Effects of seafloor and laboratory dissolution on the Mg/Ca composition of *Globigerinoides sacculifer* and *Orbulina universa* tests — A laser ablation ICPMS microanalysis perspective

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**A B S T R A C T**

Partial or selective dissolution of planktonic foraminiferal tests on the seafloor has been shown to alter original test Mg/Ca compositions and thus may limit the accuracy of Mg/Ca-based thermometry for reconstructions of past sea surface temperatures. We have employed laser ablation ICPMS to determine the extent of dissolution-caused changes in Mg/Ca distribution across individual chamber walls of the planktonic foraminifera *Globigerinoides sacculifer* and *Orbulina universa*. *G. sacculifer* samples collected from a core-top depth transect in the NE Indian Ocean and laboratory dissolution experiments show little if any evidence of preferential removal of Mg-rich calcite layers by progressive dissolution of the tests. We attribute the absence of selective dissolution to the banded distribution of Mg across the chamber walls of these foraminiferal species and to the minimal presence of calcite crusts with relatively low-Mg composition on the outer surfaces of tests. Mg/Ca microanalyses of *G. sacculifer* from core-top samples further indicate that for samples collected above the calcite lysocline the effect of post depositional dissolution on Mg/Ca sample mean values is minimal and within the uncertainty of Mg/Ca thermometry (i.e. ±0.4 mmol/mol; ±0.8 °C at ~28 °C). Comparison with previously published results for *G. sacculifer* supports these observations. Simple modelling of *G. sacculifer* test dissolution indicates that selective removal of calcite with high-Mg/Ca values from within the final chamber of *G. sacculifer* test appears insufficient to cause the ~10% decrease in Mg/Ca values observed above calcite lysocline. These changes in test composition might be related to development of partial or selective dissolution as a function of Δ[CO$_3$$^2-$] of a thin diagenetic surface coating which has a relatively high-Mg/Ca composition (i.e. 20–25 mmol/mol).

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1. Introduction

The Mg/Ca composition of planktonic foraminiferal tests is now a well-established proxy for past seawater temperatures (Elderfield and Ganssen, 2000; Anand et al., 2003). However, the accuracy and reliability of Mg/Ca thermometry may be affected by partial test dissolution on the seafloor (Barker et al., 2003; Rosenthal et al., 2004; Barker et al., 2005). A decrease in bulk test Mg/Ca composition has been documented with progressive test dissolution in deep-sea sediment core-tops (Savin and Douglas, 1973; Lohmann, 1995; Brown and Elderfield, 1996; Rosenthal and Lohmann, 2002; Dekens et al., 2002; Regenberg et al., 2006), in laboratory dissolution experiments using dilute acid (Brown and Elderfield, 1996), and during dissolution of tests in a “flow-through-ICPMS” analysis system (Benway et al., 2003). The effects of seafloor dissolution have also been documented above the calcite lysocline, where it causes an approximate 12% decrease in test Mg/Ca value per km of water depth in the modern ocean. This translates into a depth-dependent temperature bias of about −1.3 °C per km (Dekens et al., 2002; Rosenthal and Lohmann, 2002; Benway et al., 2003; de Villiers, 2003). Likewise, de Villiers (2003) demonstrates a 1–2 °C offset between Mg/Ca-based surface temperature reconstructions from cores collected in close proximity but at different water depths.

There is little agreement as to whether and how Mg/Ca compositions should be corrected for water depth, for carbonate ion concentration, or for test mass loss, to account for the resulting reduction in Mg/Ca due to partial test dissolution. Core-top studies have reported linear relationships between foraminiferal tests Mg/Ca composition and bottom water carbonate ion concentration [CO$_3$$^2-$], with different relationships occurring in different ocean basins and regions (Dekens et al., 2002; Rosenthal and Lohmann, 2002). To complicate matters, several recent studies have questioned whether test dissolution actually occurs above the lysocline (Regenberg et al., 2006; Rosenthal et al., 2004; Barker, 2005).

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2.1.1. Method

Tests of *G. sacculifer* (non-sac forms only) were picked from core-top samples (size fraction >400 µm) collected along a depth transect between 400 and 3500 m water depth off the northwest Australian margin (Fig. 1, and Table 1) (Kuhnt et al., 2006). All the cores were obtained in close proximity to each other, in a region with a relatively small sea surface temperature range (i.e. <3.5 °C) (Antonov et al., 2006). The calcite compensation and lysocline depths for the studied region were reported at ~4.5 km and 3.1 km, respectively (Peterson and Prell, 1985; Martinez et al., 1998; Ding et al., 2006; Naik and Naidu, 2007). In addition, *G. sacculifer* tests were extracted from a plankton pump sample collected immediately above the depth transect. Sampling location are summarised in Table 1.

