

# Comparison of foraminiferal cleaning procedures for Mg/Ca paleothermometry on core material deposited under varying terrigenous-input and bottom water conditions

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[1] A down-core comparison of two commonly applied foraminiferal cleaning procedures for Mg/Ca paleothermometry has been conducted using well-preserved *Globigerinoides ruber* white (250–300  $\mu\text{m}$ ) from core material deposited under varying terrigenous-input and bottom water conditions. This study demonstrates that in the majority of investigated core materials, both cleaning methods yield fairly comparable results of Mg/Ca ratios. However, Fe and Mn phases are effectively removed by the cleaning procedure containing a reductive step. In a core interval indicating gradual transition of terrigenous deposition and pore water conditions, the cleaning procedure without a reductive step results in anomalously higher Mg/Ca ratios accompanied by high Fe/Ca and Mn/Ca ratios, indicating the presence of high-Mg contaminants. Considering that the Mg/Ca deviation of the comparison study is the cumulative sum of (1) the difference in cleaning efficiency of the applied methods, (2) the cleaning-method-dependent partial dissolution of Mg, and (3) the heterogeneity of subsamples, we suggest that selective Mg loss from well-preserved *Globigerinoides ruber* shells caused by the reductive sample treatment is not substantial enough to significantly bias paleotemperature estimation. Thus, for core material deposited under varying sources and amounts of terrigenous material and bottom water conditions favorable for formation of authigenic mineral phases, the use of cleaning methods that do include a reductive step yields more effective cleaning results by successful removal of mineral phases that may contain high Mg.

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**Theme:** Development of the Foraminiferal Mg/Ca Proxy for Paleoceanography

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## 1. Introduction

[2] The application of Mg/Ca ratios of foraminiferal shells as a proxy for paleotemperature estimation has been constantly on the increase since Nürnberg *et al.* [1996] and Lea *et al.* [1999] quantitatively demonstrated the exponential relationship of Mg/Ca ratios to temperature at the calcification depth range of foraminifers. Growing numbers of calibration studies consistently reveal a temperature sensitivity of Mg/Ca ratios in planktonic foraminifers of about 10% per °C [Anand *et al.*, 2003; Dekens *et al.*, 2002; Elderfield and Ganssen, 2000; Lea *et al.*, 1999, 2000; Mashiotto *et al.*, 1999; Nürnberg *et al.*, 1996; Russell *et al.*, 2004]. Along with the refinement of analytical techniques for bulk foraminiferal Mg/Ca high-precision measurements [de Villiers *et al.*, 2002; Rosenthal *et al.*, 1999; Wara *et al.*, 2003], the successful removal of clays, organic matter, and coatings of authigenic mineral phases represents an important step for obtaining reliable Mg/Ca temperature estimates. As shown by an interlaboratory comparison study [Rosenthal *et al.*, 2004], most laboratories throughout North America and Europe apply modified versions of cleaning methods [Barker *et al.*, 2003; Martin and Lea, 2002] previously developed for Cd, Zn, and Ba analysis on foraminiferal calcite [Boyle, 1981; Boyle and Keigwin, 1985; Lea and Boyle, 1991]. The Mg/Ca cleaning method described by Martin and Lea [2002] includes a reductive step for removal of oxide coatings, while that described by Barker *et al.* [2003] does not. Comparison studies that have investigated the effect of a reductive reagent on selective Mg dissolution from foraminiferal calcite have so far yielded contradicting conclusions; Hastings *et al.* [1998] and Martin and Lea [2002] showed that the reductive step does not significantly lower the Mg/Ca value of foraminiferal calcite, whereas Barker *et al.* [2003] reported 10-15% lower Mg/Ca ratios in reductively cleaned samples attributed to corrosiveness of the reducing reagent. Comparing results of homogenized samples analyzed by various laboratories that employ the above mentioned cleaning methods, Rosenthal *et al.* [2004] showed a Mg/Ca decrease in reductively cleaned samples that resulted in a difference of 0.6°C when converted to temperature.

