# Effect of preservation state of planktonic foraminifera tests on the decrease in Mg/Ca due to reductive cleaning and on analytical yield

Heather J.H. Johnstone* [1]

[1] MARUM – Center for Marine Environmental Sciences and Faculty of Geosciences, University of Bremen, Germany

*Corresponding author
Email: hjohnstone@marum.de
Fax: +49 (0)421-218-65454
Tel: +49 (0)421 218 65440

William Lee [2]
[2] MACSI, Department of Mathematics and Statistics, University of Limerick, Limerick, Ireland
Email: william.lee@staffmail.ul.ie
Tel: +00353 (0)61 23 4798

Thorsten Kiefer [3]
[3] PAGES International Office, Bern, Switzerland
Email: thorsten.kiefer@pages.unibe.ch
Tel: +41 (0)31 631 56 08

Michael Schulz [1]
[1] MARUM – Center for Marine Environmental Sciences and Faculty of Geosciences, University of Bremen, Germany
Email: mschulz@uni-bremen.de
Tel: +49 (0)421 21865444

Harry Elderfield [4]
[4] Godwin Laboratory, Department of Earth Sciences, University of Cambridge, UK
Email: harrye@esc.cam.ac.uk
Tel: +44 (0)1223 33406

WORDS (abs, intro, methods, results disc, conc, fig caps)

subm Nov 2009; 6,939

Feb 2015; 6,238

## Abstract

Four species of planktic foraminifera from core-tops spanning a depth transect on the Ontong Java Plateau were prepared for Mg/Ca analysis both with (Cd-cleaning) and without (Mg-cleaning) a reductive cleaning step. Reductive cleaning caused etching of foraminiferal calcite, focused on Mg-rich inner calcite, even where tests had already been partially dissolved at the seafloor. Despite corrosion, there was no difference in Mg/Ca of *P. obliquiloculata* between cleaning methods. Reductive cleaning decreased Mg/Ca by an average (all depths) of ~4% for *G. ruber* and ~10% for *N. dutertrei*. Mg/Ca of *G. sacculifer* (above the calcite saturation horizon only) was 5% lower after reductive cleaning.The decrease in Mg/Ca due to reductive cleaning appeared insensitive to preservation state for *G. ruber*, *N. dutertrei* and *P. obliquiloculata*. Mg/Ca of Cd-cleaned *G. sacculifer* appeared less sensitive to dissolution than that of Mg-cleaned. Mg-cleaning is adequate, but SEM and analysis of contaminants, Al/Ca, Fe/Ca and Mn/Ca, show that Cd-cleaning is more effective for porous species. Lower analytical yield after Cd-cleaning for *G. ruber*, *G. sacculifer* and *N. dutertrei* confirmed this to be the more aggressive method. Strongest correlation between analytical yield and $\Delta[CO_3^{2-}]$ in core-top samples was for Cd-cleaned *G. ruber* (r =0.88 , p=0.020) and *P. obliquiloculata* (r= 0.68, p= 0.030). In a down-core record (correlation, r, between yield values > 30% and dissolution index, XDX, was -0.61, p =0.002). Where analytical yield is < 30% most Mg-cleaned Mg/Ca values are biased by dissolution.

## 1. Introduction

The seawater temperature proxy based on the ratio of Mg to Ca in foraminiferal calcite was developed during the 1990s and is now a routine part of paleoceanography [*Nürnberg,* 1995*; Nürnberg et al.,* 1996; *Rosenthal* 1997; *Hastings et al.,* 1998; *Mashiotta et al.,* 1999; *Lea et al.,* 1999; *Elderfield and Ganssen*, 2000]. Thorough cleaning of the foraminifera tests is necessary before analysis to remove contaminants which would otherwise bias trace-metal concentrations. Cleaning methods in current use derive from the protocol of *Boyle* [1981]. Cleaning involves first breaking open the test chambers, then fragments are then rinsed several times with water. This removes fine clays and any other sedimentary material trapped inside the test. An oxidative cleaning step (hydrogen peroxide buffered with sodium hydroxide) is necessary to remove organic material. A reductive cleaning step (anhydrous hydrazine-ammonium hydroxide-ammonium citrate solution) removes coatings of metal oxides. Test fragments undergo further rinsing with water followed by a weak acid leach before the sample is finally dissolved for analysis. When Mg/Ca is the main interest, a simplified method which excludes the reductive step is often used. This method is referred to as “Mg-cleaning”, while the method including a reductive step is called “Cd-cleaning”. Contaminant phases which contain Mg, such as marine clays and some metal oxide coatings [*Pena et al*., 2005; *Weldeab et al*., 2006], are associated with Fe, Al and Mn and these  elements are often monitored for quality control.

A number of studies find that the two cleaning methods give slightly different Mg/Ca values even where Mn and Fe values show that samples are not contaminated The interlaboratory comparison study of *Rosenthal et al.* [2004] used several species of planktonic foraminifera (*G. ruber, G. sacculifer*, *P. obliquiloculata* , *G. bulloides, O. universa*) and concluded that Mg/Ca was generally ~15% lower when Cd-cleaning rather than Mg-cleaning was used. . This is in agreement with *Barker et al*. [2003] who found that Mg/Ca after Cd-cleaning could be 10-15 % lower than with Mg-cleaning. This amount, or a fixed value of 0.2 mmol/mol is often used is a conversion factor between the two methods [*Elderfield et al*., 2006; *Sadekov et al*., 2010].

Detailed examination suggests species specific, or study specific, differences in the offset between the two cleaning methods. *Martin and Lea* [2002] found that reductive cleaning made no difference to the Mg/Ca of (poorly preserved) *Uvigerina* species, but lead to a 10% decrease in the Mg/Ca of (well preserved) *Cibicidoides wuellerstorfi*. *Barker et al.* [2003] confirmed no offset in *Uvigerina* but *Yu et al*. [2007] found a 10% decrease in Mg/Ca with Cd-cleaning for three species of benthic foraminifera including *Uvigerina* species and *C. wuellerstorfi*. *Barker et al.* [2003] found large offsets (> 15%) for *G. ruber*, *Globorotalia hirsuta* and *Neogloboquadrina pachyderma*, ~10 % for *G. truncatulinoides* and *G. inflata* , and no offset for *G. sacculifer* or *G. bulloides*. Studies using Laser Ablation (LA), rather than bulk solution, also found no difference in Mg/Ca after reductive cleaning for *G. bulloides* [*Marr et al*., 2013] and *O. universa* [*Vetter et al*., 2013].

Mg-cleaning has the advantage that the method requires less time. It also avoids the use of the very toxic reagent hydrazine and leads to less loss of sample during cleaning;

however, there is no doubt that Cd-cleaning is more effective at removing contaminants [*Boyle*, 1981; *Weldeab et al*., 2006; *Pena et al*., 2005]. For these reasons, both methods are likely to remain in common use and it is important to understand what controls the offset in Mg/Ca.

One explanation for the decrease in Mg/Ca after Cd-cleaning is that the reagent hydrazine dissolves test calcite slightly. Dissolution of planktonic foraminifera at the sea floor results in lower Mg/Ca, attributed to 'selective dissolution', as calcite containing Mg is more soluble than pure calcite [*Lorens et al.*, 1977; *Russell et al*., 1994; *Brown & Elderfield*, 1996; *Hastings et al*., 1998; *Rosenthal et al.*, 2000 *Dekens et al.*, 2002; *Regenberg et al*., 2006]. It has been suggested, therefore, that lower Mg/Ca after Cd-cleaning is caused by dissolution of test calcite by the reagents used in reductive cleaning [*Barker et al.,* 2003; *Rosenthal et al*., 2004] *Yu et al.* [2007] established that the citrate added to buffer the reducing agent (hydrous hydrazine), when applied in isolation of the reducing agent, can dissolve foraminiferal calcite.

