



Characterization of Mg/Ca distributions in planktonic foraminifera species by electron microprobe mapping

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[1] The distribution of Mg/Ca within the tests of eight modern planktonic foraminifer species has been characterized using electron microprobe mapping. Species include several that are commonly used for estimation of past seawater temperatures (*Globigerinoides ruber*, *G. sacculifer*, *Neogloboquadra incompta* (synonym of *N. pachyderma* dex.), *N. dutertrei*, and *G. truncatulinoides*). Each of the investigated species displays large variations in Mg/Ca composition within individual tests. However, the pattern of Mg/Ca variation is notably different between symbiont-bearing and symbiont-free species. In symbiotic species, cyclic Mg/Ca compositional banding occurs that is characterized by narrow (<1–3 μm), high-Mg/Ca (typically 8–11 mmol/mol) bands, intercalated between broader low Mg/Ca (typically 1–5 mmol/mol) bands. This factor of 2–3 difference equates to an apparent calcification temperature change of 10°C or more. Such temperature changes are considered highly improbable and suggest vital effects significantly modify the incorporation of Mg/Ca into the tests of symbiont-bearing species. These vital effects remain poorly understood and demand further careful evaluation as they may need to be accounted for when making reliable reconstructions of past oceanic temperatures. Symbiont-free species typically have fewer and broader compositional bands that may reflect more closely changes in calcification temperature as these species migrate within a water column.

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1. Introduction

[2] The use of the Mg/Ca composition of planktonic foraminifera tests as a proxy for past seawater temperature relies on significant variations in bulk test Mg/Ca composition being controlled by

calcification temperature [e.g., Nürnberg *et al.*, 1996; Rosenthal *et al.*, 1997; Lea *et al.*, 1999, 2000; Elderfield and Ganssen, 2000; Anand *et al.*, 2003; Barker *et al.*, 2005]. Experimental studies confirm that test Mg/Ca composition is far more sensitive to seawater temperature changes than

other variables which include salinity and pH or $[\text{CO}_3^{2-}]$ concentration [Lea *et al.*, 1999; Russell *et al.*, 2004]. However, mounting evidence points to the possibility that biological controls (vital effects) may exert a strong influence on the Mg/Ca composition of foraminiferal calcite [Erez, 2003]. Correlations between bulk test Mg/Ca composition and size in some foraminifer species have been attributed to an increase in calcification rate with size [Elderfield *et al.*, 2002] or an increase of symbiont activity with test size [Hönisch and Hemming, 2004]. Recent microanalytical studies further reveal the development of cyclic, high and low Mg/Ca banding within the tests of a single planktonic species (*Orbulina universa*) and a benthic species (*Amphistegina lobifera*). In both cases, the compositional variation that occurs across these bands exceeds what can be explained by temperature change [Erez, 2003; Eggins *et al.*, 2004]. The very limited extent of such detailed observations, taken together the differing interpretations that have been drawn from such results [cf. Erez, 2003; Eggins *et al.*, 2004], demand that a much better knowledge of the nature and extent of Mg/Ca variability within other foraminifer species be obtained in order to develop a fuller understanding of the cause(s) of Mg/Ca variability and the uncertainties associated with Mg/Ca paleoseawater thermometry. In this study, we make an important contribution to this knowledge base, by mapping in detail the distribution of Mg/Ca within tests of a range of symbiotic and asymbiotic planktonic foraminifer species. This represents a significant advance upon existing knowledge for which similar detailed insight into Mg/Ca distribution is only available for *Orbulina universa*, a species that is of relatively minor significance to paleoceanography and which can be regarded as atypical, both in terms of its test development and unusually high bulk Mg/Ca composition.

[3] This study builds upon a large number of earlier microanalytical studies, mostly using the electron microprobe, and which are notable for almost exclusively having employed point analysis strategies. These studies have established that the outer (gametogenic) calcite crust precipitated by many planktonic species typically has a lower Mg/Ca composition (by up to a factor of 3) than the inner (ontogenetic) layers of the test [Duckworth, 1977; Lohmann and Rosenthal, 1993; Puechmaille, 1994; Brown and Elderfield, 1996; Elderfield and Ganssen, 2000; Jha and Elderfield, 2000; Hathorne *et al.*, 2003], although this finding has been contradicted by the reported increase of

Mg concentration (by up to 230%) in gametogenic calcite that was precipitated by *Globigerinoides sacculifer* under controlled temperature laboratory experiments [Nürnberg *et al.*, 1996]. These observations have been augmented recently by studies employing techniques such as PIXE [Gehlen *et al.*, 2004], SIMS [Allison and Austin, 2003], and particularly laser ablation ICPMS [e.g., Eggins *et al.*, 2003, 2004; Hathorne *et al.*, 2003]. The latter technique is notable for documenting systematic changes in the Mg/Ca composition of sequentially precipitated chambers and between ontogenetic and gametogenic layers in planktonic species, including *Neogloboquadrina dutertrei* and *Globigerinoides sacculifer*. These changes appear to be consistent with variations in calcification temperature during life-cycle related migration of these species through the water column.

2. Construction of Planktonic Foraminifera Tests and Terminology Used in This Study

[4] Most modern planktonic foraminifera undergo test construction via the sequential addition of chambers. The walls of each chamber initially comprise two calcite layers (i.e., a bilamellar wall), that are secreted on either side of an organic sheet/template (commonly referred to as the primary organic membrane or POM). Additional layers are deposited onto the outer surface of existing chambers, as each subsequent chamber is added to the test during ontogenetic growth [Reiss, 1958; Bé and Hemleben, 1970; Hemleben, 1977]. A final, often thick layer of calcite is deposited upon the outer surface of each chamber that is exposed in the last whorl just prior to gametogenesis [Bé and Lott, 1964; Bé *et al.*, 1966]. This final layer is referred to as gametogenic calcite (as distinct from prior ontogenetic calcite layers) and in some species can comprise as much as 250% of the pre-existing (ontogenetic) test mass [Caron *et al.*, 1990]. A schematic illustration of the characteristic arrangement of chambers and calcite layers in the final whorl of a planktonic foraminifer test and a detailed cross section through a chamber wall is shown in Figure 1.

