

Mg/Ca ratios of single planktonic foraminifer shells and the potential to reconstruct the thermal seasonality of the water column

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[1] Mg/Ca ratios of surface and subsurface dwelling foraminifera provide valuable information about the past temperature of the water column. Planktonic foraminifera calcify over a period of weeks to months. Therefore, the range of Mg/Ca temperatures obtained from single specimens potentially records seasonal temperature changes. We present solution-derived Mg/Ca ratios for single specimens of the planktonic foraminifera species *Globigerinoides ruber* (pink), *Globigerinoides ruber* (white), and *Globorotalia inflata* from a sediment trap off northwest Africa (20°45.6'N, 18°41.9'W). Cleaning of single specimens was achieved using a flow-through system in order to prevent sample loss. Mg/Ca ratios of surface dwelling *G. ruber* (pink) show strong seasonality linked to sea surface temperature. Mg/Ca ratios of *G. ruber* (white) do not show such seasonality. Subsurface dwelling *G. inflata* flux is largest during the main upwelling season, but Mg/Ca ratios reflect annual temperatures at intermediate water depths. The sediment trap time series suggests that changes in the range of Mg/Ca ratios exhibited by single specimens of *G. ruber* (pink) and *G. inflata* from the sedimentary record should provide information on the past temperature range under which these species calcified. Statistical analysis suggests detectable changes in the Mg/Ca range are ≥ 0.80 mmol/mol (*G. ruber* (pink)) and ≥ 0.34 mmol/mol (*G. inflata*). For *G. ruber* (pink), such changes would indicate changes in the seasonal sea surface temperature range $>4^{\circ}\text{C}$ or a shift in the main calcification and reproductive period. For *G. inflata*, such changes would indicate $>1.7^{\circ}\text{C}$ changes in the thermocline temperature or a change in the depth habitat.

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1. Introduction

[2] Planktonic foraminifer Mg/Ca ratios are important for reconstructing changes in sea surface temperature (SST) [e.g., Elderfield and Ganssen, 2000; Dekens et al., 2008] and water column temperatures [e.g., Cléroux et al., 2007, 2008] related to climatic change. Numerous studies have shown that the Mg content of the shells of foraminifera correlates positively with the water temperature during calcification [e.g., Nürnberg et al., 1996; Lea, 1999; Elderfield and Ganssen, 2000; Anand et al., 2003; Cléroux et al., 2007;

Dekens et al., 2008]. Mg/Ca temperature calibrations are based on laboratory experiments [e.g., Nürnberg et al., 1996], core top calibrations [e.g., Elderfield and Ganssen, 2000; Cléroux et al., 2007; Groeneveld and Chiessi, 2011] or sediment trap studies [Anand et al., 2003; McConnell and Thunell, 2005]. As such the Mg/Ca ratio of planktonic foraminifera shells is commonly used as a proxy for reconstructing the temperature at the depth in which the utilized species preferentially calcify. The calcification depth of planktonic foraminifera differs for various species. Therefore, a thorough understanding of foraminifer ecology and species specific calibration is needed in order to reconstruct past ocean temperatures with confidence.

[3] *Globigerinoides ruber* (pink) is a tropical to subtropical species [Hemleben et al., 1989] and lives predominantly in the upper 50 m of the water column [e.g., Bé, 1977] preferentially calcifying in the upper 25 m [e.g., Ravelo et al., 1990; Anand et al., 2003; Tedesco et al., 2007; Steph et al., 2009]. Ganssen and Kroon [2000] suggest *G. ruber* (pink) is

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restricted to temperatures above 20°C, while Žarić *et al.* [2005] report a wider tolerance range of 16.4°C–29.6°C.

[4] *Globigerinoides ruber* (white) is a tropical to transitional, mixed layer dwelling species [e.g., Bé, 1977; Ganssen and Kroon, 2000; Mohtadi *et al.*, 2009] and has a slightly wider temperature tolerance range than *G. ruber* (pink). It possesses photosynthetic algal symbionts and favors a life in the photic zone, where it is found in significant numbers [Fairbanks *et al.*, 1982], migrating between the upper photic zone and the chlorophyll maximum [Wilke *et al.*, 2009].

[5] *Globorotalia inflata* is a transitional to subpolar species [Hemleben *et al.*, 1989], and lives in waters with a temperature range between 8 and 18°C [e.g., Bé and Hamlin, 1967; Farmer *et al.*, 2010]. It is very abundant in the upwelling region off northwest Africa, where it constitutes 25% of the recent sedimentary planktonic foraminifers [Diester-Haass *et al.*, 1973, Appendix Table 1]. The apparent calcification depth of *G. inflata* is suggested to vary between 100 and 600 m [Erez and Honjo, 1981; Elderfield and Ganssen, 2000; Ganssen and Kroon, 2000; Anand *et al.*, 2003; Chiessi *et al.*, 2007; Groeneveld and Chiessi, 2011]. Like many species, *G. inflata* adds crust calcite to its primary calcite test at greater depth and colder temperatures [e.g., Caron *et al.*, 1990]. This can bias geochemical signals to a deeper apparent calcification depth [Groeneveld and Chiessi, 2011; van Raden *et al.*, 2011], although the difference in Mg/Ca between crust and primary calcite cannot be explained entirely by depth migration [Hathorne *et al.*, 2009]. *G. inflata* has been abundantly found in the subsurface seasonal thermocline and the mixed layer, coincident with the maximum chlorophyll *a* concentration [Ravelo *et al.*, 1990; Wilke *et al.*, 2006]. As such, *G. inflata* has been used to reconstruct water temperatures around the seasonal thermocline [Cléroux *et al.*, 2007, 2008]. *G. inflata* has small symbiotic algae [Gastrich, 1987], restricting it to the photic zone during at least part of its life cycle.

[6] Planktonic foraminifera calcify over a period of a couple of weeks to months [e.g., Bé and Spero, 1981; Hemleben *et al.*, 1989], with the reproductive cycle often triggered by the synodic lunar cycle [e.g., Spindler *et al.*, 1979; Bijma and Hemleben, 1990]. Single specimens thus potentially record short-term temperature variations. However, in standard geochemical analyses, this potential is not exploited, as traditionally, multiple (about 10 to 30) specimens are analyzed at once. This is necessary in order to obtain a representative average temperature, and to achieve sufficient material for a reliable analysis since a substantial amount of material can be lost during standard cleaning procedures [Boyle, 1981; Lea and Boyle, 1991; Barker *et al.*, 2003]. Analyses using standard cleaning techniques can therefore only provide average temperatures, which may additionally be biased toward the main reproductive period of the species.

[7] The importance of single-shell $\delta^{18}\text{O}$ analyses of planktonic foraminifera for paleoceanographic questions is becoming increasingly recognized [Spero and Williams, 1989] and such analyses have been applied to quantify past El Niño–Southern Oscillation (ENSO) and thermocline variance [Koutavas *et al.*, 2006; Leduc *et al.*, 2009]. Recently, laser ablation inductively coupled plasma-mass

spectrometry (LA-ICP-MS) has been used to investigate interspecimen Mg/Ca variability in surface dwelling foraminifera [Sadekov *et al.*, 2008; Wit *et al.*, 2010; Marr *et al.*, 2011]. These studies suggest the variability is partly related to seasonal and interannual changes in sea surface temperature and that it resembles the seasonal range of temperatures at the sea surface. However, the interpretation of changes of the Mg/Ca variability for paleoceanographic reconstructions requires natural Mg/Ca variability, not linked to environmental change, to be well defined. Here we constrain this natural Mg/Ca variability for *G. ruber* (pink), *G. ruber* (white) and *G. inflata* from a sediment trap time series.

[8] In this study, we utilized a flow-through system [Haley and Klinkhammer, 2002], enabling Mg/Ca measurements on single shells of planktonic foraminifera from a sediment trap off Cape Blanc, Mauritania, northwest Africa, (20°45.6'N, 18°41.9'W). We test several Mg/Ca temperature equations for their applicability to single specimens of three planktonic foraminiferal species (*G. ruber* (white), *G. ruber* (pink), *G. inflata*) and investigate the potential of single tests to assess short-term temperature variations. We further evaluate and explain the variability in Mg/Ca temperatures among single specimens of these species, with a focus on their potential applicability in paleoceanographic studies.

