



Mg/Ca- ΔCO_3^{2-} pore water-temperature calibration for *Globobulimina* spp.: A sensitive paleothermometer for deep-sea temperature reconstruction



Syee Weldeab^{a,*}, Adam Arce^a, Sabine Kasten^b

^a Department of Earth Science, University of California, Santa Barbara, CA 93106, USA

^b Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Am Handelshafen 12, 27570 Bremerhaven, Germany

ARTICLE INFO

Article history:

Received 22 August 2015
Received in revised form 7 January 2016
Accepted 8 January 2016
Available online xxxx
Editor: D. Vance

Keywords:

benthic foraminiferal Mg/Ca
paleothermometry
Globobulimina spp.
carbonate ion concentration of pore water
eastern equatorial Atlantic
reconstruction of deep sea temperature

ABSTRACT

Existing benthic foraminiferal Mg/Ca-temperature calibrations are surrounded by substantial uncertainties mainly due to low temperature sensitivity of Mg/Ca in most benthic foraminifers and the effect of carbonate ion concentration on benthic foraminiferal Mg/Ca. Here we present Mg/Ca analysis of Rose Bengal stained and exceptionally well-preserved tests of the infaunal benthic foraminifer *Globobulimina* spp. from 39 eastern equatorial Atlantic core top samples. Mg/Ca in *Globobulimina* spp. varies between 2.5 mmol/mol and 9.1 mmol/mol corresponding to bottom water temperatures (BWT) between 1.8 °C and 19.1 °C and ΔCO_3^{2-} pore water between 33.7 ± 4 and -34.3 ± 4 $\mu\text{mol/kg}$ in sediment depths between 1 and 10 cm. Mg/Ca and BWT are linearly correlated with a best fit of $\text{Mg/Ca} [\text{mmol/mol}] = (0.36 \pm 0.02) * \text{BWT} [^\circ\text{C}] + 2.22 \pm 0.19$ ($r^2 = 0.92$, p -value: $11 * 10^{-20}$, and $n = 39$). Using total alkalinity and pH data of pore water samples from 64 Atlantic multi-corer sites, we obtained ΔCO_3^{2-} pore water data from the depth habitat range of *Globobulimina* spp. (≥ 1 cm ≤ 10 cm below sediment surface). We show that ΔCO_3^{2-} pore water is significantly lower than and linearly co-varies with the ΔCO_3^{2-} of the overlying bottom water: ΔCO_3^{2-} pore water = $(0.67 \pm 0.05) * \Delta\text{CO}_3^{2-}$ bottom water - (39.84 ± 1.98) ; $r^2 = 0.75$, p -value: $6 * 10^{-20}$, $n = 64$. We found a Mg/Ca sensitivity of 0.009 ± 0.0044 mmol/mol per $\mu\text{mol/kg}$ ΔCO_3^{2-} pore water and Mg/Ca temperature sensitivity of 0.32 ± 0.06 mmol/mol/°C after a correction for the ΔCO_3^{2-} pore water effect. This study provides a robust Mg/Ca-temperature calibration, highlights that ΔCO_3^{2-} pore water is spatially and most likely temporally variable, and contradicts the notion that infaunal foraminiferal Mg/Ca is relatively immune from ΔCO_3^{2-} changes in the overlying bottom water. Furthermore, comparison of down core Mg/Ca data of *Cibicides pachyderma* and *Globobulimina* spp. demonstrates that the high temperature sensitivity of Mg/Ca in *Globobulimina* spp. presents a more robust paleothermometer to reconstruct past changes in the thermal state of the deep ocean.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Deep-sea temperature reconstruction primarily relies on benthic foraminiferal Mg/Ca paleothermometry and is a key component of concerted efforts to establish a comprehensive understanding of Earth's past climate changes (Elderfield et al., 2010; Lear et al., 2000, 2010; Marchitto and deMenocal, 2003; Martin et al., 2002; Skinner and Elderfield, 2007; Sosdian and Rosenthal, 2009). However, the relatively low Mg concentration and low temperature sensitivity of Mg/Ca in the widely used benthic foraminifer species,

as well as the strong imprint of carbonate ion concentration changes on benthic foraminiferal Mg/Ca impedes a precise Mg/Ca-bottom water temperature (BWT) calibration and robust estimates of past bottom water temperature (Bryan and Marchitto, 2008; Curry and Marchitto, 2008; Elderfield et al., 2010, 2006; Lear et al., 2002; Marchitto et al., 2007; Marchitto and deMenocal, 2003; Rosenthal et al., 1997, 2006). *Globobulimina affinis*, an infaunal benthic foraminifer whose depth habitat varies between 0.5 cm and 10 cm below surface sediment (Jorissen et al., 1995; McCorkle et al., 1997; Schmiedl et al., 2000, 2004), appears to be a promising species for BWT reconstructions because of its relatively high Mg/Ca (Skinner and Elderfield, 2007; Skinner et al., 2003). There exists, however, no core top-based Mg/Ca-BWT calibration for *Globobulimina affinis* or other *Globobuliminid*, a primarily

* Corresponding author.

E-mail address: Weldeab@geol.ucsb.edu (S. Weldeab).

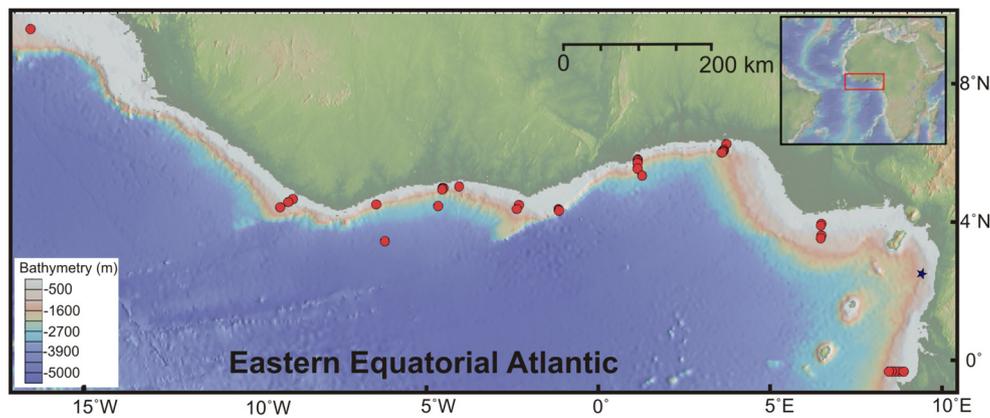


Fig. 1. Map of the Gulf of Guinea indicating location of core top samples (red filled circles) and MD2707 down core sediment (blue star). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

continental margin genus that been extant since at least the Cretaceous (Jorissen et al., 1995; McCorkle et al., 1997; Schmiedl et al., 2000, 2004). Furthermore, the lack of systematic investigation of CO_3^{2-} concentration in pore water and its relationship to that of the overlying bottom water prevents the evaluation of several factors. While ΔCO_3^{2-} bottom water ($\Delta\text{CO}_3^{2-} = \text{CO}_3^{2-}$ in situ $- \text{CO}_3^{2-}$ saturation) is spatially highly variable and has strong effect on epi-benthic foraminiferal Mg/Ca (Elderfield et al., 2006), the quantitative relationship between ΔCO_3^{2-} pore water and ΔCO_3^{2-} of the overlying bottom water is unknown and therefore the effect of the former on the Mg/Ca of infaunal benthic foraminifers is poorly constrained. Here we present a core top-based Mg/Ca–BWT calibration for *Globobulimina affinis* and *Globobulimina cf. pacifica*. Moreover, we evaluate the relationship between ΔCO_3^{2-} in pore water and the overlying bottom water in the Atlantic and quantify the effect of ΔCO_3^{2-} pore water on Mg/Ca of *Globobulimina* spp.

2. Setting, material and methods

2.1. Hydrography

This study focuses on core top sediment samples that were collected from the Gulf of Guinea, eastern equatorial Atlantic (Fig. 1). Bottom water temperature (BWT), salinity, and bottom water ΔCO_3^{2-} vary from 19.1 °C to 1.8 °C, 35.8 psu to 34.5 psu, and 101 $\mu\text{mol/kg}$ to 8.4 $\mu\text{mol/kg}$, respectively (Figs. 2A–E). Between the shallowest water depth (68 m) and the upper boundary (500 m) of the Antarctic Intermediate Water (AAIW), salinity, temperature, and ΔCO_3^{2-} decline synchronously. Within the water depth interval occupied by Antarctic Intermediate Water (AAIW), salinity and ΔCO_3^{2-} increase by 0.5 psu and 20 $\mu\text{mol/kg}$ with little change in BWT. Below 4 °C, BWT, ΔCO_3^{2-} , and salinity decline synchronously (Figs. 2D–E).