3. Methods

[5] We have used a Cameca SX100 electron microprobe to map the distribution of Mg and Ca within the tests of several planktonic foraminifer species, including the symbiont-bearing species

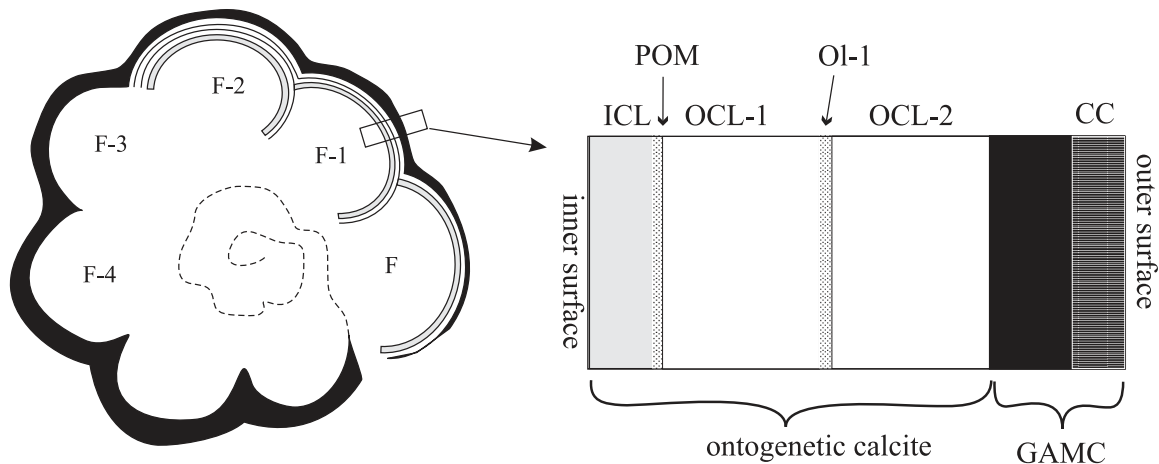


Figure 1. Schematic illustration of the test and chamber wall construction in planktonic foraminifera (adapted from Hemleben *et al.* [1977] and Erez [2003]). Note that a new layer is deposited over the test exterior with the addition of each new chamber to the test during ontogenesis. Further calcite deposition can occur at and following gametogenesis (gametogenic calcite and calcite crust). The terminology and associated acronyms used in this study are as follows: F, final chamber; F-1, chamber prior to final chamber; ICL, inner calcite layer; POM, primary organic membrane; OCL, outer calcite layer; Ol, organic layer; GAMC, gametogenic calcite; CC, calcite crust.

Globigerinoides ruber (d'Orbigny, 1839), *G. sacculifer* (Brady, 1877), *G. conglobatus* (Brady, 1879), *Orbulina universa* (d'Orbigny, 1839) and the non-symbiotic species *Neogloboquadrina incompta* (Cifelli, 1961) (synonym of *N. pachyderma* dex.), *N. dutertrei* (d'Orbigny, 1839), *Globorotalia menardii* (Parker, Jones and Brady, 1865) and *G. truncatulinoides* (d'Orbigny, 1839). All taxa, except *Neogloboquadrina incompta*, were selected from one core-top sample (Fr10-95-GC14; 20°02.71'S, 112°39.73'E; water depth of 997 m (see Martinez *et al.* [1998] for more details). *Neogloboquadrina incompta*, specimens were taken from a core-top sample from a more temperate region (MD2607; 36°57.64'S, 137°24.39'E, water depth 865 m [Gingele *et al.*, 2004]). Tests were cleaned by gentle ultrasonication in reagent grade methanol to remove adhering detrital material and were then mounted in epoxy and polished for electron microprobe analysis. The Cameca SX-100 electron microprobe was operated in WDS (wavelength dispersive spectrometry) mode using four spectrometers to simultaneously measure the elements Mg ($K\alpha$, TAP), Ca ($K\alpha$, PET), Sr ($L\alpha$, LPET), and P ($K\alpha$, LPET). A tightly focused electron beam was employed with an accelerating voltage of 15 kV and beam current of 20 nA to produce an excitation volume that is as small as possible ($\sim 2 \mu\text{m}$ diameter) without compromising the ability to measure both Mg and Ca. Test cross sections ranging up to $150 \mu\text{m} \times 150 \mu\text{m}$

were mapped using a $1 \mu\text{m}$ step size and 1 s accumulation time. Mg/Ca compositions were quantified following the procedure of Eggins *et al.* [2004], by applying a constant calibration factor determined by comparison of measured Mg/Ca intensity ratios to Mg/Ca values analyzed in the same tests by laser ablation-ICPMS. Typical integrated counts for Mg and Ca were 50 and 5000 respectively for a calcite Mg/Ca composition of 10 millimol/mol, which equates to a counting statistic uncertainty of $\sim 15\%$ (1σ) for a pixel of this composition. Wall cross sections were mapped for between 3 and 15 specimens of each species, of which representative results are shown below. In addition, we have used a Cambridge-S360 (Electron Microscopy Unit, Australian National University) to image and identify the presence of calcite crusts/gametogenic calcite on tests of *Orbulina universa* using the criteria described by Bé [1980].

4. Results

[6] Each foraminiferal species investigated in this study displays significant Mg/Ca variation in test wall cross sections, and species belonging to different genera can be seen to have characteristic patterns of Mg/Ca heterogeneity (Figure 2 and Figure 4). In general, symbiont-bearing species exhibit a cyclic, banded structure that comprises thinner layers with high Mg/Ca values that are intercalated between thicker layers with lower

