Controls on stable isotope and trace metal uptake in *Neogloboquadrina pachyderma* (sinistral) from an Antarctic sea-ice environment

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Abstract

The polar foraminifera *Neogloboquadrina pachyderma* (sinistral) dominates assemblages from the high latitude Southern Ocean, which is a key region for paleoclimate studies. Here, we use *N. pachyderma* (s.) harvested from sediment traps off the West Antarctic Peninsula to construct a seasonal time series for the calibration of calcite proxies in a high latitude seasonal sea-ice environment where temperature is decoupled from other environmental parameters. We have used a combination of $\delta^{18}O_{CaCO3}$ and $\delta^{13}C_{CaCO3}$ to decipher the calcification temperature and salinity, which reflect that *N. pachyderma* (s.) live in surface waters throughout the year, and at the ice-water interface in austral winter. Further, our results demonstrate that, during winter, the uptake of trace metals into *N. pachyderma* (s.) calcite is influenced by secondary environmental conditions in addition to temperature

during periods of sea-ice. We suggest an elevated carbonate ion concentration at the ice-water interface resulting from biological utilisation CO_2 could influence calcification in foraminifera. We demonstrate that for *N. pachyderma* (s.) Mg/Ca and Sr/Ca ratios are linear functions of calcification temperature and $[CO_3^{2-}]$. *N. pachyderma* (s.) Mg/Ca ratios exhibit temperature sensitivity similar to previous studies (~ 10 % per °C) and a sensitivity to $[CO_3^{2-}]$ of ~ 1 % per μmol kg^{-1}). Sr/Ca ratios are less sensitive to environmental parameters, exhibiting < 1% increase per °C and per 10 μmol kg^{-1}. We show how a multi-proxy approach could be used to constrain past high latitude surface water temperature and $[CO_3^{2-}]$.

Keywords: *N. pachyderma*; isotopes; trace metals; sea-ice; carbonate ion

1 Introduction

Atmospheric gases trapped in bubbles within ice cores show the partial pressure of carbon dioxide (pCO_2) was 80 ppmV lower during the Last Glacial Maximum (LGM) compared with modern values (Siegenthaler et al., 2005). Of the many hypotheses proposed to account for this CO_2 shift, a significant focus has been placed on past changes in productivity, chemistry and circulation in the Southern Ocean (Anderson et al., 2002; Sigman and Boyle, 2000). Accordingly, there is a clear motivation to obtain reliable information about these processes in the past Southern Ocean. The stable isotopic and trace metal composition of planktonic foraminiferal calcite provide important geochemical tools for reconstructing past changes in sea surface conditions. In particular, *Neogloboquadrina pachyderma* (sinistral) is a species of interest as it dominates modern planktonic assemblages in the high latitudes and Southern Ocean sediments. However, inference of past calcification conditions from *N. pachyderma* (s.) chemistry can

51 be ambiguous, in part because the species can live in a variety of habitats, including sea-
52 ice. Open water *N. pachyderma* (s.) are generally considered pycnocline dwellers, but can
53 calcify below the mixed layer, occupying a wide range of depths shallower than 200 m
54 (Kohfeld et al., 1996). In sea-ice conditions, *N. pachyderma* (s.) are associated in high but
55 patchy cell concentrations with the bottom community of sea-ice diatoms, which grows
56 in the more porous layers at the ice-water interface (Lipps and Krebs, 1974). In the
57 autumn, the adults conduct gametogenesis, such that juveniles appear in the upper part
58 of the water column and become incorporated into the forming frazil ice (Spindler and
59 Dieckmann, 1986).
60 There is an increasing appreciation that multiple factors control stable isotope and trace
61 metal chemistry of foraminifera. In particular, the role of carbonate ion concentration,
62 $[CO_3^{2-}]$, and salinity on the uptake of trace metals (Mg, Sr and Li) into planktonic
63 foraminiferal calcite is not fully understood (Ferguson et al., 2008; Lea et al., 1999;
64 Marriott et al., 2004; Mortyn et al., 2005; Russell et al., 2004). Further, Southern Ocean
65 waters are undersaturated with respect to calcite such that foraminifera have a low
66 preservation potential in slowly accumulating sediments. This, in turn, means that there
67 is a paucity of calibration studies involving high latitude species in the literature. Here,
68 we present a multi-proxy calibration study of *N. pachyderma* (s.) from the West Antarctic
69 Peninsula (WAP) collected using sediment traps. We use the stable isotopic composition
70 of the calcite to determine where the foraminifera calcify and to demonstrate that trace
71 metal uptake depends on factors other than temperature and salinity, such as $[CO_3^{2}]$,
72 during periods of sea-ice cover. We have calculated $[CO_3^{2-}]$ from measurements of
73 Dissolved Inorganic Carbon (DIC) and pH for a limited period of the year, and inferred
74 $[CO_3^{2-}]$ throughout the year using B/Ca ratios and shell weights, which agree on a
75 consistent change in $[CO_3^{2-}]$ at the depth of calcification throughout the year. This
76 allows other trace metal proxies, Mg/Ca, Sr/Ca and Li/Ca, to be calibrated for

77 temperature and [CO_3^{2-}] using linear regression. Our multi-proxy approach potentially
78 allows temperature and [CO_3^{2-}] effects to be deconvolved, such that these parameters can
79 be constrained in the past using high latitude foraminifera from marine sediment cores.

80 2 Materials and methods

81 A set of moorings was deployed in Marguerite Bay, WAP, in January 2005 from the
82 British Antarctic Survey vessel RRS James Clark Ross (840 m water depth). The site is
83 close to the Rothera Oceanographic and Biological Time-Series (RaTS) site (Clarke et al.,
84 2008) (Figure 1), an on-going programme featuring quasi-weekly water column profiling
85 and discrete water sampling. The mooring comprised a suite of oceanographic
86 instrumentation, including a sediment trap at 200 m with bottle closure times configured
87 to sample sinking particles throughout the year at fortnightly to bimonthly periods (Table
88 1). The bottles were pre-loaded with 2% buffered formalin to preserve organic material.
89 The sediment trap bottles were recovered the following year and stored at 4°C.
90 Foraminifera were picked from the sediment trap splits by K. Weston (University of East
91 Anglia, UK). *N. pachyderma* (s.) specimens were present in sediment trap bottles from
92 summer to winter months, confirming their presence in the water column throughout the
93 year. The foraminiferal organic matter and calcite were well preserved and some
94 individuals were present connected as growth chains, which suggests insignificant
95 transport in the water column.
96
97 Light microscopy, Scanning Electron Microscopy (SEM) imaging and probe analysis
98 were used to assess the microstructural scale preservation of one or two foraminifera per
99 trap bottle. Light microscope analyses show these sediment trap foraminifera are
100 "glassy" rather than "frosty" (Sexton et al., 2006) and SEM images confirm they are well
101 preserved without either dissolution due to calcite undersaturation or secondary calcite

precipitation (Figure 2). Energy Dispersive Spectrometry (EDS) shows Al, Mg and Fe levels are below detection implying no surface contamination. Foraminifera shell size was estimated by eye (compared to sieved *N. pachyderma* fractions) and was found to occupy a narrow size range (~ 212-300 μm). Encrusted specimens (Figure 2B) were not included in analysis to avoid any contribution from secondary or gametogenic calcite, which may have a different chemical composition to the other calcite layers (Brown and Elderfield, 1996; Eggins et al., 2003; Elderfield and Ganssen, 2000; Kohfeld et al., 1996; Ni et al., 2007; Nurnberg et al., 1996; Sadekov et al., 2005).

