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Reduced calcification in modern Southern Ocean planktonic foraminifera

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Anthropogenic carbon dioxide has been accumulating in the oceans, lowering both the concentration of carbonate ions and the pH (ref. 1), resulting in the acidification of sea water. Previous laboratory experiments have shown that decreased carbonate ion concentrations cause many marine calcareous organisms to show reduced calcification rates[2–5]. If these results are widely applicable to ocean settings, ocean acidification could lead to ecosystem shifts. Planktonic foraminifera are single-celled calcite-secreting organisms that represent between 25 and 50% of the total open-ocean marine carbonate flux[6] and influence the transport of organic carbon to the ocean interior[7]. Here we compare the shell weights of the modern foraminifer *Globigerina bulloides* collected from sediment traps in the Southern Ocean with the weights of shells preserved in the underlying Holocene-aged sediments. We find that modern shell weights are 30–35% lower than those from the sediments, consistent with reduced calcification today induced by ocean acidification. We also find a link between higher atmospheric carbon dioxide and low shell weights in a 50,000-year-long record obtained from a Southern Ocean marine sediment core. It is unclear whether reduced calcification will affect the survival of this and other species, but a decline in the abundance of foraminifera caused by acidification could affect both marine ecosystems and the oceanic uptake of atmospheric carbon dioxide.

Anthropogenic CO_2 changes the carbonate chemistry and the pH of the surface ocean including decreasing the saturation state of carbonate minerals in sea water[1], thus making biological precipitation of carbonate shells more difficult[8]. The ecological effects of this change in ocean carbonate chemistry are largely unknown and need to be quantified[9]. Increased CO_2 in laboratory manipulations results in reduced calcification rates in planktonic foraminifera[2] and other marine carbonate organisms including some, but not all, coccolithophorids[3,10], corals[4] and pteropods[5]. Earlier studies of down-core and core-top sediment in the North Atlantic suggest that higher atmospheric CO_2 reduces the calcification rate of planktonic foraminifera[11], although other variables such as temperature, salinity and nutrient availability may also influence calcification rates[12,13].

The Southern Ocean shows large surface-ocean gradients in carbonate chemistry, primary production, temperature, salinity and nutrients, and contains ~40% of the global ocean inventory of anthropogenic CO_2 (ref. 1). Anthropogenic CO_2 enrichment of ~60 μmol kg^{-1} as dissolved inorganic carbon in the subantarctic Southern Ocean[1] corresponds to a carbonate ion concentration ($[CO_3^{2-}]$) decrease of ~36 μmol kg^{-1} (equivalent to a pH decrease of 0.14) (see Supplementary Information S1). This high water-column inventory of anthropogenic CO_2, with relatively small changes in other variables such as temperature[14], makes the subantarctic Southern Ocean an ideal field area to examine the response of marine calcifying organisms to increasing anthropogenic CO_2. Furthermore, the South Tasman Rise region in which this study was conducted is an area where Southern Ocean fronts are dynamically linked to topographic features such as the rise and mid-ocean ridge[15] and where latitudinal positions of water masses and fronts are relatively insensitive to wind forcing[16]. It is also the site of several long-term sediment-trap deployments in the central subantarctic zone[17] (SAZ) and repeat hydrographic sections[15], providing long-term particle-flux observations and observations of ocean carbonate chemistry in the same water masses.

As water-column comparisons alone span only the past 3–4 decades and require assumptions about the pre-industrial state of the ocean[18], we combine sediment-trap and Holocene planktonic foraminiferal shell weights to detect changes in the calcification of planktonic foraminifera since pre-industrial times. This same approach has also been used in this region to detect the isotopic signature of anthropogenic CO_2 in planktonic foraminiferal stable carbon isotopes[19]. We also use a sediment core to illustrate how planktonic foraminiferal shell weights have responded to past changes in atmospheric pCO_2 over the past 50,000 years. This setting provides a 'natural experiment' using microfossils of extant marine species living in the modern ocean and having experienced the geochemical perturbations of the Quaternary period[20].