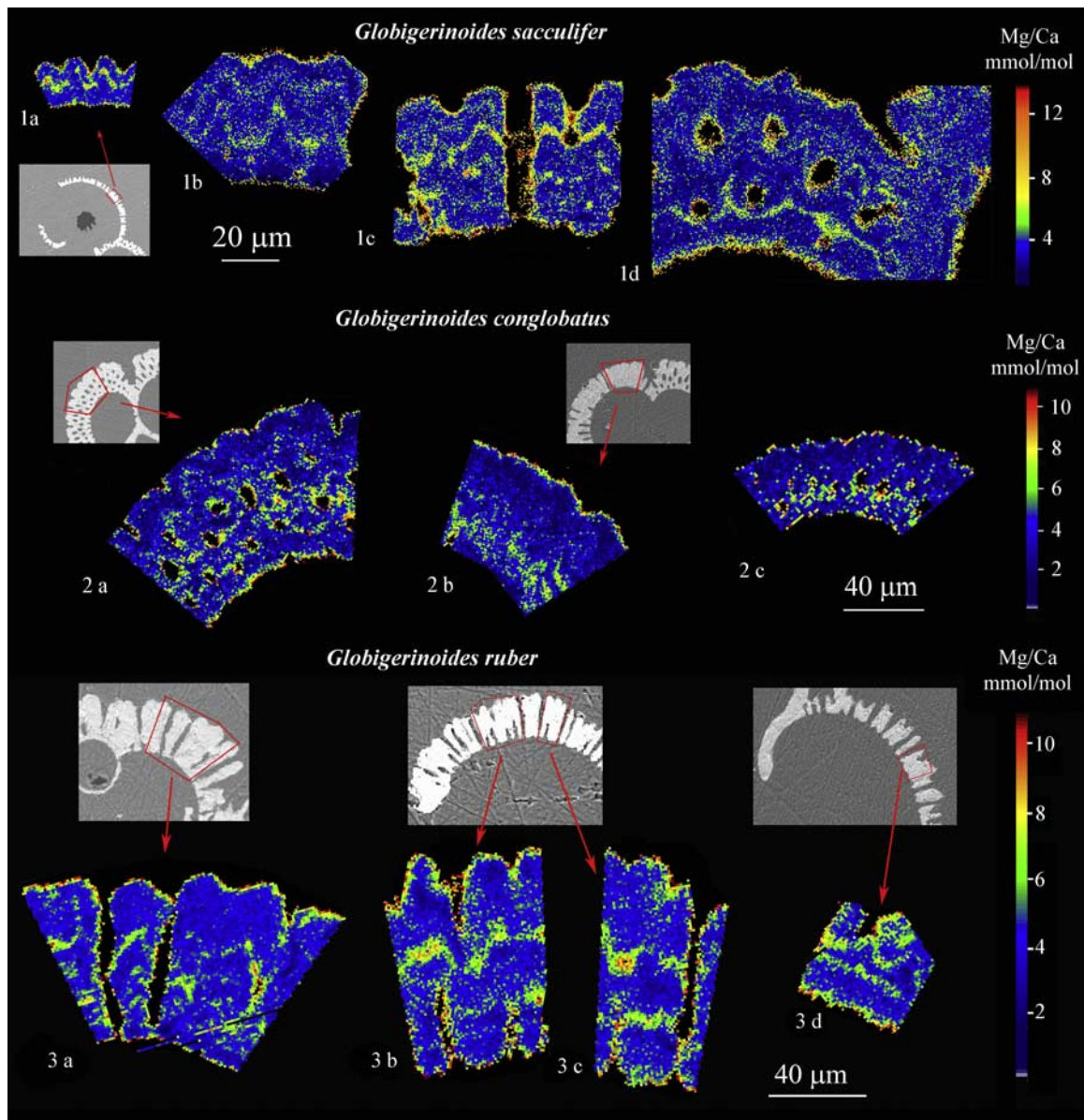


Figure 2. Maps of Mg/Ca values in chamber wall cross sections of symbiont-bearing species measured by electron microprobe (see text for analytical details). Color scales show the measured Mg/Ca values in millimoles/mole. (1a–1d) *Globigerinoides sacculifer* (Brady). 1a and 1b correspond to the F-1 and F-3 chambers in one individual and 1c and 1d to F-3 chambers in other individuals. (2a–2c) *Globigerinoides conglobatus*. (3a–3d) *Globigerinoides ruber*. Accompanying SEM images show the positions of the mapped sections of each test. The scale bars relate to the Mg/Ca maps.

Mg/Ca values. In contrast, symbiont-barren species tend to have thicker layers, lack cyclic banding, and display smaller variation in Mg content across their tests. It should be noted that due to the larger excitation volume for Mg than Ca in calcite, an artificially high Mg/Ca value is seen within a micron or so of test edges in all the microprobe maps. Unfortunately, this precludes the discrimination of this artifact from possible near-surface

enrichment of Mg or any uniformly distributed surface contamination [Eggins *et al.*, 2003; Gehlen *et al.*, 2004].

4.1. *Globigerinoides ruber*, *G. sacculifer*, and *G. conglobatus* (Figure 2)

[7] Analyzed samples of the genus *Globigerinoides* display patterns of convoluted Mg/Ca banding

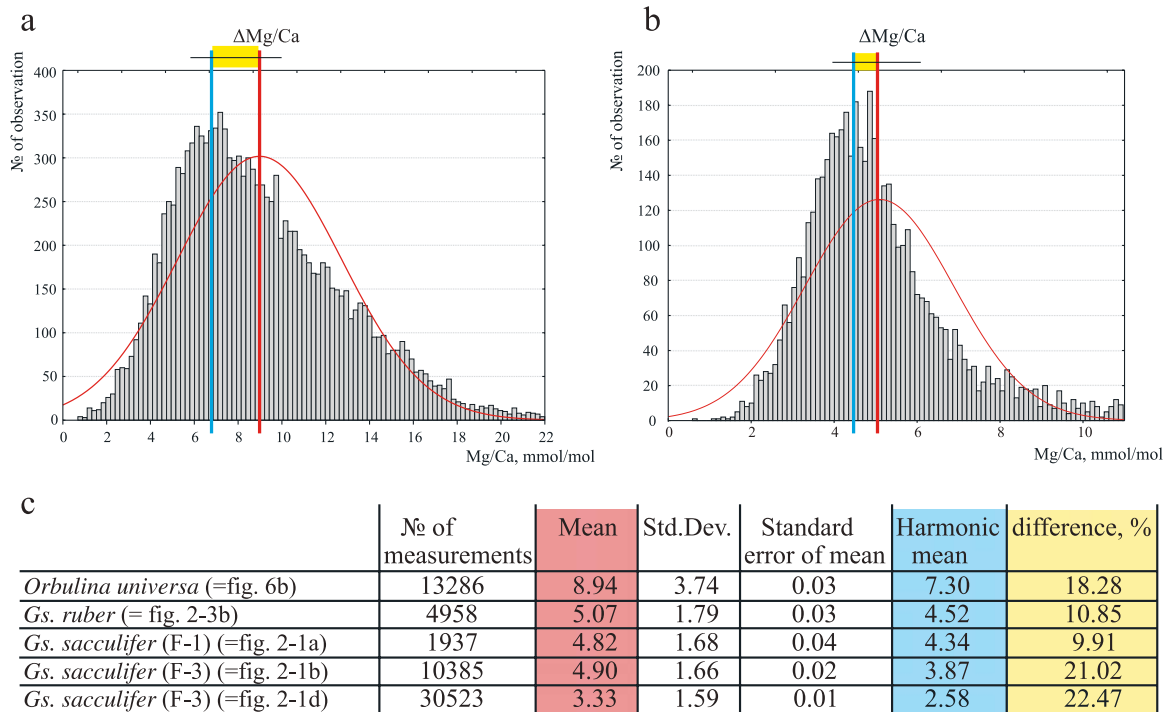


Figure 3. Frequency histograms of individual Mg/Ca values measured in cross sections of selected chamber walls of single foraminifer tests: (a) *Orbulina universa* (corresponding chamber cross section is shown in Figure 6b); (b) *Globigerinoides ruber* (corresponding chamber cross section is shown in Figure 2 (3a)); (c) tabulated arithmetic mean and harmonic mean Mg/Ca values, variability statistics, for selected chamber wall sections. The difference in percentage between the arithmetic and harmonic mean values is shown in the final column.