Total shell weights were measured (±1 μg) and the mean weight calculated per shell. The shell sizes and weights are typical of cold water *N. pachyderma* (s.) from open water and sea-ice (Barker and Elderfield, 2002; Donner and Wefer, 1994; Spindler and Dieckmann, 1986).

The oxygen and carbon isotopic composition of five to six foraminifera (> 250 μm) per bottle were analysed using a VG Isogas Prism II mass spectrometer with an on-line VG Isocarb common acid bath preparation system (Oxford University). Samples are first cleaned for organic matter using hydrogen peroxide and acetone and dried at 60°C for at least 30 minutes. In the instrument they are reacted with purified phosphoric acid at 90°C. Calibration to Pee Dee Belemnite (PDB) standard via NBS-19 is made daily using the Oxford in-house (NOCZ) Carrara marble standard. Reproducibility of replicated standards is usually better than 0.1‰ for $\delta^{13}C$ and $\delta^{18}O$.

There was insufficient material to analyse different size fractions for trace metals, so the remaining foraminifera were crushed gently between two clean glass plates and cleaned for clays by sonicating in 18 MΩ water. The process was repeated two more times with 18 MΩ water and twice with reagent grade methanol.

Oxidising stage

Due to the nature of the sediment trap samples, the oxidising stage of the foraminifera cleaning procedure was adapted for higher organic matter content (Anand et al., 2003). 0.25 ml of 50% H_2O_2 (made up with 0.2 M NaOH, making a final solution of 0.1 M NaOH) was added to each sample and placed in a hot water bath (70 °C) for a total of 45 minutes, and the samples rinsed twice with 18 MΩ water.

Final weak acid leach, dissolution and analysis

100-250 ml quartz distilled (QD) 0.001 N HNO_3 was added to each sample, sonicated and supernatant removed. This was repeated up to four times, and finally rinsed with QD water. The samples were dissolved on the day of analysis using 250 ml QD 0.1 N HNO_3, sonicated, centrifuged to settle any remaining particles and transferred to a clean tube for analysis. Trace metal analysis was carried out by Q-ICP-MS (University of Cambridge), which have been tested by an interlaboratory comparison study by M. Greaves and J. Yu using external, matrix-matched standards (Rosenthal et al., 2004). Long term reproducibility is 1.4% for Mg/Ca, 0.9% for Sr/Ca, 2.4% for Li/Ca and 4.2% for B/Ca ratios (Yu et al., 2005).

$\delta^{18}O_{water}$ of the water column

As part of RaTS, full-depth profiles of temperature and salinity were collected at the shallow mooring site on a quasi-weekly basis, using a SeaBird SBE19 conductivity-temperature-depth (CTD) sensor. Profiling was conducted from a small boat during summer and through a hole cut in the ice during winter. Discrete water samples were drawn from 15 m depth using a Niskin bottle closed with a messenger weight. These were sealed for transportation to the UK for oxygen isotope analysis. In addition, full-depth profiles of oxygen isotopes were obtained each December as part of hydrographic casts conducted during visits of RRS James Clark Ross to Rothera. Full details of the RaTS CTD profiling procedures and data quality, oxygen isotope analysis methods and

153 data are described elsewhere (Clarke et al., 2008; Meredith et al., 2008; Meredith et al.,
154 2004).

155 3 Results and discussion

156 3.1 Reconstructing foraminiferal habitat from stable isotopes

157 In order to understand the controls on trace metal uptake into N. pachyderma (s.), it is
158 essential to constrain the depth and ambient environmental conditions at calcification.
159 Here we define the foraminifera habitat using the $\delta^{18}O_{CaCO3}$ and $\delta^{13}C_{CaCO3}$, which can be
160 combined with RaTS CTD profiles to determine calcification temperature and salinity.

161 *3.1.1 Calcification depth from $\delta^{18}O$*

162 *a) Simulating $\delta^{18}O_{water}$ profiles*

163 We can use $\delta^{18}O_{CaCO3}$, with the Shackleton paleotemperature equation, to determine
164 habitat depth because vertical profiles for both temperature and $\delta^{18}O_{water}$ are available for
165 Marguerite Bay. Stable isotopic values for the calcite range from 0.66 to 1.48 ‰ and 2.60
166 to 3.26 ‰ for $\delta^{13}C$ and $\delta^{18}O$ respectively (Table 1; Figure 3). Measured $\delta^{18}O_{water}$ range
167 from -0.2 to -0.8 ‰, with more depleted values observed in surface waters. Typically,
168 isotopically lighter waters occur near the surface during the austral fall ($\delta^{18}O_{water}$ ~ -0.8
169 ‰), with isotopically heavier waters found during the austral spring ($\delta^{18}O_{water}$ ~ -0.5 to -
170 0.6 ‰), reflecting the seasonal cycles in precipitation, glacial melt and sea-ice/upper
171 ocean processes (Meredith et al., 2008). A simulated full-depth $\delta^{18}O_{water}$ field was
172 produced from the approximately weekly time series of discrete samples taken at 15 m
173 depth and the full-depth $\delta^{18}O_{water}$ profiles collected during December of each year. For
174 this, the quasi-linear relationship between salinity and $\delta^{18}O_{water}$ for Marguerite Bay was

used along with the approximately weekly full-depth salinity and temperature profiles that were collected at the same time as the $\delta^{18}O_{water}$ samples (Meredith et al., 2008). The Mixed Layer Depth (MLD) to which the upper water column is homogenised by surface processes was derived from each of the weekly profiles, and all values within the mixed layer were set to the $\delta^{18}O_{water}$ value at 15 m for each cast. Beneath the mixed layer, $\delta^{18}O_{water}$ from the full-depth casts was regressed on salinity, and this was used to convert the measured salinity from the weekly profiles into simulated $\delta^{18}O_{water}$ piecewise in 50 m sections. Combined, this produced full-depth $\delta^{18}O_{water}$ profiles at approximately weekly intervals (Figure 5a).

