



Refining benthic foraminiferal Mg/Ca-temperature calibrations using core-tops from the western tropical Atlantic: Implication for paleotemperature estimation

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[1] Benthic foraminiferal Mg/Ca has been shown to have great potential as a proxy for reconstructing deep water temperatures. However, the exact relationship between Mg uptake in benthic foraminifera and temperature is still ambiguous, and further exploration and refinement is much needed to reduce uncertainties associated with the method. Here, we present new core-top Mg/Ca data from benthic foraminiferal species from the lower part of the thermocline in the western tropical Atlantic (northern Brazilian margin). This area is unusual in that the changes in carbonate chemistry along the transect are very small, making it an ideal region for isolating and studying the role of temperature in the incorporation of Mg into the benthic shells. Our results show that benthic foraminiferal Mg/Ca largely reflects temperature in this area. Our data are combined with previously published data to produce new and improved Mg/Ca calibration equations for a number of benthic foraminiferal species within the Atlantic Ocean. Our study provides the first *C. wuellerstorfi* Mg/Ca data for the 4–6°C temperature range and indicates that *C. wuellerstorfi* Mg/Ca is strongly controlled by temperature. As a result, the newly established *C. wuellerstorfi* calibration over the entire 0–6°C temperature range is significantly improved with respect to previously published *C. wuellerstorfi*



calibrations limited to the coldest part between 0 and 4°C. Other benthic species (*Cibicidoides kullenbergi*, *Globocassidulina subglobosa*, *Uvigerina peregrina*, and *Oridorsalis umbonatus*) have also been studied, although these results are less conclusive.

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1. Introduction

[2] Over the past decade, Mg/Ca ratios measured in benthic foraminiferal shells have been used to estimate the temperature of the deep seawater in which the foraminifera calcified [Billups and Schrag, 2002; 2003; Bryan and Marchitto, 2008; Elderfield et al., 2006; 2010; 2012; Lea et al., 2000; Lear et al., 2000; Marchitto and deMenocal, 2003; Martin et al., 2002; Skinner et al., 2003; Sosdian and Rosenthal, 2009; Katz et al., 2011]. Independent temperature estimates from Mg/Ca ratios, in combination with the oxygen isotopic composition of the foraminiferal calcite ($\delta^{18}\text{O}_{\text{calcite}}$), can help constrain the oxygen isotopic composition of seawater ($\delta^{18}\text{O}_{\text{seawater}}$), which itself reflects changes in the local hydrography [Duplessy et al., 1991; Waelbroeck et al., 2002]. The use of Mg/Ca paleothermometry on planktonic foraminiferal for reconstructing sea surface temperatures is now widespread [Anand et al., 2003; von Langen et al., 2005; Lea et al., 1999; Mashiotta et al., 1999; Nürnberg et al., 1996; Russell et al., 2004], but extensive studies during the last decades have also suggested that the same method may be applied to benthic species, in order to generate records of bottom water temperature (BWT) in a wide range of temperatures [Elderfield et al., 2006; Healey et al., 2008; Kristjánssdóttir et al., 2007; Lear et al., 2002; Marchitto et al., 2007; Martin et al., 2002; Rosenthal et al., 2006; 2011; Skinner et al., 2003; Yu and Elderfield, 2008].

[3] However, using benthic foraminifera Mg/Ca to reconstruct BWT is complicated: glacial-interglacial temperature variations in intermediate and deep waters are small compared to those seen at the surface, and as a result, the calibrations have to be far more tightly constrained in order to minimize uncertainties.

[4] A number of core-top and culture calibration studies on epifaunal and infaunal benthic species have been performed over the last 15 years (Table 1 and Figure 1 and references therein) and show positive correlations with temperature (e.g., Figure 1). Previously published benthic foraminifera Mg/Ca-temperature calibrations based on a range of species from the *Cibicidoides* genus cover a large temperature range, from -1.1 to 18.4°C (Table 1 and references therein). Previous studies have shown that the relationship describing Mg incorporation in shell calcite as a function of temperature is species specific [Elderfield et al., 2006; Lear et al., 2002; Rosenthal et al., 1997]. Calibrations based on multispecies Mg/Ca ratios thus include uncertainties due to interspecies differences. It is notable that existing Atlantic datasets contain a relatively large number of *Cibicidoides* spp. measurements from waters colder than 4°C (see histogram in Figure 1) but only a few measurements below 1°C or above 4°C . As a result, existing calibrations of *Cibicidoides* spp. are poorly constrained outside of this small 1 to 4°C window. Other studies that focus exclusively on *Cibicidoides wuellerstorfi* (a common deep and intermediate water species [Murray, 1991]) cover the colder part of the temperature range ($<4^\circ\text{C}$) and suggest that the slope of the Mg/Ca-temperature calibration is steeper than that of the mixed *Cibicidoides* spp. calibration (Table 1 and Figure 1). The first possibility proposed to explain this difference was that *C. wuellerstorfi* Mg/Ca has a higher sensitivity to temperature compared to mixed *Cibicidoides* spp. Mg/Ca. However, the difference between *C. wuellerstorfi* and the mixed species calibration has led many to highlight seawater carbonate saturation as a potentially significant control on Mg incorporation into the test of this particular species [Lear et al., 2004; Martin et al., 2002]. Elderfield et al.

Table 1. Published Mg/Ca-Temperature Calibrations

Reference	Species	Method	Mg/Ca-Temperature Relationship	Temperature Range (°C)
Billups and Schrag [2002]	<i>C. wuellerstorfi</i> <i>C. kullenbergi</i>	No leaching	$Mg/Ca = 0.32T + 0.76$	1.6–5.34 [1]
Elderfield et al. [2006]	<i>Cibicidoides</i> spp.	Oxidative	$Mg/Ca = 0.90 \exp(0.11 \text{ BWT})$	–1.1–18 [2]
Healey et al. [2008]	<i>C. wuellerstorfi</i>	Reductive	$Mg/Ca = 0.781 \exp(0.23 \text{ BWT})$	0.95–3.8 [3]
Lear et al. [2002]	<i>Cibicidoides</i> spp. including <i>C. wuellerstorfi</i>	Reductive	$Mg/Ca = 0.867 \exp(0.109 \text{ BWT})$	0.8–18.4 [4]
Marchitto et al. [2007]	<i>C. pachyderma</i>	Reductive	$Mg/Ca = 0.116T + 1.2$	5.8–18.6 [5]
Martin et al. [2002]	<i>Cibicidoides</i> spp.	Reductive	$Mg/Ca = 1.22 \exp(0.109 \text{ BWT})$	–1.1–18 [6]
after Healey et al. [2008]	<i>C. wuellerstorfi</i>		$Mg/Ca = 0.652 \exp(0.28 \text{ BWT})$	1.8–3 [7]
Raitzsch et al. [2008]	<i>C. wuellerstorfi</i>	Laser ablation	$Mg/Ca = 0.830 \exp(0.145 \text{ BWT})$	0.39–3.88 [8]
	<i>C. kullenbergi</i>	Laser ablation	$Mg/Ca = 0.627 \exp(0.143 \text{ BWT})$	0.43–14.85 [9]
Rathburn and De Decker [1997]	<i>C. wuellerstorfi</i>	Sonication	$Mg/Ca = 0.342T + 1.39$	2.25–5.87 [10]
Rosenthal et al. [1997]	<i>C. pachyderma</i>	Leaching	$Mg/Ca = 1.36 \exp(0.1 \text{ BWT})$	4.5–18 [11]
Russell et al., [2004] (as cited by Martin et al., [2002])	<i>C. wuellerstorfi</i>	Leaching	$Mg/Ca = 0.953 \exp(0.206 \text{ BWT})$	0.4–2.8 [12]
Yu and Elderfield [2008]	<i>C. wuellerstorfi</i>	Oxidative	$Mg/Ca = 0.59 \exp(0.28 \text{ BWT})$ (without carbonate ion saturation correction)	0.98–4.26 [13]

