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## Reduced calcification of marine plankton in response to increased atmospheric CO<sub>2</sub>

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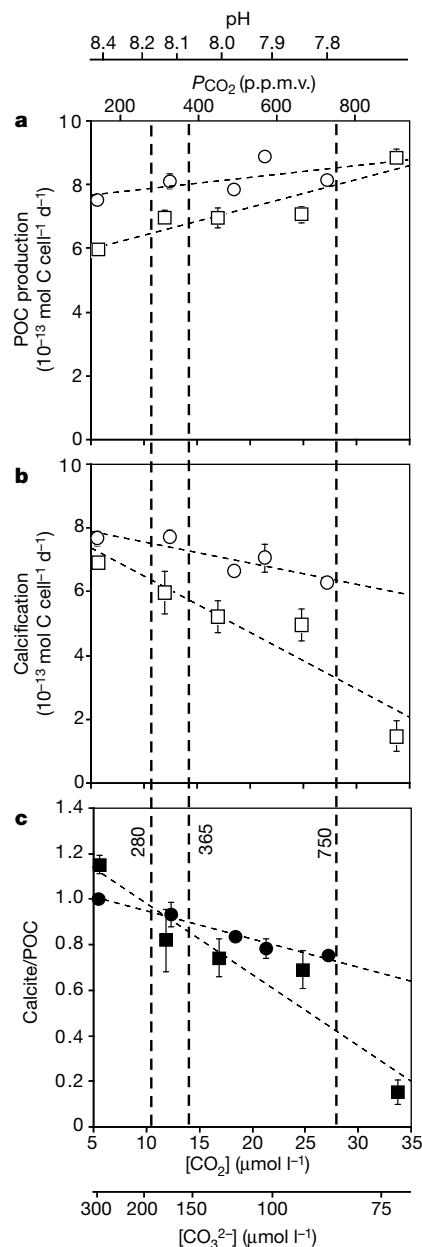
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The formation of calcareous skeletons by marine planktonic organisms and their subsequent sinking to depth generates a continuous rain of calcium carbonate to the deep ocean and underlying sediments<sup>1</sup>. This is important in regulating marine carbon cycling and ocean-atmosphere CO<sub>2</sub> exchange<sup>2</sup>. The present rise in atmospheric CO<sub>2</sub> levels<sup>3</sup> causes significant changes in surface ocean pH and carbonate chemistry<sup>4</sup>. Such changes have been shown to slow down calcification in corals and coralline macroalgae<sup>5,6</sup>, but the majority of marine calcification occurs in planktonic organisms. Here we report reduced calcite production at increased CO<sub>2</sub> 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<sub>2</sub> levels. We suggest that the progressive increase in atmospheric CO<sub>2</sub> concentrations may therefore slow down the production of calcium carbonate in the surface ocean. As the process of calcification releases CO<sub>2</sub> to the atmosphere, the response observed here could potentially act as a negative feedback on atmospheric CO<sub>2</sub> levels.

By the end of the next century, the expected increase in atmospheric CO<sub>2</sub> (ref. 3) will give rise to an almost threefold increase in surface ocean CO<sub>2</sub> concentrations relative to pre-industrial values. This will cause CO<sub>3</sub><sup>2-</sup> concentrations and surface water pH to drop by about 50% and 0.35 units, respectively<sup>4</sup>. Changes of this magnitude have been shown to significantly slow down calcification of temperate and tropical corals and coralline macroalgae<sup>5,6</sup>. Although coral reefs are the most conspicuous life-supporting calcareous structures, the majority of biogenic carbonate precipitation (>80%) is carried out by planktonic microorganisms<sup>1</sup>, particularly coccolithophorids<sup>7</sup>. These unicellular microalgae are major contributors to marine primary production and an important component of open ocean and coastal marine ecosystems<sup>8</sup>. 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<sup>9</sup>, whereas *E. huxleyi*, one of the most prominent producers of calcium carbonate in the world ocean<sup>10</sup>, forms extensive blooms covering large areas in temperate and subpolar latitudes<sup>9,11</sup>.