2. Study Area

[9] The study area off Cape Blanc (northwest Africa) is dominated by the seasonal migration of the Inter Tropical Convergence Zone (ITCZ), accompanied by a strong seasonal SST contrast (Figure 1). The amplitude of the annual SST cycle (Figure 2) derived from the advanced very high resolution radiometer at 20°22.5'N and 18°22.5'W (<http://www.ncdc.noaa.gov>) was 9.6°C during the deployment period with highest temperatures in mid-September (27.7°C) and lowest temperatures in mid-March (18.1°C). This large annual amplitude of SST is ideal for our study. The main surface current in the study area is the Canary Current, which flows south along the northwest African coast as the eastern branch of the North Atlantic Subtropical Gyre. The Canary Current is modulated by southwestward directed trade winds (Figure 1) which blow throughout the year between 20°N and 25°N [Schemainda *et al.*, 1975] and cause perennial upwelling off Cape Blanc. Upwelling is strongest in late spring and autumn [Ganssen and Sarnthein, 1983; Pelegri *et al.*, 2005]. As a result of the steady trade winds and Ekman pumping, surface waters are transported offshore and replaced by upwelled waters. The upwelled water off northwest Africa consists of two distinct water masses: the North Atlantic Central Water (NACW) and the South Atlantic Central Water (SACW). Generally, to the south of 24°N, upwelled water is dominated by low salinity (35.6–35.9‰) SACW [Mittelstaedt, 1983] transported by a northward flowing undercurrent at a depth between 200 m and 400 m [Hagen, 2001]. To the north, upwelled water consists of the higher salinity (36.1–36.4‰) North Atlantic Central Water (NACW) [Mittelstaedt, 1983]. The nutrient contrast between NACW and SACW is expressed by nitrate increasing southward from 5 to 20 mmol/m³ [Pérez-Rodríguez *et al.*, 2001; Pelegri *et al.*, 2005]. Off Cape

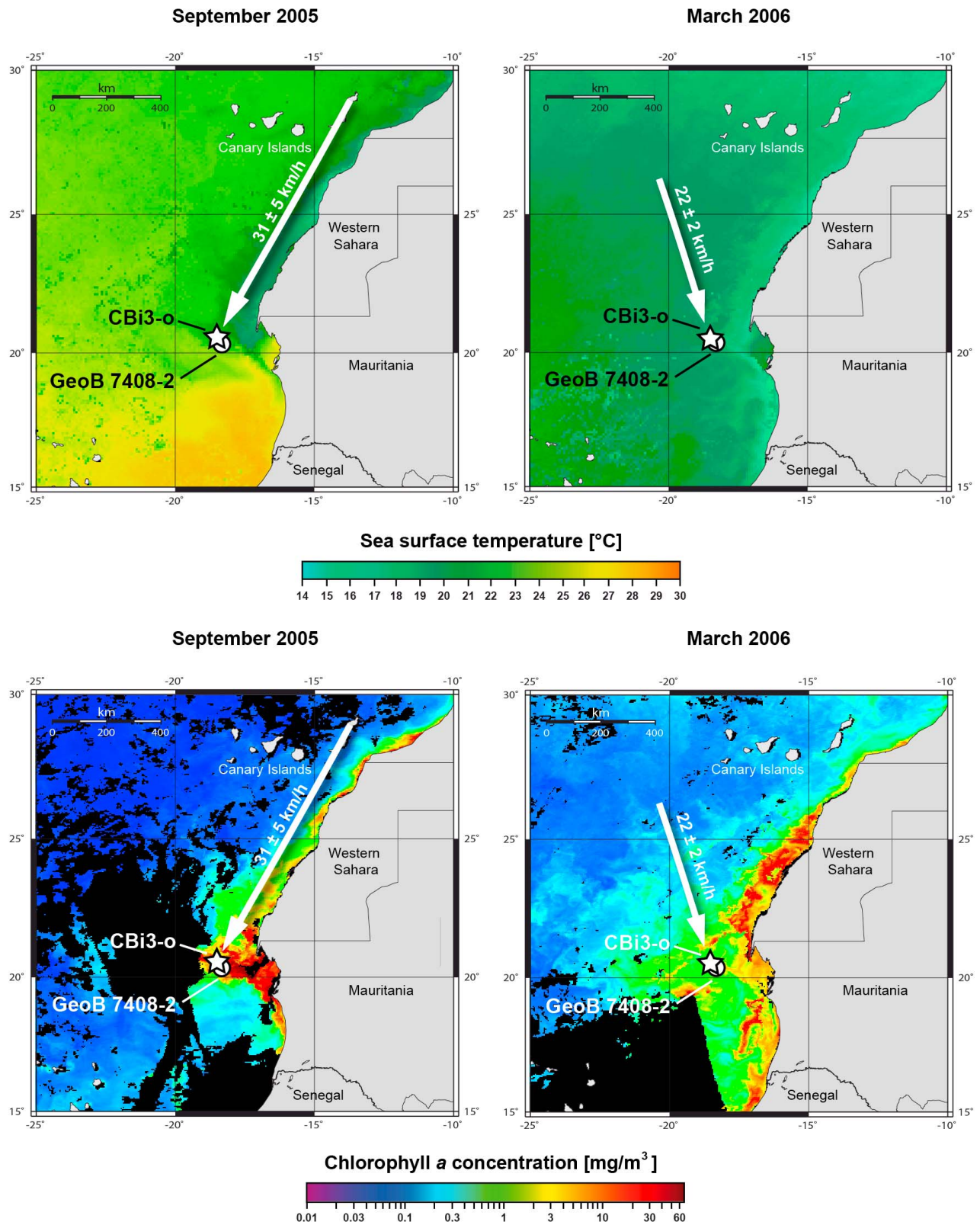


Figure 1. Map of the study area with SST, chlorophyll *a* concentrations, and surface winds. The sediment trap (indicated by a star) is located at 20°45.6'N, 18°41.9'W off Cape Blanc, northwest Africa. The location of core top GeoB 7408-2 is indicated by a circle. SSTs and chlorophyll *a* concentrations reflect the period from 22 to 29 September 2005 and from 14 to 21 March 2006, respectively. Arrows indicate average wind direction during the respective period, and the average wind speed and standard deviation (1σ) are given.

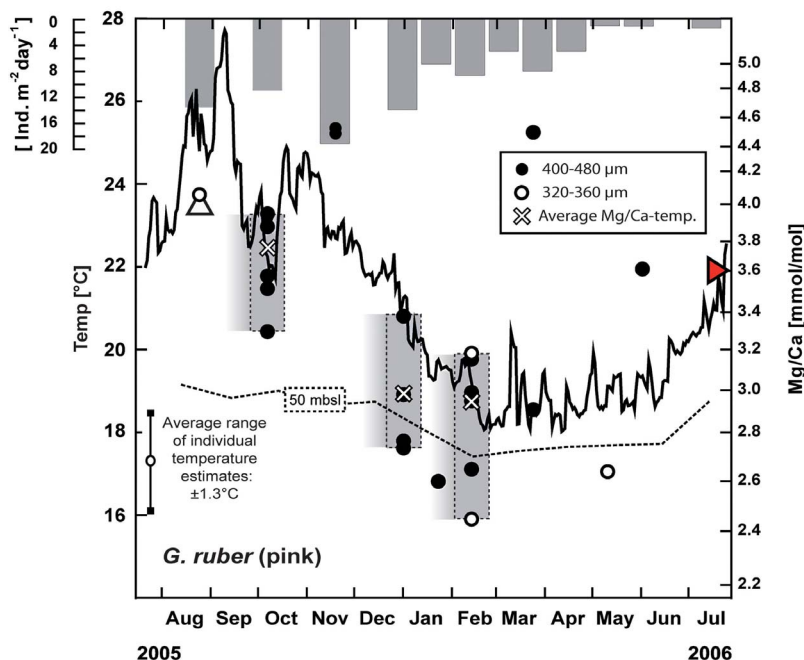


Figure 2. Single-specimen Mg/Ca ratios and Mg/Ca temperatures of *G. ruber* (pink) compared to SST. The black solid line shows the daily SST and is derived from the advanced very high resolution radiometer at 20°22.5'N, 18°22.5'W. The dashed line indicates monthly averaged temperatures at a depth of 50 m from the WOA 05. The gray bars indicate the range of individual Mg/Ca temperatures, when the *Regenberg et al.* [2009] calibration after the ACD of *Mulitza et al.* [2004] is used. Shaded gray bars indicate two weeks, which corresponds to the period during which the majority of the shell mass is precipitated. All individual data points are calculated after the *Regenberg et al.* [2009] calibration. The gray bars at the top indicate the shell flux of *G. ruber* (pink) to the sediment trap. Where no bars are shown, no *G. ruber* (pink) were collected. The white triangle indicates the Mg/Ca temperature derived from the multispecimen analysis of 10 specimens. The red triangle on the axis indicates the flux-weighted annual mean Mg/Ca ratio.