[3] Using well-preserved sample of core material deposited under varying conditions of both bottom water and the source and amount of terrigenous input, we present results of a down-core comparison of commonly used cleaning methods [Barker

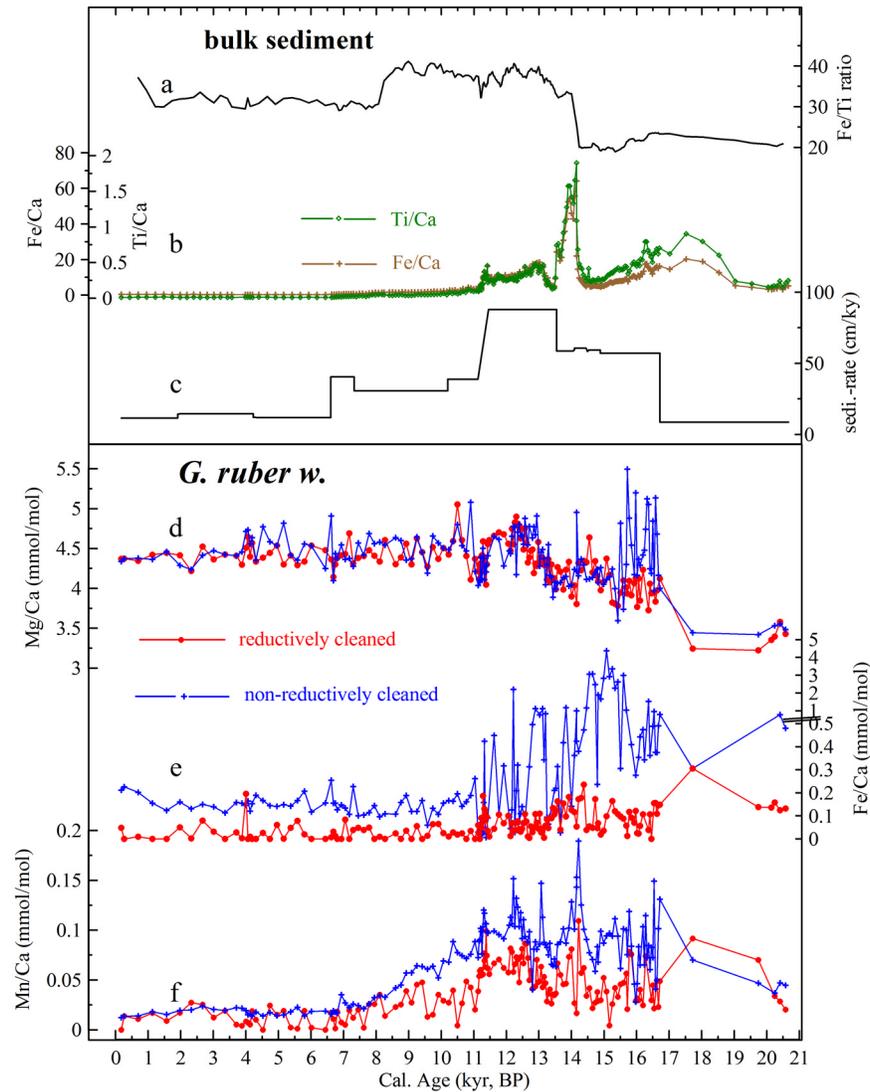
*et al.*, 2003; Martin and Lea, 2002]. Thus the core material provides an ideal opportunity to assess the cleaning effectiveness and the effect of Mg dissolution during sample preparation. A paleoceanographic discussion and interpretations based on the Mg/Ca temperature reconstruction is published in a separate paper [Weldeab *et al.*, 2006].

