



## A secondary ionization mass spectrometry calibration of *Cibicidoides pachyderma* Mg/Ca with temperature

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[1] An evaluation of *C. pachyderma* Mg/Ca using a new suite of warm water multicores from the Florida Straits shows that the slope of Mg/Ca with temperature is shallower than previously thought. Using secondary ionization mass spectrometry, we have documented that the distribution of magnesium within the polished walls of foraminiferal tests is Gaussian, suggesting that the Mg/Ca in these samples is not affected by the addition of a secondary high-magnesium calcite in the walls. The Mg/Ca within a typical *C. pachyderma* test varies by about  $\pm 20\%$  ( $1\sigma/\mu \cdot 100$ ), and the variability increases slightly in tests with higher Mg/Ca. The regression of *C. pachyderma* Mg/Ca with temperature has a slope of  $0.13 \pm 0.05$  mmol mol<sup>-1</sup> per °C, indistinguishable from the slope observed in inductively coupled plasma–mass spectrometry measurements from a different subset of the same multicores, but about one half the slope of previously published calibrations. The largest differences between the calibrations comes at the warm water end of the regression, where previously published *C. pachyderma* Mg/Ca values from Little Bahama Bank are at least 3 mmol mol<sup>-1</sup> higher than observed in these new cores. The reasons for this difference are not fully known but are most likely related to diagenesis at Little Bahama Bank.

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### 1. Introduction

[2] The use of paired measurements of foraminiferal metal/calcium ratios (Mg/Ca) and  $\delta^{18}\text{O}$  has been growing quickly because the combined proxies have the potential to quantify the contribution that salinity has on foraminiferal  $\delta^{18}\text{O}$ . For many

planktonic foraminiferal species, Mg/Ca calibrations with temperature are quite robust [Nurnberg *et al.*, 1996; Dekens *et al.*, 2002; Rosenthal and Lohmann, 2002; Anand *et al.*, 2003], but for benthic foraminifera the calibrations pose some significant problems [Rosenthal *et al.*, 1997; Martin *et al.*, 2002; Lear *et al.*, 2002; Marchitto and

*deMenocal*, 2003]. In addition, sample preparation procedures may theoretically affect the metal/calcium ratio [Martin and Lea, 2002; Barker et al., 2003; Elderfield et al., 2006; Yu et al., 2007] since sample cleaning procedures include partial dissolution of the foraminiferal test and the potential loss of soluble mineral phases with higher metal concentrations.

[3] In this paper we apply a different approach to acquiring metal/calcium ratios using secondary ionization mass spectrometry (SIMS). Several recent papers have exploited this approach, one specifically studying core top benthic foraminifera [Allison and Austin, 2003] and another studying small Holocene, Cenozoic and Cretaceous planktonic foraminifera [Bice et al., 2005]. In the first application of this technique to benthic foraminifera, Allison and Austin [2003] measured Mg/Ca and Sr/Ca in several specimens of the shallow water benthic foraminifer *Ammonia batavus*. They quantified the variability within the tests for the species:  $\sim 15$  to  $20\%$   $1\sigma$  (relative standard deviation) for Mg/Ca and  $\sim 5\%$   $1\sigma$  (RSD) for Sr/Ca. They also observed that the measured Mg/Ca values were lower than expected for the in situ temperature of the sample when compared to other benthic foraminiferal species calibrations (no independent calibrations of *A. batavus* exist).

[4] Bice et al. [2005] produced Mg/Ca for planktonic foraminifera in Holocene, Cenozoic and Cretaceous age sediments in various states of preservation, including samples with obvious calcite spar cements. They compared SIMS measurements of the primary and secondary calcite with chemically treated bulk samples measured by inductively coupled plasma–mass spectrometry (ICP-MS). Bice et al. [2005] demonstrated that in unaltered samples, the SIMS and ICP-MS methodologies produced the same mean Mg/Ca values for the samples and that in contaminated or altered samples, the primary calcite could be measured by SIMS, while the bulk samples were biased by the higher Mg/Ca values of the contaminants or overgrowths.

[5] In this paper we develop a modern calibration of the benthic foraminiferal species *Cibicidoides pachyderma* using the SIMS approach and compare the results with traditional ICP-MS measurements from the same samples [Marchitto et al., 2007]. We are using a new suite of well-dated multicores from the Florida and Bahamas margins of the Florida Straits. Our goal is to document the reliability of the SIMS approach and to evaluate

previous calibrations of *C. pachyderma* Mg/Ca with in situ water temperature.