Blanc, the Canary Current detaches from the coast, promoting the development of a large filament of upwelled water extending up to 500 km offshore [*Pérez-Rodríguez et al.*, 2001; *Pelegri et al.*, 2005], which travels over the sediment trap site. Independent of its source, the temperature of the upwelled water ranges between 15°C and 17°C [*Mittelstaedt*, 1983].

3. Material and Methods

3.1. Sample Collection

[10] Samples were obtained from a sediment trap moored ~170 km off Cape Blanc (20°45.6'N, 18°41.9'W) at 1277 m below sea level (mbsl), 1416 m above seafloor (Figure 1). The sediment trap with a surface opening of 0.5 m² was equipped with 20 collecting cups and poisoned with HgCl₂. Samples were collected in intervals of 21.5 days between 25 July 2005 and 28 September 2006. Recovery and redeployment took place during R/V *Poseidon* cruise 344 [*Fischer et al.*, 2008]. Every cup was divided into 5 aliquots using a rotating splitter, of which one was used for this study. When possible, additional aliquots were used to obtain enough specimens for analysis. The shallow depth of the sediment trap precludes any dissolution of the samples. Specimens of ~420 μm size (as used in this

study) sink at 1295 m day⁻¹ [*Takahashi and Bé*, 1984] and thus reach the sediment trap within about one day. With an approximate eddy kinetic energy of 40 cm² s⁻² at the study site [*Hecht and Hasumi*, 2008] the horizontal averaging scale for a sediment trap at 1000 m depth ranges between 1 and 10 km [*Siegel et al.*, 1990].

[11] The top centimeter of multicore GeoB 7408-2 at 20°17.4'N, 18°15.0'W from a water depth of 1935 m, obtained during R/V *Poseidon* cruise 272 [*Meggers et al.*, 2002] was used to study sedimentary shells. Individual specimens were picked and their size and morphology noted under the binocular microscope. Most *G. inflata* (d'Orbigny) specimens had four chambers in the last whorl and had moderately thickened walls. All *G. ruber* specimens were strictly from the *G. ruber sensu stricto* morphotype [*Wang*, 2000].

3.2. Cleaning Procedures

[12] As the foraminifera originate from a sediment trap that was located well above the seafloor, only oxidative cleaning was performed as organic matter can contaminate Mg/Ca measurements [e.g., *Hastings et al.*, 1996; *Barker et al.*, 2003]. We used a flow-through system [*Haley and Klinkhammer*, 2002] run offline to clean single specimens with minimal sample loss. Sample loss is signifi-

cant using traditional cleaning techniques [Boyle, 1981; Barker *et al.*, 2003] especially with small sample sizes. In the flow-through system, we placed single specimens between two PTFE filters and subjected them to a constant flow (2 mL min^{-1}) of suprapure H_2O_2 (30%) diluted to 1% in 0.1 M analytical grade NaOH (heated to $\sim 60^\circ\text{C}$) for >20 min. The samples were then rinsed for 46 min in a flow (6 min at 4 mL min^{-1} , then 40 min at 1 mL min^{-1}) of pure water ($>18 \text{ M}\Omega \text{ cm}$). To avoid dissolution during rinsing, the pH of the deionized water was kept above 7 by adding a few drops of suprapure NH_3 solution. After cleaning individuals were taken off the filter, examined under the binocular microscope to determine if they remained intact during cleaning, before being transferred to clean vials and dissolved in $500 \mu\text{L}$ thermally distilled (TD) 0.075 M HNO_3 . Samples that broke during cleaning are not considered. After centrifugation for 10 min at 6000 rpm the sample solution was transferred to clean vials for measurement.

[13] For multispecimen analysis of sediment samples, 10 *G. inflata* specimens were picked from the 400–480 μm size fraction. Cleaning was applied according to Barker *et al.* [2003]. The solution was then centrifuged (10 min at 6000 rpm) and transferred into clean tubes and diluted for measurement.

3.3. Data Acquisition

[14] Mg/Ca ratios were acquired using two approaches: The thin shells of *G. ruber* (pink and white) produced solutions with low Ca concentrations requiring Mg/Ca ratios to be determined with the more sensitive inductively coupled plasma mass spectrometry (ICP-MS) technique. The Ca concentrations of the sample solutions were first measured on a Perkin-Elmer Optima 3300R inductively coupled plasma-optical emission spectrometer (ICP-OES) equipped with an ultrasonic nebulizer U-5000 AT (Cetac Technologies Inc.) at the faculty of Geosciences, University of Bremen. Samples for ICP-MS analysis were then diluted to have Ca concentrations of 2 or 5 ppm. Standard solutions with the same Ca concentration were prepared gravimetrically from single element solutions to have Mg/Ca ratios of 4.90 mmol/mol (for measurements of *G. ruber* (pink and white)) and 1.92 mmol/mol (for measurements of *G. inflata*). Mg/Ca ratios were determined using the method of Rosenthal *et al.* [1999] from intensities measured on a Thermo-Finnigan Element 2 sector field ICP-MS at the University of Bremen. During this study the measured Mg/Ca ratios of carbonate reference materials ECRM 752-1 and JCT-1 diluted like the samples, were on average 3.69 mmol/mol ($n = 19$; $\sigma = 0.03 \text{ mmol/mol}$), and 1.28 mmol/mol ($n = 7$; $\sigma = 0.01 \text{ mmol/mol}$), respectively. This is in good agreement with the reported Mg/Ca ratios of 3.75 mmol/mol for the ECRM 752-1 [Greaves *et al.*, 2008] and 1.25 mmol/mol for the JCT-1 [Okai *et al.*, 2004]. All blanks analyzed were below the average detection limits of 0.011 ppb Mg and 1.49 ppb Ca.

[15] The relatively thick shells of *G. inflata* contained enough CaCO_3 for the determination of Mg/Ca ratios using ICP-OES. Potential drift was monitored by analysis of an in-house standard solution. Values from different ICP-OES analytical sessions were normalized using this standard solution.

[16] Mg/Ca ratios of *G. ruber* (pink), *G. ruber* (white) and *G. inflata* were used to calculate temperatures during cal-

cification using the calibrations listed in Table S1 in the auxiliary material.¹ Shell mass was calculated from the Ca concentration of the sample solution assuming that Ca in the sample solution derives solely from CaCO_3 of the dissolved specimen [Yu *et al.*, 2008].

3.4. Statistics

[17] To approximate the value that would be expected in the sedimentary record, Mg/Ca values of the cups that contained enough specimens for analysis were flux-weighted by multiplying each value by the ratio of the flux of that cup to the total flux, and then summing the respective values to produce a single value. This must be considered a first order approximation since the Mg/Ca ratio could not be measured for foraminifera from every cup so some periods of the year are not considered.