*Barker et al*. [2003] raised the question of whether the offset in Mg/Ca between cleaning methods is sensitive to preservation state of tests. Until now, this issue has not been directly addressed. Although *Rosenthal et al*., [2004] included *G. ruber* and *G. sacculifer* from a deep site in their cleaning comparison study, the different cleaning methods were carried out in different labs and they did not address the topic specifically. *Bian and Martin* [2010] used *N. dutertrei* samples with a range of preservation states from a depth transect, and compared protocols with different amounts of citrate in the reductive cleaning reagent, but did not compare to standard Mg-cleaning.

*Barker et al*. [2003] suggested that the magnitude of the offset may be less for foraminifera from dissolved sediments. This would be the case if the decrease in Mg/Ca caused by reductive cleaning was sensitive to Mg concentration such that the offset in Mg/Ca between the two methods would be greater for well-preserved, high Mg/Ca, tests than for partially dissolved tests with low initial Mg/Ca. In this scenario, reductive cleaning would give a more reproducible result, insensitive to slight prior dissolution of the test, although less representative of initial Mg/Ca. Alternatively, partial dissolution of the test at the sea floor could allow greater penetration of corrosive reagents during cleaning, meaning that reductive cleaning would cause more dissolution, and associated leaching of Mg, in poorly preserved tests. The primary question of this study is: (1) Does preservation state of a sample control the decrease in Mg/Ca caused by reductive cleaning?

The second part of this study addresses the question:
(2) Does analytical yield of a sample indicate the preservation state of foraminifera tests? Cleaning has a high attrition rate, and analytical yield (the percentage of the sample which reaches the instrument) can be a small fraction of the original. There is anecdotal evidence that more material is lost from samples which are poorly preserved. Yield may be as much as 80% for well-preserved tests cleaned by the Mg method but can fall to less than 10% for poorly preserved tests exposed to the more rigorous Cd-cleaning (M.

Greaves, pers. com.). The effect of dissolution on Mg/Ca is a major drawback of this proxy. *Tachikawa et al*. [2008] suggest that yield may be worth monitoring as a dissolution indicator. They found that low yield (<20%) meant Mg/Ca was biased by, supralysoclinal, dissolution. However calibrations comparing yield to deep water calcite saturation are so far lacking.

## 2. Material and Methods

In order to address the two questions posed in the introduction we compare the effect of the two cleaning methods on the Mg/Ca of four species of planktonic foraminifera from a depth transect on the Ontong Java Plateau (OJP). Samples span a range of deep water calcite saturation states ($\Delta[CO_3^{2-}]$) from +13 to -20 µmol/kg. $\Delta[CO_3^{2-}]$ is defined as the difference between $[CO_3^{2-}]_{\text{IN SITU}}$ (measured $[CO_3^{2-}]$ at the site) and $[CO_3^{2-}]_{\text{SATURATION}}$ (calculated $[CO_3^{2-}]$ value at saturation at the site). $\Delta[CO_3^{2-}]$ values in Table 1 are from *Johnstone et al.* [2010]. The calcite saturation horizon is the depth where $\Delta[CO_3^{2-}]$ is equal to zero. This is around 2700 m water depth at this site. The calcite tests of planktonic foraminifera are noticeably dissolved below this depth.

Four species of planktonic foraminifera were used: *Globigerinoides ruber* (white), *Globigerinoides sacculifer* (with no sac-like final chamber), *Neogloboquadrina dutertrei* and *Pulleniatina obliquiloculata*. The four species are different physically. *G. ruber* and *G. sacculifer* have an open porous texture with surface ridges but little or no outer crust. *N. dutertrei* is also porous, but has a thick outer crust. *P. obliquiloculata* has a smooth veneer on top of its calcite crust and no obvious pores [*Hemleben et al.*, 1989].

Each sample consisted of 21 - 52 tests from the 300-355 µm size fraction, ~30 tests for Mg-cleaning and ~40 tests for Cd-cleaning, in accordance with the usual protocol. Most of the samples had previously been scanned by CT (computed tomography) for another study [*Johnstone et al.,* 2011]. CT is a non-destructive technique and did not affect element to Ca ratio presented here. Samples were weighed before being crushed. This was used as initial mass in the calculation of analytical yield (this assumes that test mass consisted only of calcite and that contaminants are negligible). Mass of calcite after cleaning was calculated from the Ca concentration of the analyzed sample.

All samples were cleaned and analyzed at the Godwin Laboratory, University of Cambridge and were cleaned according to the protocols used there. The Mg-cleaning method is based on *Barker et al.* [2003]. The method for Cd-cleaning is based on that of *Boyle* [1981]. There were some slight variations to the published methods, as follows. In both cleaning methods the “coarse silicates removal” step was carried out directly after the deionised water and methanol rinses. The reductive step was carried out before the oxidative step in the Cd-cleaning method. In order to isolate the effect of reductive cleaning Mg-cleaned samples received an extra oxidative step in lieu of the reductive step. This ensured that the number of rinses and amount of sample manipulation was the same for the two sets of samples.

After cleaning, samples were analyzed, first by ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry) to obtain Ca concentrations and also Fe/Ca. Samples were then diluted to a constant Ca concentration and analyzed using the ICP-MS (Inductively Coupled Plasma - Mass Spectrometry) method developed for B/Ca analysis [*Yu et al*., 2005]. All core-top samples were cleaned and analysed over the same two week period. This manuscript deals only with Ca, Mg, Sr, Fe, Mn and Al. Other element data (Li, B, Zn, Cd, Ba, U) exists for these samples exist and will be reported elsewhere [*Yu et al.*, in prep.]. At selected depths, an extra sample was cleaned for SEM (scanning electron microscope) examination to observe the physical effect of cleaning on the tests.

Regressions between parameters ($\Delta[CO_3^{2-}]$, Mg/Ca, analytical yield) were estimated by Slopes.exe program [REF]. Ordinary least squares Bisector method is presented.

The effect of reductive cleaning on yield and on element to Ca ratios (Mg/Ca, Sr/Ca, Mn/Ca, Fe/Ca, Al/Ca) was evaluated by comparison of pairs of samples where each pair consisted of one Mg-cleaned and one Cd-cleaned sample from the same depth. Differences (of average) were considered statistically significant when a one sided t-test gave $p < 0.1$. When this was the case, the null hypothesis (reductive cleaning does not result in a lower value) was rejected.

Samples from a core taken from deep (4157 m) in the Indian Ocean WIND 28K (10$^o$ 09.2’ S, 51$^o$ 46.2’ E) [*McCave*, 2001] were used to further examine the relationship between analytical yield and dissolution.

## 3. Results

### 3.1 Observations from Scanning Electron Microscopy

SEM images show that even after Mg-cleaning, pores of *G. ruber* (not shown), *G. sacculifer* (Figures 1a) and *N. dutertrei* (Figure 2c, 2e) occasionally contained coccoliths or other sediment. Cd-cleaned tests had empty pores. Cd-cleaning was the more corrosive method and caused slight dissolution of calcite, particularly around the pores and at broken edges of tests (Figures 1b, 1d, 2d, 2f, 3b, 3f). Well-preserved tests from shallow sites of all four species had corrosion and damage to the inner calcite after reductive cleaning (Figures 1d, 2d, 3b). The outer surface of well-preserved tests of *G. ruber* (not shown), *G. sacculifer* (Figure 1b) and to a lesser extent, *N. dutertrei* (Figure 2b) also showed more corrosion after Cd-cleaning than after Mg-cleaning (Figures 1a, 2a). The outer surface of *P. obliquiloculata* appeared undamaged by either cleaning method.