## 2. Rationale

[6] Several recent developments link large scale changes in ocean hydrology with changes in ocean circulation and climate. The most important and direct observation is by Adkins et al. [2002], who showed that the salinity gradients between glacial deep water masses were reversed during the last glacial period. Southern ocean deep waters were much saltier than deep waters produced in the North Atlantic, opposite the pattern observed today. This is an indication that the freshwater budget of the southern ocean was very different from today, perhaps due to brine rejection during sea ice formation and enhanced export of sea ice from the southern ocean [Adkins et al., 2002; Otto-Bliesner et al., 2007]. Deep waters near the freezing point of seawater and large geographic gradients in water mass salinity imply that the glacial deep water density differences were dominated by the salt distribution. These changes in deep ocean circulation were accompanied by large changes in surface salinity. During periods of reduced North Atlantic overturning, surface salinities increased in the Caribbean [Schmidt et al., 2004] and the warm pool of the Pacific Ocean [Stott et al., 2002, 2004] on both orbital and millennial timescales, while surface waters in the subpolar North Atlantic experienced significantly lower salinities. These large changes in salinity (and hydrological cycle) may have played a major role in creating the different deep water mass geometry observed during the glacial period [Curry and Oppo, 2005].

[7] Unfortunately, the direct observation of past changes in deep water salinity is limited to a few locations where pore water chlorinity has been measured. A rapidly growing research strategy, however, supplements these direct observations with calculated salinities based on paired measurements of foraminiferal  $\delta^{18}\text{O}_c$  and Mg/Ca. This is particularly true for studies of surface water hydrography [e.g., Stott et al., 2002, 2004; Schmidt et al., 2004] where the calibrations of planktonic foraminiferal Mg/Ca versus sea surface temperature are well documented and apparently robust [Nurnberg et al., 1996; Dekens et al., 2002; Rosenthal and Lohmann, 2002; Anand et al., 2003]. Using a similar research strategy for benthic foraminifera, calibrations have been developed for several species [Rosenthal et al., 1997; Martin et al., 2002; Lear et al., 2002; Marchitto and deMenocal, 2003],

although the calibrations are more difficult to apply because the slope of Mg/Ca versus temperature is low at low temperatures ( $<5^{\circ}\text{C}$ ) where most benthic foraminifera live. At higher temperatures, the slopes appear to increase, but high variability within samples has made interpretation of the calibrations difficult. *Marchitto and deMenocal* [2003] pointed out these difficulties by showing that an exponential calibration and a linear calibration, both equally valid interpretations of the calibration data, lead to two different interpretations of the history of deep water temperatures for Labrador Sea Water in the North Atlantic. Differences in sample cleaning procedures, the existence of surface contamination with high magnesium, and possible high-magnesium phases in the primary foraminiferal calcite also pose difficulties in applying this approach.

[8] The calibrations are only as good as the suite of samples they are based on and nearly every calibration of benthic foraminiferal Mg/Ca versus temperature is very dependent on a suite of samples collected in Northwest Providence Channel on the southern margin of Little Bahama Bank (OCE205 [*Slowey and Curry*, 1995]). This cruise was the first dedicated coring program of thermocline water depths and it recovered a suite of high-quality box cores that spanned water column temperatures from  $<5^{\circ}\text{C}$  to  $>18^{\circ}\text{C}$ . Samples from this cruise have been used in many benthic foraminiferal element ratio calibrations since. *Rosenthal et al.* [1997] published an early calibration of Mg/Ca (as well as other elements) for benthic foraminifera using the OCE205 suite of cores. *Martin et al.* [2002] used some of the *Rosenthal et al.* [1997] Bahamas data in their calibration of *Cibicoides*. *Lear et al.* [2002] used the same samples with an improved cleaning technique to reevaluate the calibration for several benthic foraminiferal species. *Marchitto and deMenocal* [2003] used several of the *Lear et al.* [2002] OCE205 core top measurements in their reevaluation of the *C. pachyderma* Mg/Ca:temperature calibration. These benthic foraminiferal calibrations are dependent on the Bahamas suite of samples to the extent that in the *Lear et al.* [2002] calibration, 9 of 11 measurements of *C. pachyderma* Mg/Ca in cores at  $12^{\circ}\text{C}$  or higher come from OCE205 cores from the Bahamas. The other two come from shallow cores collected near Hawaii. *Lear et al.* [2002] noted that at higher temperatures, the Mg/Ca values for the *C. pachyderma* were very scattered at the Bahamas and suggested that the variability may result from diagenetic alteration of the primary elemental signal or down-slope movement of foraminiferal tests, leading them to reject some high Mg/Ca measurements in their calibration.

miniferal tests, leading them to reject some high Mg/Ca measurements in their calibration.