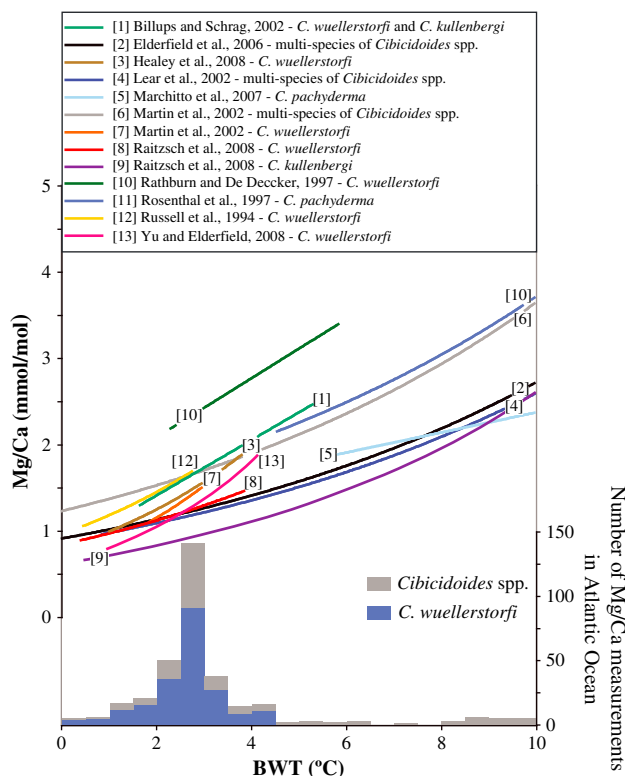


Figure 1. Single or multispecies of *Cibicidoides* spp. Mg/Ca-temperature calibration between 0 and 10°C. Numbers between brackets refer to calibrations listed in Table 1. The histogram shows the number of Mg/Ca measurement of *Cibicidoides* spp. (in gray) and *Cibicidoides wuellerstorfi* (in blue) in the Atlantic Ocean. The labeled numbers correspond to references in which the calibration equations have been used (see details in Table 1).

[2006] showed that samples from the Norwegian Sea (subzero temperature and high carbonate ion saturation state $\Delta[CO_3^{2-}]$) give anomalous ratios (large

range in Mg/Ca with little change in temperature), which led them to propose and establish the first empirical relationship between the $\Delta[CO_3^{2-}]$ and Mg/Ca

in *C. wuellerstorfi*, based on core-top samples. Since then, an increasing number of studies evaluating the effect of $\Delta[\text{CO}_3^{2-}]$ on the Mg/Ca of benthic foraminifera have been conducted [Healey et al., 2008; Raitzsch et al., 2008; Yu and Elderfield, 2008]. Published studies show that Mg/Ca in *C. wuellerstorfi* and *Cibicidoides kullenbergi* (= *Cibicidoides mundulus*) shells are strongly affected by low $\Delta[\text{CO}_3^{2-}]$ (defined as the difference between the measured carbonate ion concentration $[\text{CO}_3^{2-}]$ and the carbonate ion concentration at calcite saturation $[\text{CO}_3^{2-}]_{\text{sat}}$), for BWT less than 4°C [Elderfield et al., 2006; Raitzsch et al., 2008; Yu and Elderfield, 2008]. Yu and Elderfield [2008] further assessed the influence of BWT and $\Delta[\text{CO}_3^{2-}]$ on core-top samples from across the global ocean. They suggested that *C. wuellerstorfi* Mg/Ca ratios show a weak correlation with BWT but a strong one with $\Delta[\text{CO}_3^{2-}]$, whereas *C. kullenbergi* Mg/Ca ratios show no correlation with changes in BWT or $\Delta[\text{CO}_3^{2-}]$.

[5] Calibrations have also been published on infaunal species, which live within the sediment, such as *Uvigerina* species [Bryan and Marchitto, 2008; Elderfield et al., 2006; 2010; Lear et al., 2002; Yu and Elderfield, 2008], *Hyalinea balthica* [Rosenthal et al., 2011], *Oridorsalis umbonatus* [Healey et al., 2008; Lear et al., 2002; Rathman et al., 2004; 2008], the argonitic species *Hoeglundina elegans* [Rosenthal et al., 2006], and other species from the Arctic (*Islandiella norcrossi/helenae*, *Melonis barleeanus*, and *Cassidulina neoteretis*) [Kristjánsdóttir et al., 2007; Lear et al., 2002]. According to Elderfield et al. [2006; 2010], shallow infaunal species seem to be far less affected by changes in $\Delta[\text{CO}_3^{2-}]$ than epifaunal species, largely because they calcify in pore waters within the sediment. The infaunal species *O. umbonatus* and *Melonis* spp. exhibit temperature sensitivities similar to those observed in benthic epifaunal species, whereas other infaunal species have a lower sensitivity. After correction for the $\Delta[\text{CO}_3^{2-}]$ effect on Mg/Ca ratios, the temperature sensitivity of epifaunal foraminiferal species appears lower and similar to the sensitivity found for *Uvigerina* spp. [Raitzsch et al., 2008; Yu and Elderfield, 2008].

[6] Factors other than seawater $\Delta[\text{CO}_3^{2-}]$ can also control Mg incorporation during calcite shell growth of benthic foraminiferal species, including salinity [Dissard et al., 2010; Kisakürek et al., 2008], pH [Russell et al., 2004], and microenvironment variations [Bentov and Erez, 2006; Erez, 2003]. Although

it is known that test size might influence the Mg/Ca ratios in planktonic foraminiferal species [Elderfield et al., 2002], no studies have yet been conducted on benthic species. Although the effect of temperature on Mg/Ca ratios might, therefore, be the dominant factor for some benthic foraminiferal species, it is clearly important to assess the potential impact of other such factors.

[7] In order to address these questions, we present new benthic foraminiferal Mg/Ca results from core-top samples from a short depth transect (600–1000 m) from the western equatorial Atlantic Ocean, along the northern Brazilian margin. The core-top locations have a small temperature range of 4–6°C, but the sites are unusual in that they exhibit only very minor changes in $\Delta[\text{CO}_3^{2-}]$. This essentially removes any concern over the potential impact of $\Delta[\text{CO}_3^{2-}]$ on Mg incorporation and allows us to study the key relationship of Mg/Ca to temperature. Hence, this study aims to further constrain the controls involved in benthic foraminiferal Mg incorporation (e.g., temperature versus $\Delta[\text{CO}_3^{2-}]$).

[8] We first examine the Mg/Ca-BWT relationships of six benthic species in order to assess the temperature sensitivity of each species. We then summarize new and published *C. wuellerstorfi* core-top Mg/Ca measurements from the Atlantic Ocean [Elderfield et al., 2006; Raitzsch et al., 2008; Yu and Elderfield, 2008]. Our study provides the first *C. wuellerstorfi* Mg/Ca data for the 4–6°C temperature range. The new *C. wuellerstorfi* results, together with published *C. wuellerstorfi* data, lead us to revise the published Mg/Ca-BWT calibration and extend the temperature range above 4°C.