Between 15 and 20 tests from each core-top sample were selected for LA-ICPMS Mg/Ca analysis. Only the final chambers of *G. sacculifer* tests were analysed for Mg/Ca composition. These chambers were first severed using a scalpel, and then cleaned by ultrasonicking in methanol for 2–3 min to remove clay and other adhering detrital material. The chamber surfaces were examined under a high-magnification stereo-microscope for the presence of remaining surface contamination, and cleaned again when necessary. The LA-ICPMS analyses were conducted following the method described in (Eggins et al., 2003; Sadekov et al., 2008). The terminology (e.g. sample mean Mg/Ca, average test Mg/Ca value, range of Mg/Ca values) used in this work follows that of our previous works (Sadekov et al., 2008; Sadekov et al., 2009) and is briefly summarised below.

The final chamber of each foraminifera test was analysed 2–5 times to produce profiles of Mg/Ca values across the test. The mean of these profiles has been calculated and reported as the average Mg/Ca value. Fifteen to twenty foraminifera were analysed from each sample station (i.e. core-top, or plankton pump sample) and the population mean of the average Mg/Ca values from each station is calculated and reported as the sample mean Mg/Ca value. Following the above hierarchy, the
sample mean range of Mg/Ca values was calculated based on the range between 5th and 95th percentile of each Mg/Ca profile.

2.1.2. Results

The pattern of Mg/Ca variation across the walls of *G. sacculifer* tests comprises alternating layers of relatively low and high-Mg composition. Both the number of these layers and their Mg/Ca compositions vary significantly from specimen to specimen, similar to observations made in our previous study (Sadekov et al., 2009). No significant changes to this pattern of Mg/Ca variation within tests are observed down the depth transect. Furthermore, although we did not measure changes in size-normalized test weights, based on the length of the LA profiles there are no systematic changes in test thickness for the studied core-tops and all values are within error bar of thickness measurements.

The sample mean Mg/Ca values are used to compare the *G. sacculifer* Mg/Ca compositions of different core-top samples (Fig. 2). Each core-top

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**Fig. 2.** Left panel: changes in the range of Mg/Ca values across *Globigerinoides sacculifer* tests (horizontal bars) and the average Mg/Ca compositions of the final test chambers (grey diamonds) down the core-top sample depth transect. The mean Mg/Ca value obtained for each core-top sample (black squares) is shown along with its 95% confidence interval. The thick red line shows the linear regression fit through the sample mean Mg/Ca values. Triangles show the average Mg/Ca values from plankton pump sample. To account for the difference between the plankton pump collection temperature (27.8 °C) and mean annual sea surface temperature of the core-top samples (∼28.5 °C) (Antonov et al., 2006; Locarnini et al., 2006), a correction factor (i.e. 7% increase in Mg/Ca values per 1 °C) has been applied. Right panel: frequency distributions of individual Mg/Ca values that comprise the compositional profiles of all tests measured from each core-top sample. The frequency distribution (dashed curve) of the plankton pump sample (station 1) is overlain for comparison.
sample is notable for the large spread (variability) of individual test compositions, which typically range from about 2.0 to 6.1 mmol/mol. The mean and the range of the Mg/Ca compositions calculated for each core-top sample show no systematic variation with water depth above the lysoclone, being indistinguishable from each other within 95% confidence. The deepest core-top sample (i.e. 3355 m), located just below the hydrographic lysoclone (Δ[C\(\text{CO}_3^{2-}\)]_bottom water \approx 0; Fig. 1), has an Mg/Ca composition that is shifted by a small but nonetheless significant extent toward lower Mg/Ca value than the samples from above the lysoclone.

Frequency distributions have been constructed from the individual Mg/Ca ratio measurements that comprise the chamber wall profiles measured on all tests from each core-top sample (Fig. 2). These frequency distributions show similar semi-normal, unimodal distributions for Stations 1, 6, 7 and 8, whereas other core-top samples from above the lysoclone show more complex distributions. Of note is the distribution for Stations 1, 6, 7 and 8, whereas other core-top samples from above the lysoclone, being indistinguishable from each other within 95% confidence. The deepest core-top sample (i.e. 3355 m), located just below the hydrographic lysoclone (Δ[C\(\text{CO}_3^{2-}\)]_bottom water \approx 0; Fig. 1), has an Mg/Ca composition that is shifted by a small but nonetheless significant extent toward lower Mg/Ca value than the samples from above the lysoclone.