[9] Given the doubts about the quality of the OCE205 samples, a reevaluation of the *C. pachyderma* Mg/Ca:temperature calibration seems justified. In this paper, we address this calibration issue using a new suite of cores which provide many well-dated multicore samples in high-temperature thermocline waters. These cores form a subset of the material used for a recent ICP-MS calibration of *C. pachyderma* Mg/Ca [*Marchitto et al.*, 2007].

### 3. Methods

#### 3.1. Study Area

[10] The multicores for this study were collected from the western and eastern sides of the Florida Straits (Figure 1) on R/V *Knorr* 166-2 as part of a study to reconstruct past density gradients and geostrophic flow through the straits [*Lynch-Stieglitz et al.*, 1999; *Lund et al.*, 2006]. The cores are from shallow water depths (200 to 800 m) and sample large gradients in upper water column physical properties (temperatures from 5 to  $20^{\circ}\text{C}$  and salinities 34.9 to 36.7 psu [*Marchitto et al.*, 2007]). The multicores from the southern Florida margin intersect lower salinity waters with an equatorial Atlantic origin and the multicores from the western margin of Great Bahamas Bank intersect higher salinity waters with a subtropical North Atlantic origin [*Schmitz and Richardson*, 1991]. AMS radiocarbon dates were produced for many of the multicores [*Lund and Curry*, 2004, 2006; *Marchitto et al.*, 2007]. Sedimentation rates are higher on the Bahamas side of the straits (20 to several hundred  $\text{cm ka}^{-1}$ ) than on the southern Florida margin (10 to 50  $\text{cm ka}^{-1}$ ). AMS  $^{14}\text{C}$  measurements in many of the core tops record the effects of atmospheric nuclear weapons testing and as a result have  $^{14}\text{C}/^{12}\text{C}$  ratios much higher than 1950 values ( $F_{\text{modern}} > 1$ ). The hydrographic data for the bottom waters immediately above each core site have been presented by *Marchitto et al.* [2007]. The auxiliary material<sup>1</sup> data table for this paper, Table S1, includes bottom water temperature, salinity, and other core location information.

#### 3.2. SIMS Approach

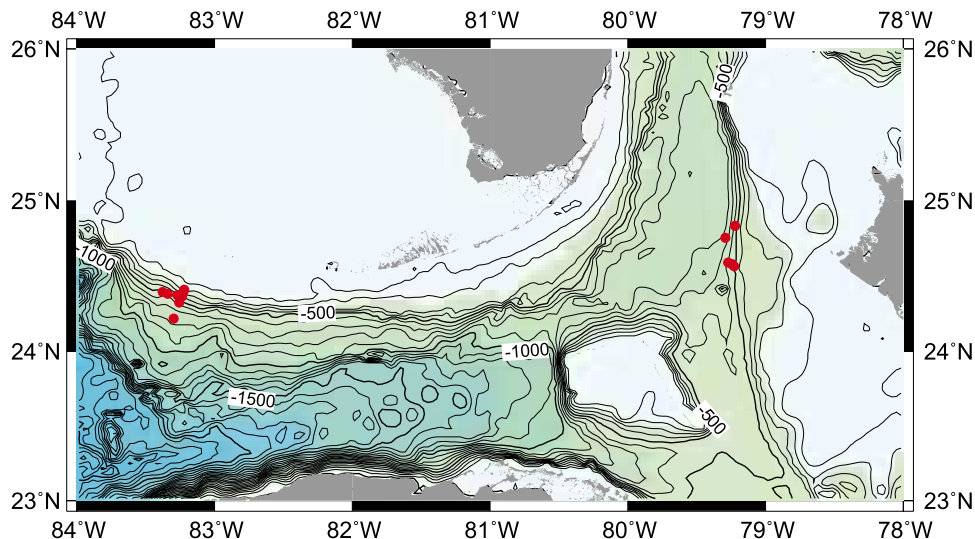
[11] We are following the same methodology as outlined by *Bice et al.* [2005]. Foraminiferal sam-

<sup>1</sup>Auxiliary materials are available at <ftp://ftp.agu.org/apend/gc/2007gc001620>.





