

Mg/Ca thermometry in planktic foraminifera: Improving paleotemperature estimations for G. bulloides and N. pachyderma left

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Key Points:
- New Mg/Ca-temperature calibration for *G. bulloides* for mid and high latitudes of both hemispheres
- New Mg/Ca-temperature calibration for *N. pachyderma* left in Southern Ocean sites away from sea ice
- *G. bulloides* calcifies deeper in the Southern Ocean than in the North Atlantic

Supporting Information:
- Supporting Information S1
- Table S1
- Table S2

Correspondence to:
N. Vázquez Riveiros,
natalia.vazquez@lsce.ipsl.fr

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Mg/Ca thermometry in planktic foraminifera: Improving paleotemperature estimations for *G. bulloides* and *N. pachyderma* left

Natalia Vázquez Riveiros[1], Aline Govin[1], Claire Waelbroeck[1], Andreas Mackensen[2], Elisabeth Michel[1], Santiago Moreira[1], Thomas Bouinot[1], Nicolas Caillon[1,3,4], Ayche Orgun[1], and Margaux Brandon[1]

[1]Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CNRS-CEA-UVSQ, Université Paris-Saclay, Gif-sur-Yvette, France, [2]Alfred Wegener Institute, Helmholtz Center for Polar and Marine Research, Bremerhaven, Germany, [3]Now at Laboratoire de Glaciologie et Géophysique de l'Environnement University of Grenoble Alpes, Grenoble, France, [4]CNRS, Laboratoire de Glaciologie et Géophysique de l'Environnement, Grenoble, France

Abstract Planktic foraminiferal Mg/Ca ratios have become a fundamental seawater temperature proxy in past climate reconstructions, due to the temperature dependence of Mg uptake into foraminiferal calcite. However, empirical calibrations for single species from methodologically consistent data are still lacking. Here we present species-specific calibrations of Mg/Ca versus calcification temperature for two commonly used species of planktic foraminifera: *Globigerina bulloides* and *Neogloboquadrina pachyderma* left, based on a series of Southern Ocean and North Atlantic core tops. Combining these new data with previously published data, we derive an integrated *G. bulloides* Mg/Ca-temperature calibration for mid and high latitudes of both hemispheres between 2 and 18°C, where $Mg/Ca = 1.006 \pm 0.032 * e^{0.065 \pm 0.003 * Tiso}$ ($R^2 = 0.82$). *G. bulloides* is found to calcify deeper in the Southern Ocean (~ 200 m) than in the North Atlantic (top 50 m). We also propose a Mg/Ca temperature calibration to describe the temperature response in *N. pachyderma* left that calcified away from the influence of sea ice in the Southern Ocean, valid between ~ −1 and 9°C, of the form $Mg/Ca = 0.580 \pm 0.016 * e^{0.084 \pm 0.006 * Tiso}$ ($R^2 = 0.70$). These calibrations account for uncertainties on Mg/Ca measurements and calcification temperature that were carefully estimated and propagated using Monte Carlo iterations. The 1σ propagated error in Mg/Ca-derived temperatures is 1.1°C for *G. bulloides* and 0.9°C for *N. pachyderma* left for the presented data sets. Geographical extension of genotypes must be assessed when choosing to develop regional or global calibrations.

1. Introduction

Planktic foraminiferal Mg/Ca ratios have become a fundamental seawater temperature proxy in past climate reconstructions [*Lea*, 2014]. This is due to the temperature dependence of Mg uptake into foraminiferal calcite, which results in increasing foraminiferal Mg/Ca ratios with increasing growth temperature [e.g., *Anand et al.*, 2003; *Lea et al.*, 1999; *Nürnberg*, 1995]. Various attempts have been conducted to calibrate foraminiferal Mg/Ca ratios as a function of temperature, including culture, core top, and sediment trap approaches. They have given rather consistent results [*Lea*, 2014], although differences in methodological techniques can introduce offsets that need to be assessed and accounted for where possible.

Calibrations based on cultured foraminifera have the advantage that the environmental variables that regulate calcification, such as temperature, can be controlled. However, culturing experiments may underrepresent the natural environment, hence potentially impacting on natural chamber growth and calcification mechanisms [*Barker et al.*, 2005]. Using foraminifera that come directly from the water column (collected either by nets or sediment traps) circumvents this problem. Nonetheless, sediment core tops are the type of samples that most resembles the material used to reconstruct past changes in the ocean. The foraminifera present in sediment core tops have undergone a complete life cycle and the formation of secondary calcite, and can be used to substantiate the temperature sensitivity exhibited by culturing experiments. Calibrations derived from core top material thus provide important insight into proxy behavior that is directly comparable to downcore material, complementing calibrations derived from water column samples.

Calcification depth and season may differ greatly between species, affecting their respective temperature preference ranges [*Jonkers and Kucera*, 2015; *Mortyn and Charles*, 2003]. Recent studies have pointed out that biological processes exert a major influence on the partitioning of metals in biogenic carbonates, thus highlighting the need for species-specific empirical calibrations [*Anand et al.*, 2003; *Lea et al.*, 1999]. However, single-species calibrations, especially from high-latitude environments, remain sparse [*Barker et al.*, 2005]. The commonly used calibration of *Elderfield and Ganssen* [2000], valid between 8 and 20°C, mixes eight planktic species and was developed mostly from North Atlantic core tops. However, species of planktic foraminifera differ markedly in habitat, ecological preferences, and physiology. Their unique behavior defines their distribution as well as the geochemistry of their test, which results in different rates of Mg incorporation with increasing temperature that multispecies calibrations cannot account for.

Globigerina bulloides and *Neogloboquadrina pachyderma* (left coiling) are the two most commonly used species for paleoreconstructions in high and midlatitudes. *G. bulloides* is a bipolar spinose species that inhabits transitional to subpolar waters, while *N. pachyderma* left appears in colder waters of subpolar regions and becomes predominant in polar environments, often forming 100% of the total foraminiferal assemblage [*Bé and Tolderlund*, 1971]. Together they form a continuum in the cold-end spectrum of sea surface temperatures (SST), where calibrations are lacking.

The first Mg/Ca calibration for *G. bulloides* was developed by *Lea et al.* [1999] using specimens cultured between 16 and 25°C. This calibration was later extended to colder temperatures (9°C) by adding data from two Southern Ocean core tops [*Mashiotta et al.*, 1999]. The only dedicated *G. bulloides* monospecific calibration based exclusively on core top material has been developed from a few (10) measurements in the North Atlantic, and it is valid between ~10 and 18°C [*Cléroux et al.*, 2008]. However, *G. bulloides* is known to present peak abundances in waters between 3 and 19°C, having been recorded in temperatures as low as 0°C and as high as 27°C [*Bé*, 1977; *Bé and Tolderlund*, 1971; *Hemleben et al.*, 1989]. It is actually most abundant in water masses at high southern latitudes [*Hillbrecht*, 1996], where it occupies a lower temperature range compared to the North Atlantic [*Bé and Tolderlund*, 1971]. The cold end of this species' temperature range is therefore still missing from currently available calibrations.

N. pachyderma left has been the object of few geochemical studies, and most of them are centered in the North Atlantic and Arctic Seas [e.g., *Kozdon et al.*, 2009; *Meland et al.*, 2005; *Nyland et al.*, 2006]. The first (and to our knowledge, only) Southern Ocean core top study was the pioneer report of *Nürnberg* [1995], that examined Mg/Ca in this species from material from the Southeast Atlantic and the Norwegian Sea by electron microprobe analysis. This type of technique allows detailed investigation of the potentially significant heterogeneity of Mg/Ca distribution within the foraminiferal tests. However, most of the Mg/Ca data used for reconstructions are nowadays obtained by analysis of calcite solutions by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or ICP- Mass Spectrometry (MS). Because differences in cleaning and measuring techniques produce different results, it is therefore necessary to establish calibrations with data derived from comparable substrates and analytical techniques as the paleorecords on which these calibrations will be applied.

The aim of this study is to establish monospecific calibrations for two species of planktic foraminifera (*G. bulloides* and *N. pachyderma* left) collected from core top material. The calibrations are based on samples cleaned and measured in a homogeneous way, in order to provide consistent SST reconstructions in sites from mid to high latitudes.

2. Material and Methods

A set of 47 core tops from the Atlantic, Indian, and Pacific sectors of the Southern Ocean, from latitudes between 36 and 78°S, have been analyzed for oxygen stable isotope composition and trace element concentrations in *G. bulloides* and *N. pachyderma* left (Figure 1 and Table 1). The study area covers temperate to polar waters, with annual SST ranging between −2 and 18°C. The water depth of the cores ranges from ~400 to 3800 m. Due to variations in the abundance of these two species in the foraminiferal assemblages, only 18 Southern Ocean sites presented enough *G. bulloides* specimens for analysis, while 39 sites were measured for *N. pachyderma* left.