that comprise continuous to semi-continuous, narrow high Mg/Ca bands intercalated between thicker but low Mg/Ca bands. The high Mg/Ca bands can be seen, through careful inspection, to conform to the progressive development of increasing topography (spine bases and pores) on the test's outer surface as the chamber walls have thickened (Figure 2: 1–3). Moreover, the narrow, high Mg/Ca bands are observed in all but the last chamber, and the number of these high Mg/Ca bands is observed to increase with chamber position in the final whorl relative to that of the final chamber. For example, chamber F-1 in *G. sacculifer* has only one high Mg/Ca band (Figure 2: 1a) whereas F-3 (Figure 2: 1c) has at least three high Mg/Ca bands. A similar association between band numbers and chamber position is observed in *G. ruber* (Figure 2: 3a–3d). The high Mg/Ca bands are notable for being relatively narrow (<1–3 μm) and for having Mg/Ca values around 8 ± 2 mmol/mol, compared to the intervening thicker calcite layers which have much lower Mg/Ca, (i.e., 4 ± 2 mmol/mol; see Figure 2: 1b and 3b–3c). Cross sections from the apical

parts of *G. ruber* and *G. conglobatus* tests have a thick outer layer with a lower Mg/Ca ratio which we interpret to be a calcite crust. In the case of *G. conglobatus*, this outer crust layer has a Mg/Ca value equal to $\sim 1.5 \pm 0.5$ mmol/mol (Figure 2: 2a–2b). In the case of *G. ruber*, this thick outer layer has Mg/Ca values similar to the low-Mg/Ca bands within the inner parts of the test wall (i.e., $\sim 3.5 \pm 1$ mmol/mol, Figure 2: 3a).

[8] The Mg/Ca maps presented in Figure 2 reveal that the high Mg/Ca comprises a small but significant proportion, in the range 10–30%, of most chamber wall sections. These high Mg/Ca bands skew the mean chamber wall compositions away from a more uniform low Mg/Ca wall composition, an effect that can be estimated by comparing the difference between the arithmetic mean and harmonic mean for the distribution of Mg/Ca values recorded in the chamber wall map (Figure 3). For the F-1 chamber of *G. ruber*, the geometric Mg/Ca mean value is about 10% higher than that of the harmonic mean. For the F-3 chamber of the same

individual, this offset increases to 21% (or about 1.03 mmol/mol higher Mg/Ca).

4.2. *Globorotalia menardii* and *G. truncatulinoides* (Figure 4: 1–2)

[9] The symbiont-free species *G. menardii* and *G. truncatulinoides* are characterized by thick, outer crust layers with relatively uniform and low Mg/Ca values (typically <2 mmol/mol; see Figure 4). These outer crust layers typically account for more than 40% of the chamber wall thickness in apical parts of the test. The inner ontogenetic parts of the chamber walls generally have higher Mg/Ca compositions (4–6 mmol/mol, Figure 4: 1b and 2a, 2c) and, in some cases, distinct layering with different Mg/Ca values occurs parallel to test surfaces. The latter is particularly obvious in a cross section through the keel of the *G. menardii* specimen in Figure 4 (1a, 1c). This individual has an innermost layer with a Mg/Ca of 5 ± 0.5 mmol/mol that extends into the centre of the keel as a long, thin wedge. This is overgrown by a lower Mg/Ca layer (4 ± 0.5 mmol/mol) that is particularly thick in the keel region, where it shows evidence for being associated with initial development of a bulbous keel form. A layer with high Mg/Ca (7 ± 1 mmol/mol) then occurs, followed by a final outermost layer which has very low Mg/Ca (1.5 ± 0.5 mmol/mol) (Figure 4: 1a, 1c). Multiple layers with distinct Mg/Ca compositions can also be seen in the example of *G. truncatulinoides* (Figure 4: 2a). The innermost layer, which is also contiguous with the septum that divides the chambers in this section, has a Mg/Ca value of $\sim 5 \pm 0.5$ mmol/mol. A relatively thick and poorly defined layer with an intermediate Mg/Ca composition (4 ± 1 mmol/mol) then occurs prior to an outermost layer of similar thickness which has very low Mg/Ca (1.5 ± 1 mmol/mol). We correlate the latter with the development of a final calcite crust on this specimen. In another specimen of *G. truncatulinoides*, a single thin Mg/Ca layer with elevated Mg/Ca occurs near the inner wall surface, followed by an intermediate layer with uniform low Mg/Ca, and an outer layer with yet lower Mg/Ca (Figure 4: 2b and 2c). A series of three thin bands are prominent within the intermediate layer on the corresponding map of measured Ca intensity, which we attribute to the presence of organic membranes sandwiched between successive calcite layers deposited during ontogenetic test growth. An enlargement of this part of the wall section shows that the high Mg/Ca layer occurs immediately

below the first low Ca intensity band, but no other Mg/Ca band can be discerned. (Figure 4: 2b–2d).

4.3. *Neogloboquadrina dutertrei* and *N. incompta* (Figure 4: 3–4)

[10] Mapped *N. dutertrei* and *N. incompta* specimens show only limited Mg/Ca variation across chamber wall cross sections. Each of the specimens investigated displays only two distinct layers. The innermost of these layers is characterized by a moderately high Mg/Ca (4 ± 1 mmol/mol), whereas the equally thick or thicker outer layer (crust) has a significantly lower Mg/Ca composition (1.5 ± 1 mmol/mol).

4.4. *Orbulina universa* (Figure 5 and Figure 6)

[11] The distribution of Mg/Ca through the chamber walls of *Orbulina universa* has been described in detail in a previous study [Eggins *et al.*, 2004], such that herein our focus has been to try to distinguish possible differences in the composition of gametogenic calcite from that of the outermost calcite crust, and to confirm the position of the primary organic membrane relative to observed Mg/Ca banding. The distribution of measured Mg/Ca values across the test walls of two different individuals, one with large euhedral crystal forms that are typical of calcite crust development on the outer test surface [Bé, 1980] (Figure 5a), and another with a smooth veneer of calcite and “spine holes” characteristic of individuals that have undergone gametogenesis [Bé, 1980] (Figure 5a), are shown in Figure 4. In both examples, an outermost layer with a similar low Mg/Ca value is observed (4 ± 1 mmol/mol). It should be noted that individuals with a calcite crust also have “spine holes” and thus also underwent gametogenesis (Figure 5a). The position of the primary organic membrane (POM), which is readily identified on SEM and backscattered X-ray images near the inner test wall surface, in each case is found to correlate with a band of low to very low Mg/Ca concentration (3.5 ± 0.5 mmol/mol) (Figure 6b).