The Holocene sediment samples used in this study are from the SAZ (between 45° S and 50° S and 144° E and 151° E) from water depths between 1,600 and 4,500 m (Fig. 1). These Holocene core-top samples were used as a pre-industrial baseline to determine planktonic foraminiferal shell weights before the industrial revolution. Sediment-trap data from five moorings (at 46°46′ S, 142°04′ E, 4,600 m water depth, with traps at 1,000, 2,000 and 3,800 m below sea surface) deployed between 1997 and 2004 in the central SAZ were used to represent the late industrial era. A sediment core (GC17; 47°45′ S, 145°49′ E, 3,001 m water depth) was collected above the top of the calcite saturation horizon (see Supplementary Information S2) and a timescale was constructed from accelerator mass spectrometry radiocarbon dates and planktonic foraminiferal $\delta^{18}O$. Measured shell weights for the planktonic foraminiferal species *Globigerina bulloides* were determined for all samples used in this study. We selected *G. bulloides* because the seasonal range in $\delta^{18}O$ for modern subantarctic *G. bulloides* implies a near-surface habitat[21] where the ocean has high anthropogenic CO_2 concentrations[1], and *G. bulloides* is continuously present throughout the Late Pleistocene epoch[22]. This species has no symbiotic algae, which have been shown to modify calcifiers'

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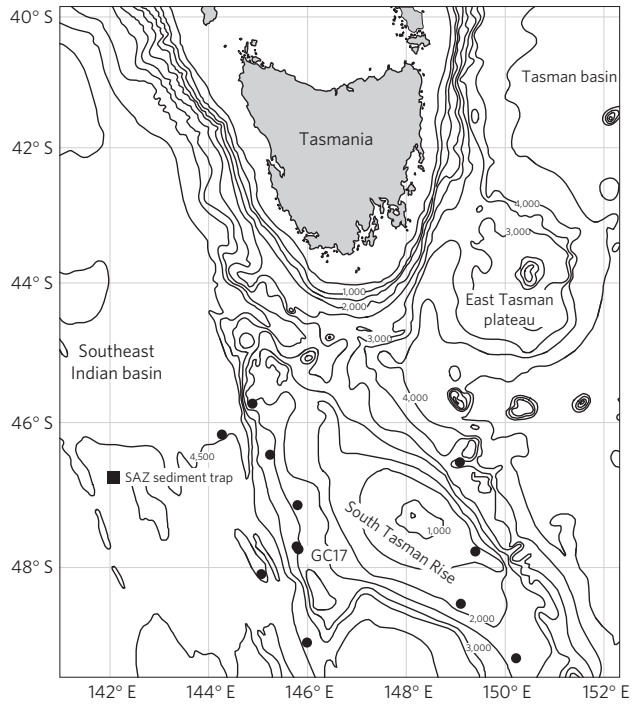

Figure 1 | Location of Holocene core-top samples, sediment-trap mooring and sediment core GC17 used in this study. Core-top samples (filled circles) and sediment-trap mooring (46°46′ S, 142°04′ E; filled square) are located in the SAZ. Bathymetry (500 m contours) sourced from the General Bathymetric Chart of the Oceans data set.