Prior to performing the dilute-acid dissolution experiments, the Mg/Ca composition of distribution of Mg/Ca values within each test fragment was characterised by LA-ICPMS using the method described in Eggins et al. (2003) and Sadekov et al. (2008). Each test fragment was then cleaned again by ultrasonication in methanol and weighed using a microbalance. Each test fragment was stored in a vial containing dilute nitric acid (0.1 or 0.17 mM HNO\(_3\)) for a period of up to a week. The acid concentrations were chose following the work of Brown and Elderfield, 1996 who originally proposed the selective dissolution model, and thus our results can be directly compared with that study. Details of the dissolution experiments performed on each fragment are summarised in Table 2.

After the dissolution experiments each test fragment was washed in distilled water and reweighed (where possible) to determine the weight lost. These fragments were then analysed a final time by LA-

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Chambers' mass (mg)</th>
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<th>Mg/Ca distribution on Figs. 3–5</th>
<th>Mg/Ca (mmol/mol)</th>
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<tr>
<td>Specimen #1</td>
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<td>24 h</td>
<td>2.5 ml (0.0001 M HNO(_3))</td>
<td>Fig. 3</td>
<td>8.40 ± 0.07</td>
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<td>2.5 ml (0.0001 M HNO(_3))</td>
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<tr>
<td>Specimen #3</td>
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<td>3 ml (0.00017 M HNO(_3))</td>
<td>Fig. 4</td>
<td>6.20 ± 0.08</td>
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2.2. Laboratory dissolution of O. universa and G. sacculifer

2.2.1. Method

To examine the effects of dilute-acid dissolution on bulk Mg/Ca compositions and internal Mg/Ca, we selected six tests of G. sacculifer (non-sac forms only) and four tests of O. universa from sample 6 (Table 1), which was collected at 2000 m water depth off the northwest Australian margin. The age of this core-top sample is 1950 ± 60 uncalibrated C\(^{14}\) years, based on an analysis at the Australian Nuclear Science and Technology Organisation—ANSTO using the method of Fink et al., 2004. We used LA-ICPMS to analyse the final spherical chamber of O. universa and the final or penultimate chambers of G. sacculifer, which had been severed using a scalpel. These chambers were broken into large fragments that were individually cleaned by ultrasonication in methanol prior to Mg/Ca analysis using the method outlined in Section 2.1.1.

Prior to performing the dilute-acid dissolution experiments, the Mg/Ca composition of distribution of Mg/Ca values within each test fragment was characterised by LA-ICPMS using the method described in Eggins et al. (2003) and Sadekov et al. (2008). Each test fragment was then cleaned again by ultrasonication in methanol and weighed using a microbalance. Each test fragment was stored in a vial containing dilute nitric acid (0.1 or 0.17 mM HNO\(_3\)) for a period of up to a week. The acid concentrations were chose following the work of Brown and Elderfield, 1996 who originally proposed the selective dissolution model, and thus our results can be directly compared with that study. Details of the dissolution experiments performed on each fragment are summarised in Table 2.

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ICPMS to determine the changes in bulk Mg/Ca composition and internal distribution of Mg/Ca values.

2.2.2. Results

The results of the dissolution experiments are shown in Figs. 3–5. In all cases, dissolution results in thinning of test walls (i.e. shortening of the LA-ICPMS profiles), with the removal of specific layers being particularly obvious in some cases. Loss of up to 40–50% in fragment weight was accompanied by only 10–25% decrease in wall thickness based on the length and form of Mg/Ca profiles. Interestingly, the outer surface of some tests appears to dissolve up to ~3–5 times faster than the inner surface. This preferential outer-surface dissolution is particularly prominent in G. sacculifer (Figs. 3 and 5).

While, dilute-acid dissolution results in substantial chamber wall thinning by progressive removal of surface calcite layers, it does not appear to modify the Mg/Ca composition of the interior parts of the test. No evidence for preferential dissolution of high-Mg/Ca layers is observed. Nevertheless, the chamber mean Mg/Ca compositions tend to decrease with increasing test dissolution, with exceptions occurring in only three cases (i.e. for O. universa specimens #1 (24 h) and #4 (24 h) and Globigerinoides sacculifer specimen #4 (24 h)) which undergo small (2–4%) increases in Mg/Ca (Fig. 5A). These particular samples are notable for having well developed outer crust layers with relatively low-Mg/Ca compositions (Figs. 3A and 5A).

