CO_2 emissions into the atmosphere, this may mean that there will be no place in the future oceans for many of the species and ecosystems that we know today.

3 **Oceans play a very important role in the global carbon cycle and Earth's climate system.**

a There are potentially important interactions between changes in the state of the oceans (including their pH) and changes in the global climate and atmospheric chemistry. Our knowledge of these impacts and effects is currently poor and requires urgent consideration.

b Both ocean acidification and climate change result from increasing atmospheric CO_2 emissions. Effects of climate change, particularly increases in ocean temperature, will impact on marine ecosystems. Occurring at the same time, the impacts of climate change will be additional to (and possibly synergistic with) those due to increased CO_2 and ocean acidification.

acidification could be substantial.

a Serious damage to coral reef ecosystems, and the human activities that are based on them, such as fisheries and recreation, could amount to economic losses of many billions of dollars per year. This will have very serious impacts on the vulnerable societies that depend upon these ecosystems.

b Ocean acidification is likely to have significant impacts on some marine fish and shellfish species. It is very hard to determine the economic value of many of these impacts, but would present a risk to some unknown fraction of the global economic value of these resources (about $100 billion per year).

c Ocean acidification will probably cause significant changes in the whole marine biogeochemical system and the ecosystem services that it provides, to an extent and in ways that cannot at present be foreseen.

d Changes to the stability of coastal reefs in tropical and subtropical parts of the globe may lead to serious decreases in coastal protection over longer time periods. These changes could fundamentally change the nature of entire coastlines and the resources available to human societies that depend on these coastal reefs.

5 **Reducing the scale of future changes to the chemistry and acidity of the oceans is only possible by preventing the accumulation of CO_2 in the atmosphere.**

a Solutions other than preventing CO_2 emissions reaching the atmosphere, such as adding chemicals to counter the effects of acidification, are likely to be only partly effective and only at a very local scale. It would be impossible at a regional or global level, and could also cause damage to the marine environment.

b There are many possible approaches to preventing the accumulation in the atmosphere of CO_2 produced by human activities: for example improved energy efficiency, use of renewable energy and carbon sequestration in geological reservoirs. Some approaches, such as direct injection of CO_2 into the deep oceans, have the potential to further exacerbate chemical changes to the oceans.

c **Unless significant reductions are made in global emissions of CO_2 (to ensure atmospheric CO_2 concentration is under twice its current levels by 2100) the entire**

undersaturated for aragonite, which is required by some organisms to make carbonate skeletons and shells. Further increases in atmospheric concentration of CO_2, above this doubling, would make the impacts progressively worse for the oceans as a whole.

6 **We conclude on the basis of current evidence that ocean acidification is an inevitable consequence of continued emissions of CO_2 into the atmosphere, and the magnitude of this acidification can be predicted with a high level of confidence. However, its impacts, particularly on marine organisms, are much less certain and require a substantial research effort.**

a Research into the impacts on ocean with a high CO_2 concentration is in its infancy and needs to be developed rapidly. Among the priority areas for further research are: the identification of those species, functional groups and ecosystems that are most sensitive to increased surface ocean CO_2, and the rate at which organisms can adapt to these changes; the interaction of increased CO_2 in the surface oceans with other factors such as temperature, the carbon cycle, sediment processes, and the balance of reef accretion and erosion; feedbacks of increased ocean surface CO_2 on air–sea exchange of CO_2, dimethylsulphide and other gases important for climate and air quality; and larger-scale manipulation experiments on the effect of increased CO_2 on biota in the surface oceans.

7 **Ocean acidification is a powerful reason, in addition to climate change, for reducing global CO_2 emissions.**

1 **There is a clear risk of significant adverse effects of ocean acidification.** We recommend that this risk should be taken into account by policy makers and other relevant national and international bodies (perhaps including the United Nations Framework Convention on Climate Change) at all discussions and negotiations about climate and other global changes.

2 **Any targets set for CO_2 emission reductions should take account of the impact on ocean chemistry and acidification as well as climate change.** We recommend that if the risk of irreversible damage arising from ocean acidification is to be avoided, particularly in the Southern Ocean, the cumulative future emissions of CO_2 from human activities to the atmosphere must be considerably less than 900 Gt C by 2100.

3 Ocean acidification and its impacts on the oceans needs to be taken into account by the Intergovernmental Panel on Climate Change and kept under review by international scientific bodies such as the Intergovernmental Oceanic Commission, the Scientific Committee on Oceanic Research and the International Geosphere-Biosphere Programme.

4 Tackling ocean acidification cannot be done by any country alone. We believe that the UK could and should take a lead internationally on both policy and research. However, it will only be able to do so by developing and extending its research activity and its international scientific networks.

5 Marine ecosystems are likely to become less robust as a result of the changes to the atmosphere outlined in this report and will probably to be more vulnerable to other environmental impacts (for example climate change, deteriorating water quality, coastal deforestation, fisheries and pollution). **This increased fragility and sensitivity of marine ecosystems needs to be taken into consideration during the development of any policies that relate to their conservation, sustainable use and exploitation, or effects on the communities that depend on them.**

6 Research into ocean chemical changes needs additional investment. Given the potential impacts of these changes, we recommend that a major internationally coordinated research effort (including monitoring) should be launched. The scale of this needs to be commensurate with that on the effects of climate change arising from enhanced greenhouse emissions. The impacts of ocean acidification are additional to, and may exacerbate, the effects of climate change. For this reason, the necessary funding should be additional and must not be diverted from research into climate change.

7 International research collaboration should be enhanced, particularly on the questions associated with effects of enhanced atmospheric CO_2 on ocean chemistry and the resulting impacts on sensitive organisms, functional groups and ecosystems. These efforts need to focus on establishing a better understanding of the various metabolic processes at different parts of the life cycle and how these are expressed at an ecosystem level. Approaches required include global monitoring as well as laboratory, mesocosm and field studies. Models that include effects of pH over a range of scales from the level of the organism to that of the ecosystem will also be necessary. Greater understanding of the likely changes to the oceans resulting from acidification will help inform the management strategies by which human populations can mitigate or adapt to these changes, and can also be linked to climate change models to predict synergistic impacts. The existing research projects of the Surface Ocean–Lower Atmosphere Study (SOLAS) and the Integrated Marine Biogeochemistry and Ecosystem Research Project (IMBER) should be part of any new initiative.

8 **Action needs to be taken now to reduce global emissions of CO_2 to the atmosphere to avoid the risk of large and irreversible damage to the oceans. We recommend that all possible approaches be considered to prevent CO_2 reaching the atmosphere. No option that can make a significant contribution should be dismissed.**

acid–base chemistry of the CO_2–carbonate system in the sea

A1 *The meaning of pH*

The term pH describes the acidity of a liquid. It is defined as:

$$pH = -\log_{10} [H^+] \qquad (1)$$

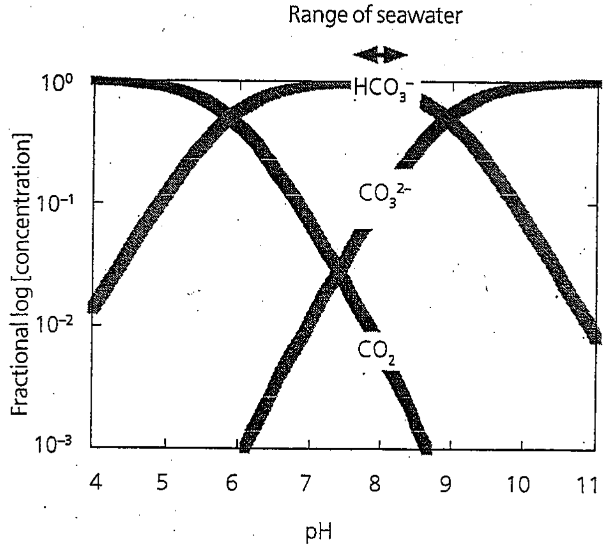
This negative logarithmic dependence on hydrogen ion concentration, $[H^+]$, in moles per litre means that if $[H^+]$ increases 10-fold then pH decreases by 1 unit. The square brackets refer to the concentration of H^+ and subsequently for the concentration of other substances.

Water has the formula H_2O. Only a small proportion of the water molecule splits up into H^+ and OH^-. In pure water, the amounts of $[H^+]$ and $[OH^-]$ are equal and the concentration of each is 10^{-7} in the units mole per litre. This means that a neutral solution has pH = 7. Acid solutions have an excess of $[H^+]$ and a pH less than 7. Alkaline (basic) solutions have an excess of $[OH^-]$ and pH greater than 7, up to 14.

A2 *Dissolved inorganic carbon in seawater*

As CO_2 dissolves in seawater, it reacts with seawater to produce H^+ and various negatively charged forms of dissolved carbon (see Figure A). Carbon dioxide dissolved in seawater first reacts with the water molecule (H_2O) to form carbonic acid (H_2CO_3). Not all the CO_2 dissolved in seawater reacts to make carbonic acid and therefore seawater contains dissolved gaseous CO_2; a point that is easily appreciated from a familiarity with carbonated drinks (which are solutions of carbonic acid). According to Henry's Law, in a simple aqueous solution we would expect the concentration of CO_2 in the air to be proportional to that in the solution of carbonic acid.

Figure A. Relative proportions of the three inorganic forms of CO_2 dissolved in seawater. Note the ordinate scale (vertical axis) is plotted logarithmically.



$$[CO_2] + [H_2O] \Rightarrow [H_2CO_3] \qquad (2)$$

Carbonic acid is an acid because it can split up into its constituents, releasing an excess of H^+ to solution and so driving pH towards lower values. Carbonic acid splits up by adding one H^+ to solution along with HCO_3^- (a bicarbonate ion):

$$[H_2CO_3] \Rightarrow [H^+] + [HCO_3^-] \qquad (3)$$

This increase in H^+ causes some CO_3^{2-} (called carbonate ion) to react with H^+ to become HCO_3^-:

$$[H^+] + [CO_3^{2-}] \Rightarrow [HCO_3^-] \qquad (4)$$

Thus, the net effect of the dissolution of CO_2 in seawater is to increase concentrations of H^+, H_2CO_3 and HCO_3^-, while decreasing concentrations of CO_3^{2-}.

The decrease in carbonate ion concentration $[CO_3^{2-}]$ has important consequences for the chemistry of carbonate minerals commonly used by marine biota to form shells or skeletons. The formation and dissolution of carbonate minerals can be represented as:

$$\begin{gathered} \leftarrow \text{mineral formation} \\ CaCO_3 \Leftrightarrow [Ca^{2+}] + [CO_3^{2-}] \qquad (5) \\ \text{dissolution} \rightarrow \end{gathered}$$

Because the dissolution of CO_2 in seawater decreases $[CO_3^{2-}]$, this reaction moves to the right, impeding the formation of carbonate minerals and promoting their dissolution. Dissolution of carbonate minerals (Equation 5) provides carbonate ions that can react to consume H^+ according to Equation 4. Thus, the dissolution of carbonate minerals tends to decrease $[H^+]$ (increase pH), counteracting some of the pH effects of added CO_2 (see A3).

A3 *The carbonate buffer and seawater pH*

The term 'carbonate buffer' is used to describe how the dissolved inorganic carbon system in seawater acts to diminish changes in ocean H^+ concentration, and thus pH. If a process, such as CO_2 dissolution (Equations 2 and 3), adds H^+ to seawater, some of the added H^+ reacts with

(Equation 4). Because initially most of the added H^+ would be consumed in this way, the change in pH is much less than it would otherwise be. But this process also consumes some carbonate ion; therefore this pH-buffering capacity would diminish as CO_2 concentrations increase. Because CO_2 is absorbed at the sea surface, it is the surface oceans that are most affected.

On the longer time scales of ocean mixing, interaction with $CaCO_3$-rich sediments tends further to buffer the chemistry of the seawater so that changes in pH are lessened. For example, if the deep oceans start to become more acidic such as through the addition of CO_2, which decreases concentrations of CO_3^{2-}, some carbonate ion will be dissolved from sediments (Equation 5).

The carbonate buffer acts to stabilise the average pH of seawater at approximately pH = 8 because of the following two processes: (i) uptake of CO_2 from the atmosphere (for example from volcanoes and now, importantly, from fossil fuel burning) and (ii) interaction of seawater with oceanic sediments composed of $CaCO_3$. Because $CaCO_3$ is abundant in sediments, the pH of the deep oceans cannot change by large amounts over timescales of 10 000 years. However, over historical surface ocean pH can occur.

A4 The calcium carbonate saturation horizon

As discussed in this report, small organisms living in open ocean waters construct shells or plates of $CaCO_3$ that, on death of the organism, fall to the sea floor. Their preservation in sea floor sediments depends on the solubility of $CaCO_3$ in seawater and on the concentration of carbonate ions.

There is a critical concentration of carbonate ions in seawater (the saturation concentration) below which $CaCO_3$ will start to dissolve. Because $CaCO_3$ solubility increases with decreasing temperature and increasing pressure, the critical concentration occurs at a depth, the 'saturation horizon', below which seawater is under-saturated and $CaCO_3$ will tend to dissolve and above which seawater is super-saturated and $CaCO_3$ will tend to be preserved. Because the $CaCO_3$ mineral calcite is less soluble than the form aragonite, the aragonite saturation horizon is shallower. Because added CO_2 decreases the carbonate ion concentration, the saturation horizons will become shallower with increasing releases of human-derived CO_2 to the atmosphere.

To inform the study we issued an open call for evidence in August 2004. We are very grateful to those who responded to this call and to those who provided additional information at the request of the Working Group.

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Dr Peter Haugan	University of Bergen
Dr Donald Hawthorn	Personal submission
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Albedo	Proportion of sunlight reflected by the Earth back into space. A reduction or increase of the Earth's albedo has an impact on global warming
Algae	Photosynthetic organisms lacking characteristic features of land plants, including phytoplankton and seaweeds
Anoxic	Without oxygen
Aragonite	Form of $CaCO_3$ with orthorhombic (crystal system based on three unequal axes at right angles to each other) symmetry in its crystal stucture
Archaea	Single-celled creatures that, with bacteria, make up a category of life called the prokaryotes (organisms composed of a cell having no nuclear membrane)
Bacteria	Single-celled creatures that, with archaea, make up a category of life called the prokaryotes (organisms composed of cells having no nuclear membrane)
Benthic	Bottom dwelling
Bioturbation	The disturbance and mixing of the sediments by animals as they move through them
$CaCO_3$	Calcium carbonate. Compound used in the formation of shells and plates of marine organisms
Calcite	Form of $CaCO_3$ with a trigonal (rhombohedral) symmetry in its crystal structure
CCS	Carbon capture and storage
Cephalopoda	A class of molluscs including squids, cuttlefish and octopuses
Cetacea	An order of large aquatic mammals including whales, dolphins and porpoises
CH_4	Methane
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
Coccolithophore	Calcifying planktonic algae
Demersal	Living near the bottom of the sea
DIC	Dissolved inorganic carbon
Dinoflagellate	Members of the algal class Dinophyceae, occuring as members of the marine phytoplankton and as photosynthetic symbionts in some benthic marine foraminifera and invertebrates
Dissociation	The capacity for certain compounds to form ions including H^+; this causes, and is caused by, pH changes
DMS	Dimethylsulphide, a breakdown product of DMSP which is volatile and can, in the atmosphere, be chemically transformed to compounds that can increase cloud formation
DMSP	Dimethylsulphoniopropionate a compound produced by some marine phytoplankton organisms, and whose breakdown produces DMS in globally significant quantities.
Euphotic zone	Zone of the sea where light penetration is sufficient for photosynthesis

GLODAP	Global Data Analysis Project
GRP	Gross regional product
Gt	Gigatonne (10^9 tonnes)
Gymnosomata	Carnivorous marine planktonic molluscs which feed exclusively on pteropods
Halocarbon	A compound in which the hydrogen of a hydrocarbon is replaced by halogens
Halogen	Any of the group of elements fluorine, chlorine, bromine, iodine and astatine
HCO_3^-	Bicarbonate ion
H_2CO_3	Carbonic acid
H_2O	Water
IPCC	Intergovernmental Panel on Climate Change
Krill	A small shrimp-like planktonic crustacean of the order Euphausiacea, important as food for fish, and for some whales and seals
Henry's Law	The concentration of a solute gas in a solution at a given temperature and salinity is directly proportional to the partial pressure of that gas above the solution
Hypercapnia	CO_2-induced acidification of body fluids
LLNL	Lawrence Livermore National Laboratory
Mesocosm	Experimental apparatus or enclosure designed to approximate natural conditions for tonnes of seawater, and in which environmental factors can be manipulated
Microcosm	Experimental apparatus or enclosure designed to approximate natural conditions for kilograms of seawater, and in which environmental factors can be manipulated
$Mg(OH)_2$	Magnesium hydroxide
Orthorhombic	Crystal structure based on three unequal axes at right angles to each other
N_2O	Nitrous oxide
Oxic	Containing oxygen
Pelagic	Living in the middle depths and surface waters of the sea
pH	A measure of the acidity of a solution; a pH below 7 indicates acidity, and above 7 denotes alkalinity
Planktonic	Of plankton, floating or drifting organisms
Protist	A member of the Protista, a group of unicellular organisms regarded as intermediate between, or more properly distinct from, plants and animals.
Protozoan	A member of the Protozoa, a group of protists with animal-like features

Pteropods	Planktonic marine molluscs with wing-like extensions to the foot, commonly called sea butterflies. The herbivorous Thecosomata typically have an aragonitic shell and are the organisms referred to in the text as Pteropods. The carnivorous Gymnosomata lack a shell and are sometimes considered to be pteropods
Saturation horizon	A natural boundary in seawater, above which $CaCO_3$ can form, and below, it dissolves. The boundary forms through the interplay of several variables, including pH
Speciation	In the context of this report, it is the chemical form of an element in seawater
Surface ocean	Near surface waters where exchange of CO_2 occurs
Symbionts	Partners in a symbiotic association
Symbiosis	Close spatial and functional association of different organisms over much or all of their lives
Thecosomata	Herbivorous planktonic marine molluscs with an aragonitic shell, considered in the text to be equivalent to pteropods
Trigonal	Three-sided; having three fold symmetry
UNFCCC	United Nations Framework Convention on Climate Change
Upwelling	Bulk movement of water from the deep ocean to the surface as part of global ocean circulation or, on a smaller scale, as part of other upward water movements

Ainsworth E A & Long S P (2005). *What have we learned from 15 years of free-air CO_2 enrichment (FACE)? A meta-analytic review of the responses of photosynthesis, canopy properties and plant production to rising CO_2.* New Phytologist **165**, 351–372

Anderson D M & Archer D (2002). *Glacial-interglacial stability of ocean pH inferred from foraminifer dissolution rates.* Nature **416**, 70–73

Arp G, Reimer A & Reitner J (2001). *Photosynthesis-induced biofilm calcification and calcium concentrations in Phanerozoic oceans.* Science **292,** 1701–1704

Banta G T, Giblin A E, Hobbie J E & Tucker J (1995). *Benthic respiration and nitrogen release in Buzzards Bay, Massachusetts.* Journal Marine Research **53**, 107–135

Barker S & Elderfield H (2002). *Foraminiferal calcification response to glacial-interglacial changes in atmospheric CO_2.* Science **297**, 833–836

Barnes R S K & Hughes R N (1988). *An introduction to marine ecology.* Blackwell Scientific Publications: Oxford

Beardall J & Raven J A (2004). *The potential effects of global climate change in microalgal photosynthesis, growth and ecology.* Phycologia **43**, 31–45

Beer S, Bjork M, Hellblom F & Axelsson L (2002). *Inorganic carbon utilization in marine angiosperms (seagrasses).* Functional Plant Biology **29**, 237–240

Bergman N M, Lenton T M & Watson A J (2004). *COPSE: a new model of biogeochemical cycling over Phanerozoic time.* American Journal of Science **304**, 397–437

Berner E K & Berner R A (1996). *Global Environment. Water, Air and Geochemical Cycles.* Prentice Hall: Upper Saddle River, New Jersey

Berner R A (1994). *Geocarb-II - a revised model of atmospheric CO_2 over Phanerozoic time.* American Journal of Science **294**, 56–91

Berry L, Taylor A R, Lucken U, Ryan K P & Brownlee C (2002). *Calcification and inorganic carbon acquisition in coccolithophores.* Functional Plant Biology **29**, 289–299

Bijma J, Spero H J & Lea D W (1999). *Reassessing foraminiferal stable isotope geochemistry: Impact of the oceanic carbonate system (experimental results).* In *Use of proxies in paleoceanography: examples from the south Atlantic* (eds Fischer G & Wefer G) 489–512. Springer-Verlag: Berlin, Heidelberg

Bijma J, Hönisch B & Zeebe R E (2002). *Impact of the ocean carbonate chemistry on living foraminiferal shell weight: comment on 'Carbonate ion concentration in glacial-age deep waters of the Caribbean Sea' by Broecker W S & Clark E - art no 1064.* Geochemistry Geophysics Geosystems **3**, 1064–1064

Booth C E, McDonald D G & Walsh P J (1984). *Acid-base balance in the sea mussel* Mytilus edulis. *I. Effects of hypoxia and air-exposure on haemolymph acid-base status.* Marine Biology Letters **5,** 347–358

Bopp L, Aumont O, Belviso S & Monfray P (2003). *Potential impact of climate change on marine dimethyl sulfide emissions.* Tellus **55B**, 11–22

Boyd P W, Watson A J, Law C S, Abraham E R, Trull T, Murdoch R, Bakker D C E, Bowie A R, Buesseler K O, Chang H, Charette M, Croot P, Downing K, Frew R, Gall M, Hadfield M, Hall J, Harvey M, Jameson G, LaRoche J, Liddicoat M, Ling R, Maldonado M T, McKay R M, Nodder S, Pickmere S, Pridmore R, Rintoul S, Safi K, Sutton P, Strzepek R, Tanneberger K, Turner S, Waite A, & Zeldis J (2000). *A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization.* Nature **407**, 695–702

Boyd P & Doney S C (2003). *The impact of climate change and feedback process on ocean carbon cycle. Ocean Biogeochemistry:* In *Ocean Biogeochemistry: the role of the ocean carbon cycle in global change* (ed Fasham M J R) 157–193. Springer, Germany

Brovkin V, Bendtsen J, Claussen M, Ganopolski A, Kubatzki C, Petoukhov V & Andreev A (2002). *Carbon cycle, vegetation and climate dynamics in the Holocene: experiments with the CLIMBER-2 model.* Global Biogeochemical Cycles **16**, 86

Brown A (2004). *On Asia's coasts, progress destroys natural defenses.* The Wall Street Journal December 31, New York, USA

Brown H, Wickins J F & MacClean M H (1991). *The effect of water hardness on growth and carapace mineralisation of juvenile freshwater prawns, Macrobrachium rosenbergii de Man.* Aquaculture **95**, 329–345

Brownlee C & Taylor A (2004). *Calcification in coccolithophores: a cellular perspective.* In *Coccolithophores: from molecular processes to global impacts* (eds Thierstein H R & Young Y R), 31–49. Springer: Berlin

Bryan K (1969). *Numerical method for the study of the world ocean circulation.* Journal of Computational Physics **4**, 1687–1969

Caribbean. World Resources Institute, Washington, USA

Burkhardt S, Zondervan I & Riebesell U (1999). *Effect of CO_2 concentration on C:N:P ratio in marine phytoplankton: a species comparison*. Limnology and Oceanography **44**, 683–690

Burkhardt S, Amoroso F G, Riebesell U & Sültemeyer D (2001). *CO_2 and HCO_3^- uptake in marine diatoms acclimated to different CO_2 concentrations*. Limnology and Oceanography **46**, 1378–1391

Caldeira K & Rau G H (2000). *Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: geochemical implications*. Geophysical Research Letters **27(2)**, 225–228

Caldeira K & Wickett M E (2003). *Anthropogenic carbon and ocean pH*. Nature **425**, 365

Caldeira K & Wickett M E (in press). *Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean*. Journal of Geophysical Research (Oceans). Article Number 2004JC002671RR.

