Surface and subsurface seawater temperature reconstruction using Mg/Ca microanalysis of planktonic foraminifera *Globigerinoides ruber*, *Globigerinoides sacculifer*, and *Pulleniatina obliquiloculata*

Aleksey Sadekov,1,2 Stephen M. Eggins,1 Patrick De Deckker,1 Ulysses Ninnemann,3 Wolfgang Kuhnt,4 and Franck Bassinot5

Received 22 July 2008; revised 1 April 2009; accepted 17 April 2009; published 3 July 2009.

1 Laser–ablation inductively coupled plasma–mass spectrometry microanalyses of Mg/Ca across individual final chambers of three planktonic foraminifera species, *Globigerinoides ruber*, *G. sacculifer*, and *Pulleniatina obliquiloculata*, reveal significant interspecies differences in test Mg concentrations. Whereas these three species have similar Mg/Ca values at low sea surface temperatures (~22°C), they diverge markedly at high sea surface temperatures (~29°C). Explanations for these differences in species Mg/Ca values based on detailed comparison of species intratest Mg/Ca distributions suggest that compositional variability within tests cannot account for the observed deviation of species Mg/Ca values in warm-water equatorial regions. Multiple regression modeling and δ18O analysis of *Globigerinoides sacculifer* tests indicate that interspecies differences in Mg/Ca values result from different depth habitats. The average Mg/Ca values of *G. ruber* final chambers reflect the temperature of the surface mixed layer (0–25 m), whereas those of *G. sacculifer* and *Pulleniatina obliquiloculata* correlate best with subsurface temperatures at 50–75 m and 100–125 m water depths, respectively. Mg/Ca calibration to the temperatures at these depths reveals a similar temperature control on Mg test composition in all species. Combining our results with Mg/Ca values from published culturing experiments, we derive a generalized equation for the effect of temperature and seawater salinity on foraminiferal Mg/Ca. We also show that the Mg/Ca composition of specific calcite layers within foraminifer tests, including the low-Mg/Ca layers of *Globigerinoides ruber* and *G. sacculifer* and the cortex layer of *Pulleniatina obliquiloculata*, correlates with seawater temperature and can be used as an additional proxy for seawater temperature.

Citation: Sadekov, A., S. M. Eggins, P. De Deckker, U. Ninnemann, W. Kuhnt, and F. Bassinot (2009), Surface and subsurface seawater temperature reconstruction using Mg/Ca microanalysis of planktonic foraminifera *Globigerinoides ruber*, *Globigerinoides sacculifer*, and *Pulleniatina obliquiloculata*, Paleoceanography, 24, PA3201, doi:10.1029/2008PA001664.

1. Introduction

Planktonic foraminifera Mg/Ca thermometry has been developed as a powerful tool in paleoceanography to reconstruct past ocean temperatures [Elderfield and Ganssen, 2000; Lea, 2003]. A consistent increase in bulk foraminiferal test Mg/Ca composition with seawater temperature (i.e., ~9 ± 1% per °C) has been observed for different planktonic foraminifer species obtained from deep-sea sediment core tops [Rosenthal et al., 1997; Hastings et al., 1998; Elderfield and Ganssen, 2000; Lea et al., 2000; Rosenthal et al., 2000; Dekens et al., 2002; Rosenthal and Lohmann, 2002], plankton net and sediment trap samples [Anand et al., 2003; McKenna and Prell, 2004; McConnell and Thunell, 2005], and also laboratory culture experiments [Nürnberg et al., 1996; Lea et al., 1999; Mashiota et al., 1999]. However, while the exponential nature of this temperature dependency is consistent with fundamental thermodynamic considerations, the reasons for its much greater sensitivity to temperature compared to inorganically precipitated calcite [Mucci and Morse, 1983; Mucci, 1987; Nürnberg et al., 1996] and the very low Mg content of planktonic foraminifer calcite, remain enigmatic. In view of these differences, it has been suggested that Mg incorporation into planktonic foraminifer calcite is tightly controlled by biochemical processes [Nürnberg et al., 1996; Rosenthal et al., 1997; Lea et al., 1999]. These biochemical processes or so-called “vital effects” have been shown to be species-specific. For example, Dekens et al. [2002] found *Globigerinoides ruber* Mg/Ca compositions to be on average 5–15% higher than those of *G. sacculifer*, and 49–55% higher than for *Neogloboquadrina dutertrei* taken from the same temperature range in the tropics. A similar set of observations based on sediment trap samples led Anand et al. [2003] to develop separate Mg/Ca thermometer calibrations for different species of planktonic foraminifera.
2. Materials and Methods

The three species of planktonic foraminifera selected for this study have distinct habitat depths within the water column. *Globigerinoides ruber* and *G. sacculifer* are spinose, symbiont-bearing species which inhabit surface (0–50 m) and subsurface (20–75 m) waters, respectively [Fairbanks et al., 1980; Erez and Honjo, 1981; Hemleben et al., 1989; Ravelo and Fairbanks, 1992]. The life cycle of *Pul­leniatina obliquiloculata* is less constrained but this species has been reported to spend its early ontogenetic stage in the mixed layer and to later migrate to greater depths where it adds a distinctive final outer calcite layer called the “cortex” [Erez and Honjo, 1981; Hemleben et al., 1989; Ravelo and Fairbanks, 1992]. Oxygen isotope studies indicate calcification depths for these species of 0–50 m for *Globigerinoides ruber*, 0–75 m for *G. sacculifer*, and 60–150 m for *Pulleniatina obliquiloculata* [Erez and Honjo, 1981; Fairbanks et al., 1982; Ravelo and Fairbanks, 1992; Spero et al., 2003; Field, 2004; Kuroyanagi and Kawahata, 2004; Cléroux et al., 2007; Huang et al., 2008].