2. Oceanographic Setting

[9] The study area is located on the upper continental slope off northeastern Brazil at ~4°S (Figure 2a). This ocean margin is characterized by well-oxygenated bottom water, where organic matter fluxes are generally low. Productivity in the western tropical North Atlantic is considered to be similar to that of the oligotrophic open ocean, with a carbon production of 20–90 $\mu\text{mol C.kg}^{-1}$ [Cooley and Yager, 2006]. Because of the oligotrophic conditions characterizing this area, some benthic foraminiferal species generally considered as deep-sea taxa, such as *C. wuellerstorfi*, *O. umbonatus*, and *Globocassidulina* spp., are found in fair numbers in the upper part of this transect (see section 3.1). Western tropical Atlantic surface waters are warm and saline. The

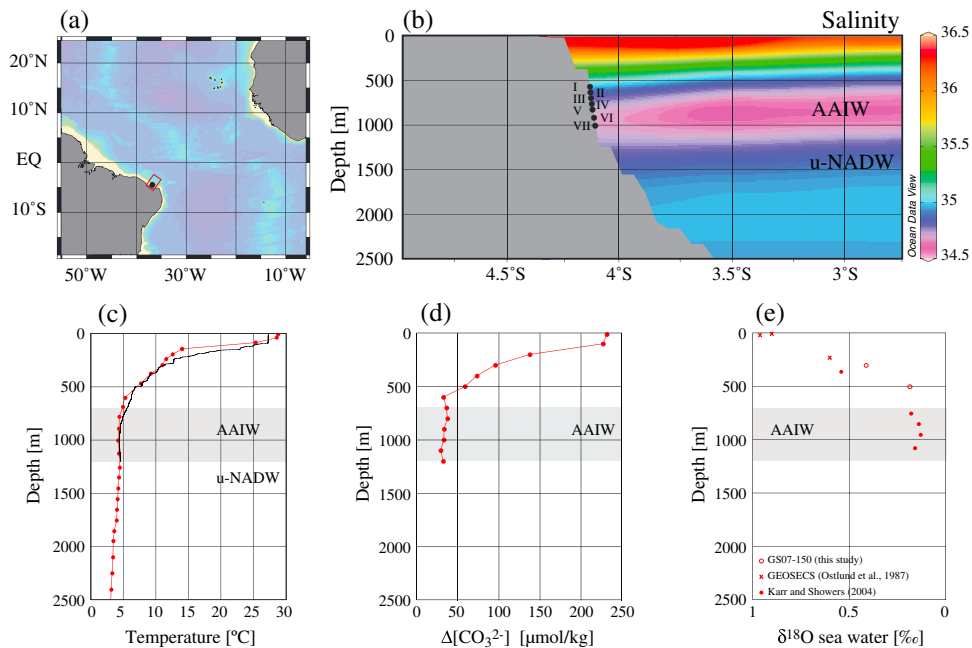


Figure 2. (a) Location of sediment transect cores (black circle) and profile chemistry section (red box). (b) Distribution of salinity (psu) in the modern tropical western Atlantic Ocean (generated with Ocean Data View) [Schlitzer, 2010]. The black circles show the location and water depths of core-tops used for this study (see location information in Table 2). (c) Temperature. (d) $\Delta[\text{CO}_3^{2-}]$ profile calculated with the software CO2sys version 14 [Lewis and Wallace, 1998] and with data (temperature, salinity, phosphorous, and nitrate) from World Atlas Ocean 2009 [Antonov *et al.*, 2010; Garcia *et al.*, 2010a; 2010b; Locarnini *et al.*, 2010] and data (alkalinity and TCO₂) from Goyet *et al.* [2000]. (e) $\delta^{18}\text{O}$ of seawater in the water column [this study; Ostlund *et al.*, 1987; Karr and Showers, 2002]. AAIW: Antarctic intermediate water; u-NADW: upper North Atlantic deep water.

upper 200 m of the water column is dominated by the North Brazilian Current, characterized by low nutrient content, with some supply from South Equatorial Current waters [Peterson and Stramma, 1991]. Below, South Atlantic Current waters from the South Atlantic subtropical gyre (200–500 m depth) help to transport heat and salt to the North Atlantic Ocean. The main thermocline is situated in the upper 500 m and spans a temperature interval from more than 25°C at the surface to less than 10°C in its lower part. Below the main thermocline, the dominant water mass is Antarctic Intermediate Water (AAIW), which is recognized by a prominent salinity minimum between ~700 and ~1200 m depth in the study area (Figure 2b). Hydrographic observations by Silva *et al.* [2009] indicate seasonal changes of ~2°C in the top 50 m of the water column. Below the seasonal thermocline, water properties are uniform throughout the year [Arz *et al.*, 1998; Levitus *et al.*, 1994].

[10] The CTD (conductivity-temperature-depth) cast (station 13) (04°15.403S; 37°03.083W; 1250 m depth), performed during the (R/V) G.O. Sars 2007 cruise, shows a temperature profile

similar to the annual temperature profiles from the World Ocean Atlas 2009 [Antonov *et al.*, 2010; Garcia *et al.*, 2010a; 2010b; Locarnini *et al.*, 2010] (Figure 2c), confirming that these profiles adequately describe the physical properties along the margin where our samples were collected. During the same cruise, seawater samples were collected near the coring sites (03°46.443S; 37°03.857W) at 300 and 500 m water depth. The oxygen isotopic ratio of these water samples is similar to the values described for nearby sites in the global seawater $\delta^{18}\text{O}$ database edited by Schmidt *et al.* [1999] and available at <http://data.giss.nasa.gov/o18data/> (e.g., Figure 2e [Karr and Showers, 2002; Ostlund *et al.*, 1987]).

[11] AAIW is characterized by low $\Delta[\text{CO}_3^{2-}]$ and low salinity (~34.5). There are no large variations in salinity, carbonate ion saturation, and $\delta^{18}\text{O}_{\text{seawater}}$, which might have a secondary influence on the Mg/Ca ratio along the coring transect (Figures 2d and 2e). The temperature range is also rather small, but this allows us to test the sensitivity of the Mg/Ca method over a temperature range of about 2°C (between 4 and 6°C).

3. Materials and Methods

[12] Surface sediment samples from the depth transect were collected using a multicorer during the 2007 RETRO GS07-150 cruise, with the research vessel (R/V) *G.O. Sars*. Multicores were retrieved from seven sites located between 600 and 1000 m depth on the upper continental slope off northeastern Brazil at about 4°S and 37°W (Figures 2a and 2b and Table 2). The surface sediment samples analyzed in this study correspond to the top 0–0.5 cm interval of the multicore. Based on Accelerator Mass Spectrometry (AMS) ¹⁴C ages of surface sediments from gravity cores retrieved in the same area, *Arz et al.* [1998; 1999] indicated a late Holocene age, with sedimentation rates of 15 cm/1000 years. AMS ¹⁴C dates based on monospecific samples of *Globigerinoides sacculifer* in the seven multicores were measured in the Rafter Radiocarbon Laboratory in New Zealand and give a calibrated radiocarbon age of between 271±28 and 2897±49 years before present (BP) (Table 2). Radiocarbon ages were calibrated using the Calib6.01 software and the marine 09 calibration curve, with a standard reservoir correction of 400 years given by the calibration program [*Reimer et al.*, 2009]. As multicoring does not disturb the sediment-water interface, we are confident that the analyzed samples from the depth transect are true surface sediment samples and thus representative of modern or late Holocene conditions. Aragonitic pteropod shells are present in all multicore samples, suggesting negligible post-depositional dissolution.

[13] Carbonate calculations of the system include the effects of temperature, salinity, pressure, phosphate, silicate, alkalinity, and total DIC (dissolved inorganic carbon), using the software CO2sys version 14 [*Lewis and Wallace*, 1998]. DIC is corrected for anthropogenic CO₂. Except for temperature, which has been measured with CTD, chemistry data were estimated using the nearest stations in the Global Ocean Data Analysis Project database [*Key et al.*, 2004].