Cerling T E (1991). *Carbon dioxide in the atmosphere: evidence from Cenozoic and Mesozoic paleosols*. American Journal of Science **291**, 377–400

Cesar H, Beurkering P, Pintz S, Dierking J (2002). *Economic Valuation of Hawai's Coral Reefs. NOAA Final Report (FY2001-2002)*. World Resources Institute: Washington, USA

Chabanet P (2002). *Coral reef fish communities of Mayotte (Western Indian Ocean) two years after the impact of the 1998 bleaching event*. Marine and Freshwater Research **53**, 107–113

Coale K H, Johnson K S, Fitzwater S E, Gordon R M, Tanner S, Chavez F P, Ferioli L, Sakamoto C, Rogers P, Millero F, Steinberg P, Nightingale P, Cooper D, Cochlan W P, Landry M R, Constantinou J, Rollwagen G, Trasvina A, Kudela R (1996). *A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment In the equatorial Pacific-Ocean*. Nature **383,** 495–501

Collins S & Bell G (2004). *Phenotypic consequences of 1 000 generations of selection at elevated CO_2 in a green alga*. Nature **431**, 566–569

Cox M D (1984). *Primitive equation. 3-dimensional model of the ocean*. Group Technical Report 1, GFDL/NOAA. Princeton University, New Jersey, USA

controls on benthic-pelagic coupling of nutrient fluxes and recycling in a coastal upwelling system. Marine Ecology Progress Series **235**, 15-8

Dason J S & Colman B (2004). *Inhibition of growth in two dinoflagellates by rapid changes in external pH*. Canadian Journal of Botany 82, 515–520

Del Giorgio P A & Williams P J LeB (2005). *The global significance of respiration in aquatic ecosystems: from single cells to the biosphere*. In *Respiration in Aquatic Ecosystems* (eds Del Giorgio & LeB Williams P J) Oxford University Press: Oxford

Denman K, Hofmann E & Marchant H (1996). *Marine biotic responses to environmental change and feedbacks to climate* In: *Climate change 1995, the science of climate change* (eds Houghton J T, Meira Filho L G, Callander B A, Harris N, Kattenberg A, Maskell K) Cambridge University Press: 483–515

Dickson A G & F J Millero (1987). *A comparison of the equilibrium constants for the dissociation of carbonic aci in seawater media*. Deep Sea Research **34**, 1733–1743

Dong Q X, Endeline B, Allen S K & Tiersch T R (2002). *Factors affecting sperm motility of tetraploid Pacific oysters*. Journal of Shellfish Research **21**, 719–723

Elderfield H (2002). *Carbonate Mysteries*. Science **296**, 1618–1620

Engel A (2002). *Direct relationship between CO_2 uptake and the transparent exoplymer particles production in natural phytoplankton*. Journal of Plankton Research **24**, 49–53

Engel A, Thoms S, Riebesell U, Rochelle-Newall E & Zondervan I (2004). *Polysaccharide aggregation as a potential sink of marine dissolved organic carbon*. Nature **428**, 929–932

Engel A, Zondervan I, Aerts K, Beaufort L, Benthien A, Chou L, Delille B, Gattuso J-P, Harly J, Heemaan C, Hoffmann L, Jacquet S, Nejstgaard J, Pizay M-D, Rochelle-Newall E S, Schneider U, Terbrueggen A & Riebesell U (2005). *Testing the direct effect of CO_2 concentration on marine phytoplankton: a mesocosm experiment with the coccolithophorid Emiliania huxleyi*. Limnology and Oceanography **50 (2)**, 493–507

Erez J (2003). *The sources of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies*. In *Biomineralization* (eds Dove P M, De Yoreo J J & Weiner S). Mineralogy and Geochemistry **54**, 115-149 *heteropod molluscs and aragonite production in the open ocean: Implications for the marine carbonate cycle.* Journal of Marine Research **48**, 209–222

FAO (2004). *The State of World Fisheries and Aquaculture*. FAO: Rome Italy

Feely R A, Sabine C L, Lee K, Berelson W, Kleypas J, Fabry, V J & Millero F J (2004). *Impact of anthropogenic CO_2 on the $CaCO_2$ system in the ocean.* Science **305**, 362–366

Fenchel T M & Riedl R J (1970). *The sulfide system: a new biotic community underneath the oxidized layer of marine sand bottoms.* Marine Biology **7**, 255–268

Field C B, Behrenfield M J, Randerson J T & Falkowski P (1998). *Primary production of the biosphere: integrating terrestrial and oceanic components.* Science **281**, 237–240

Fisheries (1998). *NMFS declares commercial fisheries failure in Alaska's Bristol Bay salmon fishery*. Fisheries **2**

Flynn K J (2001). *A mechanistic model for describing multi-nutrient, light, temperature interactions in photoplankton.* Journal of Plankton Research **23**, 977–997

Freiwald A, Fossa J H, Grehan A, Koslow T, Roberts J M (2004). *Cold-water coral reefs: out of sight no longer out of mind.* No. 22 in Biodiversity Series. UNEP–WCMC: Cambridge, UK

Furukawa Y (2001). *Biogeochemical consequences of macrofauna burrow ventilation*. Geochemical Transactions (supplement). ACS Division of Geochemistry Symposium, Biogeochemical consequences of dynamic interactions between benthic fauna, microbes and aquatic sediments, San Diego, CA

Gardner W D, Richardson M J, Smith W O (2000). *Seasonal patterns of water column particulate organic carbon and fluxes in the Ross Sea, Antarctica.* Deep-Sea Research Part II **47**, 3423–3449

Gattuso J-P, Allemand D & Frankignoulle M (1999). *Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: a review on interactions and control by carbonate chemistry.* American Zoologist **39(1)**, 160–183

Gervais F & Riebesell U (2001). *The effect of phosphorus limitation on elemental composition and stable carbon isotope fractionation in a diatom growing under different CO_2 concentrations.* Limnology and Oceanography **46**, 497–504

Giordano M, Beardall J & Raven J A (2005). *CO_2 concentrating mechanisms in algae: mechanism, environmental modulation, and evolution.* Annual Review of Plant Biology **56**, 99–131

Gonzalez Davila M, Santana-Casiano J M, Rueda M J. Llinas O & Gonzalez E F (2003) *Seasonal and interannual variability of sea-surface carbon dioxide species at the European Station for Time Series in the Ocean at the Canary Islands (ESTOC) between 1996 and 2000.* Global Biogeochemical Cycles **17**, article number 1076

Green M A, Jones M E, Boudreau C L, Moore P L, Wsetman B A (2004) *Dissolution mortality of juvenile bivalves in coastal marine deposits*. Limnology and Oceanography **49(3)**, 727–734

Gruber N, Sarmiento J L & Stocker T F (1996). *An improved method for detecting anthropogenic CO_2 in the oceans.* Global Biogeochemical Cycles **10(4)**, 809–837

Hein M & Sand-Jensen K (1997). *CO_2 increases oceanic primary production*. Nature **388**, 526–527

Heinze C (2004). *Simulating oceanic $CaCO_3$ export production in the greenhouse.* Geophysical Research Letters **31**, L16308

Hinga K R (2002). *Effects of pH on coastal phytoplankton.* Marine Ecology Progress Series **238**, 281–300

Hitchcock GL, Pane P, Smith S, Luo J & Ortner P B (2002). *Zooplankton spatial distributions in costal waters of the northern Arabian Sea, August 1995.* Deep-Sea Research **49**, 2403–2423

Hoegh-Guldberg O (1999). *Climate change, coral bleaching and the future of the world's coral reefs.* Marine and Freshwater Research **50**, 839–866

Hoegh-Guldberg H & Hoegh-Guldberg O (2004). *Biological, Economic and Social Impacts of Climate Change on the Great Barrier Reef*. World Wide Fund for Nature: Brisbane, Australia

Holligan P M, Fernandez E, Aiken J, Balch W M, Boyd P, Burkill P H, Finch M, Groom S B, Malin G, Muller K, Purdie D A, Robinson C, Trees C C, Turner S M & van der Wal P. (1993). *A biogeochemical study of the coccolithophore, Emiliania huxleyi, in the North Atlantic.* Global Biogeochemical Cycles **7(4)**, 879–900

Holmen K (2000). *The global carbon cycle*. In *Earth system science: biogeochemical cycles to global change* (eds Jacobson MC, Charlson R J Rodhe H, Orians G) p283. Elsevier: USA

Houghton J T, Ding Y, Griggs D J, Noguer M, van der Linden P J, Dai X, Maskell K & Johnson C A (eds) (2001). *Climate change 2001: the scientific basis. Contribution of Working Group I to the Third Assessment Report of the International Panel on Climate Change.* Cambridge University Press: Cambridge, UK and New York, USA *impact of two species of bioturbating shrimp (Callianassa subterranea and Upogebia deltaura) on sediment denitrification*. Journal of the Marine Biological Association of the United Kingdom **84**, 629–632

Huesemann M H, Skilmann A D & Crecelius E A (2002). *The inhibition of marine nitrification by ocean disposal of carbon dioxide.* Marine Pollution Bulletin **44**, 142–148

Institut Pierre Simon Laplace (2005). International Carbon-cycle Model Intercomparison Project Phase 3 (OCMIP3). Institut Pierre Simon Laplace: Orme, France Available online at: http://www.ipsl.jussieu.fr/OCMIP/phase3/#NOCES

Iglesias-Rodriguez M D, Brown C W, Doney S C, Kleypas J, Kolber D, Kolber Z, Hayes P K & Falkowski P G (2002). *Representing key phytoplankton functional groups in ocean carbon cycle models: coccolithophores*, Global Biogeochemical Cycles **16(4)**, 47-1 to 47–20

Ingermann R L, Robinson M L, Cloud J G & Ando M (2003). *Respiration of steelhead trout sperm: sensitivity to pH and carbon dioxide*. Journal of Fish Biology **62(1)**, 13–23

IPCC (2000). *Special Report on Emission Scenarios. A Special Report of Working Group III of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, UK

IPCC (2001). *The Third assessment report of the Intergovernmental Panel on Climate Change (IPCC).* Cambridge University Press: Cambridge, UK, and New York, USA

Ishimatsu A, Kikkawa T, Hayashi M, Lee K S & Kita J (2004). *Effects of CO_2 on marine fish: larvae and adults*. Journal of Oceanography **60**, 731–741

Key R M, Kozyr A, SabineC L, Lee K, Wanninkhof R, Bullister J, Feely R A, Millero F, Mordy C, Peng T-H (2004). *A global ocean carbon climatology: results from GLODAP*. Global Biogeochemical Cycles **18**, GB4031

Kheshgi H S (1995). *Sequestering atmospheric carbon dioxide by increasing ocean alkalinity*. Energy-The International Journal **20(9)**, 915–922

Kikkawa T, Kita J & Ishimatsu A (2004). *Comparison of the lethal effect of CO_2 and acidification on red sea bream (Pagrus major) during the early developmental stages.* Marine Pollution Bulletin **48**, 108–110

Klaas C & Archer D E (2002). *Association of sinking organic matter with various types of mineral ballast in the deep sea: implications for the rain ratio.* Global Biogeochemical Cycles **16**, article number 1116

effect of global change on ocean carbon uptake. Tellus Series B Chemical and Physical Meteorology **47**, 490-500

Kleypas J A, Buddemeier R W, Archer D, Gattuso J-P, Langdon C & Opdyke B N (1999a). *Geochemical consequences of increased atmospheric carbon dioxide on coral reefs.* Science **284**, 118–120

Kleypas J A, McManus J & Menez L (1999b). *Using environmental data to define reef habitat: where do we draw the line?* American Zoologist **39**, 146–159

Kleypas J A, Buddemeier R W & Gattuso J-P (2001). *The future of coral reefs in an age of global change.* International Journal of Earth Sciences **90**, 426–437

Kleypas J A, Buddemeier R W, Eakin M, Gattuso J-P, Guinotte J, Hoegh-Guldberg O, Iglesias-Prieto R, Jokiel P, Langdon C, Skirving W & Strong A E (2005). *Comment on coral reef calcification and climate change: the effect of ocean warming. Response to McNeil et al 2004.* Geophysical Research Letters **32**, article number L08601

Kokita T, Nakazono A (2001). *Rapid response of an obligately corallivorous filefish Oxymonacanthus longirostris (Monacanthidae) to a mass coral bleaching event.* Coral Reefs **20**, 155–158

Kübler J E, Johnston A M & Raven J A (1999). *The effects of reduced and elevated CO_2 and O_2 on the weed Lomentaria articulata.* Plant Cell and Environment **22**, 1303–1310

Kurihara H, Shimode S & Shirayama Y (2004a). *Sub-lethal effects of elevated concentration of CO_2 on planktonic copepods and sea urchins.* Journal of Oceanography **60**, 743–750

Kurihara H, Shimode S & Shirayama Y (2004b). *Effects of raised CO_2 concentration on the egg production rate and early development of two marine copepods (Arctia steuri* and *Acartia erythraea*). Marine Pollution Bulletin **49**, 721–727

Lalli C M & Gilmer R W (1989). *Pelagic snails*. Stanford University Press: Stanford, USA

Langdon C, Takahashi T, Marubini F, Atkinson M, Sweeney C, Aceves H, Barnett H, Chipman D & Goddard J (2000). *Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef.* Global Biogeochemical Cycles **14**, 639–654

Langdon C, Broecker W S, Hammond D E, Glenn E, Fitzsimmons K, Nelson S G, Peng T H, Hajdas I & Bonani G (2003). *Effect of elevated CO_2 on the community metabolism of an experimental coral reef.* Global Biogeochemical Cycles **17**, article number 1011

Langenbuch M & Pörtner H O (2002). *Changes in metabolic rate and N excretion in the marine invertebrate Sipunculus nudus under conditions of environmental hypercapnia: identifying effective acid–base variables*. Journal of Experimental Biology **205**, 1153–1160

Langenbuch H & Pörtner H O (2003). *Energy budget of hepatocytes from Antarctic fish (Pachycara brachycephalum and Lepidonotothen kempi) as a function of ambient CO_2: pH-dependent limitations of cellular protein biosynthesis?* Journal of Experimental Biology **206**, 3895–3903

Laque F L (1975). *Marine Corrosion: causes and prevention*. John Wiley: New York, USA

LeBrasseur R J (1966). *Stomach contents of salmon and steelhead trout in the northeastern Pacific ocean*. Journal of the Fisheries Resesearch Board of Canada **23**, 85–100

Leclercq N, Gattuso J-P & Jaubert J (2000). *CO_2 partial pressure controls the calcification rate of a coral community*. Global Change Biology **6**, 329–334

Leclercq N, Gattuso J-P & Jaubert J (2002). *Primary production, respiration, and calcification of a coral reef mesocosm under increased CO_2 partial pressure*. Limnology and Oceanography **47**, 558–564

Lindahl U, Ohman M C & Schelten C K (2001). *The 1997/1998 mass mortality of corals: effects on fish communities on a Tanzanian coral reef.* Marine Pollution Bulletin **42**, 127–131

Lindinger M I, Lauren D J and McDonald D G (1984). *Acid-base balance in the sea mussel,* Mytilus edulis. *III. Effects of environmental hypercapnia on intra- and extracellular acid-base balance.* Marine Biology Letters **5**, 371–381

Liss P S, Malin G, Turner S M & Holligan P M (1994). *Dimethyl sulphide and Phaeocystis: a review*. Journal of Marine Systems **5**, 41–53

Lough J M & Barnes D J (2000). *Environmental controls on growth of the massive coral porites*. Journal of Experimental Marine Biology and Ecology **245**, 225–243

Lowenstam H A (1981). *Minerals formed by organisms.* Science **211**, 1126–1130

Luo J, Du T & Liu C (2004). *The influence of pH and salinity in hatching rate of egg sac of Babylonia areolate and the effect of different diet on the development, survival rate of the larvae.* Marine sciences/Haiyang Kexue **28(6)**, 5–9

Malin G & Steinke M (2004). *Dimethyl sulphide production: what is the contribution of cocolithophores?* In *Coccolithophores – from Molecular Processes to Global Impact.* (eds Thierstein H R & Young J R) 127–164. Springer-Verlag: Berlin

Martin-Jezequel V, Huonnic F, Delille B & Riebesell U (2004). *Impact of the pCO_2 level on microalgae. Comparison of past, present & future situations during mesocosms experiments.* I: phytoplanktonic development, 2004. SOLAS open science conference, 13–16 October 2004. SOLAS, Halifax, Canada

Marubini F & Atkinson M J (1999). *Effects of lowered pH and elevated nitrate on coral calcification*. Marine Ecology Progress Series **188**, 117–121

Marubini F, Barnett H, Langdon C & Atkinson M J (2001). *Dependence of calcification on light and carbonate ion concentration for the hermatypic coral Porites compressa*. Marine Ecology Progress Series **220**, 153–162

Marubini F, Ferrier-Pages C & Cuif J-P (2002). *Suppression of growth in scleractinian corals by decreasing ambient carbonate ion concentration: a cross-family comparison*. Proceedings of the Royal Society of London B. **270**, 179–184

McNeil B I, Matear I & Barnes D J (2004). *Coral reef calcification and climate change: the effect of ocean warming*. Geophysical Research Letters **31**, L22309

Merico A, Tyrrell T, Brown C W, Groom S B & Miller P I (2003). *Analysis of satellite imagery for Emiliania huxleyi blooms in the Bering Sea before 1997*. Geophysical Research Letters **30**, article number 13371337

Millennium Ecosystem Assessment (2005). *Millennium Ecosystem Assessment synthesis report: ecosystems and human well-being*. Island Press: Washington, USA

Morel F M M, Milligan A J & Saito M A (2003). *Marine bioinorganic chemistry: the role of trace metals in the oceanic cycles*. In *The Oceans and Marine Geochemistry* - Treatise on Geochemistry (eds Holland H D & Turekian K K). Elsevier-Pergamon: Oxford, UK

Mouvet C & Bourg A C M (1983). *Speciation (including adsorbed species) of copper, lead, nickel and zinc in the Meuse River: observed results compared to values calculated with a chemical equilibrium computer program*. Water Research **17**, 641–649

Mucci A & Morse J W (1990). *Chemistry of low-temperature abiotic calcites: experimental studies on coprecipitation, stability, and fractionation*. Aquatic Science **3**, 217–257

Nedwell D B & Walker T R (1995). *Sediment - water fluxes of nutrients in an Antarctic coastal environment: Influences of bioturbation*. Polar Biology **15**, 57–64

