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

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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 $\text{Mg/Ca}[\text{mmol/mol}] = (0.36 \pm 0.02) * \text{BWT} [^\circ\text{C}] + 2.22 \pm 0.19$ ($r^2 = 0.92$, $p = 11 * 10^{-20}$, 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. ($\geq 1 \text{ cm} \leq 10 \text{ cm}$ 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) ; $r^2=0.75$, $p: 6*10^{-20}$, $n=64$. We found a Mg/Ca sensitivity of $0.009 \pm 0.0044 \text{ mmol/mol per } \mu\text{mol/kg } \Delta\text{CO}_3^{2-}$ pore water and Mg/Ca temperature sensitivity of $0.32 \pm 0.06 \text{ mmol/mol/}^\circ\text{C}$ 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.

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; Lear et al., 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; Elderfield et al., 2006; Lear et al., 2002; Marchitto et al., 2007; Marchitto and deMenocal, 2003; Rosenthal et al., 1997; Rosenthal et al., 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; Schmiedl et al., 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 continental margin genus that been extant since at least the Cretaceous (Jorissen et al., 1995; McCorkle et al., 1997; Schmiedl et al., 2000; Schmiedl et al., 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 $\Delta CO_3^{2-}{}_{\text{bottom water}}$ ($\Delta CO_3^{2-} = CO_3^{2-}{}_{\text{in situ}} - CO_3^{2-}{}_{\text{saturation}}$) is spatially highly variable and has strong effect on epi-benthic foraminifer Mg/Ca (Elderfield et al., 2006), the quantitative relationship between $\Delta CO_3^{2-}{}_{\text{pore water}}$ 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 (Figure 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 (Figures 2 A-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 (Figures 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 $\pm 0.002^\circ\text{C}$ (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 $\pm 0.1^{\circ}\text{C}$ (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 $63\mu\text{m}$ sieve and dried. For this study, Rose Bengal stained and well-preserved tests of *Globobulimina affinis* and *Globobulimina cf pacifica* (Figure 3) were selected from the sample fraction $\geq 250\mu\text{m} \leq 400\mu\text{m}$ 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* (Figure 3) as *Globobulimina spp.*. In a 400 cm long segment of MD2707 core sediment ($02^{\circ}30.11'\text{N}$, $09^{\circ}23.68'\text{E}$, 1295 m water depth), we selected *Globobulimina spp.* (*Globobulimina affinis* and *Globobulimina cf pacifica*, $\geq 250\mu\text{m} \leq 400\mu\text{m}$) and *Cibicides pachyderma* ($\geq 250\mu\text{m} \leq 400\mu\text{m}$) 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 $\pm 0.4\%$ (0.003 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 $\sim 4^\circ\text{C}$. 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 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: $\text{alk} = [(V_{\text{HCl}} \cdot C_{\text{HCl}}) - 10^{-\text{pH}} \cdot (V_0 + V_{\text{HCl}}) / f_{\text{H}^+}] / V_0$ (Schulz, 2006). V_{HCl} and C_{HCl} denote to the volume and molality 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 Oceneanographic MATLAB Toolbox (IOC et al., 2010). Density values were used to convert total alkalinity unit from mmol(eq)/l to $\mu\text{mol/kg}$. 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 CO2-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 mmol/mol and 8.2 mmol/mol (Figure 4). The deepest sample (4307 m water depth) shows a Mg/Ca value of 2.5 $\mu\text{mol/mol}$. Mn/Ca and Al/Ca display values of 6-179 $\mu\text{mol/mol}$ and of 7-278 $\mu\text{mol/mol}$, 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 $\mu\text{mol/mol}$ and 662 $\mu\text{mol/mol}$, 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 ($\geq 1 \leq 10$ 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-} porewater values of up to -83 $\mu\text{mol/kg}$ and 21 $\mu\text{mol/kg}$, respectively. The ΔCO_3^{2-} porewater trends within the sediment depth profiles also vary significantly, with some profile showing a continuous ΔCO_3^{2-} porewater down core decline and others revealing minimum values centered around a sediment depth of 3 cm. ΔCO_3^{2-} porewater is, on average, lower by 39.84 $\mu\text{mol/kg}$ 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 $\text{Mg/Ca}[\text{mmol/mol}] = (0.36 \pm 0.02) * \text{BWT}[^{\circ}\text{C}] + 2.22 \pm 0.19$, $n=39$, $r^2=0.92$, and $p=11 * 10^{-20}$ (Figure 4A). With a relatively weaker correlation coefficient ($r^2=0.88$) Mg/Ca in *Globobulimina* spp is also exponentially correlated to BWT: $\text{Mg/Ca}[\text{mmol/mol}] = (2.85 \pm 0.06) * \exp((0.067 \pm 0.004) * \text{BWT}[^{\circ}\text{C}])$. 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 $^{\circ}\text{C}$ relative to that of the Skinner and Elderfield (2007) calibration (Figure 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 (Figure 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 (Figures 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-} (Figures 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 Figure 2D), the data demonstrate that Mg/Ca and salinity do not correlate significantly ($r^2=0.05$, p-values: 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; Elderfield et al., 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; Elderfield et al., 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 (Figure 5 A). The collection sites of the 64 multi-corer sediments encompass water depths between