b) Predicting $\delta^{18}O_{CaCO3}$

The $\delta^{18}O_{CaCO3}$ was predicted using Shackleton's 1974 equation and assuming the simulated values of $\delta^{18}O_{water}$:

$$\left(\delta^{18}O_{CaCO3}\right)_{pred} = \left\{\delta^{18}O_{water} + 21.9 - \sqrt{310.61 + 10T}\right\} - v \quad (1)$$

where v is a correction factor to account for vital effects. The $\delta^{18}O_{water}$ values were corrected to PDB using Equation 2 (Bemis et al., 1998):

$$\delta^{18}O_{water} = 0.9998 \times \delta^{18}O_{SMOW} - 0.2 \quad (2)$$

For *N. pachyderma* (s.) the vital offset has been estimated as between 0.5 and 1.3 ‰ (Bauch et al., 1997; Kohfeld et al., 2000; Ortiz et al., 1996; Simstich et al., 2003; Smith et al., 2005; Volkmann, 2000). A temperature dependent vital offset based on measured ambient $\delta^{18}O_{water}$ (Bauch et al., 1997) was used with RaTS site sea-surface temperatures to correct the $\delta^{18}O_{CaCO3}$ measurements (Table 2). The vital offsets are similar between Arctic (Bauch et al., 1997) and Antarctic *N.pachyderma* (s.) (Kohfeld et al., 1996; Mortyn and Charles, 2003) despite evidence for cryptic speciation (Darling et al., 2007). The associated error is estimated to be ± 0.2 ‰.

c) Reconstructing calcification depths

Although the error on the vital effect is relatively large, the depth of calcification can be estimated by matching the measured and predicted values of $\delta^{18}O_{CaCO3}$ (Figure 5b, c). Furthermore, we can derive the temperature and salinity from the CTD profiles in order to calibrate the trace metal proxies with ambient environmental conditions at the depth of calcification. Although this is relatively straightforward in sea-ice free months, it is more difficult to assign ambient salinity values in winter given the foraminifera may be living in the sea-ice brine channels or at the ice-water interface (Lipps and Krebs, 1974). Sea-ice formation does not affect $\delta^{18}O_{water}$ significantly, so will have only a minor influence on $\delta^{18}O_{CaCO3}$ (Weiss et al., 1979). However, the extent of open exchange between the sea-ice habitat and the underlying seawater, and thus the ambient salinity, can be determined using the carbon isotopic composition of the foraminiferal calcite.

3.1.2 Winter sea-ice habitat from $\delta^{13}C$

The primary controls on $\delta^{13}C_{CaCO3}$ are the carbon isotopic composition of DIC in the ambient water, the organic matter on which the foraminifera feed, temperature and $[CO_3^{2}]$ (Kohfeld et al., 2000). The $\delta^{13}C_{DIC}$ is lighter in winter than in summer as a result of reduced gas exchange with the atmosphere due to sea-ice cover (Lynch-Stieglitz et al., 1995). As the sea-ice becomes persistent, gas exchange with the atmosphere is effectively shut off, and the $\delta^{13}C_{CaCO3}$ values become depleted by ~ 0.8‰ (Table 1). As the air temperature rises to -5 to -9°C, the sea-ice breaches the porosity threshold (Golden et al., 1998; Perovich et al., 2004) and becomes an open, interconnected system allowing the replenishment of lighter carbon from the seawater interface. Increased gas exchange with the atmosphere enriches the carbon isotopic composition of DIC, organic matter and foraminiferal calcite (Delille et al., 2007).

The carbon isotopic composition of the food source will depend on where the foraminifera are feeding, particularly in winter. $\delta^{13}C_{org}$ values from sea-ice brine algae collected from the isotopically closed upper layers of sea-ice by sackhole drilling are heavier than surface water values due to Rayleigh fractionation of carbon during biological utilisation in a closed system (Gibson et al., 1999; Carson et al., in prep). However, the observed variations in $\delta^{13}C_{CaCO3}$ here suggest that the dietary $\delta^{13}C_{org}$ does not become significantly heavier from summer to winter (Figure 3), and that the foraminifera are feeding in a system openly exchanging with the underlying water. Furthermore, if the foraminifera lived in the less consolidated bottom layers of platelet ice they would be more likely to escape the sea-ice and sink to the sediment traps. It is reasonable, therefore, to assume that during winter the foraminifera analysed lived at the ice-water interface and experienced surface water temperatures and salinities that remain relatively constant at the inferred foraminiferal habitat throughout the year (Figure 5b).

3.2 Controls on trace metal uptake in N.pachyderma (s.)

The Mg/Ca, Sr/Ca, B/Ca and Li/Ca ratios vary between 0.77-1.06 mmol/mol, 1.37-1.41 mmol/mol, 50-75 μmol/mol and 17.4-19.8 μmol/mol respectively (Figure 4). The trace metal seasonal profiles show a peak in austral winter, which is not observed in the surface temperature profile or stable isotopic composition (Figure 3, 4; Table 1). We have inferred from the isotopic composition of the calcite that the foraminifera calcify at the ice-water interface, suggesting against any temperature, salinity or Rayleigh fractionation effects on foraminifera chemistry. If our assumption is correct, it would suggest that there is some additional factor influencing calcification during the period of sea-ice cover, such as $[CO_3^{2}]$. Here, we will reconstruct the ambient $[CO_3^{2}]$ of the calcifying foraminifera, before discussing the effect on tract metal uptake.

3.3.1 Shell weight and boron uptake

Culture experiments have shown stable isotope and trace metal uptake into planktonic foraminifera may also be a function of [CO_3^{2-}], in addition to temperature and salinity (Russell et al., 2004; Spero et al., 1997). Although the carbonate system was not fully constrained throughout the year in Marguerite Bay, we have calculated [CO_3^{2-}] from available data of Dissolved Inorganic Carbon (DIC) and pH measured at the RaTS site (Carson et al., in prep). [CO_3^{2-}] values are calculated using a simple speciation model (carbcalc 5e, Boyle, 2005) for seawater at 15 m depth and brine from upper sea-ice layers collected by sackhole drilling.

We infer in the previous section that the winter habitat of *N.pachyderma* (s.) is at the ice-water interface, which likely represents the chemical transition between the low [CO_3^{2-}] of the surface waters and the extremely high [CO_3^{2-}] of the closed system upper layers of sea-ice. Qualitatively, therefore, the effect of the presence of sea-ice on the growth habitat of *N.pachyderma* (s.) is to elevate ambient [CO_3^{2-}] (Figure 6). Quantitatively, we can infer [CO_3^{2-}] at the site of calcification from shell weights (Barker and Elderfield, 2002) and the B/Ca ratio (Yu et al., 2007). We cannot use the predictable relationship between temperature and [CO_3^{2-}] in open seawater in the Southern Ocean (King and Howard, 2004) because it is unlikely to hold in seasonal sea-ice environments. Both sea-ice and the ice-water interface are known to exhibit undersaturation of CO_2 as a result of biological activity and brine expulsion (Delille et al., 2007; Gleitz et al., 1995; Papadimitiou et al., 2007), leading to a decoupling between [CO_3^{2-}] and temperature.