2.3. Flow-through ICPMS dissolution of O. universa

Flow-through dissolution experiments were conducted on the final chambers of O. universa that were taken from the same core-top sample used for the dilute-acid dissolution experiments described in the preceding section. Prior to flow-through-ICPMS analysis, each test was cleaned and analysed by LA-ICPMS following the same method used in Section 2.2.1. Three specimens with very distinct intra-test Mg/Ca distributions were selected for analysis. Specimen #1 had a thick, low-Mg/Ca (3.5–4 mmol/mol) crust layer developed on both its inner and outer surfaces (Fig. 6A). Specimen #2 had very large amplitude variations between low and high-Mg layers and a relatively high mean Mg/Ca composition (10.6 mmol/mol) (Fig. 6A). Specimen #3 showed a wide range of Mg/Ca compositions clustered about three discrete values of ~4, 9 and 12 mmol/mol (Fig. 6A). Flow-through-ICPMS analyses were performed on these tests according to the method described in Haley and Klinkhammer (2002) and Klinkhammer et al. (2004). The results of both LA-ICPMS and flow-through-ICPMS analyses of each of these O. universa tests are compared in Fig. 6.

There are significant differences in the mean Mg/Ca values and the range of Mg/Ca variation of each test measured by LA-ICPMS and by flow-through-ICPMS (Fig. 6). LA-ICPMS is clearly able to locate and resolve much greater compositional variation than flow-through-ICPMS under the conditions of these experiments.
Fig. 4. Comparison of Mg/Ca chamber wall profiles measured through *Orbulina universa* tests (specimens #4, 2 and 3) that have been subjected to dissolution in dilute nitric acid for varying time periods. A) Comparison of the Mg/Ca profiles prior to dissolution (0 h) and after dissolution times up to 168 h. All profiles are plotted from the inner (left) to the outer (right) test surface. Numbers indicate the time in hours that each test fragment was immersed in dilute nitric acid. Arrows indicate the extent of maximum dissolution (test wall thinning) obtained for each dissolution time. Note the different extents to which the outer and inner test surfaces have been dissolved (thinned). Different types of the line (i.e., solid, dashed, punctulated) represent repetitive Mg/Ca profiles across the test fragment. B) Comparison of Mg/Ca composition profiles for the different dissolution times applied to each specimen/test fragment. Note that the amplitude of Mg/Ca variation across the layers is preserved irrespective of the varying dissolution times.
Fig. 5. Comparison of Mg/Ca chamber wall profiles measured through *Globigerinoides sacculifer* (specimens #2, 3, 4 and 6) that have been subjected to dissolution in dilute nitric acid for varying time periods. A) Comparison of the Mg/Ca profiles prior to dissolution (0 h) and after dissolution times up to 72 h. All profiles are plotted from the inner (left) to the outer (right) test surface. Numbers indicate the time in hours that each test fragment was immersed in dilute nitric acid. Arrows indicate the extent of maximum dissolution (test wall thinning) obtained for each dissolution time. Note the different extents to which the outer and inner test surfaces have been dissolved (thinned). Different line types (i.e. solid, dashed, punctulated) represent repetitive Mg/Ca profiles across the test fragment. B) Comparison of Mg/Ca composition profiles for the different dissolution times applied to each specimen/test fragment. Note that the amplitude of Mg/Ca variation across the layers is preserved irrespective of the varying dissolution times.
The time-resolved evolution of the solute composition measured with progressive test dissolution by flow-through-ICPMS analysis clearly shows that there is no preferential dissolution of high-Mg/Ca test components. This is evident in the flow-through-ICPMS profile recorded for specimen #1 which starts with low-Mg/Ca values (3.5–4 mmol/mol) that gradually increase toward the end of the profile (Fig. 6B). This initial low-Mg/Ca value can be correlated with the low-Mg/Ca composition of the crust layer observed in the LA-ICPMS profiles, consistent with surface layers having dissolved before the interior test parts. The other specimens show more complex flow-through dissolution profiles, that include multiple changes to and from relatively low-Mg/Ca values (~8 mmol/mol) and high-Mg/Ca values (9 and 11 mmol/mol). No straightforward link can be drawn between the flow-through dissolution profile and the LA-ICPMS compositional profiles for specimens #2 and #3, except that neither shows evidence for selective dissolution of Mg-rich calcite.

3. Discussion

3.1. Dilute-acid dissolution

Artificial dissolution experiments were previously used by some studies to help interpret seafloor dissolution processes (Bé et al., 1975; Hecht et al., 1975; Brown and Elderfield, 1996; Hönisch, 2002; Benway et al., 2003), despite the significant differences in calcite saturation state and dissolution rates that exist between dissolution on the seafloor and that in the laboratory experiments. For example, Hecht et al. (1975) showed that changes in planktonic foraminiferal species assemblages due to seafloor dissolution can be reproduced by laboratory dissolution experiments. Bé et al. (1975) also demonstrated that progressive test dissolution in the laboratory can be linked to test structural changes observed in core-top samples collected from different water depths.