The response of these two species to CO<sub>2</sub>-related changes in seawater carbonate chemistry was examined under controlled



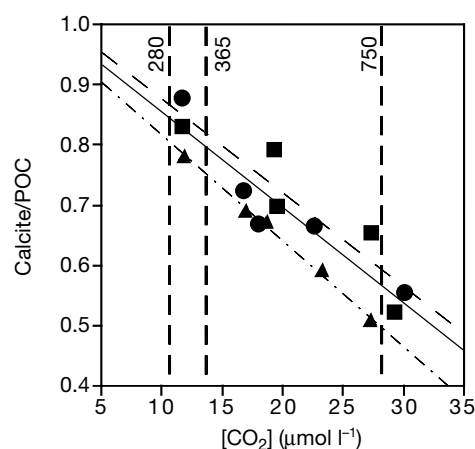
**Figure 1** Response of organic and inorganic carbon production to CO<sub>2</sub> concentration in laboratory-cultured coccolithophorids. **a**, Particulate organic carbon (POC) production; **b**, calcification; and **c**, the ratio of calcification to POC production (calcite/POC) of the coccolithophorids *Emiliania huxleyi* (circles) and *Gephyrocapsa oceanica* (squares) as a function of CO<sub>2</sub> concentration, [CO<sub>2</sub>]. Bars denote  $\pm 1$  s.d. ( $n = 3$ ); dotted lines represent linear regressions. Also indicated are corresponding ranges of pH,  $p_{\text{CO}_2}$ , and [CO<sub>3</sub><sup>2-</sup>]. We note that DIC and total alkalinity differed slightly between experimental sets for the two species; values for pH,  $p_{\text{CO}_2}$ , and [CO<sub>3</sub><sup>2-</sup>], therefore, are only approximations. Vertical lines indicate  $p_{\text{CO}_2}$  values of 280, 365 and 750 p.p.m.v., representing pre-industrial, present day and future concentrations.

laboratory conditions. The carbonate system of the growth medium was manipulated by adding acid or base to cover a range from pre-industrial  $\text{CO}_2$  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<sup>12</sup>, 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  $\text{CO}_2$ -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

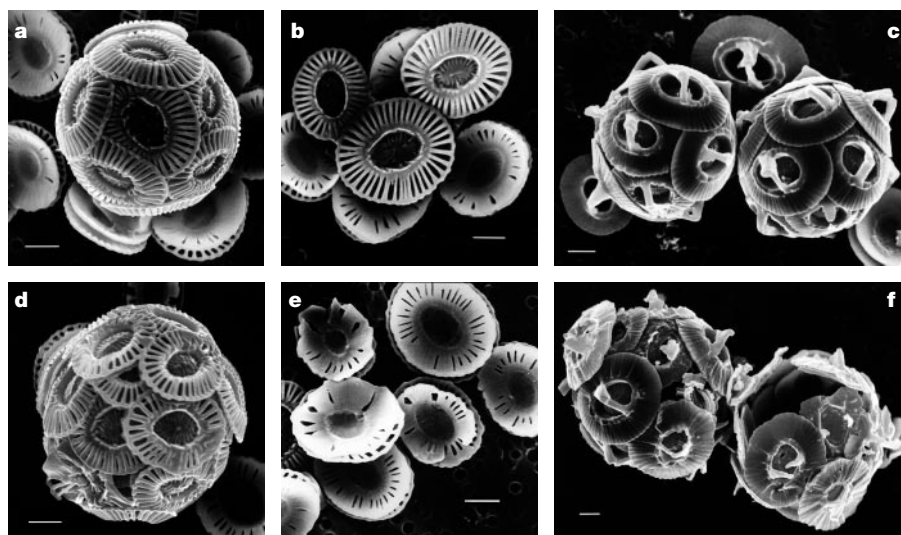
with increasing  $\text{CO}_2$  concentrations (Fig. 3). Coccolith undercalcification and malformation is a common phenomenon frequently observed both in natural environments and under laboratory conditions<sup>13</sup>. The systematic trend in the relative abundance of malformed coccoliths and coccospheres 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  $\text{CO}_2$ -related responses of natural plankton assemblages collected in the subarctic north Pacific, a region where coccolithophorids are major contributors to primary production<sup>14</sup>. After incubation of replicate samples at  $p_{\text{CO}_2}$  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- $\text{CO}_2$  relative to low- $\text{CO}_2$  treatments in four independent experiments (Fig. 4). A similar  $\text{CO}_2$ -dependent response was obtained under



**Figure 2** Ratio of calcification to POC production (calcite/POC) of *Emiliania huxleyi* as a function of  $\text{CO}_2$  concentration,  $[\text{CO}_2]$ . Cells were incubated at photon flux densities of 30, 80 and  $150 \mu\text{mol m}^{-2} \text{s}^{-1}$  (denoted by circles, squares and triangles and corresponding

solid, dashed, dash-dotted regression lines, respectively). Bars denote  $\pm 1$  s.d. ( $n = 3$ ); lines represent linear regressions. Vertical lines indicate  $p_{\text{CO}_2}$  values of 280, 365 and 750 p.p.m.v.