5. Discussion

[12] Several existing hypotheses might be used to explain the presence of systematic Mg/Ca heterogeneity within tests of planktonic foraminifera, including (1) change in calcification temperature due to foraminifer migration through the water column [Lohmann and Schweitzer, 1990; Lohmann

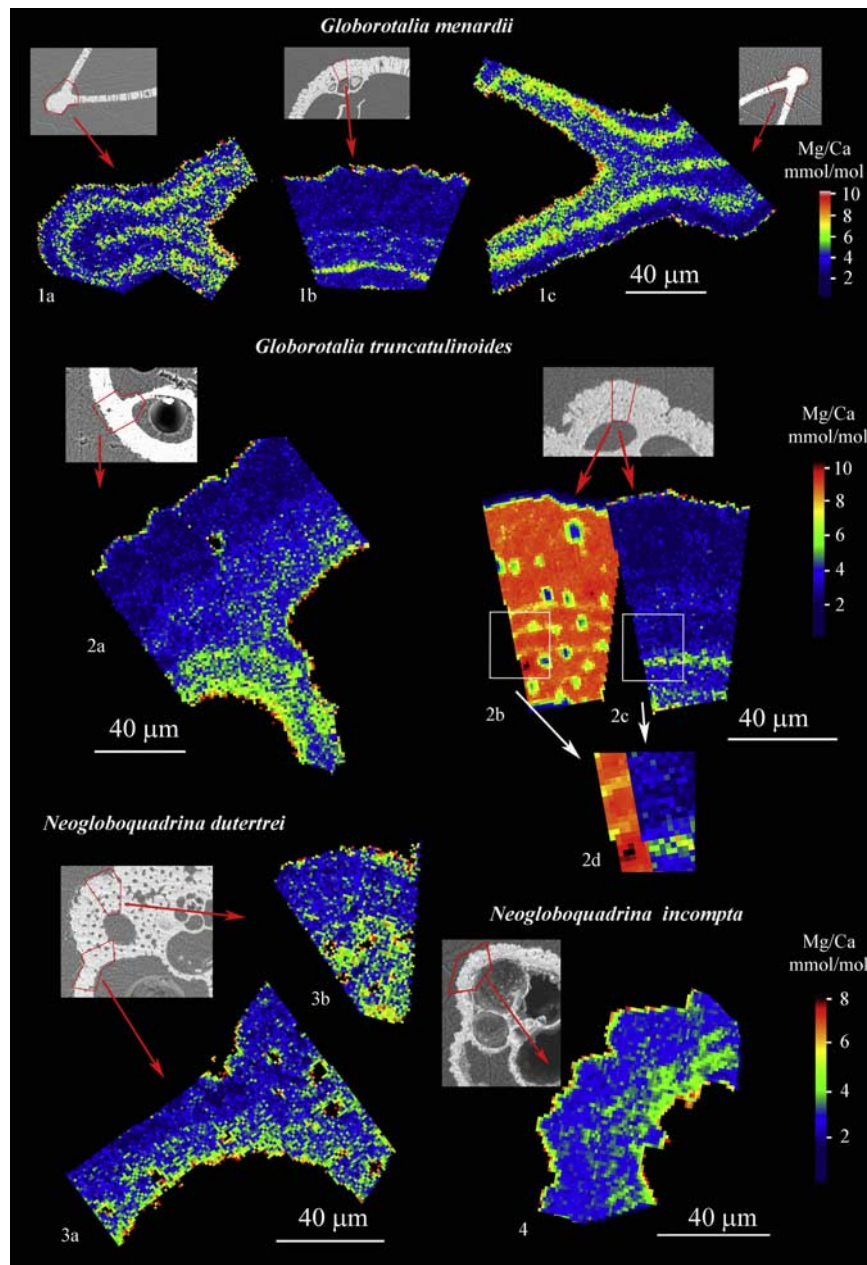


Figure 4. Maps of Mg/Ca values in chamber wall cross sections of symbiont-barren species measured by electron microprobe (see text of analytical details). Color scales show the measured Mg/Ca values in millimoles/mole. (1a–1c) *Globorotalia menardii*. (2a–2d) *Globorotalia truncatulinoides* (a) cross section through two adjoining chambers and the intervening septum, (b) map of measured Ca intensity showing evidence for multiple Ca-poor layers which are interpreted to be embedded organic layers, (c) Mg/Ca map of the same test cross section as b; (d) enlargement of the area within b and c containing the inferred organic layers. (3a–3b) *Neogloboquadrina dutertrei*. (4) *Neogloboquadrina incompta*. Accompanying SEM images show the positions of the mapped sections on each test. The scale bars relate to the Mg/Ca maps.

and Rosenthal, 1993; Lohmann, 1995; Eggins et al., 2003]; (2) diurnal changes in calcification chemistry (specifically pH and $[\text{CO}_3^{2-}]$) arising from the interplay of algal symbiont photosynthetic activity and net respiration of symbionts and the host foraminifer [Eggins et al., 2004]; and (3) the

precipitation of two distinct calcite compositions (one high-Mg and the other low-Mg) via different calcification pathways [Erez, 2003]. In addition, a number of other simple possibilities that arise with reservoir fractionation effects [Elderfield et al., 1996] and changes in calcite