In addition, unpublished data from the North Atlantic [*Bouinot*, 2011] are presented here for the first time, with the aim of comparing the Southern Ocean data set with Northern Hemisphere data. *Bouinot* [2011] analyzed *G. bulloides* samples in eight core tops from the North Atlantic between 41° and 58°N (Table 1 and

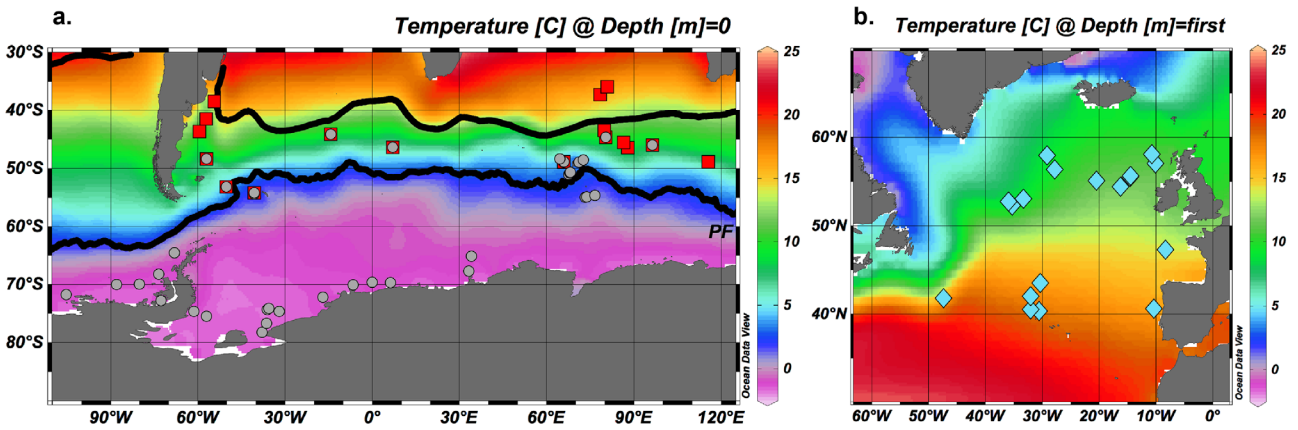


Figure 1. Maps showing core top locations and mean annual SST from the World Ocean Atlas 2009 [*Locarnini et al.*, 2010]. (a) Southern Ocean sites. Red squares indicate core top samples with *G. bulloides*; grey circles indicate samples with *N. pachyderma* left. The black lines indicate the positions of the Polar Front (PF) and the Subtropical Front (STF) [*Orsi et al.*, 1995]. (b) North Atlantic sites. Blue diamonds indicate samples with *G. bulloides* [*Bouinot*, 2011; *Cléroux et al.*, 2008].

Figure 1), following the methods described below. Both data sets (Southern Ocean and North Atlantic) were complemented with the published North Atlantic measurements of *Cléroux et al.* [2008] (details in section 4.1).

All core tops have been carefully selected to ensure they contain sediments of Late Holocene age, following the MARGO recommendations [*Kucera et al.*, 2005] (Table 1). Briefly, four Late Holocene (0–4 ky) intervals or chronozones are defined according to the uncertainty level of their chronological controls. Levels 1 and 2 are samples with radiometric dates or varves on the intervals 0–2 ky and 0–4 ky, respectively, or the presence of Rose Bengal stained foraminifera indicating that they were alive at the time of collection (Level 2). Level 3 includes samples with stratigraphic controls on the interval 0–4 ky, or with radiometric dates within the interval 4–8 ky. Stratigraphic controls of the lowest certainty level (4) include samples recovered from large box corers or multicorers that allow the recovery of undisturbed sediment surface (e.g., some ANT and M29 core tops), or other stratigraphic constraints [*Kucera et al.*, 2005].

2.1. Trace Element Analysis

Samples of *G. bulloides* or *N. pachyderma* left were picked from the 250 to 315 and 200 to 250 μm size fractions, respectively, for trace element analysis. Only nonencrusted specimens were selected, that is, foraminifera that were not covered (totally or partially) by a shiny "crystalline" calcite crust visible under the binocular microscope [e.g., *Groeneveld and Chiessi*, 2011]. The shells were gently crushed between glass plates, homogenized, split into aliquots equivalent to ~30 specimens, and cleaned following the method described by *Barker et al.* [2003] to eliminate contamination from clays and organic matter. Mg/Ca analyses were performed on a Varian Vista Pro ICP-OES at the LSCE (Gif-sur-Yvette, France) following the procedure of *de Villiers et al.* [2002]. The standards used for the intensity ratio calibration range between 0.5 and 12.0 mmol/mol of Mg/Ca, at a constant Ca concentration of 40 ppm. Precision for measured Mg/Ca ratios determined from replicate runs of an internal standard solution of Mg/Ca = 4.985 mmol/mol is 0.6% (1σ, relative standard deviation (RSD), n = 91). The accuracy of Mg/Ca measurements was established by an interlaboratory calibration study of carbonate reference materials [*Greaves et al.*, 2008].

Absence of silicate and Mn-Fe-oxide contamination was controlled by measuring Fe, Al, and Mn content, with maximum allowed Fe/Mg or Fe/Ca values of 0.1 mol/mol and 0.1 mmol/mol, respectively, for high Mg/Ca samples. Due to values above these thresholds, core MD84-561 and one replica of core MD12-3401Q were removed from the data set of *N. pachyderma* left. Plotting Mg/Ca against Al/Ca, Fe/Ca and Mn/Ca does not show any discernible trend that would indicate detrital contamination (supporting information Figure S1 and Tables S2 and S3).

After removal of contaminated samples, 18 Southern Ocean core tops were retained for the *G. bulloides* Mg/Ca data set (45 replicas), and 38 core tops for the *N. pachyderma* left data set (100 replicas) (supporting information Tables S1 and S2). Pooled standard deviations (1σ uncertainty) obtained on *G. bulloides* and *N. pachyderma* left replicated Mg/Ca analyses are, respectively, ± 0.14 and ± 0.06 mmol/mol.