Pagani M, Lemarchand D, Spivack A & Gaillardet J (2005). *A critical evaluation of the boron isotope-pH proxy: the accuracy of ancient ocean pH estimates*. Geochimica et Cosmochimica Acta **69**, 953-961 *fluxes determine particulate organic carbon fluxes or vice versa?* Geochemistry Geophysics Geosystems **5**, article number Q04002

Pauly D, Christensen V, Dalsgaard J, Froese R, Torres F (1998). *Fishing down marine food webs*. Science **279**, 860–863

Pearson P N & Palmer M R (2000). *Atmospheric carbon dioxide concentrations over the past 60 million years,* Nature **406**, 695–699

Pitcher G & Calder D (2000). *Harmful algal blooms of the southern Benguela current: a review and appraisal of monitoring from 1989 to 1997.* South African Journal of Marine Science **22**, 255–271

Politi Y, Arod T, Klein E, Weiner S & Addadi L (2004). *Sea urchin spine calcite forms via a transient amorphous calcium carbonate phase.* Science **306**, 1161–1164

Pörtner H O & Reipschläger A (1996). *Ocean disposal of anthropogenic CO_2: physiological effects on tolerant and intolerant animals.* In *Ocean storage of CO_2. Environmental Impact (eds* Ormerod B & Angel M) 57–81. IEA Greenhouse Gas R&D Programme: Cheltenham, UK

Pörtner H O & Zielinski (1998). *Environmental constraints and the physiology of performance in squids.* South African Journal of Marine Science **20**, 207–221

Pörtner H O, Bock C & Reipschläger A (2000). *Modulation of the cost of pHi regulation during metabolic depression: a 31P-NMR study in invertebrate (Sipunculus nudus) isolated muscle.* Journal of Experimental Biology **203**, 2417–2428

Pörtner, H O, Langenbuch M & Reipschläger A (2004). *Biological impact of elevated ocean CO_2 concentrations: lessons from animal physiology and Earth history.* Journal of Oceanography **60**, 705–718

Rau G H & Caldeira K (1999). *Enhanced carbonate dissolution: a means of sequestering waste CO_2 as ocean bicarbonate.* Energy Conversion and Management **40(17)**, 1803–1813

Rau G H & Caldeira K (2002). *Minimizing effects of CO_2 storage in oceans.* Science **276**, 275–276

Raven J A (1986). *Physiological consequences of extremely small size for autotrophic organisms in the sea.* In *Photosynthetic Picoplankton* **214**. (eds Platt T & Li W K W) 583. Canadian Bulletin of Fisheries and Aquatic Sciences: Ottawa, Canada

Raven J A & Waite A (2004). *The evolution of silicification in diatoms: inescapable sinking and sinking as escape?* New Phytologist **162**, 45-61

reefs: a comparison with rain forests. In *Biodiversity II: Understanding and protecting our biological resources.* (eds Reaka-Kudla M L, Wilson D E & Wilson E O). Joseph Henry Press: Washington

Rhoads D C & Young D K (1970). *The influence of deposit-feeding organisms on sediment stability and community trophic structure.* Journal Marine Research **28**, 150–178

Ridgwell A J (2001). *Glacial-interglacial perturbations in the global carbon cycle.* PhD thesis, University of East Anglia, Norwich, UK

Riebesell U, Zondervan I, Rost B, Tortell P D, Zeebe R & Morel F M M (2000). *Reduced calcification of marine plankton in response to increased atmospheric CO_2.* Nature **407**, 364–367

Rost B, Riebesell U, Burkhardt S & Sültemeyer D (2003). *Carbon acquisition by bloom-forming marine phytoplankton.* Limnology and Oceanography **48**, 55–67

Rost B, Riebesell U (2004). *Coccolithophores and the biological pump: responses to environmental changes* pp76–99. In: *Coccolithophores – From molecular processes to global impact.* Springer.

Royal Society & Royal Academy of Engineering (1999). *Nuclear energy: the future climate.* Document 10/99, Royal Society, Royal Academy of Engineering: London

Royal Society (2002). *Economic Instruments for the reduction of carbon dioxide emissions.* Document 26/02, Royal Society: London

Royal Society (2003). *Royal Society response to the House of Lords Inquiry into the practicalities of developing renewable energy.* Document number 22/03, Royal Society: London

Royal Society (2005). *Royal Society response to the Defra review of the UK climate change programme.* Document 02/05, Royal Society: London

Sabine C L, Feely R A, Gruber N, Key R M, Lee K, Bullister J L, Wanninkhof R, Wong C S, Wallace D W R, Tilbrook B, Millero F J, Peng T H, Kozyr A, Ono T & Rios A F (2004). *The oceanic sink for anthropogenic CO_2.* Science **305**, 367–371

Sanyal A, Hemming N G, Hanson G N & Broecker W S (1995). *Evidence for a higher pH in the Glacial ocean from boron isotopes in foraminifera.* Nature **373**, 234–236

Sarmiento, J L, Le Quéré C & Pacala S W (1995). *Limiting future atmospheric carbon-dioxide.* Global Biogeochemical Cycles **9**, 121–137

Sarmiento J L & Le Quéré C (1996). *Oceanic carbon dioxide uptake in a model of century-scale global warming.* Science **274**, 1346-1350

Sarmiento J L, Hughes T M C, Stouffer R J & Manabe S (1998). *Simulated response of the ocean carbon cycle to anthropogenic climate warming*. Nature **393**, 245–249

Schippers P, Lürling M & Sheffer M (2004). *Increase of atmospheric CO_2 promotes phytoplankton*. Ecology Letters **7**, 446–451

Seibel B A & Dierssen H M (2003). *Tip of the iceberg: Cascading trophic impacts of reduced biomass in the Ross Sea, Antarctica.* Biological Bulletin **202**, 93–97

Seibel B A & Fabry V J (2003). *Marine biotic response to elevated carbon dioxide*. Advances in Applied Biodiversity Science **4**, 59–67

Shirayama Y, Kurihara H, Thornton H, Yamamoto T, Ohta M, Okita K & Shimode S (2004). *Impacts on ocean life in a high-CO_2 world.* Paper presented at SCOR–UNESCO sponsored symposium, The ocean in a high-CO_2 world, SCOR-UNESCO, Paris, 2004

Smyth T J, Tyrrell T & Tarrant B (2004). *Time series of coccolithophore activity in the Barents Sea, from twenty years of satellite imagery*. Geophysical Research Letters . **31**

Spalding M D, Ravilious C & Green E P (2001). *World atlas of coral reefs.* Prepared by the UNEP World Conservation Monitoring Centre. University Press of California Press: Berkeley, USA

Takeuchi I (1972). *Food animals collected from the stomachs of three salmonoid fishes Oncorhynchus and their distribution in the natural environments in the northern North Pacific.* Bulletin of the Hokkaido Region Fisheries Research Laboratory **38**, 1–119

Tortell P D, Giocoma R D, Sigman D M, Morel F M M (2002). *CO_2 effects on taxonomic composition and nutrient utilization in an Equatorial Pacific phytoplankton assemblage*. Marine Ecology Progress Series **236**, 37–43

Tyrrell T, Holligan P M & Mobley C D (1999). *Optical impacts of oceanic coccolithophore blooms*. Journal of Geophysical Research – Oceans **104**, 3223–3241

Tyrrell T & Merico A (2004). *Emiliania huxleyi: bloom observations and the conditions that induce them*. In *Coccolithophores – from molecular processes to global impact* (eds Thierstein H R & Young J R) 75–97. Springer-Verlag: Berlin

Ware J R, Smith S V & Reakakudla M L (1992). *Coral reefs: sources or sinks of atmospheric CO_2?* Coral Reefs **11**, 127–130

Widdicombe S & Austen MC (1998). *Experimental evidence for the role of Brissopsis lyrifera (Forbes, 1841) as a critical species in the maintenance of benthic diversity and the modification of sediment chemistry.* Journal of Experimental Marine Biology and Ecology **228(2)**, 241–255

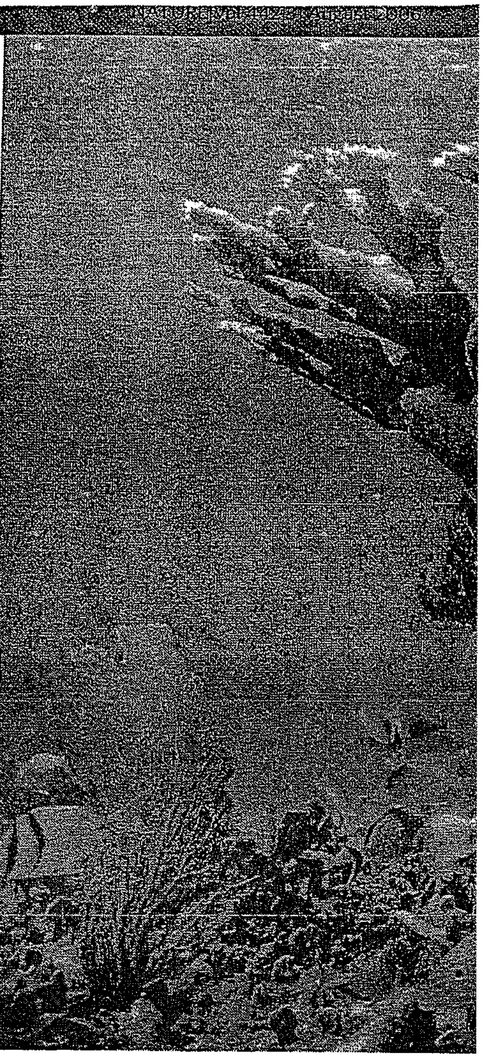
Widdicombe S, Austen M C, Kendall M A, Warwick R M & Jones M B (2000). *Bioturbation as a mechanism for setting and maintaining levels of diversity in subtidal macrobenthic communities*. Hydrobiologia **440**, 369–377

Zeebe R E & Wolf-Gladrow D (2001). *CO_2 in seawater: equilibrium, kinetics, isotopes.* Elsevier Oceanography Series. Elsevier: Amsterdam

Zondervan I, Zeebe R E, Rost B & Riebesell U (2001). *Decreasing marine biogenic calcification: a negative feedback on rising atmospheric pCO_2*. Global Biogeochemical Cycles **15**, 507-516

SICK SEAS

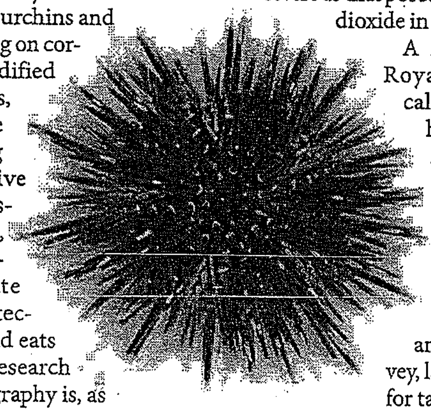
The rising level of carbon dioxide in the atmosphere is making the world's oceans more acidic. **Jacqueline Ruttimann** reports on the potentially catastrophic effect this could have on marine creatures.



It's not hard to imagine a tonne of water: it is a week's worth of not-very-deep baths. Getting to grips with a billion tonnes of water is more of a challenge. That would be a similar bath for every man, woman and child on the planet; a week's worth of flow for the Nile. To really expand your mind, go further still, to a billion billion tonnes — enough water to give every human a day's worth of the Nile instead of a shallow bath. There are dwarf planets that weigh less than a billion billion tonnes. Yet Earth's oceans weigh more.

If it is hard to imagine something so vast, it is perhaps even harder to imagine changing it. But humanity is changing the oceans. From the tropics to the Arctic, the seas are sucking up human-driven emissions of carbon dioxide — about half of the excess belched into the atmosphere over the past two centuries from fossil-fuel burning and cement manufacturing plants[1]. When carbon dioxide dissolves in water, carbonic acid is produced: as a result the oceans are becoming more acidic. "It's basic chemistry," says Joanie Kleypas, a marine ecologist at the National Center for Atmospheric Research in Boulder, Colorado. "It's hard to say that this is not happening."

Over the past few years, scientists have documented how increasingly acidic seas could eat away the armour of many creatures — blunting the spikes on sea urchins and dissolving the covering on corals. In artificially acidified waters, some animals, such as squid, have problems swimming because the corrosive water affects their respiration rate. Others, particularly tiny organisms with carbonate shells, lose their protective shields as the acid eats away at them[2]. But research into low-pH oceanography is, as yet, sparse. "We're just starting to grapple with what low pH will mean for ocean communities," says Jim Barry, a marine biologist at the Monterey Bay Aquarium Research Institute (MBARI) in Moss Landing, California.



This ocean acidification is unlike the atmospheric warming also being caused by carbon dioxide in that it is fairly predictable; plotting its future course requires little more than school chemistry, as opposed to sophisticated modelling. The rate of acidification is pretty much unprecedented. Before the industrial revolution, the rise in the level of carbon dioxide in the atmosphere was relatively slow — giving oceans time to circulate the waters being made more acidic in the shallows with acid-neutralizing carbonate sediments in the depths.

In the past few decades, carbon dioxide has been building up far more quickly, and the ocean is becoming acidified at a rate that outpaces the action of sedimentary antacids. The rate of change is perhaps 100 times anything seen in the past hundreds of millennia, as suggested by isotope studies of ancient sediments. In the century to come, sea creatures will find themselves in conditions that their ancestors never had to face. These organisms have never been forced to adapt to lower pH, says Ulf Riebesell, a marine biogeochemist at the Leibniz Institute for Marine Sciences in Germany. "They've never seen this before in their evolution."

Acid attack

The acidified waters eat away at the carbonate skeletons that protect many marine organisms. By some estimates, calcification rates will decrease by up to 60% by the end of this century. If so, carbon dioxide in the ocean could represent a chemical threat to the biosphere as severe as that posed by the build up of carbon dioxide in the atmosphere.

A 2005 report from the Royal Society in London called for more research to help quantify the threat. Another report, released last month by three US research agencies, the National Science Foundation, the National Oceanic and Atmospheric Administration, and the US Geological Survey, laid out research strategies for tackling the problem. And the Intergovernmental Panel on Climate Change (IPCC) — the international body tasked with quantifying the effects of climate change — is flagging ocean acidification as a problem for the first time in its next report, due in early 2007

In 1800, the carbon dioxide in the atmosphere was 280 parts per million, and the oceans' pH averaged 8.16. Today there are 380 parts per million of carbon dioxide in the atmosphere, and the pH of the oceans is on average 8.05. Estimates suggest the pH could drop to 7.9 by the end of the century. The drop from 8.16 to 7.9, says Kleypas, "doesn't sound like much, but it's a lot." Each one-step change on the pH scale indicates a tenfold change in acidity.

Just as terrestrial ecologists experiment by growing plants in high concentrations of carbon dioxide, so marine biologists are beginning to investigate what life in the less-alkaline ocean may be like.

In a fjord in southwest Norway, Riebesell has set up an outdoor laboratory consisting of a raft with what look like giant milk cartons moored to it. The containers, known as 'mesocosms', are 50-litre vessels filled with coccolithophores — photosynthesizing plankton, or phytoplankton, with carbonate coverings. Riebesell immerses the coccolithophores into tanks that are aerated with the projected levels of carbon dioxide in the next 50 and 100 years. He calls them "the oceans of the future".

The coccolithophores' outer casings — tiny hubcaps known as coccoliths — are made of the carbonate mineral calcite. Riebesell found that exposing coccolithophores to three times the present-day atmospheric level of carbon dioxide caused nearly half of their protective coating to disintegrate[3].

Such changes don't bode well for one of the ocean's most abundant types of phytoplankton,

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Fragile lives: acidified seas could dissolve corals and blunt the spines of sea urchins (left).

and what's bad for phytoplankton is likely to be bad for the food webs they sustain. By aggregating on the surface of waste from the upper levels of the ocean (mainly fish droppings), the coccoliths help it to sink down to the seabed communities, which recycle its nutrients into the ocean. Weakening the coccoliths could have knock-on effects on nutrient cycling.

Most at risk

Riebesell is now looking at the effects of increasing acidity on plankton eggs and larvae; other researchers are studying the dangers posed to larger animals, such as sea urchins and snails. In one experiment, marine biologist Yoshihisa Shirayama, at Kyoto University in Japan, placed sea urchins and snails separately into 30-litre tanks filled with water containing 550 parts per million of carbon dioxide. Within three months, the creatures dropped in weight by roughly 8%. Their calcite spines became blunted, says Shirayama, and so brittle that they broke off easily when handled.

If carbon dioxide levels in the tanks were quickly lowered, the animals eventually recovered. If they were exposed to high levels over the long term, such as for a year, most of them died[4]. "It's obvious that animals cannot adapt to large change in carbon-dioxide concentration," says Shirayama.

Other disturbing news comes from experiments led by MBARI's Barry. For most of his career, carbon dioxide has just been a tool: he used to carry a fire extinguisher to intertidal zones so he could bubble the gas through the sea water, put the animals living in it to sleep and thus capture them more easily. Now he's looking at carbon dioxide as a threat.

> "People should know that the consequences of what we're doing in the next decade will last for thousands of years." — Ken Caldeira

Working with his postdoctoral fellow Eric Pane, Barry has been studying how two crab species respond to elevated levels of carbon dioxide. Preliminary results suggest that the shallow-water Dungeness crab, (*Cancer* species), does much better than the deep-sea Tanner crab (*Chionoecetes* species), as measured by how long it takes their metabolism to recover from a high dose of carbon dioxide. That difference points out a key point about the acidifying oceans, says Barry: "Deep-sea animals are probably much more sensitive to changes than animals found in shallow water."

Barry and Pace presented their findings on the crab studies in July, at a deep-sea biology symposium in Southampton, UK. In related work, Barry has found that microscopic animals living in seafloor sediments seem to decline after being exposed to a drop in of just 0.1 for one month. Oddly, they see recover after a week or two — perhaps, Barry says, because fewer of them are being eaten by larger animals, which may have died off, or because they have more to eat themselves as the dead bodies of other small creatures, killed by the pH change, drift to the sea floor.

Mass die-off

Also at risk in the deep sea are cold-water corals, some of the slowest growing corals on Earth. Corals are particularly vulnerable to acidification because reefs are built out of aragonite, a carbonate mineral that is more soluble than the calcite used by coccolithophores and sea urchins. "Deep-water corals could soon be in trouble," says James Orr, an oceanographer at the Laboratory for Clima and Environmental Science in Gif-sur-Yv France. By the end of the century, two-thirds of deep-water corals — as opposed to virtually none today — could be exposed to sea water that is corrosive to aragonite[5].

Because carbonate is more soluble in high pressures and cold water, increased acidity has a greater effect at depth. But Orr's studies suggest that aragonite will be unstable at all depths throughout the Southern Ocean by 2100. Once the corals go, so too may other species that rely on them for resources such as shelter.

Despite such dire models, not all scien are convinced that ocean acidification wil a major problem. In May, a paper in *Geophysical Research Letters* suggested that the rising carbon dioxide would have minimal biological impact in the ocean[6]. Hugo Loáiciga, a hydrologist at the University of California, Santa Ba bara, argued that sediment carbonates wou be able to buffer the predicted acidification.

But it seems most experts disagree. A response, signed by 25 leaders in the field of ocean acidification, rebutted each of Loáiciga's points in detail. The experts also argued that many marine organisms would be sensitive to a drop of 0.2 pH units — a change Loáiciga had said would be essentially unimportant.

Ken Caldeira, an Earth-systems modeller at the Carnegie Institution of Washington in Stanford, California, who led the response, says the public needs to know now that this is a problem, and that it is unprecedented in its scale. In one model, Caldeira and his colleague Michael Wickett from the Lawrence Livermore National Laboratory, California, simulated the effects of an unregulated pulse of fossil-fuel burning that peaks around the year 2100.

The atmospheric carbon-dioxide level pe shortly after the highest rate of burning. T

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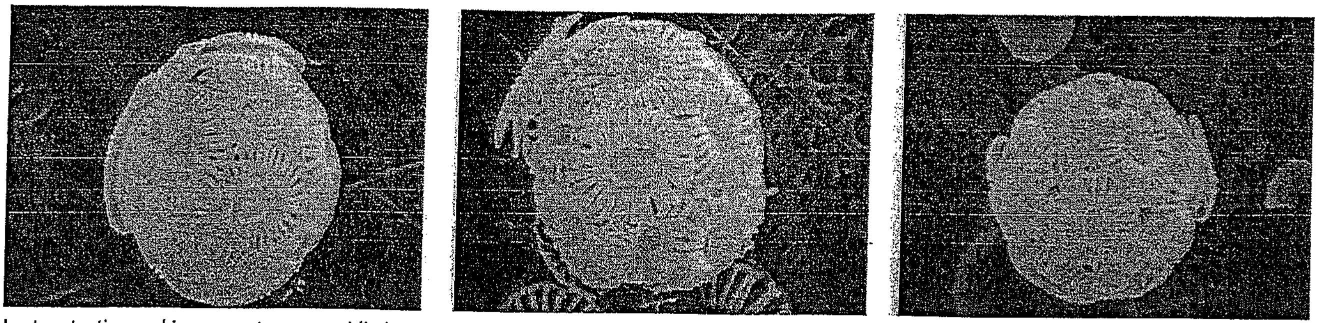


J. CUBILLOS

Lost protection: making sea water more acidic (centre and right) dissolves the outer casings of coccolithophores, tiny plankton that form the basis of food webs.