3.1. Mg/Ca Analysis

[14] The sediment samples were washed and wet sieved at 63 and 150 μm. Samples were then dry-sieved at 250, 315, and 400 μm for *C. wuellerstorfi* and *C. kullenbergi* and at 250 μm for some of the infaunal species, to obtain 7–25 benthic foraminifer specimens per sample. Six benthic foraminiferal species (*Cibicides wuellerstorfi*, *Cibicides kullenbergi*, *Globocassidulina subglobosa*, *Uvigerina*

peregrina, *Oridorsalis umbonatus*, and *Bulimina inflata*) were picked from the >150 μm fraction. *U. peregrina*, *O. umbonatus*, and *G. subglobosa* are shallow infaunal species. *C. wuellerstorfi* has an epifaunal microhabitat and is thus exposed to the ambient bottom water conditions, which here are characterized by a low organic matter flux to the sediment [*Altenbach and Sarnthein*, 1989]. In the Northeastern Atlantic, *C. wuellerstorfi* has been found between 1360 and 4280 m [*Murray et al.*, 1991] but may be present in small numbers around 1000 m [*Fontanier et al.*, 2013; *Eberwein and Mackensen*, 2006]. A recent study from New Zealand demonstrates that high relative abundances of *C. wuellerstorfi* have been found from upper bathyal to upper abyssal depths (400–3000 m) [*Hayward et al.*, 2010]. The distribution of benthic species is controlled by two principal factors: the supply of organic matter and oxygen content [*Jorissen et al.*, 1995; *Levin and Gage*, 1998; *Van der Zwaan et al.*, 1999]; however, current intensity, sediment grain size, and the dominant water masses in the area are also known to affect the representation and abundance of the species [*Jorissen et al.*, 2007]. In our study area, the presence of *C. wuellerstorfi* in waters shallower than 1000 m may be explained by the exceptionally low organic matter flux to the sea floor, which is typical for the continental slope off northeastern Brazil (see section 2). *C. wuellerstorfi* is able to live in shallow waters above 1000 m depth in this region. The very high abundance of *Globocassidulina* spp., which is generally considered as an oligotrophic taxon [*Schmiedl et al.*, 1997; *Mackensen et al.*, 1995], confirms the low export production in this region, with only intermittent organic matter input.

[15] Sample weights greater than 0.175 mg are required for each Mg/Ca analysis. In this study, measured samples generally weighed 0.300–0.400 mg (typically corresponding to ~15–20 shells). We separated specimens by size fraction to test the potential size effect on Mg/Ca ratios. We crushed foraminiferal shells between two glass plates to break the chambers and homogenized them before splitting them into sub-samples for Mg/Ca replicates and δ¹⁸O analyses. Some samples did not contain sufficient material to conduct both Mg/Ca and δ¹⁸O replicates.

[16] The crushed foraminifera were cleaned for contaminant phases following the procedure developed by *Barker et al.* [2003]. This method includes a clay removal step, oxidation of the organic matter, and surface leaching. The samples were analyzed for Mg/Ca, Fe/Ca, and Mn/Ca by using a Thermo Finnigan IRIS inductively coupled plasma optical

Table 2. Core-Top Locations^a

Core	Lat. (°S)	Long. (°W)	WD (m)	BWT (°C)	Salinity	$[\text{CO}_3^{2-}]$ -calcite ($\mu\text{mol/kg}$)	Sample Depth (cm)	Species	AMS ¹⁴ C ages (years BP)	Errors	Cal. Ages (years BP)	Errors	Size Fraction				
GS07-150-22/1MC (I)	04°16.231	37°09.051	598	6.06	34.5	33.2	0-0.5	<i>G. Saccatijfer</i>	3123	30	2897	49	-				
							core-top						-				
							core-top						150-200				
							core-top						150-250				
							core-top						150-250				
							core-top						150-250				
							core-top						250-315				
							core-top						250-315				
							core-top						315-400				
							core-top						250-400				
GS07-150-21/1MC (II)	04°15.981	37°08.711	656	5.67	33.6	0-0.5	<i>G. Saccatijfer</i>	2633	20	2317	30	150-250					
core-top	200-250																
core-top	250-315																
core-top	250-315																
core-top	250-400																
GS07-150-20/1MC (III)	04°15.655	37°08.243	700	5.38	37.5	0-0.5						<i>G. Saccatijfer</i>	2653	30	2328	24	150-250
core-top	150-250																
core-top	200-250																
core-top	250-315																
core-top	250-315																
core-top	315-400																
core-top	315-400																
core-top	250-400																
GS07-150-26/2MC (IV)	04°15.267	37°07.761	750	4.92	37	0-0.5	<i>G. Saccatijfer</i>	2078	20	1651	40						150-200
core-top	200-250																
core-top	150-250																
core-top	150-250																
core-top	150-250																
core-top	250-315																
core-top	250-315																
core-top	315-400																
core-top	250-400																
GS07-150-19/1MC (V)	04°14.868	37°07.197	800	4.64	36.4	0-0.5						<i>G. Saccatijfer</i>	727	30	368	45	150-200
core-top	200-250																



Table 2. (continued)

	Mg/Ca (mmol/mol)						$\delta^{18}\text{O}$ (‰)					
	<i>U. Peregrina</i>	<i>B. Inflata</i>	<i>O. Umbonatus</i>	<i>G. Subglobosa</i>	<i>C. kullenbergi</i>	<i>C. wuellerstorfi</i>	<i>U. Peregrina</i>	<i>B. Inflata</i>	<i>O. Umbonatus</i>	<i>G. Subglobosa</i>	<i>C. kullenbergi</i>	<i>C. wuellerstorfi</i>
2.10	2.28	-	-	-	-	-	2.04	2.10	-	-	-	-
-	2.34	-	-	-	-	-	-	2.48	-	-	-	-
-	-	-	-	4.46	-	-	-	-	-	1.98	-	-
-	-	3.10	3.37	-	2.95	2.95	-	-	2.66	-	1.66	1.35
-	-	2.88	-	-	-	-	-	-	-	-	-	-
-	-	2.66	-	-	-	-	-	-	-	-	-	-
-	-	-	-	4.14	2.41	2.41	-	-	-	1.91	1.41	1.41
-	-	-	-	-	2.53	2.53	-	-	-	-	1.68	1.68
-	-	-	-	-	3.07	3.07	-	-	-	-	1.77	1.77
-	-	-	-	-	3.91	3.91	-	-	-	-	1.87	1.87
-	-	2.32	1.74	-	-	-	-	2.41	2.63	-	-	-
-	-	2.71	-	-	-	-	-	2.43	-	-	-	-
-	-	-	1.93	-	2.55	2.55	-	-	2.40	-	1.81	1.81
-	-	-	-	5.06	-	-	-	-	-	1.95	-	-
-	-	-	-	-	2.76	2.76	-	-	-	-	-	-
-	-	-	-	-	2.04	2.04	-	-	2.28	-	1.96	1.96
-	-	-	1.71	-	-	-	-	-	-	-	-	-
-	-	-	1.75	-	2.56	2.56	-	-	2.52	-	0.91	0.91
-	-	-	-	-	2.23	2.23	-	-	-	-	1.96	1.96
-	-	-	-	4.83	-	-	-	-	-	1.98	-	-
-	-	-	-	3.76	2.24	2.24	-	-	-	2.03	-	-
-	-	-	-	-	2.31	2.31	-	-	-	-	2.02	2.02
-	-	-	-	-	2.44	2.44	-	-	-	-	1.87	1.87
-	-	-	-	-	2.30	2.30	-	-	-	-	1.97	1.97
-	-	-	1.70	-	-	-	-	-	2.66	-	-	-
1.14	2.48	-	-	-	-	-	2.60	2.88	-	-	-	-
-	-	-	-	4.80	-	-	-	-	-	-	-	-
-	-	-	-	4.77	-	-	-	-	-	2.04	-	-
-	-	2.44	1.80	-	2.44	2.44	-	-	2.60	-	2.07	2.07
-	-	-	-	-	2.65	2.65	-	-	-	-	2.06	2.06
-	-	-	-	-	2.55	2.55	-	-	-	-	2.12	2.12
-	-	-	-	-	1.80	1.80	-	-	-	-	1.97	1.97
-	-	-	-	-	2.45	2.45	-	-	-	-	2.10	2.10
-	-	-	-	-	2.00	2.00	-	-	-	-	1.96	1.96
-	-	2.61	1.50	-	-	-	-	2.62	2.78	-	-	-
1.33	1.86	-	-	-	-	-	2.86	2.79	-	-	-	-

Table 2. (continued)

Core	Lat. (°S)	Long. (°W)	WD (m)	BWT (°C)	Salinity	$\Delta[\text{CO}_3^{2-}]$ -calcite ($\mu\text{mol/kg}$)	Sample Depth (cm)	Species	AMS 14C ages (years BP)	Errors	Cal. Ages (years BP)	Errors	Size Fraction					
GS07-150-18/1MC (VI)	04°13.827	37°05.945	898	4.3	34.47	34.7	core-top	<i>G. Sacculifer</i>	619	30	271	28	150–250					
							core-top						150–250					
							core-top						250–315					
							core-top						250–315					
							core-top						315–400					
							core-top						315–400					
GS07-150-17/2MC (V)	04°12.986	37°04.518	1000	4.17	34.56	33	0–0.5	<i>G. Sacculifer</i>	1303	20	796	38	150–200					
							core-top						200–250					
							core-top						150–250					
							core-top						250–315					
							core-top						250–315					
							core-top						315–400					
							core-top						315–400					
							4–4.5						<i>G. Sacculifer</i>	1303	20	796	38	150–200
							core-top											200–250
							core-top											150–250
							core-top											250–315
							core-top											250–315
core-top	315–400																	

^aBWT from the CTD was taken during the cruise RETRO GS07-150.