For this study, *Globigerinoides ruber*, *G. sacculifer* (nonsac forms) and *Pulleniatina obliquiloculata* tests were obtained from nine core top samples spanning a large latitude gradient (equator to 30°S) and an annual sea surface temperature, is required for accurate reconstruction of the water column temperatures using Mg/Ca thermometry.

Planktonic foraminifera migrate within the water column during their life cycle and consequently, record varying calcification temperatures as they precipitate their calcite tests [Fairbanks et al., 1982; Bijma and Hemleben, 1994; Field, 2004; Kuroyanagi and Kawahata, 2004]. Multiple opening-closing plankton net and oxygen isotope studies indicate that different species prefer to inhabit different depth intervals within the water column [Fairbanks and Wiebe, 1980; Fairbanks et al., 1982; Ravelo and Fairbanks, 1992; Kuroyanagi and Kawahata, 2004]. These habitat depth preferences may contribute to differences between species-specific Mg/Ca temperature calibrations. It also has been shown in culturing experiments that some species precipitate a distinctive final layer of calcite prior to gametogenesis [Bé et al., 1977; Bé, 1980; Caron et al., 1987, 1990]. In nature this final “gametogenic” calcification event is believed to occur in relatively deep water [Bé, 1980; Duplessy et al., 1981; Blanc and Bé, 1981; Dekens et al., 2002]. If so, it may record a colder temperature signal characterized by lower Mg/Ca values. It follows that the extent to which this gametogenic calcite is variably developed in different species may bias their bulk test Mg/Ca compositions and also account for interspecies differences in Mg/Ca composition [Dekens et al., 2002]. Resolving the influence of the “habitat depth” versus biochemical vital effects on the Mg/Ca composition of planktonic foraminifers, and its sensitivity to temperature, is required for accurate reconstruction of the water column temperatures using Mg/Ca thermometry.

Conventional application of Mg/Ca thermometry relies on the bulk analysis of samples comprising 10–30 foraminiferal tests of the same species [Elderfield and Ganssen, 2000; Lea et al., 2000; Rosenthal et al., 2000; Dekens et al., 2002; Anand et al., 2003; Barker et al., 2005]. This approach averages the temperature signal recorded by individual tests comprising the sample population. Bulk analyses cannot discriminate different temperature signals incorporated at different habitat depths within individual tests. New microanalysis techniques, such as laser ablation—inductively coupled plasma—mass spectrometry (LA-ICP-MS), provide the ability to investigate the nature of differences in Mg/Ca composition by profiling Mg/Ca distribution across individual test chambers [Eggins et al., 2003; Reiehert et al., 2003]. In this study, we have employed LA-ICP-MS to determine and compare the Mg/Ca compositions of different test parts (chambers and wall layers) for three species of planktonic foraminifera *Globigerinoides ruber*, *G. sacculifer* and *Pulleniatina obliquiloculata*, that were obtained from the same core top samples. We explore the potential for using the Mg/Ca compositions of specific test layers as proxies for seawater temperature. Our results provide insight into the nature of differences in Mg/Ca values in these planktonic foraminiferal species and the extent to which habitat depth preferences versus biological vital effects determine their Mg/Ca composition.
temperature range (from 21.8°C to 29.4°C [Locarnini et al., 2006] (see Table 1)). These samples correspond to a range of upper water column structures, varying from a strongly stratified, shallow thermocline at the equator to a much thicker, mixed surface layer off the southwestern margin of Australia. All core top samples are located well above calcite lysocline in this region [Peterson and Prell, 1985] and contained well-preserved foraminiferal tests.

Mg/Ca profiles were measured only in the final chambers of *G. ruber*, *G. sacculifer* and *P. obliquiloculata* tests. This strategy reflects laboratory studies that report planktonic foraminifera form new chambers every 1–3 days [Bé et al., 1977; Caron et al., 1987; Spero, 1988; Spero and Lea, 1993; Lea et al., 1999] and continue to add calcite layers to preexisting chambers. Consequently, the final chamber is likely to display the fewest layers and least Mg/Ca variation because of migration through the water column. Sample preparation and LA-ICP-MS analyses were carried out according to procedures described in previous work [Sadekov et al., 2006]. Table 1 summarizes the number of analyzed tests of each species.

The depth resolution of LA-ICP-MS profile analyses was optimized by ablating excised final chambers of *G. ruber* and *G. sacculifer* tests from the inside to the outside surface. Because of their smooth surface topography, the final chambers of *P. obliquiloculata* were ablated from the

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**Figure 1.** Typical Mg/Ca profiles across the final chamber walls of *Globigerinoides sacculifer* and *G. ruber* tests. Profiles are grouped into types according to the number of high- and low-Mg/Ca layers within the final chamber. All tests have been ablated (profiled) from the inner to the outer surface (left to right). Filled boxes correspond to the type of layer distribution in Figure 2.
outside to inside surface. After LA-ICP-MS analysis, test fragments from the final chambers of *G. sacculifer* were removed from the carbon tape and cleaned in methanol prior to $\delta^{18}O$ isotope analysis. These isotopic measurements were carried out at the stable isotope laboratory at Department of Earth Sciences, University of Bergen using a Finnigan MAT 253 mass spectrometer coupled to an automated Kiel carbonate preparation device. The in-house standard measured with the samples was Carrera Marble (CM03). The isotopic values are calibrated to VPDB using NBS-19 and NBS-18. The long-term analytical precision (1 sigma) of the working standards over a time interval of several months is equal to or better than 0.1‰.

To ensure the recent origin (i.e., late Holocene) of the studied material, ages of the core top samples (Table 1) were established with $^{14}C$ dating at the Poznań Radiocarbon Laboratory, Poland, and at the Australian Nuclear Science and Technology Organisation (ANSTO) [Fink et al., 2004; Olley et al., 2004]. The CALIB5.0 program was used to calibrate $\delta^{14}C$ dates into calendar ages. The age of the core top sample from the Ontong Java Plateau was taken from Berger et al. [1987].