The mean shell weights range from ~6 μg per shell to ~14 μg per shell (Figure 6). The pristine nature of the foraminifera suggests variability in the shell weight profile, also reflected in the shell geochemistry, is a result of environmental conditions rather than dissolution or encrustation effects (Figure 2). Specifically, there is a peak in midwinter

between June and October, where shell weights increase ~4 μg per shell (Figure 6). According to the calibration of Barker & Elderfield (2002) this shell weight change corresponds to an increase in $[CO_3^{2-}]$ of ~ 40 μmol kg^{-1} (note though that this calibration is for *N. pachyderma* (dextral)). This feature is unrelated to changes in the contribution of different size fractions (Figure 6), which suggests the geochemical variation is not a function of shell size or ontogeny.

B/Ca, thought to be a measure of $[CO_3^{2-}]$, is a relatively new proxy (Foster, 2008; Yu and Elderfield, 2005; Yu et al., 2007). Boron is taken up into foraminifera calcite as the borate ion ($B(OH)_4^-$) (Hemming & Hansen, 1992), which exchanges with boric acid as a function of pH resulting in both the B/Ca ratio and B isotopic fractionation (Yu et al., 2007). The borate ion substitutes for CO_3^{2-} in the calcite lattice according to Equation 3:

$$\left(\frac{[Ca(HBO_3)]}{[CaCO_3]}\right) = K_D\left(\frac{[B(OH)_4^-]}{[HCO_3^-]}\right) \quad (3)$$

Hence, as $[HCO_3^-]$ decreases (i.e. $[CO_3^{2-}]$ increases), $B(OH)_4^-$ uptake increases (Gaillardet and Allègre, 1995).

In this study, B/Ca shows a strong peak in mid-winter, which we suggest occurs at a time when there are neither significant temperature nor salinity changes in the water column at the depth of calcification (Figure 6). There is no change in the B/Ca ratio during the period of cooling into winter, suggesting there is no significant temperature effect here on boron uptake into calcite. This contradicts other studies that have shown a temperature dependence on B uptake into foraminiferal calcite (Yu et al., 2007). However, the water temperature variation experienced here is low (approximately 2°C), suggesting that other factors dominate in this case.

The B/Ca ratio has been shown in other plankonic foraminifera (*Globigerinoides inflata*) to relate to $[CO_3^{2-}]$ according to Equation 4 (Yu et al., 2007), where the numbers in parentheses show 95% confidence intervals.

297 $$[CO_3^{2-}] = 0.8647(\pm 0.16)(B/Ca) + 108.29(\pm 11.2) \quad (4)$$

298 Although there are thought to be species-specific dependence on B incorporation into
299 foraminiferal calcite, the latitudinal trend and range in B/Ca ratios for *G. inflata* and *N.*
300 *pachyderma* (s.) are similar (Yu, pers. com.). Hence, in the absence of a published
301 calibration, we have used the *G. inflata* relationship (Equation 4) to reconstruct temporal
302 changes in $[CO_3^{2-}]$ in Marguerite Bay (Figure 6).
303 The B/Ca data indicate an increase in $[CO_3^{2-}]$ (decrease in PCO_2) in the winter during the
304 period of sea-ice coverage of 30-40 μmol kg^{-1}. Whilst it is possible that the temperature
305 and $[CO_3^{2-}]$ effect could compensate each other at certain times of year, a peak in $[CO_3^{2-}]$
306 at the site of calcification inferred from the B/Ca ratios is consistent with the calculated
307 $[CO_3^{2-}]$ and shell weight variations (Figure 6).
308 In summary, the shell weight and B/Ca ratios are consistent with the foraminifera living
309 at the ice-water interface over winter. Sea-ice and the ice-water interface are known to
310 exhibit undersaturation of CO_2 as a result of biological activity and expulsion (Delille et
311 al., 2007; Gleitz et al., 1995; Papadimitiou et al., 2007; Figure 6), leading to the mid-
312 winter increase in $[CO_3^{2-}]$. We suggest the extremely high $[CO_3^{2-}]$ calculated for the upper
313 layers in sea-ice are not matched by the predictions from shell weights and B/Ca because
314 the degree of CO_2 utilisation is less extreme at the ice-water interface where the
315 foraminifera calcify. The change in $[CO_3^{2-}]$ is likely to change foraminiferal oxygen
316 isotopes by less than 0.1 ‰ (Spero et al., 1997), consistent with our $\delta^{18}O_{CaCO3}$ variations
317 (Figure 3; Table 1), but may have an influence on trace metal uptake.
318

319 ***3.3.2 Carbonate ion effect on trace metal uptake***

320 Mg/Ca, Sr/Ca and Li/Ca ratios share similar "w-shaped" profiles, including both high
321 summer values and a midwinter peak also observed in the shell weight and B/Ca ratio

profiles, which suggests metal uptake is controlled by multiple environmental controls including calcification temperature and $[CO_3^{2-}]$. Here, the sensitivity of Mg/Ca, Sr/Ca and Li/Ca ratios to the different environmental parameters can be estimated and constrained by linear regression with calcification temperature and $[CO_3^{2-}]$. Although the Mg/Ca ratio is generally assumed to be an exponential function of calcification temperature (Elderfield and Ganssen, 2000), the model here focuses on the low temperature domain and so a linear approximation is valid.

Moving averages of calcification temperature and $[CO_3^{2-}]$, calculated from $\delta^{18}O_{CaCO3}$ and the B/Ca ratio respectively (Figure 6), were used to solve Equations 5-6 by fit of least mean squares for Mg/Ca and Sr/Ca ratios (Figure 7).

$$\frac{Mg}{Ca} = 0.11(\pm 0.02)T + 0.011(\pm 0.002)[CO_3^{2-}] - 0.69(\pm 0.2)$$

$r^2 = 0.33$ ($n=13$, $p<0.05$)

(5)

$$\frac{Sr}{Ca} = 0.008(\pm 0.002)T + 0.0015(\pm 0.0002)[CO_3^{2-}] + 1.14(\pm 0.25)$$

$r^2 = 0.57$ ($n=13$, $p<0.05$)

(6)

There is no significant relationship between the predicted and measured Mg/Ca when the linear regression is carried out for T and $[CO_3^{2-}]$ separately ($r^2 < 0.1$). Unfortunately, there are not sufficient data points to conduct rigorous statistical testing, but uncertainties have been estimated by optimising the sum of the least mean squares by varying each parameter in turn to ±5% of the optimal value. (Note: this method does not produce a good fit for Li/Ca ratios, $r^2 < 0.1$). A positive correlation between Mg/Ca residuals and shell weight, an independent measure of $[CO_3^{2-}]$, provides further evidence for a significant $[CO_3^{2-}]$ effect on *N. pachyderma (s.)* trace metal uptake (Figure 8).