Table 2. (continued)

	Mg/Ca (mmol/mol)						$\delta^{18}\text{O}$ (‰)					
	<i>U. Peregrina</i>	<i>B. Inflata</i>	<i>O. Umbonatus</i>	<i>G. Subglobosa</i>	<i>C. kullenbergi</i>	<i>C. wuellerstorfi</i>	<i>U. Peregrina</i>	<i>B. Inflata</i>	<i>O. Umbonatus</i>	<i>G. Subglobosa</i>	<i>C. kullenbergi</i>	<i>C. wuellerstorfi</i>
-	-	-	-	-	4.50	-	-	-	-	2.06	-	-
-	-	-	-	4.10	-	-	-	-	-	1.98	-	-
-	-	-	1.61	-	2.40	-	-	-	2.75	-	2.13	-
-	-	-	-	-	2.11	-	-	-	-	-	2.13	-
-	-	-	-	3.96	2.32	-	-	-	-	2.10	2.26	-
-	-	-	-	-	1.88	-	-	-	-	-	2.14	-
-	-	-	-	-	2.05	-	-	-	-	-	-	-
-	-	-	-	-	2.10	-	-	-	-	-	2.04	-
-	-	2.26	1.51	-	-	-	-	-	2.67	-	-	-
1.33	1.70	-	-	-	-	2.70	2.94	-	-	-	-	-
-	-	-	-	5.18	-	-	-	-	-	2.08	-	-
-	-	-	-	3.25	-	-	-	-	-	2.16	-	-
-	-	2.90	1.65	-	2.08	-	-	2.49	2.72	-	2.16	-
-	-	-	-	3.71	2.16	-	-	-	-	1.98	-	-
-	-	-	-	-	1.95	-	-	-	-	-	2.15	-
-	-	-	-	-	1.81	-	-	-	-	-	2.19	-
-	-	2.27	1.51	-	-	-	-	2.52	2.68	-	-	-
1.14	1.74	-	-	-	-	2.86	2.93	-	-	-	-	-
-	-	-	-	4.29	-	-	-	-	-	2.33	-	-
-	-	-	-	4.10	-	-	-	-	-	2.27	-	-
-	-	3.01	1.73	-	-	-	-	-	2.84	-	2.46	-
-	-	-	-	4.40	1.91	-	-	-	-	2.36	2.02	-
-	-	-	-	-	2.09	-	-	-	-	-	2.32	-
-	-	-	-	-	2.03	-	-	-	-	-	2.14	-
-	-	2.31	1.49	-	-	-	-	2.95	2.78	-	-	-

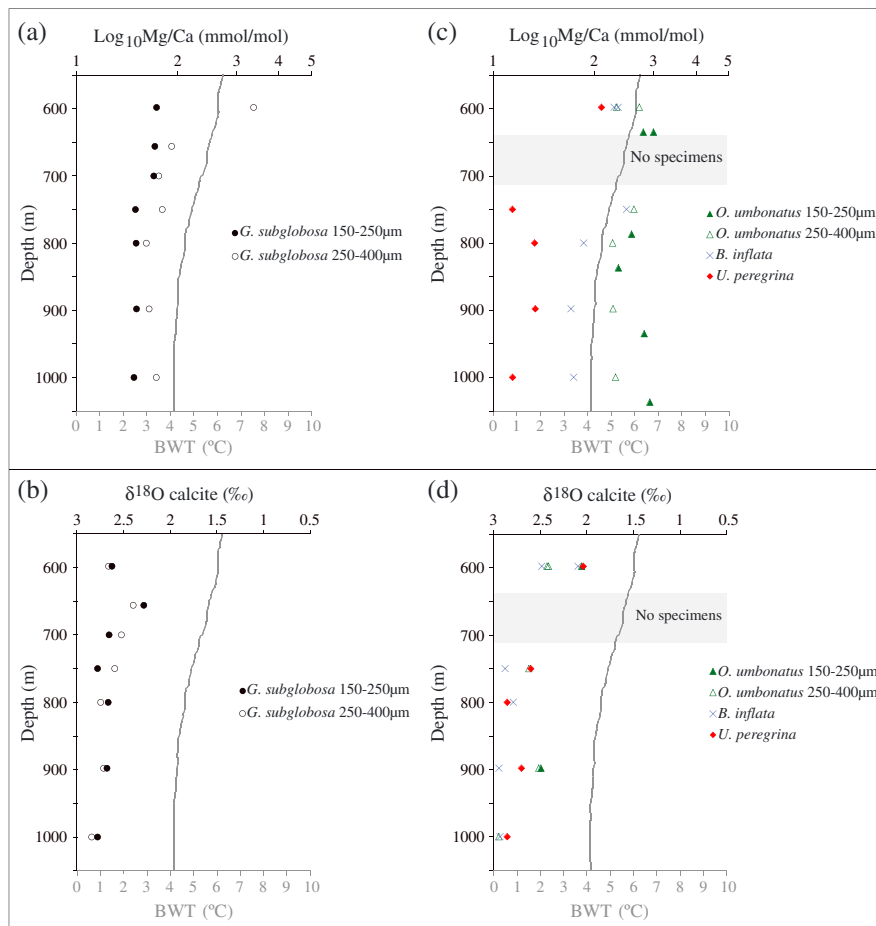


Figure 3. (a, c) Shell Mg/Ca and (b, d) δ¹⁸O for infaunal foraminiferal species plotted against water depth. The Mg/Ca axis is adjusted to the temperature axis by using an exponential relationship (adopted from Elderfield *et al.* [2006]).

emission spectrometer at Bergen GeoAnalytical Facility at the Department of Earth Sciences, University of Bergen. For every six to eight samples, known standard solutions were analyzed to correct for instrumental biases and analytical drift of the instrument.

[17] Long-term instrumental precision of elemental ratio data (determined by 60 replicate analyses of a standard solution containing Mg/Ca=1.020 mmol/mol) is ±0.043 mmol/mol (1σ) or 0.81% (relative standard deviation (RSD)). The pooled standard deviation of the duplicate Mg/Ca determination for the epifaunal species *C. wuellerstorfi* (based on 63 replicates (from 7 to 25 specimens)) is equivalent to an overall average precision of 5% (pooled RSD), including artifacts from cleaning, picking, and sample heterogeneity, in addition to instrumental precision. The epifaunal species *C. kullenbergi* has not been replicated. For the infaunal species, only *O. umbonatus* has been replicated and the average precision is equivalent to

7.1% (pooled RSD). Measured Mg/Ca values show no correlation with Fe/Ca and Mn/Ca, indicating the absence of contamination due to insufficient cleaning or the presence of diagenetic coatings or silicates. Fe/Ca is <0.1 mmol/mol on all except for the *C. kullenbergi* Mg/Ca analyses. However, there is no trend between Mg/Ca and Fe/Ca in *C. kullenbergi* ($r^2 = 0.1$).