Table 1. Core Top Locations and Stratigraphic Controls

Sample Name	Latitude	Longitude	Depth (m)	Species[a]	Age Control[b]	Reference Age Control
ANTVI/3 1622-1	−78.25	−37.81	1104	*NpL*	4	This study
ANTII/4 1220-3	−76.75	−36.32	996	*NpL*	4	This study
ANTII/4 1212-1	−75.52	−56.90	425	*NpL*	2	This study
ANTIV/3 1423-1	−74.70	−61.32	478	*NpL*	4	This study
ANTV/4 1489-3	−74.66	−31.97	602	*NpL*	4	This study
ANTIV/3 1416-1	−74.33	−36.02	1527	*NpL*	4	This study
ANTV/4 1494-3	−74.18	−35.49	1944	*NpL*	2	This study
ANTXI/3 2531-1	−72.83	−72.58	757	*NpL*	4	This study
ANTIV/3 1373-2	−72.25	−16.88	1237	*NpL*	2	This study
ANTXI/3 2544-1	−71.80	−105.19	546	*NpL*	2	This study
ANTIV/3 1391-1	−70.10	−6.50	1797	*NpL*	4	This study
ANTXI/3 2540-1	−70.06	−87.93	1822	*NpL*	2	This study
ANTXI/3 2526-1	−70.01	−80.06	580	*NpL*	4	This study
ANTIX/3 2037-2	−69.71	6.27	1646	*NpL*	4	This study
ANTIX/3 2064-2	−69.65	0.02	1580	*NpL*	4	This study
ANTXI/3 2525-1	−68.27	−73.44	453	*NpL*	4	This study
ANTVIII/6 1818-5	−67.75	33.31	805	*NpL*	4	This study
ANTVIII/6 1815-2	−65.14	34.23	1539	*NpL*	2	This study
ANTVI/2 1560-1	−64.61	−68.01	830	*NpL*	2	This study
MD84-551	−55.02	73.28	2230	*NpL*	1	*Pichon et al.* [1992]
MD84-552	−54.92	73.83	1780	*NpL*	4	*Dezileau et al.* [2000]
MD84-553	−54.68	76.63	1504	*NpL*	4	This study
MD87-744	−54.45	−40.52	1975	*NpL*	4	This study
MD87-745	−54.25	−40.48	1920	*Gb, NpL*	4	This study
ANTXI/2 2519-1	−53.22	−50.10	596	*Gb, NpL*	2	This study
MD80-304	−51.07	67.73	1930	*NpL*	3	This study
MD88-795	−50.84	68.02	1870	*NpL*	4	This study
MD84-563	−50.72	68.15	1720	*NpL*	4	*Gersonde et al.* [2005]
MD04-2717G	−48.96	65.93	1500	*Gb, NpL*	4	This study
MD04-2721	−48.95	71.13	845	*NpL*	1	This study
MD04-2718	−48.89	65.96	1428	*Gb, NpL*	4	This study
MD88-774	−48.88	115.67	3330	*Gb*	4	This study
MD84-568	−48.60	72.67	2241	*NpL*	4	This study
M29/1 2726-3	−48.39	−56.93	1405	*Gb, NpL*	2	This study
MD12-3394	−48.38	64.59	2320	*NpL*	4	This study
MD02-2488	−46.47	88.02	3469	*Gb*	4	This study
ANTIX/4 2083-1	−46.37	7.04	1955	*Gb, NpL*	2	This study
MD00-2374	−46.03	96.48	3250	*Gb, NpL*	2	This study
MD94-103	−45.58	86.53	3600	*Gb*	2	*Sicre et al.* [2005]
MD12-3401Q	−44.68	80.39	3445	*Gb, NpL*	4	This study
MD07-3076Q	−44.15	−14.23	3770	*Gb, NpL*	1	*Skinner et al.* [2010]
M29/1 2712-2	−43.67	−59.33	1228	*Gb*	2	This study
MD97-2101	−43.50	79.84	3200	*Gb*	2	*Crosta et al.* [2005]
M29/1 2709-7	−41.54	−57.06	1078	*Gb*	2	This study
M29/1 2703-7	−38.51	−54.20	1187	*Gb*	4	This study
MD76-118	−37.32	78.48	2048	*Gb*	4	This study
MD97-2100	−35.97	80.93	2510	*Gb*	4	This study
SU90-03P	40.50	−32.00	2475	*Gb*	4	*Chapman and Shackleton* [1998]
MD95-2039	40.58	−10.33	3381	*Gb*	3	*Schonfeld et al.* [2003]
CH69-K9	41.76	−47.35	4100	*Gb*	1	*Labeyrie et al.* [1999]
MD08-3182	52.70	−35.94	3757	*Gb*	1	This study
NA87-22	55.50	−14.50	2161	*Gb*	1	*Waelbroeck et al.* [2001]
MD03-2674	56.36	−27.81	2829	*Gb*	4	This study
MD95-2005	57.03	−10.06	2130	*Gb*	3	*Cléroux et al.* [2008]
F II KR 03	57.93	−29.13	2215	*Gb*	4	This study

[a]Gb: *G. bulloides*; NpL: *N. pachyderma* left.

[b]Chronostratigraphic control following the recommendations of MARGO [*Kucera et al.*, 2005]; radiometric controls on the 0–2 ky and 0–4 ky are indicated by 1 and 2, respectively; 3 indicates radiometric controls within the interval 4 − 8 ky or other stratigraphic control (e.g., % *G. hirsuta* left coiling) within 0 − 4 ky; and 4 indicates other stratigraphic constraints (e.g., $\delta^{18}O$ stratigraphy). Presence of Rose Bengal stained benthic foraminifera is indicated by 2.

2.2. Sample Dissolution

Carbonate dissolution at the sea floor is a potential bias that may affect the Mg/Ca content of core top samples, due to the preferential dissolution of Mg-rich calcite [*Brown and Elderfield*, 1996]. Core tops studies have shown a lowering of the Mg/Ca content of planktic foraminiferal shells with increasing water depth of the samples, due to the decrease in carbonate saturation levels [*Dekens et al.*, 2002; *Regenberg et al.*, 2006].

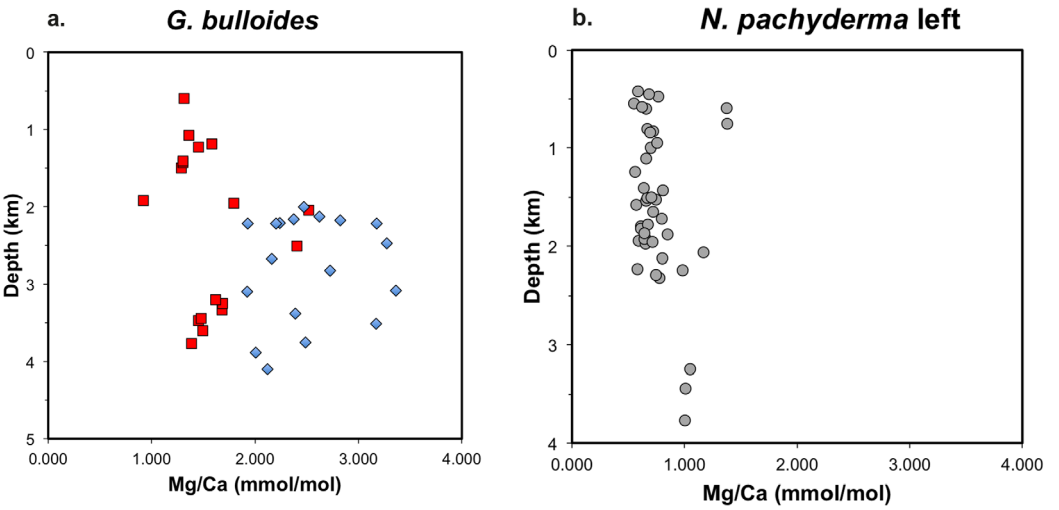


Figure 2. Variation of foraminiferal Mg/Ca (mmol/mol) with water depth (km) of the core tops. (a) *G. bulloides* samples. Red squares: Southern Ocean sites ($R^2 = 0.03$); blue diamonds: North Atlantic sites ($R^2 = 0.01$). (b) *N. pachyderma* left samples ($R^2 = 0.05$).

Moreover, Mg/Ca has been shown to decrease with carbonate ion concentration of seawater ($[CO_3^{2-}]$) even above the calcite saturation horizon in waters supersaturated with respect to pure calcite ($\Delta[CO_3^{2-}] > 0$ μmol/kg) [*Hertzberg and Schmidt*, 2013; *Regenberg et al.*, 2014]. Based on the analysis of a global data set of core tops, *Regenberg et al.* [2014] have suggested that Mg/Ca ratios of planktic foraminifera start to decrease in bottom waters below a critical threshold of $\Delta[CO_3^{2-}] = 21.3 \pm 6.6$ μmol/kg.

The core tops presented here do not show any obvious correlation of Mg/Ca content with water depth ($R^2 = 0.03$ for Southern Ocean *G. bulloides*; 0.01 for North Atlantic *G. bulloides*; 0.05 for *N. pachyderma left;* Figure 2), suggesting that all the samples are above dissolution depths. To verify the influence of the calcite saturation state of bottom waters in our samples, we have estimated at each site the bottom water departure from calcite saturation, $\Delta[CO_3^{2-}]$, based on bottle Global Ocean Data Analysis Project (GLODAP) $[CO_3^{2-}]$ data at nearby sites [*Key et al.*, 2004] and using the revised empirical equation of $[CO_3^{2-}]$ at saturation ($[CO_3^{2-}]_{sat}$) of *Bassinot et al.* [2004].

Carbonate ion concentration at each station is above the saturation line (Figure 3a), though the degree of calcite saturation for five of the *G. bulloides* and two of the *N. pachyderma* left stations is below the threshold proposed by *Regenberg et al.* [2014] (Figure 3b). However, $\Delta[CO_3^{2-}]$ does not show any correlation with Mg/Ca content ($R^2 = 0.13$ for North Atlantic *G. bulloides* samples; 0.02 for Southern Ocean *G. bulloides*