## 2. Material and Methods

[4] GeoB3129 and GeoB3911 cores were recovered from the same site (4°36.8'S, 36°38.2'W) at the continental margin off north-eastern Brazil at a water depth of 830 m. The two sediment cores were combined to create a composite core (GeoB 3129–3911) with the chronology established by 16 Accelerator Mass Spectrometer (AMS) datings [Arz *et al.*, 1999b], and as a composite covering the last 20.5 thousand years before present (kyr B.P.). The preservation of planktonic foraminifers throughout the core is excellent.

[5] Two sample series (A and B) were prepared for this study. Sample series A was prepared following the cleaning protocol developed by Barker *et al.* [2003]. Briefly, approximately 60 individuals of *Globigerinoides ruber* white (250–300 µm) were gently crushed and transferred into acid-leached 0.5-ml vials. Samples were rinsed with ultrapure water several times and ultrasonically treated. The samples were then rinsed with twice-distilled methanol and treated ultrasonically again, followed by treatments with hot oxidizing solutions (hydrogen peroxide buffered with sodium hydroxide). After every step the samples were rinsed with ultrapure water and ultrasonically treated. Afterward, the samples were checked under the microscope for silicate grains and strongly discolored test fragments, and these were removed using a fine-haired brush. Thereafter, the samples were transferred into new acid-leached vials and leached with weak (0.001 N) nitric acid solution. The samples were dissolved using 0.075 N nitric acid. Immediately after the dissolution of carbonate test fragments, the sample solutions were transferred into acid-leached 2-ml vials.

[6] The preparation of sample series B, which comprises parallel subsamples to sample series A, was conducted following cleaning procedures described by Martin and Lea [2002]. However, alkaline chelation using buffered DTPA (Di-ethylene-tetra-penta-acid) was omitted and samples were microscopically checked for foreign material and strongly discolored foraminiferal shell material



**Figure 1.** (a) Fe/Ti (3-point running average), (b) Ti/Ca and Fe/Ca, and (c) sedimentation rate of bulk sediment in Geo B3129/3911 [Arz *et al.*, 1999a]. (d) Mg/Ca, (e) Fe/Ca, and (f) Mn/Ca ratios of reductively (red lines, sample series B) and nonreductively (blue lines, sample series A) cleaned foraminiferal calcite (*G. ruber w.*, size fraction: 250–300  $\mu\text{m}$ ) versus age model (kyr B.P.) in core Geo B3129/3911. Note break in y axis in Figure 1e.

before the weak-acid leaching step. Thus the cleaning methods we compared differ only in the addition of a reduction step (anhydrous hydrazine-ammonium hydroxide-ammonium citrate solution) for the B series.

[7] The Mg/Ca measurements were conducted on ICP-OES (Perkin Elmar Optima 3300 R). For stabilization and minimizing the matrix effect, an internal standard (yttrium) was added and samples were diluted to equal Ca concentration depending on the Ca concentration from a preliminary ICP-OES measurement. Standards and replicate analyses of samples gave a mean reproducibility of  $\pm 0.07$  Mg/Ca mmol/mol. Parallel to Mg/Ca ratios,

Sr/Ca, Fe/Ca, Mn/Ca, and Ba/Ca were also analyzed. Fe/Ca and Mn/Ca ratios were used for monitoring the cleaning result.

### 3. Results

[8] This study focuses on element ratios in *G. ruber w.* However, selected element ratios and deposition rate of bulk sediment are presented in Figures 1a–1c in order to provide information related to bulk composition of the core material. While Fe/Ca and Ti/Ca ratios of the bulk sediment (Figure 1b) show the variation of terrigenous input relative to carbonate content [Arz *et al.*,



1999a], the variation of Fe/Ti ratio of bulk sediment may indicate change in composition, source, and, to a lesser degree, change in bottom water conditions leading to mobilization of Fe phases. Covariance of parameters of the bulk sediment with elemental ratios of *G. ruber* will be discussed later in section 4.

