Earth and Planetary Science Letters 278 (2009) 67–77

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

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

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ARTICLE INFO

Article history:
Received 17 March 2008
Received in revised form 18 November 2008
Accepted 20 November 2008
Available online 13 January 2009

Editor: P. DeMenocal

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

ABSTRACT

The polar foraminifera *Neogloboquadrina pachyderma* (sinistral) dominates assemblages from the high latitude Southern Ocean, which plays a key role in determining past climate due to the tight linkage between Antarctic temperature and atmospheric CO_2. 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 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 cover. We propose an elevated carbonate ion concentration at the ice–water interface resulting from biological utilisation of CO_2 could influence calcification in foraminifera. Our calculations suggest that for *N. pachyderma* (s.) Mg/Ca, Sr/Ca ratios and Li/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 (~10–20%/°C) and a sensitivity to $[CO_3^{2-}]$ of ~1%/μmol kg^{-1}. Sr/Ca ratios are less sensitive to environmental parameters, exhibiting ~5% increase/°C and ~0.5%/10 μmol kg^{-1}. The relationship between Li/Ca ratios and both temperature and $[CO_3^{2-}]$ is less significant with ~10% increase in Li/Ca ratio/°C and 10 μmol kg^{-1}. We show how a multi-proxy approach could be used to constrain past high latitude surface water temperature and $[CO_3^{2-}]$.

1. Introduction

Atmospheric gases trapped in bubbles within ice cores show the partial pressure of carbon dioxide (pCO_2) was 80 ppm V lower during the Last Glacial Maximum (LGM) compared with modern values (Petit, 1999; 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 be ambiguous, in part because the species can live in a variety of habitats, including sea-ice. Open water *N. pachyderma* (s.) are generally considered pycnocline dwellers, but can calcify below the mixed layer, occupying a wide range of depths shallower than 200 m (Kohfeld et al., 1996). In sea-ice conditions, *N. pachyderma* (s.) are associated in high but patchy cell concentrations with the bottom community of sea-ice diatoms, which grows in the more porous layers at the ice–water interface (Lipps and Krebs, 1974). In the autumn, the adults conduct gametogenesis, such that juveniles appear in the upper part of the water column and become incorporated into the forming frazil ice (Spindler and Dieckmann, 1986).

There is an increasing appreciation that multiple factors control stable isotope and trace metal chemistry of foraminifera. In particular, the role of carbonate ion concentration, $[CO_3^{2-}]$, and salinity on the uptake of trace metals (Mg, Sr and Li) into planktonic foraminiferal calcite is not fully understood (Ferguson et al., 2008; Lea et al., 1999; Marriott et al., 2004; Mortyn et al., 2005; Russell et al., 2004). Further, Southern Ocean waters are undersaturated with respect to calcite such that foraminifera have a low preservation potential in slowly

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doi:10.1016/j.epsl.2008.11.026

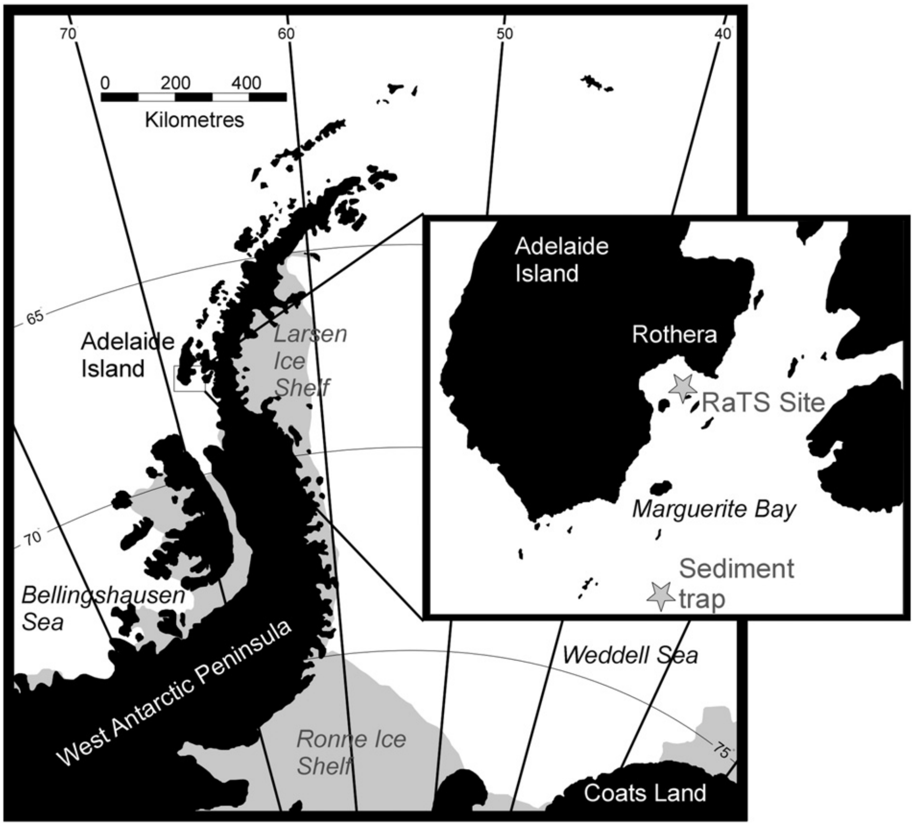

Fig. 1. Map showing the sediment trap and RaTS site (see text for details) off the West Antarctic Peninsula.

accumulating sediments. This, in turn, means that there is a paucity of calibration studies involving high latitude species in the literature. Here, we present a multi-proxy calibration study of *N. pachyderma* (s.) from the West Antarctic Peninsula (WAP) collected using sediment traps. We use the stable isotopic composition of the calcite to determine where the foraminifera calcify and to demonstrate that trace metal uptake depends on factors other than temperature and salinity, such as $[CO_3^{2}]$, during periods of sea-ice cover. We have calculated $[CO_3^{2-}]$ from measurements of Dissolved Inorganic Carbon (DIC) and pH for a limited period of the year, and inferred $[CO_3^{2-}]$ throughout the year using B/Ca ratios and shell weights, which agree on a consistent change in $[CO_3^{2-}]$ at the depth of calcification throughout the year. This allows other trace metal proxies, Mg/Ca, Sr/Ca and Li/Ca ratios, to be calibrated for temperature and $[CO_3^{2-}]$ using linear regression. Our multi-proxy approach potentially allows temperature and $[CO_3^{2-}]$ effects to be deconvolved, such that these parameters can be constrained in the past using high latitude foraminifera from marine sediment cores.