3. Results and Discussion

3.1. Comparison of Mg/Ca Variation Within *G. ruber*, *G. sacculifer*, and *P. obliquiloculata*

*G. ruber* and *G. sacculifer* show very similar patterns of Mg/Ca variation (Figure 1), that are characterized by alternating layers with relatively low and high Mg/Ca ratio values. These layers are typically between 1 and 6 $\mu$m thick, and the number of layers varies from specimen to specimen and tends to increase with test wall thickness. *G. ruber* typically has thinner tests and most (50–95%) final chambers have 2 or 3 layers. *G. sacculifer* has significantly fewer specimens with only two layers (cf. *G. ruber*), and between 10 and 60% of final chambers have four or more layers. No systematic relationships between different core top samples and the number of layers in the final chamber of these species were found (Figure 2).

The Mg/Ca profiles in a majority (55–85%) of *P. obliquiloculata* tests display a distinct, low-Mg/Ca layer at their outer surface (Figures 3 and 4). This corresponds with the presence of a smooth microperforate surface calcite layer, or cortex, which is observed to have between 3 and 10 times lower Mg/Ca than the inner parts of the test wall. Repeated LA-ICP-MS analyses show very good reproducibility for Mg/Ca values measured in the cortex layer, permitting its composition to be characterized and used as a specific geochemical signal of *P. obliquiloculata* tests. We subsequently use the term “cortex Mg/Ca composition” to refer to the average Mg/Ca value of the cortex layer as distinct from the integrated (profile average) composition of the final chamber of *P. obliquiloculata*.

The interior of *P. obliquiloculata* tests, including tests without a cortex layer, display a pattern of intercalating low-Mg and high-Mg layers that is similar to *G. ruber* and *G. sacculifer*. However, in *P. obliquiloculata* the variation of Mg/Ca values is less systematic than in the two *Globigerinoidea* species and also shows larger amplitude Mg/Ca changes from layer to layer. We use the term “internal Mg/Ca composition” to refer to the profile average Mg/Ca composition of *P. obliquiloculata* tests, that excludes any outer cortex layer where developed. These internal Mg/Ca compositions are characterized by relatively poor reproducibility in repeated LA-ICP-MS analyses.

3.2. Low-Mg/Ca Layer Compositions in *G. ruber* and *G. sacculifer*

The presence of alternating low-Mg and high-Mg layers were first identified by Erez [2003] in the shallow water dwelling, symbiotic benthic foraminifera *Amphistegina lobifera*. The development of similar Mg layering within the planktonic foraminifera *Orbulina universa* was documented shortly thereafter by Eggins et al. [2004] and subsequently in other planktonic foraminifera including *Globigerinoides ruber*, *G. sacculifer* and *Pulleniatina obliquiloculata* [Eggins et al., 2004; Anand and Elderfield, 2005; Sadekov et al., 2005; Kunioka et al., 2006; Sadekov et al., 2008]. There are two main competing hypotheses regarding the origin of this Mg layering: the “organic membrane” hypothesis proposed by Erez [2003] and the “pH variation” hypothesis proposed by Eggins et al. [2004].
The organic membrane hypothesis proposes that high-Mg layers correspond to calcite enriched with organic material and formed under a distinct biomineralization condition than the low-Mg calcite. These high-Mg layers are argued to be precursors to, and responsible for, initiating the calcification of the low-Mg calcite, which comprises the major proportion of the test. Kunioka et al. [2006] used NanoSIMS to suggest that high-Mg layers in the inner parts of *Pulleniatina obliquiloculata* tests are associated with calcite layers enriched in organic compounds that had been marked with protein staining solution.

The pH variation hypothesis is based on diurnal changes in pH and calcite saturation state that take place within the microenvironment of algal symbiont-bearing foraminifera [Rink et al., 1998], and on culturing experiments which show a dependency of bulk foraminiferal Mg/Ca composition on seawater pH [Lea et al., 1999; Russell et al., 2004]. A 0.1 pH unit increase produces a 5–7% decrease in foraminiferal test Mg concentration [Lea et al., 1999; Russell et al., 2004]. New culture experiment results confirm that the low-Mg layers in *O. universa* are precipitated during the day and high-Mg layers at night [Eggins et al., 2007], consistent with the modifying effects of symbiont photosynthetic activity on carbonate chemistry within the foraminiferal microenvironment [Rink et al., 1998]. It is worth noting that significant pH fluctuations might also be produced by varying respiration rates due to feeding or other changes in metabolic activity of both symbiotic and nonsymbiotic foraminifera.

Herein, we will not reexamine the origin of Mg/Ca variability within foraminiferal tests, but rather to explore the potential use of the low-Mg/Ca layer compositions as a temperature proxy. As previously shown for *Globigerinoides ruber* [Sadekov et al., 2008], the composition of the first low-Mg/Ca layer can be reproducibly measured by LA-ICP-MS, as can the first low-Mg calcite layer composition in *G. sacculifer* tests (Figure 1). Accordingly, it is feasible to assess the relationships between seawater temperature and these low-Mg calcite layer compositions in *G. ruber* and *G. sacculifer*, and with the final chamber Mg/Ca compositions. Given the hypothesized origins of these low-Mg/Ca layers, any temperature signal recorded by these layers may be viewed as either an unmixed signal (free of high-Mg calcite) or the Mg/Ca temperature signal biased by symbiotic activity.

**Figure 3.** Typical Mg/Ca profiles across the final chamber walls of *Pulleniatina obliquiloculata* tests. All tests have been ablated (profiled) from the outer to the inner surface (left to right). (a–c) Profiles through tests with well-developed, low-Mg/Ca (0.5–1 mmol/mol) cortex layer on the outer test surface. (d) Profile across a test displaying relatively narrow compositional variation.