[9] In the time interval 4–0 kyr, the Mg/Ca ratios show fairly comparable results between the two cleaning methods (Figure 1d). From 11 to 4 kyr, sample series A cleaned without the reduction step generally showed slightly higher Mg/Ca values than series B (Figure 1d). In series A, this interval also exhibits higher Fe/Ca and Mn/Ca ratios than that of series B, varying from 0.2 to 0.1 mmol/mol and 0.02 to 0.09 mmol/mol, respectively (Figures 1e and 1f). The reductively cleaned sample series B shows Fe/Ca and Mn/Ca values less than 0.1 and 0.05 mmol/mol during this time, respectively (Figures 1e and 1f).

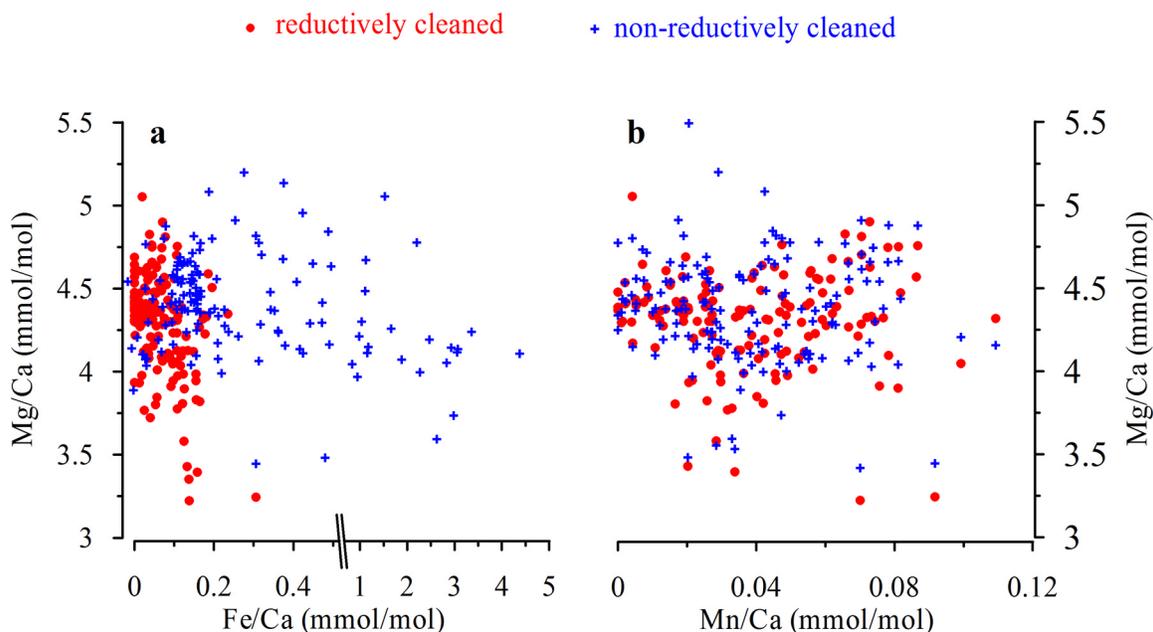
[10] In the time intervals 12.5–11, 15.5–13.3, and 21–17.8 kyr, the deviation of Mg/Ca ratios between the reductively and nonreductively cleaned sample series generally does not exceed a value of 0.25 mmol/mol. However, the Fe/Ca and Mn/Ca ratios in sample series A show high values in these time intervals, reaching up to 3 mmol/mol and 0.15 mmol/mol, respectively (Figures 1e and 1f). In contrast, the highest Fe/Ca and Mn/Ca values of the reductively cleaned sample series reach 0.2 and 0.1 mmol/mol, respectively, in the same intervals (Figures 1e and 1f).