346 Although further work is required to produce a rigorous calibration, our data can be used
347 to estimate the sensitivity of *N. pachyderma* (s.) calcite Mg/Ca and Sr/Ca ratios to
348 temperature and [CO_3^{2-}]. The Mg/Ca ratios in this environment show similar
349 temperature sensitivity (~ 10 % per °C) to open water *N. pachyderma* (Elderfield and
350 Ganssen, 2000; Nurnberg, 1995; von Langen et al., 2005). Although some laboratory
351 and field studies suggest a salinity effect on Mg/Ca ratios (Ferguson et al., 2008), such an
352 effect cannot be tested here as there is little variability in calcification salinity. Sr/Ca is
353 less sensitive to environmental conditions than the Mg/Ca ratio (< 1% increase per °C
354 and per 10 μmol kg^{-1}) (Figure 7). This is consistent with previous culture experiments,
355 plankton tow and core top samples of non-globorotaliid foraminifera that demonstrate a
356 weak temperature effect on Sr uptake into planktonic foraminiferal calcite and an
357 increase in the Sr/Ca ratio with increasing pH (Mortyn et al., 2005; Russell et al., 2004).
358 *Implications for glacial-interglacial SST reconstructions*
359 The influence on *N. pachyderma* (s.) Mg/Ca ratios (and the uptake of other trace metals)
360 by environmental parameters other than temperature (e.g. [CO_3^{2-}]) has implications for
361 glacial-interglacial SST reconstructions in regions where sea-ice cover varies on similar
362 timescales. This includes:
363 1) Regions of the subantarctic Southern Ocean that are outside the modern Seasonal Sea-
364 Ice Zone (SIZ) but were within the winter sea-ice extent during cooler periods;
365 2) Regions of coastal Antarctica that are within the modern SIZ but were covered by
366 multi-year ice during cooler periods.
367 Downcore records from the subantarctic Pacific indicate a change in *N. pachyderma* (s.)
368 Mg/Ca ratio of ~ 0.2 mmol/mol on a glacial-interglacial timescale (Mashiotta et al.,
369 1999), which is of similar amplitude to seasonal changes from this study. Diatom
370 population analysis (Gersonde et al., 2005) indicate that the core was near the edge of the
371 LGM winter sea-ice extent, such that the site may have experienced seasonal variation in

372 $[CO_3^{2-}]$ in the absence of temperature variation. The time averaging of such seasonality
373 in sediments requires further investigation for the robust interpretation of Southern
374 Ocean foraminiferal trace metal proxies.

375 4 Summary and conclusions

376 Here, we constrain the controls on geochemical proxies based on the high latitude
377 planktonic foraminifera, *Neogloboquadrina pachyderma* (s.) using time series sediment trap
378 samples from the West Antarctic Peninsula. $\delta^{18}O_{CaCO3}$ and $\delta^{13}C_{CaCO3}$ can be used to
379 demonstrate that the foraminifera calcify at the ice-water interface in winter, which
380 exchanges openly with seawater, and to reconstruct calcification temperature and salinity.
381 Our results show that trace metal uptake during calcification is influenced by factors
382 other than ambient temperature and salinity, especially during periods of sea-ice cover.
383 We suggest, using B/Ca ratios and shell weight data, that there is an increase in $[CO_3^{2-}]$
384 during periods of sea-ice cover and that Mg/Ca, Sr/Ca and Li/Ca ratios are functions of
385 temperature and $[CO_3^{2-}]$. *N. pachyderma* (s.) Mg/Ca exhibits similar temperature
386 sensitivity to previous studies (~ 10 % per °C) and a $[CO_3^{2-}]$ sensitivity of ~ 10 % per 10
387 μmol kg^{-1}. Sr/Ca is less sensitive to environmental parameters, exhibiting < 1% increase
388 per °C and per 10 μmol kg^{-1}. Seasonal variation in habitat, and associated changes in
389 ambient conditions with depth in the water column and the ice-water interface, adds a
390 further degree of uncertainty to paleoceanographic reconstructions based on Mg/Ca
391 ratios. However, more reliable estimates of past sea surface temperatures can be
392 achieved by taking into account changes in sea-ice cover. Further work on the time
393 averaging of seasonal variability in calcite chemistry is justified in order to decode
394 Southern Ocean paleoclimate records.
395
396

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Figure captions:

Figure 1: Map showing the sediment trap and RaTS site (see text for details) off the West Antarctic Peninsula.

Figure 2: SEM images of foraminifera A) showing non-encrusted specimen from June; B) showing encrusted specimen from May and C) an internal view showing good preservation and lack of secondary calcite.

Figure 3: A) Mean surface temperature and salinity (data from British Antarctic Survey); B) $\delta^{18}O_{CaCO3}$ and $\delta^{13}C_{CaCO3}$ results for *N. pachyderma* (s.). The hatched bar indicates the period of persistent sea-ice.

578

579 Figure 4: Trace metal results for *N. pachyderma* (s.) calcite, each plotted against surface
580 temperature and salinity. The hatched bar indicates the period of persistent sea-ice.

581

582 Figure 5: A) predicted $\delta^{18}O$ of water, with values given relative to SMOW. B) Predicted $\delta^{18}O$ of
583 foraminiferal calcite. A temperature dependent vital effect between 0.6 and 1.1‰ has been
584 applied to the data.
585 The measured $\delta^{18}O_{CaCO3}$ values can then be compared to the model to estimate habitat depths.
586 The white bars indicate the error on the $\delta^{18}O_{CaCO3}$ measurements (0.1‰) and indicate the most
587 likely depths for calcification, and the black error bars show the error on the vital effect (±0.2‰).
588 C) Reconstructed temperatures and salinities for the conditions at which the foraminifera calcify
589 calculated from the $\delta^{18}O$ depth profile.