**Figure 4.** Relative proportion of *Pulleniatina obliquiloculata* tests with and without a low-Mg/Ca cortex layer.
Figure 5 illustrates the difference between the low-Mg/Ca layer and average final chamber Mg/Ca compositions of *G. ruber* and *G. sacculifer*. The regression line fits for both species are remarkably similar and have the relationship $\frac{Mg}{Ca}_{low} = 0.78(\pm0.01) \cdot \frac{Mg}{Ca}_{average}$ (Mg/Ca$_{low}$ and Mg/Ca$_{average}$ are Mg/Ca values of the low-Mg calcite layer and the profile average compositions, respectively). The low-Mg/Ca layer offset from the chamber Mg/Ca composition could be explained by the pH bias during precipitation of the low-Mg/Ca layers. According to the experiments of Lea et al. [1999] and Russell et al. [2004], a 22% lower Mg/Ca composition would correspond to a 0.4 $\pm$ 0.1 unit increase in seawater pH. The size of this pH change is broadly consistent with the half-cycle amplitude in diurnal pH variation (0.4 pH unit) that has been measured for *G. sacculifer* [Jorgensen et al., 1985]. Accordingly, a temperature signal if present, recorded by *G. ruber* and *G. sacculifer* low-Mg/Ca layers could be interpreted as photosynthesis biased average Mg/Ca composition, and fit to an equation of the form

$$\frac{Mg}{Ca}_{low} = K \cdot \left[B \cdot \exp(A \cdot \text{Temperature})\right]_{Mg/\text{Ca}_{average}}$$  

where K is a constant that represents the mean low-Mg/Ca layer bias for *G. ruber* and *G. sacculifer* (i.e., 0.78 $\pm$ 0.01).

This correction factor applies only to entire sample population level and not to individual foraminifers, which have varying offsets (see Figure 5) possibly due to varying pH amplitudes arising from different symbiont numbers and number densities.

3.3. Relationships Between Mg/Ca Composition and Sea Surface Temperature

Mean Mg/Ca values for the different measured calcite compositions (i.e., Mg/Ca$_{average}$, Mg/Ca$_{low}$, Mg/Ca$_{cortex}$) from each core top sample have been used to assess the relationships with annual sea surface temperature (SST) (Figure 6 and Table 2). In all cases, an exponential function best describes the relationship between annual SST and the various Mg/Ca compositions, except for the internal Mg/Ca compositions of *P. obliquiloculata* (i.e., cortex layer excluded), which show no significant correlation with SST (Figure 6c). The final chamber Mg/Ca$_{average}$ compositions of *G. ruber* and *G. sacculifer* show very high correlation coefficients with SST, with $r^2$ values of 0.99 and 0.98, respectively. This contrasts with the poor correlation ($r^2 = 0.25$) found for *P. obliquiloculata* (Figure 6a). All three
species are notable for having very similar Mg/Ca\textsubscript{average} values at the coldest sample site (SST of $\sim$22$^\circ$C), that diverge markedly at higher temperatures and the equator (SST of $\sim$29$^\circ$C). The Mg/Ca\textsubscript{average} compositions of $G$. \textit{ruber} at the equatorial sites are approximately 15% higher than $G$. \textit{sacculifer} and 38% higher than $P$. \textit{obliquiloculata} (Figure 6a). This is consistent with the differences between these species noted previously [Dekens et al., 2002; Anand et al., 2003; Huang et al., 2008; Regenberg et al., 2009].

[20] The low-Mg/Ca layer compositions of $G$. \textit{ruber} and $G$. \textit{sacculifer} show similar exponential increases with SST with sensitivities of 9% and 7% in Mg/Ca per $^\circ$C (for $G$. \textit{ruber} and $G$. \textit{sacculifer}, respectively). These sensitivities are slightly higher than sensitivities of 8% and 6% determined for their Mg/Ca\textsubscript{average} compositions. The smaller preexponential coefficients (Figure 6b) reflect the bias constant (K) noted in section 3.2.

[21] The cortex layer (Mg/Ca\textsubscript{cortex}) compositions of $P$. \textit{obliquiloculata} correlate significantly better with SST ($r^2 = 0.57$) than either the final chamber average or the interior Mg/Ca compositions for this species. The regression indicates a comparatively small 5% increase in the cortex Mg/Ca composition per $^\circ$C increase in SST (Figure 6c). It is also noted that the difference between the interior Mg/Ca composition and both the cortex and final chamber average compositions of $P$. \textit{obliquiloculata} diminish with increasing SST. This can be attributed to a decrease in the relative proportion of cortex layer calcite with increasing SST (e.g., decrease from 25% to 14% as SST increases from 22 to 29$^\circ$C, based on mass balance constraints).


[22] Our results show systematic differences between the Mg/Ca calibrations obtained for $G$. \textit{ruber}, $G$. \textit{sacculifer} and $P$. \textit{obliquiloculata}. These are broadly consistent with species composition differences observed in previous studies that have been attributed to (1) differences in the seasonal growth preferences of species [Stott et al., 2002; McConnell and Thunell, 2005]; (2) differences in the intratest distribution of Mg/Ca values, in particular the development of gametogenic crusts [Dekens et al., 2002; Anand et al., 2003; Anand and Elderfield, 2005]; (3) differences in species biomineralization processes [Bentov and Erez, 2006]; and (4) differences in species depth habitat preferences and migration patterns [Dekens et al., 2002; Regenberg et al., 2006]. Our results permit a critical evaluation of these hypotheses.