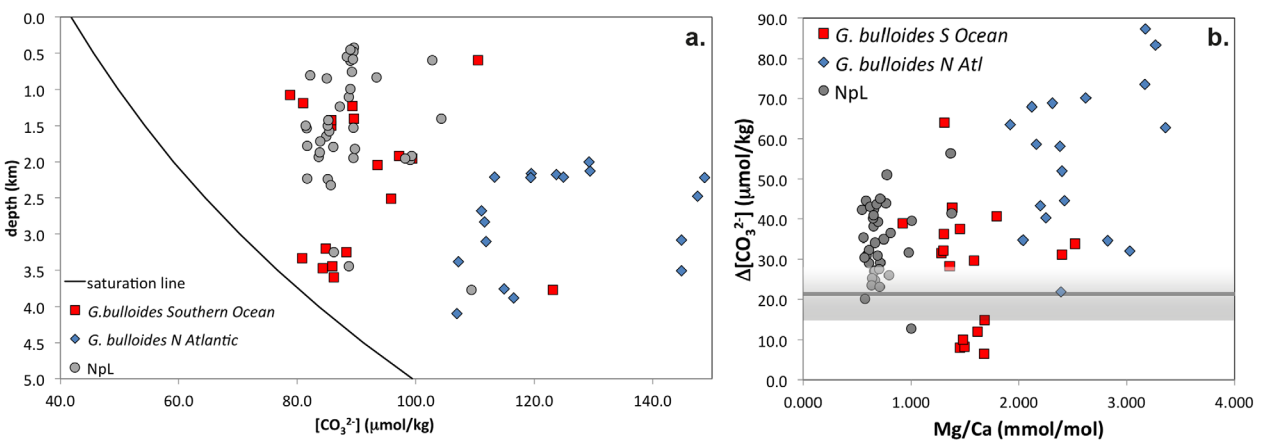


Figure 3. (a) Carbonate ion concentration ($[CO_3^{2-}]$, μmol/kg) at each station versus depth (km). The black line shows the calcite saturation line calculated using the $[CO_3^{2-}]_{sat}$ equation of *Bassinot et al.* [2004]. (b) Degree of calcite saturation ($\Delta[CO_3^{2-}]$, μmol/kg) versus measured foraminiferal Mg/Ca (mmol/mol). Grey horizontal line and shadow shows the critical threshold of $\Delta[CO_3^{2-}] = 21.3 \pm 6.6$ μmol/kg defined by *Regenberg et al.* [2014]. Red squares: Southern Ocean *G. bulloides* sites; blue diamonds: North Atlantic *G. bulloides* sites; grey circles: Southern Ocean *N. pachyderma* left sites. Correlation coefficients for (b) $R^2 = 0.13$ for North Atlantic *G. bulloides* samples; 0.02 for Southern Ocean *G. bulloides* samples; 0.06 for *N. pachyderma* left samples.

samples; 0.06 for *N. pachyderma* left samples; Figure 3b). Together with visual examination of the samples indicating good preservation, this lack of correlation points to a lack of significant dissolution.

2.3. Stable Isotope Analysis

Planktic foraminiferal specimens were handpicked in the 250–315 μm size fraction for *G. bulloides* and 200–250 μm size fraction for *N. pachyderma* left on LSCE samples, and in the 125–315 μm size fraction for AWI (Bremerhaven, Germany) samples. LSCE samples were cleaned in a methanol ultrasonic bath for a few seconds and roasted under vacuum at 380°C for 45 min prior to analysis, in order to eliminate impurities [*Duplessy*, 1978].

Planktic foraminiferal $^{18}O/^{16}O$ ratios ($\delta^{18}O$ hereafter, expressed in ‰ versus Vienna Pee-Dee Belemnite, VPDB) were measured at the LSCE on Finnigan $\Delta+$ and Elementar Isoprime mass spectrometers, and at AWI on Finnigan MAT253 mass spectrometers. VPDB is defined with respect to NBS-19 calcite standard ($\delta^{18}O = -2.20‰$). The mean external reproducibility (1σ) of carbonate standards for $\delta^{18}O$ is ± 0.05 and ± 0.08 ‰ at LSCE and AWI, respectively. Measured NBS-18 $\delta^{18}O$ are -23.20 ± 0.20 ‰ VPDB at the LSCE and -23.08 ± 0.13 ‰ VPDB at AWI.

In total, 18 Southern Ocean core tops were analyzed for $\delta^{18}O$ in *G. bulloides* (28 replicas), and 38 for *N. pachyderma* left (59 replicas) (supporting information Tables S1 and S2). The pooled standard deviation for replicas of $\delta^{18}O$ measurements is 0.22‰ for *G. bulloides*, and 0.10‰ for *N. pachyderma* left.

2.4. Isotopic Temperature

G. bulloides has traditionally been assigned a "near surface" habitat [*King and Howard*, 2005]. However, plankton tows from the Southeast Atlantic have shown that this species may occupy a more variable water depth than initially thought, and it is often found associated with phytoplankton blooms [*Mortyn and Charles*, 2003]. *N. pachyderma* left is also considered a surface dweller, but it can be found down to 250 m, close to pycnocline depths [*King and Howard*, 2005; *Kohfeld et al.*, 1996]. In order to avoid uncertainties related to the calcification habitat of the species, we have chosen to calculate their isotopic temperatures (i.e., temperatures of calcification at equilibrium with sea water) and use them to calibrate the Mg/Ca data against the temperature at which the foraminifera calcify. We have computed isotopic temperature with the paleotemperature equation of *Shackleton* [1998], using the measured $\delta^{18}O$ of the foraminifera and $\delta^{18}O$ of the water in which they calcified:

$$T_{iso} = 16.0 - 4.38 * (\delta^{18}O_c - \delta^{18}O_{sw}) + 0.10 * (\delta^{18}O_c - \delta^{18}O_{sw})^2 \quad (1)$$

T_{iso} is the isotopic temperature in °C, and $\delta^{18}O_c$ and $\delta^{18}O_{sw}$ are the $\delta^{18}O$ of the foraminiferal calcite in ‰ VPDB and of the seawater in ‰ SMOW, respectively. A correction factor of -0.27 ‰ was applied to convert from the SMOW to the VPDB scale [*Hut*, 1987].

The values of $\delta^{18}O_{sw}$ at each station were extracted from the gridded data set of *LeGrande and Schmidt* [2006]. Since the calcification depth of both species is not exactly known, and may vary from one location to the other [e.g., *Mortyn and Charles*, 2003; *Simstich et al.*, 2003], several tests were performed by averaging the $\delta^{18}O_{sw}$ values at each station over different depths. The mean ($\pm$ standard deviation) difference between $\delta^{18}O_{sw}$ averaged over 0–50 m and over 0–500 m is 0.02 ± 0.09 ‰ for the stations with *G. bulloides* data and -0.04 ± 0.04 ‰ for the stations with *N. pachyderma* left data, indicating that the choice of water depth is not critical. We have thus chosen to use the averaged value over the first 50 m of the water column at each location, and we took the uncertainty related to this assumption into account in the calculation of the propagated isotopic temperature error (see below). In this way, no a priori assumptions are made about the calcification depth of the species.

The total 1σ uncertainty of the $\delta^{18}O_{sw}$ value at each site has been estimated as the quadratic sum of the error of the GISS data set (considered to be 0.20‰, in order to account for the sparseness of the data in some regions) and the site-specific difference between $\delta^{18}O_{sw}$ averaged over the first 50 m or over the first 500 m at each station. This uncertainty ranges between 0.27 and 0.20‰, and is 0.21‰ on average. The 1σ error of $\delta^{18}O_c$ is the quadratic sum of the standard deviations of replicated measurements and the mean external reproducibility of $\delta^{18}O$ analysis (section 2.3). The 1σ error of T_{iso} calculated from the paleotemperature equation of *Shackleton* [1998] (equation (1)) has been computed using the law of propagation of error

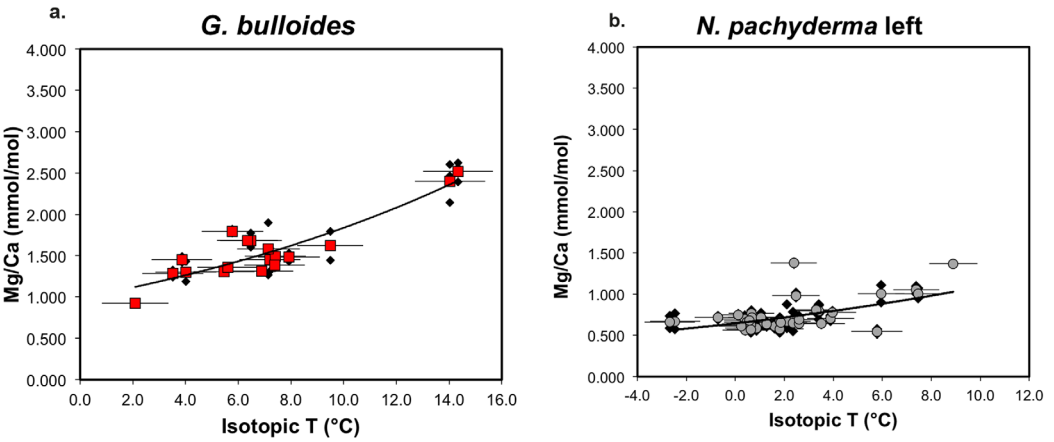


Figure 4. Mg/Ca (mmol/mol) versus isotopic temperature (°C). (a) *G. bulloides* Southern Ocean data. Red squares are site averages and black diamonds are replicas. Black thick line indicates exponential regression computed on averaged values of all Southern Ocean sites (equation (2), $R^2 = 0.75$). (b) *N. pachyderma* left data. Grey circles are site averages and black diamonds are replicas. Black thick line indicates the exponential regression computed on averaged values at all sites (equation (3), $R^2 = 0.35$). Error bars in both graphs are 1σ uncertainties in T_{iso}.