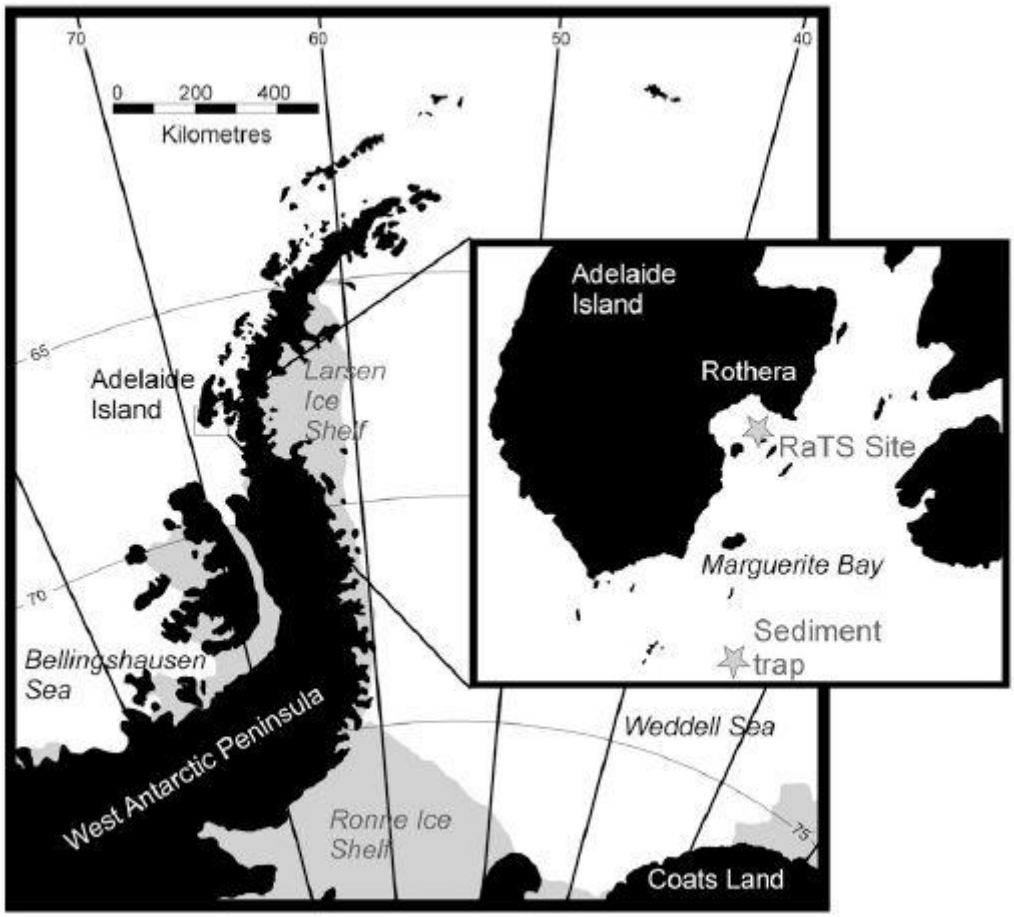
590

591 Figure 6: Measures of carbonate ion concentration in seawater. A) B/Ca; B) $[CO_3^{2-}]$ calculated
592 using B/Ca and the calibration of (Yu et al., 2007). The error bars show 95% confidence
593 intervals (Equation 4); C) $[CO_3^{2-}]$ in seawater (15 m depth; black triangles) and sea-ice brine from
594 upper layers of ice collected by sackhole drilling (grey triangles), calculated using measured values
595 of alkalinity and DIC (data from Carson et al., in prep) and carbcalc 5e (Boyle, 2005); D) mean
596 shell weights for all size fractions; E) numbers of shells in each size fraction (< 250 μm in black
597 circles; > 250 μm in white circles) demonstrating the trends in shell weights are not a result of
598 changes in the proportion of each size fraction. The hatched box shows the period of persistent
599 sea-ice.

600

601 Figure 7: Controls on trace metal uptake into *N. pachyderma* (s.). A) Calcification temperature
602 and $[CO_3^{2-}]$, calculated from $\delta^{18}O_{CaCO3}$ and B/Ca ratios respectively (Figure 3 and 4). The data
603 are smoothed using a moving average. B) Measured Mg/Ca (black triangles) and Mg/Ca
604 predicted using Equation 5 (white triangles). C) Measured Sr/Ca (black circles) and Sr/Ca

605 predicted using Equation 6 (white circles). The hatched box shows the period of persistent sea-
606 ice.
607
608 Figure 8: Mg/Ca residuals plotted against mean shell weight, which can be used as an
609 independent measure of [CO_3^2]. The Mg/Ca residuals are calculated here by subtracting the
610 Mg/Ca ratio predicted using the exponential relationship given by (Elderfield and Ganssen, 2000)
611 and calcification temperature from the measured Mg/Ca value (white circles). Mg/Ca residuals
612 are also calculated here by subtracting the Mg/Ca temperature effect and constant term show in
613 Equation 5 (black circles). The Mg/Ca residuals correlate significantly with shell weight (r^2 =
614 0.52, $p < 0.05$, $n = 13$).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60
50
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Kilometres
65
70
75
Adelaide
Island
Larsen
Ice
Shelf
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Sea
West Antarctic Peninsula
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Adelaide
Island
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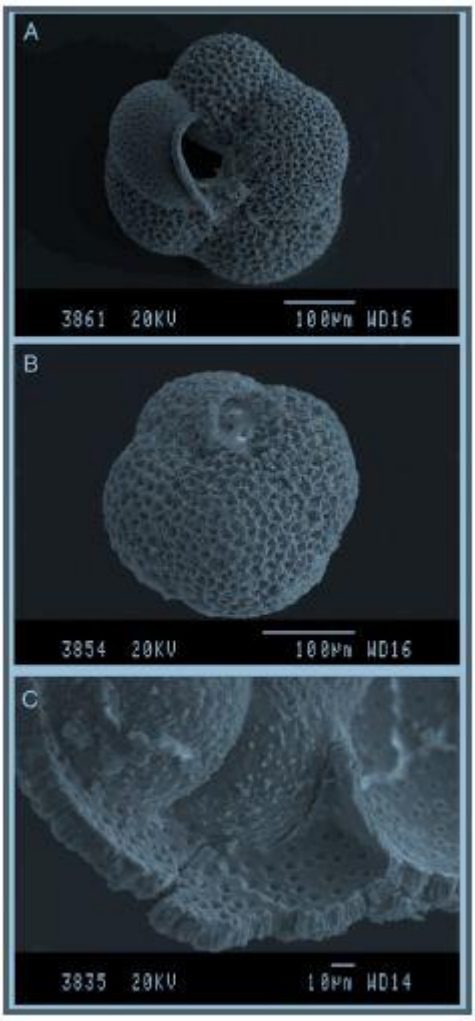
RaTS Site
Marguerite Bay
Sediment
trap