2.2. Core top and down core samplings

Core top samples were retrieved from water depths between 68 m and 4307 m using a giant box corer during RV Meteor Cruise M 6-5 in 1988 (Lutze et al., 1988). BWT was measured 1.5 m above the sediment surface of each sampling site with a thermometer that has an uncertainty of ± 0.002 °C (Lutze et al., 1988). Immediately after recovery of the box corer, pore-water temperature at a depth between 4 and 5 cm below surface sediment was measured with a probe thermometer that has an uncertainty of ± 0.1 °C (Lutze et al., 1988). Bottom water and pore water temperatures linearly correlate with $r^2 = 0.99$ and slope of 0.94 ± 0.02 (Lutze et al., 1988). Onboard, subsampling of the box cores was limited to

a sediment depth of 2 cm. Sediments were preserved and stained on board with a solution of 2 g Rose Bengal in 1 L of methanol (Altenbach et al., 2003). The material was then washed through a 63 μm sieve and dried. For this study, Rose Bengal stained and well-preserved tests of *Globobulimina affinis* and *Globobulimina cf. pacifica* (Fig. 3) were selected from the sample fraction ≥ 250 μm ≤ 400 μm and gently crushed to open the chambers for effective cleaning. We combined *Globobulimina affinis* and *Globobulimina cf. pacifica* because the abundance of either one of these species was not high enough for a robust trace element analysis. In the following discussion, we will refer to *Globobulimina affinis* and *Globobulimina cf. pacifica* (Fig. 3) as *Globobulimina* spp. In a 400 cm long segment of MD2707 core sediment (02°30.11'N, 09°23.68'E, 1295 m water depth), we selected *Globobulimina* spp. (*Globobulimina affinis* and *Globobulimina cf. pacifica*, ≥ 250 μm ≤ 400 μm) and *Cibicides pachyderma* (≥ 250 μm ≤ 400 μm) and analyzed their trace element compositions. The preservation state of both *Globobulimina* spp. and *Cibicides pachyderma*, as judged by visually inspection under the microscope, is excellent.

2.3. Cleaning and trace element analysis

Tests of *Globobulimina* spp. and *Cibicides pachyderma* were cleaned using the UCSB standard foraminifera cleaning procedure that includes oxidative and reductive steps but without the DTPA (diethylene triamine pentaacetic acid) step (Martin and Lea, 2002). Trace elements were analyzed by the isotope dilution/internal standard method (Martin and Lea, 2002) using a Thermo Finnigan Element2 sector inductively coupled plasma mass spectrometer (ICP-MS). Analytical reproducibility, assessed by analyzing consistency standards matched in Mg/Ca ratios to dissolved foraminifera solutions, is $\pm 0.4\%$ (0.03 mmol/mol) (1σ). Al/Ca, Fe/Ca and Mn/Ca were used to check the cleaning efficiency.

2.4. Calculation of ΔCO_3^{2-} pore water

We used total alkalinity and pH measurements in porewater to calculate carbonate ion concentration in 64 multi-corer samples that were collected across the Atlantic Ocean (30.193N–44.475S, 14.004E–54.258W, and water depth 605–5817 m) during numerous cruises by the Geochemistry working group at the University of Bremen. The method of porewater sampling and total alkalinity and pH measurements is described in detail, for example, in Schulz (2006) and Hensen et al. (1997). Here we provide a brief summary. To re-establish the in situ temperature onboard of the research vessel, the multi-corer sediments were kept at ~ 4 °C. pH values of the freshly cut sediment surface were determined using punch-in electrodes. Then the sediments were sliced in 0.5-to-1 cm thick

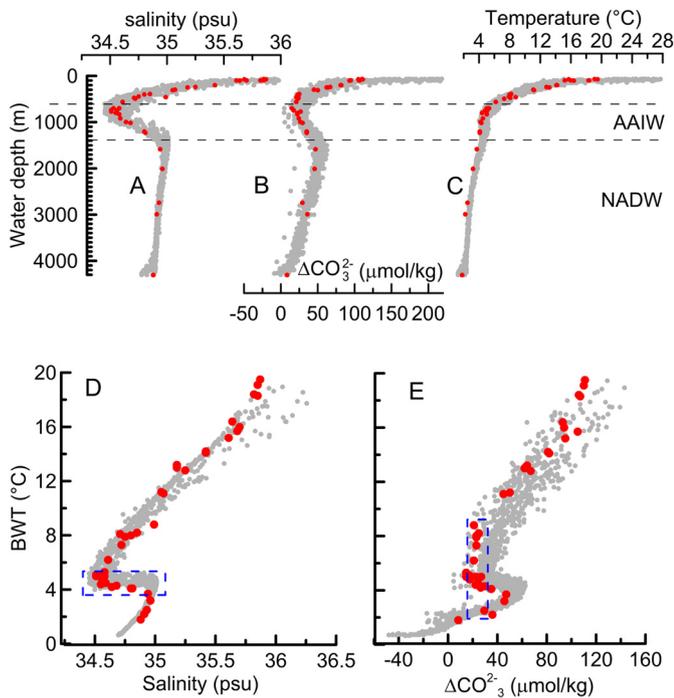


Fig. 2. A–C: Salinity, ΔCO_3^{2-} , and temperature across the Gulf of Guinea water depth. Red dots indicate bottom water values over the sampling sites (Fig. 1) and small grey dots indicate available data (latitude: 10.84N–5.72S and longitude: 338.77E–306.35E) from the Gulf of Guinea. D–E: Bottom Water Temperature (BWT)–salinity and BWT– ΔCO_3^{2-} relationships. All data sets shown in Figs. 2A–E were retrieved from the Global Ocean Data Analysis Project (GLODAP) (Key et al., 2004) and ΔCO_3^{2-} was calculated using the CO_2 -CALC software (Robbins et al., 2010). Blue rectangles mark ranges used to isolate the temperature and salinity imprint in Mg/Ca. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

sample and porewater was extracted by compression using a filter with a mesh size of 0.1–0.2 μm (Schulz, 2006). Total alkalinity was analyzed immediately after fluid extraction using titration. Adequate amount of 0.001 M hydrochloric acid was added to 1 ml porewater and the pH was brought to 3.5. The alkalinity was calculated as follows: $\text{alk} = [(V_{\text{HCl}} * C_{\text{HCl}}) - 10^{-\text{pH}} * (V_0 + V_{\text{HCl}})] / f_{\text{H}^+} / V_0$ (Schulz, 2006). V_{HCl} and C_{HCl} denote to the volume and molarity of added hydrochloric acid; pH, V_0 , f_{H^+} describe the pH value the solution attains after accounting for the addition of hydrochloric acid, the volume of the porewater, and the activity coefficient for H^+ -ions in solution, respectively (Schulz, 2006). The density of bottom water was calculated using the Gibbs Seawater MATLAB

Toolbox (IOC et al., 2010). Density values were used to convert total alkalinity unit from $\text{mmol}(\text{eq})/\text{l}$ to $\mu\text{mol}/\text{kg}$. CO_3^{2-} in situ in pore water were calculated using measurements of total alkalinity and pH measurements in pore water, pressure at bottom water depth, bottom water salinity and temperature (Antonov et al., 2010; Locarnini et al., 2010). Bottom water ΔCO_3^{2-} was calculated using Global Ocean Data Analysis Project (GLODAP) data set (Key et al., 2004) and the CO_2 -CALC software (Robbins et al., 2010). ΔCO_3^{2-} in pore water (ΔCO_3^{2-} pore water) is presented here as the difference between CO_3^{2-} in situ in pore water and CO_3^{2-} saturation value of the overlying bottom water.