## KNR166-2 Multicore Stations

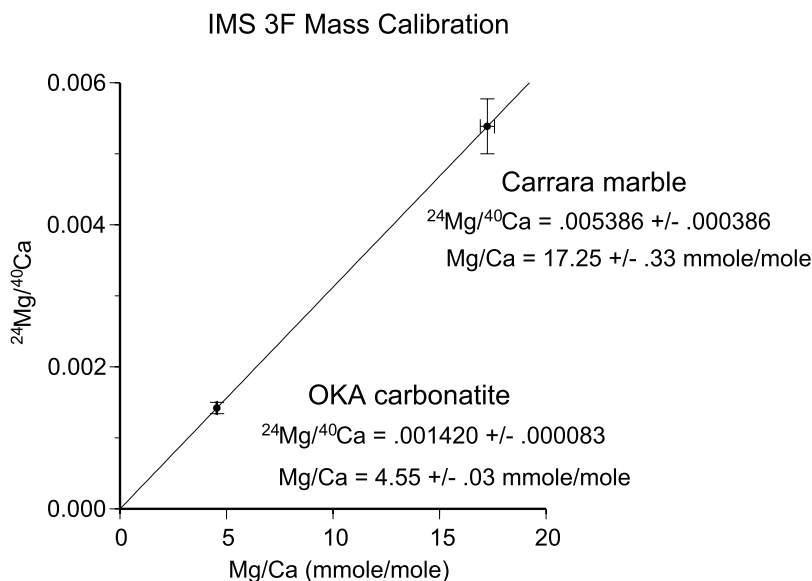


**Figure 1.** KNR166 multicore locations from the southern Florida margin and the western margin of Great Bahamas Bank.

ples were removed from sediment samples that had been disaggregated in distilled water. No chemical cleaning technique was applied. We produced polished sections of the benthic foraminiferal taxon *C. pachyderma* and measured a variety of metal/Ca ratios using a Cameca IMS 3f ion microprobe at the Woods Hole Oceanographic Institution. The process involves sputtering a polished surface of a mineral (in this case  $\text{CaCO}_3$ , but best known and evaluated for a variety of silicates) using a negatively charged primary beam ( $\text{O}^-$ ) 10  $\mu\text{m}$  in diameter and accelerating the sputtered positively charged ions through a double-focusing mass spectrometer system for direct ion counting. For our procedure, we began each analysis by cleaning an area of the test wall with a 25  $\mu\text{m}$  rasterized ion beam to remove potential laboratory contamination caused during the sample preparation and polishing. The ion beam width was then reduced to 10  $\mu\text{m}$  in the middle of the cleaned 25  $\mu\text{m}$  area. Sample locations were away from the edges of the test walls to avoid sampling adhered sedimentary material and surface diagenetic overgrowths. We measured six isotopes ( $^{23}\text{Na}^+$ ,  $^{24}\text{Mg}^+$ ,  $^{25}\text{Mg}^+$ ,  $^{26}\text{Mg}^+$ ,  $^{40}\text{Ca}^+$  and  $^{88}\text{Sr}^+$ ) in four sets of scans with counting times of 20 seconds each (except for  $^{40}\text{Ca}^+$  which requires only 2 seconds of counting to achieve stable measurements in counts per second). Isobaric interferences (such as  $^{24}\text{Mg}^{16}\text{O}^+$  on  $^{40}\text{Ca}^+$  and  $^{44}\text{Ca}_2^+$  on  $^{88}\text{Sr}^+$ ) were suppressed by energy filtering by applying a small acceleration offset of  $-70$  V to the secondary ion beam [Shimizu and Hart, 1982;

Swart, 1990]. Each spot measurement took about 15 minutes to perform and for each foraminiferal test four or five measurements were generally made. As a result it takes about one hour or more to determine robust mean Mg/Ca and Sr/Ca values for an individual foraminiferal test.