2. Materials and methods

A set of moorings was deployed in Marguerite Bay, WAP, in January 2005 from the British Antarctic Survey vessel RRS James Clark Ross (840 m water depth). The site is close to the Rothera Oceanographic and Biological Time-Series (RaTS) site (Clarke et al., 2008) (Fig. 1), an on-going programme featuring quasi-weekly water column profiling and discrete water sampling. The mooring comprised a suite of oceanographic instrumentation, including a sediment trap at 200 m

Table 1

Stable isotope and trace metal results for the sediment trap *N. pachyderma* (s.) present for each numbered bottle from the upper trap of the deep mooring site in Marguerite Bay

#	Bottle opens	Bottle closes	Stable isotopes		ICPMS results						Vista ICP-OES results		
			$\delta\ ^{13}C_{CaCO3}$ ‰	$\delta\ ^{18}O_{CaCO3}$ ‰	Li/Ca μmol/mol	B/Ca μmol/mol	Mg/Ca	Al/Ca μmol/mol	Mn/Ca μmol/mol	Sr/Ca	Fe/Ca	Sr/Ca	Mg/Ca
1	1/26/2005	2/7/2005	1.48	2.60	18.9	50.8	1.07	−0.91	30.4	1.380	0.16	1.37	1.06
2	2/7/2005	2/21/2005	1.09	3.09	18.3	56.6	1.02	−1.23	12.9	1.383	0.02	1.38	0.99
3	2/21/2005	3/1/2005	0.88	2.93	18.7	50.4	0.92	−0.64	6.0	1.387	0.05	1.41	0.89
4	3/1/2005	4/1/2005	1.09	3.16	17.7	51.7	0.96	−0.92	5.1	1.382	0.07	1.40	0.91
5	4/1/2005	5/1/2005	1.34	3.26	18.2	55.1	0.79	−0.12	6.2	1.367	0.10	1.41	0.77
6	5/1/2005	6/1/2005	0.66	2.91	17.9	56.1	0.85	−1.38	8.1	1.378	0.03	1.41	0.83
7	6/1/2005	7/15/2005	0.81	3.02	19.0	62.7	1.00	1.09	6.0	1.388	0.05	1.41	0.98
8	7/15/2005	9/1/2005	0.99	2.96	19.8	72.1	1.04	5.11	3.3	1.384	0.04	1.41	1.03
9	9/1/2005	10/1/2005	0.98	2.97	17.9	77.4	0.99	4.02	6.0	1.395	0.02	1.41	0.97
10	10/1/2005	11/1/2005	0.75	3.07	17.4	59.0	0.91	6.19	4.6	1.395	0.12	1.41	0.89
11	11/1/2005	11/15/2005	0.94	3.03	17.5	68.3	0.87	0.67	2.9	1.387	0.02	1.41	0.87
18	1/3/2006	1/18/2006	1.10	3.18	18.7	45.2	1.00	−1.61	10.9	1.369	0.26	1.37	0.99
19	1/18/2006	2/1/2006	1.16	3.15	17.7	53.3	0.90	−1.23	10.1	1.371	0.11	1.38	0.92
blk					−5.7	−551.3	−0.41	−148	−2.0	0.003			

Trace metal results are in mmol/mol unless stated. Results from both Q-ICP-MS and Vista ICP-OES are shown for comparison. Blanks (blk) are shown for the Q-ICP-MS results. Note the low Al/Ca and Mn/Ca, suggesting no clay contamination. Also shown are the opening and closing dates of each sediment trap bottle.

with bottle closure times configured to sample sinking particles throughout the year at fortnightly to bimonthly periods (Table 1). The bottles were pre-loaded with 2% buffered formalin to preserve organic material. The sediment trap bottles were recovered the following year and stored at 4 °C. Foraminifera were picked from the sediment trap splits by K. Weston (University of East Anglia, UK). *N. pachyderma* (s.) specimens were present in sediment trap bottles from summer to winter months, confirming their presence in the water column throughout the year.

Light microscopy, Scanning Electron Microscopy (SEM) imaging and probe analysis were used to assess the microstructural scale preservation of one or two foraminifera/trap bottle. Light microscope analyses show these sediment trap foraminifera are "glassy" rather than "frosty" (Sexton et al., 2006) and SEM images confirm they are well preserved without either dissolution due to calcite undersaturation or secondary calcite precipitation (Fig. 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). Rare encrusted specimens (Fig. 2B) were not included in analysis to avoid any contribution from secondary or gametogenic calcite, which may have a different chemical composition than 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).