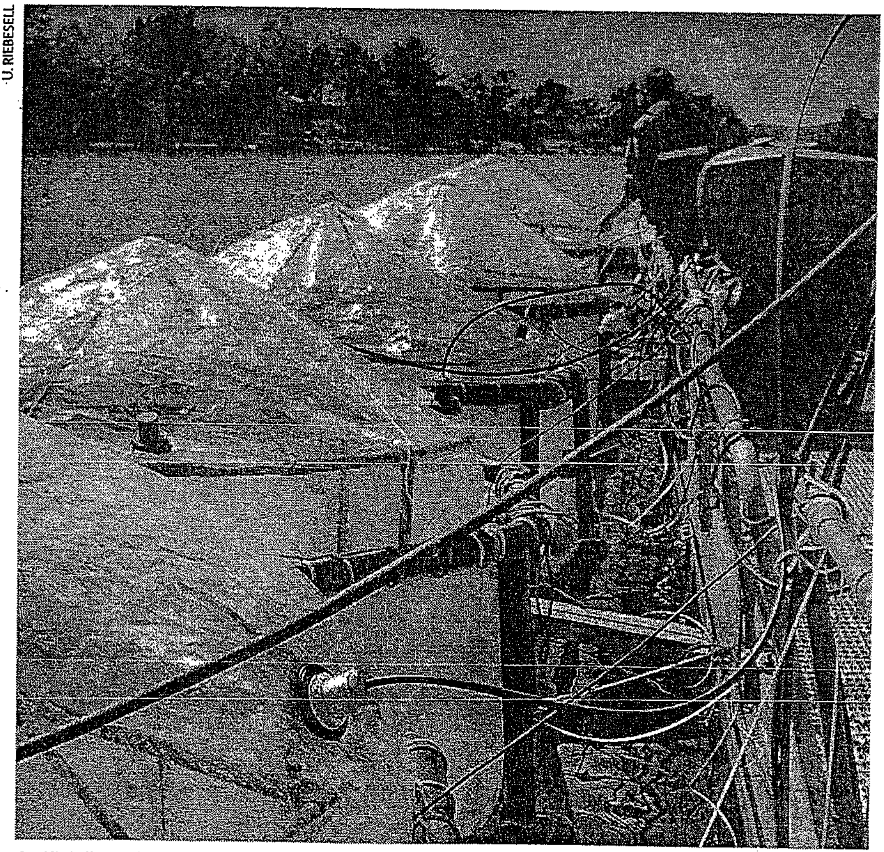
it slowly subsides as the carbon is picked up by the ocean — which slowly becomes more acidic at depth. At the surface, the pH might stop falling by 2750. A kilometre or so deep, however, the pH would still be dropping at the beginning of the next millennium[7]. "People should know that the consequences of what we're doing in next decade will last for thousands of years," says Caldeira.

In the meantime, researchers have a great deal to do trying to understand what the first decades of change could bring about. "So few studies have been done," says Victoria Fabry, an oceanographer at California State University in San Marcos. "We've really just scratched the surface." As an example, Fabry says lab studies on calcifying plankton are in such short supply that researchers have investigated only about 2% of all species.

The July report produced by the US research agencies suggests paths for future studies. These include merging experiments done in the laboratory with those in the field, as well as identifying the effects of acidification on keystone species such as coral and plankton and how changes to such species could affect the rest of the ecosystem. The report also notes the need to study the problem at all spatial scales; currently, most studies are focused on either the large-scale biogeochemical level or effects on individual organisms. Studies of ecosystems are in short supply.

A world of problems

To try to rectify that, some researchers are pushing for large-scale field experiments, such as marine versions of the open-air experiments in carbon-dioxide enrichment that have been taking place in forests for many years. Barry and his MBARI colleagues are working to develop one of these experiments in the free ocean — it will be essentially a deep-sea cage set in a plume of water enriched in carbon dioxide.



U. RIEBESELL

Artificially acidified tanks of sea water are shedding light on the effects of lower pH on sea creatures.

In addition, disciplines are starting to merge. Oceanographers are beginning to collaborate with chemists to quantify the acidification reactions, and with engineers to develop robotic submersibles to collect deep-sea organisms for study. Social scientists are starting to get involved as well. The next Pacific Science Congress, to be held in Okinawa, Japan, in June 2007, will bring together natural scientists and social scientists to discuss how residents of coastal areas might adapt.

With more attention on the problem, a new possibility has raised its head. Ocean acidification might not just run in parallel with global warming — it could amplify it. The chalky coccolithophores, when blooming, lighten the surface of the oceans, which means more sunlight is reflected into space. Reduce their number and even if other phytoplankton take their place, that lightness will be gone.

Coccolithophores are also responsible for many of the clouds over oceans. They produce a lot of dimethylsulphide, which accounts for much of the aerosolized sulphate in the atmosphere above the oceans. Sulphate particles act as 'seeds' around which cloud droplets grow[8]. Remove them, and you could remove a significant fraction of the world's clouds, warming the planet yet further[9].

Human imagination cannot easily cope with the vastness of the oceans, or the complexities that change within them can bring about. But human industry faces no such obstacle in making change unavoidable for centuries to come. ■

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Additional reporting is by Alexandra Witze.

1. Tedesco, T., Feely, R. A., Sabine, C. L. & Cosca, C. E.; available at www.research.noaa.gov/spotlite/archive/spot_gcc.html (2005).
2. Orr, J. C. *et al. Nature* **437**, 681–686 (2005).
3. Riebesell, U. *et al. Nature* **407**, 364–367 (2000).
4. Shirayama, Y. & Thornton, H. *J. Geophys. Res.* **110**, C09S08 (2005).
5. Guinotte, J. M. *et al. Front. Ecol. Environ.* **4**, 141–146 (2006).
6. Loáiciga, H. A. *Geophys. Res. Lett.* **33**, L10605 (2006).
7. Caldeira, K. & Wickett, M. E. *Nature* **425**, 365 (2003).
8. Charlson, R. J. *et al. Nature* **326**, 655–661 (1987).
9. Gunson, J. R. *et al. Geophys. Res. Lett.* doi:10.1029/2005GL024982 (2006).

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The Oceanic Sink for Anthropogenic CO_2

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Using inorganic carbon measurements from an international survey effort in the 1990s and a tracer-based separation technique, we estimate a global oceanic anthropogenic carbon dioxide (CO_2) sink for the period from 1800 to 1994 of 118 ± 19 petagrams of carbon. The oceanic sink accounts for ~48% of the total fossil-fuel and cement-manufacturing emissions, implying that the terrestrial biosphere was a net source of CO_2 to the atmosphere of about 39 ± 28 petagrams of carbon for this period. The current fraction of total anthropogenic CO_2 emissions stored in the ocean appears to be about one-third of the long-term potential.

Since the beginning of the industrial period in the late 18th century, i.e., over the anthropocene (*1*), humankind has emitted large quantities of CO_2 into the atmosphere, mainly as a result of fossil-fuel burning, but also because of land-use practices, e.g., deforestation (*2*). Measurements and reconstructions of the atmospheric CO_2 history reveal, however, that less than half of these emissions remain in the atmosphere (*3*). The anthropogenic CO_2 that did not accumulate in the atmosphere must have been taken up by the ocean, by the land biosphere, or by a combination of both. The relative roles of the ocean and land biosphere as sinks for anthropogenic CO_2 over the anthropocene are currently not known. Although the anthropogenic CO_2 budget for the past two decades, i.e., the 1980s and 1990s, has been investigated in detail (*3*), the estimates of the ocean sink have not been based on direct measurements of changes in the oceanic inventory of dissolved inorganic carbon (DIC).

Recognizing the need to constrain the oceanic uptake, transport, and storage of anthropogenic CO_2 for the anthropocene and to provide a baseline for future estimates of oceanic CO_2 uptake, two international ocean research programs, the World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Study (JGOFS), jointly conducted a comprehensive survey of inorganic carbon distributions in the global ocean in the 1990s (*4*). After completion of the U.S. field program in 1998, a 5-year effort was begun to compile and rigorously quality-control the U.S. and international data sets, including a few pre-WOCE data sets in regions that were data limited (*5*). The final data set consists of 9618 hydrographic stations collected on 95 cruises, which represents the most accurate and comprehensive view of the global ocean inorganic carbon distribution available (*6*). As individual basins were completed, the ocean tracer–based ΔC* method (*7*) was used to separate the anthropogenic CO_2 component from the measured DIC concentrations (*8–10*). Here we synthesize the individual ocean estimates to provide an ocean data-constrained global estimate of the cumulative oceanic sink for anthropogenic CO_2 for the period from ~1800 to 1994 (*11*).

Distribution and inventories of anthropogenic CO_2 in the ocean. The objectively gridded individual sample estimates were vertically integrated to produce the column inventory map shown in Fig. 1. Because the global survey had limited data coverage in the marginal basins and the Arctic Ocean (north of 65°N), these areas were excluded from the mapped regions. The cumulative oceanic anthropogenic CO_2 sink in 1994, for the ocean region shown in Fig. 1, is 106 ± 17 Pg C. Accounting for the excluded regions, we estimate a global anthropogenic CO_2 sink of 118 ± 19 Pg C. The uncertainty in the total inventory is based on uncertainties in the anthropogenic CO_2 estimates and mapping errors (*11*).

Figure 1 shows that this anthropogenic CO_2 is not evenly distributed throughout the oceans. The highest vertically integrated concentrations are found in the North Atlantic. As a result, this ocean basin stores 23% of the global oceanic anthropogenic CO_2, despite covering only 15% of the global ocean area (table S1). By contrast, the Southern Ocean south of 50°S has very low vertically integrated anthropogenic CO_2 concentrations, containing only 9% of the global inventory. More than 40% of the global inventory is found in the region between 50°S and 14°S

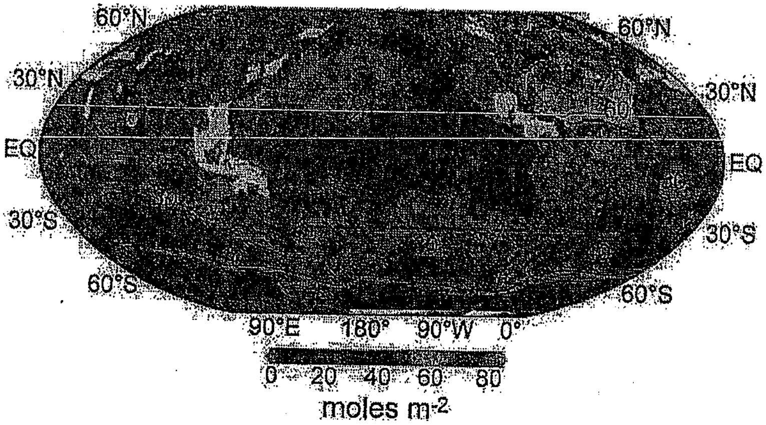

Fig. 1. Column inventory of anthropogenic CO_2 in the ocean (mol m^{-2}). High inventories are associated with deep water formation in the North Atlantic and intermediate and mode water formation between 30° and 50°S. Total inventory of shaded regions is 106 ± 17 Pg C.

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because of the substantially higher vertically integrated concentrations and the large ocean area in these latitude bands (Fig. 1, table S1). About 60% of the total oceanic anthropogenic CO_2 inventory is stored in the Southern Hemisphere oceans, roughly in proportion to the larger ocean area of this hemisphere.

Figure 2 shows the anthropogenic CO_2 distributions along representative meridional sections in the Atlantic, Pacific, and Indian oceans for the mid-1990s. Because anthropogenic CO_2 invades the ocean by gas exchange across the air-sea interface, the highest concentrations of anthropogenic CO_2 are found in near-surface waters. Away from deep water formation regions, the time scales for mixing of near-surface waters downward into the deep ocean can be centuries, and as of the mid-1990s, the anthropogenic CO_2 concentration in most of the deep ocean remained below the detection limit for the ΔC^* technique.

Variations in surface concentrations are related to the length of time that the waters have been exposed to the atmosphere and to the buffer capacity, or Revelle factor, for seawater (*12*, *13*). This factor describes how the partial pressure of CO_2 in seawater (PCO_2) changes for a given change in DIC. Its value is proportional to the ratio between DIC and alkalinity, where the latter term describes the oceanic charge balance. Low Revelle factors are generally found in the warm tropical and subtropical waters, and high Revelle factors are found in the cold high latitude waters (Fig. 3). The capacity for ocean waters to take up anthropogenic CO_2 from the atmosphere is inversely proportional to the value of the Revelle factor; hence, the lower the Revelle factor, the higher the oceanic equilibrium concentration of anthropogenic CO_2 for a given atmospheric CO_2 perturbation. The highest anthropogenic CO_2 concentrations (~60 μmol kg^{-1}) are found in the subtropical Atlantic surface waters because of the low Revelle factors in that region. By contrast, the near-surface waters of the North Pacific have a higher Revelle factor at comparable latitudes and consequently lower anthropogenic CO_2 concentrations primarily because North Pacific alkalinity values are as much as 100 μmol kg^{-1} lower than those in the North Atlantic (Fig. 3).

About 30% of the anthropogenic CO_2 is found at depths shallower than 200 m and nearly 50% at depths above 400 m. The global average depth of the 5 μmol kg^{-1} contour is ~1000 m. The majority of the anthropogenic CO_2 in the ocean is, therefore, confined to the thermocline, i.e., the region of the upper ocean where temperature changes rapidly with depth. Variations in the penetration depth of anthropogenic CO_2 are dete mined by how rapidly the anthropogenic CO that has accumulated in the near-surface waters is transported into the ocean interior. This transport occurs primarily along surfaces of constant density called isopycnal surfaces.

The deepest penetrations are associated with convergence zones at temperate latitudes where water that has recently been in contact with the atmosphere can be transported into the ocean interior. The isopycnal surfaces in these regions tend to be thick and inclined, providing a pathway for the movement of anthropogenic CO_2-laden waters into the ocean interior. Low vertical penetration is generally observed in regions of upwelling, such as the Equatorial Pacific, where intermediate-depth waters, low in anthropogenic CO_2, are transported toward the surface. The isopycnal layers in the tropical thermoclin tend to be shallow and thin, minimizing the movement of anthropogenic CO_2-laden waters into the ocean interior.

Figure 4A shows the distribution of anthropogenic CO_2 on a relatively shallow isopycnal surface (see depths in Fig. 2) with a potential density (σ_θ) of 26.0. About 20% of the anthropogenic CO_2 is stored in waters with potential densities equal to or less than that of this surface. The highest concentrations are generally found closest to where this density intersects the surface, an area referred to as the outcrop. Concentrations decrease away from these outcrops in the Indian and Pacific oceans, primarily reflecting the aging of these waters, i.e., these waters were exposed to lower atmospheric CO_2 concentrations when they were last in contact with the atmosphere. The Atlantic waters do not show this trend because the 26.0 σ_0 surface is much shallower and therefore relatively well connected to the ventilated surface waters throughout most of the Atlantic (Figs. 2A and 4A).

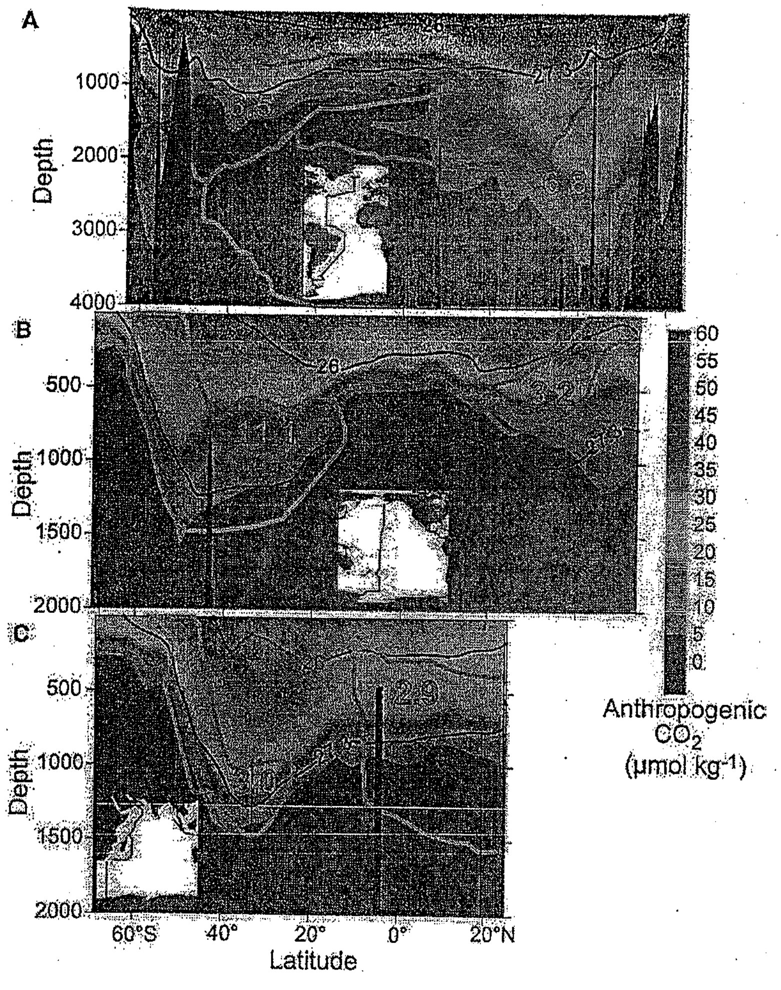

Fig. 2. Representative sections of anthropogenic CO_2 (μmol kg^{-1}) from (A) the Atlantic, (B) Pacific, and Indian (C) oceans. Gray hatched regions and numbers indicate distribution of intermediate water masses (and North Atlantic Deep Water) on the given section and the total inventory of anthropogenic CO_2 (Pg C) within these water masses. The southern water masses in each ocean represent Antarctic Intermediate Water. The northern water masses represent the North Atlantic Deep Water (A), North Pacific Intermediate Water (B), and Red Sea/Persian Gulf Intermediate Water (C). The two bold lines in each panel give the potential density [σ_θ = (density − 1) × 1000] contours for the surfaces shown in Fig. 4. Insets show maps of the cruise tracks used. Note that the depth scale for (A) is twice that of the other figures, reflecting the deeper penetration in the North Atlantic.

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The formation and transport of mode and intermediate waters is the primary mechanism for moving anthropogenic CO_2 to intermediate depths. The spatial distribution of anthropogenic CO_2 in these intermediate waters is illustrated with the 27.3 σ_θ surface (Fig. 4B), whose mean depth is about 900 m. As with the 26.0 σ_θ surface, anthropogenic CO_2 concentrations decrease away from the outcrop. On this deeper surface, however, slower ventilation results in stronger gradients and large areas where the anthropogenic CO_2 is below detection level. The Atlantic contains substantially higher anthropogenic CO_2 concentrations on the 27.3 σ_θ surface than the other basins, due in part to faster ventilation, but also because of the more favorable Revelle factor. Although the formation of intermediate, mode, and deep waters provides the primary mechanism for moving anthropogenic CO_2 into the ocean interior, the magnitude and distribution of the anthropogenic signal can be quite different depending on the nature of the water mass. As examples, some of the dominant intermediate water masses are outlined in Fig. 2 (*14*).

Antarctic Intermediate Water (AAIW) is formed in the Southern Ocean from upwelled Circumpolar Deep Water in the vicinity of the Subantarctic Front between 45° and 55°S and is then subducted and transported northward at intermediate depths. Immediately north of the AAIW, sub-Antarctic Mode Water (SAMW) forms north of the sub-Antarctic Front and contains a greater component of subtropical water than AAIW and is also subducted into the main thermocline of the ocean interior. While at the surface, these water masses appear to take up large amounts of anthropogenic CO_2 from the atmosphere as a result of both high wind speeds enhancing gas transfer and low initial anthropogenic CO_2 content. These subducted intermediate and mode waters contain high concentrations of anthropogenic CO_2, which are transported equatorward and downward, as clearly evidenced by the deepening of anthropogenic CO_2 penetration in Fig. 2. This transport plus the large volumetric contribution of the water masses to the Southern Hemisphere thermocline leads to high anthropogenic CO_2 inventories, estimated to exceed 20 Pg C (*14*).

About 3.2 Pg of anthropogenic carbon is found in the North Pacific Intermediate Water (NPIW). Unlike the AAIW that typically delineates the lower limit of the anthropogenic penetration, a substantial amount of anthropogenic CO_2 can be found deeper than the NPIW at the latitude of the section shown in Fig. 2B. NPIW is not the only intermediate-type water mass formed in the North Pacific, and the complex interplay of different intermediate-type waters in the North Pacific makes it difficult to attribute the anthropogenic signal to any one specific intermediate water mass in this region.

Nearly 3 Pg C can be found in the intermediate waters of the northern Indian Ocean (Fig. 2C). The Indian Ocean differs from the other oceans because of its land-locked northern boundary. Anthropogenic CO_2 in the tropical north Indian Ocean generally penetrates deeper than in the tropical Atlantic and Pacific. This primarily reflects the introduction of relatively young, dense waters that are high in anthropogenic CO_2 from the Red Sea and the Persian Gulf (*8*, *15–16*). Excess evaporation in these regions increases the salinity and density of the waters, which sink and carry the anthropogenic CO_2 with them. As these waters flow into the northern Indian Ocean at intermediate depths, they mix and spread equatorward across the northern Indian Ocean.