Our results demonstrate that laboratory dissolution, in vitro and using flow-through-ICPMS, does not discriminate between high and low-Mg calcite layers in G. sacculifer and O. universa tests. Rather these methods simply dissolve exposed surfaces. Whether these laboratory dissolution observations apply to natural processes and whether seafloor dissolution of foraminiferal tests is also indiscriminant of Mg/Ca requires careful consideration, as significant differences in calcite dissolution kinetics occur under different saturation states and consequently between artificial and natural conditions (Berner and Morse, 1974; Morse and Arvidson, 2002; Hales, 2003).

Calcium carbonate dissolution kinetics are complex and can be non-linear with respect to solution chemistry (Berner and Morse, 1974; Keir, 1980; Morse and Arvidson, 2002; Gehlen et al., 2005). During calcite dissolution by dilute acids (pH ≪ 5) the rate of reaction is controlled by the diffusion rate of chemical reactants in the solvent phase to and from the calcite crystal surfaces (De Giudici, 2002; Morse and Arvidson, 2002). Atomic force microscopy (AFM) and vertical scanning interferometry (VSI) demonstrate that these surface processes can be strongly influenced by Mg$^{2+}$ concentration in the solvent as well as the calcite surface Mg/Ca ratio, due to
exchange and hydration kinetics (Davis et al., 2000; Arvidson et al., 2006). Therefore, natural dissolution on the seafloor could be much more selective toward calcite layers with high-Mg/Ca values than dissolution with dilute acids, and therefore results of artificial dissolution on test geochemistry from this study and earlier studies should be interpreted with caution.

3.2. Changes in G. sacculifer Mg/Ca values above the calcite lysocline

The selective dissolution of more Mg-rich test parts has become a widely-accepted explanation for the observed decrease in bulk test Mg/Ca compositions during seafloor dissolution. However, our results show little if any evidence for such selective dissolution in core-top samples collected above the calcite lysocline. Differences in the sample tests’ wall-thickness, mean Mg/Ca values and changes to the range of Mg/Ca values within individual tests are not statistically significant. This indicates that in carbonate-rich sediments as in our transect, selective dissolution of G. sacculifer tests is either not occurring above the calcite lysocline or that its effect is within the detectable resolution of our analytical technique. Given the calculated uncertainties of the core-top sample mean Mg/Ca compositions, in our samples with standard errors of about ±0.2 mmol/mol (see Appendix A), the effect of seafloor dissolution above the calcite lysocline on G. sacculifer tests (Brown and Elderfield, 1996; Rosenthal and Boyle, 1993; Rosenthal and Lohmann, 2002; Dekens et al., 2002; Rosenthal et al., 2003; Regenberg and Elderfield, 2005; Sadekov et al., 2008) is developed on the Mg/Ca compositions by approximately 15% compared to the oxidative cleaning methods. This difference is consistent with studies that have employed different cleaning methods prior to Mg/Ca analysis. Samples subjected to reductive cleaning produced have consistently lower Mg/Ca values than samples subjected to oxidative cleaning. This indicates that in carbonate-rich sediments as in our transect, selective dissolution of more Mg-rich test parts has become a widely-accepted explanation for the observed decrease in bulk test Mg/Ca compositions during seafloor dissolution. The selective dissolution of more Mg-rich test parts has become a widely-accepted explanation for the observed decrease in bulk test Mg/Ca compositions during seafloor dissolution.
of Mg/Ca thermometry. The size of this dissolution effect is broadly consistent with a previously published result from Sierra Leone Rise (Rosenthal and Lohmann, 2002) (e.g. 0.013 mmol/mol per Δ[CO$_3^{2-}$] μmol/kg). Whether or not the Mg/Ca values of G. sacculifer should be corrected for this small dissolution effect depends on its origin. For example, if this ~10% decrease in Mg/Ca values above the calcite lysocline is due to seaﬂoor dissolution of foraminiferal calcite then it should be considered in Mg/Ca thermometry applications. However, if observed changes are caused by dissolution/removal of contaminant phases present on test surfaces then an improvement of the cleaning technique may be required rather than a dissolution correction. A number of plausible test dissolution scenarios have been modelled to shed light on the origin of the ~10% decrease in G. sacculifer Mg/Ca values observed above the lysocline. These different scenarios have been modelled using the laser ablation ICPMS data from this work with the following characteristics (for mathematical details please see Appendix B).

3.2.1. Surface (non-selective) dissolution

Dissolution proceeds via the progressive removal of the exposed inner and outer surfaces of G. sacculifer tests. To model this process we used Mg/Ca data for stations 1 and 4 which formed the initial condition of the model {X$_1$, X$_2$, X$_m$, X$_n$} for each test, where X$_i$ is Mg/Ca values of i measurement across the test. The data was subject to stepwise modification where each step removes successive increments, data-point X$_1$, X$_2$, X$_m$ and X$_n$. This modification reflects dissolution of the exposed test surface on outer (X$_1$, X$_2$, X$_m$, X$_n$) and inner (X$_n$) sides of a test. Three times faster dissolution rate was assumed for outer tests surface following our observations in dilute-acid experiment (see Section 2.2).