[18] For the interpretation of the average Mg/Ca ratios from 123 specimens of *G. inflata* that were collected throughout the year, it is necessary to calculate if the average is representative and acceptably accurate. The accuracy of the calculation of the average Mg/Ca ratio is given by e (equation (1)), at the 95% confidence level, specified by $\alpha = 0.05$. σ^2 is the variance and n the number of samples:

$$e = \sqrt{\frac{z^2(1 - \frac{\alpha}{2})\sigma^2}{n}} \quad (1)$$

[19] We use the quantile $z_{0.975} = 1.96$ for a standardized normal distribution, which can be approximately assumed for random samples with $n > 30$. Equation (1) uses the variance σ^2 of the total statistical population. Since we only have data on a subpopulation, we have to approximate σ^2 using equation (2), where x_i is the respective sample, \bar{x} is the average of all samples and $E(S^2)$ is the expected value of σ^2 :

$$S^2 = \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2 \quad (2)$$

The 95% confidence interval of the average Mg/Ca ratio is calculated according to equation (3), where s is the standard deviation of all samples. Again, we use the quantile $z_{0.975} = 1.96$, defining the 95% confidence level, with $\alpha = 0.05$:

$$\left[\bar{x} - z \left(1 - \frac{\alpha}{2} \right) \frac{s}{\sqrt{n}}, \bar{x} + z \left(1 - \frac{\alpha}{2} \right) \frac{s}{\sqrt{n}} \right] \quad (3)$$

In order to estimate the change of the variance that would be statistically significant and therefore detectable, we calculate the confidence interval of the variance, according to equation (4), where S is the standard deviation, n is the number of samples and $\alpha = 0.05$ defines the level of confidence of 95%:

$$\left[\frac{(n-1)^*S^2}{\chi^2/(n-1, \frac{\alpha}{2})}, \frac{(n-1)^*S^2}{\chi^2/(n-1, 1 - \frac{\alpha}{2})} \right] \quad (4)$$

Since Mg/Ca ratios lack symmetry, mean values and variance were calculated in logarithmic space and then reconverted to sample space. To minimize the effects of

¹Auxiliary materials are available in the HTML. doi:10.1029/2010PA002091.

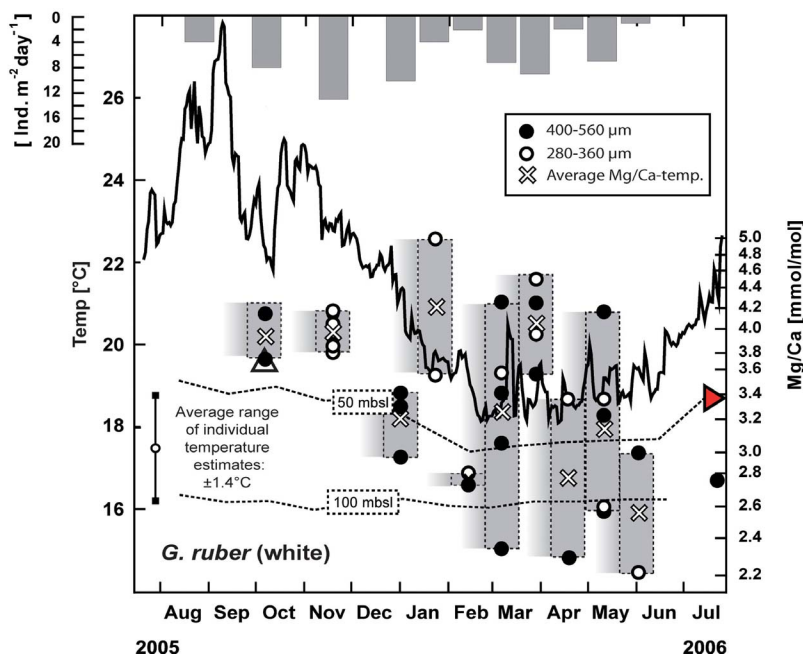


Figure 3. Single-specimen Mg/Ca ratios and Mg/Ca temperatures of *G. ruber* (white) compared to SST. Black line shows the daily SST and is derived from the advanced very high resolution radiometer at 20°22.5'N, 18°22.5'W. Shaded gray bars indicate two weeks, which corresponds to the period during which the majority of the shell mass is precipitated. Dashed lines indicate monthly averaged temperatures at depths of 50 m and 100 m from the WOA 05. Mg/Ca temperatures are calculated after the Elderfield and Ganssen [2000] calibration. The gray bars at the top indicate the shell flux of *G. ruber* (white) to the sediment trap. Where no bars are shown, no *G. ruber* (white) were collected. The white triangle indicates the Mg/Ca temperature derived from the multispecimen analysis of 10 specimens. The red triangle on the axis indicates the flux-weighted annual mean Mg/Ca ratio.

potential outliers, we do not interpret data lying further than 2σ from the sample mean.

4. Results

4.1. *G. ruber* (pink)

[20] Unbroken specimens of *G. ruber* (pink) were analyzed from 9 out of 16 cups (Table S2). Individual Mg/Ca ratios of *G. ruber* (pink) show strong seasonal differences ranging between 2.45 mmol/mol (November 2005) and 4.53 mmol/mol (February 2006) (Figure 2).

[21] Mg/Ca ratios of single specimens of the surface dweller *G. ruber* (pink) show strong variability within the sampling intervals, with a maximum intracup range of 0.73 mmol/mol during February 2006 (Table S2). The mean deviation of individual measurements from the average Mg/Ca ratio within the sampling intervals was 0.27 mmol/mol. Mg/Ca values show no systematic differences between larger and smaller specimens within the limited size range investigated. Two outliers in December 2005 and March 2006 with Mg/Ca ratios corresponding to temperatures more than 4°C different from the measured SST (see section 5.2.1, *G. ruber* (pink)) are not included in the discussion. A multispecimen analysis from the cup spanning the period 15 August 2005 to 6 September 2005 yields a Mg/Ca ratio of 3.98 mmol/mol.

[22] *G. ruber* (pink) was collected throughout the year with highest fluxes between August 2005 and December

2005 (maximal 19 individuals $\text{m}^{-2} \text{day}^{-1}$ during November 2005). During the time of highest fluxes, highly variable flux rates were observed and in some cups no *G. ruber* (pink) were found at all. The estimation of flux rates is based on samples collected from splits that contained a substantial amount of plankton and other collected material. Some specimens might therefore have been overlooked and the interpretation of flux rates should be made with some caution. The flux weighted annual Mg/Ca ratio is 3.57 mmol/mol.

4.2. *G. ruber* (white)

[23] Unbroken specimens of *G. ruber* (white) were analyzed from 11 out of 16 cups (Table S2). The highest Mg/Ca ratio of 4.94 mmol/mol was recorded in January 2006 (Figure 3) and the lowest Mg/Ca ratio of 2.20 mmol/mol was recorded in June 2006. Within the sampling intervals, Mg/Ca ratios of single specimens of *G. ruber* (white) show pronounced variability, with a maximum intracup range of 1.91 mmol/mol in March 2006 (Figure 3). On average, the deviation of individual measurements from the average Mg/Ca ratio within the sampling intervals was 0.45 mmol/mol. Mg/Ca values show no systematic differences between larger and smaller specimens or between different sampling intervals. A multispecimen analysis from the cup spanning the period 27 September 2005 to 9 October 2005 yields a Mg/Ca ratio of 3.65 mmol/mol.