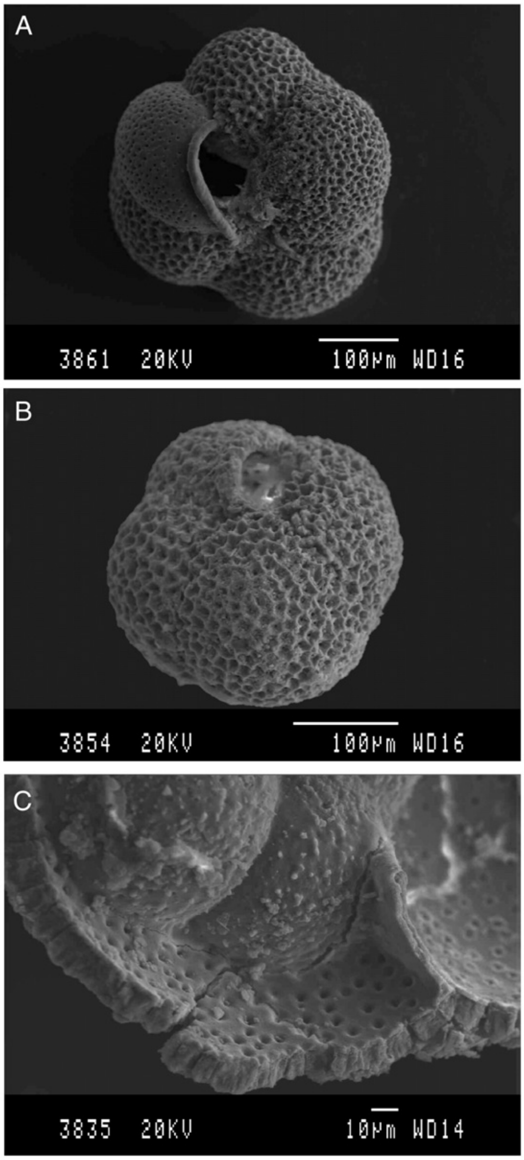

Fig. 2. SEM images of foraminifera A) showing non-encrusted specimen from June; B) showing encrusted specimen from May and C) an internal view showing good preservation and lack of secondary calcite.

Total shell weights were measured (±1 μg) and the mean weight calculated/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 (ranging from 250 to 300 μm in size)/bottle were analysed using a VG Isogas Prism II mass spectrometer with an online VG Isocarb common acid bath preparation system (Oxford University). Samples were first cleaned for organic matter using hydrogen peroxide and acetone and dried at 60 °C for at least 30 minutes. In the instrument they were 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.

2.1. 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 min, and the samples rinsed twice with 18 MΩ water.

2.2. 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).

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

As part of RaTS, full-depth profiles of temperature and salinity were collected 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 data are described elsewhere (Clarke et al., 2008; Meredith et al., 2008; Meredith et al., 2004).

3. Results and discussion

3.1. Reconstructing foraminiferal habitat from stable isotopes

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

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

3.1.1.1. Simulating $\delta^{18}O_{water}$ profiles. $\delta^{18}O_{CaCO3}$ can be calculated from the temperature and $\delta^{18}O_{water}$ data available for Marguerite Bay (Shackleton, 1974) and used to determine habitat depth. Stable isotopic values for the calcite range from 0.66 to 1.48‰ and 2.60 to 3.26‰ for $\delta^{13}C$ and $\delta^{18}O$ respectively (Table 1; Fig. 3). Measured $\delta^{18}O_{water}$ range from −0.2 to −0.8‰, with more depleted values observed in surface waters. Typically, isotopically lighter waters occur near the surface during the austral fall ($\delta^{18}O_{water} \sim -0.8$‰), with isotopically heavier waters found during the austral spring ($\delta^{18}O_{water} \sim$ −0.5 to −0.6‰), reflecting the seasonal cycles in precipitation, glacial melt and sea-ice/upper ocean processes (Meredith et al., 2008). A simulated full-depth $\delta^{18}O_{water}$ field was produced from the time series of discrete samples taken at 15 m depth and the full-depth $\delta^{18}O_{water}$ profiles collected during December of each year. For this, the quasi-linear relationship between salinity and $\delta^{18}O_{water}$ for Marguerite Bay was used along with 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 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 into simulated $\delta^{18}O_{water}$ piecewise in 50 m sections (Fig. 4a).

3.1.1.2. Predicting $\delta^{18}O_{CaCO3}$. The $\delta^{18}O_{CaCO3}$ was predicted using Eq. (1) (Shackleton, 1974) and assuming the simulated values of $\delta^{18}O_{water}$:

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

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

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

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‰.

3.1.1.3. 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 $\delta^{18}O_{CaCO3}$ (Fig. 4B,C). This is relatively straightforward in sea-ice free months, but it is more difficult to assign ambient salinity values in winter given the foraminifera may be living in the sea-ice brine

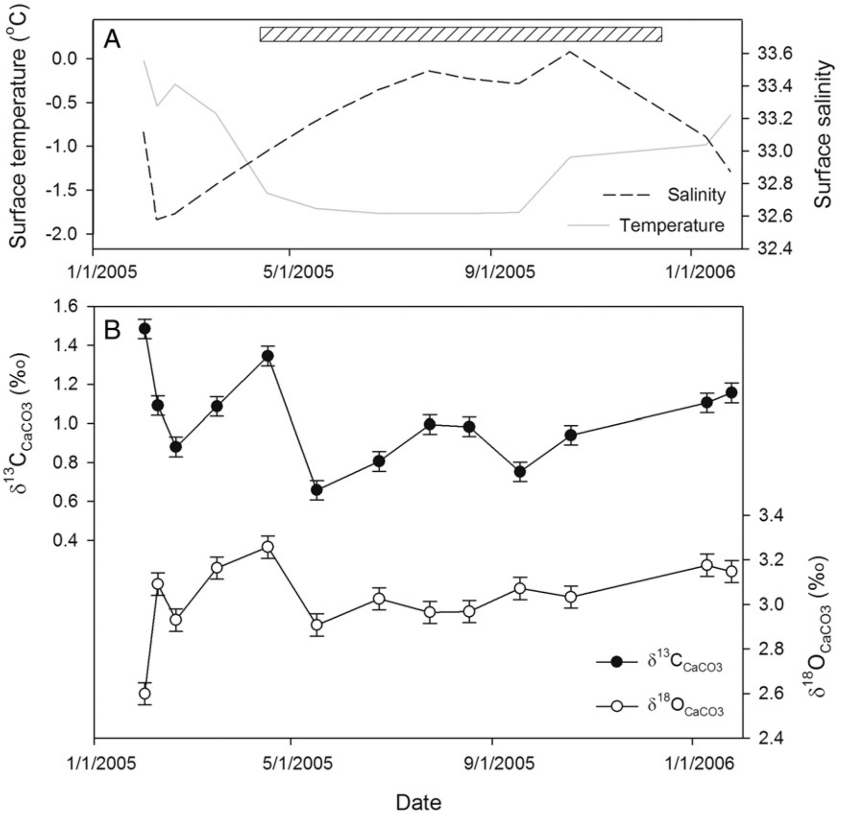

Fig. 3. A) Mean surface temperature and salinity (data from British Antarctic Survey); B) $\delta^{18}O_{CaCO3}$ and $\delta^{13}C_{CaCO3}$ results for *N. pachyderma* (s.). All values are referenced to Pee Dee Belemnite (PDB). The hatched bar indicates the period of persistent sea-ice.