[*Ku*, 1966] considering that errors on $\delta^{18}O_{sw}$ and $\delta^{18}O_c$ are independent, and it amounts on average to 1.1°C for *G. bulloides* and 1.0°C for *N. pachyderma* left.

2.5. Mg/Ca-Temperature Calibrations

Experiments on inorganic calcite have indicated an exponential temperature dependence of the incorporation of Mg into calcite of ~3% per °C [*Oomori et al.*, 1987], with Mg/Ca calibrations often expressed as Mg/Ca (mmol/mol) = B * exp(A*T(°C)). In this equation, B is the species-specific preexponential constant, and A represents the temperature sensitivity of Mg incorporation into foraminiferal calcite.

Experiments with cultured foraminifera, on the other hand, have indicated a higher sensitivity of 8–10% per °C, pointing at the influence of biological factors in the incorporation of shell Mg [*Lea et al.*, 1999; *Rosenthal*, 2007]. Empirical calibrations for planktic foraminifera have often used this culturing-derived sensitivity to calculate regression lines with an exponential constant set to 0.1 [e.g., *Elderfield and Ganssen*, 2000]. However, independent calibrations have shown different sensitivities for the organic calcite of planktic species, including much lower values down to ~6% Mg/Ca per °C for *G. bulloides* and *N. pachyderma* left from sediment trap and core top studies [*Anand et al.*, 2003; *Jonkers et al.*, 2013; *Marr et al.*, 2011; *McConnell and Thunell*, 2005]. We have therefore decided not to fix the constants of the calibration equations, in order to empirically calculate the temperature sensitivity of *G. bulloides* and *N. pachyderma* left from our data sets.

The A and B coefficients of the regression equations were calculated for each species by performing 1000 Monte Carlo iterations of a least square regression. This approach allows us to propagate the uncertainties associated with both the calculation of T_{iso} and Mg/Ca measurements. Specifically, we have added for each iteration random noise to site-average T_{iso} and Mg/Ca values within their respective uncertainty ranges (see sections 2.1 and 2.4 for the calculation of uncertainties on Mg/Ca and T_{iso} values, respectively). The given B, A, and R^2 values are the median values of the 1000 iterations, and their associated nonparametric errors are the 68% confidence intervals calculated from the 84% and 16% percentiles (1σ errors).

3. Results

Measured Mg/Ca was plotted against calculated isotopic temperature for each Southern Ocean species (Figure 4). The site-averaged results are summarized in supporting information Table S1 (replica values given in supporting information Table S2).

G. bulloides Mg/Ca in the Southern Ocean sites varies between 0.921 and 2.521 mmol/mol (Figure 4a). Mg/Ca and isotopic temperature exhibit an exponential relationship between ~ 2 and 14°C that follows the equation:

Table 2. Published Mg/Ca-Temperature Relationships Compared With Data From This Study (in bold)

	Mg/Ca = B exp(AT)					
Species	B	A	R^2	Error on T (°C)	T range (°C)	Reference
Multispecies	0.520 (±0.010)	0.1			8–22°C	Elderfield and Ganssen [2000]
G. bulloides	0.474	0.107	0.98	0.8	10–25°C	Mashiotta et al. [1999]
G. bulloides	**1.006 (±0.032)**	**0.065 (±0.003)**	**0.82**	**1.1**	**2–18°C**	**This study (equation (4))**
N. pachyderma left	0.406	0.083			0–15°C	Nürnberg [1995]
***N. pachyderma* left**	**0.580 (±0.016)**	**0.084 (±0.006)**	**0.70**	**0.9**	**−1 − 9°C**	**This study (equation (5))**

$$Mg/Ca = 0.996\,(\pm 0.038) * \exp(0.061\,(\pm 0.005) * T_{iso})\; R^2 = 0.75 \quad (2)$$

N. pachyderma left Mg/Ca values are lower than in *G. bulloides*, in accordance with the lower isotopic temperatures (Figure 4b). However, they also cover a much smaller Mg/Ca range (between 0.546 and 1.378 mmol/mol), despite similar amplitude in the isotopic temperature variations of both species (11.6°C in *N. pachyderma* left versus 12.2°C in *G. bulloides*). The exponential regression of Mg/Ca and T_{iso} for *N. pachyderma* left for our Southern Ocean core tops (Figure 4b) takes the form:

$$Mg/Ca = 0.642\,(\pm 0.010) * \exp(0.061\,(\pm 0.005) * T_{iso})\; R^2 = 0.35 \quad (3)$$

This equation is indistinguishable from a linear regression (not shown). The low correlation coefficient of the *N. pachyderma* left data ($R^2 = 0.35$) seems to indicate a poor response of Mg/Ca in this species to ambient temperature changes in this temperature range.

4. Discussion

4.1. Mg/Ca in *G. bulloides*

The calibration of *G. bulloides* obtained from Southern Ocean core tops presented here (equation (2)) has a sensitivity coefficient of ~6% per °C, lower than in previously published calibrations that include this species (~10%) [*Elderfield and Ganssen*, 2000; *Mashiotta et al.*, 1999] (Table 2). However, the multispecies calibration of *Elderfield and Ganssen* [2000] was developed from core tops of the North Atlantic between 30 and 60°N, and the monospecific calibration of *Mashiotta et al.* [1999] only included two Southern Ocean core tops, the remainder being cultured data. This may suggest a different response of Mg incorporation by this species in different areas of the ocean.

To ascertain if the low response of Southern Ocean *G. bulloides* to temperature is a regional effect or not, we have compared our data set with other available Mg/Ca data sets. In order to avoid the accumulation of errors due to differences in cleaning and measuring techniques, only calibrations derived from core tops using the cleaning method of *Barker et al.* [2003] and measured by ICP spectrometers are considered here.

As discussed in section 2, *Bouinot* [2011] has analyzed *G. bulloides* samples with the same approach in North Atlantic core tops (Table 1 and supporting information Tables S1 and S2). In addition, *Cléroux et al.* [2008] have developed a calibration for *G. bulloides* from 10 core tops in the North Atlantic between 40° and 58°N, using the same methodology as in the present study. Their calibration was developed by comparing Mg/Ca in these core tops with isotopic temperatures calculated from measured $\delta^{18}O_c$ and $\delta^{18}O_{sw}$ extracted from *LeGrande and Schmidt* [2006]. Other calibrations commonly used for *G. bulloides* are either based on mixed planktic foraminifera [*Elderfield and Ganssen*, 2000], or on data sets cleaned and/or measured by other techniques [*Marr et al.*, 2011], not derived from core tops [*Jonkers et al.*, 2013; *Lea et al.*, 1999], or a combination of these factors [*Mashiotta et al.*, 1999; *McConnell and Thunell*, 2005].

Grouping the Southern Ocean data set presented in equation (2) with the *Cléroux et al.* [2008] and *Bouinot* [2011] data sets extends the temperature range of this calibration to 2–18°C, with sites located in both hemispheres. The bipolarity of *G. bulloides* has been established by the finding of the same two subpolar/transitional genotypes (Types IIa and IIb) in both hemispheres [*Darling and Wade*, 2008; *Darling et al.*, 2000], justifying the pooling of northern and southern sites. On the basis of our complete data set, we propose a new exponential Mg/Ca temperature calibration to describe the temperature response in *G. bulloides* (Figure 5, Table 2) of the form:

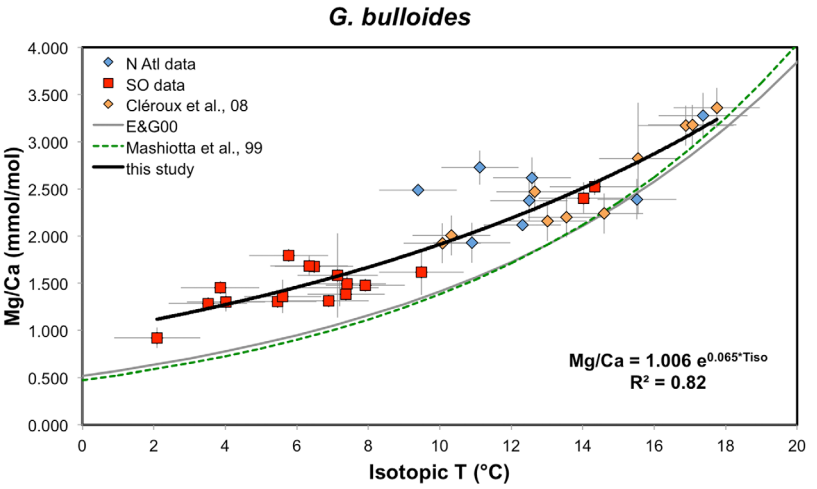


Figure 5. Mg/Ca (mmol/mol) versus isotopic temperature (°C) for *G. bulloides*. All symbols are site averages; red squares are new Southern Ocean data; blue diamonds are new North Atlantic data presented in this study [*Bouinot*, 2011]; orange diamonds are the data set of *Cléroux et al.* [2008] with T_{iso} recalculated as explained in section 2.4. Black thick line indicates the regression including all sites (equation (4)). The regression curves of *Mashiotta et al.* [1999] (*G. bulloides*, green-dashed line) and *Elderfield and Ganssen* [2000] (multispecies, grey line) are also shown for comparison.