Although tests from deep sites had already undergone dissolution at the sea floor, reductive cleaning caused further corrosion. Again, the inner calcite of all four species was affected. Inner calcite of poorly preserved tests appeared friable and etched after reductive cleaning (Figure 2j, 3f). The outer surface of *G. ruber* (not shown) and *G. sacculifer* (Figure 1f) from deep sites was more corroded after Cd-cleaning than after Mg-cleaning (Figure 1e). The outer surface of *N. dutertrei* and *P. obliquiloculata* from deep sites did not appear to be further corroded by reductive cleaning (Figures 2g, 2h, 3d).

*Sensitivity of Mg/Ca to* $\Delta[CO_3^{2-}]$

Mg/Ca of all four species decreased with decreasing calcite saturation of deep water ($\Delta[CO_3^{2-}]$) (Figure 4). Regressions between Mg/Ca and $\Delta[CO_3^{2-}]$) were similar for both cleaning methods for *G. ruber*, *N. dutertrei* and *P. obliquiloculata*. Mg/Ca of Cd-cleaned *G. sacculifer* appeared less sensitive to $\Delta[CO_3^{2-}]$ than Mg-cleaned samples (Figure 4).

### 3.3 Effect of reductive cleaning on Mg/Ca, indicators of contamination (Al/Ca, Fe/Ca and Mn/Ca), pairwise comparisons

Data from 29 out of 33 potential pairs was available for comparison (one sample was lost during cleaning and in three other cases slightly different sample depths were run for Mg-cleaning and Cd-cleaning methods. In a further three cases samples were too small to run on the ICP-MS so there is no Al/Ca data). Pairwise comparison of sample means (Table 3) showed Cd-cleaning resulted in lower Mg/Ca than Mg-cleaning for two of the four foraminifera species. Mean Mg/Ca, for all depths, was 0.17 mmol/mol, or ~10%, lower after Cd-cleaning than Mg-cleaning for *N. dutertrei* and 0.18 mmol/mol, ~4%, lower for *G. ruber*. The decrease in mean Mg/Ca due to reductive cleaning did not quite reach statistical significance for *G. sacculifer* (0.10 mmol/mol, or 3%, $\alpha = 0.10$). In this species, there was a significant difference in Mg/Ca between cleaning methods in samples from above the calcite saturation horizon, where Mg/Ca was on average 0.21mmol/mol, ~5%, less for Cd-cleaned rather than Mg-cleaned samples. There was no difference in the offset between methods in samples from above and below the calcite saturation horizon for any other species. There was no decrease in average Mg/Ca between the two cleaning methods for *P. obliquiloculata*.

The highest values of Al/Ca, Fe/Ca and Mn/Ca were found in Mg-cleaned samples from above the calcite saturation horizon. Samples from deep sites at the Ontong Java Plateau tended to have lower levels of contamination particularly Fe/Ca and Mn/Ca.

Mean Fe/Ca and Mn/Ca were lower after reductive cleaning for all four species (Figure 5). Fe concentrations did not reach the detection limit of the ICP-OES for most of the reductively cleaned samples. Where Fe did not reach the detection limit, a value of zero has been used for Fe/Ca in order to compare samples. Comparison of sample means showed reductive cleaning lowered Fe/Ca by 93% for *G. ruber*; 94% for *G. sacculifer*; 72% for *N. dutertrei*. There was no significant decrease for *P. obliquiloculata*. A negative value was recorded for Mn/Ca when Mn concentration was less than the zero standard on the ICP-MS. This was the case for several of the reductively cleaned samples. In these cases a value of zero was used for pairwise comparison between cleaning methods, but not in the plot (Figure 5). Reductive cleaning lowered mean Mn/Ca by 83% for *G. ruber*; 97% for *G. sacculifer*; 81% for *N. dutertrei* and 53% for *P. obliquiloculata*. Mean Al/Ca was lower after reductive cleaning by 71% for *G. ruber*; 23% for *G. sacculifer* and 66% for *N. dutertrei*. Cleaning method made no difference to Al/Ca of *P. obliquiloculata*.

### 3.4 Relationship of analytical yield with $\Delta[CO_3^{2-}]$ and with MgCa

Analytical yield (Table 3, Figure 6) was greater after Mg-cleaning than after Cd-cleaning for *G. ruber* (Mg-cleaning 32%; Cd-cleaning 16%), *G. sacculifer* (37%; 29%) and *N.*

*dutertrei* (36%; 25%). Yield was not significantly different between methods for *P. obliquiloculata* (27%; 35%).

Regressions estimated between analytical yield of core top samples and $\Delta[CO_3^{2-}]$ all show a positive relationship. Correlation was not significant at the 0.1 level for *G. ruber* and *P. obliquiloculata* cleaned by the Mg-method. The relationship may be mediated by sample mass. There is a strong correlation between $\Delta[CO_3^{2-}]$ and mass of the initial sample and analytical yield is moderately correlated to sample mass. Yield of Mg-cleaned *G. sacculifer* and *N. dutertrei* and Cd-cleaned *G. ruber, G. sacculifer* and *N. dutertrei* have a stronger correlation with $\Delta[CO_3^{2-}]$ than with sample mass.

For the down core record, WIND28K, yield and dissolution index, XDX, of *G. sacculifer* show a weak but statistically significant, correlation($r = -0.32$, $p = 0.020$). Correlation was stronger when the dataset was restricted to values of yield >30% ($r = -0.61$, $p = 0.002$). Correlation between sample mass and XDX was strong ($r = -0.78$, $p = <0.001$). There was some correlation between yield and total sample mass ($r= 0.21$, $p = 0.130$) and yield and average mass ($r = 0.31$, $p = 0.030$).

*Mg/Ca and yield*

Correlation between yield and Mg/Ca for the OJP core-top samples was less than that between $\Delta[CO_3^{2-}]$ and Mg/Ca (Figure 4). Correlation was significant, $p <0.050$, for *N. dutertrei* and *P. obliquiloculata* (Table 3).

## 4. Discussion

### 4.1. Cause of decreased Mg/Ca after reductive cleaning: selective dissolution or more effective contaminant removal

The physical corrosion of tests revealed by SEM, and the decrease in analytical yield, of Cd-cleaned compared to Mg-cleaned samples for three out of four species (Figs1, 2, 3, 6; Table 2) supports previous reports that reductive cleaning causes dissolution of foraminiferal calcite [*Barker et al*., 2003; *Yu et al*., 2007; *Marr et al*., 2013; *Vetter et al*., 2013; *Sadekov et al*., 2010]. There was some evidence that this dissolution preferentially corroded Mg-rich areas of test calcite. Chemical mapping has illustrated that *N. dutertrei* and *P. obliquiloculata* have a low Mg outer crust [*Sadekov et al*., 2005; *Kunioka et al*., 2006; *Sadekov et al.*, 2010]. In our samples, SEM shows that the outer crust calcite of *N. dutertrei* and *P. obliquiloculata* was less corroded by reductive cleaning than the inner parts of the test (Figures 2b, 2d, 3b, 3d). This 'selective dissolution' did not necessarily lead to change in Mg/Ca. *P. obliquiloculata* were corroded by reductive cleaning, yet there was no significant difference in Mg/Ca between cleaning methods in this species. It appears that tests can be partially dissolved by reductive cleaning without this significantly affecting Mg/Ca.