**Figure 3** Scanning electron microscopy (SEM) photographs of coccolithophorids under different  $\text{CO}_2$  concentrations. **a, b, d, e**, *Emiliania huxleyi*; and **c, f**, *Gephyrocapsa oceanica* collected from cultures incubated at  $[\text{CO}_2] \approx 12 \mu\text{mol l}^{-1}$  (**a–c**) and at  $[\text{CO}_2] \approx 30–33 \mu\text{mol l}^{-1}$  (**d–f**), corresponding to  $p_{\text{CO}_2}$  levels of about 300 p.p.m.v. and 780–850 p.p.m.v., respectively. Scale bars represent  $1 \mu\text{m}$ . Note the difference in the

coccolith structure (including distinct malformations) and in the degree of calcification of cells grown at normal and elevated  $\text{CO}_2$  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.

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  $p_{\text{CO}_2}$ , 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  $\text{CO}_2$  to the surrounding water<sup>15</sup>, whereby the increase in  $\text{CO}_2$  concen-

tration, 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  $\text{CO}_2$  released per mole  $\text{CaCO}_3$  precipitated<sup>16</sup> (assuming temperature  $T = 15^\circ\text{C}$ , and salinity  $S = 35$ ). Following the predictions of future atmospheric  $\text{CO}_2$  rise, this value will 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  $\text{CO}_2$  to the atmosphere. In the case of reduced calcification, this positive feedback is reversed. Assuming a pre-industrial pelagic inorganic carbon production of  $0.86 \text{ Gt C y}^{-1}$  (ref. 17) and a  $\text{CO}_2$ -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  $\text{CO}_2$  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  $p_{\text{CO}_2}$ . Although it is presently not clear what the physiological and ecological role of coccolith formation is<sup>18</sup>, we propose that  $\text{CO}_2$ -dependent changes in calcification may affect cellular processes such as acquisition of inorganic carbon<sup>19</sup> and nutrients<sup>20</sup> as well as trophic interactions, and particle sinking rate<sup>21,22</sup>. 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  $\text{CO}_2$  storage in the upper ocean<sup>3,15,23</sup>, thus providing a negative feedback for changes in atmospheric  $p_{\text{CO}_2}$ . Such a feedback should be taken into account when predicting the role of the ocean in mitigating future anthropogenic  $\text{CO}_2$  increases or in reconstructing the relation between ocean productivity and glacial-interglacial variations in  $p_{\text{CO}_2}$ .