3.2. Stable Isotopes Analysis

[18] Stable isotope analyses were conducted on the same sample material as the trace element analyses. The foraminifera shell fragments were cleaned in alcohol in an ultrasonic bath and dried at 60°C. The isotope measurements were carried out at the stable isotope laboratory at the Department of Earth Sciences at University of Bergen. Between ~30 and 50 µg of foraminifera were analyzed for each sample on a Finnigan MAT 253 mass spectrometer

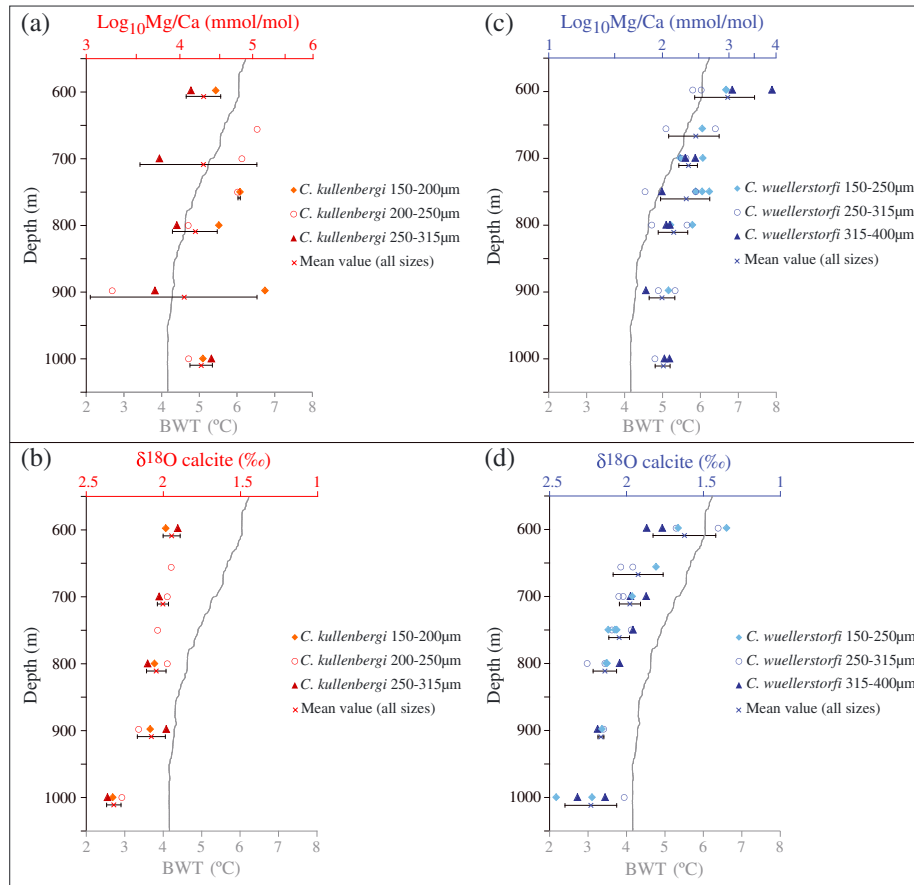


Figure 4. (a, c) Shell Mg/Ca and (b, d) $\delta^{18}\text{O}$ for epifaunal foraminiferal species plotted against water depth. The Mg/Ca axis is adjusted to the temperature axis by using an exponential relationship (adopted from Elderfield *et al.* [2006]).

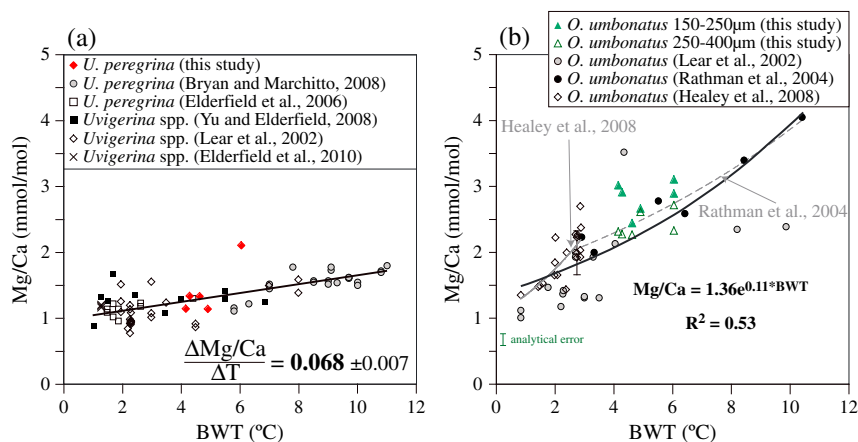


Figure 5. Mg/Ca versus temperature: (a) *U. peregrina* and *Uvigerina* spp. and (b) *O. umbonatus*.

coupled to an automated Kiel carbonate preparation device. The isotopic values were calibrated to Vienna Pee Dee Belemnite using the standards NBS19 and NBS18. The long-term $\delta^{18}\text{O}$ analytical precision (1σ) of the standard is $\pm 0.08\%$.

4. Results

[19] Figure 3 shows Mg/Ca ratios and $\delta^{18}\text{O}$ of calcite plotted versus water depth for all the infaunal foraminifera species studied. *Globocassidulina*

subglobosa shows a nearly constant Mg/Ca value (1.79 ± 0.47 mmol/mol) along the slope for the two size fractions analyzed; it seems not to be significantly affected by test size or by temperature (Mg/Ca = 1.98 ± 0.62 mmol/mol for the 150–250 μm size fraction; 1.59 ± 0.12 mmol/mol for the 250–355 μm size fraction) (Figure 3a). The $\delta^{18}\text{O}$ value of *G. subglobosa* tends to be lower in the upper part of the depth transect, except the upper site at 600 m, which displays higher values (Figure 3b).

[20] Mg/Ca ratios of *O. umbonatus* are systematically lower in the 250–400 μm size fraction (2.41 ± 0.19 mmol/mol) than in the 150–250 μm size fraction (2.83 ± 0.25 mmol/mol). This difference is particularly apparent in the two deepest sites (17/1MC - 1000 m and 18/2MC - 900 m) (Figure 3c). In the 150–250 μm size fraction, Mg/Ca values from the upper site are similar to those from the lower sites, with minimum values found at 750 and 800 m depths. The Mg/Ca values for the 250–400 μm size fraction seem in line with temperature, with Mg/Ca for the uppermost sites (750–600 m) displaying a slightly higher Mg/Ca ratio (mmol/mol) compared to that for the deeper sites. Overall, however, there is no clear relationship between Mg/Ca and temperature for *O. umbonatus*. There is a lack of *O. umbonatus* $\delta^{18}\text{O}$ measurements in the 150–250 μm size fraction, as too few specimens were obtained to achieve reliable measurements (Figure 3d). In the 250–400 μm size fraction, there is $\sim 0.8\text{‰}$ change toward lighter values in $\delta^{18}\text{O}$ from the deepest site to the shallow site, corresponding to $\sim 2^\circ\text{C}$ if the $\delta^{18}\text{O}$ of the water is constant. However, the pattern of *O. umbonatus* $\delta^{18}\text{O}$ changes versus depth is not regular and does not follow temperature.

[21] The size effect in *U. peregrina* and *B. inflata* has not been tested due to their limited abundances in the samples. Results for these species are therefore a composite of all size fractions (Figures 3c and 3d). Core-top data for these two species show a slight decrease in Mg/Ca with decreasing BWT. The $\delta^{18}\text{O}$ of these species also tends to exhibit lighter $\delta^{18}\text{O}$ at shallower sites.