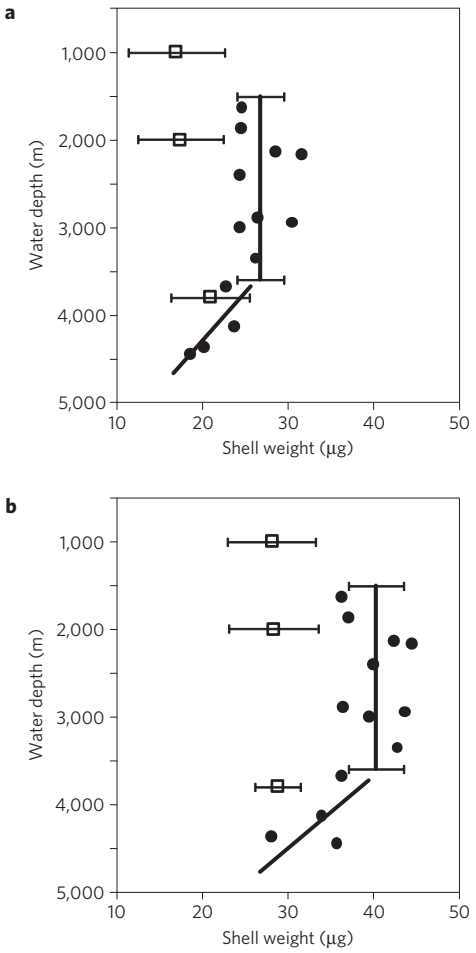

Figure 2 | SAZ Holocene core-top (filled circles) and average flux-weighted sediment-trap shell weights (open squares) for *G. bulloides*. **a**, Pre-industrial *G. bulloides* (300–355 μm) shell weight is 26.8 ± 2.8 μg (1 s.d.; $n = 9$ measurements of 50 or more shells) and modern average flux-weighted shell weight is 17.4 ± 5.0 μg (1 weighted s.d.; $n = 50$ measurements of 1–39 shells). **b**, Pre-industrial *G. bulloides* (355–425 μm) shell weight is 40.3 ± 3.2 μg (1 s.d.; $n = 9$ measurements of 50 or more shells) and modern average flux-weighted shell weight is 28.3 ± 5.3 μg (1 weighted s.d.; $n = 25$ measurements of 1–13 shells). Shell weights are also shown for traps at 1,000 and 3,800 m below sea surface. Error bars represent one standard deviation of the means (weighted mean for sediment-trap samples; arithmetic mean for core-top samples). See Supplementary Information S5,S6 for data.

response to CO_2 (ref. 8). The shell weights for *G. bulloides* were determined on shells within two narrow size ranges (300–355 μm and 355–425 μm; see the Methods section) as a means of accounting for shell size as a covariate of weight.

Using Holocene core-top *G. bulloides* to represent pre-industrial conditions and sediment-trap *G. bulloides* to reflect the industrial era, we detected a significant reduction in the shell weight of this planktonic foraminifer (Fig. 2). At water depths shallower than ~3,600 m (above the top of the foraminiferal lysocline; Fig. 2), Holocene shell weights for *G. bulloides* (300–355 μm) average 26.8 ± 2.8 μg (1 s.d.; $n = 9$ measurements of 50 or more shells). In contrast, the average flux-weighted sediment-trap shell weight for *G. bulloides* (300–355 μm) between 1997 and 2004 was 17.4 ± 5.0 μg (1 weighted s.d.; $n = 50$ individual sediment-trap cups, for which all shells were analysed) (Fig. 2a). We used flux-weighted averages from sediment-trap samples to compare with sediment records as the latter implicitly represent long-term flux-weighted averages. Using the simple arithmetic average of the sediment-trap shell weights for *G. bulloides* (15.6 ± 4.9 μg for the 300–355 μm size range) would suggest an even larger difference between the sediment and sediment-trap shell weights, and makes no difference to the estimates of the variance. Flux-weighted SAZ sediment-trap foraminiferal $\delta^{18}O$ values confirm that sedimentary isotopic records are strongly weighted towards the season of maximum production[21] and provide independent validation for the use of flux-weighted shell weights to account for seasonal changes in foraminiferal production and shell weights.

There are seasonal planktonic foraminiferal flux and shell-weight variations (minimum weight 8.8 μg, maximum weight 25.8 μg in the 300–355 μm size range). Maximum *G. bulloides* fluxes[23] and weights occur in spring and early summer, coinciding with the beginning of seasonal drawdown of carbon and the concomitant shift towards higher carbonate saturation states, and implies a slightly higher sensitivity than we infer from the core-top/sediment trap comparison[24]. Although carbonate chemistry may not be the only driver of foraminiferal shell-weight seasonality, we note that the impact of anthropogenic CO_2 persists throughout the year in these water masses. We examined the distribution of individual foraminiferal shell weights in a core-top sample to compare the distribution of shell weights in surface sediments with the seasonal variability in sediment traps (Fig. 3). The major differences in the distribution of shell weights between sediment traps and core-top sediments occur between the heaviest values in the populations in both size fractions. Although there is overlap between the shell-weight records, there is little overlap amongst the heaviest weight classes. Thus, it is the maximum shell weights rather than the minimum weights that are driving changes in the average shell weights of core tops, so that the seasonal variations are not the cause of the core-top versus sediment-trap differences. This pattern also argues against dissolution having removed the lightest shells in surface sediments.