[11] The most marked deviations in Mg/Ca ratios between the two cleaning methods occur in the time intervals of 16.7–15.3 kyr and, to a lesser degree, 20.3–16.7 kyr, with differences up to 0.8 mmol/mol (Figure 1d). High Mg/Ca values in these two intervals are accompanied by higher Fe/Ca ratios in sample series A, varying between 0.35 and 3 mmol/mol. In contrast, the Fe/Ca and Mn/Ca ratios obtained in sample series B are less than 0.15 and 0.1 mmol/mol, respectively (Figures 1e and 1f).

#### 4. Discussion

[12] The results of this comparison study revealed three intervals in the core material that exhibit differences either in the Mg/Ca ratios between the two cleaning methods, differences in the variation and magnitude of Fe/Ca and Mn/Ca ratios, differences in the co-variance of Fe/Ca and Mn/Ca ratios with Mg/Ca ratios, or some combination of these

factors (Figures 1d–1f). The principal causes for discrepancy in the Mg/Ca values in this comparison study can be attributed to the different degree of cleaning effectiveness of the applied methods, cleaning method-dependent partial dissolution of Mg in foraminiferal calcites, and heterogeneity of subsamples. Due to excellent preservation condition of the planktonic foraminifers throughout the entire core, we rule out varying susceptibility of samples to the reductive reagent. Change in the amount and composition of terrigenous input and the presence of authigenic phases (Mn-Fe-oxides, pyrite, and secondary minerals such as ferric oxyhydroxides), which vary through the investigated time interval (Figure 1a), affect the cleaning effectiveness of both methods. When compared to the elemental ratios and deposition rate of bulk sediment (Figures 1a–1c), the increase of Fe/Ca and Mn/Ca ratios of the nonreductively cleaned samples of *G. ruber* tests coincides with sections of high deposition rate and relative high Fe/Ca and Ti/Ca ratios in the bulk sediment (11.5–21 kyr). However, pronounced increases of Fe/Ca and Ti/Ca in the bulk sediment (Figure 1b; 13.5–14.5 kyr) not accompanied by a proportionally increased deposition rate does not correspond with a proportionate increase in Fe/Ca in *G. ruber* analysis. In intervals where the deposition rate and the Fe/Ca and Ti/Ca ratios reveal low values (Figure 1b), Fe/Ca ratios in the nonreductively cleaned samples reach their lowest values. Foraminiferal Mn/Ca ratios, however, are relatively high and accompanied by varying Fe/Ti ratios (Figure 1a) in the bulk sediment (20.5–8 kyr), implying a causal relationship between Mn/Ca in the foraminiferal calcite with the Fe/Ti in the bulk sediment. Assuming that high Fe/Ca and Ti/Ca in bulk sediment indicate high terrigenous input relative to biogenic carbonate, and variation of Fe/Ti is related to change in the composition of terrigenous materials, higher burial rates accompanied by high terrigenous input (11–17 kyr) likely induced changes in the pore water chemistry that may have caused mobilization and the consequent formation of Fe and Mn phases that are not successfully removed in the nonreductively cleaned samples. Mn/Ca values in both cleaning procedures reveal similar trends indicating a close relationship to changes in the composition of terrigenous detritus, though values in the reductively cleaned sample series are lower than those in the nonreductively cleaned sample series (11–17 kyr). Whether the relatively enhanced Mn/Ca value is related to Mn-oxides, Mn-carbonate overgrowth, or other Mn phases is, in this study, difficult to assess. However, the lower Mn/Ca