3. Results

Mg/Ca in *Globobulimina* spp. from water depths between 68 m and 103 m show values between 9.1 $\mu\text{mol}/\text{mol}$ and 8.2 $\mu\text{mol}/\text{mol}$ (Fig. 4). The deepest sample (4307 m water depth) shows a Mg/Ca value of 2.5 $\mu\text{mol}/\text{mol}$. Mn/Ca and Al/Ca display values of 6–179 $\mu\text{mol}/\text{mol}$ and of 7–278 $\mu\text{mol}/\text{mol}$, respectively. Mg/Ca and Mn/Ca show a negative correlation ($r = -0.5$); and Mg/Ca and Al/Ca show no significant correlation ($r^2 = 0.03$). With values varying between 53 $\mu\text{mol}/\text{mol}$ and 662 $\mu\text{mol}/\text{mol}$, Fe/Ca show elevated values, but are not significantly correlated with Mg/Ca ($r^2 = 0.01$).

We generated ΔCO_3^{2-} pore water data from 64 multi-corer sediment profiles (1–10 cm) that were collected from Atlantic water depth varying between 605 m and 5817 m. While overlap exists, samples from deepest and shallowest water show negative and positive ΔCO_3^{2-} pore water values of up to $-83 \mu\text{mol}/\text{kg}$ and 21 $\mu\text{mol}/\text{kg}$, respectively. The ΔCO_3^{2-} pore water trends within the sediment depth profiles also vary significantly, with some profile showing a continuous ΔCO_3^{2-} pore water down core decline and others revealing minimum values centered around a sediment depth of 3 cm. ΔCO_3^{2-} pore water is, on average, lower by 39.84 $\mu\text{mol}/\text{kg}$ and highly correlated to the ΔCO_3^{2-} bottom water (see discussion in Chapter 4.3)

4. Discussion

4.1. Mg/Ca–temperature calibration

Our regression analysis shows that the relationship between Mg/Ca in *Globobulimina* spp. and BWT is best explained by a linear correlation with a best fit of $\text{Mg/Ca} [\text{mmol}/\text{mol}] = (0.36 \pm 0.02) * \text{BWT} [^{\circ}\text{C}] + 2.22 \pm 0.19$, $n = 39$, $r^2 = 0.92$, and p -value = $11 * 10^{-20}$ (Fig. 4A). With a relatively weaker correlation coefficient

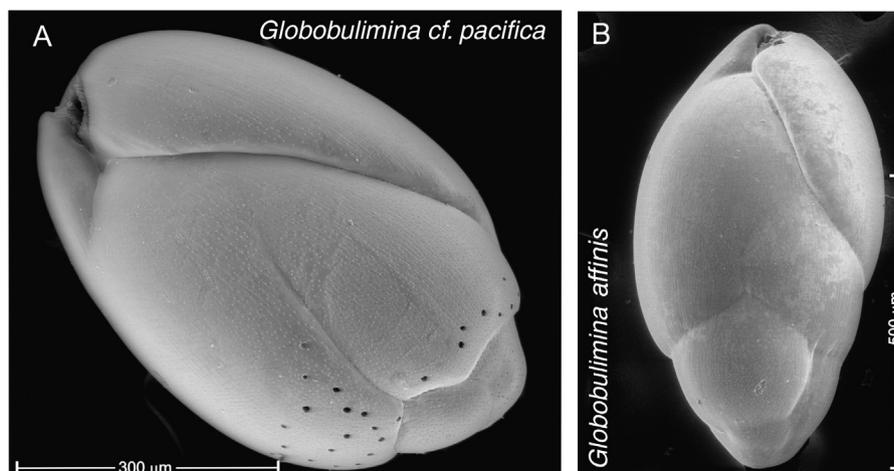


Fig. 3. Scanning Electron Microscope (SEM) image of (A) *Globobulimina cf. pacifica* and (B) *Globobulimina affinis* selected from Gulf of Guinea core top samples.

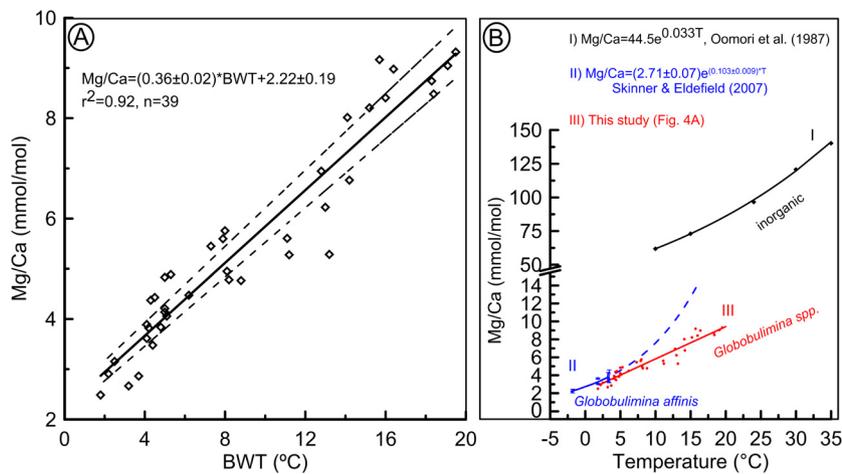


Fig. 4. A) Mg/Ca analyzed in tests of *Globobulimina* spp. from Gulf of Guinea core top samples plotted versus bottom water temperature (BWT). Bold and dotted lines indicate the best fit regression line ($\text{Mg/Ca [mmol/mol]} = (0.36 \pm 0.02) * \text{BWT [}^\circ\text{C]} + (2.22 \pm 0.19)$, $r^2 = 0.92$, $n = 39$ and p -value of $11 * 10^{-20}$) and its uncertainty (1σ), respectively. B: I) relationship of Mg/Ca and calcification temperature of inorganically precipitated calcites (Oomori et al., 1987). II) Relationship of Mg/Ca in *Globobulimina affinis* from Last Glacial Maximum, Last Interglacial and modern-to-late Holocene samples and corresponding estimates of bottom water temperature (Skinner and Elderfield, 2007) (for more details see caption of Fig. 1 in Skinner and Elderfield, 2007). The dotted line indicates an extension of calibration curve outside the data used to establish the calibration equation. III) This study, as described in Fig. 4A.

($r^2 = 0.88$) Mg/Ca in *Globobulimina* spp. is also exponentially correlated to BWT: $\text{Mg/Ca [mmol/mol]} = (2.85 \pm 0.06) * \exp((0.067 \pm 0.004) * \text{BWT [}^\circ\text{C]})$. For Mg/Ca values between 2 and 4 mmol/mol, our linear calibration equation yields, on average, temperature estimates that are higher by 1.3 °C relative to that of the Skinner and Elderfield (2007) calibration (Fig. 4B). The deviation of temperature estimates from our linear calibration equation becomes extremely large when the calibration by Skinner and Elderfield (2007) is applied for Mg/Ca values larger than 5 mmol/mol (Fig. 4B).

4.2. Exploring salinity influence on Mg/Ca

We note that over a significant fraction of the investigated data set BWT, salinity, and ΔCO_3^{2-} are positively correlated (Figs. 2D–E). Changes in salinity are known to affect Mg incorporation into foraminiferal calcite. There is an emerging consensus that salinity change of one psu causes a 2–8% Mg change in planktonic foraminiferal calcite (Hönisch et al., 2013; Kisakürek et al., 2008; Lea et al., 2000; Nürnberg et al., 1996). In contrast, results of benthic foraminifer culturing experiments are inconsistent. While one culturing study focusing on *Ammonia tepida* suggests a 2.2–2.5% Mg increase per salinity unit rise (Dissard et al., 2010), another study on *Planoglabratella opercularis* and *Quinqueloculina yabei* found no significant salinity influence (Toyofuku et al., 2000).