$$\mathrm{Mg/Ca} = 1.006\,(\pm 0.032) * \exp(0.065\,(\pm 0.003) * T_{iso})\; R^2 = 0.82 \quad (4)$$

The average 1σ error of the regression is estimated to be 0.3°C. It is calculated by propagating the nonparametric 1σ errors obtained on A and B coefficients and accounting for the high interdependence (correlation coefficient of −0.93) between A and B, using the law of propagation of uncertainties [*Ku*, 1966]. Propagating the measurement error on *G. bulloides* Mg/Ca values ($\sigma_{Mg/Ca\ Gb} = 0.14$ mmol/mol), in addition to the regression error, leads to an average error on the expected temperatures derived from this calibration ($1\sigma_{TMg/Ca}$) of 1.1°C within the temperature range 2–18°C (± 2.2°C at 2°C and ± 0.7°C at 18°C). This *G. bulloides* Mg/Ca-isotopic temperature calibration therefore accounts for and propagates all sources of uncertainty (random errors associated to Mg/Ca and $\delta^{18}O_c$ replicates, error in the calculation of $\delta^{18}O_{sw}$ at each site, and uncertainty related to the exponential regression), and not only the uncertainty of the exponential fit.

The temperature sensitivity of Mg incorporation in our *G. bulloides* calibration is still only 6.5 ± 0.6% per °C, lower than in previous studies, especially when compared to cultured specimens [*Lea et al.*, 1999] or to North Atlantic core tops [*Cléroux et al.*, 2008]. This is likely the result of the extension of the exponential regression of this species to lower temperatures. The preexponential constant, on the other hand, is high (1.006 ± 0.032), close to constants calculated from sediment trap studies or core tops from the Southwest Pacific Ocean [*Anand et al.*, 2003; *Jonkers et al.*, 2013; *Marr et al.*, 2011]. As suggested above, the differences between our data and previously published calibration curves may be due to differences in sample pretreatment (which may include reductive steps that decrease the Mg/Ca content of the shells), to differences in sample provenance (sediment traps versus core tops), or to the distribution of *G. bulloides* data relative to other measured species in multispecies calibrations. If we set the exponential constant of our equation to 0.1, the preexponential constant is lowered to 0.628, closer to the values derived by *Elderfield and Ganssen* [2000] or *Mashiotta et al.* [1999]. However, the coefficient of determination (R^2) decreases from 0.82 to 0.62, indicating a poorer goodness of fit of the regression.

The core tops used to generate *G. bulloides* data are mostly located south of 32°S and north of 40°N, indicating that equation (4) is valid in mid and high latitudes of both hemispheres. Even though most lower-latitude sites are outside of the distributional range of this species, *G. bulloides* has also been shown to thrive in lower-latitude upwelling regions dominated by high-productivity seasons [*Bé*, 1977; *Naidu and Malmgren*, 1996]. The inclusion of core tops from temperate to tropical regions, as well as the inclusion of core tops from the Pacific Ocean, may help to reduce the uncertainty of this calibration, and to validate it in a global context. In addition, the discrimination between the genotypes of *G. bulloides* has been shown to reduce the prediction errors in SST reconstructions based on planktic foraminiferal counts [*Kucera and*

Darling, 2002]. Differentiating between *G. bulloides* genotypes may therefore also help reducing the uncertainties in Mg/Ca calibrations.

Measured *G. bulloides* Mg/Ca values are higher than predicted from their isotopic temperatures if they are calculated from published calibrations [*Elderfield and Ganssen*, 2000; *Mashiotta et al.*, 1999] (Figure 5). Sediment trap and plankton tow studies have also noted similar high Mg/Ca values in *G. bulloides* [*Jonkers et al.*, 2013; *Martínez-Botí et al.*, 2011] that have been ascribed to the presence of "anomalous Mg/Ca excess" in water-column shells of the North Atlantic that may not necessarily be preserved in the sediment [*Jonkers et al.*, 2013; *Martínez-Botí et al.*, 2011]. However, the occurrence of Mg/Ca data between ~ 1 and 4 mmol/mol is frequent in the Atlantic and Pacific Oceans [*Elderfield and Ganssen*, 2000; *Jonkers et al.*, 2013; *Marr et al.*, 2011; *Martínez-Botí et al.*, 2011; *Skinner and Elderfield*, 2005, raw data; this study]. This seems to indicate that values within this range are not necessarily anomalous, but rather common and not necessarily related to high-salinity regions such as the Mediterranean Sea, where Mg/Ca ratios are extremely high [*van Raden et al.*, 2011]. The increased goodness of fit of the bipolar calibration (equation (4)) with respect to the Southern Ocean calibration (equation (2)) indicates that regional differences likely do not play an important role on the incorporation of Mg in the test of *G. bulloides*, at least in the areas considered in this study.

4.2. Mg/Ca in *N. pachyderma* left

Mg/Ca and isotopic temperature of *N. pachyderma* left from all Southern Ocean core tops are poorly correlated ($R^2 = 0.35$, Figure 4). Similarly to the sensitivity we have found for *G. bulloides* (section 4.1), the temperature sensitivity of *N. pachyderma* left is lower in our study (6.1 ± 0.5% per °C) than in most previously published calibrations (~10%), [*Kozdon et al.,* 2009; *Nürnberg*, 1995], although sediment trap data from the Irminger Sea with T_{iso} between ~ 4 and 6°C have shown a similar response of 6% per °C [*Jonkers et al.*, 2013].

Nürnberg [1995] developed a first relationship between Mg/Ca and water temperature for this species, using core top data from the Atlantic sector of the Southern Ocean and from the Norwegian Sea. He found similar sensitivities of ~9% per °C in both hemispheres, although he noted that data derived from sampling sites annually covered by sea ice in the Arctic deviated from the general trend. However, Mg/Ca in that study was measured by electron microprobe analysis, making the comparison with our data set complicated. More recently, *Meland et al.* [2006] found a lack of temperature control on *N. pachyderma* left Mg/Ca values in cold-water areas of the Nordic Seas. They attributed this result in part to annual sea ice cover influencing seawater chemistry and thus Mg/Ca ratios, which prompted *Kozdon et al.* [2009] to propose a new temperature calibration only for Norwegian Sea waters. These latter authors found that reliable Mg/Ca-based temperature estimates from this species are limited to foraminifera that have calcified in water masses with peak summer temperatures above ~3°C. However, *N. pachyderma* left was found to prefer gradually deeper habitats with increasing surface water temperatures, which limits its utility as a temperature indicator. *Hendry et al.* [2009], in sediment traps off the Antarctic peninsula, showed that the calcite of *N. pachyderma* left is influenced by factors other than temperature during periods of sea ice cover, and suggested that high carbonate ion concentrations at the ice-water interface affect Mg incorporation in the shells.

Traditionally, planktic foraminifera have been selected based on their morphological types, and separated into different morphospecies based on their test shape. However, genetic studies show that individual morphospecies may present distinct genotypes that are adapted to different environments, and may therefore present different behaviors as paleoproxies [*Darling and Wade*, 2008]. *N. pachyderma* left has been shown to present seven different genotypes whose speciation has likely developed in response to Quaternary climate dynamics [*Darling et al.*, 2007], which suggests that proxies developed from different genotypes of this taxon should be calibrated independently [*Darling et al.*, 2004]. Considering the Southern Hemisphere genotypes, Type IV has been found to be the only one adapted to overwintering in sea ice [*Darling et al.*, 2004]. This genotype may correspond to the *N. pachyderma* left shown by *Hendry et al.* [2009] to exhibit poor correlation between test Mg/Ca and ambient temperature.