[22] Figure 4 presents the Mg/Ca ratios and $\delta^{18}\text{O}$ of calcite versus water depth for the epifaunal *C. wuellerstorfi* and *C. kullenbergi*. *Cibicidoides kullenbergi* Mg/Ca shows a rather large scatter, both for different water depths (when a single size fraction is considered) and for different size fractions (Figure 4a). Our *C. kullenbergi* Mg/Ca values are significantly higher than other published Mg/Ca values from the Atlantic Ocean [Elderfield et al.,

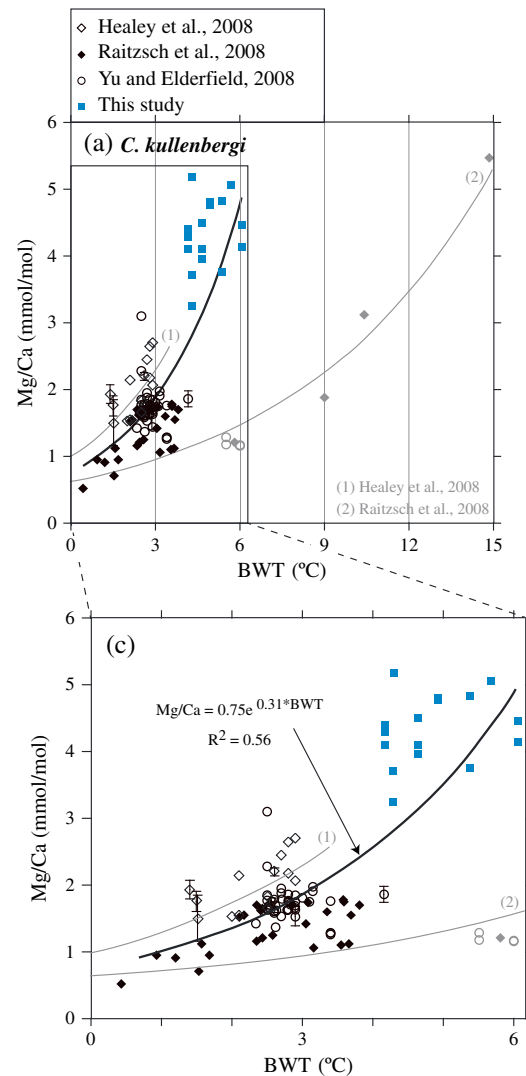


Figure 6. Core-top *C. kullenbergi* Mg/Ca versus BWT from Atlantic sites from different sources. Published temperature calibrations (gray lines) on *C. kullenbergi* are shown.

2006; Lear et al., 2003; Raitzsch et al., 2008; Yu and Elderfield, 2008]. The temperature difference between this study area and those used in the previous studies in the Atlantic may account for some of this difference. In spite of rigorous cleaning, iron contamination is apparent in *C. kullenbergi* measurements, with Fe/Ca ratios 10 times higher than the recommended maximum ratio [Barker et al., 2003]. However, there is no significant correlation between Mg/Ca and Fe/Ca ($r^2=0.1$). This is unlikely to be the result of inadequate cleaning since the cleaning procedure for *C. kullenbergi* was identical to that of *C. wuellerstorfi*. Also, the measured *C. kullenbergi* $\delta^{18}\text{O}$ values do not show

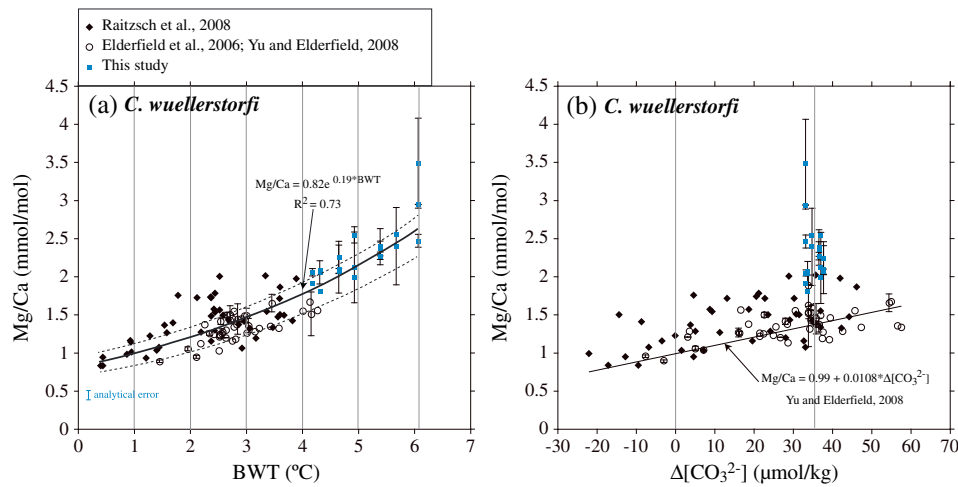


Figure 7. (a) Core-top *C. wuellerstorfi* Mg/Ca versus BWT from Atlantic sites from different sources. The black error bars associated to the marks represent standard errors. The dark line represents the Mg/Ca-temperature calibration for ~0–6°C temperature range. Dashed lines bracket the 95% confidence interval. (b) Core-top *C. wuellerstorfi* Mg/Ca versus $\Delta[CO_3^{2-}]$ from Atlantic sites from different sources.

the same large scatter as the measured *C. kullenbergi* Mg/Ca (Figure 4b).

[23] Figure 4c shows a decrease in *C. wuellerstorfi* Mg/Ca values with decreasing BWT. There is no apparent size effect in the dataset for the three size fractions tested (Figure 4c). These results clearly suggest a positive relationship between Mg/Ca and calcification temperature, and a higher temperature sensitivity than observed for other species in this study (Figures 3c and 4c). *Cibicidoides wuellerstorfi* $\delta^{18}\text{O}$ values are also seen to increase with increasing water depth, closely following observed temperatures along the transect (Figure 4d).

5. Discussion

[24] Since the bottom waters associated with our core transect are characterized by very little variability in all properties except temperature, we expect this to be the dominant control on Mg/Ca and $\delta^{18}\text{O}$ for the different species included in this study.

5.1. Mg/Ca of Infaunal Species

[25] For most of the infaunal species, our results do not clearly indicate on how Mg/Ca and $\delta^{18}\text{O}$ respond to changes in physical properties (i.e., temperature) within the water column. In the upper part of the transect, we observe a tendency for high Mg/Ca ratios (mmol/mol) to correlate with higher BWT (Figure 3). Infaunal foraminiferal $\delta^{18}\text{O}$ also show slightly lower values moving upward in the water column.

[26] To extend the temperature range of our calibration, we combined different datasets from different regions of the world ocean (Figure 5) [Bryan and Marchitto, 2008; Elderfield et al., 2010; Healey et al., 2008; Lear et al., 2002; Rathman et al., 2004]. Yu and Elderfield [2008] have attributed a small difference of 0.09 mmol/mol between results obtained using the oxidative versus the reductive cleaning methods [Boyle and Keigwin, 1985; 1986]. As we have used the oxidative method [Barker et al., 2003], we applied the +0.09 mmol/mol correction to the *Uvigerina* species and *O. umbonatus* datasets to allow us to directly compare all the data [Bryan and Marchitto, 2008; Healey et al., 2008; Lear et al., 2002]. The combined Mg/Ca linear regression for *Uvigerina* spp. and *U. peregrina* measurements indicates only a weak dependence on temperature, with a slope of $\sim 0.068 \pm 0.007$ mmol/mol/°C, over a temperature range of 1–11°C (Figure 5a). As shown by Bryan and Marchitto [2008], there does not appear to be significant interspecies differences within the genus *Uvigerina*, in contrast to the clear differences observed between *Cibicidoides* species [Elderfield et al., 2006].

[27] Our *O. umbonatus* Mg/Ca data agree well with the dataset from Rathman et al. [2004] (Figure 5b). Most of the *O. umbonatus* Mg/Ca ratios from Lear et al. [2002] have lower values than those from Rathman et al. [2004] study. They are also lower than our values, despite the adjustment made to account for the different cleaning methods. The Mg/Ca data from Healey et al. [2008] show a higher sensitivity than the other data [this study;

Lear *et al.*, 2002; Rathman *et al.*, 2004], and this cannot only be attributed to the different cleaning method used. Moreover, the *O. umbonatus* Mg/Ca ratios also show differences related to test size. This suggests that there may be an ontogenic effect on the *O. umbonatus* temperature response. Further work is required to clarify the Mg/Ca-temperature relationship for *O. umbonatus* and to better constrain the warmest part of the calibration (6–11°C).