Figure 6. Relationships between sea surface temperature and sample mean Mg/Ca values of different test components: (a) average final chamber Mg/Ca compositions of \textit{Globigerinoides sacculifer}, $G$. \textit{ruber}, and \textit{Pulleniatina obliquiloculata}; (b) low-Mg/Ca layer compositions of \textit{Globigerinoides sacculifer} and $G$. \textit{ruber}; and (c) \textit{Pulleniatina obliquiloculata} cortex, average final chamber, and internal Mg/Ca composition. See text for definitions of these test components and the methodology used to estimate their Mg/Ca compositions.
3.4.1. Seasonal Species Preferences

[25] The largest differences between the Mg/Ca compositions of *G. ruber*, *G. sacculifer* and *P. obliquiloculata* are observed in samples from equatorial regions which have the highest SSTs (Figure 6). Calcification temperatures estimated from the average Mg/Ca values for the equatorial core top samples are 28.2°C for *G. ruber*, 26.3°C for *G. sacculifer* on the basis of Dekens et al.’s [2002] thermometer calibrations, and 24.0°C for *P. obliquiloculata* (on the basis of Anand et al.’s [2004] thermometer calibration). These differences in calcification temperatures would require the seasonal SST variation to be 1.9–4.2°C, which is significantly larger than the seasonal ranges in the equatorial Indo-Pacific region (i.e., less than 1.5°C) [Locarnini et al., 2006]. Importantly, time series sediment trap studies from the equatorial Pacific show that *G. ruber*, *G. sacculifer* and *P. obliquiloculata* have similar seasonal preferences, with peaks in abundances during August–September and December–January [Kuroyanagi et al., 2002]. Seasonal preferences are therefore an unlikely explanation for the observed compositional differences between these species.

3.4.2. Species Differences in Intratest Mg/Ca Distribution

[24] Species-specific differences in Mg/Ca distribution within tests, in particular the occurrence of a calcite crust layer precipitated in deeper parts of the water column, is a commonly suggested explanation for interspecific differences in bulk test Mg/Ca compositions [Dekens et al., 2002; Regenberg et al., 2006]. For example, the presence of the encrusting cortex layer with low Mg/Ca values in *P. obliquiloculata* tests can explain the relatively low average test Mg/Ca values of this species. However, to account for the differences between the Mg/Ca thermometer calibrations of *P. obliquiloculata* and the other species, the proportional contribution of the encrusting cortex layer to the chamber wall composition should increase with increasing water temperature. This is the reverse of what is observed, that is, a decreasing contribution with increasing SST (Figure 6c; see also section 3.3).

[25] It is difficult to explain the observed deviation between the temperature calibrations of *G. ruber* and *G. sacculifer* at high temperatures given their similar chamber wall Mg/Ca profile characteristics (Figure 1). No distinctive low-Mg/Ca encrusting layer is observed in either *G. sacculifer* or *G. ruber* that could otherwise account for the differences in the Mg/Ca average temperature calibrations between these species. However, it is possible that a subtle difference occurs in the relative proportion (or thickness) of low-Mg and high-Mg calcite layers within *G. ruber* and *G. sacculifer* tests with increasing temperature (e.g., along the lines proposed by Bentov and Erez [2006] to account for the temperature sensitivity of Mg partitioning into foraminiferal calcite). To assess this possibility, we have conducted mass balance calculations to estimate the relative proportions of measured low-Mg/Ca and high-Mg/Ca calcite layer compositions that are required to account for the observed changes in Mg/Ca average compositions (Figure 7). The results for *G. ruber* and *G. sacculifer* (see Figure 7) indicate that the proportion of low-Mg/Ca layers is independent of temperature and is approximately constant at 45% and 55% of the chamber wall, respectively. These calculations assume that each final chamber comprises a mix of a single low-Mg/Ca and single high-Mg/Ca layer composition, and is reliant on the ability of LA-ICP-MS to resolve these two end-member layer compositions. Subject of these limitations, the absence of any trends in Figure 7 suggests that no significant temperature control is exerted on the relative development of high-Mg/Ca and low-Mg/Ca layers (Figure 7).

3.4.3. Species-Specific Differences in Biominalization Control of Mg Incorporation

[26] The Mg/Ca values of *G. ruber*, *G. sacculifer* and *P. obliquiloculata* are approximately 2 orders of magnitude lower than Mg/Ca values in inorganically precipitated calcite [Katz, 1973; Nürnberg et al., 1996]. To precipitate these low-Mg/Ca calcite compositions from seawater, foraminifera may need to reduce the Mg$^2+$ activity in the calcifying fluid [Rosenthal et al., 1997; Zeebe and Sanyal, 2002; Lea, 2003]. Several mechanisms have been proposed (see review by Bentov and Erez [2006]), including modification of pinocytedose seawater by transmembrane transport of Mg$^2+$ and complexion with organic molecules (e.g., ATP) [Zeebe and Sanyal, 2002; Bentov and Erez, 2005, 2006]. The extent of this Mg activity reduction and its relationship with temperature can be estimated for each species using the average Mg/Ca values of test calcite, by assuming that all calcite precipitates inorganically from biologically modified seawater. It is then straightforward
Figure 7. The percentage of low-Mg calcite comprising final chamber compositions of *Globigerinoides sacculifer* and *G. ruber*, calculated using mass balance constraints based on the measured average final chamber composition and extreme high and low Mg/Ca layers. The percentage was calculated for different SST (29.1, 25.2, and 21.7 °C) to estimate changes in relative proportion of low- and high-Mg calcite with temperature. Unless otherwise indicated, vertical axes show the percent of low Mg/Ca values, and horizontal axes correspond to specimen number.
Figure 8. (a) Calculated Mg/Ca composition of the calcifying fluid required to precipitate calcite tests of *Globigerinoides ruber* (squares), *G. sacculifer* (diamonds), and *Pulleniatina obliquiloculata* (circles) with average Mg/Ca values obtained in this study (details about the calculation are explained in the text). (b) Percentage of Mg$^{2+}$ removed or complexed during seawater modification at the calcification site and its dependence on seawater temperature (based on Mg/Ca values calculated for calcifying fluid in Figure 8a) for the three studied species (symbols are same as in Figure 8a). Slope of the regression lines (dashed lines) shows decreasing efficiency of biochemical reactions in reducing Mg$^{2+}$ activity with temperature. Note also that the magnitude of this decrease is different for different species.