Nineteen of the 38 Southern Ocean core tops included in the calculation of equation (3) are situated on the Antarctic margin, and therefore subject to the possible influence of sea ice. If these core top samples are excluded from the regression, the goodness of fit improves markedly:

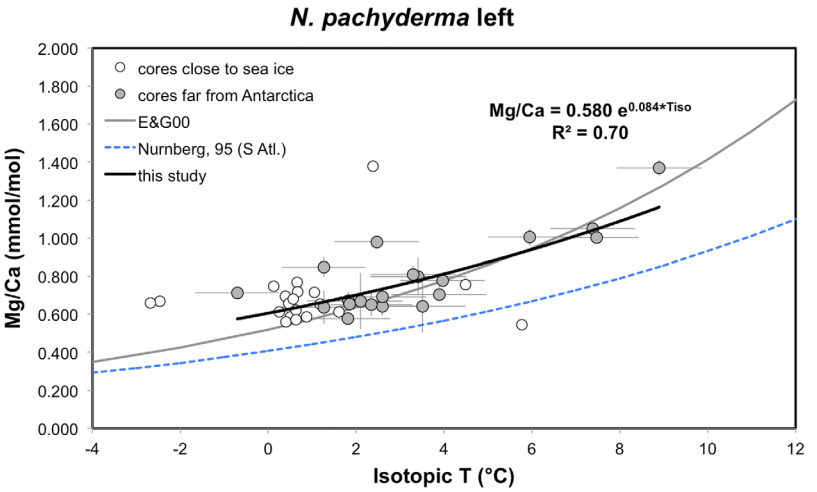


Figure 6. Mg/Ca (mmol/mol) versus isotopic temperature (°C) for *N. pachyderma* left. Circles are site averages, grey for sites north of 60°S and away from the influence of sea ice, and white for sites close to the Antarctic margin. Black line indicates the exponential regression including sites not affected by sea ice (grey circles, equation (5)). The regression curves of *Nürnberg* [1995] (South Atlantic *N. pachyderma* left, blue dashed line) and *Elderfield and Ganssen* [2000] (multispecies, grey line) are also shown for comparison.

$$\mathrm{Mg/Ca} = 0.580\,(\pm 0.016) * \exp(0.084\,(\pm 0.006) * \mathrm{T_{iso}})\,R^2 = 0.70 \quad (5)$$

The sensitivity of *N. pachyderma* left Mg/Ca to temperature (8.4 ± 0.6% per °C) is higher when cores from the Antarctic margin are excluded (Figure 6 and Table 2), and very close to that of the South Atlantic data set of *Nürnberg* [1995].

The combination of our "far from Antarctic sea ice" Southern Ocean data with the data sets of *Nürnberg* [1995] and/or the complete data set of *Kozdon et al.* [2009] actually lowers the fit of the calibration ($R^2 < 0.50$) and the exponential constant. In the case of the study of *Nürnberg* [1995], the differences between data sets may be ascribed to methodological issues that increase the scatter of the regression. On the other hand, *Kozdon et al*. [2009] have used the same cleaning and measuring techniques as in the present study, so the data set should be comparable with the Southern Ocean. However, *Darling et al*. [2007] and *Darling et al*. [2004] have shown that Northern and Southern Hemisphere populations of *N. pachyderma* left present different genotypes. These two genotypes have not mixed since ice-sheet build-up during the Quaternary (~1.8 My ago) [*Darling et al.*, 2007], and may therefore present different responses of Mg incorporation into their tests.

On the basis of these considerations, we propose a new exponential Mg/Ca temperature calibration to describe the temperature response in *N. pachyderma* left that calcified away from the influence of sea ice in the Southern Ocean (equation (5), Table 2). The 1σ error of the regression (obtained by propagating the nonparametric 1σ errors associated with coefficients A and B, and accounting for the high interdependence (correlation coefficient of −0.83) between A and B) is 0.4°C. Propagating the measurement uncertainty on *N. pachyderma* left Mg/Ca values ($\sigma_{\mathrm{Mg/Ca\ NpL}} = 0.06$ mmol/mol), in addition to the regression uncertainty, leads to an average error on the expected temperatures derived from this calibration ($1\sigma_{\mathrm{TMg/Ca}}$) of 0.9°C within the temperature range −1–9°C (± 1.5°C at −1°C and ± 0.7°C at 9°C).

4.3. Calcification Depths

If we compare *G. bulloides* isotopic temperatures from Southern Ocean and North Atlantic core tops with annual mean temperature values for the upper 50 m of the water column at the core sites extracted from the World Ocean Atlas 2009 (WOA09) [*Locarnini et al.*, 2010], we find an average difference of 0.1 ± 2.1°C. A similar value is observed if we compare Mg/Ca-derived temperature and WOA09 temperature, with *G. bulloides* Mg/Ca-derived temperatures (calculated with equation (4)) on average 0.2 ± 2.8°C lower than annual mean temperature over the upper 50 m of the water column. Note that the choice of WOA database has a negligible impact in this differences, since comparison of WOA09 and WOA13 SST for high latitude sites indicates a root mean standard deviation of only 0.2°C [*Capron et al.*, 2014].

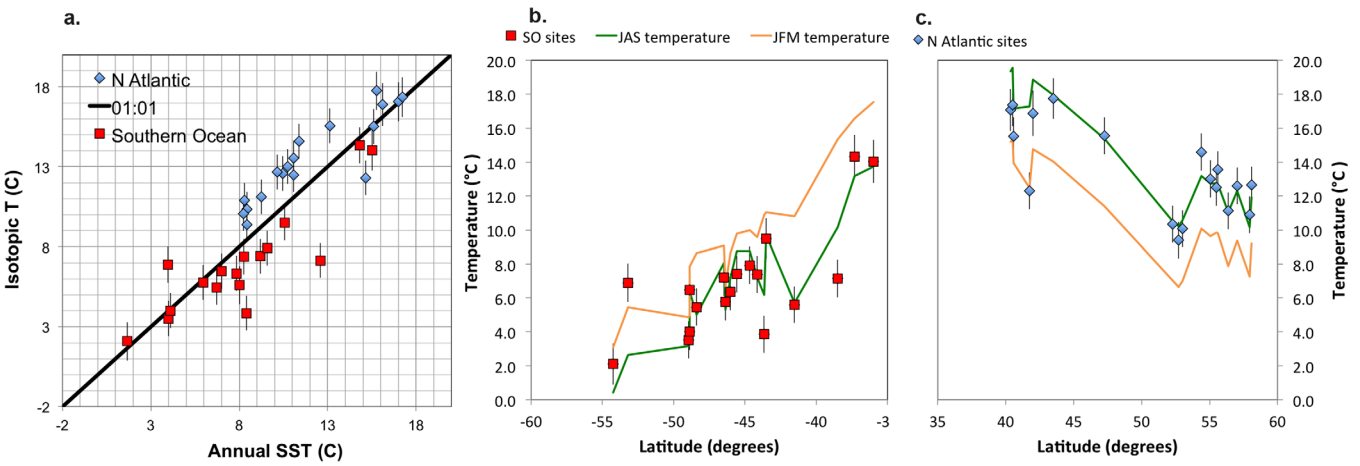


Figure 7. (a) Isotopic temperature of *G. bulloides* (°C) versus annual SST (°C) of the upper 50 m of the water column extracted from WOA09 [*Locarnini et al.*, 2010] at the location of the North Atlantic and Southern Ocean sites. Black line indicates 1:1 relation. (b and c) Isotopic temperature of *G. bulloides* (°C) versus latitude of the core top sites in the Southern Ocean (b) and the North Atlantic (c). Orange line is January–March (JFM) temperature; green line is July–September temperature (JAS) from the WOA09 [*Locarnini et al.*, 2010]. Red squares are sites located in the Southern Ocean and blue diamonds are sites in the North Atlantic.

However, there is a noticeable difference between Southern Ocean and North Atlantic sites. Isotopic temperatures of Southern Ocean sites are on average 1.0°C lower than annual temperature, whereas North Atlantic sites are on average 1.3°C higher (Figure 7a). When isotopic temperatures are plotted against January–February–March (JFM) and July–August–September (JAS) WOA09 temperatures, all sites fall close to the JAS temperatures of the upper 50 m of the water column (Figure 7b), suggesting that calcification takes place during the summer season in the North Atlantic, and the winter season in the Southern Ocean. This behavior of *G. bulloides* is puzzling, since sediment trap data from the Southern Ocean have reported that this species calcifies from spring to summer [*Jonkers and Kucera*, 2015; *King and Howard*, 2003; *Marchant et al.*, 2004].

Another explanation for this mismatch is that *G. bulloides* is living at a greater depth than the upper 50 m in the Southern Ocean. In order to calculate the approximate calcification depth of *G. bulloides* at each site, reconstructed temperatures were compared with interpolated water column temperature vertical profiles at each site. These "synthetic" temperature vertical profiles were constructed by selecting WOA09 temperature-depth profiles situated within ± 1.5° longitude and latitude from each core top site, and interpolating the temperature at each WOA09 depth at the actual core top site with inverse distance weighting (using R statistical software) [*R Core Team*, 2015]. Once the interpolated vertical temperature profile was built at each sample location, calcification depth was estimated by linearly interpolating the depth that corresponded to the calculated calcification temperature.