Addressing the suggestion of *Barker et al.* [2003] outlined in the introduction, there was no difference in the regression between $\Delta[CO_3^{2-}]$ and Mg/Ca of Mg-cleaned and Cd-cleaned samples for three out of the foraminiferal species analysed. The exception was *G. sacculifer*, where regressions trended toward smaller offset for poorly preserved samples. In this species, Mg/Ca of Cd-cleaned samples appeared less sensitive to the effect of dissolution, decreasing by 0.021 (± 0.002) mmol/mol per unit $\Delta[CO_3^{2-}]$ compared to 0.041 (±0.010) for Mg-cleaned samples.

In our study, the average (for all depths) decrease in Mg/Ca due to reductive cleaning, was less than the general correction factor of 15% suggested by *Rosenthal et al.* [2004], for all four species examined. The average offset for *G. ruber* in this study of 4% (Figure 4, Figure 5) is less than the 15% found by *Barker et al*. [2003] for well-preserved *G. ruber* from the Arabian Sea. It may be that our sample set does not encompass truly well-preserved samples, *G. ruber* from even the shallowest sites on the Ontong Java Plateau appear slightly dissolved [*Johnstone et al.*, 2010] and Mg/Ca of the shallowest samples do not represent annual average SST at the OJP (Figure 4). Therefore, we cannot completely exclude the possibility that there is a preservation effect in this species, although, for the range of dissolution covered by our sample set, there was no trend toward a smaller offset with decreased calcite saturation.

For *G. sacculifer*, there was no significant difference between Mg-cleaned and Cd-cleaned samples when considering the whole sample set. This is in agreement with *Barker et al*. [2003] who also found no difference in this species, but differs from *Rosenthal et al*. [2004] who found 8 %. For samples above the CSH, Mg-cleaned *G. sacculifer* were 5% higher than Cd-cleaned. However, this is probably within the error of the Mg/Ca method which is often assumed to be ±5 % [eg *Anand et al*., 2003].

The effect on Mg/Ca of dissolution during cleaning is not predicted by dissolution at the seafloor. *N. dutertrei* and *P. obliquiloculata* from the Ontong Java Plateau show a similar sensitivity to the effect of natural dissolution on Mg/Ca (Figure 4). However, on average, Mg/Ca of *N. dutertrei* was ~10% lower after reductive cleaning, suggesting this species is very sensitive to cleaning protocol, while that of *P. obliquiloculata* was unaffected by cleaning method (Figure 4). Again this differs from *Rosenthal et al*., [2004] who found an 8% decrease with Cd-cleaning in *P. obliquiloculata*.

Efficiency of contaminant removal may contribute to the difference in Mg/Ca between cleaning methods. Although these OJP core top samples were cleaned adequately by Mg-cleaning (Fe/Ca and Al/Ca levels were never indicative of contamination), SEM of our samples shows that Cd-cleaning is the more effective method, while Mg-cleaning can leave coccolith plates and detritus in test pores (Figures 1a, 2c). Decreased Al/Ca after reductive cleaning in *G. ruber, G. sacculifer* and *N. dutertrei* in this study (Figure 5) also confirms work of *Boyle*, [1981] that Cd-cleaning also removes sediment from tests more effectively than Mg-cleaning. Metal oxide phases are more likely to occur in down core samples, but even in these Pacific core-top samples Mn/Ca was lower after Cd-cleaning (Figure 5). These oxides can contribute contaminant Mg [*Pena et al*., 2006; *Weldeab et al.,* 2006]. The slight calcite dissolution associated with reductive cleaning may actually be advantageous to remove authogenic calcites, which can be high in Mg, and any incorporated particles.

The tendency of tests to collect sediment or other contamination, may depend on morphology. *Barker et al*. [2003] demonstrated that *G. bulloides*, with its porous texture and open form, was more prone to clay contamination than other species. Previous studies have noted that pores are sites of contaminants [*Pena* et al., 2008; *Vetter et al*., 2013]. In this present study, the smooth surface of *P. obliquiloculata* (Figure 3d) was never seen to be contaminated with sediment, unlike the porous tests of *G. ruber*, *G. sacculifer* (Figure 1) and *N. dutertrei* (Figure 2). In contrast to the three species above, Al/Ca (and Mg/Ca) of *P. obliquiloculata* was similar for both cleaning methods (Figure 5) suggesting that there was little clay to be removed. We do not suggest that clay removal accounts for all of the difference in Mg/Ca between cleaning methods as what is removed does not fit the element ratio of typical marine clays. For example illite is roughly 2% Mg, 2% Fe, 10% Al, ie contains ~5 times more Al than Mg, whereas reductive cleaning removed ~6-7 times more Mg than Al or Fe (Table 3).

The study specific, rather than species specific, differences in Mg/Ca between cleaning methods support the supposition of *Rosenthal et al*., [2004] that minor differences in cleaning protocol affect Mg/Ca.  In this study the "silicate removal step" was carried out for all samples, and in some laboratory protocols this step is omitted. Additionally the "oxidative step" was carried out twice in the Mg-cleaning method. We speculate that the intensity of sample crushing may also affect results. Recent studies using LA show that dissolution thins the walls of tests, but that high Mg bands persist in partially dissolved *G. ruber*  [*Tachikawa et al*., 2008], *G. sacculifer*  [*Sadekov et al*., 2010], *O. universa* [*Vetter et al.*, 2013; *Sadekov et al*., 2010], and *G. bulloides* [*Marr et al*., 2013]. Finer crushing potentially exposes more Mg-rich areas to corrosive reagents. Sensitivity to reagents may also be influenced by intrinsic characteristics of the test, such as arrangement of Mg or crystallinity, which vary between samples. Likelihood of contamination and the amount of Mg in contaminant phases also varies with locality. A universal correction factor therefore may not be appropriate. Where high accuracy is required, comparisons should be made for the particular protocols and samples involved.

## 4.2 Analytical yield as a potential indicator of sample dissolution and bias of Mg/Ca derived temperatures

Maximum yield from core-top samples was ~60%, so a significant part of the original sample was never analyzed, even in well-preserved tests cleaned by the gentlest (Mg-cleaning) method. Presumably part of the not-analysed fraction is clay, silicates and other contaminants. SEM showed that samples from below the calcite saturation horizon contained less detritus than those from shallower sites and are less likely to give high Al/Ca (Al/Ca > 30 μmol/mol) (Table 2). Most of the loss of material in poorly preserved samples therefore must be from the tests themselves. Samples from deep sites were noticeably more friable than well-preserved tests. They were easy to crush and formed small powdery fragments which remained on the surface of the cleaning solution and could potentially be discarded with the solution.

### *Does analytical yield decrease with decreasing* $\Delta[CO_3^{2-}]$

Correlation between $\Delta[CO_3^{2-}]$ and analytical yield (Table 3) confirms anecdotal evidence that analytical yield tends to be lower for poorly preserved samples (Figure 6, Table 3)

In order to further test the utility of the relationship between yield and test preservation, we compared analytical yield of (Mg-cleaned) *G. sacculifer* to a record of preservation for a down core record for which Mg/Ca has been published [*Kiefer et al.,* 2006, *Johnstone et al*., 2014]. Sediment core WIND 28K [*McCave*, 2001] spans the past 150 ka. It was retrieved from 4,175 m water depth in the Indian Ocean from a site currently bathed in corrosive Circumpolar Deep Water. $\Delta[CO_3^{2-}]$ proxy, XDX, is based on the appearance of tests in CT scans and shows that tests are poorly preserved throughout much of the core [*Johnstone et al*., 2014] (Figure 7). Good preservation (low XDX values) in WIND28K occurs during the deglaciations – generally times of good calcite preservation in Indian and pacific oceans [e.g. *Berger*, 1977] - and early in Marine Isotope Stage 3 – also a period of enhanced calcite preservation in the deep Indian Ocean [*Anderson et al*., 2008]. There is a weak correlation between yield and preservation state as indicated by XDX, (r = -0.32, p = 0.020). Considering only a subset of the data, where yield is >30%, gives a stronger correlation (r = -0.61, p = 0.002). This suggests that low yield can occur for any sample, but high yield tends to be associated with better preserved samples.