In our attempt to evaluate the Mg/Ca–salinity relationship, we use bottom water salinity because there is no direct measurements of pore water salinity available from the sediment depth of our sample collections. Chlorinity-based salinity estimates of pore water indicate that salinity of pore water and that of the overlying bottom water (Insua et al., 2014) are, with an uncertainty of ± 0.1 psu, identical. Given that the focus of this study is on the upper 2 cm of undisturbed core top sediment, we assume that pore water salinity is similar to that of the overlying Gulf of Guinea seawater. Isolating the salinity effect on Mg uptake of *Globobulimina* spp. from those of temperature and ΔCO_3^{2-} is complicated by the fact that in a significant part of the data set, bottom water salinity is strongly correlated to BWT and ΔCO_3^{2-} (Figs. 2D–E). It should be noted, however, that while the magnitude of BWT variation within the investigated sites is 17.3 °C, the maximum change in salinity is only 1.3 psu. In order for this salinity change to result in a Mg/Ca change of 6.6 mmol/mol, the Mg uptake in *Globobulimina* spp. calcite must be extremely sensitive to salinity. However, limiting the evaluation to an interval where BWT (varying between

5.1 °C and 4.1 °C) and salinity do not positively co-vary (blue rectangle in Fig. 2D), the data demonstrate that Mg/Ca and salinity do not correlate significantly ($r^2 = 0.05$, p -value: 0.51, $n = 11$). We note also that this depth interval is marked by an increase of ΔCO_3^{2-} pore water from -28 to -8 $\mu\text{mol/kg}$ (see next chapter). While both the increase of salinity and ΔCO_3^{2-} by 0.4 psu and 20 $\mu\text{mol/kg}$, respectively, should lead to an increase of Mg/Ca, the value of Mg/Ca drops from 4.8 to 3.5 mmol/mol. This result shows that in an interval that is marked by a relatively rapid increase in salinity and ΔCO_3^{2-} , a gradual decline of BWT exerts the dominant control on Mg/Ca. While the above analysis does not support an extremely strong salinity sensitivity of Mg/Ca in *Globobulimina* spp., we emphasize that the low number of samples ($n = 11$) and narrow salinity range (34.51–33.9 psu) limits the robustness of the conclusion regarding a possible subtle salinity effect.

4.3. ΔCO_3^{2-} in pore water and its effect on infaunal foraminiferal Mg/Ca

Several studies indicate that changes in ΔCO_3^{2-} have a significant effect on epi-benthic foraminiferal Mg/Ca (Bryan and Marchitto, 2008; Elderfield et al., 2010, 2006; Marchitto et al., 2007; Rosenthal et al., 2006). In contrast, it has been hypothesized that the effect of bottom water ΔCO_3^{2-} on Mg/Ca in the infaunal benthic foraminifers *Uvigerina* spp. is relatively weak (Elderfield et al., 2010, 2006). This hypothesis is based on the assumption that concentration of ΔCO_3^{2-} pore water tends toward zero in the calcification depth of *Uvigerina* spp. (Elderfield et al., 2010; Martin and Sayles, 1996). Here, we first investigate the relationship between ΔCO_3^{2-} pore water and the ΔCO_3^{2-} of the overlying bottom water in 64 Atlantic Ocean multi-corer samples (Fig. 5A). The collection sites of the 64 multi-corer sediments encompass water depths between 605 m and 5817 m, as well as sites with variable accumulation rates, primary productivity and organic matter remineralization rates, and sediments bathed by all water masses of the Atlantic Ocean (thermocline, AAIW, North Atlantic Deep Water, and Antarctic Deep Water) (Fig. 5 A). Therefore, we consider the pore water data to be representative for the Atlantic Basin. Here the discussion focuses on pore water data from sediment depths between 1 cm and 10 cm below the surface sediment, covering the maximum habitat depth range of *Globobulimina* spp. and most of the infaunal benthic foraminifers (Jorissen et al., 1995; McCorkle et al., 1997; Schmiedl et al., 2000, 2004). The 64 pro-

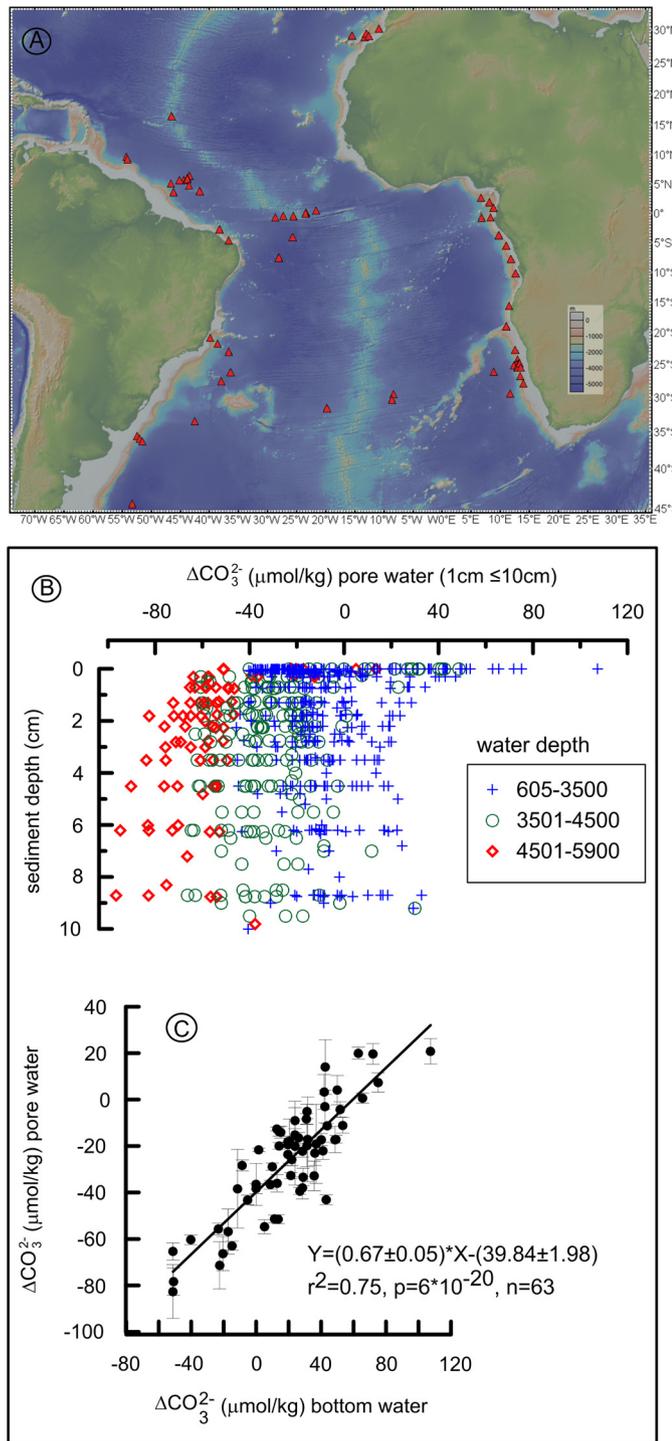


Fig. 5. A) Location of multi-corer sites used in this study. B) ΔCO_3^{2-} pore water concentrations calculated from total alkalinity and pH measurements in the pore water of multi-corer sediments collected across the Atlantic Ocean (latitude: 30.193N–44.475S and longitude: 14.004E–54.258W). Published data of total alkalinity and pH measurements were obtained from <http://www.pangaea.de> (Hensen, 1996; Hensen et al., 1997, 1998, 2000). C) ΔCO_3^{2-} pore water concentration (as shown in Fig. 5A) plotted versus ΔCO_3^{2-} concentration of the overlying bottom water. Bold line indicates the best fit regression line (ΔCO_3^{2-} pore water [$\mu\text{mol}/\text{kg}$] = $(0.67 \pm 0.05) * \Delta\text{CO}_3^{2-}$ bottom water [$\mu\text{mol}/\text{kg}$] - (39.84 ± 1.98) , $r^2 = 0.75$, $4 * 10^{-18}$, $n = 62$). Vertical bars indicate the deviation (1σ) from average ΔCO_3^{2-} values (dots) of 5–10 measurements along a multi-corer sediment depth (see Fig. 5A).