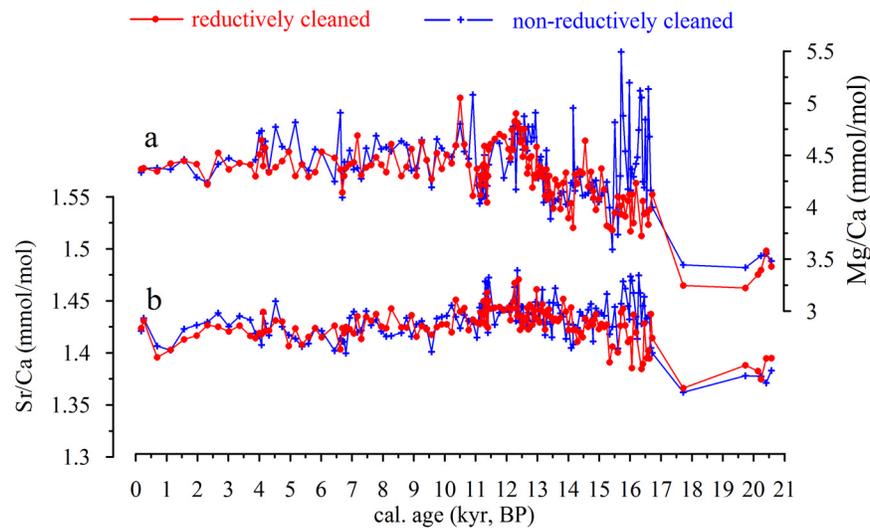


**Figure 2.** (a) Mg/Ca versus Fe/Ca and (b) Mg/Ca versus Mn/Ca of reductively (red dots) and nonreductively (blue cross) cleaned foraminiferal calcite in GeoB 3129/3911 core. Note break in x axis in Figure 2a.

values (on average below 0.07 mmol/mol) in the reductively cleaned sample series compared to that of nonreductively cleaned sample series indicate that part of Mn phases is soluble in the reductive reagent, i.e., almost certainly Mn-oxide.

[13] The assessment of cleaning effectiveness of the two methods is here solely based on the Fe/Ca and Mn/Ca ratios, which are related to the presence of contaminants that may contain elevated Mg. On the basis of the results shown in Figures 1d–1f, it is evident that the cleaning method with a reduction step is more effective in the removal or minimization of Fe and Mn phases and that the reductive reagent does not significantly cause dissolution of lattice-bound Mg in *G. ruber* tests. This latter conclusion is deduced from the Mg/Ca difference ( $\Delta$ Mg/Ca) between both methods (Figure 4) that, considering analytical uncertainty and heterogeneity of subsamples, for the most part ranges between  $-0.25$  and  $+0.25$  mmol/mol (Figure 4a). It is also evident that the highest values of Fe/Ca and Mn/Ca in the nonreductive cleaning method do not necessarily correspond with intervals of highest  $\Delta$ Mg/Ca. For instance, the time interval 15.5–14.2 kyr shows the highest values of Fe/Ca in series A (about 3 mmol/mol), and the corresponding Mg/Ca ratios do not significantly differ from the reductively cleaned sample series, which show low Fe/Ca values (0.05–0.15 mmol/mol) (Figures 1e, 1f, and 2a). In contrast, series A Mg/Ca ratios are significantly higher for the time

interval 16.75–15.5 kyr than from 15.5–14.2 kyr, although the Fe/Ca values (0.3–0.5 mmol/mol) are lower. This illustrates that the composition of the contaminants and their effect on the Mg/Ca ratios varied with climate changes in the catchment areas of the river system that is the main source of terrigenous input to the core site [Arz *et al.*, 1999b; Behling *et al.*, 2000; Jennerjahn *et al.*, 2004]. The formation of authigenic Mn-Fe-oxide coatings and/or pyrite, promoted by changes in the bottom water conditions, represents another major source of contamination for trace element analyses of the foraminiferal calcite [Boyle, 1981; Martin and Lea, 2002]. In fact, a microscopic check of the samples revealed an increase in the presence of spheroidal mineral phases, most likely micro-pyrites or secondary mineral phases such as ferric oxyhydroxides, in the time interval from 11–17 kyr. Although attempt was made to manually remove these mineral phases and other foreign materials under the microscope, we assume that the presence of secondary ferric oxyhydroxides associated with the oxidation of pyritic phases [Childs *et al.*, 1998, and references therein] embedded in the pores of the foraminiferal shell fragments and leached during sample dissolution may be responsible for the high Fe/Ca ratios in sample series A (Figure 1d). Supporting this assumption, the poor co-variance of the Fe/Ca and Mg/Ca ratios (Figure 2a) in the sample series prepared without reduction reagent argues for con-