Figure 9. Reconstruction of the calcification depth of final test chambers of *Globigerinoides sacculifer*, *G. ruber*, and *Pulleniatina obliquiloculata* based on the regression of Mg/Ca composition against seawater temperatures from different depth intervals within the upper water column (for details see text). Shaded intervals indicate those depth intervals which show the best regression fits and thus inferred calcification depths for each species. Blue arrows indicate the depth interval inferred for *Globigerinoides sacculifer* calcification on the basis of $\delta^{18}$O analyses (see Figure 10 for further details).
to calculate the Mg/Ca activity ratio values of the calcifying fluid using a value of 5.15 mol/mol for seawater Mg/Ca [Broecker and Peng [1982], which describe a partition coefficient of magnesium in calcite and its relationship with temperature (Figure 8a).

\[ \text{Mg/Ca}_{\text{calcifying fluid}} = \left( \frac{\text{Mg/Ca}_{\text{calcite}}}{D_{\text{Mg}}} \right) \]  

\[ D_{\text{Mg}} = 0.0009 \cdot T \, ^{\circ}C + 0.035 \]  

Mg/Ca values of the calcifying fluid increase with temperature in G. ruber and G. sacculifer, but have little or no change for P. obliquiloculata. These species-specific changes in the Mg/Ca values of the calcifying fluid can be interpreted as a decrease in efficiency of the biochemical reaction responsible for Mg\(^{2+}\) reduction at the calcification site (Figure 8b). Bentov and Erez [2006] suggested that temperature may cause an increase in diffusion rate or that ATP hydrolysis can reduce the efficiency of biochemical removal of Mg ions from the calcifying fluid and consequently increase calcite Mg/Ca values. While it is possible these factors (e.g., diffusion or ATP hydrolysis) could respond differently to seawater temperature changes

Figure 10. Reconstructed calcification depths for the final chambers of Globigerinoides sacculifer tests based on their measured \(\delta^{18}O\) compositions. Predicted \(\delta^{18}O\) calcite values based on temperature and salinity for different intervals within the upper 200 m of the water column. Red squares are measured \(\delta^{18}O_{\text{calcite}}\) of last chambers of G. sacculifer for each sediment sample. Calculations were made using the equations of Mulitza et al. [1998] for temperature and Fairbanks et al. [1997] for salinity dependences of \(\delta^{18}O_{\text{calcite}}\) and \(\delta^{18}O_{\text{water}}\). A constant correction of \(-0.27\%\) was applied to convert SMOW to PDB scales following Bemis et al. [1998].

Table 3. Summary of Calcification Depths Estimated for the Final Chambers of Globigerinoides sacculifer Tests Using \(\delta^{18}O\) Values and Different Published Calibration for \(\delta^{18}O\) Calcite and Water Temperature and \(\delta^{18}O\) Water and Salinity

<table>
<thead>
<tr>
<th>Works Used to Calculate (\delta^{18}O) Calcite From Seawater Temperature</th>
<th>Works Used to Calculate (\delta^{18}O) of Water From Seawater Salinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spero et al. [2003]</td>
<td>85 ± 16</td>
</tr>
<tr>
<td>Multiza et al. [2003]</td>
<td>80 ± 14</td>
</tr>
<tr>
<td>Duplessy et al. [1981]</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>Bemis et al. [1998]</td>
<td>&gt;</td>
</tr>
<tr>
<td>low light Orbulina</td>
<td>&gt;</td>
</tr>
<tr>
<td>high light Orbulina</td>
<td>63 ± 18</td>
</tr>
<tr>
<td>Shackleton [1974]</td>
<td>&gt;</td>
</tr>
<tr>
<td>Erez and Honjo [1981]</td>
<td>&gt;</td>
</tr>
</tbody>
</table>

\(a\) Depth is in meters plus or minus standard error of the mean depth for studied samples. The results for equations used in this study are bold.
in each species and therefore account for differences between species-specific Mg/Ca thermometers, this is highly speculative and a topic for future studies on foraminiferal biomineralization.

### 3.4.4. Differences in Species’ Habitat Preference

[27] The effects of foraminiferal habitat preferences on the test chemistry of different species are well known from oxygen isotope studies [Fairbanks and Wiebe, 1980; Fairbanks et al., 1980; Blanc and Bé, 1981; Fairbanks et al., 1982; Ravelo and Fairbanks, 1992], and have been suggested to be a factor contributing to interspecies differences in Mg/Ca composition [Dekens et al., 2002; Regenberg et al., 2006; Cléroux et al., 2007, 2008; Huang et al., 2008].

[28] To test the effects of species depth habitat preferences on Mg/Ca compositions, we used a similar approach to the recent study of Farmer et al. [2007] employing oxygen isotopes compositions. The rationale for this approach is that the depth interval and associated water temperature which best represents the observed Mg/Ca compositions should minimize residual deviations and provide the best regression fit for Mg/Ca versus temperature. Accordingly, we compare the regression fits for the measured Mg/Ca compositions of each species with mean annual temperatures at different water depth intervals for each core top sampling site [Locarnini et al., 2006]. The regression fit results obtained from this comparison of the measured test component compositions of the three species are shown in Figure 9. The best fits (highest correlation coefficients) for G. ruber and G. sacculifer and P. obliquiloculata were obtained with temperatures corresponding to depth intervals of 0–25 m, 0–50 m and 100–125 m, respectively. Analyses of δ18O composition obtained on the same final test chambers of G. sacculifer indicate that calcification temperatures for the formation of the final chamber are consistent with the 50–75 m depth interval (Figure 10 and Table 3), which is slightly deeper than the depth derived from Mg/Ca compositions. Interestingly, if the sample from Ontong Java Plateau is omitted, leaving only the core tops samples from Indian Ocean, the revised regression fit indicates a consistent calcification depth of 50–75 m for G. sacculifer (Figure 9). This depth interval (i.e., 50–75 m) is also more in line with the results of previous studies [Fairbanks et al., 1982; Ravelo and Fairbanks, 1992; Bijma and Hemleben, 1994; Bijma et al., 1994; Faul et al., 2000; Lončarić et al., 2006; Regenberg et al., 2009].