3.2.2. Selective dissolution of Mg-rich parts

Dissolution proceeds by progressive removal of the most Mg-rich parts of a test. To model this process we used Mg/Ca data for stations 4 and 6 which formed the initial condition of the model {X$_1$, X$_2$, X$_m$, X$_n$} for each test, where X$_i$ is Mg/Ca values of i measurement across the test. The data was subject to stepwise modification where each step removes one data-point with the highest Mg/Ca value from each profile (i.e. X$_{in}$→X$_{i1}$), each step proceeds as {X$_1$, X$_2$, X$_m$, X$_n$}→{X$_{i1}$, X$_{i2}$, X$_m$, X$_n$} after each step.

3.2.3. Mg-rich surface veneer

This model is based on previous studies (Eggins et al., 2003; Sadekov et al., 2008) which observed the presence of a thin surface layer that has Mg/Ca values in the range of 20–100 mmol/mol. Herein we assume gradual removal of thin (0.1–0.2 μm thick) surface layer with a value of 20 or 25 mmol/mol. To model this process we used Mg/Ca data for stations 1 and 6 which formed initial condition of the model {X$_1$, X$_2$, X$_m$, X$_n$} for each test, where X$_i$ is Mg/Ca values of i measurement across the test. The data was subject to stepwise modification where each step adds one data-point to each Mg/Ca profile with Mg/Ca value 20 for station X or 25 for station X (i.e. X$_{ir}$ for station X or 25 for station X). Each step proceeds as {X$_1$, X$_2$, X$_m$, X$_n$}→{X$_{ir}$, X$_{ir}$, X$_m$, X$_n$} after each step). The result of the model were recalculated to make last step of the model (e.g. tests with Mg-rich veneer) as first and the initial model condition (e.g. tests with no Mg-rich veneer) as last to follow the assumption of gradual dissolution on the Mg-rich veneer with time.

Results for each of these models are summarised in Fig. 8 which shows a change in Mg/Ca value as a function of relative wall thinning calculated from the length of LA-ICP MS profiles (Eggins et al., 2003). Given the maximum reported relative weight lost (approximately equals relative test thinning) for G. sacculifer tests collected above the calcite lysocline is ~30% (Broecker and Clark, 2001; Rosenthal and Lohmann, 2002), our modelling reveals that test dissolution is unable to account even for the small ~10% decrease in Mg/Ca values regardless of the dissolution pattern (selective to Mg-rich test parts or non-selective). Furthermore, as only well-preserved tests are used for Mg/Ca analyses, it is unlikely that the data compiled in Fig. 7 derive from tests that have been subjected to as much as 30% dissolution. Such test dissolution is visible even at low magnification (see figures in Bé et al., 1975; Hecht et al., 1975) and is usually accompanied by significant test fragmentation (Bé et al., 1975; Hecht et al., 1975). Therefore, we conclude that heterogeneity of Mg/Ca values across final chambers of G. sacculifer test is not sufﬁcient to produce the observed decrease of Mg/Ca values during progressive test dissolution.

Fig. 8. Relative changes in the sample mean Mg/Ca value and the sample mean test thickness derived from modelling G. sacculifer test dissolution and contamination on the seaﬂoor (details of the models are discussed in the text and Appendix B). Dashed lines are best fit to the modelled Mg/Ca values. Lines and symbols are labelled (e.g. St.1 or St.2) according to the samples used in modelling. Best fit lines for surface contamination model (squares) show Mg/Ca composition of the assumed contamination layer (e.g. 20 mmol/mol or 25 mmol/mol). Grey shading indicates the range of Mg/Ca changes from Fig. 7B (horizontal) and the range of reported changes in G. sacculifer test weights (vertical) above calcite lysocline (Broecker and Clark, 2001; Rosenthal and Lohmann, 2002). Note that both dissolution models are unable to reproduce the observed ~10% decrease in Mg/Ca values (Fig. 7B) within an acceptable limit for test dissolution (i.e. <30%) above the calcite lysocline.
In contrast to the two dissolution models results, the removal of a thin Mg-rich surface veneer 0.15 μm thick (e.g. less than 2% of the test thickness) with Mg/Ca composition of 20 mmol/mol can readily produce ~10% decrease of sample mean Mg/Ca values. This relatively thin layer might be composed of residual organic material or diagenetic Mg-rich carbonate or other inorganic precipitate (Boyle, 1983; Morse et al., 1979). The amount and composition of this secondary precipitate present on test surfaces should depend on the calcite saturation level of bottom water (i.e. thicker precipitate in more supersaturated bottom water and thinner to absent in under-saturated bottom water). Both decrease in the relative thickness and in Mg content of the secondary precipitate with decreasing A[CO$_3^{-}$]$_{bottom}$ water. Consequently may produce a trend similar to that observed in the supra-lysocline $G$. sacculifer Mg/Ca. Accordingly, we suggest that the variable development and removal of an Mg-rich surface veneer is potentially responsible for the changes in $G$. sacculifer Mg/Ca values above the calcite lysocline that have been observed here and in early studies (Rosenthal and Boyle, 1993; Brown and Elderfield, 1996; Dekens et al., 2002; Rosenthal and Lohmann, 2002; Rosenthal et al., 2003; Regenberg et al., 2006). If correct, this would underscore the importance of cleaning methods used in Mg/Ca thermometry.