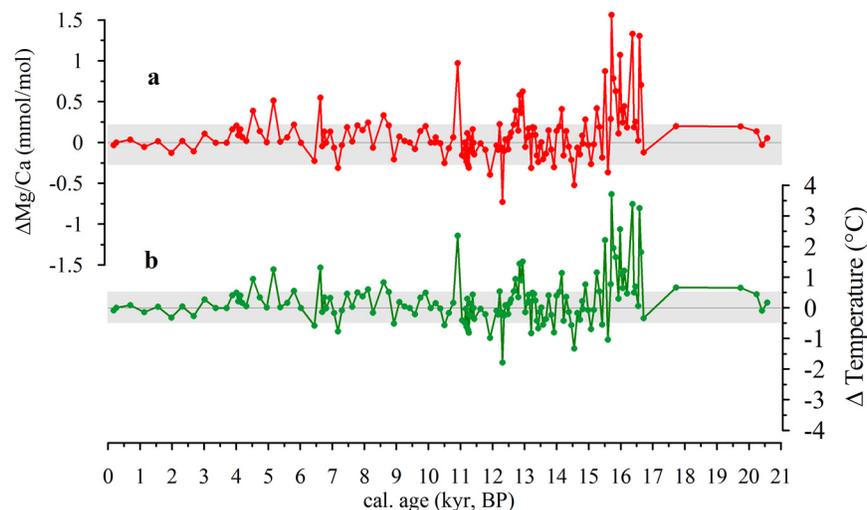


**Figure 3.** (a) Mg/Ca and (b) Sr/Ca ratios of reductively (red lines) and nonreductively (blue lines) cleaned foraminiferal calcite versus age model (kyr B.P.) in GeoB 3129/3911 core.

taminants with high Fe and relatively low Mg content. The intervals that show relatively high Mg/Ca values (compared to reductively prepared samples) and are accompanied by higher Fe/Ca and Mn/Ca ratios are likely controlled by contaminants (coatings) that contributed significant amounts of Mg. Alternatively, clay minerals trapped by oxide coatings or by ferric oxyhydroxides and leached during sample dissolution may also have been responsible for the pronounced higher Mg/Ca ratios. Corroborating the latter assumption, Sr/Ca ratios, which are less affected by Fe-Mn-oxides [Barker *et al.*, 2003], reveal higher values coincid-

ing with the highest Mg/Ca values in sample series A (Figure 3).

[14] The Holocene interval is most useful in assessing lattice-bound Mg loss during sample preparation because of the relatively low Fe/Ca and Mn/Ca values in sample series A, indicating a limited presence of contaminants, and because of the lower offset of Mg/Ca ratios relative to the values obtained with reductively cleaned samples. The average difference of Mg/Ca between the two cleaning methods is less than 0.25 mmol/mol (Figure 4a), and when converted to temperature, the difference is generally less than 0.5°C



**Figure 4.** (a)  $\Delta$ Mg/Ca and (b)  $\Delta$ Mg/Ca temperature (nonreductively minus reductively cleaned sample series) in foraminiferal calcite versus cal. age (kyr B.P.) in core GeoB 3129/3911. Mg/Ca temperature is calculated on the basis of the calibration equation (Mg/Ca [mmol/mol] =  $0.38 \cdot \exp(0.09 \cdot T [^{\circ}\text{C}])$ ) developed by Anand *et al.* [2003]; Gray bars in Figures 4a and 4b indicate range of  $\pm 0.25$  mmol/mol and  $\pm 0.5^{\circ}\text{C}$ , respectively.