[28] To summarize, our results suggest that, although the *O. umbonatus* Mg/Ca temperature sensitivity is potentially high, other factors such as test size [this study] and $\Delta[\text{CO}_3^{2-}]$ from pore water [Spero *et al.*, 1997] may substantially influence the Mg/Ca values. More studies on *O. umbonatus* Mg/Ca are thus necessary before Mg/Ca from this species can be used as a reliable temperature recorder.

5.2. Mg/Ca of Epifaunal Species

[29] We separate *C. wuellerstorfi* and *C. kullenbergi* because they have different behavior with respect to trace element incorporation. This will be further discussed in the following sections.

5.2.1. *C. kullenbergi*

[30] Although our results exhibit unusually high Mg/Ca values in Figure 4a, we examine the new *C. kullenbergi* Mg/Ca data together with other published Atlantic Mg/Ca studies [Elderfield *et al.*, 2006; Raitzsch *et al.*, 2008; Healey *et al.*, 2008; Yu and Elderfield, 2008] (Figure 6). Again, we have applied the same +0.09 mmol/mol correction to samples cleaned with the reductive method [Elderfield *et al.*, 2006; Healey *et al.*, 2008; Yu and Elderfield, 2008]. We observe a large scatter in *C. kullenbergi* Mg/Ca through the 0–15°C temperature range (Figure 6). We obtain the following equation:

$$\text{Mg/Ca}(\text{mmol/mol}) = 0.75 \pm 0.08 \times \exp[0.31 \pm 0.03 \times \text{BWT}(\text{°C})] \quad (1)$$

$$R^2 = 0.56$$

[31] This calibration equation does not include the published data between 5 and 15°C (see Figure 6 and data represented in gray). By increasing the number of data points in the 4–6°C range (where data were previously seriously lacking), we show that our calibration has much steeper slopes than the calibration of Raitzsch *et al.* [2008] but agrees well with the exponential relationship determined by Healey *et al.* [2008] for the same species. Although *C. kullenbergi* exhibits very

high Fe/Ca values and we cannot entirely exclude a potential contamination, this species Mg/Ca does appear to exhibit strong temperature sensitivity. *Cibicidoides kullenbergi* certainly has some potential for reconstructing temperature based on Mg/Ca, but more studies will be needed to confirm these results.

5.2.2. *C. wuellerstorfi*

[32] We examine our *C. wuellerstorfi* Mg/Ca data from the Brazilian margin alongside published Atlantic Mg/Ca data from Elderfield *et al.* [2006], Raitzsch *et al.* [2008], and Yu and Elderfield [2008] (Figure 7). The Norwegian Sea data are discounted here for the reason mentioned previously. We also exclude core M35024-6 from the Caribbean basin (17°N, 66°W, depth 4.71 km, $T = 4.35^\circ\text{C}$, $S = 34.98$, $\Delta[\text{CO}_3^{2-}] = 3.1 \mu\text{mol/kg}$), since it shows anomalously low Mg/Ca values for warm temperatures (see Yu and Elderfield [2008] for further details). To avoid introducing noise due to different cleaning methods, we only considered *C. wuellerstorfi* Mg/Ca data obtained using the oxidative technique [this study, unpublished data; Elderfield *et al.*, 2006; Yu and Elderfield, 2008] and laser ablation [Raitzsch *et al.*, 2008].

[33] Combining published *C. wuellerstorfi* Mg/Ca values from the 0–4°C temperature range with our Mg/Ca data from the 4–6°C range, we obtain the following relationship over the entire 0–6°C range (Figure 7a):

$$\text{Mg/Ca}(\text{mmol/mol}) = 0.82 \pm 0.04 \times \exp[0.19 \pm 0.01 \times \text{BWT}(\text{°C})] \quad (2)$$

$$R^2 = 0.73$$

[34] Our results show that *C. wuellerstorfi* Mg/Ca temperature has a steeper regression slope compared to those presented for mixed *Cibicidoides* spp. studies [Elderfield *et al.*, 2006], reinforcing the conclusion that the temperature sensitivity of *C. wuellerstorfi* is much higher than that of mixed *Cibicidoides* spp. (Figure 1 and calibration equation (2)). As previously discussed, Elderfield *et al.* [2006] suggested that the difference between *C. wuellerstorfi* and mixed *Cibicidoides* spp. calibrations (including the Norwegian Sea data) might be related to $\Delta[\text{CO}_3^{2-}]$ effect. Also, other studies suggest that BWT does not drive *C. wuellerstorfi* Mg/Ca ratios at low temperatures (below 3°C) due to the effect of $\Delta[\text{CO}_3^{2-}]$ [Yu and Elderfield, 2008; Raitzsch *et al.*, 2008]. Yu and Elderfield [2008] therefore recommend separating the

temperature signal and the $\Delta[\text{CO}_3^{2-}]$ effect on the epifaunal benthic Mg/Ca ratios. Ideally, temperature calibrations should be produced in areas where the $\Delta[\text{CO}_3^{2-}]$ can be controlled or is constant. As we have shown previously, the northeastern Brazilian margin is unusual in that it is characterized by a homogeneous $\Delta[\text{CO}_3^{2-}]$ between ~500 and 1200 m (Figures 2d and 7b). Consequently, we have produced the Mg/Ca-temperature calibration extension for *C. wuellerstorfi* in a context where the parameter considered most likely to complicate Mg/Ca paleothermometry, i.e., $\Delta[\text{CO}_3^{2-}]$ is controlled. When combining these new data with existing *C. wuellerstorfi* Mg/Ca data, we observe that the low temperature data do not appear anomalous but are consistent with the exponential curve describing the warmer temperature data. This lends strong support to the temperature control on *C. wuellerstorfi* Mg/Ca. However, we recommend that Mg/Ca calibration work in the future should focus on the temperature extremities of the calibration, where the data are sparse.

[35] Salinity variations are also very small over the Brazilian depth transect. It is therefore reasonable to assume that salinity is unlikely to exert a major control on Mg/Ca in our area either. However, the salinity effect on Mg incorporation into benthic foraminiferal calcite is poorly constrained in the literature [Dissard *et al.*, 2010; Toyofuku *et al.*, 2000] and further work is required to understand its potential impact on benthic foraminifer Mg/Ca ratios.

6. Conclusions

[36] In this study, we present new benthic foraminiferal Mg/Ca-BWT calibrations based on additional data from the western tropical Atlantic Ocean. We have produced benthic foraminiferal Mg/Ca data for the 4–6°C temperature range, using core-top samples from an area characterized by very low variability in water mass properties such as $\Delta[\text{CO}_3^{2-}]$ and salinity. This allows for more reliable calibrations of Mg/Ca versus BWT for the benthic species studied. We have also examined the species-specific Mg/Ca-BWT sensitivity as well as test size effects on Mg/Ca ratios.

[37] Our results suggest that the temperature sensitivity of the infaunal species *O. umbonatus* is higher than that of the infaunal species *Uvigerina peregrina*. However, there may be an ontogenic effect on Mg incorporation for *O. umbonatus* at the deepest sites.

Our results also show that *C. kullenbergi* Mg/Ca-temperature calibrations may have potential but need further study.

[38] Combining our new *C. wuellerstorfi* data with published data, we have extended the existing Mg/Ca-temperature calibration for this species over the temperature range from 4 to 6°C in the Atlantic Ocean. *Cibicidoides wuellerstorfi* Mg/Ca exhibits higher temperature sensitivity over the 0–6°C temperature range than mixed *Cibicidoides* spp. Mg/Ca. Since $\Delta[\text{CO}_3^{2-}]$ is homogeneous and stable in this region, we can essentially remove the question of its influence above 4°C and show that temperature is indeed the major control on *C. wuellerstorfi* Mg/Ca.

[39] Although further work is required in other parts of the Atlantic Ocean to confirm this calibration, our results clearly indicate that among the six most commonly used benthic species, *C. wuellerstorfi* has the greatest potential for reconstructing BWT between 0 and 6°C and more robustly above 4°C.

Acknowledgments

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