channels or at the ice–water interface (Lipps and Krebs, 1974). Sea-ice formation does not affect δ $^{18}O_{water}$ significantly, so will have only a minor influence on δ $^{18}O_{CaCO3}$ (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 δ ^{13}C. The primary controls on δ $^{13}C_{CaCO3}$ 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 δ $^{13}C_{DIC}$ 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 δ $^{13}C_{CaCO3}$ values become depleted by ~0.8‰ (Table 1). As the air temperature rises to −5 to −9 °C in austral spring (October to November), the sea-ice breaches the porosity threshold (Golden et al., 1998; Perovich et al., 2004) and becomes an open, interconnected

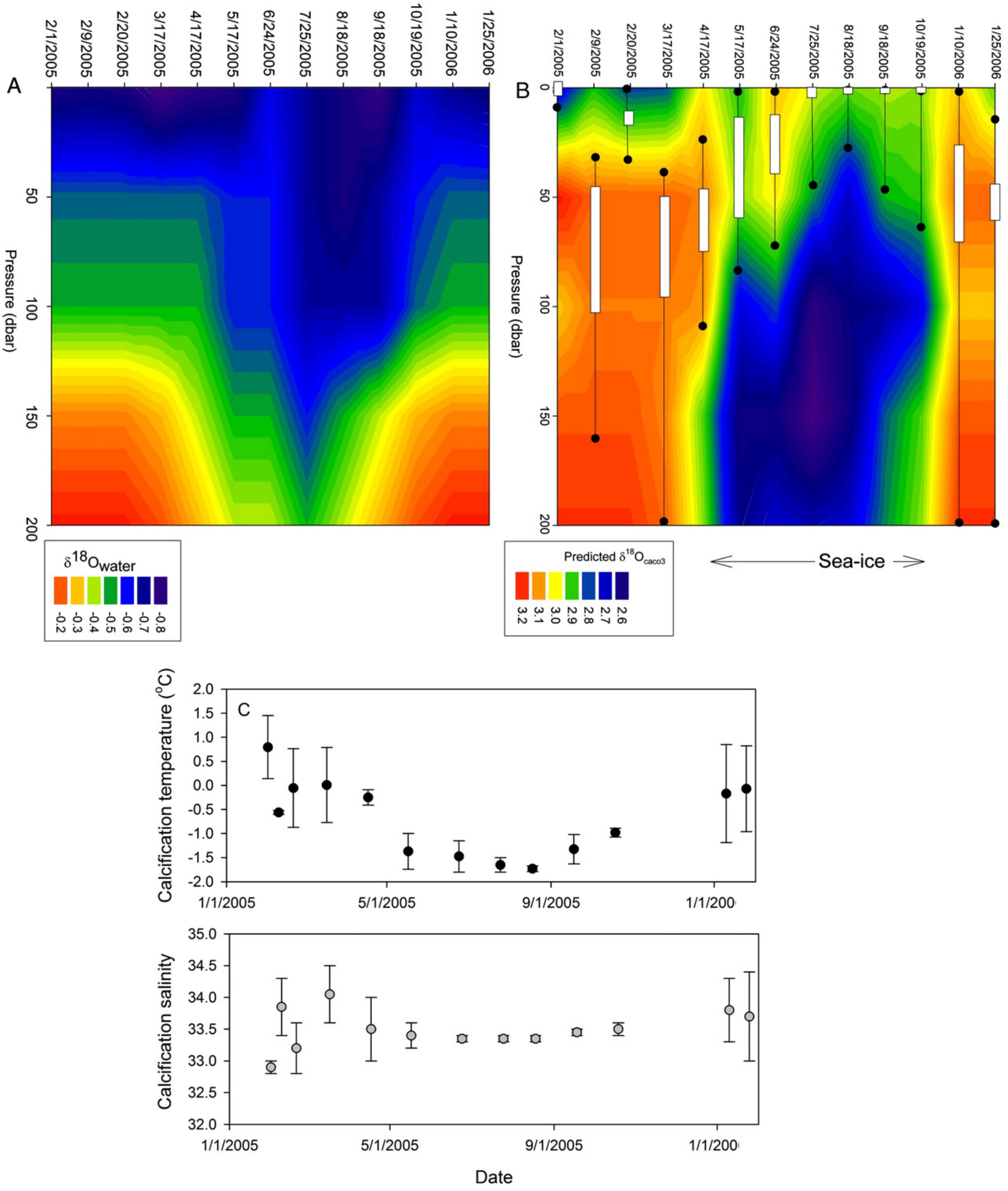

Fig. 4. A) predicted δ ^{18}O of water, with values given relative to Standard Mean Ocean Water (SMOW). B) Predicted δ ^{18}O of foraminiferal calcite. A temperature dependent vital effect between 0.6 and 1.1‰ has been applied to the data. The measured δ $^{18}O_{CaCO3}$ values can then be compared to the model to estimate habitat depths. The white bars indicate the error on the δ $^{18}O_{CaCO3}$ measurements (0.1‰) and indicate the most likely depths for calcification, and the black error bars show the error on the vital effect (±0.2‰). C) Reconstructed temperatures and salinities for the conditions at which the foraminifera calcify calculated from the δ ^{18}O depth profile.