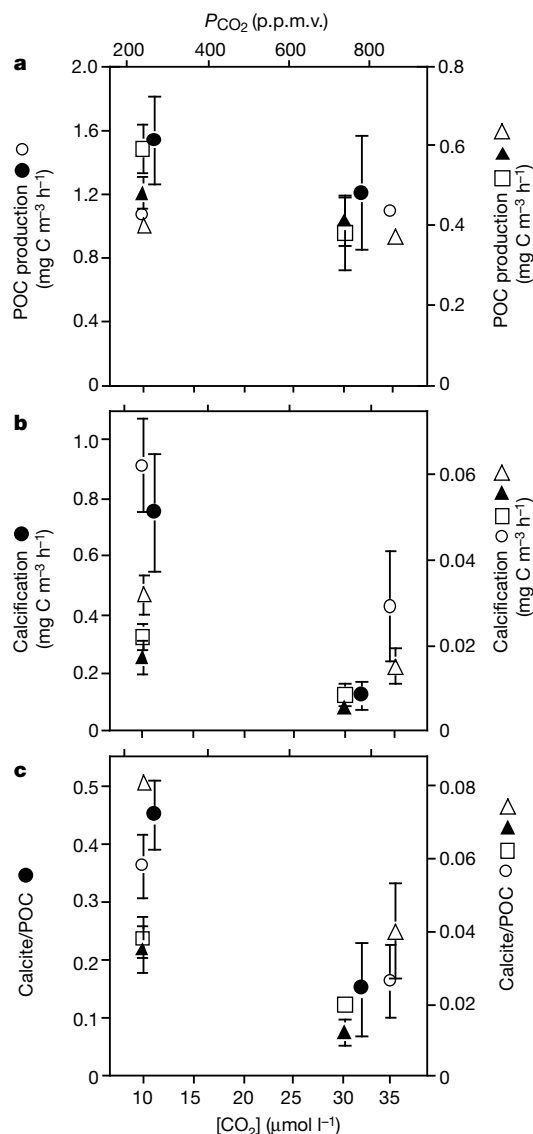
## Methods

### 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  $15^\circ\text{C}$  in filtered ( $0.2 \mu\text{m}$ ) sea water enriched with nitrate and phosphate to concentrations of 100 and  $6.25 \mu\text{mol l}^{-1}$ , 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  $150 \mu\text{mol m}^{-2} \text{ s}^{-1}$ , light/dark (L/D) cycle = 16/8 h (Fig. 1) and of 150, 80 and  $30 \mu\text{mol m}^{-2} \text{ s}^{-1}$ , L/D = 24/0 (Fig. 2). Dissolved inorganic carbon (DIC) was measured coulometrically in duplicate (UIC model 5012)<sup>25</sup>. Alkalinity was determined in duplicate through potentiometric titration<sup>26</sup>. pH,  $\text{CO}_2$  and  $\text{CO}_3^{2-}$  concentrations were calculated from alkalinity, DIC and phosphate concentrations ( $T = 15^\circ\text{C}$ ;  $S = 31$ ) 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,  $500^\circ\text{C}$ ) QM-A filters (pore width is about  $0.6 \mu\text{m}$ ) and stored at  $-25^\circ\text{C}$ . 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 ( $13 \pm 1^\circ\text{C}$ ).  $\text{CO}_2$  concentrations in samples were manipulated by either bubbling with commercially prepared  $\text{CO}_2$ /air mixtures (Station P26, 1998/1999) or by the addition of high-purity (trace-metal-clean) HCl/NaOH. Low  $\text{CO}_2$  samples contained about  $10 \mu\text{M CO}_2$  ( $\sim 250 \text{ p.p.m.v.}$ ) with a pH of about 8.20 while high  $\text{CO}_2$  treatments contained approximately  $33 \mu\text{M CO}_2$  ( $\sim 800 \text{ p.p.m.v.}$ ) with a pH of about 7.75. Total alkalinity ( $\sim 2180 \mu\text{Eq l}^{-1}$ ) was unaffected by  $\text{CO}_2$  bubbling while HCl and NaOH additions changed alkalinity by  $-6.4\%$  and  $+3.4\%$ , respectively.  $\text{CO}_2$



**Figure 4** Effects of  $\text{CO}_2$  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 ( $50^\circ\text{N}$ ,  $145^\circ\text{W}$ ) 1998, 6.8-day  $\text{CO}_2$  pre-conditioning (filled circles). Station P26 1999, 2-day  $\text{CO}_2$  pre-conditioning (squares). Station P26 1999, 9-day  $\text{CO}_2$  pre-conditioning (filled triangles). Station P20 ( $43^\circ 30' \text{N}$ ,  $138^\circ 40' \text{W}$ ) 1999, 1.5-day  $\text{CO}_2$  pre-conditioning (open triangles). Station Z9 ( $55^\circ\text{N}$ ,  $145^\circ\text{W}$ ) 1999, 1.5-day pre-conditioning (open circles). In all five experiments, POC production did not differ significantly between  $\text{CO}_2$  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.



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  $\mu\text{Ci }^{14}\text{C}$  (50 mCi mmol<sup>-1</sup>) for 6–9 hours, harvested onto 0.4- $\mu\text{m}$  polycarbonate filters, and immediately frozen in scintillation vials at  $-20^\circ\text{C}$ . In the laboratory, filter samples were acidified with either 10% HCl or  $\text{H}_3\text{PO}_4$  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  $^{14}\text{C}$  uptake in dark control bottles as well as filtered seawater blanks.

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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<sup>1–4</sup>. 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<sup>2–4</sup>. 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<sup>5</sup>. 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<sup>6–11</sup>. 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<sup>12–19</sup>. This decadal pattern has been referred to as the Pacific Decadal Oscillation<sup>19</sup> (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<sup>15–18</sup>. 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,