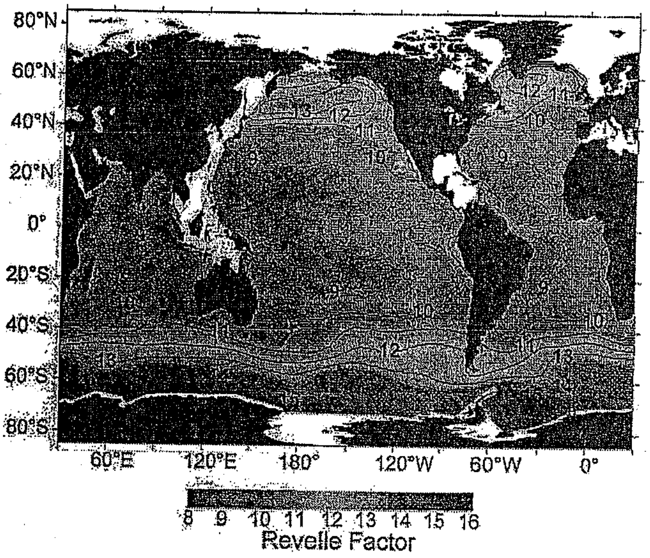

Fig. 3. Map of the 1994 distribution of Revelle factor, $(\delta P_{CO_2}/\delta DIC)/(P_{CO_2}/DIC)$, averaged for the upper 50 m of the water column. A high Revelle factor indicates that, for a given atmospheric CO_2 perturbation, the oceanic equilibrium concentration of anthropogenic CO_2 will be lower than that for low–Revelle factor waters. The current Revelle factors are about one unit higher than they were in the preindustrial ocean.

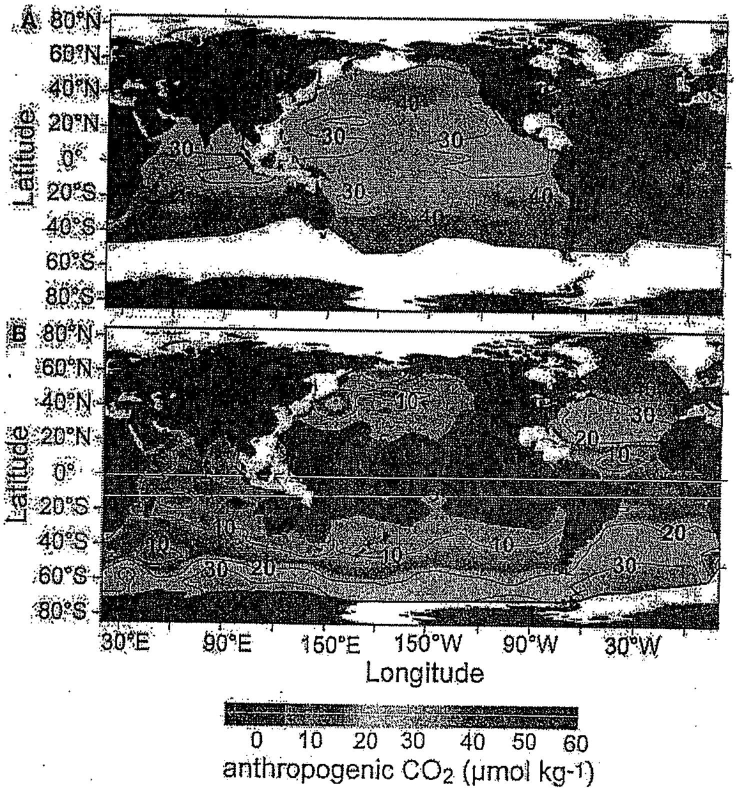

Fig. 4. Maps of anthropogenic CO_2 on the (A) 26.0 and (B) 27.3 potential density surfaces. Bold lines at the edge of the colored region indicate areas where the density surface outcrops. The highest values are generally observed closest to the outcrop and decrease toward the equator.

2-558

Globally, only 7% of the total anthropogenic CO_2 is found deeper than 1500 m. The only place where large concentrations of anthropogenic CO_2 penetrate to mid and abyssal depths is the North Atlantic, as a result of the formation and downward spreading of Labrador Sea Water and North Atlantic Deep Water (NADW). Moving southward away from the formation region, the concentration of anthropogenic CO_2 in NADW decreases because the older waters were exposed to lower atmospheric CO_2 perturbations, and because of mixing with adjacent bottom waters containing little or no anthropogenic CO_2. In total, nearly 7 Pg of anthropogenic carbon is associated with NADW (*14*). Thus, NADW contains substantially less anthropogenic CO_2 than AAIW, even though NADW has a tremendous impact on the large-scale circulation of the ocean.

There is little anthropogenic CO_2 associated with Antarctic Bottom Water, although exact reconstructions of the anthropogenic CO_2 concentration in this water mass were hampered because of limited carbon data available in regions where these bottom waters are forming. The low anthropogenic CO_2 inventories in these water masses are thought to result from a very high Revelle factor (Fig. 3), the limited contact with the surface before being transported into the ocean interior, and the physical barriers to CO_2 uptake from the presence of sea-ice (*17*). In addition, the anthropogenic CO_2 signals acquired at the surface are quickly diluted with older waters that contain no anthropogenic CO_2 as they sink into the abyssal ocean.

Because most of the deep ocean waters have not been in contact with the atmosphere during the anthropocene (*18*), the 1994 inventory of anthropogenic CO_2 in the ocean is only ~15% of the inventory it would have if the average surface concentration of anthropogenic CO_2 (56 μmol kg^{-1}) were found throughout the ocean. This scenario, however, does not account for the Revelle factor, which makes the uptake capacity of the deep and intermediate waters much lower than that of the surface waters. Calculating the DIC increase from an 80 parts per million (ppm) change in global ocean PCO_2 values (equivalent to the 1994 atmospheric CO_2 increase from preindustrial) implies that the 1994 inventory is ~30% of the ocean potential at that time.

The ocean's role in the global carbon cycle. The global ocean inventory estimated here permits us, for the first time, to place observational constraints on the anthropogenic CO_2 budget for the anthropocene. In particular, it permits us to estimate the magnitude of the time-integrated terrestrial carbon balance, which cannot be easily deduced from observations. We first consider the anthropogenic budget terms that are relatively well constrained. Over the anthropocene, about 244 ± 20 Pg C was emitted into the atmosphere as a result of the burning of fossil fuels and cement production (*19*) (Table 1). About two-thirds of these emissions have remained in the atmosphere, increasing the atmospheric CO_2 concentration from about 281 ± 2 ppm in 1800 (*20*) to 359 ± 0.4 ppm in 1994 (*21*), which translates to an increase of 165 Pg C. Subtracting our ocean inventory estimate of 118 ± 19 Pg C and the atmospheric inventory change from the integrated fossil-fuel emissions constrains the net carbon balance of the terrestrial biosphere to be a net source of 39 ± 28 Pg C for the period between 1800 and 1994. Therefore, the ocean has constituted the only true net sink for anthropogenic CO_2 over the past 200 years. Without this oceanic uptake, atmospheric CO_2 would be about 55 ppm higher today than what is currently observed (~380 ppm).

The terrestrial net source represents a balance between CO_2 emissions from land-use change, and an uptake of CO_2 by the terrestrial biosphere. Emissions from land-use change are ill-constrained. By comparing carbon storage between potential natural vegetation and present-day land cover, de Fries *et al.* (*22*) estimated a total loss of about 180 to 200 Pg C since the mid-holocene. Using a carbon accounting model for land-use change, Houghton and Hackler (*2*) estimated a carbon loss of about 143 Pg C for the period from 1850 to 1994, with an uncertainty of about 50%. Extrapolating their estimate back to 1800 gives a loss of about 160 Pg C for the anthropocene. Comparisons of land-use change emissions between different estimates for the past two decades reveal, however, that Houghton and Hackler's estimates tend to be nearly twice as large as those of others (*23*). Taking this factor into account and the large uncertainty associated with these estimates, we adopt a range of 100 to 180 Pg C for land-use change emissions between 1800 and 1994. With this range, we infer that the terrestrial biosphere must have taken up between 61 and 141 Pg C from the atmosphere over the anthropocene.

Table 1. Anthropogenic CO_2 budget for the anthropocene (1800 to 1994) and for the decades of the 1980s and 1990s.

CO_2 sources and sinks	1800 to 1994 (Pg C)*	1980 to 1999 (Pg C)¶
Constrained sources and sinks		
(1) Emissions from fossil fuel and cement production	244† ± 20	117 ± 5
(2) Storage in the atmosphere	−165‡ ± 4	−65 ± 1
(3) Uptake and storage in the ocean	−118§ ± 19	−37 ± 8
Inferred net terrestrial balance		
(4) Net terrestrial balance = [−(1) − (2) − (3)]	39 ± 28	−15 ± 9
Terrestrial balance		
(5) Emissions from land-use change	100 to 180‖	24 ± 12
(6) Terrestrial biosphere sink = [−(1) − (2) − (3)] − (5)	−61 to −141	−39 ± 18

*Errors as estimated by respective sources; errors of sums and differences are calculated by quadratic error propagation. †From (*19*), with an error estimate of ±8%. ‡Calculated from the change in atmospheric PCO_2 (1800: 281 ± 2 ppm; 1994: 359 ± 0.4 ppm). §This study includes anthropogenic CO_2 storage in marginal seas and the Arctic Ocean. ‖Based on (*2*); see text for details. ¶From (*23*), integrated for the period 1980 to 1999.

It is interesting to contrast this anthropogenic CO_2 budget over the anthropocene with that over the past two decades (*23*). Note that the emissions from fossil fuel ar cement production in the decades of ti. 1980s and 1990s are nearly half of the anthropocene emissions (Table 1). The airborne fraction, i.e., the fraction of the combined fossil-fuel and land-use emissions that remains in the atmosphere, is statistically indistinguishable between the two periods, i.e., 39 to 48% for the anthropocene versus ~46% for 1980 to 1999 (Table 1). There is an indication, although not statistically significant, that the ocean-uptake fraction has decreased from 28 to 34% to about 26%, whereas the sink strength of the terrestrial biosphere appears to have remained constant within the large uncertainty bounds (18 to 33% versus 28%).

Future changes. On the time scales of several thousands of years, it is estimated that ~90% of the anthropogenic CO_2 emission will end up in the ocean (*24*). Because of the slow mixing time of the ocean, however, the current oceanic uptake fraction is only about one-third of this value. Studies of the coupled carbon-climate system have suggested that on decadal time scales, the ocean may become a less efficient sink for anthropogenic CO_2 because of positive feedbacks in the coupled carbon-climate system (*25*)—consistent with the suggestion of a decreasing ocean-uptake fraction noted from Table 1.

There is a potential for both positive and negative feedbacks between the ocean and atmosphere, including changes in both the physics (e.g., circulation, stratification) and biology (e.g., export production, calcification) of the ocean. These processes are still not well understood. On the time scales of decades to centuries, however, most of the known chemical feedbacks are positive. If the surface ocean PCO_2 concentrations continue to increase in proportion with the atmospheric CO_2 increase, a doubling of atmospheric

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CO_2 from preindustrial levels will result in a 30% decrease in carbonate ion concentration and a 60% increase in hydrogen ion concentration. As the carbonate ion concentration decreases, the Revelle factor increases and the ocean's ability to absorb more CO_2 from the atmosphere is diminished. The impact of this acidification can already be observed today and could have ramifications for the biological feedbacks in the future (*26*). If indeed the net feedbacks are primarily positive, the required socioeconomic strategies to stabilize CO_2 in the future will be much more stringent than in the absence of such feedbacks. Future studies of the carbon system in the oceans should be designed to identify and quantitatively assess these feedback mechanisms to provide input to models that will determine the ocean's future role as a sink for anthropogenic CO_2.

References and Notes

1. P. J. Crutzen, E. F. Stoermer, *Global Change Newslett.* 41, 12 (2000).
2. R. A. Houghton, J. L. Hackler, in *Trends: A Compendium of Data on Global Change* (Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, TN, 2002), http://cdiac.esd.ornl.gov/trends/landuse/houghton/houghton.html.
3. C. Prentice *et al.*, in *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, J. T. Houghton *et al.*, Eds. (Cambridge Univ. Press, New York, 2001), pp. 183–237.
4. D. W. R. Wallace, in *Ocean Circulation and Climate*, G. Siedler, J. Church, W. J. Gould, Eds. (Academic Press, San Diego, CA, 2001), pp. 489–521.
5. R. M. Key *et al.*, in preparation.
6. Bottle data and 1° gridded distributions are available through the GLODAP Web site (http://cdiac.esd.ornl.gov/oceans/glodap/Glodap_home.htm).
7. N. Gruber, J. L. Sarmiento, T. F. Stocker, *Global Biogeochem. Cycles* 10, 809 (1996).
8. C. L. Sabine *et al.*, *Global Biogeochem. Cycles* 13, 179 (1999).
9. C. L. Sabine *et al.*, *Global Biogeochem. Cycles* 16, 1083, 10.1029/2001GB001639 (2002).
10. K. Lee *et al.*, *Global Biogeochem. Cycles* 17, 1116, 10.1029/2003GB002067 (2003).
11. Materials and methods are available as supporting material on *Science* Online.
12. R. Revelle, H. E. Suess *Tellus* 9, 18 (1957).
13. T. Takahashi, J. Olafsson, J. G. Goddard, D. W. Chipman, S. C. Sutherland, *Global Biogeochem. Cycles* 7, 843 (1993).
14. Five intermediate water masses and NADW were defined using the following temperature (T) and salinity (S) properties: Pacific AAIW: $33.8 < S < 34.5$ and $2 < T < 10$; NPIW: $S < 34.3$ and $5 < T < 12$; Indian AAIW: $33.8 < S < 34.5$ and $2 < T < 10$; Red Sea Water: $S > 34.8$ and $5 < T < 14$; Atlantic AAIW: $33.8 < S < 34.8$ and $2 < T < 6$; NADW: $34.8 < S < 35$ and $1.5 < T < 4$. Water mass inventories were determined by summing up the gridded anthropogenic CO_2 values within a region defined by the T and S limits using the Levitus World Ocean Atlas 2001 salinity and temperature fields.
15. A. Papaud, A. Poisson, *J. Mar. Res.* 44, 385 (1986).
16. S. Mecking, M. Warner, *J. Geophys. Res.* 104, 11087 (1999).
17. A. Poisson, C.-T. A. Chen, *Deep-Sea Res. Part A* 34, 1255 (1987).
18. M. Stuiver, P. D. Quay, H. G. Ostlund, *Science* 219, 849 (1983).
19. G. Marland, T. A. Boden, R. J. Andres, in *Trends: A Compendium of Data on Global Change* (Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, TN, 2003), http://cdiac.esd.ornl.gov/trends/emis/meth_reg.htm.
20. D. M. Etheridge *et al.*, *J. Geophys. Res.* 101, 4115 (1996).
21. C. D. Keeling, T. P. Whorf, in *Trends: A Compendium of Data on Global Change* (Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, TN, 2004), http://cdiac.esd.ornl.gov/trends/co2/sio-keel.htm.
22. R. S. de Fries, C. B. Field, I. Fung, G. J. Collatz, L. Bounoua, *Global Biogeochem. Cycles* 13, 803 (1999).
23. C. L. Sabine *et al.*, in *The Global Carbon Cycle: Integrating Humans, Climate, and the Natural World. SCOPE 62*, C. B. Field, M. R. Raupach, Eds. (Island Press, Washington, DC, 2004), pp. 17–44.
24. D. E. Archer, H. Kheshgi, E. Maier-Reimer, *Global Biogeochem. Cycles* 12, 259 (1998).
25. N. Gruber *et al.*, in *The Global Carbon Cycle: Integrating Humans, Climate, and the Natural World. SCOPE 62*, C. B. Field, M. R. Raupach, Eds. (Island Press, Washington, DC, 2004), pp. 45–76.
26. R. A. Feely *et al.*, *Science* 305, 362 (2004).
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Supporting Online Material
www.sciencemag.org/cgi/content/full/305/5682/367/DC1
Materials and Methods
Fig. S1
Table S1

2 March 2004; accepted 8 June 2004

Mapping the Antigenic and Genetic Evolution of Influenza Virus

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The antigenic evolution of influenza A (H3N2) virus was quantified and visualized from its introduction into humans in 1968 to 2003. Although there was remarkable correspondence between antigenic and genetic evolution, significant differences were observed: Antigenic evolution was more punctuated than genetic evolution, and genetic change sometimes had a disproportionately large antigenic effect. The method readily allows monitoring of antigenic differences among vaccine and circulating strains and thus estimation of the effects of vaccination. Further, this approach offers a route to predicting the relative success of emerging strains, which could be achieved by quantifying the combined effects of population level immune escape and viral fitness on strain evolution.

Much of the burden of infectious disease today is caused by antigenically variable pathogens that can escape from immunity induced by prior infection or vaccination. The degree to which immunity induced by one strain is effective against another is mostly dependent on the antigenic difference between the strains; thus, the analysis of antigenic differences is critical for surveillance and vaccine strain selection. These differences are measured in the laboratory in various binding assays (*1–3*). Such assays give an approximation of antigenic differences, but are generally considered unsuitable for quantitative analyses. We present a method, based on the fundamental ideas described by Lapedes and Farber (*4*), that enables a reliable quantitative interpretation of binding assay data, increases the resolution at which antigenic differences can be determined, and facilitates visualization and interpretation of antigenic data. We used this method to study quantitatively the antigenic evolution of influenza A (H3N2) virus, revealing both similarities to, and important differences from, its genetic evolution.

Influenza viruses are classic examples of antigenically variable pathogens and have a seemingly endless capacity to evade the immune response. Influenza epidemics in humans cause an estimated 500,000 deaths worldwide per year (*5*). Antibodies against the viral surface glycoprotein hemagglutinin (HA) provide protective immunity to influenza virus infection, and this protein is therefore the primary component of influenza vaccines. However, the antigenic structure of HA has changed significantly over time, a process known as antigenic drift (*6*), and in most years, the influenza vaccine has to be up

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Effect of increased atmospheric CO_2 on shallow water marine benthos

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[1] The decision to sequester CO_2 in the deep ocean should ultimately be based not only upon what would happen to deep sea marine biota but also upon what would happen to surface organisms if nothing were done to limit atmospheric CO_2. Thus such a decision should be based on a proper understanding of long-term chronic effects, from the global-scale perturbation in near-surface ocean CO_2, in addition to acute effects, from large local increases in CO_2 caused by purposeful sequestration. Here we focus on the long-term chronic effects of CO_2 on shallow water benthic organisms that have calcium carbonate shells. With two duplicate 6 month manipulative experiments, we demonstrate that a 200 ppm increase in CO_2 adversely affects the growth of both gastropods and sea urchins. Thus even moderate increases in atmospheric CO_2 that could well be reached by the middle of this century will adversely affect shallow water marine benthic organisms. This provides another reason, beyond concerns for climate, to enhance efforts to limit increases in atmospheric CO_2 to the lowest possible levels.

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1. Introduction

[2] As one option of mitigating rapid increasing atmospheric CO_2, it has been proposed to sequester CO_2 in the deep sea [*Handa and Ohsumi*, 1995; *Haugan and Drange*, 1992; *Herzog and Edmond*, 1994; *Hoffert et al.*, 1979; *Kita and Ohsumi*, 2004; *Marchetti*, 1977; *Ohsumi*, 2004]. Higher concentrations of CO_2 in seawater that would come with purposeful ocean sequestration suggests that marine organisms could be affected [*Barry et al.*, 2004; *Carman et al.*, 2004; *Ormerod and Angel*, 1996; *Omori et al.*, 1998; *Takeuchi et al.*, 1997; *Shirayama*, 1997]. However, related physiological studies of the impacts of high CO_2 on deep sea organisms are inadequate to estimate related ecological impacts.

[3] During the 21st century, atmospheric CO_2 is likely to increase by more than 200 ppm; without serious reduction of fossil fuel emissions, the increase could be as high as 2000 ppm [*Intergovernmental Panel on Climate Change* (*IPCC*), 2001]. Increasing atmospheric CO_2 leads to lower surface ocean pH. We may thus speak of an acidification of the surface seawater (i.e., an increase in the number of hydrogen ions [H^+]) although surface ocean seawater will almost certainly never become acidic (pH < 7). Such acidification could affect shallow water organisms [*Ishimatsu et al.*, 2004; *Kurihara et al.*, 2004; *Pörtner et al.*, 2004]. Some may consider an increase of atmospheric CO_2 by 200 ppm to be moderate, but even that may produce chronic health problems in shallow water marine organisms. *Riebesell et al.* [2000] found notable effects of increased CO_2 concentrations on coccolithophores [*Riebesell*, 2004]. Here we focus on the effects on marine organisms exposed for 6 months to surface seawater in contact with atmospheric CO_2 of 560 ppm. This represents a 200 ppm increase above today's level, which is what the *IPCC* [2001] proposed would need to be maintained to avoid catastrophic climatic change. We focus our study on the potential impacts of elevated CO_2 at this level on shallow water benthos.