Table 2
Applied vital offsets, *v*, applied to measurements for this study, estimated from SST

Bottle	SST °C	Measured $\delta\ ^{18}O_{CaCO3}$‰	Vital effect ‰
1	−0.0	2.60	0.6
2	−0.5	3.09	0.6
3	−0.3	2.93	0.6
4	−0.6	3.16	0.6
5	−1.5	3.26	0.7
6	−1.7	2.91	0.9
7	−1.8	3.02	0.9
8	−1.8	2.96	0.9
9	−1.8	2.97	0.9
10	−1.8	3.07	0.8
11	−1.1	3.03	0.8
12	−1.0	3.18	0.6
18	−0.6	3.15	0.6
19			

The vital effect was calculated using the relationship from Bausch et al. (1997):

$$v = 0.20(\pm 0.08)T - 0.63(\pm 0.01)$$

(r=0.65), where numbers in parentheses indicate 95% confidence intervals. The associated error is estimated to be ±0.2‰.

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 (Fig. 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 (Fig. 4B).

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

The Mg/Ca, Sr/Ca, B/Ca and Li/Ca ratios measured by Q-ICP-MS vary between 0.77–1.06 mmol/mol, 1.371–1.395 mmol/mol, 45.7–77.5 µmol/mol and 17.4–19.8 µmol/mol respectively (Fig. 5). The trace metal seasonal profiles show a peak in austral winter, which is not observed in the calcification temperature or salinity conditions (Figs. 3, 5). This would suggest that there is some additional factor influencing test composition 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 trace metal uptake.

3.2.1. 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 can calculate $[CO_3^{2-}]$ from available data of Dissolved Inorganic Carbon (DIC), pH, temperature and salinity measured at the RaTS site (Carson et al., in prep). $[CO_3^{2-}]$

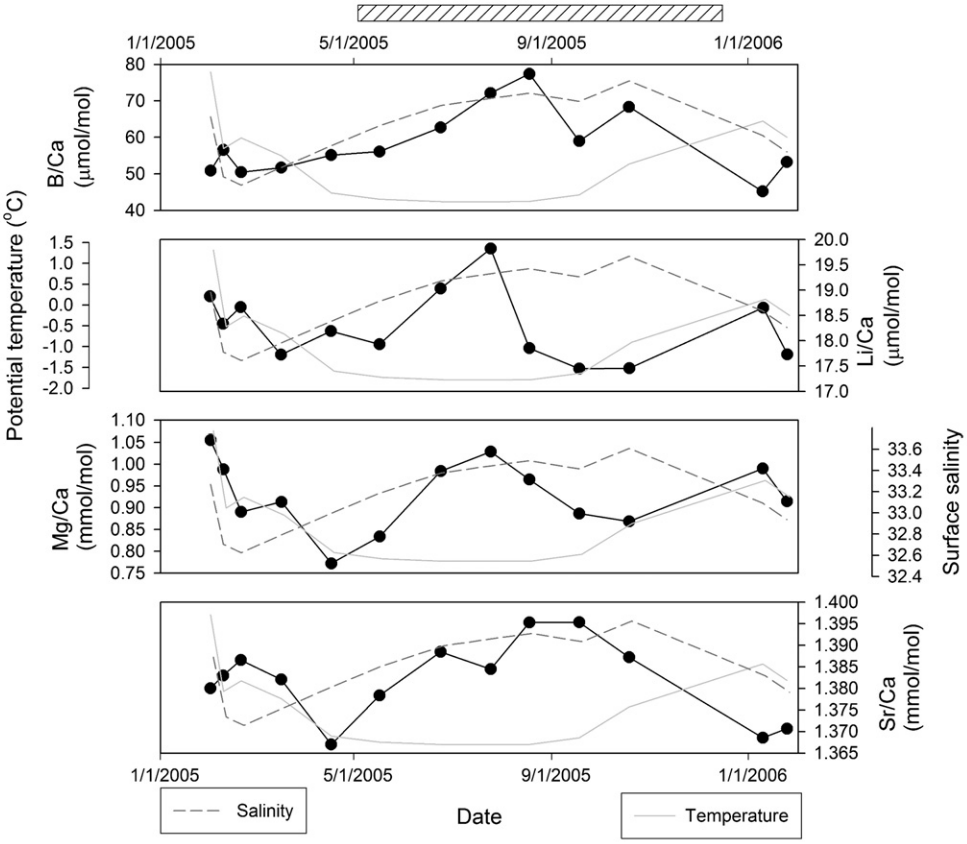

Fig. 5. Trace metal results for *N. pachyderma* (s.) calcite measured by Q-ICP-MS, each plotted against surface temperature and salinity. The hatched bar indicates the period of persistent sea-ice.

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 (Fig. 6). Sea-ice brine was collected by sackhole drilling, which involves partially drilling through the ice, taking care not to penetrate the ice–water interface, and collecting the brine that drains into the resulting hole. Note that brine DIC and pH measurements are only available for a limited period during winter due to restricted sampling.

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 $[CO_3^{2-}]$ we have calculated for the closed system upper layers of sea-ice. 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. Qualitatively, therefore, the effect of the presence of sea-ice on the growth habitat of *N.pachyderma* (s.) is to elevate ambient $[CO_3^{2-}]$ (Fig. 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).

3.2.1.1. Shell weights. The mean shell weights range from ~6 μg to ~14 μg/shell (Fig. 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 (Fig. 2). Specifically, there is a peak in mid-winter between June and October, where shell weights increase ~4 μg/shell (Fig. 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 (Fig. 6), which suggests the geochemical variation is not a function of shell size or ontogeny.