[24] *G. ruber* (white) was collected throughout the year with only moderate annual variability (maximal

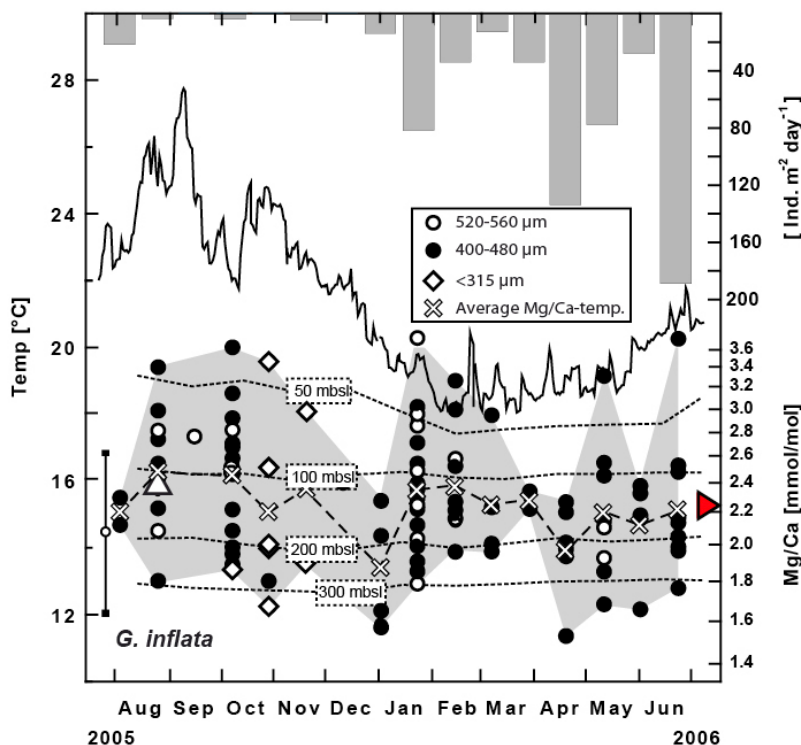


Figure 4. Single-specimen Mg/Ca ratios, Mg/Ca temperatures, and flux rates of *G. inflata* off Cape Blanc. The black line indicates the daily SST and is derived from the advanced very high resolution radiometer at $20^\circ 22.5' \text{N}$, $18^\circ 22.5' \text{W}$. The narrow-spaced dashed lines indicate monthly averaged temperatures at the shown depths from the WOA 05. Crosses connected with a wide-paced dashed line indicate average Mg/Ca temperatures. The vertical bar indicates the average range of individual temperature estimates of $\pm 2.5^\circ\text{C}$. Mg/Ca temperatures are calculated after the Elderfield and Ganssen [2000] calibration. The gray bars at the top indicate the shell flux of *G. inflata* to the sediment trap. The white triangle indicates the Mg/Ca temperature derived from the multispecimen analysis of 10 specimens. The red triangle on the axis indicates the flux-weighted annual mean Mg/Ca ratio.

13 individuals $\text{m}^{-2} \text{day}^{-1}$ during November 2005). Between August 2005 and November 2005 strong changes in flux rates were observed and in some cups, no *G. ruber* (white) specimens were found at all. As noted above, the interpretation of flux rates should be made with some caution. The flux weighted annual Mg/Ca ratio is 3.38 mmol/mol.

4.3. *G. inflata*

[25] Unbroken specimens of *G. inflata* were analyzed from all 16 cups (Table S2). The highest Mg/Ca ratio of 3.72 mmol/mol was recorded in January 2006, while the lowest Mg/Ca ratio of 1.53 mmol/mol was recorded in April 2006 (Figure 4). A seasonal trend between different sampling intervals for *G. inflata* is not apparent, however strong variations in the Mg/Ca ratio occur within each of the sampling intervals. The largest intracup range in the Mg/Ca ratio of *G. inflata* of 1.95 mmol/mol is recorded during June 2006 (Figure 4). On average, the deviation of individual values around the average Mg/Ca ratio of a sampling interval is 0.64 mmol/mol. A multispecimen analysis from the cup spanning the period from 15 August 2005 to 6 September 2005 yields a Mg/Ca ratio of 2.42 mmol/mol.

[26] We found pronounced differences in the flux of *G. inflata* at the study site (Figure 4). From August 2005

to January 2006, few specimens were collected (maximal 21 individuals $\text{m}^{-2} \text{day}^{-1}$). From January 2006 to the end of June 2006, fluxes increased to reach a maximum of 188 individuals $\text{m}^{-2} \text{day}^{-1}$ during June 2006. The flux weighted Mg/Ca ratio is 2.23 mmol/mol. The Mg/Ca ratio of a multispecimen core top sample from GeoB 7408-2 is 2.23 mmol/mol.

5. Discussion

5.1. Seasonal Shell Abundance

[27] *G. ruber* (pink) and *G. ruber* (white) were collected throughout the year (Figures 2 and 3). Fluxes of both species were very variable. Higher fluxes between August 2005 and January 2006 were found for both species, however this is more pronounced for *G. ruber* (pink) than for *G. ruber* (white). Fluxes of *G. inflata* between January 2006 and June 2006 were much higher than and nearly a mirror image of the fluxes of *G. ruber* (pink). The differences in abundance are assumed to result from the exceptional seasonal changes in the study area. In the upper water column, these changes are controlled by large differences in SST. The large Cape Blanc upwelling filament is also important. In September 2005, the filament moved right over the sediment trap

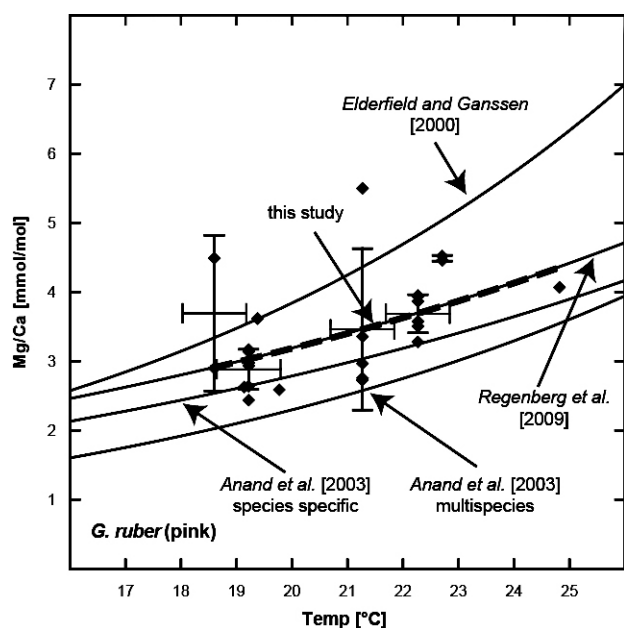


Figure 5. Comparison of *G. ruber* (pink) Mg/Ca ratios from this study to published Mg/Ca temperature calibrations. The lines represent Mg/Ca temperature calibrations of Elderfield and Ganssen [2000], Anand et al. [2003], and Regenberget al. [2009] using the ACD of Mulitza et al. [2004]. Mg/Ca ratios of *G. ruber* (pink) from this study are shown as diamonds, and the exponential fit to these ratios is shown as a dashed line. Vertical error bars show sample standard deviation; horizontal error bars show root-mean-square error (degrees Celsius) of the advanced very high resolution radiometer derived SST from in situ SST as given by She et al. [2007].

(Figure 1), with high nutrient concentrations at the surface evident by high chlorophyll *a* concentrations. Conversely, in March 2006, the filament was absent in the study area (Figure 1). Water temperatures, the thermal stratification of the water column and nutrient availability are likely to act in concert to control shell fluxes at the study site.

[28] *G. ruber* (pink) was most abundant during summer/fall with warm sea surface temperatures. This is in agreement with the study of Wilke et al. [2009] who showed that *G. ruber* (pink) is most abundant when surface mixed layer temperatures are higher than 20°C. Additionally, the strong thermal stratification during the summer has been reported to favor *G. ruber* [Sautter and Sancetta, 1992]. High nutrient levels evident by high chlorophyll *a* concentrations (Figure 1) are also expected to favor the development of *G. ruber* (pink).

[29] In contrast, *G. inflata* flux rates were lowest between August 2005 and January 2006. Since *G. inflata* records very similar Mg/Ca temperatures throughout the year, water temperatures are expected to play a minor, if any, role in controlling flux rates. It is assumed that nutrient availability controls flux rates of *G. inflata* in the study area. CTD casts show that the maximum chlorophyll *a* concentration at different seasons is found above 50 mbsl (Figure S1). It is suggested that *G. inflata* cannot make use of the high nutrient concentrations during times of a well stratified

water column in summer. Contrastingly, during the main upwelling season in winter/spring, *G. inflata* is more suited to the low nutrient concentrations (Figure 1) than *G. ruber* (pink and white).