files reveal that ΔCO_3^{2-} pore water is significantly lower relative to the ΔCO_3^{2-} of the overlying bottom water (p -value: $6 * 10^{-20}$, Figs. 5B and 5C). The ΔCO_3^{2-} profiles along the sediment depth show a rapid decline in the first the upper 3–4 cm (Fig. 5B). While some profiles show a continuous drop of ΔCO_3^{2-} from shallower to deeper sediment depth, others show that the sediment interval with the lowest ΔCO_3^{2-} values is confined to the upper 2–4 cm (Fig. 5B). One factor that has a strong control on the ΔCO_3^{2-} variability is the depth distribution of the main water masses of the Atlantic (AAIW, NADW, and AADW). These depth intervals between 4500 m and 5900 m and 605 m and 3500 m show the most undersaturated and most oversaturated water with respect to the carbonate ion concentration, respectively (Fig. 5B). Within and between the broadly-defined depth intervals (Fig. 5B), there is large variation of ΔCO_3^{2-} pore water most likely indicating a spatial variation of water depth occupied by the major water masses of the Atlantic, changes in primary productivity, and remineralization of organic matter within the upper 10 cm sediment depth. Fig. 5C highlights that the average ΔCO_3^{2-} pore water ($\geq 1 \leq 10$ cm sediment depth) is significantly lower than, but strongly correlated to the ΔCO_3^{2-} values of the overlying bottom water (ΔCO_3^{2-} pore water = $(0.67 \pm 0.05) * \Delta\text{CO}_3^{2-}$ bottom water - (39.84 ± 1.98) , $r^2 = 0.75$, $p: 4 * 10^{-18}$, $n = 64$). The implication of this observation is that infaunal foraminifers live in pore water that is, on average, lower by $46.5 \pm 10.6 \mu\text{mol}/\text{kg}$ relative to the ΔCO_3^{2-} of the overlying bottom water. Furthermore, ΔCO_3^{2-} pore water varies spatially, reflecting the ΔCO_3^{2-} variability of the overlying water and the rate of organic matter remineralization in the surface sediments. The spatial co-variability of ΔCO_3^{2-} bottom water and ΔCO_3^{2-} pore water also implies a temporal variability. Paleocyanographic reconstruction over the last 25,000 years indicates that water masses of the Atlantic, Indian, and Pacific oceans experienced large-scale changes in ΔCO_3^{2-} bottom water (Yu et al., 2010). As shown by the present-day close relationship between ΔCO_3^{2-} bottom water and ΔCO_3^{2-} pore water (Fig. 5C), it is expected that glacial–interglacial changes in ΔCO_3^{2-} bottom water had a direct impact on ΔCO_3^{2-} pore water. According to our equation (Fig. 5C), a glacial–interglacial ΔCO_3^{2-} bottom water change of $40 \pm 5 \mu\text{mol}/\text{kg}$ in the abyssal of North Atlantic (water depth: 4045 m) (Raitzsch et al., 2011; Yu et al., 2010) corresponds to a ΔCO_3^{2-} pore water change of $26.8 \pm 5.4 \mu\text{mol}/\text{kg}$. The sensitivity of Mg/Ca in *Uvigerina* spp. to ΔCO_3^{2-} and temperature changes is estimated $0.002 \pm 0.001 \text{ mmol}/\text{mol}$ per $\mu\text{mol}/\text{kg}$ and $0.078 \pm 0.008 \text{ mmol}/\text{mol}/^\circ\text{C}$, respectively (Elderfield et al., 2010). Consequently, a glacial–interglacial ΔCO_3^{2-} pore water change of $26.8 \mu\text{mol}/\text{kg}$ in the North Atlantic contributes to a Mg/Ca change between 0.08 and 0.03 mmol/mol and causes a bias of 0.9-to-0.4 $^\circ\text{C}$ in the BWT estimates. The general implication of this finding is that glacial–interglacial changes in ΔCO_3^{2-} bottom water and ΔCO_3^{2-} pore water have a substantial impact on the Mg/Ca of infaunal foraminifers, Mg/Ca-derived BWT estimate and BWT- $\delta^{18}\text{O}$ based sea level and salinity reconstruction. Paired analysis of Mg/Ca and quantitative proxies (B/Ca, B isotope) for past changes in carbonate ion concentration can provide a potentially useful tool to correct the effect of ΔCO_3^{2-} changes on Mg/Ca.

A strong correlation between BWT and ΔCO_3^{2-} in two sections of the data set (Fig. 2E) complicates the evaluation of a possible ΔCO_3^{2-} effect on *Globulimina* spp. Mg/Ca. We pursue a two-step strategy to assess a potential ΔCO_3^{2-} effect on Mg/Ca in *Globulimina* spp. First, we isolate Mg/Ca changes ($\text{Mg}/\text{Ca}_{\text{temperature}}$) related to BWT changes by focusing on a water depth interval where BWT drops from 8.8 $^\circ\text{C}$ to 2.5 $^\circ\text{C}$ (blue rectangle in Fig. 2E)

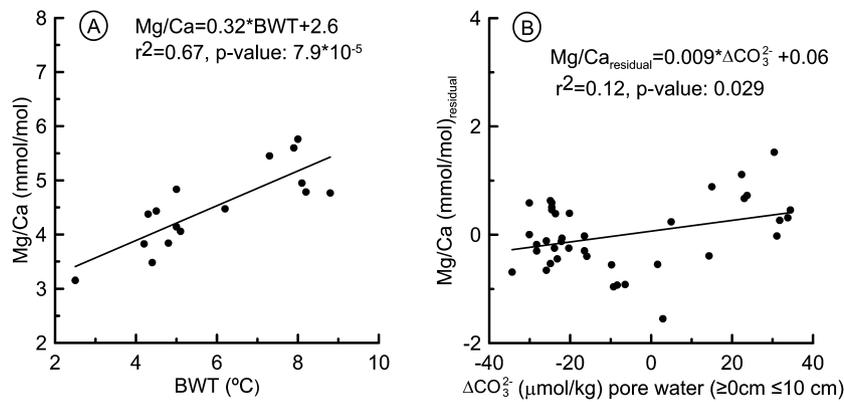


Fig. 6. A) Mg/Ca–BWT correlation ($Mg/Ca_{\text{temperature}} = 0.32 \pm 0.06 \cdot BWT + 2.6 \pm 0.37$, $r^2 = 0.67$, $n = 16$, $p\text{-value} = 0.000079$) in a depth interval where changes in salinity (34.68 ± 0.14 psu) and ΔCO_3^{2-} in pore water (-28.2 ± 2.3 mmol/kg) are relative small. B) Mg/Ca_{residual} versus ΔCO_3^{2-} pore water ($Mg/Ca_{\text{residual}} = (0.009 \pm 0.0044) \cdot \Delta CO_3^{2-}$ pore water + 0.06 ± 0.1 , $r^2 = 0.12$, $n = 16$, $p\text{-value} = 0.029$).

but salinity and pore water ΔCO_3^{2-} changes are small, showing variation of 0.4 psu (34.9–34.5 psu) and 5.6 $\mu\text{mol/kg}$ (-25.8 to -20.2 $\mu\text{mol/kg}$), respectively. We obtain a correlation equation of $Mg/Ca_{\text{temperature}} = (0.32 \pm 0.06) \cdot BWT + 2.6 \pm 0.37$ ($r^2 = 0.67$, $n = 16$, $p\text{-value} = 0.000079$) (Fig. 6A). We then subtract $Mg/Ca_{\text{temperature}}$ from the entire data set of measured Mg/Ca (Mg/Ca_{measured}) and obtain the Mg/Ca residual ($Mg/Ca_{\text{residual}} = Mg/Ca_{\text{measured}} - Mg/Ca_{\text{temperature}}$). If we interpret the Mg/Ca_{residual} to reflect Mg/Ca changes related to the variation of ΔCO_3^{2-} pore water ($Mg/Ca_{\text{residual}} = Mg/Ca - \Delta CO_3^{2-}$), we obtain the following relationship: $Mg/Ca - \Delta CO_3^{2-} = (0.009 \pm 0.0044) \cdot \Delta CO_3^{2-}$ pore water + 0.06 , $r^2 = 0.12$, $p\text{-value} = 0.029$ (Fig. 6B). The result suggests a change of 0.009 ± 0.0044 Mg/Ca per unit ΔCO_3^{2-} ($\mu\text{mol/kg}$). A ΔCO_3^{2-} glacial–interglacial change of 22 $\mu\text{mol/kg}$, as suggested for the equatorial Atlantic (water depth 2945 m) (Raitzsch et al., 2011), would give rise, on average, to Mg/Ca change of 0.19 mmol/mol. According to our calibration this corresponds to BWT changes of 0.55 °C, which is within the error estimates of the Mg/Ca–BWT calibration. The r^2 - and p -values, however, show that the correlation is weak and significant only at a significance level of $\alpha = 0.05$. We caution also that the sensitivity value of 0.009 ± 0.0044 mmol/mol per ΔCO_3^{2-} $\mu\text{mol/kg}$ may overestimate the effect of ΔCO_3^{2-} on Mg/Ca because a possible salinity effect is not taken into account and the $Mg/Ca_{\text{temperature}}$ calculation is based on a relatively limited number of samples ($n = 16$) (Fig. 6A). With an average difference of 0.04 mmol/mol/°C in the temperature sensitivity estimates between the analyzed Mg/Ca (0.36 ± 0.02 mmol/mol/°C) and ΔCO_3^{2-} -corrected Mg/Ca (0.32 ± 0.06 mmol/mol/°C) that are within error comparable, Mg/Ca in *Globobulimina* spp. provides a sensitive paleothermometry for deep ocean temperature reconstructions.