3.2.1.2. B/Ca ratios. 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

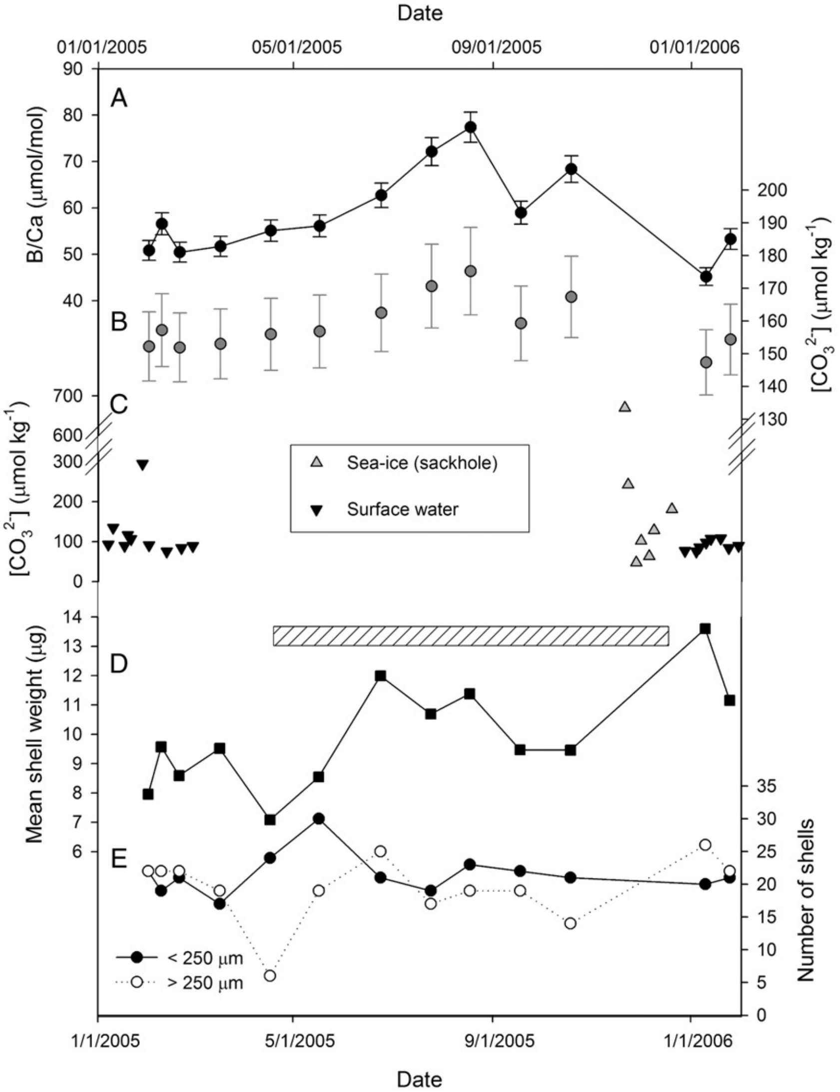

Fig. 6. Measures of carbonate ion concentration in seawater. A) B/Ca ratios; B) $[CO_3^{2-}]$ calculated using the B/Ca ratios and the calibration of (Yu et al., 2007). The error bars show 95% confidence intervals (Eq. (4)); C) $[CO_3^{2-}]$ in seawater (15 m depth; black triangles) and sea-ice brine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

fractionation (Yu et al., 2007). The borate ion substitutes for CO_3^{2-} in the calcite lattice according to Eq. (3):

$$\left(\frac{[Ca(HBO_3)]}{[CaCO_3]}\right) = K_D\left(\frac{[B(OH_4^-)]}{[HCO_3^-]}\right) \tag{3}$$

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 (Fig. 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 K), suggesting that other factors dominate in this case.

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

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

Although there are thought to be species-specific dependence on B incorporation into foraminiferal calcite (Foster, 2008), the latitudinal trend and range in B/Ca ratios for *G. inflata* and *N. pachyderma* (s.) are similar (Yu, pers. com.). Hence, in the absence of a published calibration, we have used the *G. inflata* relationship (Eq. (4)) to reconstruct temporal changes in $[CO_3^{2-}]$ in Marguerite Bay (Fig. 6). In summer, the reconstructed values of at the depth of calcification (~140–160 μmol kg^{-1}) are slightly offset from the calculated values based on DIC and pH at 15 m (~90 to 130 μmol kg^{-1}), which could be because of uncertainties in the calculations, or because the foraminifera are calcifying away from the surface. The trends in $[CO_3^{2-}]$ from shell weight and B/Ca ratios differ in the summer: the shell weights suggest highest $[CO_3^{2-}]$ in January, whereas the B/Ca ratios indicate the highest values in winter. This could reflect other secondary controls influencing shell weight, most likely temperature.

The B/Ca data indicate an increase in $[CO_3^{2-}]$ (decrease in PCO_2) in the winter during the period of sea-ice coverage of 30–40 μmol kg^{-1}. Whilst it is possible that the temperature and $[CO_3^{2-}]$ effect could compensate each other at certain times of year, a peak in $[CO_3^{2-}]$ at the site of calcification inferred from the B/Ca ratios is consistent with the calculated $[CO_3^{2-}]$ and shell weight variations (Fig. 6).

In summary, the shell weight and B/Ca ratios are consistent with the foraminifera living at the ice–water interface over winter. Sea-ice and the ice–water interface are known to exhibit undersaturation of CO_2 as a result of biological activity and expulsion (Delille et al., 2007; Gleitz et al., 1995; Papadimitiou et al., 2007; Fig. 6), leading to the mid-winter increase in $[CO_3^{2-}]$. We suggest the extremely high $[CO_3^{2-}]$ calculated for the upper layers in sea-ice are not matched by the predictions from shell weights and B/Ca because the degree of CO_2 utilisation is less extreme at the ice–water interface where the foraminifera calcify. The change in $[CO_3^{2-}]$ is likely to change foraminiferal oxygen isotopes by less than 0.1‰ (Spero et al., 1997), consistent with our $\delta^{18}O_{CaCO3}$ variations (Fig. 3; Table 1), but may have an influence on trace metal uptake.