*Does analytical yield indicate altered Mg/Ca?*

The effect of dissolution on Mg/Ca derived temperatures is a major problem for paleoceanographic reconstructions. For instance, dissolution reduces calculated temperatures for *N. dutertrei* by ~9°C from the shallowest to deepest samples from the Ontong Java Plateau [*Johnstone et al.,* 2011]. Our core-top samples suggest that for Mg-cleaned samples, Mg/Ca is not reliable where yield < 30%. Mg/Ca of these samples was biased by at least 10 %, which is equivalent to ~1 $^{o}$C (Figure 8). For Cd-cleaned samples the picture is less clear cut. *G. ruber* and *G. sacculifer* yield can be very low (<10 %) while Mg/Ca is still representative. For the more robust species, *N. dutertrei* and *P. obliquiloculata*, discarding Mg/Ca where yield was <30 % would not get rid of all biased values and would reject one good value. The value of yield below which data is unreliable is likely to vary between workers. Human input may also distort the relationship between yield and dissolution if poorly preserved or small samples were treated more carefully than samples where tests appear more robust.

Another confounding factor may be that of sample mass. This is strongly correlated to $\Delta[CO_3^{2-}]$, as tests thin and become less abundant due to dissolution (Table 3). There appears to be some correlation between sample mass and yield, at least in some species (eg *P. obliquiloculata* r = 0.8, p =0.006). In the down core, WIND28K, record correlation between yield and sample mass is also strong (r=0.-78, p = <0.001), but the correlation between yield and $\Delta[CO_3^{2-}]$ proxy XDX appears less strong (r = 0.21, p=0.130) than for the Mg-cleaned *G. sacculifer* from core-top samples (r = 0.64, p = 0.125). Further work would be required to isolate the influence of sample mass on yield.

Despite these caveats, we concur with *Tachikawa et al*., [2008], that it may be worth monitoring analytical yield as a first indicator of dissolution bias on Mg/Ca derived temperatures. Although there is a great deal of variability between individual data points, a succession of low yields may warn of a dissolved section of core.

## 5. Conclusions

(1) There was no difference in the slope of regression between $\Delta[CO_3^{2-}]$ and Mg/Ca of Mg-cleaned and Cd-cleaned samples for *G. ruber*, *N. dutertrei* or *P. obliquiloculata.* For G. *sacculifer*, Mg/Ca of Cd-cleaned samples appeared less sensitive to the effect of dissolution.

Although Mg-cleaning is an adequate cleaning method if samples are not contaminated with a high Mg phase, Cd-cleaning removes contaminants more effectively, especially for porous species. SEM showed detritus in pores of *G. ruber*, *G. sacculifer* and *N. dutertrei* after Mg-cleaning while Cd-cleaned tests had clean, empty, pores. Elements indicative of contamination, Al/Ca, Fe/Ca and Mn/Ca, were lower after Cd-cleaning cleaning in these three species. Susceptibility to contamination is sensitive to morphology. *P. obliquiloculata,* which has a very smooth outer surface, did not have coccolith plates or sediment adhering to tests. Al/Ca was not decreased by reductive cleaning in this species, suggesting there was little contamination to be removed.

Reductive cleaning causes slight dissolution of foraminifera tests. Lower analytical yield in *G. ruber*, *G. sacculifer* and *N. dutertrei* species cleaned by Cd- rather than Mg-method confirms this as the more aggressive method. Even tests which have already undergone dissolution at the sea floor showed corrosion after reductive cleaning and this corrosion was focused on inner, Mg-rich, areas of the test. This slight dissolution did not necessarily decrease Mg/Ca, as average Mg/Ca of *P. obliquiloculata* was not significantly lower after reductive cleaning. Reductive cleaning did decrease Mg/Ca in some species. Mg/Ca was on average 4% lower for *G. ruber* (average of all depths), 5 % lower for *G. sacculifer* (if only samples above the CSH are considered), and 10% lower for *N. dutertrei* (all depths) after reductive cleaning. These offsets are generally lower than those of previous studies. If the decrease in Mg/Ca due to reductive cleaning is controlled by extrinsic factors, such as amount or type of clay contamination or intrinsic factors of the test calcite, which can change through time, or to slight differences in cleaning protocol a universal, or even species specific, correction factor between methods would not apply.

(2) Weak, but significant, correlation between Analytical yield and $\Delta[CO_3^{2-}]$ in core-top samples suggests that it may be worth monitoring this property as a first indicator of test preservation and dissolution bias on Mg/Ca. Mg/Ca values of Mg-cleaned samples were unreliable below 30 % recovery. The precise value is no doubt operator dependent. Analytical yield of Cd-cleaned samples, particularly of fragile species, can be low (<10%) but offer reliable Mg/Ca.

**Figure 1.** SEM image of cleaned *G. sacculifer* tests. Left hand side: tests cleaned using Mg-cleaning method; right hand side: tests cleaned using Cd-cleaning method. Samples are from shallow (1616 m), panels (a) to (d); and deep (3400 m), panels (e) and (f), sites on the Ontong Java Plateau. White scale bars are 10 µm long.

(a) Test from a shallow site contains coccoliths and detritus after Mg-cleaning (white arrow) trapped in the pores. (b) Cd-cleaned sample is cleaner, but surface appears etched. Side view of broken test wall shows that inner calcite is more damaged by Cd-cleaning (d) than Mg-cleaning (c).

(e) Mg-cleaned test from a deep site (3400 m) shows some dissolution damage to outer surface. (f) Cd-cleaning causes additional dissolution to the outer surface, even in tests which have already been slightly dissolved at the seafloor.

**Figure 2**. SEM images of cleaned *N. dutertrei* tests. Left hand side: tests cleaned by Mg-cleaning method; right hand side: tests cleaned using Cd-cleaning method. Samples are from a shallow (1616 m) site, panels (a) to (f), and a deep (3400 m) site, panels (g) to (j) on the Ontong Java Plateau. White scale bars are 10 µm long.

(a) Outer wall of Mg-cleaned test (a) from shallow site (1616 m) shows less etching than Cd-cleaned test (b). (c and e) Cd-cleaning is the more effective cleaning method. Mg-cleaned samples can retain coccoliths and other detritus (white arrows) in the pores. (d) Side view of wall of Cd-cleaned test shows that inner calcite is slightly dissolved and separating into layers. The outer calcite is not affected and is still solid. Inner calcite of Mg-cleaned tests shows damage mainly around the pores (e), whereas Cd-cleaned tests show more widespread etching of the inner calcite (f).

(g, h) The outer surface of tests from a deep site (3400 m) show etching and pitting, due to dissolution at the seafloor, irrespective of cleaning method. Inner calcite, where present, appears porous and dissolved (i). Inner calcite was often completely separated from the outer crust. (j) shows the inside of an empty outer crust..