4.4. Application of the new Mg/Ca–BWT calibration to down core date sets

We apply the calibration developed in this study to the *Globobulimina affinis* Mg/Ca time-series from the Iberian Margins (Skinner et al., 2003) and compare the BWT estimates with those that were obtained using Mg/Ca-calibrations for *Globobulimina affinis* (Skinner and Elderfield, 2007; Skinner et al., 2003) (Fig. 7). A potential caveat in this comparison is that our calibration is based on *Globobulimina affinis* and *Globobulimina cf. pacifica*, whereas the calibration by Skinner et al. (2003) uses only *Globobulimina affinis*. Another caveat is that calibration temperature studies by Skinner et al. (2003) and Skinner and Elderfield (2007) are based largely on assumptions of LGM and Last Inter-

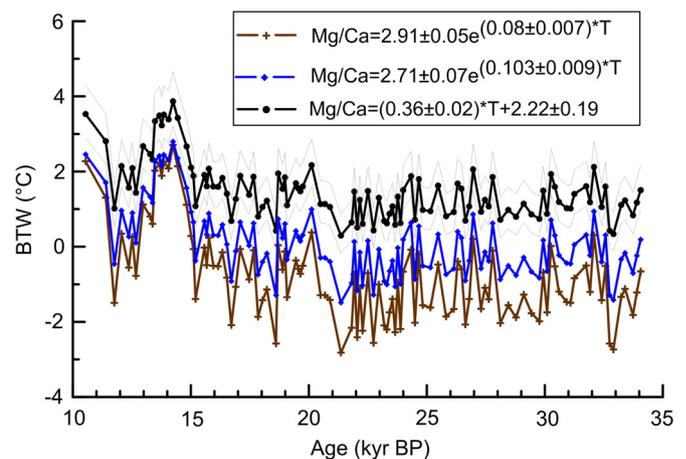


Fig. 7. BWT estimates using *Globobulimina affinis* Mg/Ca time-series analyzed in samples from a core sediment that was retrieved from the Iberian Margin (Skinner et al., 2003). Brown line: BWT estimates as published by Skinner et al. (2003). Blue and black lines indicate BWT estimates calculated using calibration equations developed by Skinner and Elderfield (2007) and in this study, respectively. Thin gray lines indicate uncertainty (1sigma) of the BWT estimates (black line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

glacial bottom water temperature. Keeping these caveats in mind, the comparison reveals that the BWT time-series obtained using our linear calibration equation is higher by 2.2 ± 0.4 °C relative to the BWT time-series discussed in Skinner et al. (2003) (Fig. 7). Consequently, applying our calibration the Last Glacial Maximum (LGM: 19–23 kyr BP) BWT estimate is 1.2 ± 0.5 °C and early Holocene–LGM BWT difference is 2 °C compared to Skinner et al. (2003) estimate of -1.2 °C and 4.2 °C, respectively. We note, however, that applying the calibration equation by Skinner and Elderfield (2007) to the *Globobulimina affinis* Mg/Ca time-series (Skinner et al., 2003), the temperature offset between the linear and exponential calibration equation is reduced to 1.4 ± 0.2 °C (Fig. 7). Taken together, the application of our calibration leads to a significantly different estimate of LGM bottom water cooling and the magnitude of glacial–interglacial thermal changes. With a change of 0.36 ± 0.02 mmol/mol/°C (Fig. 4), the temperature sensitivity of Mg/Ca in *Globobulimina* spp. is 2.8–3 and 4.3–5.5 times higher than those of *Cibicides* spp. (0.12–0.13 mmol/mol/°C) and *Uvigerina* spp. (0.065–0.085 mmol/mol/°C) (Bryan and Marchitto, 2008; Curry and Marchitto, 2008; Elderfield et al., 2010, 2006; Marchitto et al., 2007; Rosenthal et al., 2006). To demonstrate the effect of varying temperature sensitivities of benthic

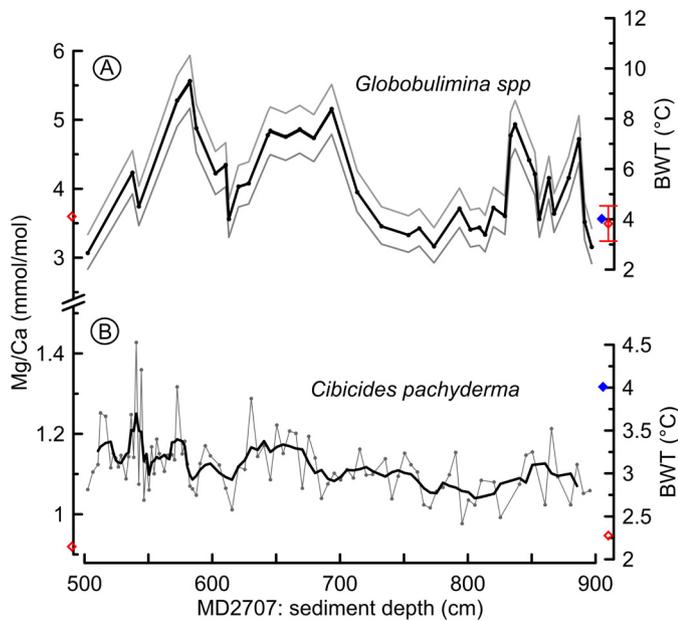


Fig. 8. Left y-axis shows Mg/Ca analyzed in (A) *Globobulimina* spp. and (B) *Cibicides pachyderma* from MD2707 down core samples. A) Right y-axis shows Mg/Ca-based BWT estimates (bold line) and uncertainty (grey line) based on the Mg/Ca-temperature calibration we have developed in this study. B) Right y-axis shows BWT estimates based on the Mg/Ca analysis in *Cibicides pachyderma* and Mg/Ca-temperature calibration developed by Marchitto and deMenocal ($\text{Mg/Ca} = 0.25 * \text{BWT} + 0.35$) (Marchitto and deMenocal, 2003); note the Mg/Ca-temperature calibration (Marchitto and deMenocal, 2003) does not provide uncertainty estimates. Open red diamonds on the left and right y-axes indicate Mg/Ca values in *Globobulimina* spp. and *Cibicides pachyderma* in MD2707 core top sample and the corresponding Mg/Ca-based BWT estimates, respectively. Filled blue diamonds indicate instrumentally determined modern BWT (4°C) over MD2707 core site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

foraminiferal Mg/Ca on temperature reconstruction, we analyzed Mg/Ca in the tests of *Globobulimina* spp. and *Cibicides pachyderma* in Gulf of Guinea sediment core MD2707 (Fig. 8) (Weldeab et al., 2007). Estimates of ΔCO_3^{2-} effect on Mg/Ca in both *Globobulimina* spp. (0.009 mmol/mol/ $\mu\text{mol/kg}$) (this study) and *Cibicides* spp. (0.0085 mmol/mol/ $\mu\text{mol/kg}$) (Elderfield et al., 2006) are similar. If we assume that salinity changes affect the Mg/Ca in both genera comparably, the major difference between the down core records may be related mainly to a single factor. Temperature sensitivity of Mg/Ca in *Globobulimina* spp. is 2.8–3 times higher relative to Mg/Ca in *Cibicides* spp. (0.12–0.13 mmol/mol/°C) (Bryan and Marchitto, 2008; Curry and Marchitto, 2008; Elderfield et al., 2010, 2006; Marchitto et al., 2007; Rosenthal et al., 2006). Moreover, even though the Mg/Ca sensitivity to changes in ΔCO_3^{2-} in both genera is comparable, due to the different Mg/Ca temperature sensitivity, a glacial–interglacial change of ΔCO_3^{2-} by 22 $\mu\text{mol/kg}$ in the equatorial Atlantic (Raitzsch et al., 2011) would bias a BWT estimate by 1.5°C and 0.55°C in *Cibicides* spp. and *Globobulimina* spp., respectively. The marked changes in the down core Mg/Ca record of *Globobulimina* spp. are virtually indistinguishable in the Mg/Ca record of *Cibicides pachyderma* due to the relatively small Mg/Ca changes (± 0.09 mmol/mol from the average of 1.13 mmol/mol, $n = 107$). The conversion of *Globobulimina* spp. and *Cibicides pachyderma* Mg/Ca into BWT estimates indicates temperature changes up to 5°C and 1.5°C, respectively. We note that the paleoceanographic significance and the time frame of the Mg/Ca record will be discussed in the context of a multiproxy record in a separate manuscript. Moreover, the BWT estimate (2.2°C) based on Mg/Ca (0.92 mmol/mol) in *Cibicides pachyderma* from Gulf of Guinea core top samples (MD2707: 390 years BP) (Weldeab et al., 2007) underestimates the modern BWT (4°C) by 1.8°C (Fig. 7).