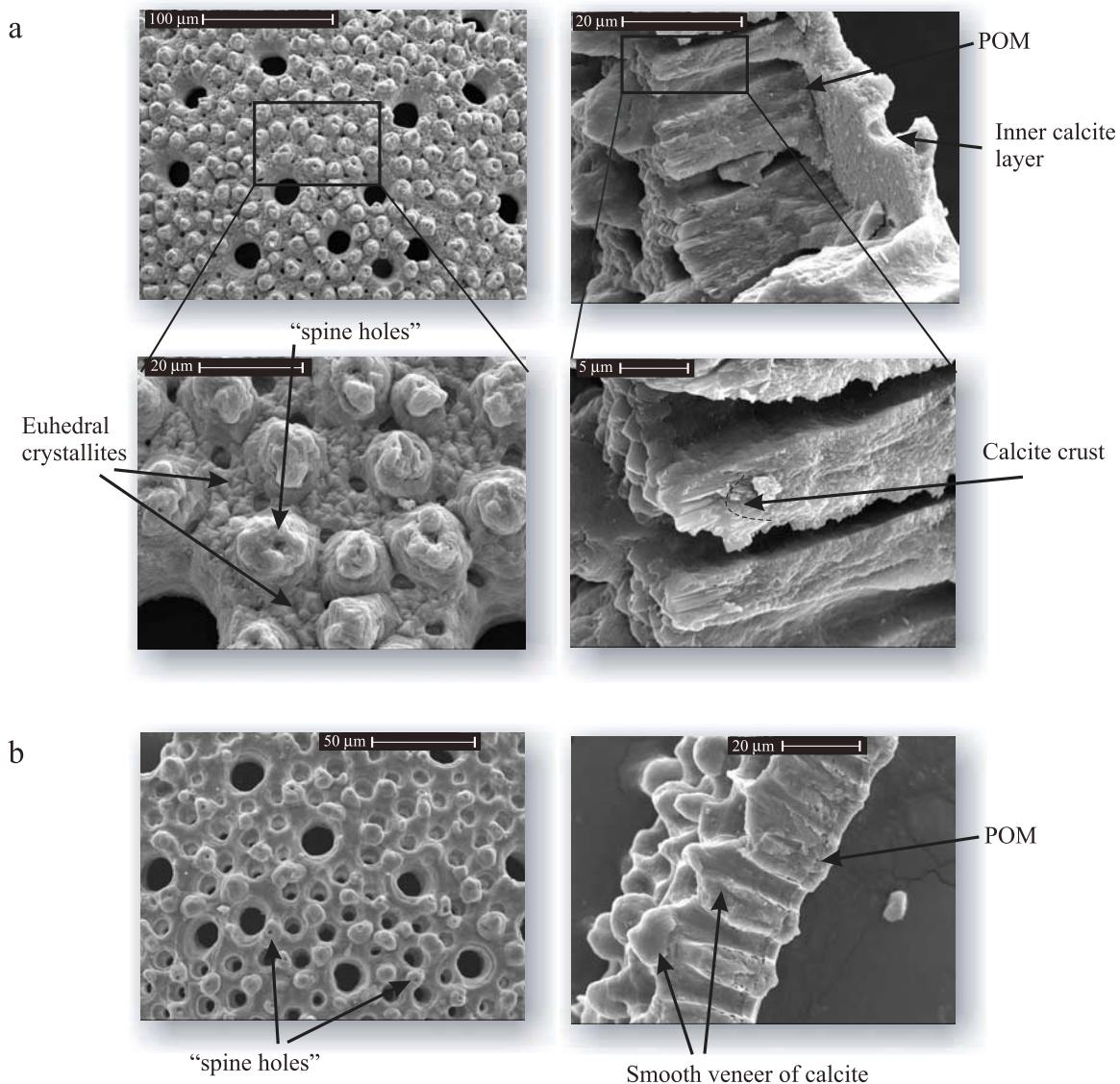


Figure 5. SEM images showing the characteristic surface morphology and internal structure of *Orbulina universa* tests with (a) gametogenetic calcite and (b) calcite crust. Both specimens show the presence of “spine holes” typical for tests which have undergone gametogenesis [Bé, 1980].

saturation state under biological control of $[Mg^{2+}]$, $[Ca^{2+}]$ or $[CO_3^{2-}]$ activities also warrant consideration. The present study provides a basis for critical evaluation of these various hypotheses, despite a lack of detailed constraints upon the possible changes in conditions under which these natural tests were calcified.

5.1. pH Change in the Foraminiferal Microenvironment

[13] Eggins *et al.* [2004] attributed the Mg/Ca banding in *Orbulina universa* to a daily pH cycle within the calcifying foraminifer’s microenvironment, in response to the interplay between daytime

photosynthetic activity of algal symbionts and net respiration of the symbionts and the host foraminifera. This hypothesis is based on observed changes in the bulk chemistry of foraminifera tests that have been cultured under different seawater pH [Lea *et al.*, 1999; Russell *et al.*, 2004], and microsensor measurements and theoretical studies that indicate large diurnal changes in pH (and thus carbonate ion chemistry), from low nighttime pH to high daytime pH, within the foraminiferal microenvironment [Jørgensen *et al.*, 1985; Rink *et al.*, 1998; Wolf-Gladrow *et al.*, 1999]. The Mg/Ca banding that we have documented in tests of *Globigerinoides* sp. could be interpreted in a similar way, with changes in photosynthesis and

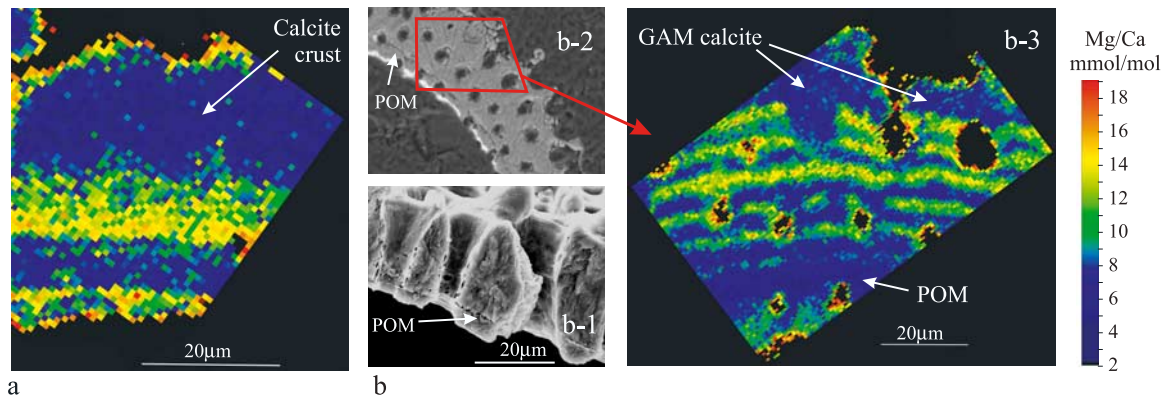


Figure 6. Maps of Mg/Ca values measured by electron microprobe in chamber wall cross sections of selected *Orbulina universa* tests with (a) gametogenetic calcite and (b) calcite crust. These maps correspond to SEM images of the same test shown in Figure 5. The position of the POM can be clearly seen in the SEM image (Figure 5: b-1) and corresponds to the low-Mg layer on the microprobe-map (Figure 5: b-3). Color scales show the measured Mg/Ca values in millimoles/mole.

net respiration rates being recorded in the Mg/Ca composition of precipitated calcite. Clearly, the Mg/Ca variation observed in the non-symbiont bearing species clearly cannot be accounted for by this mechanism. However, it is conceivable that changes in the rate of host respiration could modify the pH within the microenvironment of these symbiont-barren species, and might accompany metabolic changes associated with the consumption of prey or nutrients [Eggins *et al.*, 2004]. We conclude that pH is a plausible explanation for Mg/Ca banding in photosynthetic symbiont-bearing species, but is at best only a possibility in the case of the asymbiotic species.