[4] Regardless of whether global warming occurs, increases in atmospheric CO_2 concentration will result in a decrease in seawater pH. As a result, it is likely that organisms with calcium carbonate shells will be affected more than others [*Shirayama*, 1997], because making calcium carbonate shells is one of the biological processes that are the most sensitive to the acidification of the seawater. In the present paper, we studied some marine organisms that have $CaCO_3$ skeletons, namely gastropods and sea urchins. Unfortunately few studies have focused on the effects of increasing CO_2 on these organisms [e.g., *Knutzen*, 1981; *Bamber*, 1990; *Adams et al.*, 1997]. Here we have used long-term exposure experiments, to evaluate if increased atmospheric CO_2 and the associated change in surface water pH will affect the growth rate and mortality of these shallow water species.

2. Materials and Methods

[5] The gastropod *Strombus luhuanus* and two sea urchins, *Hemicentrotus pulcherrimus* and *Echinometra mathaei*, were chosen as representative near-shore calcareous species. We used juveniles (<1 year old) to be able to evaluate possible changes in growth rate. We made two experiments under nearly identical conditions. However, in the second experiment, seawater temperatures were higher and initial animal body size was larger. At the beginning of

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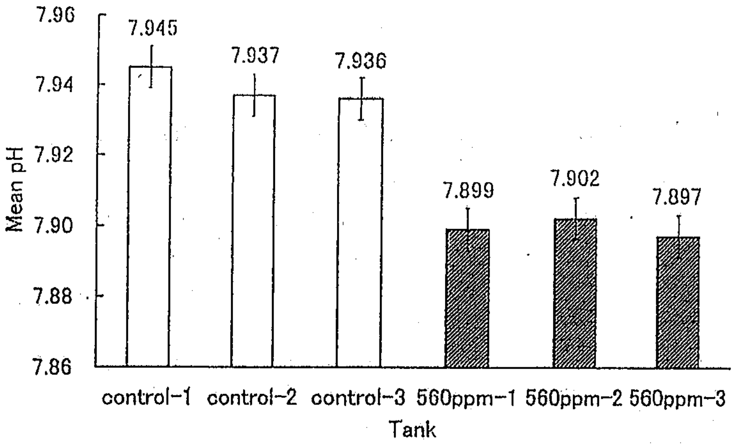

Figure 1. Mean pH of seawater in the control and high-CO_2 tanks.

these two experiments, the mean body size of *Strombus luhuanus* was 22 mm (experiment 1) and 24 mm (experiment 2) in terms of shell height; corresponding wet shell weights were 1.9 and 2.6 g. Mean body weights of *Hemicentrotus pulcherrimus* and *Echinometra mathaei* at the beginning of experiment 1 were 0.84 and 2.7 g, whereas in the experiment 2, they were 4.1 and 8.5 g.

[6] Thirty individuals (ten individuals for each species) were kept in one 30 L tank. Six tanks were prepared and hooked up to individual aeration systems. Three tanks were supplied with air to which an additional 200 ppm of CO_2 was added. The other three tanks were used as controls, i.e., they were supplied with ambient air flowing at the same rate, but with no additional CO_2. Food (sea weed and chopped krill) was supplied twice a day so that it would not be limiting. Approximately two thirds of the seawater was changed once a week using natural seawater pumped up through the subtidal intake situated near our coastal laboratory. Light exposure was not controlled. Seawater temperature was not controlled except during mid summer when it was not allowed to go beyond 30°C.

[7] Tank water pH and temperature were measured once a day. We recorded the deaths of individuals and subsequently removed them from the tanks. All individuals were marked and their growth was monitored. Once every two weeks, we measured the shell height of each snail with a slide gauge. We also measured the wet weight of the snails and the sea urchins with a digital balance. After these measurements, animals were returned to their tanks.

3. Results

3.1. Physical Data of Sea Water

[8] Throughout the first experiment, the mean water pH in the high-CO_2 tanks was significantly lower than in the control tanks (t-test, $p < 0.05$), although the difference was only 0.03 (Figure 1). Similar differences in pH were observed in the second experiment. The temperature of the seawater fluctuated with the natural conditions. In experiment 1, it ranged from 20.0° to 23.9°C, and in experiment 2, it ranged from 24.1° to 25.5°C. In both experiments, there was no significant difference in the mean water temperature among high-CO_2 and control tanks (t-test, $p > 0.05$). We used natural sea water pumped up from the subtidal zone (2 m water depth) off the shore close to our laboratory. The DIC in the control tank of the first experiment was measured as 1990 μmol/L.

3.2. Survival

[9] In the first experiment, all animals remained alive for 6 months in the control tanks. This suggests that the culture conditions were suitable for carrying out these long-term experiments (Figure 2a). In the high-CO_2 tanks, however, several individuals died after just the 10th week. For *Hemicentrotus pulcherrimus*, which proved the most sensitive to the elevated CO_2, eight individuals (27%), died before the end of experiment. For *Echinometra mathaei*, one individual died during week 14, and three individuals (10%) died before the end of experiment. For the snail *Strombus luhuanus* no individuals died during the first 20 weeks; yet three individuals (10%) died by the end of the experiment (Figure 2b).

[10] In the second experiment, survival rates for both gastropods and sea urchins in the high-CO_2 tanks were not significantly less than those in the control tanks. For the control tanks, one *Hemicentrotus pulcherrimus* individual (3.3% of the population) died during week 10, and one gastropod (3.3%) died during week 14 (Figure 3a). In the high-CO_2 tanks, one *Echinometra mathaei* individual (3.3%) died during week 8, and another two individuals (10%) died by the end of experiment. Only one individual (3.3%) of *Hemicentrotus pulcherrimus* died during week 26. For the gastropod, one individual (3.3%) died during week 8 and another one died during week 20 (Figure 3b).

3.3. Growth

[11] The growth of each individual was calculated as a percentage of relative growth 100 × ((value at time T) − (initial value))/(initial value). For example, if an animal were to double its weight, the relative growth rate would be 100%.

[12] The impact of elevated CO_2 on marine organisms was more evident in terms of growth rate than in terms of

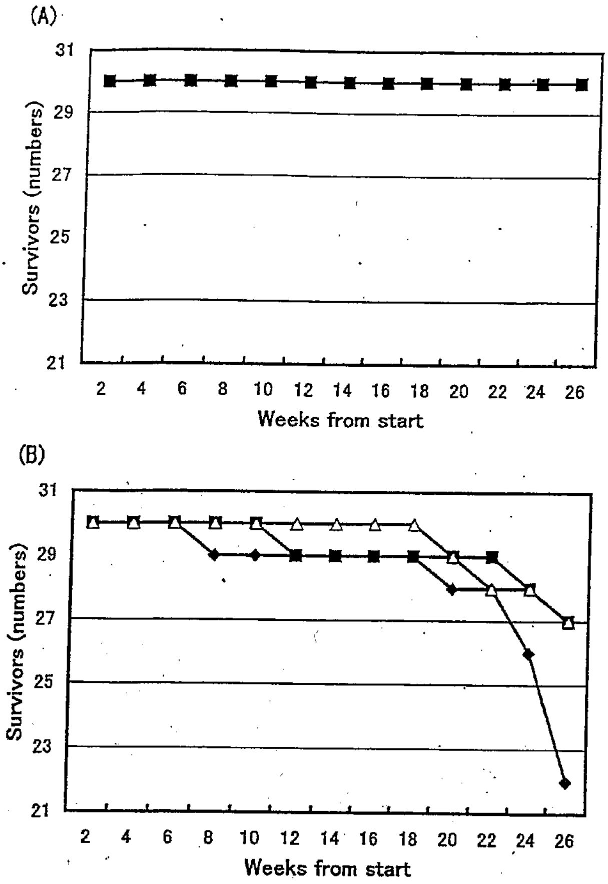

Figure 2. Survival of animals in (a) the control tanks and (b) the high-CO_2 tanks in experiment 1 (filled diamond, sea urchin *Hemicentrotus pulcherrimus*; filled square, sea urchin *Echinometra mathaei*; open triangle, snail *Strombus luhuanus*). The survival rates of animals in the high-CO_2 tanks were significantly lower than in the control tanks (two-way ANOVA, $F = 10.3$, $p = 0.0075$).

mortality rate. Under both control and high-CO_2 conditions, *Hemicentrotus pulcherrimus* grew at the same rate for 12 weeks during the first part of experiment 1. From week 14 onward, the wet weights of these animals were lower in the high-CO_2 tanks than in the control tanks (Figure 4a). In the second experiment, growth in the control and high-CO_2 tank were similar until week 14. Growth rate diverged in week 16 with animals in the high-CO_2 tank weighing significantly less than those in the control tank. After week 22, growth continued in the control tanks, but there was no significant growth in the high-CO_2 tanks (Figure 4b).

[13] The effect of elevated CO_2 on growth rate was most pronounced in *Echinometra mathaei*. During the first 12 weeks of the first experiment, there was no difference in the growth rate between the control and high-CO_2 tanks; the same was found for *Hemicentrotus pulcherrimus* (see above). Afterward, *E. mathaei* continued to grow in the control tanks, but not in the high-CO_2 tanks (Figure 5a). In the second experiment, differences in growth rates were not significant during the first 14 weeks. After week 16, animals in the control tank continued to grow, whereas the size of those in the high-CO_2 tank actually diminished. At the end of the experiment, the mean wet weight in the high-CO_2 tank was 8% less than at the beginning of the experiment (Figure 5b). A final visual inspection revealed that these sea urchin shells had become so brittle that they were easily broken during handling. Thinning of the calcium carbonate tests of the sea urchins in the high-CO_2 tank might explain part of their loss in body weight.

[14] For *Strombus luhuanus*, we measured both shell height and wet weight of the whole individual. In the two experiments, like both species of sea urchins, the growth rates in the control and high-CO_2 tanks were not substantially different in the beginning of experiments but were statistically significant at the end of experiments. In the first experiment, both shell height (Figure 6a) and wet weight (Figure 6c) were not statistically different during the first 12 weeks. However, at week 14, average values of both shell height (t-test, $p < 0.05$) and wet weight (t-test, $p < 0.01$) were significantly larger in the control tank than in the

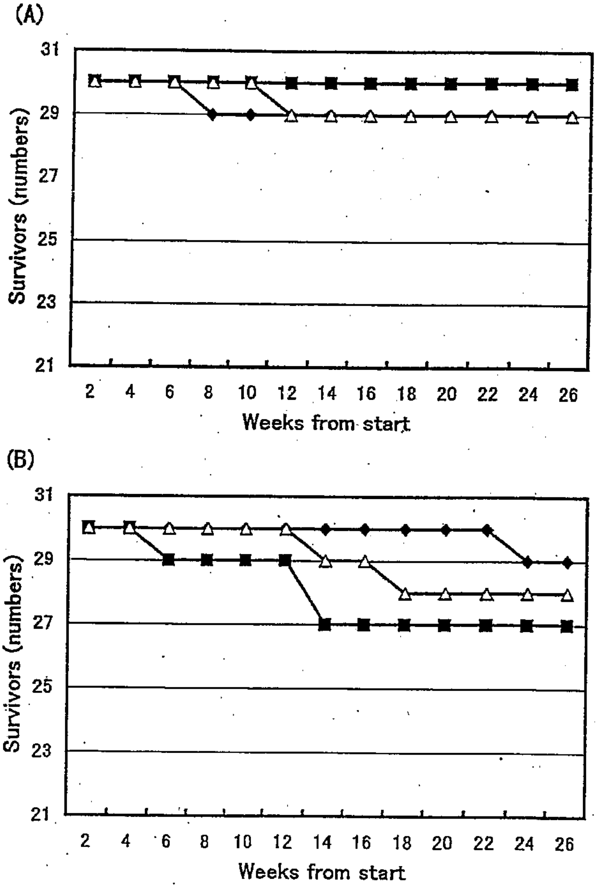

Figure 3. Survival of sea urchins in (a) the control tanks and (b) the high-CO_2 tanks in experiment 2 (filled diamond, *Hemicentrotus pulcherrimus*; filled square, *Echinometra mathaei*; open triangle, snail *Strombus luhuanus*). Survival rates of animals in the high-CO_2 tanks were not significantly lower than in the control tanks (two-way ANOVA, $F = 2.29$, $p = 0.16$).

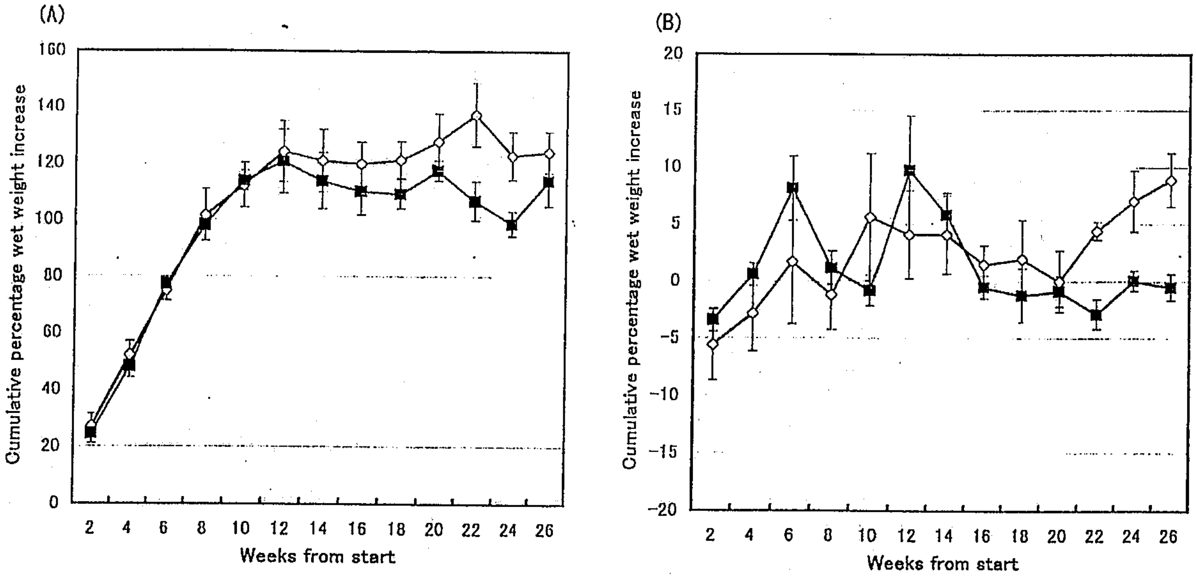

Figure 4. Relative growth rate from the wet weight of the sea urchin *Hemicentrotus pulcherrimus* (open symbol, control; filled symbol, higher CO_2 concentration) in experiments (a) 1 and (b) 2. A three-way ANOVA as a function of time (week 2–26), experiment (experiment 1 and 2), and treatment (control versus high CO_2) confirmed that increased CO_2 significantly decreased the growth rate of this sea urchin species ($F = 11.2, p < 0.001$). In addition, a significant difference was found between experiments 1 and 2 ($F = 3767, p < 0.0001$).

high-CO_2 tank, and the differences remained significant during the rest of the experiment. In the second experiment, the differences between control and elevated CO_2 conditions became statistically significant also at week 14 in the case of shell height (Figure 6b; *t*-test, $p < 0.001$). On the other hand, the differences of wet weight were significant as early as at week 8 (Figure 6d; *t*-test, $p < 0.01$). Throughout the rest of the experiment, both shell height and wet weight

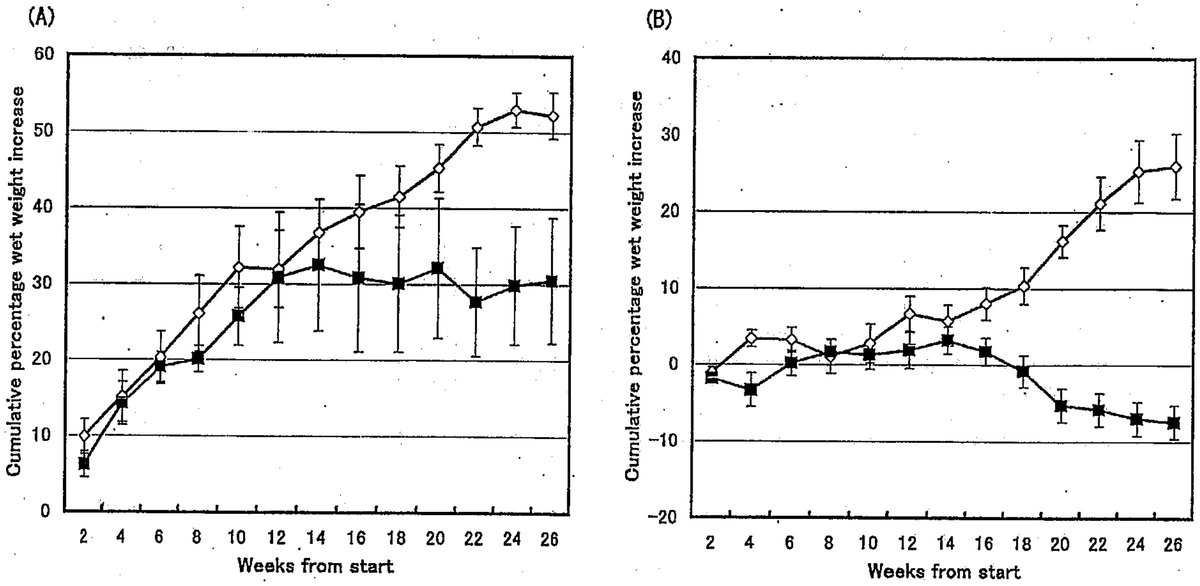

Figure 5. Relative growth rate based on the wet weight of the sea urchin *Echinometra mathaei* (open symbol, control; filled symbol, higher CO_2 concentration) in experiments (a) 1 and (b) 2. A three-way ANOVA as a function of time (week 2–26), experiment (experiment 1 and 2), and treatment (control versus high CO_2) confirmed increased CO_2 significantly decreased the growth rate ($F = 27.9, p < 0.0001$). There was also a significant difference between experiments 1 and 2 ($F = 283, p < 0.0001$).

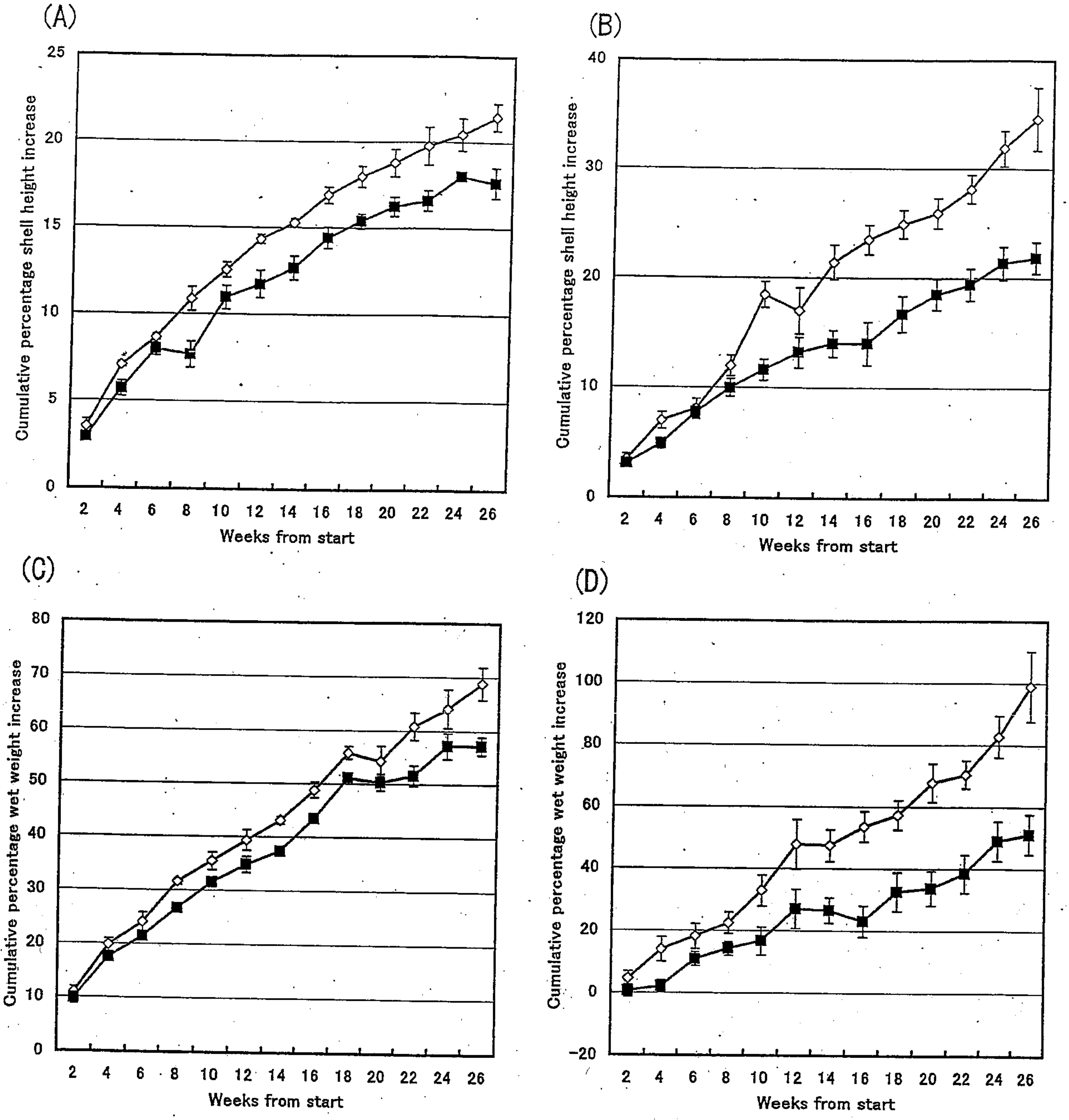

Figure 6. Relative growth rate based on shell height as well as wet weight for the snail *Strombus luhuanus* (open symbol, control; filled symbol, high CO_2) in experiments (a, c) 1 and (b, d) 2. A three-way ANOVA as a function of time (week 2–26), experiment (experiment 1 and 2), and treatment (control versus high CO_2) confirmed that increased CO_2 concentration significantly decreased the growth rate in terms of both shell height ($F = 57.0, p < 0.0001$) and wet weight ($F = 113, p < 0.0001$). There was also a significant difference between experiments 1 and 2 ($F = 30.9, p < 0.0001$ and $F = 37.9, p < 0.0001$, respectively).

were significantly larger in the control tank than in the high-CO_2 tank.