5.2. Mg/Ca Temperature Equations

5.2.1. *G. ruber* (pink)

[30] We compare measured SSTs to Mg/Ca ratios from individual *G. ruber* (pink) shells and interpret differences as a result of calcification temperature. The exponential fit to our data is remarkably similar to the Regenberget al. [2009] equation (Figure 5). Mg/Ca temperatures derived from this equation are realistic for *G. ruber* (pink) in the study area (Figure 2). Using different Mg/Ca temperature equations, Mg/Ca temperatures range between 18.1°C and 27.2°C [Anand et al., 2003] (single species), 20.7°C and 27.5°C [Anand et al., 2003] (multispecies), 15.5°C and 21.6°C [Elderfield and Ganssen, 2000], and 15.9°C and 25.4°C [Regenberget al., 2009]. It is suggested that the Regenberget al. [2009] equation is best suited for single *G. ruber* (pink) specimens in this study for several reasons: It is species specific, in contrast to the Elderfield and Ganssen [2000] equation that does not include *G. ruber* (pink). Moreover, it is based on a larger amount of specimens (20–25) than the Anand et al. [2003] calibration (5–15 specimens). It therefore is likely that the Mg/Ca ratios derived from the multispecimen analysis include a larger range of Mg/Ca ratios and this might be crucial when working with single specimens. In addition, the Regenberget al. [2009] equation was generated solely from samples originating from the tropics, the preferred habitat of *G. ruber* (pink).

[31] Using the Regenberget al. [2009] equation, maximum Mg/Ca temperatures for most individual specimens during one collecting interval closely match the advanced very high resolution radiometer derived SST (Figure 2). We assume that these temperatures correspond to individuals that calcified in the uppermost part of the water column and that highest Mg/Ca ratios represent temperatures near the sea surface during the respective interval. Our observations are in line with Tedesco et al. [2007] who state that *G. ruber* (pink) is capable of accurately estimating SSTs throughout the year.

[32] Mg/Ca temperatures from sediment trap studies [e.g., McConnell and Thunell, 2005; Mohtadi et al., 2005] rely on the multispecimen analyses of at least 10 specimens providing an averaged temperature. We conducted a multispecimen analysis using 10 specimens from the collecting cup spanning the period from 15 August to 6 September 2005 that produced a Mg/Ca temperature of 23.4°C, similar to one single specimen Mg/Ca temperature of 23.8°C derived from this period. Not enough single specimens could be analyzed from this collecting cup to derive an average Mg/Ca temperature. The flux-weighted annual Mg/Ca value of 3.57 mmol/mol of all *G. ruber* (pink) individuals analyzed corresponds to a temperature of 21.7, thus slightly lower than the annual average temperature of 22.9°C. This suggests that *G. ruber* (pink) in the study area can be used in sediment archives to reconstruct temperatures that approximate the annual average sea surface temperature.

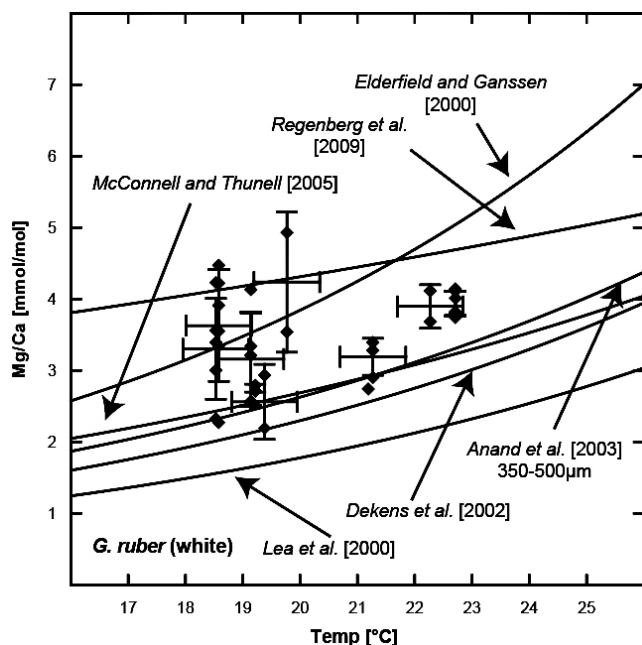


Figure 6. Comparison of *G. ruber* (white) Mg/Ca ratios from this study to published Mg/Ca temperature calibrations. The lines represent Mg/Ca temperature calibrations of Elderfield and Ganssen [2000] and Regenberg et al. [2009] using the ACD of Mulitza et al. [2004], McConnell and Thunell [2005], Anand et al. [2003], Dekens et al. [2002], and Lea et al. [2000]. Mg/Ca ratios of *G. ruber* (white) from this study are shown as diamonds. Vertical error bars show sample standard deviation; horizontal error bars show root-mean-square error (degrees Celsius) of the advanced very high resolution radiometer derived SST from in situ SST as given by She et al. [2007].

5.2.2. *G. ruber* (white)

[33] The range of Mg/Ca ratios measured from the shells of *G. ruber* (white) is large in comparison with the other species. However, the range between the lowest (2.20 mmol/mol) and highest (4.94 mmol/mol) Mg/Ca ratios is similar to that found by Sadekov et al. [2008] for *G. ruber* (1.75 mmol/mol to 5.53 mmol/mol at a site exhibiting a SST seasonality of 3.9°C).

[34] Comparison of measured SST with Mg/Ca ratios from individual *G. ruber* (white) shells (Figure 6) does not fit to any published Mg/Ca temperature equation. We can exclude that the mismatch was caused by contamination of the shells (monitored by analysis of Mn/Ca and Fe/Ca ratios) and the cleaning was identical for *G. ruber* (pink). Most Mg/Ca temperature equations [Lea et al., 2000; Dekens et al., 2002; Anand et al., 2003; McConnell and Thunell, 2005] yield temperatures substantially higher than the SST during the sampling interval at the study site and also in the adjacent areas (Figure 2). Mg/Ca temperature estimations during the time of coldest SSTs are listed in Table S3. The equations of Regenberg et al. [2009], which are dependent on different apparent calcification depths (ACDs), are an exception to the general overestimation of SSTs. However, the coldest Mg/Ca temperatures derived using the Regenberg et al. [2009] equation are unrealisti-

cally low during most of the year. The equation of Elderfield and Ganssen [2000] yields the most realistic temperatures in this study. The warmest temperatures are however still higher than the SST during the respective collecting intervals (Figure 3). Lateral advection seems unlikely due to the low horizontal averaging scale at the study site (see section 3.1). The coldest temperatures using the Elderfield and Ganssen [2000] equation correspond to unrealistically low calcification considering that *G. ruber* (white) is a symbiotic species and thrives to remain in the photic zone.

[35] An additional factor that could explain some of the variability is the pH of the ambient seawater. Lea et al. [1999] and Russell et al. [2004] have demonstrated that a 0.1 unit pH increase can account for a 6–16% decrease of the Mg/Ca ratio in the shells of *Globigerina bulloides* and *Orbulina universa*. A decreased pH in upwelled waters along the northwest African margin of 0.2 units [Weichert, 1980] could hence account for a 12–32% increase of the Mg/Ca ratios in our samples. During times of strong upwelling in late spring [e.g., Pelegri et al., 2005], this could cause an increase in Mg/Ca ratio from 3.14 mmol/mol to 4.14 mmol/mol, in line with the highest Mg/Ca ratio observed between 30 April 2006 and 22 May 2006.

[36] We conducted a multispecimen analysis consisting of 10 *G. ruber* (white) specimens from the collecting cup spanning the period from 27 September to 19 October 2005, which yielded a Mg/Ca temperature of 19.5°C. This is only 0.6°C lower than the average Mg/Ca temperature of the individual specimen analysis ($n = 2$). The flux-weighted Mg/Ca value of 3.38 mmol/mol corresponds to a temperature of 18.7°C, that is close to winter temperatures (e.g., 17 February 2006: 18.7°C). The flux weighted Mg/Ca ratio of *G. ruber* (white) in this study is however sensitive to a potential sampling bias. For example, a flux of 13 individuals $m^{-2} day^{-1}$ (as determined from 9 November to 1 December) occurring during the time of warmest SST from 25 August to 27 September, would increase the flux weighted Mg/Ca temperature by 2.7°C (using the equation of Elderfield and Ganssen [2000]). Any interpretation of the flux weighted average should therefore be made with care.