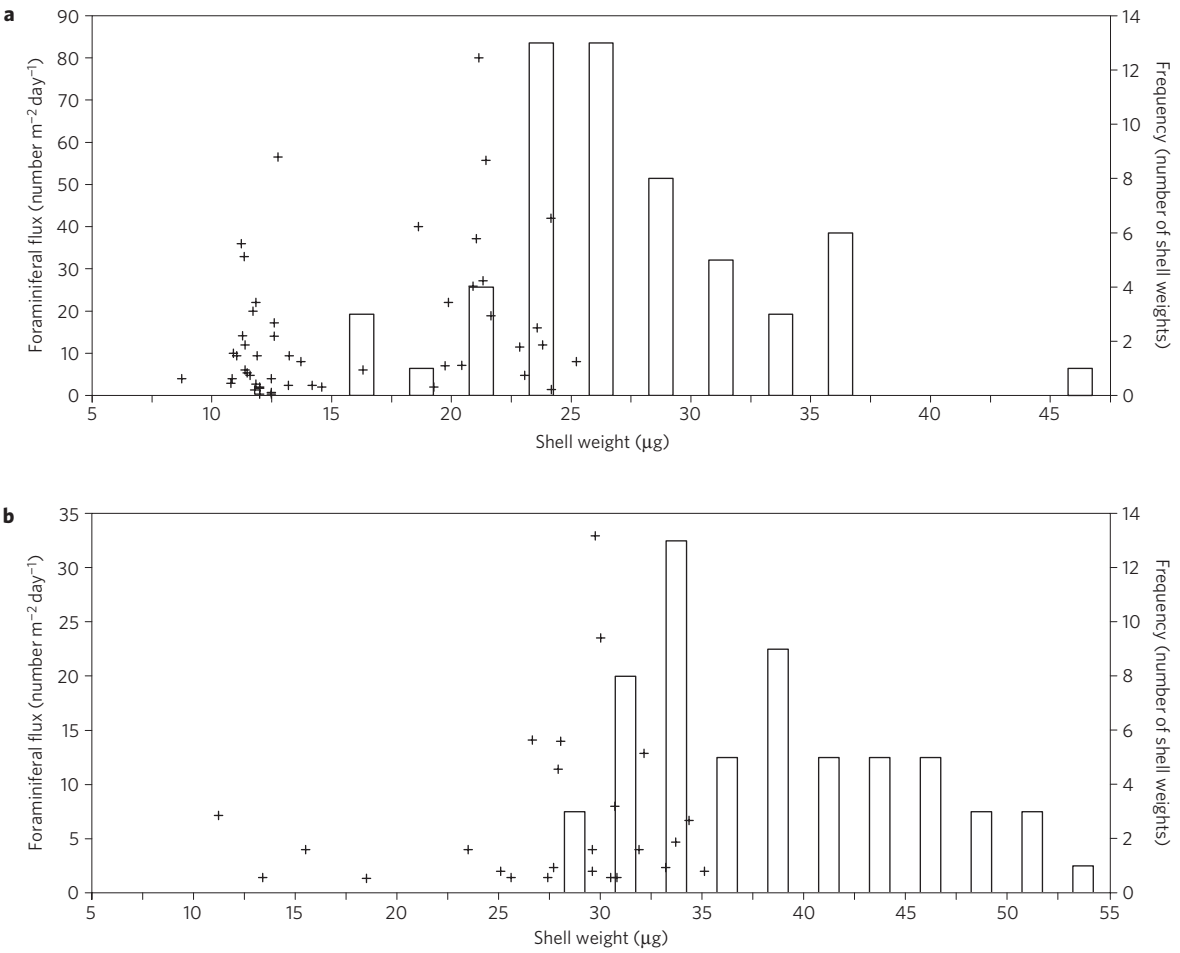

Figure 3 | *G. bulloides* shell weight and shell flux for 47° S sediment trap at 2,000 m below sea surface and the distribution of individual *G. bulloides* shell weights from core SO136-140BX. a, The 300–355 μm and **b**, 355–425 μm size ranges show a bimodal distribution of sediment-trap shell weights (+) that is due to seasonal differences in shell weight and shell flux. The distribution of individual shell weights from core-top SO136-140BX (bars) shows shell-weight variability within this core-top sample. Major differences between sediment-trap and core-top sediment samples occur in the heaviest shell-weight classes. See Supplementary Information S7 for data.

The observed average shell weight for modern *G. bulloides* represents a 35% reduction relative to Holocene shells in the 300–355 μm size range and a 30% reduction in the 355–425 μm size range (Fig. 2b). These decreases in shell weights of ~30–35% are consistent with decreases in calcification rates observed in experiments with corals[4] and other species of planktonic foraminifera[2,25] under elevated CO_2.