3.2.2. Carbonate ion effect on trace metal uptake

Mg/Ca, Sr/Ca and Li/Ca ratios share similar "w-shaped" profiles, including both high summer values and a mid-winter 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

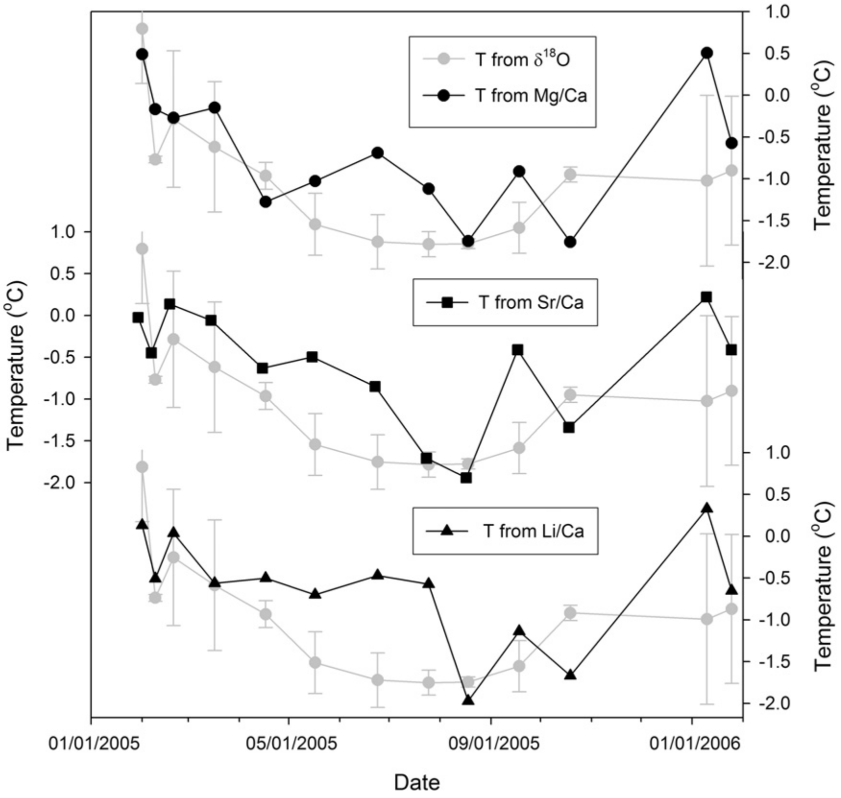

Fig. 7. Reconstructions of temperature using Mg/Ca, Sr/Ca and Li/Ca ratios. Carbonate ion concentration was calculated using B/Ca ratios (Fig. 6), and temperature calculated using measured elemental ratios and Eqs. (5)–(7) (black symbols). The grey circles show the temperature at the site of calcification estimated from $\delta^{18}O_{CaCO3}$ (Fig. 4).

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.

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

$$\frac{Mg}{Ca} = 0.19(\pm 0.01)T + 0.015(\pm 0.001)\left[CO_3^{2-}\right] - 1.3(\pm 0.1) \qquad (5)$$
$$r^2 = 0.49 \; (n = 13, \; p < 0.05)$$

$$\frac{Sr}{Ca} = 0.052(\pm 0.008)T + 0.0050(\pm 0.0001)\left[CO_3^{2-}\right] + 0.58(\pm 0.01) \qquad (6)$$
$$r^2 = 0.58 \; (n = 13, \; p < 0.05)$$

$$\frac{Li}{Ca} = 1.8(\pm 0.5)T + 0.120(\pm 0.003)\left[CO_3^{2-}\right] + 0.38(\pm 0.19) \qquad (7)$$
$$r^2 = 0.44 (n = 13, \; p < 0.05)$$

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 ($r^2<0.1$). Indeed, using previous temperature calibrations (Elderfield & Ganssen, 2000) results in a temperature overestimate of ~6–7 °C. There are insufficient 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. 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 or a common alternative factor controlling the weight and chemistry of the shells (Fig. 8).

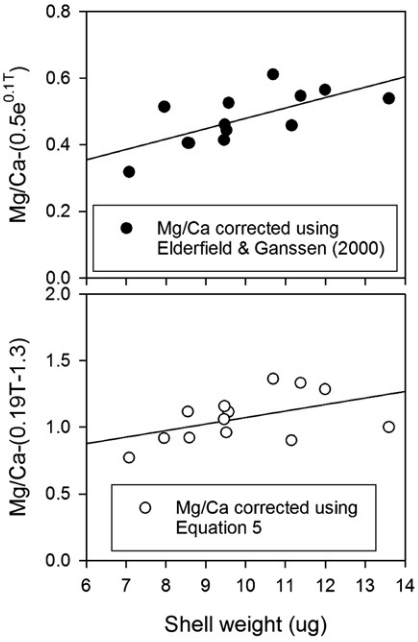

Fig. 8. Mg/Ca residuals plotted against mean shell weight, which can be used as an independent measure of $[CO_3^{2}]$. The Mg/Ca residuals are calculated here by subtracting the Mg/Ca ratio predicted using the exponential relationship given by (Elderfield and Ganssen, 2000) and calcification temperature from the measured Mg/Ca value (black circles). These residuals correlate well with shell weight ($r^2=0.47$). Mg/Ca residuals are also calculated here by subtracting the Mg/Ca temperature effect and constant term show in Eq. (5) (white circles). There is also a positive correlation between these residuals and shell weight, although it is less significant ($r^2=0.23$).