[12] Ratios of  $\text{Mg}/^{40}\text{Ca}^+$  in unknowns were then compared with the Mg/Ca ratio in standards (OKA carbonatite, Carrara marble), which we measured independently by ICP-MS without chemical cleaning. The measured  $^{24}\text{Mg}^+ / ^{40}\text{Ca}^+$  using SIMS and measured Mg/Ca concentrations using ICP-MS for the two  $\text{CaCO}_3$  samples used as primary standards for calibration are presented in Figure 2. For this instrument to make accurate Mg (or Sr) measurements the relationship should be linear and the intercept must go through the origin. With only two calibration points, it is not possible to document a linear response using these data alone. However, the linear response of SIMS system is well documented for silicate minerals at a variety of trace element concentration levels as long as the same mineral substrate is being analyzed [Shimizu, 1997]. The sputtering process fractionates the sputtered ions depending on the composition of the original substrate, a process generally termed “matrix effects”. Thus it is not possible to use a calibration curve for a silicate mineral to constrain elemental variations in different silicate or carbonate minerals. Here we use the calibration curve in Figure 2 to document the performance of the Cameca IMS 3f on a carbonate substrate. Conver-



**Figure 2.** Calibration relationship of  $^{24}\text{Mg}/^{40}\text{Ca}$  and Mg/Ca concentration ratios for two  $\text{CaCO}_3$  SIMS standards.  $^{24}\text{Mg}/^{40}\text{Ca}$  is measured by SIMS; Mg/Ca ratio is measured independently by ICP-MS (for OKA, *Bice et al.* [2005]; for Carrara, this paper). The Cameca 3f ion microprobe has a linear response over several orders of magnitude variability in Mg concentration, making it possible to accurately determine Mg/Ca ratios. For  $^{24}\text{Mg}/^{40}\text{Ca}$ , SIMS external analytical precision of the standards averages  $\pm 3.5\%$  within an analytical session. Mass spectrometer tuning parameters differ between sessions, so all Mg/Ca data are calculated on the basis of standard measurements made during a session.

sion of the  $(^{24,25,26})\text{Mg}/^{40}\text{Ca}$  isotopic ratio data to Mg/Ca ratios (in  $\text{mmol mol}^{-1}$ ) was made using the measured values for OKA, which for Mg/Ca are closer to the range observed in the *C. pachyderma*. The reported values of Mg/Ca were calculated as the mean Mg/Ca based on the three independent isotopic measurements,  $^{24}\text{Mg}/^{40}\text{Ca}$ ,  $^{25}\text{Mg}/^{40}\text{Ca}$ , and  $^{26}\text{Mg}/^{40}\text{Ca}$ .

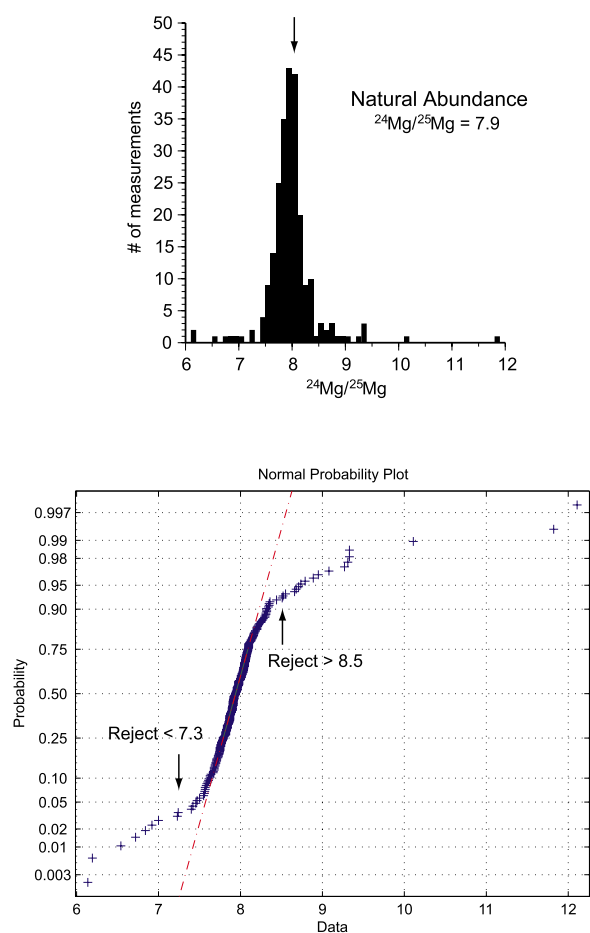
[13] A constraint on the quality of the measurement comes from analysis of the three isotopes of magnesium ( $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$ ) which occur in nature with specific abundance ratios. For our standard measurements, the  $^{24}\text{Mg}/^{25}\text{Mg}$  is  $7.9 \pm 0.2$  and the  $^{24}\text{Mg}/^{26}\text{Mg}$  is  $7.4 \pm 0.2$ , about the same as the abundance ratios seen in nature (7.77 and 7.05, respectively) (Figure 3). Fractionation in the SIMS systems preferentially biases the observed ratios toward higher  $^{24}\text{Mg}$  by fractionating  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$  in an approximate 1:2 ratio. Magnesium isotope variations within foraminifera at the per mil (‰) level are not resolvable by this methodology or instrument. Drift in the isotopic ratios is a sign of poor mass spectrometer tuning and surface contamination. For this work, we rejected  $^{24}\text{Mg}/^{25}\text{Mg}$  greater than 8.5 and less than 7.3, following *Bice et al.* [2005]. In addition, we removed from consideration any data with Na/Ca