Significant carbonate dissolution has been shown to occur in organic-rich sediments well above the calcite lysocline due to oxidation of sediment organic matter (or so called respiration) and consequent undersaturation of pore water (see Hales, 2003 and citations therein). This supra-lysocline dissolution may affect the Mg/Ca values of foraminifera and could account for the spread of $G$. sacculifer Mg/Ca values observed in Fig. 7B as well as the relatively low sample mean Mg/Ca value at station 3 (Fig. 2). However, considering the distinct difference in pattern of Mg/Ca change above and below the calcite lysocline (Fig. 7B), we suggest that the processes or rates of foraminifera dissolution which modify Mg/Ca compositions are different under saturated and under-saturated conditions.

3.3. Changes in $G$. sacculifer Mg/Ca values below the calcite lysocline

Samples from below the calcite lysocline depth show a significant 0.2 mmol/mol decrease in their mean Mg/Ca compositions per 1 mmol/kg decrease in A[CO$_3^{-}$]$_{bottom}$ water (Fig. 7B). This trend is markedly steeper than above the calcite lysocline, and implies either a change in the rate of the dissolution or the initiation of additional mechanism responsible for altering Mg/Ca values in $G$. sacculifer. We are not able to provide conclusive evidence as to the mechanism(s) responsible for the decrease in bulk test Mg/Ca compositions below the calcite lysocline. However, the change in the frequency distribution of Mg/Ca values for the single core-top sample from below the calcite lysocline, compared to the plankton tow and supra-lysocline samples in Fig. 1B, clearly indicates the loss of the test calcite with higher Mg/Ca values. To have significantly modified the samples bulk Mg/Ca composition, this dissolution should be accompanied by preferential dissolution of test chambers with relatively Mg-rich content. In addition, when using solution analysis of a large number of tests, as is typically done in paleo-reconstructions, the fragmentation/preferential removal of tests with relatively high average Mg/Ca composition may also account for the shift in bulk Mg/Ca. This is consistent with results of early studies on foraminifera dissolution, which reported different dissolution rates between test chambers and between tests within a foraminifera population (Bé et al., 1975; Hecht et al., 1975).

4. Summary

Several different approaches have been used to study foraminiferal test dissolution, including a core-top sample depth transect to 3500 m, all of which demonstrate little evidence for selective dissolution of $G$. sacculifer Mg-rich calcite. $G$. sacculifer tests taken from above the calcite lysocline show minimal if any discernable dissolution effects on sample Mg/Ca compositions. Comparison of previously published results for $G$. sacculifer are consistent with these observations and indicate that the effects of seafloor dissolution on $G$. sacculifer bulk Mg/Ca compositions result in only small changes in Mg/Ca compositions when above the calcite lysocline. The size of the compositional bias deriving from seafloor dissolution above the calcite lysocline is small compared to the uncertainty in bulk test compositions deriving from inter-test variability (e.g. ±0.4 mmol/mol, or ±0.8 °C at ~28 °C). This relative small effect of seafloor dissolution on Mg/Ca values of $G$. sacculifer may be attributed to the banded character of intra-test Mg/Ca variation and the minimal development of a crust layer on the final chambers of this species. Simple models of $G$. sacculifer tests dissolution to show that heterogeneity of Mg/Ca values across $G$. sacculifer test is unable to produce the observed decrease of Mg/Ca values in samples collected above the calcite lysocline. We suggested that these changes in Mg/Ca values may be related to the development and removal of a thin, Mg-rich veneer on test surfaces. This contrasts with modification of $G$. sacculifer Mg/Ca values below the calcite lysocline, which is probably related to preferential dissolution of tests and/or chambers with relative high-Mg/Ca composition.

Acknowledgements

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Appendix A.

Summary of station mean Mg/Ca compositions of Globigerinoides sacculifer. The average value for all stations is highlighted in grey.