4. Discussion

[15] To our knowledge, only *Michaelidis et al.* [2005] have tried to elucidate the impact of small increases in atmospheric CO_2 concentration on marine organisms through a long-term study. They monitored the growth of a mussel species, *Mytilus galloprovincialis* for three months and found that the growth of the mussel was significantly reduced by moderate hypercapnia. Here we have shown that an atmospheric CO_2 increase of just 200 ppm would have negative consequences on the

growth rates of other groups of animals, gastropod and echinoids.

[16] Sea urchins were affected more by increased CO_2 than were snails. Sensitivity among these species differed significantly in both experiment 1 (three dimensional ANOVA: $F = 1045$, $p < 0.0001$) and experiment 2 (three dimensional ANOVA: $F = 302$, $p < 0.0001$). Differences may be partly explained by the larger surface area/body weight ratio of the sea urchins and their inability to regulate changes in their internal body condition, i.e., because of their direct connection with the ambient seawater through their madreporites. Moreover, sea urchin tests are made of high magnesian calcite, which is substantially more soluble than snail shells (calcite).

[17] If the influence of elevated CO_2 were limited to reduced calcification of the $CaCO_3$ test, the shells in the experimental tank should be thinner than in the control. However, the shell height should be the same because the physiological condition of the gastropods should not have been affected, and the animals should grow at the same rate. Yet we found that increased CO_2 affected both shell height and body mass, which suggests that increased CO_2 also affected the physiology of these organisms.

[18] Stronger effects were evident in experiment 2 relative to experiment 1. The only differences were that experiment 2 had larger animals and higher seawater temperatures. Animals with higher metabolic activity are more sensitive to elevated CO_2 [*Pörtner and Reipschläger*, 1996]. The metabolic activity of poikilothermal marine animals increases with an increase in seawater temperature. Both findings are consistent with our observation of the greater influence of higher CO_2 in experiment 2, which also had higher seawater temperature.

[19] The level of pCO_2 plays an important role not only because it affects the saturation state of $CaCO_3$, but probably even more so because of its effect on the cells of animals. In shallow water ecosystems, surface water pCO_2 is lower than that in the atmosphere as a result of daytime primary productivity of both phytoplankton and benthic macroalgae. At night this balance is reversed and pCO_2 becomes higher in the seawater than in the atmosphere due to the respiration of all organisms including plants. Thus in situ, animals under an atmospheric CO_2 of 560 ppm would experience even higher pCO_2 than in our controlled study, were they not also exposed to equivalent increases due to plant respiration. Such diurnal fluctuations will also need to be accounted for in future efforts to evaluate impacts of increasing CO_2 levels on the marine ecosystem.

[20] Our results rely on experiments using only a few species. We have ignored possible interactions between species that would occur under natural conditions. To understand the impact of elevated CO_2 on shallow water marine organisms at the ecosystem level, laboratory experiments are just a beginning. It would be desirable to carry out small-scale open-water CO_2 enrichment experiments.

[21] As with corals, elevated seawater temperatures must also affect benthic organisms [*Pörtner et al.*, 2004]. The combined effects due to elevated CO_2 and elevated temperature could have a larger impact than simply adding the two effects individually, particularly in regard to the species with calcium carbonate shells.

[22] Our results are inadequate by themselves to evaluate the impact of elevated CO_2 on shallow water marine benthic ecosystems. Nonetheless, they point out the high sensitivity of some marine organisms to what many may consider as moderate increases in atmospheric CO_2. This provides an added reason, beyond worries about climate, why there is an even more pressing need to thoroughly explore all opportunities to limit atmospheric levels of this greenhouse gas.

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References

Adams, E. E., J. A. Caulfield, H. Herzog, and D. I. Auerbach (1997), Impacts of reduced pH from ocean CO_2 disposal: Sensitivity of zooplankton mortality to model parameters, *Waste Manage.*, *17*, 375–380.

Bamber, R. N. (1990), The effects of acidic seawater on three species of lamellibranch mollusks, *J. Exper. Mar. Biol. Ecol.*, *143*, 181–191.

Barry, J., K. R. Buck, C. F. Lovera, L. Kuhnz, P. J. Whaling, E. T. Peltzer, P. Walz, and P. G. Brewer (2004), Effects of direct ocean CO_2 injection on deep-sea meiofauna, *J. Oceanogr.*, *60*, 759–766.

Carman, K. R., D. Thistle, J. W. Fleeger, and J. P. Barry (2004), Influence of introduced CO_2 on deep-sea metazoan meiofauna, *J. Oceanogr.*, *60*, 767–772.

Handa, N., and T. Ohsumi (Eds.) (1995), *Direct Ocean Disposal of Carbon Dioxide*, Terrapub, Tokyo.

Haugan, P. M., and H. Drange (1992), Sequestration of CO_2 in the deep ocean by shallow injection, *Nature*, *357*, 318–320.

Herzog, H. J., and J. Edmond (1994), Disposing of CO_2 in the ocean, *Spec. Publ. R. Soc. Chem.*, *153*, 329–337.

Hoffert, M. J., Y.-C. Wey, A. J. Callegari, and W. S. Broecker (1979), Atmospheric response to deep-sea injection of fossil fuel carbon dioxide, *Clim. Change*, *2*, 53–68.

Intergovernmental Panel on Climate Change (IPCC) (2001), *Third Assessment Report*, Cambridge Univ. Press, New York.

Ishimatsu, A., T. Kikkawa, M. Hayashi, K.-S. Lee, and J. Kita (2004), Effects of CO_2 on marine fish: Larvae and adults, *J. Oceanogr.*, *60*, 731–741.

Kita, J., and T. Ohsumi (2004), Perspectives on biological research for CO_2 ocean sequestration, *J. Oceanogr.*, *60*, 695–703.

Knutzen, J. (1981), Effects of decreased pH on marine organisms, *Mar. Pollut. Bull.*, *12*, 25–29.

Kurihara, H., S. Shimode, and Y. Shirayama (2004), Sub-lethal effects of elevated concentration of CO_2 on planktonic copepods and sea urchins, *J. Oceanogr.*, *60*, 743–750.

Marchetti, C. (1977), On geoengineering and the CO_2 problem, *Clim. Change*, *1*, 59–68.

Michaelidis, B., C. Ouzounis, A. Paleras, and H. O. Pörtner (2005), Effects of long-term moderate hypercapnia on acid-base balance and growth rate in marine mussels (*Mytilus galloprovincialis*), *Mar. Ecol. Prog. Ser.*, *293*, 109–118.

Ohsumi, T. (2004), Introduction: What is the ocean sequestration of carbon dioxide?, *J. Oceanogr.*, *60*, 693–694.

Omori, M., C. P. Norman, and T. Ikeda (1998), Ocean disposal of CO_2: Potential effects on deep-sea plankton and micronekton—A review, *Plankton Biol. Ecol.*, *45*, 87–99.

Ormerod, B., and M. Angel (Eds.) (1996), *Ocean Storage of Carbon Dioxide: Environmental Impact*, Int. Energy Agency Greenhouse Gas Res. and Develop. Prog., Cheltenham, U. K.

Pörtner, H. O., and A. Reipschläger (1996), Ocean disposal of anthropogenic CO_2: Physiological effects on tolerant and intolerant animals, in *Ocean Storage of CO_2: Environmental Impact*, edited by B. Ormerod and M. Angel, pp. 57–81, Int. Energy Agency Greenhouse Gas Res. and Develop. Prog., Cheltenham, U. K.

Pörtner, H. O., M. Langenbuch, and A. Reipschläger (2004), Biological impact of elevated ocean CO_2 concentration: Lessons from animal physiology and Earth history, *J. Oceanogr.*, *60*, 705–718.

Riebesell, U. (2004), Effects of CO_2 enrichment on marine phytoplankton, *J. Oceanogr.*, *60*, 719–729.

Riebesell, U., I. Zondervan, B. Rost, P. D. Tortell, R. E. Zeebe, and F. M. M. Morel (2000), Reduced calcification of marine plankton in response to increased atmospheric CO_2, *Nature*, *407*, 364–367.

Shirayama, Y. (1997), Biodiversity and biological impact of ocean disposal of carbon dioxide, *Waste Manage.*, *17*, 381–384.

Takeuchi, K., Y. Fujioka, Y. Kawasaki, and Y. Shirayama (1997), Impacts of high concentration of CO_2 on marine organisms; a modification of CO_2 ocean sequestration, *Energy Conserv. Manage.*, *38*, S337–S341.

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CHAPTER 8

Reviewing the Impact of Increased Atmospheric CO_2 on Oceanic pH and the Marine Ecosystem

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ABSTRACT: The world's oceans contain an enormous reservoir of carbon, greater than either the terrestrial or atmospheric systems. The fluxes between these reservoirs are relatively rapid such that the oceans have taken up around 50% of the total carbon dioxide (CO_2) released to the atmosphere via fossil fuel emissions and other human activities in the last 200 years. Whilst this has slowed the progress of climate change, CO_2 ultimately results in acidification of the marine environment. Ocean pH has already fallen and will continue to do so with certainty as the oceans take up more anthropogenic CO_2. Acidification has only recently emerged as a serious issue and it has the potential to affect a wide range of marine biogeochemical and ecological processes. Based on theory and an emerging body of research, many of these effects may be non-linear and some potentially complex. Both positive and negative feedback mechanisms exist, making prediction of the consequences of changing CO_2 levels difficult. Integrating the net effect of acidification on marine processes at regional and basin scales is an outstanding challenge that must be addressed via integrated programs of experimentation and modelling. Ocean acidification is another argument, alongside that of climate change, for the mitigation of anthropogenic CO_2 emissions.

8.1 Introduction

The 1999 EU Energy Outlook to 2020 suggests that, despite anticipated increases in energy generation from renewable sources, up to 80% will still be accounted for by fossil fuels. On current trends, CO_2 emissions could easily be 50% higher by 2030. Already about 50% of anthropogenic CO_2 has been taken up by the oceans [1] and thus the oceans have been acting as a buffer, limiting atmospheric CO_2 concentrations. CO_2 in the atmosphere is relatively inert but when dissolved in seawater it becomes highly reactive and takes part in a range of chemical, physical, biological and geological reactions, some of which are predictable while some are more complex. Warming of the oceans will only have a small direct impact on the rate of oceanic uptake via changes in the solubility of CO_2. However, the oceans' capacity to absorb more CO_2 decreases as they take up CO_2.

Of all the predicted impacts attributed to this inevitable rise in atmospheric CO_2 and the associated rise in temperature (e.g. large-scale melting of ice sheets, destabilisation of methane hydrates, sea level rise, slowdown in the North Atlantic thermohaline circulation) one of the most pressing is the acidification of surface waters through the absorption of atmospheric CO_2 and its reaction with seawater to form carbonic acid [2, 3].

Predictions of atmospheric CO_2 concentrations, due to the unrestricted release of fossil fuel CO_2, by 2100 are 700 ppm [4] and by 2300 are 1900 ppm [3, 5] (based on median scenarios). This would equate to a decrease in surface ocean pH of 0.3 and 0.8 pH units from pre-industrial levels respectively [2, 3]. The top-end prediction of 1000 ppm CO_2 by 2100 would equate to a pH decrease of 0.5 units which is equivalent to a threefold increase in the concentration of hydrogen ions [5]. While climate change has uncertainty, these geochemical changes are highly predictable. Only the timescale and thus mixing scale length are really under debate. Such dramatic changes in ocean pH have probably not been seen for millions of years of the Earth's history [6, Figure 8.1].

8.2 Global Air–Sea Fluxes of Carbon Dioxide

There has been an increase in atmospheric carbon dioxide from 280 ppm in AD1800 to 380 ppm at the present day. This increase is due to a supply of anthropogenic CO_2 to the atmosphere which is currently estimated at 7 GtC yr^{-1} [4]. The observed annual increase in atmospheric CO_2 represents 3.2 GtC yr^{-1}, the balance being removed from the atmosphere and taken up by the oceans and land. There is now generally good agreement that the ocean absorbs 1.7 ± 0.5 GtC yr^{-1} [4]. Note that the rate-limiting step in the long-term oceanic uptake of anthropogenic CO_2 is not air-sea gas exchange, but the mixing of the surface waters with the deep ocean [7]. Whilst the ocean can theoretically absorb 70–80% of the projected production of anthropogenic CO_2, it would take many centuries to do so [8].

There is also a large natural annual flux of CO_2 between the ocean and the atmosphere of almost 90 GtC yr^{-1} that, pre-1800, was believed to be almost in balance. This

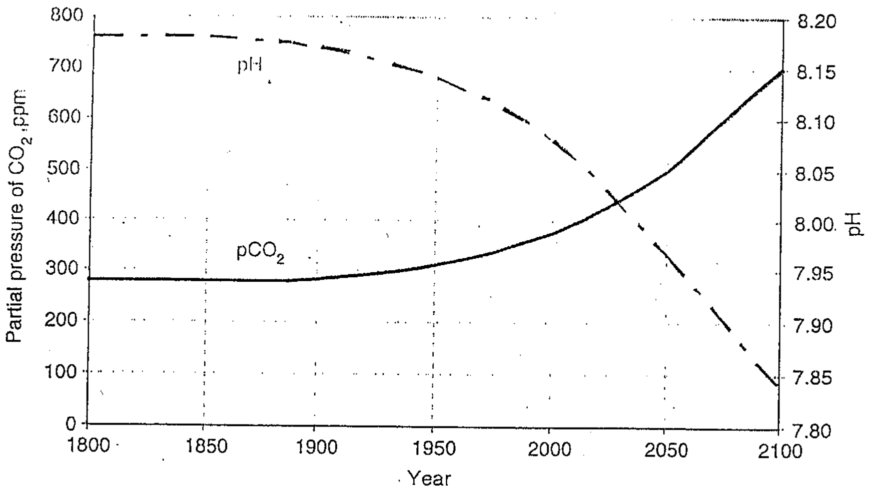

Figure 8.1 The past and projected change in atmospheric CO_2 and seawater pH assuming anthropogenic emissions are maintained at current predictions (redrawn from Zeebe and Wolf-Gladrow 2001).

huge influx and efflux is due to a combination of marine productivity and particle sinking (the biological pump) and ocean circulation and mixing (the solubility pump). Phytoplankton growth consumes dissolved inorganic carbon (DIC) in the surface seawater causing an undersaturation of dissolved CO_2 and uptake from the atmosphere. The re-equilibration time for CO_2 is slow (typically several months) due to the dissociation of CO_2 in seawater (see below). Ocean circulation also results in air-sea exchange of CO_2 as the solubility of CO_2 is temperature dependent. Warming decreases the solubility of CO_2 and promotes a net transfer of CO_2 to the atmosphere, whereas cooling results in a flux from the atmosphere to the ocean. Anthropogenic CO_2 modifies the flux from the solubility pump as CO_2 availability does not normally limit biological productivity in the world's oceans.

However, the observation that the net oceanic uptake of anthropogenic CO_2 is only about 2% of the total CO_2 cycled annually across the air-sea interface ought to be of major concern. The significant perturbations arising from this small change in flux imply that the system is extremely sensitive. Any resulting changes in the biogeochemistry of the mixed layer could have a major impact on the magnitude (or even sign) of the total CO_2 flux and hence on the Earth's climate [9].

8.3 The Carbonate System

The chemistry of carbon dioxide in seawater has been the subject of considerable research and has been summarized by Zeebe and Wolf-Gladrow [2]. Dissolved inorganic carbon can be present in any of 4 forms, dissolved carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}). Addition of CO_2 to seawater, by air–sea gas exchange due to increasing CO_2 in the atmosphere, leads initially to an increase in dissolved CO_2 (equation 8.1). This dissolved carbon dioxide reacts with seawater to form carbonic acid (equation 8.2). Carbonic acid is not particularly stable in seawater and rapidly dissociates to form bicarbonate ions (equation 8.3), which can themselves further dissociate to form carbonate ions (equation 8.4). At a typical seawater pH of 8.1 and salinity of 35, the dominant DIC species is HCO_3^- with only 1% in the form of dissolved CO_2. It is the relative proportions of the DIC species that control the pH of seawater on short to medium timescales.

$$CO_{2(atmos)} \Leftrightarrow CO_{2(aq)} \tag{8.1}$$

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \tag{8.2}$$

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \tag{8.3}$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \tag{8.4}$$

It is also important to consider the interaction of calcium carbonate with the inorganic carbon system. Calcium carbonate ($CaCO_3$) is usually found in the environment either as calcite or less commonly aragonite. Calcium carbonate dissolves in seawater forming carbonate ions (CO_3^{2-}) which react with carbon dioxide as follows:

$$\begin{aligned} CaCO_3 + CO_2 + H_2O &\Leftrightarrow Ca^{2+} + CO_3^{2-} + CO_2 + H_2O \\ &\Leftrightarrow Ca^{2+} + 2HCO_3^- \end{aligned} \tag{8.5}$$

This reaction represents a useful summary of what happens when anthropogenic carbon dioxide dissolves in seawater. The net effect is removal of carbonate ions and production of bicarbonate ions and a lowering in pH. This in turn will encourage the dissolution of more calcium carbonate. Indeed, the long-term sink for anthropogenic CO_2 is dilution in the oceans and reaction with carbonate sediments.

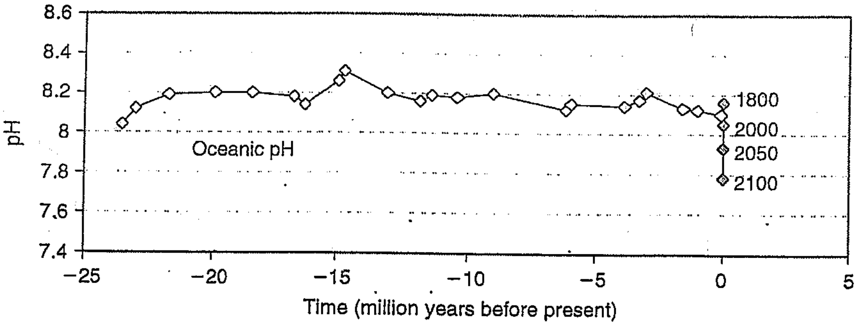

Figure 8.2 Past (white diamonds, data from Pearson and Palmer, 2000) and contemporary variability of marine pH (grey diamonds with dates). Future predictions are model derived values based on IPCC mean scenarios.

As can clearly be seen above, formation of calcite (the reverse of equation 8.5) actually produces CO_2.

Seawater at current pH levels is highly buffered with respect to carbon dioxide and has a great capacity to absorb carbon dioxide, as most of the CO_2 added will rapidly be converted to bicarbonate ions. It can be shown that if the atmospheric CO_2 levels doubled, dissolved CO_2 would only rise by 10%, with most of the remaining 90% being converted to bicarbonate ions. However, if bicarbonate ions increase, then the equilibrium of reaction 3 will be forced forwards and hence the pH of the seawater will be reduced. This is of great importance both for seawater chemistry and for the buffering capacity of seawater as it reduces the ability of seawater to buffer further CO_2 increases [2]: i.e. as the partial pressure of carbon dioxide increases the buffering capacity of seawater decreases.

The mean pH of seawater has probably changed by less than 0.1 units over the last several million years [6, Figure 8.2]. Since the start of the Industrial Revolution (circa 1800), the release of anthropogenic CO_2 to the atmosphere and subsequent flux into the surface oceans has already led to a decrease in the pH of oceanic surface waters of 0.1 unit [10, 5]. The same calculations show that the current rate of increase in atmospheric CO_2 concentration (15 ppm/decade) will cause a decrease in pH of 0.015 units/decade [11]. Globally, oceanic surface water pH varies over a range of 0.3 pH units, due to changes in temperature and seasonal CO_2 uptake and release by biota. However, the current surface ocean pH range is nearly distinct from that assumed for the inter-glacial period and the predicted pH for 2050 is nearly distinct from that of the pre-industrial period (Figure 8. 2). In some sense therefore the marine system is accelerating its entry into uncharted territory. Whilst species shifts and adaptation of physiology and community structure might maintain the system's gross functionality over longer timescales, the current rates of environmental change are far more rapid than previously experienced. We do not know if marine organisms and ecosystems will be able to adapt at these timescales.