(Figure 4b). This is similar to the findings of *Rosenthal et al.* [2004], who reported a temperature difference of about  $0.6^{\circ}\text{C}$  between nonreductively and reductively cleaned planktonic foraminiferal tests. However, we argue that the Mg/Ca difference of any comparison study is the cumulative sum of the difference in cleaning effectiveness of the methods (as indicated by Fe/Ca and Mn/Ca), Mg dissolution during sample treatment, sample heterogeneity, and analytical uncertainties. Depending on the depositional conditions of the samples from particular intervals, the effectiveness of cleaning methods and their comparability may vary. However, we suggest that dissolution of lattice-bound Mg in foraminiferal calcite caused by the cleaning reagent should equally affect all samples within the interval 0–4 kyr that shows low terrigenous input, low deposition rate, and well-preserved foraminifers and pteropods. Thus, on the basis of the time interval 0–4 kyr where the two cleaning methods show fairly comparable Mg/Ca ratios, we suggest that the application of the reductive reagent (anhydrous hydrazine-ammonium hydroxide-ammonium citrate solution) does not significantly affect the Mg/Ca ratio of foraminiferal calcite, in agreement with the findings reported by *Hastings et al.* [1998]. Consequently, the effect of Mg dissolution and Mg/Ca decrease caused by reductive sample treatment is lower than is suggested by Figure 4a. This is in contrast to the findings of *Barker et al.* [2003, 2005], who reported an up to 10–15% decrease of Mg/Ca ratios ( $1\text{--}1.5^{\circ}\text{C}$  when converted to temperature) attributed to the corrosiveness of the reductive sample treatment. On the basis of the discrepant observations, the question arises whether the preservation status of foraminifera [*Brown and Elderfield*, 1996; *de Villiers*, 2003] and/or a species-specific susceptibility to Mg dissolution affects the outcome of the different cleaning procedures and their comparability.

## 5. Summary and Conclusion

[15] We have presented a comparison of the two commonly applied cleaning methods for foraminiferal Mg/Ca analysis using well-preserved samples of core material deposited under varying terrigenous-input and bottom water conditions. We suggest that the cleaning method that does include a reductive step is more effective for removal of Fe and Mn phases that may be accompanied by high-Mg contaminants. Thus removal or minimizing of coating phases seems essential and the use of reductive reagent seems appropriate for

samples from settings that are prone to high terrigenous input of varying composition and bottom water conditions favorable for formation of authigenic phases as shown in this study and by *Pena et al.* [2005]. Our comparison study shows that there would have been an overestimation of SST in the 16.7–15.5 kyr interval if only the nonreductive cleaning procedure have been used.

[16] The effect and magnitude of Mg loss and consequent Mg/Ca decrease caused by a reductive reagent is difficult to quantify because the observed difference of Mg/Ca values in any comparison study is likely the sum of several factors (see section 4). On the basis of this study, we conclude that the decrease in Mg/Ca due to a reductive reagent is not significant enough to bias reliable paleotemperature reconstruction.

[17] Given the potential of Mg/Ca investigations on both planktonic and benthic foraminifers coupled with oxygen isotope analysis to improve our understanding of the temperature and salinity history of the oceans, it is desirable that the paleoclimate community reach a consensus on an integrated cleaning procedure, weighing the advantages, weaknesses, and concerns related to the commonly used cleaning methods [*Barker et al.*, 2003; *Martin and Lea*, 2002] and consider adding the potentially useful step of centrifugation of samples immediately after carbonate dissolution and transferring sample solution to new acid-leached vial [*Boyle*, 1981; *Greaves et al.*, 2005]. The use of integrated cleaning procedures and suitable solid standards for interlaboratory calibration, as suggested by *Greaves et al.* [2005], would certainly facilitate the interlaboratory comparison of Mg/Ca temperature reconstructions.

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