226 605 m and 5817 m, as well as sites with variable accumulation rates, primary productivity
 227 and organic matter remineralization rates, and sediments bathed by all water masses of
 228 the Atlantic Ocean (thermocline, AAIW, North Atlantic Deep Water, and Antarctic Deep
 229 Water) (Figure 5 A). Therefore, we consider the pore water data to be representative for
 230 the Atlantic Basin. Here the discussion focuses on pore water data from sediment depths
 231 between 1 cm and 10 cm below the surface sediment, covering the maximum habitat
 232 depth range of *Globobulimina spp.* and most of the infaunal benthic foraminifers
 233 (Jorissen et al., 1995; McCorkle et al., 1997; Schmiedl et al., 2000; Schmiedl et al.,
 234 2004). The 64 profiles reveal that $\Delta CO_3^{2-}{}_{\text{pore water}}$ is significantly lower relative to the
 235 ΔCO_3^{2-} of the overlying bottom water (p-value: 6×10^{-20} , Figures 5B and 5C). The
 236 ΔCO_3^{2-} profiles along the sediment depth show a rapid decline in the first the upper 3-4
 237 cm (Figure 5B). While some profiles show a continuous drop of ΔCO_3^{2-} from shallower
 238 to deeper sediment depth, others show that the sediment interval with the lowest
 239 ΔCO_3^{2-} values is confined to the upper 2-4 cm (Figure 5B). One factor that has a strong
 240 control on the ΔCO_3^{2-} variability is the depth distribution of the main water masses of the
 241 Atlantic (AAIW, NADW, and AADW). These depth intervals between 4500 m and 5900
 242 m and 605 m and 3500 m show the most undersaturated and most oversaturated
 243 water with respect to the carbonate ion concentration, respectively (Figure 5B).
 244 Within and between the broadly-defined depth intervals (Figure 5B), there is large
 245 variation of $\Delta CO_3^{2-}{}_{\text{pore water}}$ most likely indicating a spatial variation of water depth
 246 occupied by the major water masses of the Atlantic, changes in primary productivity, and
 247 remineralization of organic matter within the upper 10 cm sediment depth. Figure 5C
 248 highlights that the average $\Delta CO_3^{2-}{}_{\text{pore water}}$ ($\geq 1 \leq 10$ cm sediment depth) is significantly

249 lower than, but strongly correlated to the ΔCO_3^{2-} values of the overlying bottom water
 250 ($\Delta CO_3^{2-}{}_{\text{pore water}} = (0.67 \pm 0.05) * \Delta CO_3^{2-}{}_{\text{bottom water}} - (39.84 \pm 1.98)$, $r^2=0.75$, p :
 251 $4*10^{-18}$, $n=64$. The implication of this observation is that infaunal foraminifers live in
 252 pore water that is, on average, lower by 46.5 ± 10.6 $\mu\text{mol/kg}$ relative to the ΔCO_3^{2-} of the
 253 overlying bottom water. Furthermore, $\Delta CO_3^{2-}{}_{\text{porewater}}$ varies spatially, reflecting the
 254 ΔCO_3^{2-} variability of the overlying water and the rate of organic matter
 255 remineralization in the surface sediments. The spatial co-variability of $\Delta CO_3^{2-}{}_{\text{bottom}}$
 256 water and $\Delta CO_3^{2-}{}_{\text{porewater}}$ also implies a temporal variability. Paleoceanographic
 257 reconstruction over the last 25,000 years indicates that water masses of the Atlantic,
 258 Indian, and Pacific oceans experienced large-scale changes in $\Delta CO_3^{2-}{}_{\text{bottom water}}$ (Yu et
 259 al., 2010). As shown by the present-day close relationship between $\Delta CO_3^{2-}{}_{\text{bottom water}}$ and
 260 $\Delta CO_3^{2-}{}_{\text{pore water}}$ (Figure 5C), it is expected that glacial-interglacial changes in $\Delta CO_3^{2-}{}_{\text{bottom}}$
 261 water had a direct impact on $\Delta CO_3^{2-}{}_{\text{porewater}}$. According to our equation (Figure 5C), a
 262 glacial-interglacial $\Delta CO_3^{2-}{}_{\text{bottom water}}$ change of 40 ± 5 $\mu\text{mol/kg}$ in the abyssal of North
 263 Atlantic (water depth: 4045 m) (Raitzsch et al., 2011; Yu et al., 2010) corresponds to a
 264 $\Delta CO_3^{2-}{}_{\text{porewater}}$ change of 26.8 ± 5.4 $\mu\text{mol/kg}$. The sensitivity of Mg/Ca in *Uvigerina* spp.
 265 to ΔCO_3^{2-} and temperature changes is estimated 0.002 ± 0.001 mmol/mol/ $\mu\text{mol/kg}$ and
 266 0.078 ± 0.008 mmol/mol/ $^{\circ}\text{C}$, respectively (Elderfield et al., 2010). Consequently, a glacial-
 267 interglacial $\Delta CO_3^{2-}{}_{\text{porewater}}$ change of 26.8 $\mu\text{mol/kg}$ in the North Atlantic contributes to a
 268 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
 269 BWT estimates. The general implication of this finding is that glacial-interglacial
 270 changes in $\Delta CO_3^{2-}{}_{\text{bottom water}}$ and $\Delta CO_3^{2-}{}_{\text{porewater}}$ have a substantial impact on the Mg/Ca of
 271 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 (Figure 2E) complicates the evaluation of a possible ΔCO_3^{2-} effect on *Globobulimina* spp. Mg/Ca. We pursue a two-step strategy to assess a potential ΔCO_3^{2-} effect on Mg/Ca in *Globobulimina* spp. First, we isolate Mg/Ca changes ($Mg/Ca_{\text{temperature}}$) related to BWT changes by focusing on a water depth interval where BWT drops from 8.8 °C to 2.5 °C (blue rectangle in Figure 2E) 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 – -20.2 $\mu\text{mol/kg}$), respectively. We obtain a correlation equation of $Mg/Ca_{\text{temperature}} = 0.32 \pm 0.06$ *BWT + 2.6 $\pm$ 0.37 ($r^2 = 0.67$, $n = 16$, $p\text{-value} = 0.000079$) (Figure 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:

$$Mg/Ca - \Delta CO_3^{2-} = (0.009 \pm 0.0044) * \Delta CO_3^{2-} \text{ pore water} + 0.06, r^2 = 0.12, p\text{-value}: 0.029$$

(Figure 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 changes 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-} μ 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_{temperature} calculation is based on a relatively limited number of samples (n=16) (Figure 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) (Figure 7). A potential caveat in this comparison is that our calibration is based on *Globobulimina affinis* and *Globobulimina c.f. 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 Interglacial 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 $2.2\pm0.4^\circ\text{C}$ relative to the BWT time-series discussed in Skinner et al. (2003) (Figure 7). Consequently, applying our calibration the Last Glacial Maximum (LGM: 19-23 kyr BP) BWT estimate is $1.2\pm0.5^\circ\text{C}$ 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 $1.4 \pm 0.2^\circ\text{C}$ (Figure 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/ $^\circ\text{C}$ (Figure
 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/ $^\circ\text{C}$) and *Uvigerina spp.*
 (0.065–0.085 mmol/mol/ $^\circ\text{C}$) (Bryan and Marchitto, 2008; Curry and Marchitto, 2008;
 Elderfield et al., 2010; Elderfield et al., 2006; Marchitto et al., 2007; Rosenthal et al.,
 2006). To demonstrate the effect of varying temperature sensitivities of benthic
 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
 (Figure 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/ $^\circ\text{C}$) (Bryan and Marchitto, 2008; Curry and Marchitto, 2008;
 Elderfield et al., 2010; Elderfield et al., 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 indicate 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 (Figure 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 foraminifers, 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 foraminifers 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.

6. Acknowledgements

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Figures and figure captions

Weldeab et al.: Figure 1

Figure 1: Map of the Gulf of Guinea indicating location of core top samples (red filled circles) and MD2707 down core sediment (blue star).

Figure 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 (Figure 1) and small grey dots indicate available data (latitude: 10.84 N–5.72 S and longitude: 338.77 E–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 Figures 2A-E were retrieved from the Global Ocean Data Analysis Project (GLODAP) (Key et al., 2004) and ΔCO_3^{2-} was calculated using the CO2-CALC software (Robbins et al., 2010). Blue rectangles mark ranges used to isolate the temperature and salinity imprint in Mg/Ca.

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

Figure 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 ($Mg/Ca[mmol/mol] = (0.36 \pm 0.02) \cdot BWT[^\circ C] + (2.22 \pm 0.19)$, $r^2 = 0.92$, $n = 39$ and p-value of $11 \cdot 10^{-20}$) 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 Figure 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 Figure 4A.

Figure 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 www.pangaea.de (Hensen, 1996; Hensen et al., 1997; Hensen et al., 1998; Hensen et al., 2000). C) ΔCO_3^{2-} pore water concentration (as shown in Figure 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 [μmol/kg] = $(0.67 \pm 0.05) * \Delta CO_3^{2-}$ bottom water [μmol/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 Figure 5A).

Figure 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 ($Mg/Ca_{\text{residual}} = 0.009 \pm 0.0044 \cdot \Delta CO_3^{2-} \text{ pore water} + 0.06 \pm 0.1$, $r^2 = 0.12$, $n = 16$, $p\text{-value} = 0.029$).

Weldeab et al.: Figure 7

Figure 7: BWT estimates of *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).

Weldeab et al.: Figure 8

Figure 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 ($\text{Mg/Ca} = 0.25 \cdot \text{BWT} + 0.35$) (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 the modern BWT (4 °C) over the core site of MD2707.