8.4 Ecosystem Impacts

Although studies looking at ecosystem response are in their infancy, reduced pH is a potent mechanism by which high CO_2 could affect marine biogeochemistry [5, 12, 13]. The changes to the carbonate chemistry of the system [14, 15] may affect plankton species composition and their spatial or geographical distribution [16], principally by inhibiting calcifying organisms such as coccolithophores, pteropods, gastropods, foraminifera and corals in waters with high CO_2 [5]. Reduced calcification in cultures of two species of coccolithophores has been observed when grown at 750 ppm CO_2 [17]. Other non-calcifying organisms may grow in their place and impact the structure and processes occurring in the whole ecosystem. The main calcifiers in the ocean are the planktonic microalgae, coccolithophores [18], which secrete calcite platelets called liths. These organisms can form massive blooms, often of 100,000s km^2. They play an important role in the global carbon cycle through the transport of calcium carbonate to the marine sediments. Coccolithophores are also a major producer of dimethyl sulphide (DMS) which may have a role in climate regulation via the production of cloud condensation nuclei [19]. A reduction in the occurrence of the coccolithophore blooms that occur in large areas of the global oceans could lead to a reduced flux of DMS from the oceans to the atmosphere and hence further increases in global temperatures via cloud changes. International efforts to examine the impacts of high CO_2 in more natural enclosed seawater systems (mesocosms) with blooms of coccolithophores shows that calcification, growth rates and exudation can be affected by high CO_2 and this has implications on biogeochemical cycling, carbon export and food web dynamics [20, 21]. Over long timescales calcium carbonate is the major form in which carbon is buried in marine sediments, hence species composition is intimately linked to the strength of the biological pump and carbon burial in sediments [22, 23].

The effect of high CO_2 on tropical coral reefs has received particular attention [24, 25, 26] because calcification rates in corals (which secrete a more thermodynamically stable form of $CaCO_3$, aragonite) decline under elevated CO_2 conditions. Predictions are that coral calcification rates may decrease by 21–40% over the period 1880–2065 in response to changes in atmospheric CO_2 concentrations [27, 28, 29]. Reduction in coral calcification can result in declining coral cover and loss of the reef environments [25]. Coral reefs are essentially oases of high productivity such that they produce 10–12% of the fish caught in the tropics and 20–25% of the fish caught by developing nations [30]. The sea contributes about 90% of the animal protein consumed by many Pacific Island countries.

Calcification rates respond not only to carbonate saturation state, but also to temperature, nutrients, and light. It has been argued that increasing temperature, at least in corals, may invoke a biological response that leads to higher calcification rates in the short term. This might offset the impact of declining carbonate ion concentrations [31]. Although there is concern over these studies [5, 25] they do show the importance of looking at the impacts synergistically.

Extensive cold water corals have been discovered in the last decade in many of the world's oceans that may equal or even exceed the coverage of the tropical coral reefs [32]. A decrease in the depth below which aragonite dissolves, due to reduced carbonate ion concentrations, may make these ecosystems particularly vulnerable [33]. This effect will be greatest in the higher latitudes and impact calcifying organisms that live there [5]. For instance, pteropods are the dominant calcifiers in the Southern Ocean and are an important part of the Antarctic food web and ecosystem.

The availability of marine nutrients, necessary for primary production, is affected by pH. The form of both phosphorus and nitrogen, the key macro nutrients, are pH sensitive; acidification provoking a reduction in the available form of phosphate (PO_4^{3-}) and a decrease in ammonia (NH_3) with respect to ammonium (NH_4^+), changing the energetics of cellular acquisition. A second consequence of low pH may be the inhibition of microbial nitrification [34] with a resulting decrease in the oxidised forms of nitrogen (e.g. NO_3^-). As a result we may see a decrease in the NO_3^- dependant denitrification process which removes nitrogen from the marine system in the form of nitrogen gas. The resulting build-up of marine nitrogen (mainly as NH_4^+) may trigger eutrophication effects.

The solubility (and availability) of iron, an important micro-nutrient, is likely to increase with acidification, perhaps increasing productivity in some remote ocean basins that are currently iron limited. The net effect of these processes is likely to change the nutrient availability to phytoplankton, impacting species composition and distribution and consequently the rate of carbon cycling in the marine system. Changes to the phytoplankton community structure are likely to affect the organisms that prey on phytoplankton, including economically important species [35, 36, 37].

If the environmental CO_2 concentration is high (equivalent to three-fold increases in atmospheric CO_2 relative to pre-industrial), fish and other complex animals are likely to have difficulty reducing internal CO_2 concentrations, resulting in accumulation of CO_2 and acidification of body tissues and fluids (hypercapnia) [38]. The effects of lower level, long term increases in CO_2 on reproduction and development of marine animals is unknown and of concern. High sensitivity to CO_2 is shown by squid (Cephalopods), because of their high energy and oxygen demand for jet propulsion, with a relatively small decrease in pH of 0.25 having drastic effects (reduction of c. 50%) on their oxygen carrying capacity [39].

Experiments, using CO_2 concentration beyond that expected to be seen in the next few hundred years, have shown that decreased motility, inhibition of feeding, reduced growth, reduced recruitment, respiratory distress, decrease in population size, increased susceptibility to infection, shell dissolution, destruction of chemosensory systems and mortality can occur in high CO_2/low pH waters in the small range of higher organisms tested to date, many of which are shellfish [5]. However, further experiments are required to investigate the impacts of the CO_2 and pH levels relevant to ocean uptake of anthropogenic CO_2.

Juvenile forms of shellfish may be less tolerant to changes in pH than adults. Indeed, greater than 98% of the mortality of settling marine bivalves occurs within the first few days or weeks after settling. This is thought to be in part due to their sensitivity to the carbonate saturation state at the sediment-water interface [40]. The higher seawater CO_2 concentrations that will occur in the future may therefore enhance shell dissolution and impact recruitment success and juvenile survival.

The average carbonate saturation state of benthic sediment pore waters could decline significantly, inducing dissolution of carbonate phases within the pore-water-sediment system [14]. Further, the benthic sediment chemistry of shallow coastal seas exhibits a delicate balance between aerobic and anaerobic activity which may be sensitive to varying pelagic CO_2 loads. In short, marine productivity, biodiversity and biogeochemistry may change considerably as oceanic pH is reduced through oceanic uptake of anthropogenic CO_2.

Changes that may occur in the same time frame as increased seawater CO_2 and reduced pH, include increased seawater temperature, changes in the supply of nutrients to the euphotic zone through stronger water column stratification, changes in salinity, and sea-level rise. There are likely to be synergistic impacts on marine organisms and ecosystems. There is surprisingly little research on the potential impact of a high CO_2 ocean on marine organisms and ecosystems let alone the impact this might have when combined with other climate-induced changes. This needs to be redressed. Whilst about 28 million people are employed in fishing and aquaculture with a global fish trade of US$53,000 million [30], the marine environment provides other valuable services [41] and its existence and diversity is treasured. As the oceans play a key role in the Earth's life support system, it would seem that a better understanding of the impacts of high CO_2 on the marine environment and consideration of mitigation and stabilization choices is worthy of substantial investment.

8.5 International Recognition

The global scientific community is increasingly concerned about the impacts of a high CO_2 ocean. This community includes the International Global Biosphere Programme (*IGBP*), the Scientific Committee on Oceanic Research (*SCOR*), the Commission on Atmospheric Chemistry and Global Pollution (*CACGP*) and the International Council for Science (*ICSU*). A SCOR and IOC-funded International Science Symposium held at UNESCO, Paris on 10–12 May 2004, *Symposium on the Ocean in a High-CO_2 World*, brought together scientists working in this area for the first time. The scientific consensus has been summarised in the report *Priorities for Research on the Ocean in a High-CO_2 World* [42] and the overwhelming conclusion was that there is an urgent need for more research in this area. The Royal Society formed an international working group to report on ocean acidification and published on 30 June 2005 [5]. Commissions and conventions that are policy instruments for the protection of our seas (such as the OSPAR (Oslo–Paris) Commission and the London Convention) have held workshops on the environmental impact of placement of CO_2 in geological structures in the maritime area and recognise the significance of ocean acidification caused by uptake of anthropogenic CO_2 as a strong argument, along with climate change, for global mitigation of CO_2 emission. A report to Defra, summarising the current knowledge of the potential impact of ocean acidification (by direct uptake or by release from sub-seabed geological sequestration) concluded that there was a need for urgent research to help inform government of the potential impact of both ocean uptake of anthropogenic CO_2 and its release from maritime sea bed geological structures [43].

8.6 Conclusions

This paper outlines only a few of the potential effects that higher CO_2 may have on the marine system. Many other processes are pH sensitive: for example, changes in pH also have the potential to disrupt metal ion uptake causing symptoms of toxicity, and intra-cellular enzymatic reactions are also pH sensitive [5]. Given continued CO_2 emissions, further marine acidification is inevitable and effects on the marine ecosystem are likely to be measurable. Whilst many of the effects are nominally negative, some could be considered positive. How these may balance out is unknown. The scientific community is far from being able to predict accurately the impact of acidification on the oceans and whether an appreciable decline in resource base may occur. We also need to address the key question of whether marine organisms and ecosystems have the ability to adapt to the predicted changes in CO_2 and pH. Ocean acidification will occur within the same time scales as other global changes associated with climate impacts. These also have much potential to alter marine biogeochemical cycling.

Modelling techniques provide an important mechanism for resolving whole system impact. Indeed, several researchers cite the need for integrated modelling studies [e.g. 35]. The problem is multi-disciplinary. We need to integrate atmosphere, hydrodynamic and ecosystem modellers, to build on experimental knowledge, and require significantly more system measurements in order to validate models. UK and international momentum is building towards this challenge and many of the required collaborations are being forged. However, the provision of manpower, computer, experimental and observational resources still needs to be addressed. Mitigation of CO_2 emissions will decrease the rate and extent of ocean acidification [5]. This is another powerful argument to add to that of climate change for reduction of global anthropogenic CO_2 emissions.

REFERENCES

1. Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong, C.S., Wallace, D.W.R., Tilbrook, B., Millero, F.J., Peng, T.H., Kozyr, A., Ono, T. and Rios, A.F., 2004. The oceanic sink for anthropogenic CO_2. *Science*, **305**: 367–371.
2. Zeebe, R.E. and Wolf-Gladrow, D.A., 2001. CO_2 in seawater: equilibrium, kinetics and isotopes. Elsevier Oceanography Series. 65: pp. 346.
3. Caldeira, K. and Wickett, M.E., 2003. Anthropogenic carbon and ocean pH. *Nature*, **425**, p. 365.
4. IPCC, 2001. *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change* [Houghton, J.T., Ding, Y., Griggs, D.J., Noguer, M., van der Linden, P.J., Dai, X., Maskell, K., and Johnson C.A. (Eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, pp. 881.
5. The Royal Society, 2005. Ocean acidification due to increasing atmospheric carbon dioxide. Document 12/05 Royal Society: London.
6. Pearson, P.N. and Palmer M.R., 2000. Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature*, **406**, 695–699.
7. Sarmiento, J.L. and Sundquist, E.T., 1992. Revised budget for the oceanic uptake of anthropogenic carbon-dioxide. *Nature*, **356**, 589–593.
8. Maier-Reimer, E. and Hasselmann, K., 1987. Transport and storage of CO_2 in the ocean – An inorganic ocean-circulation carbon cycle model. *Climate Dynamics*, **2**, 63–90.
9. Nightingale, P.D. and Liss P.S., 2003. Gases in seawater. In, *The oceans and marine geochemistry. A Treatise on Geochemistry, Vol. 6* [H. Elderfield, Ed.]. Elsevier.
10. Haughan, P.M. and Drange, H., 1996. Effects of CO_2 on the ocean environment. *Energy Conservation and Management*, **6–8**, 1019–1022.

11. Ormerod, W.G., Freund, and Smith, A., 2002. Ocean storage of carbon dioxide, 2nd edn. *IEA Greenhouse Gas R&D Programme*, pp. 26.
12. Wolf-Gladrow, D.A., Riebesell, U., Burkhardt, S. and Bijma, J., 1999. Direct effects of CO_2 concentration on growth and isotopic composition of marine plankton. *Tellus*, B51, 461–476.
13. Knutzen, J., 1981. Effects of decreased pH on marine organisms. *Marine Pollution Bulletin*, 12, 25–29.
14. Andersson, A. J., Mackenzie, F. T. and Ver, L.M., 2003. Solution of shallow-water carbonates: An insignificant buffer against rising atmospheric CO_2. *Geology*, **31**, 513–516.
15. Feely, R.A., Sabine, C.L.; Lee, K., Berelson, W., Kleypas, J., Fabry, V.J. and Millero, F.J., 2004. Impact of anthropogenic CO_2 on the $CaCO_2$ system in the ocean. *Science*, **305**, 362–366.
16. Boyd, P.W. and Doney, S.C., 2002. Modelling regional responses by marine pelagic ecosystems to global climate change. *Geophysical Research Letters*, **29**, 1806, doi: 10.1029/2001GL014130.
17. Riebesell, U., Zondervan, I., Rost, B., Tortell, P.D., Zeebe, R.E. and Morel, F.M.M., 2000. Reduced calcification of marine plankton in response to increased atmospheric CO_2. *Nature*, **407**, 364–367.
18. Holligan, P. M., Fernandez, E., Aiken, J., Balch, W.M., Boyd, P., Burkill, P.H., Finch, M., Groom, S.B., Malin, G., Muller, K., Purdie, D.A., Robinson, C., Trees, C.C., Turner, S.M. and Vanerwal, P., 1993. A Biogeochemical Study of the Coccolithophore, *Emiliania huxleyi*, in the North-Atlantic. *Global Biogeochemical Cycles*, 7, 879–900.
19. Charlson, R.J., Lovelock, J.E., Andreae, M.O. and Warren, S.G., 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature*, **326**, 655–661.
20. Engel, A., Zondervan, I., Aerts, K., Beaufort, L., Benthien, A., Chou, L., Delille, B., Gattuso, J.-P., Harly, J., Heemaan, C., Hoffmann, L., Jacquet, S., Nejstgaard, J., Pizay, M.-D., Rochelle-Newall, E.S., Schneider, U., Terbrueggen, A. and Riebesell, U., 2005. Testing the direct effect of CO_2 concentration on marine phytoplankton: A mesocosm experiment with the coccolithophorid *Emiliania huxleyi*. *Limnology & Oceanography*, **50**, 493–507.
21. Delille, B., Harlay, J., Zondervan, I., Jacquet, S., Chou, L., Wollast, R., Bellerby, R.G.J., Frankignoulle, M., Borges, A.V., Riebesell, U. and Gattuso, J-P., 2005. Response of primary production and calcification to changes of pCO_2 during experimental blooms of the coccolithophorid Emiliania huxleyi. *Global Biogeochemical Cycles*, **19**, GB2023 10.1029/2004GB002318.
22. Archer, D., 1995. Upper Ocean Physics as Relevant to Ecosystem Dynamics – a Tutorial. *Ecological Applications*, **5**, 724–739.
23. Tian, R.C., Vezina, A., Legendre, L., Ingram, R.G., Klein, B., Packard, T., Roy, S., Saenkoff, C., Silverberg, N., Therriault, J.C. and Tremblay, J.E., 2000. Effects of pelagic food-web interactions and nutrient remineralization on the biogeochemical cycling of carbon: a modeling approach. *Deep Sea Research, Part II*, **47**, 637–662.
24. Kleypas, J.A., Buddemeier, R.W., Archer, D., Gattuso, J.-P., Langdon, C. and Opdyke, B.N., 1999. Geochemical Consequences of Increased Atmospheric Carbon Dioxide on Coral Reefs. *Science*, **284**, 118–120.
25. Kleypas, J.A., Buddemeier, R.W. and Gattuso, J.-P., 2001. The future of coral reefs in an age of global change. *International Journal Earth Sciences*, **90**, 426–437.
26. Marubini, F. and Atkinson M. J., 1999. Effects of lowered pH and elevated nitrate on coral calcification. *Marine Ecology Progress*, **188**, 117–121.
27. Langdon, C., Takahashi, T., Marubini, F., Atkinson, M., Sweeney, C., Aceves, H., Barnett, H., Chipman, D. and Goddard, J., 2000. Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. *Global Biogeochemical Cycles*, **14**, 639–654.w
28. Langdon, C., Broecker, W.S., Hammond, D.E., Glenn, E., Fitzsimmons, K., Nelson, S.G., Peng, T.-H., Hajdas, I. and Bonani, G., 2003. Effect of elevated CO_2 on the community metabolism of an experimental coral reef. *Global Biogeochemical Cycles*, 17, 1011, doi: 10.1029/2002GB001941.
29. Leclercq, N., Gattuso, J.-P. and Jaubert, J., 2000. CO_2 partial pressure controls the calcification rate of a coral community. *Global Change Biology*, 6, 329–334.
30. Garcia, S.M. and De Leiva Moreno, I., 2001. Global overview of marine fisheries. Report of the Conference on Responsible Fisheries in the Marine Ecosystem (ftp://ftp.fao.org/fi/DOCUMENT/reykjavik/Default.htm), Reykjavik, Iceland, 1–4 October 2001.
31. Lough, J.M. and Barnes, D.J., 2000. Environmental controls on growth of the massive coral porites. *Journal of Experimental Marine Biology and Ecology*, **245**, 225–243.
32. Freiwald, A., Fossa, J. H., Grehan, A., Koslow, T. and Roberts, J. M., 2004. Cold-water coral reefs: Out of sight no longer out of mind. No. 22 in Biodiversity Series, UNEP-WCMC, Cambridge, UK.
33. Orr, J., Bopp, L., Aumont, O., Key, R., Sabine, C., Plattner, G. K., Joos, F., Maier-Reimer, E., Weirig, M.F., Schlitzer,R., Matear, R., Slater, R., Sarmiento, J., Doney, S., Lindsay, K., Follows, M., Yool, A., Mouchet, A., Yamanaka, Y. and Ishida, A. Aragonite undersaturation in the surface Southern Ocean by 2100. Proceedings of the symposium 'The Ocean in a High CO_2 World', Paris, 10–12 May 2004.
34. Huesemann, M.H., Skillman, A.D. and Crecelius, E.A., 2002. The inhibition of marine nitrification by ocean disposal of carbon dioxide. *Marine Pollution Bulletin*, **44**, 142–148.
35. DeAngelis, D. L. and Cushman R. M., 1990. Potential application of models in forecasting the effects of climate changes on fisheries. *Transactions of the American Fisheries Society*, **119**, 224–239.
36. Frank, K.T., Perry, R.I. and Drinkwater, K.F., 1990. Predicted response of Northwest Atlantic invertebrate and fish stocks to CO_2-induced climate change. *Transactions of the American Fisheries Society*, **119**, 353–365.
37. Nejstgaard, J.C., Gismervik, I. and Solberg, P.T., 1997. Feeding and reproduction by Calanus finmarchicus and microzooplankton grazing during mesocosm blooms of diatoms and the coccolithophore *Emiliania huxleyi*. *Marine Ecology Progress*, **147**, 197–217.
38. Portner, H.O., Langenbuch, M. and Reipschlager, A., 2004. Biological impact of elevated ocean CO_2 concentrations: lessons from animal physiology and Earth history. *Journal of Oceanography*, **60**, 705–718.
39. Portner, H.O. and Reipschlager, A., 1996. Ocean dispersal of anthropogenic CO_2: physiological effects on tolerant and intolerant animals. In, *Ocean storage of CO_2*. Environmental Impact. [Omerod, B. and Angel, M., Eds.] MIT and IEA Greenhouse Gas ROD Programme, Cheltenham, Boston, pp. 57–81.
40. Green, M.A., Jones, M.E., Boudreau, C.L., Moore, R.L. and Westman, B.A., 2004. Dissolution mortality of juvenile bivalves in coastal marine deposits. *Limnology & Oceanography*, **49**, 727–734.
41. Costanza, R.R., d'Arge, R., de Groot, R., Farber, S., Grasso, M., Hannon, B., Limburg, K., Naeem, S., O'Neill, R.V., Paruleo, J., Raskin, R.G., Sutton, P. and van den Belt, M., 1997. The value of the world's ecosystem services and natural capital. *Nature*, 387, 253–260.
42. Priorities for Research on the Ocean in a High-CO_2 World. http://ioc.unesco.org/iocweb/co2panel/Docs/Research%20Priorities%20Report-Final.pdf
43. Turley, C., Nightingale, P., Riley, N., Widdicombe, S., Joint, I., Gallienne, C., Lowe, D., Goldson, L., Beaumont, N., Mariotte, P., Groom, S., Smerdon, G., Rees, A., Blackford, J., Owens, N., West, J., Land, P. and Woodason, E., 2004. Literature Review: Environmental impacts of a gradual or catastrophic release of CO_2 into the marine environment following carbon dioxide capture. (DEFRA: MARP 30 (ME2104) 31 March 2004.