5.2. Seawater Temperature

[14] Seawater temperature changes are a potential straightforward cause of the observed Mg/Ca variations and banding in planktonic foraminifera. However, required temperature changes can exceed 10–20°C, and would necessitate very large migration up and down through the water column in the case of symbiont-bearing species [Eggins *et al.*, 2004]. This is a highly improbable explanation for the origin of banding in *G. ruber* and *G. sacculifer* (and also *O. universa* [see Eggins *et al.*, 2004]) which are known to inhabit the mixed layer and upper thermocline during the mature ontogenetic stages of the life-cycles [Fairbanks *et al.*, 1982; Bé *et al.*, 1985; Deuser, 1987; Ottens, 1992; Bijma *et al.*, 1990; Bijma and Hemleben, 1994; Peeters, 2000; Tedesco and Thunell, 2003; Field, 2004].

[15] Symbiont-barren species exhibit broad and simple Mg/Ca variation, and lack the obvious cyclic

high- and low-Mg banding that characterizes the symbiont-bearing species. In general, the Mg/Ca composition of symbiont-barren species tend to increase or decrease toward the outer surface, in keeping with migration of these organisms from depth toward the surface, or vice versa. The *G. menardii* shown in Figure 4 (1c) could be interpreted to have migrated upward into warmer water before descending into much deeper and colder water where it secreted its final outer calcite crust. In contrast, the *G. truncatulinoides* specimen shown in Figure 4 (2a) could be interpreted as having migrated downward until it also precipitated a final calcite crust layer in much colder and deeper water. Similarly, the *Neogloboquadrina* specimens appear to have formed the inner parts test walls in relatively warm water before migrating downward to add a final outer calcite crust. The keel region of the *G. menardii* specimen in Figure 4 (1) would suggest a more complex change in temperature and habitat, with initial thickening being accomplished by precipitation of low-Mg calcite upon a thin high Mg/Ca blade, followed by another high Mg/Ca layer and final low Mg/Ca layer. The composition of calcite precipitated by *Globorotalia* and *Neogloboquadrina* genera might reflect temperature changes that have occurred during migration through the water column but additional mechanism should be involved to explain the distribution of Mg/Ca in the keel regions of *G. menardii*.

5.3. Erez [2003] Biomineralization Model

[16] Erez [2003] had proposed a general biomineralization model for foraminifera that invokes the precipitation of two types of calcite, one high-Mg

and the other low-Mg calcite, and has called upon this model to explain the cyclic high and low Mg/Ca banding in the large, symbiont-bearing benthic foraminifera *Amphistegina lobifera*. These two distinct calcite compositions are attributed to different calcification pathways. The high-Mg calcite is sourced from Ca-Mg-P-rich mineral granules and claimed to be intimately associated with the organic matrix, whereas the low-Mg calcite is precipitated from vacuolized seawater and claimed to be added only as layers to the outer side of the primary organic membrane [Erez, 2003]. Erez [2003] refers to the high-Mg calcite as “primary calcite” and equates it directly with precipitation of the inner calcite layer of the initial bilamellar wall (ICL in Figure 1), and refers to the low-Mg calcite as “secondary calcite” and equates it with the initial outer layer of the bilamellar wall (OCL1) and all subsequent added ontogenetic layers (OCL2, OCL3 etc.; see Figure 1). It should be noted that the proposed arrangement of high and low Mg/Ca compositions within the test wall structure is strictly inconsistent with the cyclic high-low Mg banding observed in *O. universa*, *G. ruber* and *G. sacculifer* and in the benthic species *A. lobifera*. Nonetheless, it is reasonable to accept a modification to the model whereby with the addition of each new layer during ontogenesis, both high and low Mg/Ca components are deposited. However, a critical shortcoming with the Erez [2003] model (as proposed) is revealed by our results, which show that the primary organic membrane is not intimately associated with high-Mg/Ca calcite, but rather coincides with a low Mg/Ca composition band. This can be seen clearly in some *Globigerinoides* sections (Figure 2: 1a, 3d) and is particularly obvious in *Orbulina universa* (see Figure 6b) where the POM is associated with the band that has the lowest Mg/Ca of any calcite precipitated during the ontogenetic phase of test growth. This fundamental mismatch between the model’s prediction and observations indicates that the model is either incorrect or in need of future modification to account for the Mg/Ca variation, and particularly the cyclic banding that occurs in symbiotic foraminifera species. In arriving at this conclusion, we do not dispute the underlying observations upon which the model has been based. Rather, we suggest the Mg-Ca-P-rich mineral granules identified by Erez [2003] may serve instead as a pool for calcification of low-Mg calcite rather than high-Mg calcite compositions. In support of this variation to the model, we note that the Mg-Ca-P-rich mineral granules have an Mg/Ca ratio of 2 [Erez, 2003], and therefore if dissolved back into a

calcifying fluid pool, would provide a reservoir composition with a factor of 2 to 3 lower Mg/Ca than seawater. It follows that these Mg-rich granules might be employed to modify and reduce the Mg/Ca composition of precipitated calcite by up to a factor of 2 to 3 compared to calcite that is precipitated from “unmodified” vacuolized seawater.

5.4. Other Possible Explanations for Cyclic Mg/Ca Banding

[17] If layer calcification within foraminifer tests is viewed in terms of discrete calcification events, a number of simple explanations might be invoked to produce the cyclic banding that Erez [2003] and our studies have documented. For example, calcification from a closed (or partly closed) reservoir can readily produce an increase in factor of 2–3 in Mg/Ca value of precipitated calcite, with 80–95% usage of the available Ca within the reservoir (assuming a distribution coefficient for Mg/Ca of 0.001 between calcite and the fluid [see Elderfield *et al.*, 1996]). The problem with this biomineralization model is that other elements with D values significantly <1 should also increase by a similar amount, yet we have found no evidence for such correlations between Mg/Ca and Sr/Ca or Ba/Ca using either our laser ablation-ICPMS or electron-probe mapping technique. Another possible explanation could lie in the active control of $[Mg^{2+}]$, $[Ca^{2+}]$ or $[CO_3^{2-}]$ by the foraminifer to change the degree of calcite supersaturation within the calcifying fluid and thereby switch on and off and control shell calcification. For example, $[Mg^{2+}]$ might be controlled in order to reduce the effect of poisoning on calcite precipitation, by either pumping Mg out of or by complexing Mg within the calcification fluid [see Erez, 2003]. In the process of turning calcification on and then off (i.e., increasing then reducing the degree of calcite supersaturation) using either a Mg pump or complexing agent, $[Mg^{2+}]$ will at first fall and then potentially increase again. This would produce a decrease followed by an increase in precipitated calcite Mg/Ca composition, so that, with the addition of each calcite layer (via this or a similar process involving control of $[Ca^{2+}]$ or $[CO_3^{2-}]$), a cyclic deposition of high and low Mg/Ca calcite would occur.