ratios higher than 22  $\text{mmol mol}^{-1}$  because of the observed high Na/Ca in the mounting medium [*Bice et al.*, 2005].

[14] Using this approach, external analytical precisions for standards average  $\pm 3.5\%$  ( $1\sigma$  Relative Standard Deviation, RSD) for Mg/Ca (and  $\pm 1.7\%$  for Sr/Ca). Internal precisions are better (generally  $< \pm 2\%$ ), while replicate measurements of spots from *C. pachyderma* have greater variability ( $\pm 10\%$  for Mg/Ca), probably reflecting heterogeneity within the foraminiferal test wall itself.

## 4. Results

[15] The complete data set is listed in Table S1. We measured 29 foraminiferal tests in 14 multicore tops from the Florida Straits. For each foraminiferal test we measured four to eight individual spots (Figure 4) and produced a total of 133 individual measurements of Mg/Ca (and Sr/Ca), after culling the data for quality and mounting medium contamination. Using these data we compare the SIMS measurements with chemically cleaned ICP-MS measurements made from the same multicores; we evaluate the internal variability of Mg/Ca in the *C. pachyderma* tests; and we determine the



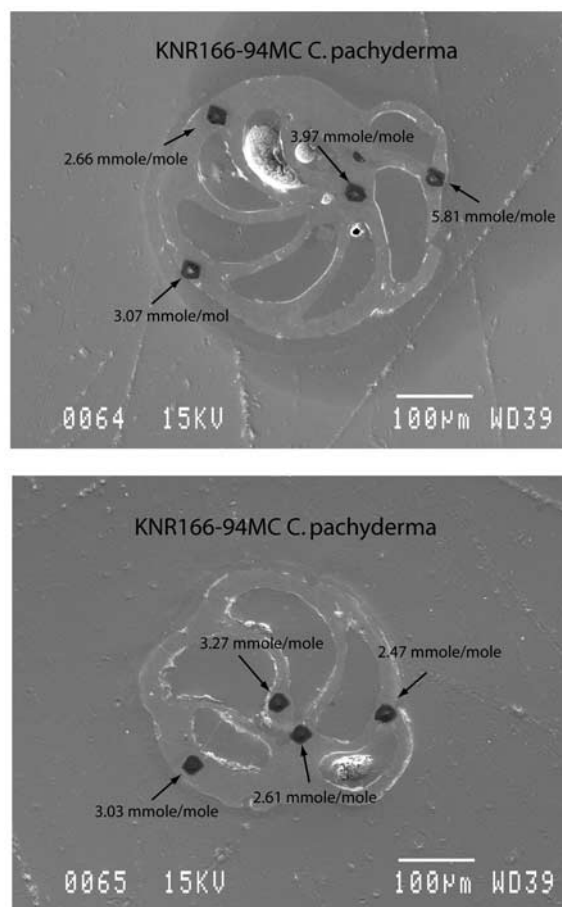
**Figure 3.** Histogram and cumulative frequency distribution plots of  $^{24}\text{Mg}/^{25}\text{Mg}$  for *C. pachyderma*. The data fall off a normal distribution for  $^{24}\text{Mg}/^{25}\text{Mg}$  greater than about 8.5 and less than about 7.3. Following the approach of *Bice et al.* [2005], we rejected data with  $^{24}\text{Mg}/^{25}\text{Mg}$  ratios outside of those bounds.

relationship of Mg/Ca to the temperature of the overlying seawater at each location.