Although further work is required to produce a rigorous calibration, our data can be used to estimate the sensitivity of *N. pachyderma* (s.) calcite Mg/Ca, Sr/Ca and Li/Ca ratios to temperature and $[CO_3^{2-}]$. The Mg/Ca ratios in this environment show similar temperature sensitivity (~10–20%/°C) to open water *N. pachyderma* (Elderfield and Ganssen, 2000; Nurnberg, 1995; von Langen et al., 2005). According to our calibrations, Mg/Ca of *N. pachyderma* (s.) show a 10–20% increase/10 μmol kg^{-1} increase in $[CO_3^{2-}]$. This contrasts to the inference of an inverse relationship between Mg/Ca and $[CO_3^{2-}]$ based on few data points from cultures of *Orbulina universa* and *Globigerina bulloides* (Russell et al., 2004), suggesting the influence of $[CO_3^{2-}]$ on trace metal uptake is species dependent. Although some laboratory and field studies suggest a salinity effect on Mg/Ca ratios (Ferguson et al., 2008), such an effect cannot be tested here as there is little variability in calcification salinity. The Sr/Ca ratio is less sensitive to environmental conditions than the Mg/Ca ratio (~5% increase/°C and ~0.5%/10 μmol kg^{-1}) (Fig. 7). This is consistent with previous culture experiments, plankton tow and core top samples of non-globorotaliid foraminifera that demonstrate a weak temperature effect on Sr uptake into planktonic foraminiferal calcite and an increase in the Sr/Ca ratio with increasing pH (Mortyn et al., 2005; Russell et al., 2004). The relationship between Li/Ca ratios and both temperature and $[CO_3^{2-}]$ is less statistically significant with ~10% increase in Li/Ca ratio/°C and 10 μmol kg^{-1}. Our results indicate Li/Ca ratios in *N. pachyderma* (s.) may be more sensitive to temperature than other species. For example, downcore measurements of Li/Ca ratios from the planktonic foraminifera *Orbulina universa* show a temperature and $[CO_3^{2-}]$ sensitivity of only 2%/°C (Hall & Chan, 2004). This might reflect species-specific variation and the difficulties in deconvolving temperature and $[CO_3^{2-}]$ in most open marine environments.

3.3. Implications for glacial–interglacial SST reconstructions

The influence on *N. pachyderma* (s.) Mg/Ca ratios (and the uptake of other trace metals) by environmental parameters other than temperature (e.g. $[CO_3^{2-}]$) has implications for glacial–interglacial SST reconstructions in regions where sea-ice cover varies on similar timescales. This includes:

1) Regions of the subantarctic Southern Ocean that are outside the modern Seasonal Sea-Ice Zone (SIZ) but were within the winter sea-ice extent during cooler periods;
2) Regions of coastal Antarctica that are within the modern SIZ but were covered by multi-year ice during cooler periods.

Downcore records from the subantarctic Pacific indicate a change in *N. pachyderma* (s.) Mg/Ca ratio of ~0.2 mmol/mol on a glacial–interglacial timescale (Mashiotta et al., 1999), which is of similar amplitude to seasonal changes from this study. Diatom population analysis (Gersonde et al., 2005) indicates that the core was near the edge of the LGM winter sea-ice extent, such that the site may have experienced seasonal variation in $[CO_3^{2-}]$ in addition to temperature variation. The time averaging of such seasonality in sediments requires further investigation for the robust interpretation of Southern Ocean foraminiferal trace metal proxies.

4. Summary and conclusions

Here, we constrain the environmental controls the stable isotope and trace metal uptake by the high latitude planktonic foraminifera, *Neogloboquadrina pachyderma* (s.) using time series sediment trap samples from the West Antarctic Peninsula. $\delta^{18}O_{CaCO3}$ and $\delta^{13}C_{CaCO3}$ were used to demonstrate that the foraminifera calcify at the ice–water interface in winter, which exchanges openly with seawater, and to reconstruct calcification temperature and salinity. Our results show that trace metal uptake during calcification is influenced by factors other than ambient temperature and salinity, especially during periods of sea-ice cover. We suggest, using B/Ca ratios and shell weight data, that there is an increase in [CO$_3^{2-}$] during periods of sea-ice cover and that Mg/Ca, Sr/Ca and Li/Ca ratios are functions of temperature and [CO$_3^{2-}$]. *N. pachyderma* (s.) Mg/Ca exhibits similar temperature sensitivity to previous studies (~10–20%/°C) and a [CO$_3^{2-}$] sensitivity of ~10%/10 μmol kg^{-1}. Sr/Ca is less sensitive to environmental parameters, exhibiting ~5% increase/°C and ~0.5%/10 μmol kg^{-1}. The relationship between Li/Ca ratios and both temperature and [CO$_3$2−] is less statistically significant with ~10% increase in Li/Ca ratio/°C and 10 μmol kg^{-1}. Seasonal variation in habitat, and associated changes in ambient conditions with depth in the water column and the ice–water interface, adds a further degree of uncertainty to paleoceanographic reconstructions based on Mg/Ca ratios. More reliable estimates of past sea surface temperature can be achieved by taking into account changes in sea-ice cover. Further work on the time averaging of seasonal variability in calcite chemistry is justified in order to decode Southern Ocean paleoclimate records.

Acknowledgements

The authors would like to thank the following: Damien Carson and Raja Ganeshram for DIC, pH and organic carbon isotopes and useful discussion (University of Edinburgh); Norman Charnley for help with stable isotope analysis ICP-MS (Department of Earth Sciences, University of Oxford); Mervyn Greaves and Jimin Yu for their help with cleaning and trace metal analysis (University of Cambridge); Mark Brandon (Open University), Keith Weston and Tim Jickells (University of East Anglia, Norwich) for help recovering and picking the sediments; Andrew Clarke (British Antarctic Survey) and Mags Wallace (Open University) for biological and physical oceanographic data; the base commander and staff of Rothera Research Station and master and crew of the RRS James Clark Ross, British Antarctic Survey. The authors would like to thank Peter deMenocal and three anonymous reviewers for insight and discussion. The work was funded as part of NERC Antarctic Funding Initiative AFI4-02. KRH is funded by NERC grant NER/S/A/2004/12390.

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