When calculated T_{iso} values are compared with mean summer (JAS for the North Atlantic and JFM for the Southern Ocean) synthetic temperature vertical profiles, the average calcification depth inferred for *G. bulloides* for all Southern Ocean sites is 183 ± 136 m. Using *G. bulloides* $T_{Mg/Ca}$ to infer calcification depth, we obtain a similar result of 237 ± 215 m (Figure 8a). On the other hand, reconstructed *G. bulloides* calcification depths in the North Atlantic sites are much shallower (44 ± 38 m if they are calculated from T_{iso} and 50 ± 61 m if reconstructed from $T_{Mg/Ca}$, Figure 8b). This indicates that, in the Southern Ocean, *G. bulloides* is not necessarily a "surface dweller" as sometimes assumed, but rather that its position in the water column is quite variable. Plankton tow data from the South Atlantic have already shown this strong variability, with measureable populations that can be as deep as 800 m [*Mortyn and Charles*, 2003].

The isotopic temperatures of *N. pachyderma* left away from the influence of sea ice are closest to spring (October–December, OND) temperatures in the Southern Ocean (average difference is 0.1 ± 2.1°C). This is in agreement with studies that have indicated that calcification for this species takes place during spring in subpolar environments [*Jonkers et al.*, 2010; *Kohfeld et al.*, 1996]. Mg/Ca-derived temperatures are within 1.9°C of isotopic temperatures, and also close to spring temperature of the upper 50 m of the water column (average difference is −0.2 ± 2.5°C).

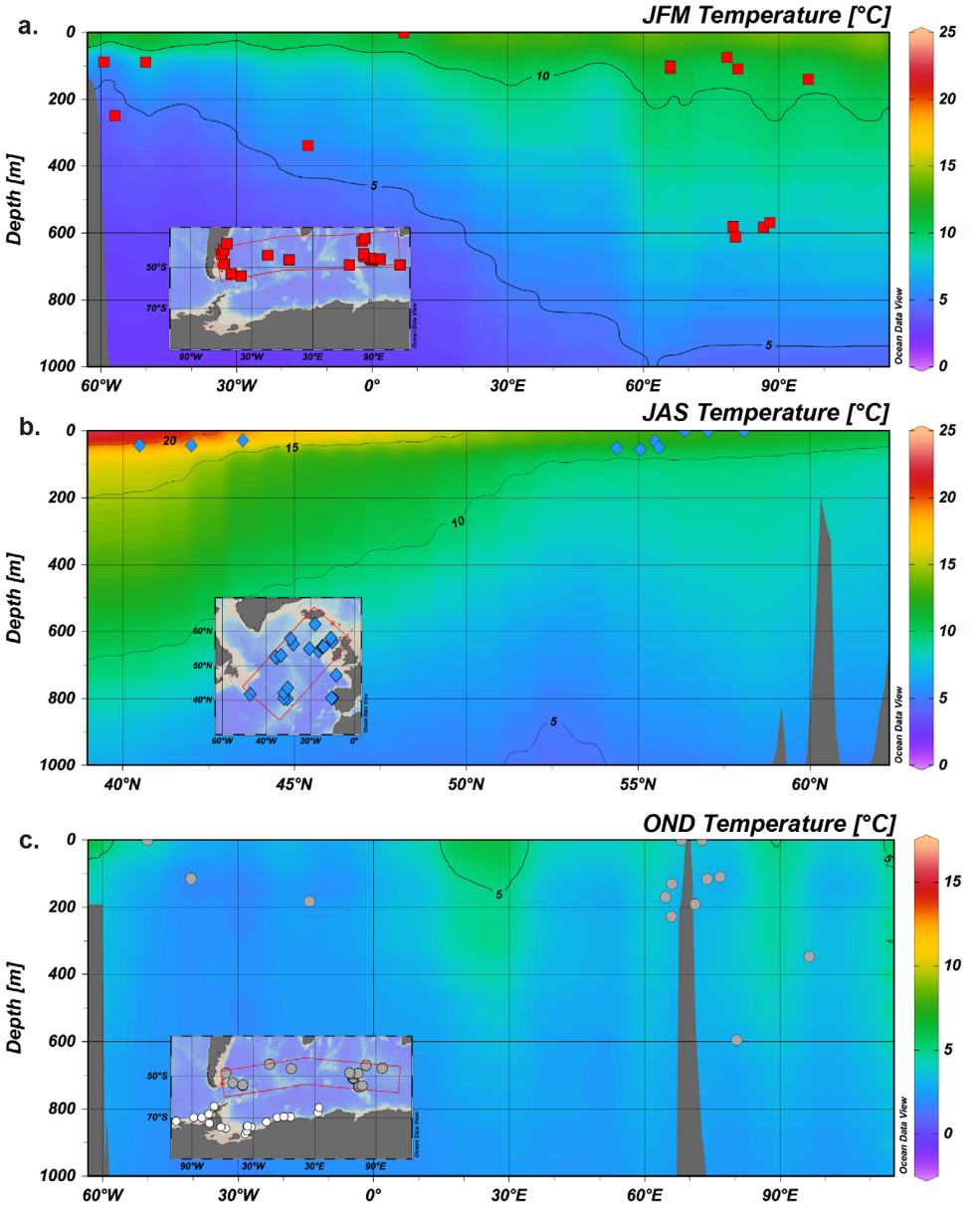


Figure 8. Calcification depths reconstructed from Mg/Ca-derived temperatures plotted over WOA09 temperature sections defined by red sections in the insets. (a) Summer (JFM) temperature meridional transect with Southern Ocean *G. bulloides* sites (red squares). (b) Summer (JAS) temperature latitudinal transect with North Atlantic *G. bulloides* sites (blue diamonds). (c) Spring (OND) temperature meridional transect with *N. pachyderma* left sites away from the influence of sea ice (grey circles). Also shown in the inset are *N. pachyderma* left sites affected by sea ice (white circles).

If we compare reconstructed *N. pachyderma* left temperatures with spring (OND) temperature vertical profiles averaged from nearby WOA09 stations, the average calcification depth inferred from T_{iso} is 110 ± 166 m, similar to calcification depth reconstructed from $T_{Mg/Ca}$ (156 ± 144 m, Figure 8c). This is in agreement with studies that have found that *N. pachyderma* left calcifies at depths of 50–200 m [*Bergami et al.*, 2009; *Kohfeld et al.*, 1996]

5. Conclusions

We have developed Mg/Ca-temperature relationships for two commonly used species in paleoceanography from mid to high latitudes, *G. bulloides* and *N. pachyderma* left. The calibrations are based on core top foraminifera that have been cleaned following the method developed by *Barker et al.* [2003] and measured by

ICP-OES. Mg/Ca ratios in both species increase exponentially with calcification temperature, with sensitivities of ~6 and 8% in Mg/Ca per degree of temperature for *G. bulloides* and *N. pachyderma* left, respectively (Table 2). These sensitivities are somewhat lower than in previously published calibrations, in particular those derived from culturing experiments or using mixed planktic species. We have carefully estimated and propagated the uncertainties on Mg/Ca measurements, calcification temperature calculations, and regression fits using Monte Carlo iterations, in order to obtain realistic estimates of the errors associated with the reconstructed temperatures.

The Mg/Ca-temperature calibration of *G. bulloides* is valid for mid and high latitudes of both hemispheres over the 2–18°C temperature range, which extends the range of previous calibrations in accord with the ecological preferences of this species. The propagated absolute error in calcification temperature is 1.1°C for our data set. *G. bulloides* is found to calcify at ~200 m depth in the Southern Ocean, while it is confined to the top 50 m of the water column in the North Atlantic.

The relation between Mg/Ca ratios and calcification temperature in *N. pachyderma* left breaks down in sites affected by sea ice, where other factors such as carbonate ion concentration or habitat depth changes may influence the incorporation of Mg [*Hendry et al.*, 2009; *Kozdon et al.*, 2009]. Arctic and Antarctic populations do not have similar temperature sensitivities, probably due to genotypic differences developed during the Early Pleistocene [*Darling et al.*, 2007]. We have therefore developed a calibration for the −1 to 9°C temperature range using Southern Ocean core tops away from Antarctic sea ice (between ~60 and 44°S) that results in an absolute temperature error of 0.9°C for our data set.

This study highlights the need of developing Mg/Ca-temperature calibrations that are methodologically consistent and based on single species. The response of the incorporation of Mg in foraminiferal tests of a single species to temperature is likely related to genotypes that have developed in response to different environmental conditions. A case-by-case assessment of the geographical extension of those genotypes is needed when choosing to develop regional versus global calibrations.

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