5.2.3. *G. inflata*

[37] We found a wide range of Mg/Ca ratios during each sampling interval (Figure 4) and interpret the varying Mg/Ca ratios as a result of different calcification depths and slight variations in crust calcite thickness. For the approximation of calcification depths, it is important to account for the influence of crust calcite on Mg/Ca ratios, because crust calcite can significantly change the Mg/Ca ratio of planktonic foraminifera [e.g., Nürnberg et al., 1996; McKenna and Prell, 2004; Hathorne et al., 2009; Groeneveld and Chiessi, 2011]. Groeneveld and Chiessi [2011] show that specimens of *G. inflata* with thick crusts yield systematically lower Mg/Ca ratios and emphasize the importance of defining a clear and narrow state of encrustation of the *G. inflata* specimens being used. SEM images show the surface texture of specimens from the sediment trap (Figure S2) suggesting moderate crust addition. We calculated the shell weights of *G. inflata*, in order to identify unusually heavy shells, since the addition of crust calcite would lead to heavier shells [Caron et al., 1990; Lohmann, 1995]. Shell weights within the respective size fractions range between 9.65 μg and 59.59 μg . Average weights within the respec-

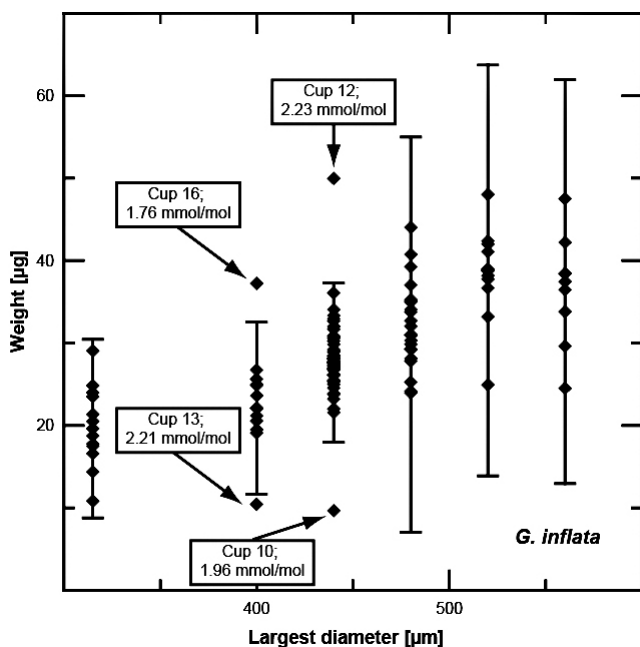


Figure 7. Size versus single-shell weight in the respective size fraction of *G. inflata* from the sediment trap (located at 20°45.6'N, 18°41.9'W). Bars indicate the range between the upper and lower quartile. Outliers and their Mg/Ca ratios are indicated.

tive size fractions are in accordance with smaller and larger shell sizes (Table S2 and Figure S3).

[38] Within size fractions, some variability of the mass of individual specimens is found (Figure 7). We compare shells of the same size to calculated shell mass, in order to identify samples that are potentially thickened by crust calcite. Samples are normally distributed, when the most lightweight and most heavy sample is excluded from the 440 μm size fraction (Shapiro-Wilk tested at a 95% level of confidence). Four outliers can be identified. The lightest and heaviest samples from the 440 μm size fraction deviate from a normal distribution. Moreover the lightest and heaviest samples from the 400 μm size fraction are outside the upper and lower quartiles. The Mg/Ca ratios of these outliers are, however, not noticeably different from all other specimens (Figure 8). We therefore conclude that there is no simple relationship between the amount of crust calcite and the Mg/Ca ratios of *G. inflata* in this study.

[39] Many studies have recognized the potential of *G. inflata* for temperature reconstructions at the base of the seasonal thermocline [e.g., Thornalley et al., 2009] but the existing temperature equations for this species differ substantially from each other [Elderfield and Ganssen, 2000; Anand et al., 2003; Cl  roux et al., 2008; Thornalley et al., 2009; Farmer et al., 2010; Groeneveld and Chiessi, 2011]. Calculation of Mg/Ca temperatures for *G. inflata* using the equations listed in Table S1 yields temperature estimates that are either too warm or too cold when compared to World Ocean Atlas temperatures [Locarnini et al., 2006]. In Table S4, we compare Mg/Ca temperature estimates from individual *G. inflata* specimens collected between 27 September and 19 October 2005 to monthly average World Ocean Atlas water column temperatures

during October [Locarnini et al., 2006]. The equations of Anand et al. [2003], Cl  roux et al. [2008], and Farmer et al. [2010] yield warmest temperatures that are 5.4  C, 6.8  C, and 13.0  C above the observed SST in the middle of the collecting period. In contrast, the equations of Elderfield and Ganssen [2000], Thornalley et al. [2009], and Groeneveld and Chiessi [2011] yield temperature estimates that fit with the water column observations (see section 5.3).

[40] A multispecimen analysis of 10 *G. inflata* specimens from the collecting cup spanning the period from 15 August to 6 September 2005, yields a Mg/Ca temperature of 16.0  C, similar to the average Mg/Ca temperature of 16.3  C from the individual specimen analyses. The close match of the average temperature derived from the multispecimen analysis and the analyses of single specimens confirms the excellent potential of our approach to measure single specimens, in order to gain information about the overall variability in Mg/Ca temperatures within a population.

[41] The average Mg/Ca temperature of *G. inflata* from the sediment trap samples reflects an annual mean temperature at a depth of about 150 m in the study area (Figure 4). The largest deviations from the average Mg/Ca temperature are measured in August 2005 (+1.1  C) and December (  1.8  C). As these periods coincide with times of low flux, they are unlikely to lead to a seasonal bias in the sedimentary record. This is supported by the multispecimen analysis of *G. inflata* from core top GeoB 7408-2, which yields a Mg/Ca ratio of 2.23 mmol/mol. The average Mg/Ca ratio of all *G. inflata* samples from the sediment trap is between 2.23 mmol/mol and 2.38 mmol/mol at a confidence level of 95% and the flux-weighted average is also 2.23 mmol/mol. The good match with the multispecimen analysis from the sedimentary record supports the assumption that there is no seasonal bias in the Mg/Ca signal of *G. inflata*.

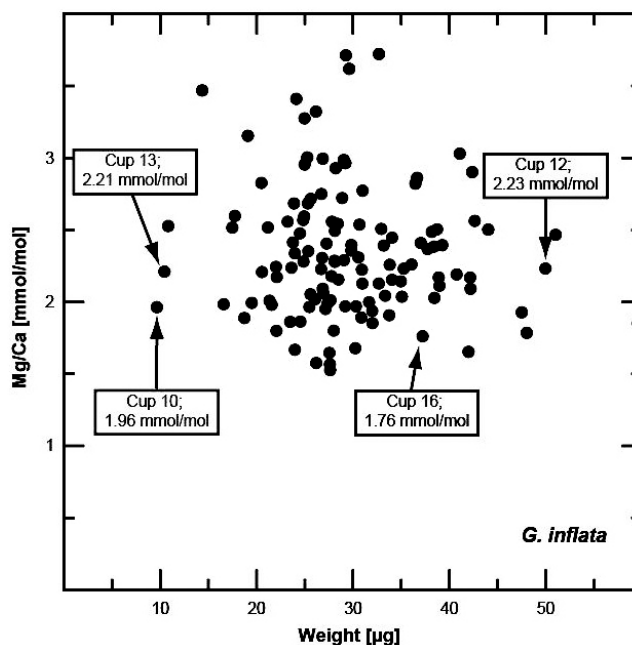


Figure 8. Weight versus single-shell Mg/Ca ratios of *G. inflata* from the sediment trap (located at 20°45.6'N, 18°41.9'W). Outliers and their Mg/Ca ratios are indicated.

5.3. Comparison of Inferred Calcification Depths to Reported Habitat Depths From Plankton Tows

[42] The Mg/Ca temperature estimates derived using the *Regenberg et al.* [2009] equation mostly correspond to a calcification depth for *G. ruber* (pink) between the surface and ~30 m. This is within the mixed layer at a habitat depth reported in tow studies for this species [e.g., *Wilke et al.*, 2009]. An exception is the lowest temperature (15.9°C) recorded in February 2006 (Figure 2). Though very low, we assume that this temperature is a realistic record of the calcification temperature at the study site, due to the low horizontal averaging scale at the study site (see section 3.1). One possibility could be that the specimen calcified within the upwelled water. Everywhere along the northwest African coast, this has a temperature of 15°C–17°C [*Mittelstaedt*, 1983].