**Figure 3.** SEM images of cleaned *P. obliquiloculata* tests. Left hand side: tests cleaned using Mg-cleaning method; right hand side: tests cleaned using Cd-cleaning method. Samples are from a shallow (1616 m) site, panels (a) (b) and (d), and a deep (2965 m) site, panels (c), (e) and (f), on the Ontong Java Plateau. White scale bars are 10 µm long. Black scale bar is 100 µm long.

Side view of broken test wall shows that Cd-cleaned test (b) is more dissolved, particularly the inner calcite, than Mg-cleaned test (a). The inner and outer calcite of *P. obliquiloculata* (also in *N. dutertrei*, not shown) tends to separate into inner and outer calcite when tests are slightly dissolved (c). *P. obliquiloculata* has a very smooth outer veneer (d).

Inner calcite of tests from the deep (2965 m) site is slightly dissolved (e). Cd-cleaned test (f) is more corroded than Mg-cleaned test (e).

**Figure 4**. Mg/Ca for four species of planktic foraminifera prepared by Mg-cleaning (blue triangles) and Cd-cleaning (red circles). Sensitivity of Mg/Ca to $\Delta[CO_3^{2-}]$ (decrease in mmol/mol per µmol/kg) is shown for each species and cleaning method. Cd-cleaned data of *Dekens et al.* [2002] (grey empty circles) shown for comparison.

**Figure 5.** Comparison of element/Ca obtained by Mg-cleaning and Cd-cleaning for four species of planktic foraminifera. Solid lines are 1:1 lines; dashed line best fit to data forced through the origin. Where analyte does not reach detection limit for Fe/Ca, a value of zero has been plotted. On average (all samples, all species) Mg/Ca are 4% lower where Cd-cleaning rather than Mg cleaning was employed. Fe/Ca and Mn/Ca are lower after reductive cleaning for all four species. Al/Ca is lower after reductive cleaning for all species except *P. obliquiloculata*.

**Figure 6**. Correlation (r) between analytical yield and deep water calcite saturation, $\Delta[CO_3^{2-}]$. For *G. ruber, G. sacculifer* and *N. dutertrei* mean analytical yield is lower after reductive cleaning. In *P. obliquiloculata* yield is similar for both cleaning methods. Slopes of regressions are given in Table 3.

**Figure 7**. Analytical yield for Mg-cleaned *G. sacculifer* from WIND28K, a core from deep (4157 m) in the Indian Ocean. Black line is $\delta^{18}O$ of *C. wuellerstorfi* [*Kiefer et al.,* 2006]. Red line is dissolution index XDX [*Johnstone et al*., 2014], indicating preservation state of *G. sacculifer* tests. Good preservation, low XDX values, occurs during the glacial terminations (marked TI and TII) and between 150 and 270 cm. Brown line is analytical yield of Mg-cleaned *G. sacculifer* (thick line is 3 point running average). Horizontal lines are running (7 values) correlation coefficient between XDX and % yield (dark green) and p value (light green). Yellow bars highlight areas where there is significant correlation, r < -5 and p < 0.01. Lower panel shows regression between XDX and % yield, where yield is > 30%.

**Figure 8**. Change in Mg/Ca due to dissolution (ΔMg/Ca) versus analytical yield for core top samples from the Ontong Java Plateau. Values from the shallowest sample (1BC3, 1,616 m water depth) in our depth transect from the Ontong Java Plateau were used as the 100 % value. The red shaded area shows where Mg/Ca is biased by more than 10% (equivalent to ~1 $^{o}$C). Where analytical yield is below 30 % (red horizontal line) the majority of Mg/Ca values are biased by dissolution.

| Core | Lat.<br>[° N] | Long.<br>[° W] | Water depth<br>[m] | $\Delta[CO_3^{2-}]$<br>[μmol/kg] |
|---|---|---|---|---|
| 1BC3 | -2.24 | -157.00 | 1616 | 13.8 |
| 1.5BC33 | -1.00 | -157.85 | 2015 | 9.3 |
| 2BC13 | -0.01 | -158.91 | 2301 | 4.9 |
| 2.5BC37 | 0.00 | -159.48 | 2445 | 4.3 |
| 3BC16 | 0.01 | -160.45 | 2959 | -2.2 |
| 3BC24 | 0.01 | -160.43 | 2965 | -2.3 |
| 4BC51 | -0.02 | -161.02 | 3411 | -5.8 |
| 4.5BC53 | -0.01 | -161.39 | 3711 | -11.8 |
| 5BC54 | -0.01 | -161.77 | 4025 | -14.7 |
| 5.5BC58 | 0.00 | -162.22 | 4341 | -22.4 |
| 6BC66 | 0.00 | -162.70 | 4400 | -23.0 |

Calcite saturation ($\Delta[CO_3^{2-}]$) from *Johnstone et al.*, [2010].