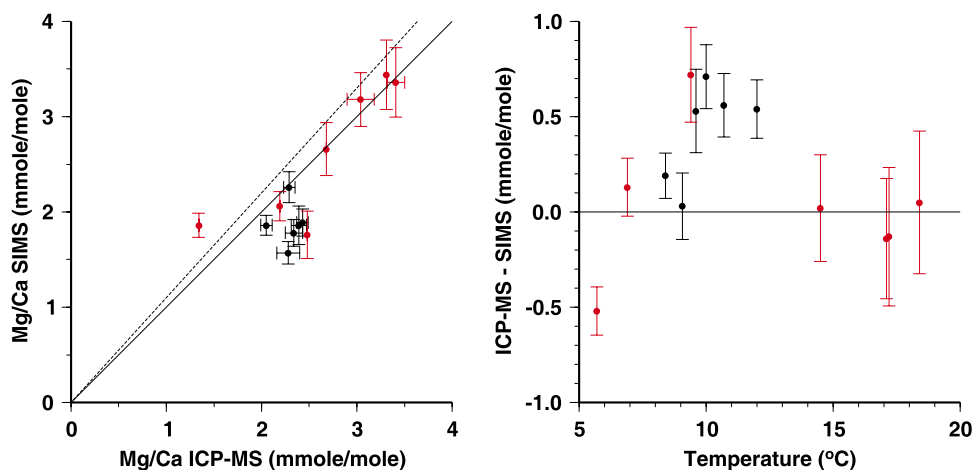
#### 4.1. Intercomparison With ICP-MS

[16] In Figure 5, we present paired values of Mg/Ca produced independently using SIMS and ICP-MS. The ICP-MS measurements were produced from cleaned *C. pachyderma* using standard oxidative and reductive cleaning protocols [Boyle and Rosenthal, 1996] and are presented by Marchitto *et al.* [2007]. The values for SIMS are the averages ( $\pm 1$  standard error) for all spots measured at a location (usually from two or three tests; see Table S1 for a complete listing of spot measurements at each location). Thirteen pairs of measurements are included in Figure 5 and seven

measurements fall within about  $0.3 \text{ mmol mol}^{-1}$  of the 1:1 concordance line. Five others fall off the 1:1 line with values about  $0.5$  to  $0.7 \text{ mmol mol}^{-1}$  higher for the ICP-MS measurements. For the full comparison, the average difference (in absolute value) between the SIMS and ICP-MS data is  $0.33 \text{ mmol mol}^{-1}$  and the root mean squared (rms) deviation is  $0.42 \text{ mmol mol}^{-1}$ . Seven of the multicore tops contain significant bomb radiocarbon, and all but one of these fall very close to



**Figure 4.** Within-test variability for two *C. pachyderma* tests from KNR166-94MC, a multicore bathed in  $18^\circ\text{C}$  subtropical gyre waters. The measurement location is the  $10 \mu\text{m}$  spot within each broader  $25 \mu\text{m}$  dark area. The mean value of the Mg/Ca ratio measured by SIMS is  $3.36 \pm 0.36 \text{ mmol mol}^{-1}$  (1 standard error =  $1\sigma/\sqrt{n} = 1.03/\sqrt{8}$ ). The value measured by ICP-MS is  $3.41 \text{ mmol mol}^{-1}$ . The within-test variability of  $\pm 1.03 \text{ mmol mol}^{-1}$  is about 30%, higher than the average within-test variability of about 20% observed in the full data set (see Figure 6). There is a small increase in the variability of Mg/Ca as a function of the mean value observed within the test ( $r = 0.37$   $p < 0.05$ ); higher mean values of Mg/Ca are accompanied by higher variability (in percent).



**Figure 5.** Intercalibration of Mg/Ca ratios based on SIMS measurements and ICP-MS measurements using *C. pachyderma* samples from the KNR166 multicores. SIMS measurements are the average ( $\pm 1$  standard error) of all “spots” measured on *C. pachyderma* tests within the core top. The ICP-MS measurement is based on several whole tests of *C. pachyderma* following standard analytical techniques [Marchitto *et al.*, 2007]. Red symbols denote core tops containing bomb radiocarbon. There is good agreement between the methods except for the cores bathed in waters from 9 to 12°C. The reason for this discrepancy is unclear. The dashed line represents the higher (by 10%) Mg/Ca values which might be expected for the SIMS data, which have not been subjected to any chemical cleaning [Yu *et al.*, 2007]. The large error bars for the SIMS data preclude testing for this possibility.

the 1:1 concordance line for the paired measurements. For the five multicores where the measurements diverge, each falls within a fairly narrow water temperature range of 9 to 12°C and most of these multicores come from the Florida margin side of the straits.