We can also examine the response of calcifying organisms to large-scale changes in CO_2 by establishing how they responded to past changes in ocean carbonate chemistry. The magnitude of atmospheric pCO_2 variations estimated from ice cores (from 180 and 280 ppmv; ref. 20) over glacial–interglacial cycles and the concomitant changes in ocean [CO_3^{2-}] (ref. 26) are similar to the anthropogenic CO_2 increase and changes in ocean chemistry[1]. Changes in the shell weights of planktonic foraminifera during these changes in ocean carbonate chemistry are reflected in the palaeoceanographic record[11,27]. Our observed sediment-trap *G. bulloides* shell-weight decrease (~30–35%) is comparable to a prediction of shell-weight change (~33%) using a Holocene shell-weight calibration to North Atlantic surface-water [CO_3^{2-}] (ref. 11) and estimated Southern Ocean water-column anthropogenic CO_2 values[1]. In our Southern Ocean sediment core, GC17, the shell-weight record for *G. bulloides* over the past 50,000 years tracks the ice core record of atmospheric pCO_2 (Fig. 4). Shell weights were highest during the Last Glacial Maximum (LGM; 18–24 kyr) and lowest during the Holocene (0–10 kyr), with a ~20% decrease in shell weight corresponding to the 80 ppmv LGM–Holocene increase in atmospheric pCO_2 (Fig. 4).

Although the decreased shell weights are consistent with the expected effects from anthropogenic ocean acidification, we cannot absolutely rule out other possible causes, and we address some of these here. The use of buffered solutions, which maintained their alkaline chemistry during collection and processing, make it unlikely that the lower shell weights result from dissolution post collection or during sample processing (see Supplementary Information S3). The constancy of *G. bulloides* shell weights and shell fluxes at the 47° S mooring[23] at 1,000, 2,000 and 3,800 m (Fig. 2), suggests the effect of water-column calcite dissolution is negligible. However, dissolution may have removed some of the lighter shells in the deepest trap, which is below the calcite saturation horizon, accounting for a slightly higher mean shell weight in that trap (Fig. 2). However, as noted above, the major differences in shell weights between sediment-trap and core-top sediments occur between the heaviest values in the populations and this pattern argues against dissolution having removed the lightest shells in surface sediments. Scanning electron micrographs show that although both the sediment-trap and Holocene *G. bulloides* have undergone gametogenesis[28] (see Supplementary Information S4), *G. bulloides* does not add gametogenetic calcite[29], so that temporal variations in this process cannot explain

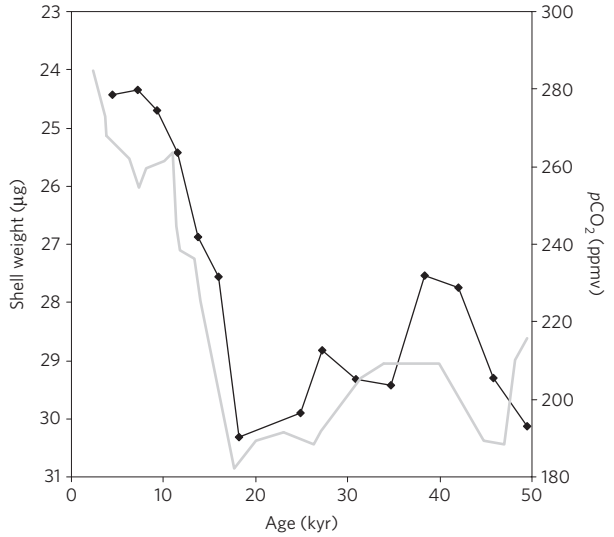

Figure 4 | Measured shell weights for *G. bulloides* (300–355 µm) in GC17 (filled diamonds) and Vostok pCO_2 record (grey solid line; ref. 20). *G. bulloides* shell weights track the Vostok pCO_2 record over the past 50,000 years. Shell weights are highest during the LGM (18–24 kyr) and glacial and lowest during the Holocene (0–10 kyr). Holocene *G. bulloides* shells (24.4 ± 0.1 µg, 1 s.d.; $n = 2$ measurements of 50 or more shells) are ~19.5% lower than LGM shells (30.3 µg; $n = 1$ measurement of 50 or more shells). See Supplementary Information S8 for age model and shell weight data.