615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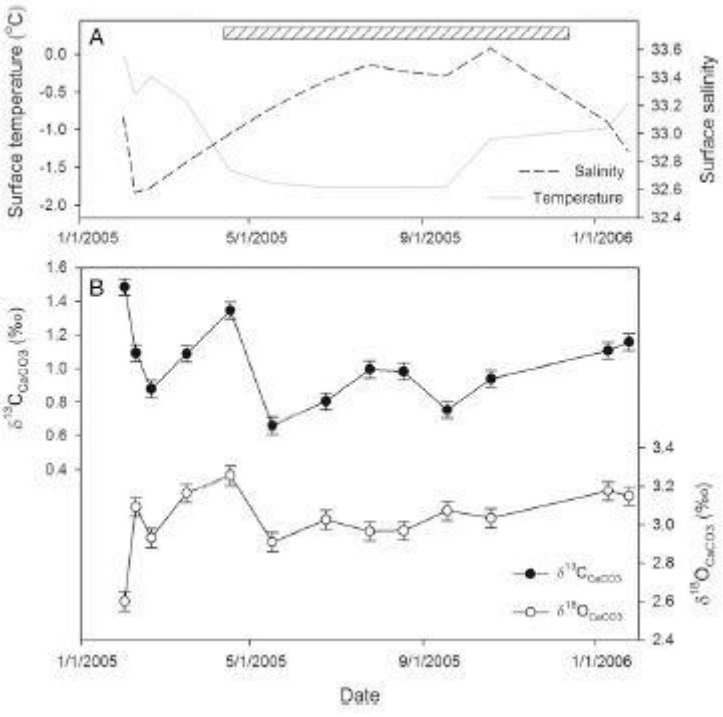
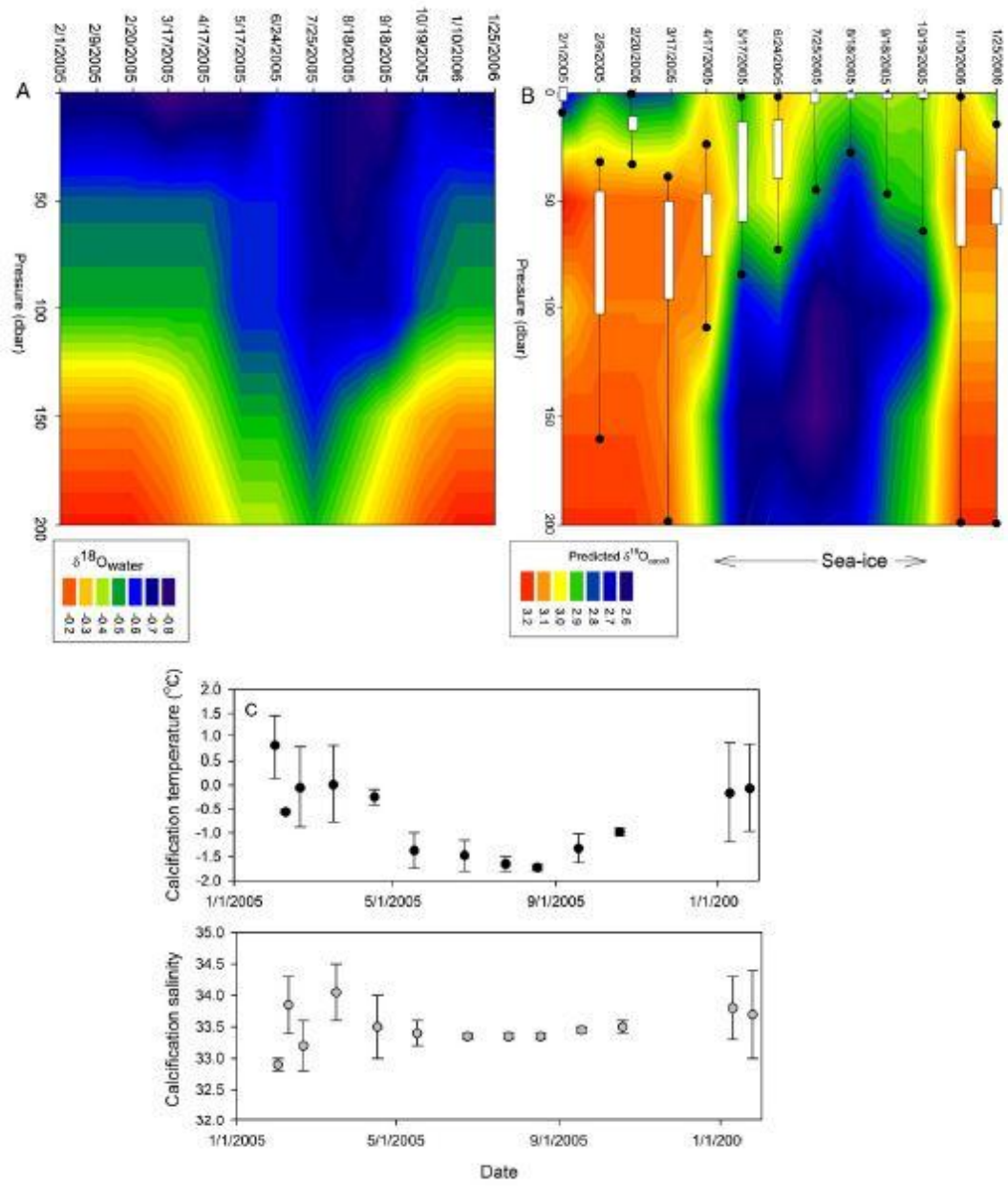
3861 20KV 100μm WD16
B
3854 20KV 100μm WD16
C
3835 20KV 10μm WD14

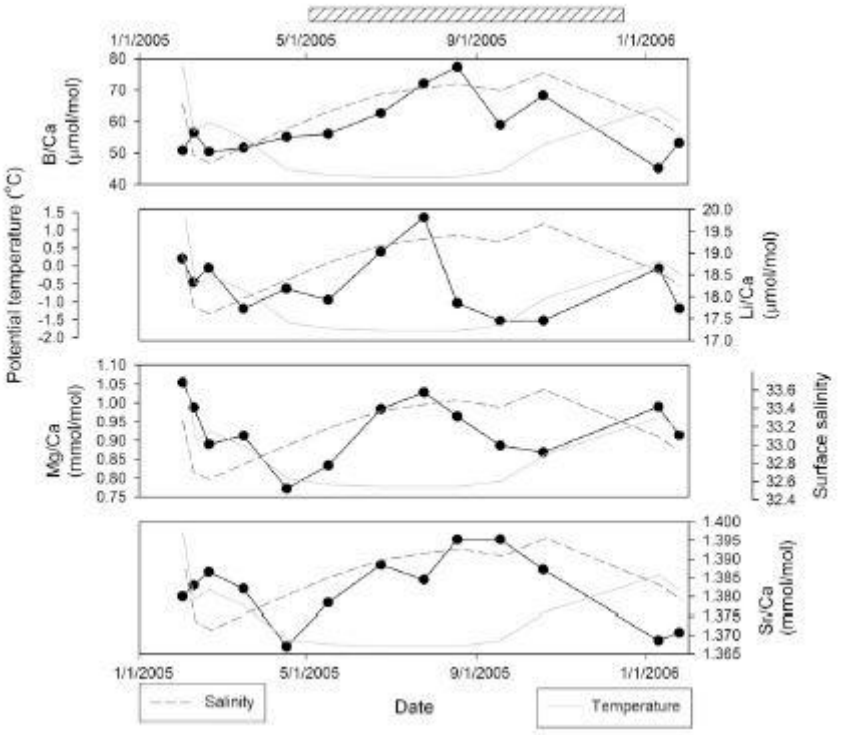
616


A
Surface temperature (°C)
Surface salinity
Salinity
Temperature
1/1/2005
5/1/2005
9/1/2005
1/1/2006
B
δ13CCaCO3 (‰)
δ18OCaCO3 (‰)
Date