**Table 1.** Details of cores used in this study.

|  |  |  | "Mg-cleaning" method * |  |  |  |  |  | "Cd |
|---|---|---|---|---|---|---|---|---|---|
| Core | Yield | Mg/Ca | Sr/Ca | Al/Ca | Mn/Ca | Fe/Ca | Yield | Mg/Ca | Sr/C |
|  | [%] | [mmol/mol] | [mmol/mol] | [µmol/mol] | [µmol//mol] | [mmol/mol] | [%] | [mmol/mol] | [mmol/ |
|  |  |  |  |  |  | ***G. ruber* (white), 300-355 µm** |  |  |  |
| **1BC3** | 38 | 4.81 | 1.51 | 92 | 4.6 | 0.029 | 33 | 4.49 |  |
| **1.5BC33** | 34 | 4.47 | 1.47 | 22 | 3.6 | 0.020 | 23 | 4.51 |  |
| **2BC13** | 26 | 4.13 | 1.43 | 26 | 5 | 0.044 | 24 | 4.13 |  |
| **2.5BC37** | 32 | 4.24 | 1.47 | 57 | 7.4 | 0.052 | 7 | 4.07 |  |
| **3BC16** | 20 | 4.18 | 1.46 | 22 | 2.3 | 0 | 2 • | 4.17 |  |
| **3BC24** | 40 | 4.28 | 1.49 | 19 | 3.3 | 0.031 | 10 | 3.65 |  |
| Average | **32** | **4.35** | **1.47** | **40** | **4.4** | **0.029** | **17** | **4.17** |  |
| Average of paired differences (Mg- minus Cd-cleaned) |  |  |  |  |  |  | **15** | **0.18** |  |
|  |  |  |  |  |  | ***G. sacculifer* (without sac), 300-355 µm** |  |  |  |
| **1BC3** | 58 | 4.02 | 1.41 | 27 | 2.8 | 0.050 | 42 | 3.90 |  |
| **1.5BC33** | 51 | 4.24 | 1.38 | 32 | 2.5 | 0.036 | 36 | 3.86 |  |
| **2BC13** | 57 | 3.76 | 1.34 | 6 | 0.9 | 0.023 | 29 | 3.58 |  |
| **2.5BC37** | 47 | 3.85 | 1.36 | 11 | 12.3 | 0.012 | 33 | 3.70 |  |
| **3BC16** | 25 | 3.41 | 1.34 | 18 | 2 | 0 | 27 | 3.58 |  |
| **3BC24** | 52 | 3.54 | 1.33 | 8 | 3.6 | 0.049 | 35 | 3.64 |  |
| **4BC51** | 35 | 3.64 | 1.34 | 21 | 1.3 | 0.019 | 1 • | 3.54 |  |
| Average | **46** | **3.78** | **1.36** | **17.57** | **3.63** | **0.03** | **29** | **3.68** |  |
| Average of paired differences (Mg- minus Cd-cleaned) |  |  |  |  |  |  | **15** | 0.09 |  |
|  |  |  |  |  |  | ***N. dutertrei*, 300-355 µm** |  |  |  |
| **1BC3** | 42 | 2.28 | 1.36 | 80 | 5.3 | 0.031 | 25 | 2.13 |  |
| **1.5BC33** | 49 | 2.10 | 1.36 | 25 | 4.1 | 0.028 | 48 | 1.93 |  |
| **2BC13** | 50 | 1.82 | 1.36 | 10 | 4.5 | 0.016 | 32 | 1.76 |  |
| **2.5BC37** | 44 | 1.97 | 1.36 | 16 | 3.4 | 0.015 | 27 | 1.73 |  |
| **3BC16** | 35 | 1.74 | 1.35 | 12 | 1.5 | 0 | 19 | 1.42 |  |
| **3BC24** | 38 | 1.75 | 1.36 | 5 | 1.4 | 0 | 20 | 1.42 |  |
| **4BC51** | 24 | 1.33 | 1.38 | 36 | 1.1 | 0 | 19 | 1.19 |  |
| **4.5BC53** | 16 | 1.44 | 1.39 | 14 | 0.5 | 0 | 22 | 1.24 |  |
| **5BC54** | 50 | 1.40 | 1.42 | 19 | 1.1 | 0.020 | not run |  |  |
| **5.5BC58** | 12 | 1.08 | 1.44 | 18 | 0.6 | 0.000 | 15 | 1.18 |  |
| **6BC66** | not run |  |  |  |  |  | 22 | 1.07 |  |
| Average | **36** | **1.69** | **1.38** | **23.50** | **2.35** | **0.011** | **25** | **1.51** |  |
| Average of paired differences (Mg- minus Cd-cleaned) |  |  |  |  |  |  | **6** | 0.04 |  |
|  |  |  |  |  |  | ***P. obliquiloculata*, 300-355 µm** |  |  |  |
| **1BC3** | 56 | 2.84 | 1.43 | 39 | 7.1 | 0.032 | 61 | 2.87 |  |
| **1.5BC33** | 41 | 2.66 | 1.42 | 12 | 4.2 | 0.021 | 54 | 2.52 |  |
| **2BC13** | 44 | 2.33 | 1.44 | 9 | 4.4 | 0.012 | 22 | 2.52 |  |
| **2.5BC37** | 0 | 0 | 0 | 0 | 0 | 0 | 33 | 2.21 |  |
| **3BC16** | not run |  |  |  |  |  | 30 | 2.14 |  |
| **3BC24** | 33 | 2.39 | 1.43 | 6 | 12.8 | 0.009 | 31 | 2.16 |  |
| **4BC51** | 11 | 1.90 | 1.35 | 11 | 2.5 | 0 | 37 | 1.82 |  |
| **4.5BC53** | 13 | 1.65 | 1.35 | 36 | 3 | 0 | 27 | 1.73 |  |
| **5BC54** | 48 | 1.62 | 1.39 | 12 | 2.6 | 0.010 | not run |  |  |
| **5.5BC58** | 3 • | 1.46 | 1.38 | n | 1.7 | 0 | 24 | 1.47 |  |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **6BC66** | 19 | 1.40 | 1.40 | 32 | 2.7 | 0 | 26 | 1.44 |
| Average | **27** | **1.83** | **1.26** | **17.44** | **4.10** | **0.008** | **35** | **2.09** |
| Average of paired differences (Mg- minus Cd-cleaned) | | | | | | | -15 | 0.01 |

Element analysis by ICP-MS, except for Fe which was by ICP-MS, or if indicated by ●
*Mg/Ca data from *Johnstone et al*. [2011]
n, not measured
0, below detection limit
Non-significant differences in paired comparison have grey background

**Table 2.** Analytical yield and Mg/Ca, Mn/Ca, Al/Ca, Fe/Ca for four species of planktic foraminifera cleaned using Mg-cleaning and Cd-cleaning methods.

| Species | Cleaning protocol | | Regression between Mg/Ca and Δ[$CO_3^{2-}$] (Fig 4) | | Regression between analytical yield and Δ[$CO_3^{2-}$] (Fig 6) | | Correlation between sample mass and Δ[$CO_3^{2-}$] | | Corre betwe sampl and analy yield |
|---|---|---|---|---|---|---|---|---|---|
| **Core-tops** | | **n** | **Slope** | **Intercept** | **Slope** | **Intercept** | **r** | **p** | **r** |
| ***G. ruber*** | Mg- cleaning | 6 | 24 ± 4 | -101 ± 20 | 0.89 ± 0.15 | -24 ± 6 | 0.99 | 0.000 | 0.51 |
| ***G. sacculifer*** | Mg- cleaning | 7 | 24 ± 6 | -88 ± 22 | 0.59 ± 0.15 | -24 ± 8 | 0.86 | 0.013 | 0.64 |
| ***N. dutertrei*** | Mg- cleaning | 10 | 30 ± 2 | -54 ± 4 | 0.82 ± 0.11 | -32 ± 5 | 0.84 | 0.002 | 0.41 |
| ***P. obliquiloculata*** | Mg- cleaning | 10 | 25 ± 1 | -56 ± 3 | 0.71 ± 0.08 | -24 ± 5 | 0.93 | 0.000 | 0.58 |
| ***G. ruber*** | Cd-cleaning | 6 | 20 ± 4 | -77 ± 18 | 0.53 ± 0.07 | -4 ± 2 | 0.92 | 0.009 | 0.67 |
| ***G. sacculifer*** | Cd-cleaning | 7 | 49 ± 5 | -176 ± 19 | 0.54 ± 0.15 | -13 ± 5 | 0.66 | 0.110 | 0.26 |
| ***N. dutertrei*** | Cd-cleaning | 10 | 35 ± 4 | -56 ± 7 | 1.29 ± 0.37 | -36 ± 9 | 0.83 | 0.003 | 0.58 |
| ***P. obliquiloculata*** | Cd-cleaning | 10 | 26 ± 2 | -59 ± 4 | 0.97 ± 0.18 | -37 ± 7 | 0.97 | 0.000 | 0.80 |

| | | | | | Regression between analytical yield and XDX | | Correlation between sample mass and XDX | | Corre betwe samp and analy yield |
|---|---|---|---|---|---|---|---|---|---|
| **WIND28K** | | | | | **r** | **p** | **r** | **p** | **r** |
| ***G. sacculifer*** | Mg- cleaning | 52 | | | -0.32 | 0.020 | -0.78 | <0.001 | 0.21 |
| | | | Subset where yield >30 % | | | | | | |
| | | 23 | | | -0.61 | 0.002 | | | |

**Table 3**. Parameters for regressions between Mg/Ca and Δ[$CO_3^{2-}$] (Fig 4) and analytical yield and Δ[$CO_3^{2-}$] (Fig 6). Also correlation (r) between sample mass and Δ[$CO_3^{2-}$], and partial correlation between analytical yield and Δ[$CO_3^{2-}$], controlling for sample mass, for core-top samples from the OJP.

## Acknowledgements

This study was funded through DFG Excellence Cluster: “The Ocean in the Earth System”. Many thanks to Jimin Yu for running samples on the ICP-MS and for helpful discussion. Thanks also to Mervyn Greaves for help in the laboratory, and to Linda Booth and Stijn de Schepper for useful comments. WL acknowledges the support of the Mathematics Applications Consortium for Science and Industry funded by the Science Foundation Ireland mathematics initiative grant 06/MI/005.