shell-weight differences between modern and Holocene shells. Similarly, the scanning electron micrographs do not show calcite overgrowths, and thus do not suggest that authigenic precipitation has added mass to foraminiferal shells in the sediment-trap cups. In addition, the oxygen isotopic composition of sediment-trap foraminifera is consistent with precipitation in surface waters and inconsistent with precipitation at the depths of the sediment traps[21]. Furthermore, the similarity between flux-weighted and core-top *G. bulloides* oxygen isotopic compositions[21] indicates that temperature effects on calcification cannot explain shell-weight differences. Likewise, multivariate dissimilarity metrics show that sediment-trap foraminiferal assemblages are similar to Holocene assemblages, suggesting no large-scale changes in water-mass distributions over the South Tasman Rise since the Holocene[23]. Core tops in this region have high percentages of fine-fraction sediments[30] suggesting no winnowing has occurred; thus, our results are not likely to be artefacts of the removal of lighter foraminiferal shells from core-top sediments by currents.

If the implied changes in calcification of *G. bulloides* occur more broadly among planktonic foraminifera, there may be significant implications for the future marine carbon cycle. The global carbonate flux due to planktonic foraminifera is ~1.3–3.2 Gt yr^{-1}, equivalent to 23–53% of the total open-marine $CaCO_3$ flux[6]. Decreasing foraminiferal shell mass would imply a corresponding reduction in calcium carbonate ($CaCO_3$) export by the surface ocean, with implications for organic carbon (C_{org}) to $CaCO_3$ rain ratios and the effectiveness of $CaCO_3$ as 'ballast' for C_{org} export[7] and the global carbon cycle.

Our results provide the first field observation for reduced calcification in Southern Ocean planktonic foraminifera and suggest that there has been a ~30–35% reduction in the calcification of one species. We suggest this is due to anthropogenic ocean acidification. Our results may not be applicable to all species of planktonic foraminifera as many taxa in this group, unlike *G. bulloides*, bear algal symbionts, which may alter their calcification response to changing ocean carbonate chemistry[8]. Foraminifera secrete calcite, the most stable and robust form of calcium carbonate. Shells of the metastable carbonate mineral aragonite, such as those of pteropods, may be more vulnerable to acidification, especially as the Southern Ocean will become undersaturated with respect to aragonite within this century[5].

Methods

Core-top and down-core *G. bulloides* shell weights were determined by picking 50 or more whole individual shells from the 300–355 and 355–425 µm size ranges. Each batch of whole foraminiferal shells was ultrasonically cleaned in methanol and oven dried at 60 °C. Any shells broken during the cleaning process were discarded and the remaining shells were counted. The shells were weighed on a microbalance (precision = 0.1 µg) and average shell weights were calculated by dividing the measured weight by the total number of whole foraminifera. Replicate shell-weight measurements were determined by selecting a separate aliquot of 50 or more shells from the same sample. The mean difference for repeat shell-weight measurements was ±1.2 µg (1 s.d.; $n = 55$). Individual *G. bulloides* shell weights from core-top SO136-140BX were determined by picking and weighing individual specimens from the 300–355 and 355–425 µm size ranges. A total of 57 specimens were weighed from the 300–355 µm size range and 60 specimens were weighed from the 355–425 µm size range. Average flux-weighted shell weights for sediment-trap *G. bulloides* were determined by picking every single whole individual shell from the 300–355 and 355–425 µm size ranges. We used the total number of whole *G. bulloides* shells picked and the measured shell weights to calculate the average flux-weighted shell weight for deployments between 1997 and 2004. Before picking, sediment-trap sample aliquots (see ref. 17 and Supplementary Information S3 for further details on sediment-trap methods and sample preparation) were soaked in 3% hydrogen peroxide solution buffered with sodium borate for no more than 1 h to dissolve any organic matter before sieving. Samples were then washed through a 150 µm sieve with deionized water buffered with sodium borate and oven dried at 60 °C. Whole *G. bulloides* shells were picked from the 300–355 and 355–425 µm size ranges and batches of shells were weighed on a microbalance.

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Author contributions

A.D.M. and W.R.H. conceived the foraminiferal shell-weight experiment; A.D.M. carried out laboratory processing; T.W.T. and S.G.B. run the Australian Antarctic Sciences Subantarctic Zone sediment trap program, including handling of moorings and laboratory processing of bulk sediment-trap samples; A.D.M. and W.R.H. wrote the manuscript, with all authors commenting.

Additional information

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