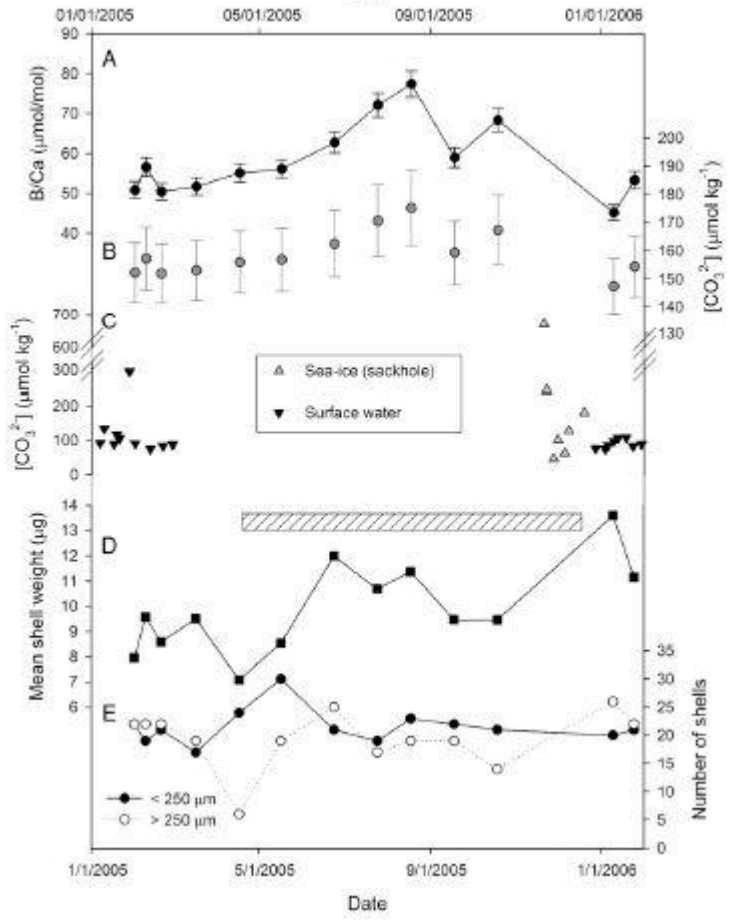
617


A
B
C
Pressure (dbar)
δ18Owater
Predicted δ18Ocarb
Sea-ice
Calcification temperature (°C)
Calcification salinity
Date
1/1/2005
5/1/2005
9/1/2005
1/1/200

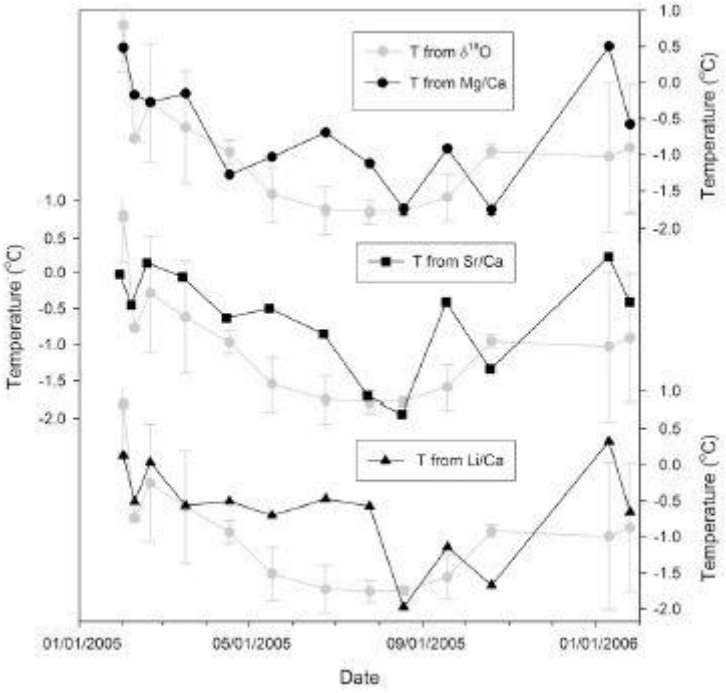
618


1/1/2005
5/1/2005
9/1/2005
1/1/2006
B/Ca (µmol/mol)
Li/Ca (µmol/mol)
Mg/Ca (mmol/mol)
Surface salinity
Sr/Ca (mmol/mol)
Potential temperature (°C)
Salinity
Temperature
Date

619


01/01/2005
05/01/2005
09/01/2005
01/01/2006
A
B
C
D
E
B/Ca (µmol/mol)
[CO3 2-] (µmol kg-1)
Sea-ice (sackhole)
Surface water
Mean shell weight (µg)
Number of shells
< 250 µm
> 250 µm
Date

620


T from δ18O
T from Mg/Ca
T from Sr/Ca
T from Li/Ca
Temperature (°C)
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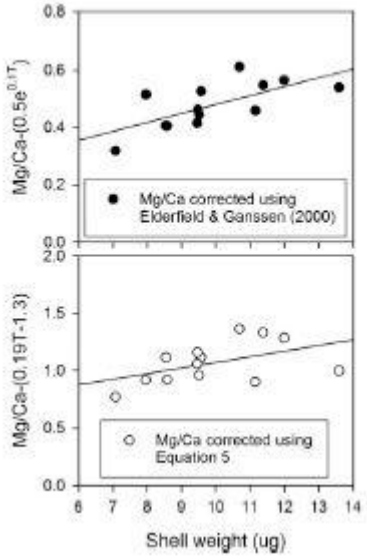
Temperature (°C)
01/01/2005
05/01/2005
09/01/2005
01/01/2006
Date

621


Mg/Ca-(0.5e^0.1T)
Mg/Ca corrected using Elderfield & Ganssen (2000)
Mg/Ca-(0.19T-1.3)
Mg/Ca corrected using Equation 5
Shell weight (ug)

622