We used a Mg/Ca–BWT calibration (Marchitto and deMenocal, 2003) that yields the closest estimate to the instrumental modern BWT. All other Mg/Ca–temperature calibrations, as summarized in (Elderfield et al., 2006), yield much lower estimates. The large deviation of existing Mg/Ca–temperature calibrations in estimating the BWT of the modern Gulf of Guinea and the large difference between Mg/Ca in *Globobulimina* spp. and *Cibicides pachyderma* in the down core BWT estimates highlights the uncertainty associated with the low temperature sensitivity of *Cibicides* spp. In conclusion, the core top calibration and the down core analysis demonstrate that the relatively high temperature sensitivity of Mg/Ca in *Globobulimina* spp. provides a robust tool to reconstruct thermal changes in the deep ocean.

5. Summary and conclusion

In this study we present the first core top-based Mg/Ca–temperature calibration for *Globobulimina* spp. Our calibration reveals that the temperature sensitivity of Mg/Ca in *Globobulimina* spp. (0.36 mmol/mol/°C) is 2.8 and 4.3–5.5 times higher than that of *Cibicides* spp. and *Uvigerina* spp., respectively. Furthermore, for the first time we establish a quantitative and robust estimate of ΔCO_3^{2-} bottom water and ΔCO_3^{2-} pore water relationship. We show that the ΔCO_3^{2-} pore water concentration varies spatially, is linearly correlated to and is lower by 46 ± 10.6 $\mu\text{mol/kg}$ than the ΔCO_3^{2-} of the overlying bottom water. Because of the close ΔCO_3^{2-} pore water and ΔCO_3^{2-} bottom water co-variation and the demonstrated sensitivity of infaunal foraminiferal Mg/Ca to changes in ΔCO_3^{2-} pore water, it is most likely that past glacial–interglacial changes in ΔCO_3^{2-} bottom water have a significant effect on Mg/Ca of infaunal foraminifera, Mg/Ca-based BWT and Mg/Ca– $\delta^{18}\text{O}$ -based salinity and sea level estimates. The impact of changes in ΔCO_3^{2-} pore water on Mg/Ca is particularly strong for infaunal benthic foraminifera that have low Mg concentration and low temperature sensitivity. Removing the Mg/Ca component related to ΔCO_3^{2-} changes, the temperature sensitivity of Mg/Ca in *Globobulimina* spp. is estimated at 0.32 mmol/mol/°C which is within the error of the sensitivity estimate 0.36 mmol/mol/°C derived from the ΔCO_3^{2-} -uncorrected Mg/Ca–BWT calibration equation. Analysis of Mg/Ca in *Globobulimina* spp. and *Cibicides pachyderma* in down core samples highlights that the relatively high temperature sensitivity of Mg/Ca in *Globobulimina* spp. provides a more robust tool to unravel and constrain the thermal history of the deep ocean.

Acknowledgements

We thank Wolfgang Kuhn for providing access to the core top samples, Georges Paradis for ICP-MS operation, Gareth Seward for SEM images, Dorothy Pak and William Gray for discussion, Gerhard Schmedl for help with the identification of *Globobulimina affinis* and cf. *pacifica* species. We also thank Matthias Zabel (MARUM – Center for Marine Environmental Sciences, University of Bremen) for making unpublished pore-water data available. We thank the three anonymous reviewers and the editor for their constructive comments on an earlier version of this paper. This study was supported by NSF grant OCE 1260696 awarded to Syee Weldeab.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.epsl.2016.01.009>. These data include Google maps of the most important areas described in this article.