[29] These best fit depth intervals are calcification depths for the final chambers and are not equivalent to species habitat depths. However, these intervals are notable for their good agreement with previously documented habitat depths for each of these species, on the basis of both plankton net and oxygen isotope studies [Fairbanks et al., 1982; Ravelo and Fairbanks, 1992; Bijma and Hemleben, 1994; Faul et al., 2000; Anand et al., 2003; Field, 2004; Kuroyanagi and Kawahata, 2004; Cléroux et al., 2008; Regenberg et al.,...
Consequently, we attribute the observed differences between species Mg/Ca thermometer calibrations to the different calcification depths of the final test chambers. The depth optimized Mg/Ca average regressions for *G. ruber* and *G. sacculifer* and *P. obliquiloculata* are notable for being statistically indistinguishable from each other (Figure 11). The depth optimized regressions for the Mg/Ca_low compositions of *G. sacculifer* and *G. ruber* are also closely similar (Figure 11). These are consistent with the similar offset observed between Mg/Ca_average and Mg/Ca_low values in section 3.2 of this work.

The absence of any significant differences between species depth optimized Mg/Ca_average and Mg/Ca_low temperatures indicates that the temperature control on Mg/Ca compositions may be identical for all three species. This indicates the possibility that a single “generalized” Mg thermometer could be applied to these species to reconstruct a temperature profile for the upper water column, and possibly minimizing errors associated with applications of different species-specific calibrations.

### 3.4.5. Generalized Mg/Ca Thermometer for Sea Surface and Upper Thermocline Temperature Reconstruction

A generalized Mg/Ca temperature equation might be best estimated from culturing experiments where water conditions are tightly controlled [Spero, 1992; Lea et al., 1999]. By using Mg/Ca analyses only from the final chambers of *G. ruber* and *G. sacculifer* and *P. obliquiloculata* it may also be possible to reduce the variability of Mg/Ca values caused otherwise by foraminiferal migration within the water column. To estimate the generalized Mg/Ca thermometer, we have applied a multiple regression model to the combined Mg/Ca data sets from culturing experiments available for studies species [e.g., Nürnberg et al., 1996; Kısakürek et al., 2008] and the Mg/Ca_average values from our work (Figure 12 and Table S1). A seawater salinity dependence was also included in the regression

**Figure 12.** Comparison of previously published thermometers for *G. ruber* and generalized Mg/Ca thermometer derived from the final chamber average Mg/Ca compositions of this work and Mg/Ca values from culturing experiments [Nürnberg et al., 1996; Kısakürek et al., 2008]. Black solid line is the generalized Mg/Ca equation at a seawater salinity of 35‰. Shaded area corresponds to the 95% confidence band of the regression. Note the agreement between the calibration of Kısakürek et al. [2008] and our generalized Mg/Ca thermometer. Dashed black lines are generalized Mg/Ca equations at seawater salinities of 33‰ and 38‰. Most published Mg/Ca thermometers plot between these dashed lines, suggesting that some of the discrepancy between Mg/Ca calibrations could be related to seawater salinity. 1, Mohtadi et al. [2009]; 2, Anand et al. [2003]; 3, Dekens et al. [2002]; 4, Whito et al. [2002]; 5, Kısakürek et al. [2008] at salinity 35‰; 6, McConnell and Thunell [2005]; 7, “warm water calibration” from Regenberg et al. [2009].
model to account for the large salinity variation that occurs for our core top sites [Antonov et al., 2006], and recent studies that show the importance of salinity for foraminifer Mg/Ca compositions [Nürnberg et al., 1996; de Menocal et al., 2007; Ferguson et al., 2008; Groeneveld et al., 2008; Kısakürek et al., 2008]. The resulting generalized equation fit, i.e.,

\[
\text{Mg/Ca}_{\text{average}} = \exp[0.057(\pm 0.012) \cdot S(\text{psu}) + 0.075(\pm 0.006) \cdot T(\text{C}) - 2.56(\pm 0.46)],
\]

accounts for 0.85% of the total Mg/Ca variability (e.g., \(R^2 = 0.85\)). It is also readily modified for application to the Mg/Ca low compositions of (1) G. ruber to estimate the surface mixed layer temperature (0–25 m depth)

\[
T_{(0–25)} = \ln(\text{Mg/Ca}_{\text{average}}) - 0.057 \cdot S + 2.56)/0.075
\]

and

\[
T_{(0–25)} = \ln(\text{Mg/Ca}_{\text{low}}/0.78) - 0.057 \cdot S + 2.56)/0.075,
\]

(2) G. sacculifer to estimate the upper thermocline temperature (50–75 m depth), and

\[
T_{(0–25)} = \ln(\text{Mg/Ca}_{\text{average}}) - 0.057 \cdot S + 2.56)/0.075
\]

Equation (4) is statistically indistinguishable from the published calibrations of Whitko et al. [2002] and Kısakürek et al. [2008] (Figure 12), and is broadly consistent with many published Mg/Ca thermometers [Hastings et al., 1998; Dekens et al., 2002; Anand et al., 2003; McConnell and Thunell, 2005; Cléroux et al., 2008; Mohtadi et al., 2009; Regenberg et al., 2009] (Figure 12).