<table>
<thead>
<tr>
<th>Samples #</th>
<th>Mean Mg/Ca mmol/mol</th>
<th>Standard deviation of the mean Mg/Ca mmol/mol</th>
<th>Standard error of the mean Mg/Ca mmol/mol</th>
<th>95% confidence interval for mean Mg/Ca mmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>3.45</td>
<td>0.55</td>
<td>0.15</td>
<td>3.22</td>
</tr>
<tr>
<td>S2</td>
<td>3.69</td>
<td>0.83</td>
<td>0.21</td>
<td>3.46</td>
</tr>
<tr>
<td>S3</td>
<td>3.47</td>
<td>0.84</td>
<td>0.22</td>
<td>3.25</td>
</tr>
<tr>
<td>S4</td>
<td>4.07</td>
<td>0.83</td>
<td>0.21</td>
<td>3.86</td>
</tr>
<tr>
<td>S5</td>
<td>3.56</td>
<td>0.71</td>
<td>0.18</td>
<td>3.38</td>
</tr>
<tr>
<td>S6</td>
<td>3.68</td>
<td>0.90</td>
<td>0.20</td>
<td>3.48</td>
</tr>
<tr>
<td>S7</td>
<td>3.95</td>
<td>0.70</td>
<td>0.16</td>
<td>3.71</td>
</tr>
<tr>
<td>S8</td>
<td>3.58</td>
<td>0.72</td>
<td>0.19</td>
<td>3.38</td>
</tr>
<tr>
<td>S9</td>
<td>3.14</td>
<td>0.74</td>
<td>0.16</td>
<td>2.92</td>
</tr>
<tr>
<td>Average</td>
<td>3.62</td>
<td>0.76</td>
<td>0.19</td>
<td>3.34</td>
</tr>
</tbody>
</table>
Appendix B.

Schematic diagram and summary of laser ablation ICPMS data format and calculation for *G. sacculifer* test dissolution and contamination modelling

**Original data format**

<table>
<thead>
<tr>
<th>specimen #1</th>
<th>specimen #2</th>
<th>...</th>
<th>specimen #i</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>#2</td>
<td>...</td>
<td>#X</td>
</tr>
<tr>
<td>Mg/(\text{Ca}^2)</td>
<td>Mg/(\text{Ca}^2)</td>
<td>...</td>
<td>Mg/(\text{Ca}^2)</td>
</tr>
<tr>
<td>Mg/(\text{Ca}^3)</td>
<td>Mg/(\text{Ca}^3)</td>
<td>...</td>
<td>Mg/(\text{Ca}^3)</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td></td>
<td>...</td>
</tr>
<tr>
<td>Mg/(\text{Ca}^n)</td>
<td>Mg/(\text{Ca}^n)</td>
<td>...</td>
<td>Mg/(\text{Ca}^n)</td>
</tr>
</tbody>
</table>

Profiles average values

| Mg/\(\text{Ca}^1\) | Mg/\(\text{Ca}^1\) | ... | Mg/\(\text{Ca}^1\) |
| Mg/\(\text{Ca}^n\) | Mg/\(\text{Ca}^n\) | ... | Mg/\(\text{Ca}^n\) |

Test average values

| Mg/\(\text{Ca}^\text{average} \text{ specimens} #_1\) | Mg/\(\text{Ca}^\text{average} \text{ specimen} #_2\) | ... | Mg/\(\text{Ca}^\text{average} \text{ specimen} #_i\) |

Sample mean value

| Mg/\(\text{Ca}^\text{sample mean} \text{ value}\) |

---

**Model 1 (surface dissolution)**

Each dissolution “step” removes:

First three data points from test outer surface (e.g. Mg/\(\text{Ca}^1\) to Mg/\(\text{Ca}^3\)) and one data point from test inner surface (e.g. Mg/\(\text{Ca}^n\)) of each distribution profile.

New Mg/\(\text{Ca}^\text{ave}\) is calculated following the same method as for original data.

---

**Model 2 (selective dissolution)**

Each dissolution “step” removes:

One data point with maximum Mg/\(\text{Ca}\) value (e.g. max [Mg/\(\text{Ca}^1\), Mg/\(\text{Ca}^3\), Mg/\(\text{Ca}^n\)]) from of each distribution profile.

New Mg/\(\text{Ca}^\text{ave}\) is calculated following the same method as for original data.

---

**Model 3 (surface contamination)**

Each contamination “step” adds:

One data point \(\text{Mg/\(\text{Ca}\)^{ave}}\geq20\) or 25 mmol/mol to each distribution profile.

New Mg/\(\text{Ca}^\text{ave}\) is calculated following the same method as for original data.
References