References

- Altenbach, A.V., Lutze, G.F., Schiebel, R., Schönfeld, J., 2003. Impact of interrelated and interdependent ecological controls on benthic foraminifera: an example from the Gulf of Guinea. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 197 (3–4), 213–238.
- Antonov, J.I., Seidov, D., Boyer, T.P., Locarnini, R.A., Mishonov, A.V., Garcia, H.E., Baranova, O.K., Zweng, M.M., Johnson, D.R., 2010. World Ocean Atlas 2009, Volume 2: Salinity. In: Levitus, S. (Ed.), NOAA Atlas NESDIS 69. U.S. Government Printing Office, Washington, D.C., 184 pp.
- Bryan, S.P., Marchitto, T.M., 2008. Mg/Ca-temperature proxy in benthic foraminifera: new calibrations from the Florida Straits and a hypothesis regarding Mg/Li. *Paleoceanography* 23 (2), PA2220. <http://dx.doi.org/10.1029/2007pa001553>.
- Curry, W.B., Marchitto, T.M., 2008. A secondary ionization mass spectrometry calibration of *Cibicides pachyderma* Mg/Ca with temperature. *Geochem. Geophys. Geosyst.* 9 (4), Q04009.
- Dissard, D., Nehrke, G., Reichert, G.J., Bijma, J., 2010. The impact of salinity on the Mg/Ca and Sr/Ca ratio in the benthic foraminifera *Ammonia tepida*: results from culture experiments. *Geochim. Cosmochim. Acta* 74 (3), 928–940.
- Elderfield, H., Greaves, M., Barker, S., Hall, I.R., Tripati, A., Ferretti, P., Crowhurst, S., Booth, L., Daunt, C., 2010. A record of bottom water temperature and seawater $\delta^{18}\text{O}$ for the Southern Ocean over the past 440 kyr based on Mg/Ca of benthic foraminiferal *Uvigerina* spp. *Quat. Sci. Rev.* 29 (1–2), 160–169.
- Elderfield, H., Yu, J., Anand, P., Kiefer, T., Nylund, B., 2006. Calibrations for benthic foraminiferal Mg/Ca paleothermometry and the carbonate ion hypothesis. *Earth Planet. Sci. Lett.* 250 (3–4), 633–649.
- Hensen, C., 1996. Frühdiagenetische Prozesse und Quantifizierung benthischer Stoff-Flüsse in Oberflächensedimenten des Südatlantiks. 88, 132 pp, urn:nbn:de:gbv:46-ep000102178* University of Bremen, Bremen.
- Hensen, C., Landenberger, H., Zabel, M., Gundersen, J.K., Glud, R.N., Schulz, H.D., 1997. Simulation of early diagenetic processes in continental slope sediments off southwest Africa: the computer model CoTAM tested. *Mar. Geol.* 144 (1–3), 191–210.
- Hensen, C., Landenberger, H., Zabel, M., Schulz, H.D., 1998. Quantification of diffusive benthic fluxes of nitrate, phosphate, and silicate in the southern Atlantic Ocean. *Glob. Biogeochem. Cycles* 12 (1), 193–210.
- Hensen, C., Zabel, M., Schulz, H.D., 2000. A comparison of benthic nutrient fluxes from deep-sea sediments off Namibia and Argentina. *Deep-Sea Res., Part 2, Top. Stud. Oceanogr.* 47 (9–11), 2029–2050.
- Hönisch, B., Allen, K.A., Lea, D.W., Spero, H.J., Eggins, S.M., Arbuszewski, J., deMenocal, P., Rosenthal, Y., Russell, A.D., Elderfield, H., 2013. The influence of salinity on Mg/Ca in planktic foraminifera – evidence from cultures, core-top sediments and complementary $\delta^{18}\text{O}$. *Geochim. Cosmochim. Acta* 121, 196–213.
- Insua, T.L., Spivack, A.J., Graham, D., D'Hondy, S., Moran, K., 2014. Reconstruction of Pacific Ocean bottom water salinity during the Last Glacial Maximum. *Geophys. Res. Lett.* 41, 2914–2919.
- IOC, SCOR and IAPSO, 2010. The international thermodynamic equation of seawater 2010: Calculation and use of thermodynamic properties, Intergovernmental Oceanographic Commission, Manuals and Guides. UNESCO (IOC/2010/MG/56Rev.) 196 pp.
- Jorissen, F.J., de Stigter, H.C., Widmark, J.G.V., 1995. A conceptual model explaining benthic foraminiferal microhabitats. *Mar. Micropaleontol.* 26 (1–4), 3–15.
- Key, R.M., Kozyr, A., Sabine, C.L., Lee, K., Wanninkhof, R., Bullister, J.L., Feely, R.A., Millero, F.J., Mordy, C., Peng, T.H., 2004. A global ocean carbon climatology: results from Global Data Analysis Project (GLODAP). *Glob. Biogeochem. Cycles* 18 (4), GB4031. <http://dx.doi.org/10.1029/2004GB002247>.
- Kisakürek, B., Eisenhauer, A., Böhm, F., Garbe-Schönberg, D., Erez, J., 2008. Controls on shell Mg/Ca and Sr/Ca in cultured planktonic foraminifera, *Globigerinoides ruber* (white). *Earth Planet. Sci. Lett.* 273 (3–4), 260–269.
- Lea, D.W., Pak, D.K., Spero, H.J., 2000. Climate impact of Late Quaternary equatorial Pacific sea temperature variations. *Science* 289, 1719–1724.
- Lear, C.H., Elderfield, H., Wilson, P.A., 2000. Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science* 287 (5451), 269–272.
- Lear, C.H., Mawbey, E.M., Rosenthal, Y., 2010. Cenozoic benthic foraminiferal Mg/Ca and Li/Ca records: toward unlocking temperatures and saturation states. *Paleoceanography* 25, PA4215. <http://dx.doi.org/10.1029/2009pa001880>.
- Lear, C.H., Rosenthal, Y., Slowey, N., 2002. Benthic foraminiferal Mg/Ca-paleothermometry: a revised core-top calibration. *Geochim. Cosmochim. Acta* 66 (19), 3375–3387.
- Locarnini, R.A., Mishonov, A.V., Antonov, J.I., Boyer, T.P., Garcia, H.E., 2010. World Ocean Atlas 2005, Volume 1: Temperature. U.S. Government Printing Office, Washington, D.C., 182 pp.
- Lutze, G.F., Aguwe, C.O.C., Altenbach, A., Hemken-Mellies, U., Kothe, C., Muehlan, N., Pflaumann, U., Samtleben, C., Sarnthein, M., Segl, M., Soltwedel, T., Stute, U., Tiedemann, R., Weinholz, P., 1988. Report of R. V. "Meteor" cruise M 6-5, Dakar - Libreville 15.1-16.2.1988. Geol. Palaeont. Institute, University of Kiel, Kiel, Germany.
- Marchitto, T.M., Bryan, S.P., Curry, W.B., McCorkle, D.C., 2007. Mg/Ca temperature calibration for the benthic foraminifer *Cibicides pachyderma*. *Paleoceanography* 22 (1), PA1203. <http://dx.doi.org/10.1029/2006pa001287>.
- Marchitto, T.M., deMenocal, P.B., 2003. Late Holocene variability of upper North Atlantic Deep Water temperature and salinity. *Geochem. Geophys. Geosyst.* 4 (12), 1100. <http://dx.doi.org/10.1029/2003GC000598>.
- Martin, P.A., Lea, D.W., 2002. A simple evaluation of cleaning procedures on fossil benthic foraminiferal Mg/Ca. *Geochem. Geophys. Geosyst.* 3 (10), 1–8.
- Martin, P.A., Lea, D.W., Rosenthal, Y., Shackleton, N.J., Sarnthein, M., Papenfuss, T., 2002. Quaternary deep sea temperature histories derived from benthic foraminiferal Mg/Ca. *Earth Planet. Sci. Lett.* 198, 193–209.
- Martin, W.R., Sayles, F.L., 1996. CaCO_3 dissolution in sediments of the Ceara Rise, western equatorial Atlantic. *Geochim. Cosmochim. Acta* 60, 243–263.
- McCorkle, D., Corliss, B.H., Farnham, C.A., 1997. Vertical distributions and stable isotopic compositions of live (stained) benthic foraminifera from the North Carolina and California continental margins. *Deep-Sea Res.* 44, 983–1024.
- Nürnberg, D., Bijma, J., Hemleben, C., 1996. Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. *Geochim. Cosmochim. Acta* 60 (5), 803–814.
- Oomori, T., Kaneshima, H., Maezato, Y., 1987. Distribution coefficient of Mg^{2+} ions between calcite and solution at 10–50 °C. *Mar. Chem.* 20, 327–336.
- Raitzsch, M., Hathorne, E.C., Kuhnert, H., Groeneveld, J., Bickert, T., 2011. Modern and late Pleistocene B/Ca ratios of the benthic foraminifer *Planulina wuellerstorfi* determined with laser ablation ICP-MS. *Geology* 39 (11), 1039–1042.
- Robbins, L.L., Hansen, M.E., Kleypas, J.A., Meylan, S.C., 2010. CO₂calc – a user-friendly seawater carbon calculator for Windows, Max OS X. and iOS (iPhone), U.S. Geological Survey Open-File report 2010–1280.
- Rosenthal, Y., Boyle, E.A., Slowey, N., 1997. Temperature control on the incorporation of Mg, Sr, F and Cd into benthic foraminiferal shells from Little Bahama Bank: prospects for thermocline paleoceanography. *Geochim. Cosmochim. Acta* 61 (17), 3633–3643.
- Rosenthal, Y., Lear, C.H., Oppo, D.W., Linsley, B.K., 2006. Temperature and carbonate ion effects on Mg/Ca and Sr/Ca ratios in benthic foraminifera: aragonitic species *Hoeglundina elegans*. *Paleoceanography* 21 (1), PA1007. <http://dx.doi.org/10.1029/2005pa001158>.
- Schmiedl, G., de Boeve, F., Buscail, R., Charrierc, B., Hemleben, C., Medernach, L., Picon, P., 2000. Trophic control of benthic foraminiferal abundance and microhabitat in the bathyal Gulf of Lions, western Mediterranean Sea. *Mar. Micropaleontol.* 40, 167–188.
- Schmiedl, G., Pfeilsticker, M., Hemleben, C., Mackensen, A., 2004. Environmental and biological effects on the stable isotope composition of recent deep-sea benthic foraminifera from the western Mediterranean Sea. *Mar. Micropaleontol.* 51 (1–2), 129–152.
- Schulz, H., 2006. Quantification of early diagenesis: dissolved constituents in pore water and signals in the solid phase. In: Schulz, H., Zabel, M. (Eds.), *Marine Geochemistry*. Springer, Berlin, Heidelberg, pp. 73–124.
- Skinner, L.C., Elderfield, H., 2007. Rapid fluctuations in the deep North Atlantic heat budget during the last glacial period. *Paleoceanography* 22 (1), PA1205. <http://dx.doi.org/10.1029/2006pa001338>.
- Skinner, L.C., Shackleton, N., Elderfield, H., 2003. Millennial-scale variability of deep-water temperature and $\delta^{18}\text{O}_{\text{dw}}$ indicating deep-water source variations in the Northeast Atlantic, 0–34 cal. ka BP. *Geochem. Geophys. Geosyst.* 4. <http://dx.doi.org/10.1029/2003GC000585>.
- Sosdian, S., Rosenthal, Y., 2009. Deep-sea temperature and ice volume changes across the Pliocene–Pleistocene climate transitions. *Science* 325 (5938), 306–310.
- Toyofuku, T., Kitazato, H., Kawahata, H., Tsuchiya, M., Nohara, M., 2000. Evaluation of Mg/Ca thermometry in foraminifera: comparison of experimental results and measurements in nature. *Paleoceanography* 15 (4), 456–464.
- Weldeab, S., Lea, D.W., Schneider, R.R., Andersen, N., 2007. 155,000 years of West African monsoon and ocean thermal evolution. *Science* 316 (5829), 1303–1307.
- Yu, J., Broecker, W., Elderfield, H., Jin, Z., McManus, J., Zhang, F., 2010. Loss of carbon from the deep sea since the last glacial maximum. *Science* 330, 1084–1087.