## 6. References

Barker, S., M. Greaves and H. Elderfield (2003), A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry, *Geochem. Geophys. Geosyst., 4*(9), 8407, doi:10.1029/2003GC000559.

Berger, W.H. (1977), Deep-sea carbonate and the late deglaciation preservation spike in pteropods and foraminifera, *Nature 269*, 301-304.

Boyle, E. (1981), Cadmium, zinc, copper and barium in foraminifera tests, *Geochim. Cosmochim. Acta, 47*, 1815–1819.

Brown, S., and H. Elderfield (1996), Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by postdepositional dissolution – evidence of shallow Mg-dependent dissolution, *Paleoceanography 11*(5), 543-551.

Dekens, P.S., D.W. Lea, D.K. Pak, and H.J. Spero (2002), Core top calibration of Mg/Ca in tropical foraminifera: Refining paleotemperature estimation, *Geochemisty Geophysics Geosystems 3*(4), 1022, doi:10.1029/2001GC000200.

Elderfield, H., and G. Ganssen (2000), Reconstruction of temperature and $\delta^{18}$O of surface ocean waters using Mg/Ca of planktonic foraminiferal calcite, *Nature, 405,* 442– 445.

Greaves, M., et al. (2008), Interlaboratory comparison study of calibration standards for foraminiferal Mg/Ca thermometry, *Geochem. Geophys. Geosyst., 9,* Q08010, doi:10.1029/2008GC001974.

Hastings, D. W., A. D. Russell, and S. R. Emerson (1998), Foraminiferal magnesium in Globeriginoides sacculifer as a paleotemperature proxy, *Paleoceanography, 13,* 161–169.

Hemleben, C., M. Spindler, and O. R. Anderson (Eds.) (1989), *Modern Planktonic Foraminifera,* 363 pp., Springer, New York.

Johnstone, H.J.H, M. Schulz, J. Yu and H. Elderfield (2010), Inside story: An X-ray microtomography method for assessing dissolution in foraminifera tests, *Marine Micropaleontogy 77*, 58-70

Johnstone, H.J.H., M. Schulz , J. Yu and H. Elderfield (2011), Calibrating computed tomography based dissolution index XDX to dissolution bias of Mg/Ca in planktic foraminifera, *Paleoceanography 26*, PA1215, doi:10.1029/2009PA001902.

Johnstone, H.J.H., T. Kiefer, H. Elderfield and M. Schulz, (2014), Calcite saturation, dissolution-corrected foraminiferal test mass and dissolution-corrected Mg/Ca reconstructed using XDX: a 150 ka record from the western Indian Ocean, *Geochemistry, Geophysics, Geosystems 15* (3), 781-797

Kiefer, T., I.N. McCave, and H. Elderfield, (2006), Antarctic control on tropical Indian Ocean sea surface temperature and hydrography, *Geophysical Research Letters, 33*, L24612, doi:10.1029/2006GL027097.

King, K. and P. E. Hare (1972), Amino acid composition of the test as a taxonomic character for living and fossil planktonic foraminifera, *Micropaleontology18*(3) 285-293.

Kunioka, D., K. Shirai, N. Takahata, Y. Sano, T. Toyofuku, and Y. Ujiie (2006), Microdistribution of Mg/Ca, Sr/Ca, and Ba/Ca ratios in *Pulleniatina obliquiloculata* test by using a NanoSIMS: Implication for the vital effect mechanism, *Geochem.Geophys. Geosyst., 7*, Q12P20, doi:10.1029/2006GC001280.

Lea, D. W., T. A. Mashiotta, and H. J. Spero (1999), Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing, *Geochem. Cosmochim. Acta. 63*, 2369–2379.

Lorens, R.B., D. F. Williams, and M. L. Bender (1977), The Early Nonstructural Chemical Diagenesis of Foraminiferal Calcite, *Journal of Sedimentary Research 47,* doi: 10.1306/212F73C9-2B24-11D7-8648000102C1865D.

Martin, P. A., and D. W. Lea (2002), A simple evaluation of cleaning procedures on fossil benthic foraminiferal Mg/Ca, *Geochem. Geophys. Geosyst., 3*(10), 8401, doi:10.1029/2001GC000280.

McCave, I.N., (2001), *R.R.S Charles Darwin Cruise 129,* Report. Department of Earth Science, University of Cambridge, UK.

Mashiotta, T. A., D. W. Lea, and H. J. Spero (1999), Glacial-interglacial changes in subantarctic sea surface temperature and $\delta^{18}$O-water using foraminiferal Mg, *Earth Planet. Sci. Lett., 170*, 417–432.

Nürnberg, D. (1995), Magnesium in tests of *Neogloboquadrina pachyderma* sinistral from high northern and southern latitudes, *J. Foraminiferal Res., 25*, 350– 368.

Nürnberg D., J. Bijma and C. Hemleben (1996), Assessing the reliability of Mg in foraminiferal calcite as a proxy for water mass temperatures, *Geochim. Cosmochim. Acta 60*, 803-814.

Regenberg, M., D. Nürnberg, S. Steph, J. Groeneveld, D. Garbe-Schönberg, R. Tiedemann and W.-C. Dullo (2006), Assessing the effect of dissolution on planktonic foraminiferal Mg/Ca ratios: Evidence from Caribbean core tops, *Geochem. Geophys. Geosyst., 7,* Q07P15, doi:10.1029/2005GC001019.

Rosenthal, Y., E. A. Boyle, and N. Slowey (1997), Environmental controls on the incorporation of Mg, Sr, F and Cd into benthic foraminifera shells from Little Bahama Bank: Prospects for thermocline paleoceanography, *Geochim. Cosmochim. Acta, 61,* 3633– 3643.

Rosenthal, Y., G.P. Lohmann, K.C. Lohmann and R.M. Sherrell (2000), Incorporation and preservation of Mg in Globigerinoides sacculifer: Implications for reconstructing the temperature and $^{18}$O /$^{16}$O of seawater, *Paleoceanography, 15*(1), 135.

Rosenthal, Y., et al. (2004), Interlaboratory comparison study of Mg/Ca and Sr/Ca measurements in planktonic foraminifera for paleoceanographic research, *Geochem. Geophys. Geosyst., 5,* Q04D09, doi:10.1029/2003GC000650.

Sadekov, A. Yu., S. M. Eggins, and P. De Deckker (2005), Characterization of Mg/Ca distributions in planktonic foraminifera species by electron microprobe mapping, *Geochem. Geophys. Geosyst., 6,* Q12P06, doi:10.1029/2005GC000973.

Tachikawa

Weldeab, S., R. R. Schneider, and M. Kölling (2006), Comparison of foraminiferal cleaning procedures for Mg/Ca paleothermometry on core material deposited under varying terrigenous-input and bottom water conditions, *Geochem. Geophys. Geosyst., 7,* Q04P12, doi:10.1029/2005GC000990.

Yu, J. M., J. Day, M. Greaves and H. Elderfield (2005), Determination of multiple element/calcium ratios in foraminiferal calcite by quadrupole ICP-MS, *Geochem. Geophys. Geosyst., 6,* Q08P01, doi:10.1029/2005GC000964.

Yu, J. M., H. Elderfield, M. Greaves, and J. Day (2007), Preferential dissolution of benthic foraminiferal calcite during laboratory reductive cleaning, *Geochem. Geophys. Geosyst., 8,* Q06016, doi:10.1029/2006GC001571.

Yu, J. M., (in prep), Dissolution effects in planktic foraminifera from the Ontong Java Plateau