[43] Mg/Ca temperatures recorded by *G. ruber* (white) using the *Elderfield and Ganssen* [2000] equation correspond to calcification depths between the surface and ~40 m (October 2005), 0 m (January 2006), ~110 m (February 2006), and ~150 m (May 2006) when compared to World Ocean Atlas data (Figure 3) [*Locarnini et al.*, 2006]. It is difficult to reconcile these calcification depths given the fact that *G. ruber* (white) has symbiotic dinoflagellates and should be restricted to the photic zone. As noted above (section 5.2.2) the calcification depths for *G. ruber* (white) should be treated with caution.

[44] Calculated apparent calcification depths of *G. inflata* mostly correspond to the upper 400 m, 500 m, and 75–500 m of the water column, using the equations of *Elderfield and Ganssen* [2000], *Groeneveld and Chiessi* [2011], and *Thornalley et al.* [2009], respectively. In this study, we use the *Elderfield and Ganssen* [2000] equation generated using North Atlantic sediment samples. When compared to World Ocean Atlas data, the majority of our data indicate a shallowest apparent calcification depth between the sea surface and 50 m, hence at the depth of the highest chlorophyll *a* concentration (Figure S1), where *G. inflata* can make use of its food source. The mean temperature estimates of the individual sampling intervals are between 16.3°C and 13.4°C, corresponding to calcification depths between about 100 m and 300 m, respectively, hence well below the seasonal thermocline which is at ~50 m (Figure S1). The interpretation of this large range of calculated calcification depths must account for *G. inflata* calcifying over a wide range of depths, reflected in the depth integrated composition of its shell [*Wilke et al.*, 2006]. It builds part of its shell in the surface mixed layer and the thermocline [*Wilke et al.*, 2006]. The fact that *G. inflata* has small symbiotic algae [*Gastrich*, 1987] suggests that it spends part of the life cycle in the photic zone. However, wall thickening at depth produces crust calcite with a lower Mg/Ca ratio that can constitute a large proportion of the final test mass. This means that apparent calcification depths can be deeper than the depth at which the individuals spent most of their lives.

5.4. Implications for Paleocceanographic Reconstructions

[45] Based on the distribution of single specimen Mg/Ca ratios of *G. ruber* (white), *G. ruber* (pink) and *G. inflata*, it

is suggested that in the study area, *G. ruber* (pink) is suitable for investigations of paleoseasonality. In contrast, *G. ruber* (white) does not appear to be applicable for this purpose in the study area using published Mg/Ca temperature equations. The inferred apparent calcification depth of *G. inflata* below the depth of the seasonal thermocline suggests this species is a recorder of subsurface temperatures. Changes in single specimen maximum and minimum calcification temperatures from sediment core samples could indicate calcification at different subsurface depths in the past.

[46] A study on single specimens of planktonic foraminifera by *Billups and Spero* [1996] demonstrates that the range of $\delta^{18}\text{O}$ values can be used in order to assess seasonal or depth-related calcification temperatures in the paleoceanographic past. *Koutavas et al.* [2006] show that a change in total variance between populations of planktonic foraminifera (*G. ruber* (white)) can provide information on ENSO and seasonal variability. Accordingly, we suggest that a change in Mg/Ca variance and Mg/Ca range can be used as an indicator for environmental variability in the study area when measured on downcore samples.

5.4.1. *G. ruber* (pink)

[47] The present-day difference between highest and lowest Mg/Ca ratios of single *G. ruber* (pink) specimens in the study area over an annual cycle is 2.08 mmol/mol (Table S2), corresponding to the difference between warmest and coldest temperatures under which the specimens calcified (Figure 2). Likewise in the sedimentary record, the difference between highest and lowest Mg/Ca ratios is expected to indicate the range of temperatures under which the specimens calcified. It is suggested that changes in the range between highest and lowest Mg/Ca ratios in the sedimentary record are a measure of interannual changes in the range between highest and lowest SST. A prerequisite for such interpretation is that potential artifacts introduced by variable sedimentation rate and bioturbation can be minimized and natural variability can be confined.

[48] The annual Mg/Ca variance of *G. ruber* (pink) in this study is 1.43 mmol/mol and the 95% confidence interval of this variance ranges from 0.88 mmol/mol to 2.73 mmol/mol. This means that when a different variance measured from sedimentary specimens (with its own confidence interval) falls outside this estimate, it would be significantly different from the variance of the sample investigated here. A hypothetical decrease of variance below this threshold of 0.88 mmol/mol would mean a decrease of variance by 38%. If we assume that the variance relative to the total range of values remains the same (69%) in the past in the study area, a significant decrease of the total variance (below 0.88 mmol/mol) requires a decrease of the Mg/Ca range from 2.08 mmol/mol to 1.28 mmol/mol. Using the equation of *Regenberg et al.* [2009], this would represent a decrease in the temperature range of 4.0°C, from 10.0°C to 6.0°C. We did not calculate what increase in the temperature range would be significant as the modern range is already large (10°C) and a substantial increase is rather unlikely.

5.4.2. *G. inflata*

[49] The annual variance of *G. inflata* in this study is 1.37 mmol/mol and the 95% confidence interval of this variance ranges from 1.08 mmol/mol to 1.80 mmol/mol.

Again, a variance of sedimentary specimens that falls outside of this confidence interval would be significantly different from the samples investigated here. A decrease of variance beyond the significance threshold of 1.08 mmol/mol would mean a decrease of variance by 21%. If we again hypothesize that the variance relative to the total range of values remains the same (85%) in the study area throughout the past, a significant decrease of the total variance below the significance threshold of 1.08 mmol/mol requires a decrease of the total Mg/Ca range from 1.62 mmol/mol to 1.28 mmol/mol. Using the equation of *Elderfield and Ganssen* [2000], this would represent a decrease in the temperature range of 1.7°C, from 7.6°C to 5.9°C. A reduction of the temperature range of this magnitude was shown by *Billups and Spero* [1996] for the western equatorial Atlantic using individual *Neoglobobulimina dutertrei* shells. *N. dutertrei* is a species that prefers oceanographic conditions similar to *G. inflata*, i.e., upwelling regions and a habitat close to the chlorophyll maximum at the bottom of the mixed layer [*Fairbanks et al.*, 1982]. Between isotopic stage 1 and 2, a decrease of the temperature range of 4.7°C in the western equatorial Atlantic was suggested *Billups and Spero* [1996]. Given the detectable change (1.7°C) of the temperature range suggested in our study, the analysis of single *G. inflata* could prove valuable for detecting changes of thermocline temperatures or calcification depths in the paleoceanographic past.

6. Conclusions

[50] Mg/Ca thermometry of single specimens of *G. ruber* (pink) is suitable in the upwelling region off Cape Blanc for tracking the seasonal amplitude of SST when applying the Mg/Ca temperature equation of *Regenberg et al.* [2009]. In contrast, Mg/Ca ratios of *G. ruber* (white) do not track seasonal SST using published Mg/Ca temperature equations. The best SST estimate is obtained when using the *Elderfield and Ganssen* [2000] equation. Mg/Ca ratios of single specimens of *G. inflata* do not exhibit any apparent seasonality and are remarkably similar throughout the year. The best SST estimate is also obtained when using the *Elderfield and Ganssen* [2000] equation for *G. inflata*.

[51] Statistical analysis of single specimen Mg/Ca ratios from this study suggests that *G. ruber* (pink) can serve as potential recorder of paleoseasonality in the sedimentary record. Single specimen Mg/Ca ratios of *G. inflata* are suggested to track changes of its habitat depth. Changes in the range between highest and lowest Mg/Ca ratios of *G. ruber* (pink) ≥ 0.80 mmol/mol (4°C) and changes in the range between highest and lowest Mg/Ca ratios of *G. inflata* ≥ 0.34 mmol/mol (1.7°C) are thought to be indicative of a change of the temperature range in which the specimens calcified.

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