5.5. Implications of Mg/Ca Heterogeneity for Paleoseawater Thermometry

[18] The occurrence of heterogeneity within planktonic foraminifer species that are used for paleo-

ceanography (particularly *Globigerinoides ruber*, *G. sacculifer*, *Neogloboquadrina incompta* and *N. dutertrei*) presents a number of potential complications for the reconstruction of paleoseawater temperature based on bulk tests geochemistry. First, variation in the relative number, thickness and composition of high Mg/Ca bands in different chambers of individual symbiotic-bearing foraminifera, may skew chamber bulk compositions by different amounts. For example, the final chamber of *Globigerinoides sacculifer* has a relatively low Mg/Ca value (no high Mg/Ca bands), whereas previous chambers (with more high Mg/Ca bands) are skewed toward increasingly higher Mg contents by up to 20–25% (equivalent to 2–3°C). Interestingly, this could explain the relationship that has been observed between increasing test size and the Mg/Ca ratio in various species [Nürnberg *et al.*, 1996; Elderfield *et al.*, 2002; Hönisch and Hemming, 2004]. Using the same rationale, it follows that the greater number and particularly the thickness of the high-Mg bands in *Orbulina* may explain why this species has seawater thermometer calibrations that are higher in Mg/Ca for a given temperature than other planktonic species. A second potential complication comes with the application of different foraminiferal cleaning strategies [Boyle, 1981; Martin and Lea, 2002; Barker *et al.*, 2003; Pak *et al.*, 2004; Pena *et al.*, 2005], which will remove the high-Mg and low-Mg bands to different extents, depending on their composition and exposure at test surfaces. This could conceivably bias bulk test Mg/Ca compositions either up or down and by amounts that could prove difficult to reproduce.

5.6. Mg/Ca Composition of Final Calcite Crust Versus Gametogenic Calcite

[19] The terms “calcite crust” and “gametogenic calcite” have been used with ambiguity since Bé [1980] first described the formation of gametogenic calcite by *G. sacculifer* and proposed that the well known “calcite crust” of *Globorotalia* could be of the same origin. The terms calcite crust and gametogenic calcite have been used synonymously by some authors [Erez *et al.*, 1991; Lohmann and Rosenthal, 1993; Lohmann, 1995; Nürnberg *et al.*, 1996; Rosenthal *et al.*, 2000; Dekens *et al.*, 2002; Benway *et al.*, 2003], but have been assumed to have distinct meanings by others [Hemleben *et al.*, 1985; Caron *et al.*, 1990; Brown and Elderfield, 1996; Hastings *et al.*, 1998; Jha and Elderfield, 2000]. Moreover, some authors have inferred gametogenic calcite as having a high-Mg content

[Brown and Elderfield, 1996; Nürnberg *et al.*, 1996; Hastings *et al.*, 1998; Jha and Elderfield, 2000; Erez, 2003] whereas others have interpreted gametogenic (crust) calcite to be strongly depleted in Mg [Lohmann and Rosenthal, 1993; Lohmann, 1995; Rosenthal *et al.*, 2000; Dekens *et al.*, 2002; Rosenthal and Lohmann, 2002; Klinkhammer *et al.*, 2004; McKenna and Prell, 2004]. The possibility that final crust calcite and gametogenic calcite, in fact, are distinct is relevant to paleoseawater thermometry, as gametogenic calcite has been linked with the deposition of Mg-rich calcite in cultured *G. sacculifer* [Nürnberg *et al.*, 1996], whereas crust calcite has almost invariably been linked with low Mg/Ca compositions [Lohmann, 1995; Rosenthal *et al.*, 2000; Dekens *et al.*, 2002; Benway *et al.*, 2003; Eggins *et al.*, 2003]. As a contribution to this debate, our analyses of specimens of *Orbulina universa* with a calcite crust and with gametogenic calcite (as defined by Bé [1980]), show that these calcite types (which occur as outermost test layers in both cases) have low Mg/Ca values (Figure 6a). Furthermore, we note that we have not found evidence for the development of a high-Mg layer on outer-surface of other analyzed species. This is consistent with the formation of both calcite types in deeper, colder water, as has been proposed previously [Orr, 1967; Fleisher, 1969; Erez and Honjo, 1981; Hemleben *et al.*, 1985; Lohmann and Schweitzer, 1990; Lohmann, 1995].

6. Conclusions

[20] Planktonic foraminifera exhibit large variations in Mg/Ca composition within their tests. Moreover, significant differences in the pattern of Mg/Ca distribution occur between species, particularly between symbiont-bearing and symbiont-barren taxa. Symbiont-bearing species are characterized by cyclic high- and low-Mg banding, with narrow (<1–3 μm), high Mg/Ca (often reaching 8–11 mmol/mol) bands intercalated between broader bands with up to a factor of 2 to 3 lower Mg/Ca. This difference in high- and low-Mg/Ca band composition equates to apparent calcification temperature changes exceeding 10°C, which can be considered beyond an acceptable range for the mixed layer and upper thermocline dwelling species such as *G. ruber* and *G. sacculifer*. The banding observed in these symbiont-bearing species has similarities to that previously documented in *O. universa* by Eggins *et al.* [2004]), with the notable distinction that *O. universa* has much thicker and higher Mg/Ca composition bands. The

latter may explain why seawater thermometer calibrations for *O. universa* are higher in Mg/Ca for a given temperature than for other planktonic species. We suggest the Mg/Ca banding that occurs in symbiont-bearing species has a similar biologically mediated origin, linked in some way to symbiont activity and associated effects on calcification chemistry. In contrast, symbiont-barren species are notable for having fewer and broader compositional bands that typically follow systematic progression to higher or lower Mg/Ca compositions. These compositional changes may reflect changes in calcification temperature as these species migrate up and down through the thermocline. We further conclude that the crust calcite and gametogenic calcite in *Orbulina universa* have similar low Mg/Ca compositions, consistent with the precipitation of both calcite variants in relatively deep and cold water compared ontogenetic calcite.

[21] The nature and extent of Mg/Ca heterogeneity within different planktonic foraminifer species is likely to be significant for the reconstruction of past oceanic temperatures due to (1) the as yet undemonstrated extent to which the test bulk Mg/Ca composition reflects the integral of the calcification temperature; (2) the variable amount by which bulk test compositions may be biased toward higher or lower Mg/Ca values by changes in the relative number, thickness and composition of high-Mg/Ca bands in different chambers of the same test and in different tests; and (3) likely bulk compositional shifts resulting from the differential removal of high Mg/Ca and low-Mg/Ca bands during test cleaning.

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