[33] Figure 13 shows an application of the generalized Mg/Ca thermometer to reconstructing seawater temperatures at different depth intervals by using the final chamber Mg/Ca compositions of (1) G. ruber to estimate the surface mixed layer temperature (0–25 m depth)

\[
T_{(0–25)} = \ln(\text{Mg/Ca}_{\text{average}}) - 0.057 \cdot S + 2.56)/0.075
\]

and

\[
T_{(0–25)} = \ln(\text{Mg/Ca}_{\text{low}}/0.78) - 0.057 \cdot S + 2.56)/0.075,
\]
and (3) *P. obliquiloculata* to estimate deeper main thermocline temperatures (100–125 m depth).

\[ T_{100-125} = \left( \ln(\text{Mg/Ca}_{\text{average}}) - 0.057 \cdot S + 2.56 \right)/0.075 \]

The calculated temperatures for the water column intervals show a good correlation with observed temperatures (Figure 13). This application is not an independent experiment because we used the same core top samples for the regression model of the generalized thermometer, in combination with other Mg/Ca data (e.g., data from culturing experiments [Nürnberg et al., 1996; Kisekurek et al., 2008]). However, Figure 13 demonstrates the applicability of the generalized Mg/Ca equation for each species separately, as well as for the low-Mg calcite of *G. ruber* and *G. sacculifer* species.

[34] Previous studies have attributed the habitat depth preferences of different planktonic foraminiferal species to their symbioses and feeding strategies, with the latter being related to depth of the chlorophyll maximum rather than absolute depth [Fairbanks et al., 1982; Ravelo and Fairbanks, 1992; Bijma and Hemleben, 1994; Faul et al., 2000; Anand et al., 2003; Field, 2004; Kuroyanagi and Kawahata, 2004]. Accordingly, the calcification depths inferred in this study for *G. sacculifer* and *P. obliquiloculata* may be valid only for temperate to tropical regions of the Indian and Pacific oceans, and the other regions with a comparable oceanography. Given the sensitivity to past changes in the depth of the chlorophyll maximum in the oceans, the ability to reconstruct accurate temperature-depth profiles may be compromised, as distinct from temperatures related to the position of the chlorophyll maximum. Further studies are required to test the *G. sacculifer* and *P. obliquiloculata* depth habitat preferences in different parts of the ocean and the applicability of this approach to paleocean reconstruction.

### 4. Conclusions

[35] LA-ICP-MS microanalysis of Mg/Ca through individual final chambers of *Globigerinoides ruber*, *G. sacculifer* and *Pulleniatina obliquiloculata* tests indicate significant interspecies differences in test Mg/Ca concentrations. Our results show that differences in intraspecies distributions of species Mg/Ca values cannot account for the observed deviation of species Mg/Ca values in warm-water equatorial regions. Results of our multiple regression modeling and previous δ18O studies of *Globigerinoides sacculifer* tests, both indicate that interspecies discrepancies in Mg/Ca thermometers result from species differences in depth habitat. The average Mg/Ca values of *G. ruber* reflect seawater temperature of the surface water mixed layer (0–25 m), whereas those of *G. sacculifer* and *Pulleniatina obliquiloculata* correlate best with temperatures at 50–75 m and 100–125 m depth, respectively. Comparison of Mg/Ca calibrations based on seawater temperatures corresponding to these depths indicates that all three species share a similar temperature control on Mg test composition. Accordingly, we have derived a generalized temperature relationship by multiple regression of our results and culture studies which is described by the equation

\[ \text{Mg/Ca}_{\text{final chamber average}} = \exp[0.057(\pm0.012) \cdot S(\text{psu}) + 0.075(\pm0.006) \cdot T(\text{C}^\circ) - 2.56(\pm0.46)]. \]

We further demonstrate that the low-Mg/Ca layer compositions of *G. ruber* and *G. sacculifer* and the cortex of *P. obliquiloculata* can also be used as proxy for water temperature.

[36] Acknowledgments. This work was funded by Australian Research Council Discovery grant DP0450358 awarded to Patrick De Deckker and Stephan Eggins. Cores were obtained through R/V *Sonne* and R/V *Franklin* cruises funded by German Ministry of Education, Science and Technology (BMBF-grant 03G0185A, *Sonne* 185 cruise) and by the Australian National Facility grant to Patrick De Deckker for cruises *Franklin* 95/10 and 96/02. Material from cores BAR9403 and SHI 9016 was provided by F. Guichard from the LSEC in Gif-sur-Yvette. Some of the AMS dates on core top samples were funded by ANSE grant 97/057R. We also thank Judith Shelley for assistance with AMS sample preparation and Rune Seraas for help with stable isotope analyses. This manuscript greatly benefited from the constructive criticism of Gerald Dickens and Gert-Jan Reichart.

### References


Bemis, B. E., H. J. Spero, J. Bijma, and D. W. Lea (1998), Reevaluation of the oxygen iso-
topic composition of planktonic foraminifera: Experimental results and revised paleotem-

Bentov, S., and J. Erez (2005), Novel observa-
tions on biomineralization processes in fora-

Bentov, S., and J. Erez (2006), Impact of biomin-


Bijma, J., and C. Hemleben (1994), Population dynamics of the planktonic foraminifer *Globi-

Bijma, J., C. Hemleben, and K. Wellnitz (1994), Lunar-influenced carbonate flux of the plank-


F. Bassinot, Laboratoire des Sciences du Climat et de l’Environnement, IPSL, CEA, CNRS, F-91989 Gif-sur-Yvette, France.

P. De Decker and S. M. Eggins, Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia.

W. Kuhn, Institut für Geowissenschaften, Christian-Albrechts-Universität zu Kiel, Olshausenstrasse 40, D-24118 Kiel, Germany.

U. Ninnemann, Department of Earth Science, University of Bergen, Allegaten 41, N-5007 Bergen, Norway.

A. Sadekov, Grant Institute of GeoSciences, University of Edinburgh, The King’s Buildings, West Mains Road, Edinburgh EH9 3PW, UK. (alessy.sadekov@ed.ac.uk)