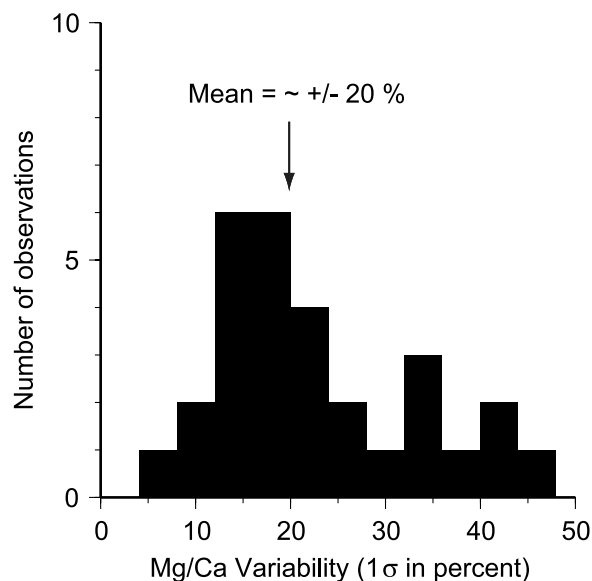
[17] At this time we cannot be sure why some of our measurements differ by more than 0.5 mmol mol<sup>-1</sup>. One possibility is difference in numbers of tests analyzed by the two techniques or the limited number of spots measured within each test. Marchitto *et al.* [2007] analyzed 4 to 14 tests for each Mg/Ca measurement. Here we have measured (usually) two tests per multicore sample. When we have two or more tests in a sample, the mean values for the tests can vary from  $\pm 0.09$  ( $1\sigma$ ) to  $\pm 0.79$  ( $1\sigma$ ), and average  $\pm 0.39$  ( $1\sigma$ ). Given this potential for large differences between individual tests, it is possible that part of the offset may result from the incomplete sampling of the *C. pachyderma* population.

[18] That the largest differences between the analytical approaches fall within a limited temperature range and are from a restricted geographic region suggests that the elevated ICP-MS values may alternatively be related to differences in sediment lithology, resulting in difficulties in chemically cleaning these samples and/or the existence of secondary calcite with a slightly higher Mg/Ca value. Surface contaminants or diagenetic over-

growths would not be detected by the SIMS technique because its measurements are made on the polished surface of interior test walls away from the edges. Marchitto *et al.* [2007] provide evidence that secondary crusts near Little Bahama Bank are extremely elevated in Mg. High magnesium cements are common to many carbonate bank facies, but so far there is no evidence for contamination or diagenetic alteration of the Florida Straits core top samples. All of the ICP-MS data pass standard data quality evaluation [Marchitto *et al.*, 2007]. Thus the reason for the small but seemingly systematic difference between the SIMS and ICP-MS measurements remains unresolved.

[19] It is also interesting that the offset between the two approaches is because of higher Mg/Ca values in samples that have undergone full oxidative and reductive cleaning [Marchitto *et al.*, 2007]. Martin and Lea [2002] performed cleaning experiments on multiple aliquots taken from single samples of *C. wuellerstorfi* and *Uvigerina*. They found that full cleaning (rather than oxidative cleaning alone) lowered the Mg/Ca values of the *C. wuellerstorfi* sample by about 0.1 mmol mol<sup>-1</sup> but left the *Uvigerina* Mg/Ca unchanged. They attributed the *C. wuellerstorfi* lowering to the removal of authigenic contaminants rather than preferential dissolution of Mg, since additional dissolution caused by an aggressive chelation step resulted in no further lowering. Yu *et al.* [2007] recently showed that full cleaning lowered





**Figure 6.** Within-test variability, expressed as a percent of the mean value, for 29 individual *C. pachyderma* tests from the KNR166 multicore samples. Within-test variability averages about 20% of the mean value with a small, but statistically significant, increase in variability (expressed as percent) in tests with higher mean values ( $r = 0.37$ ,  $p < 0.05$ ).

the Mg/Ca values of *C. wuellerstorfi*, *C. kullenbergi*, and *Uvigerina* from multiple samples by about 10% ( $\sim 0.05$ – $0.2 \text{ mmol mol}^{-1}$ ), which they concluded may be due to loss of primary Mg in the foraminiferal test. Our results, if robust, suggest that the full cleaning technique instead resulted in incomplete cleaning at least in a subset of the core locations. An offset of  $-10\%$  in the other reductively cleaned samples is difficult to rule out given the large error bars on the SIMS measurements.

#### 4.2. Internal Variability

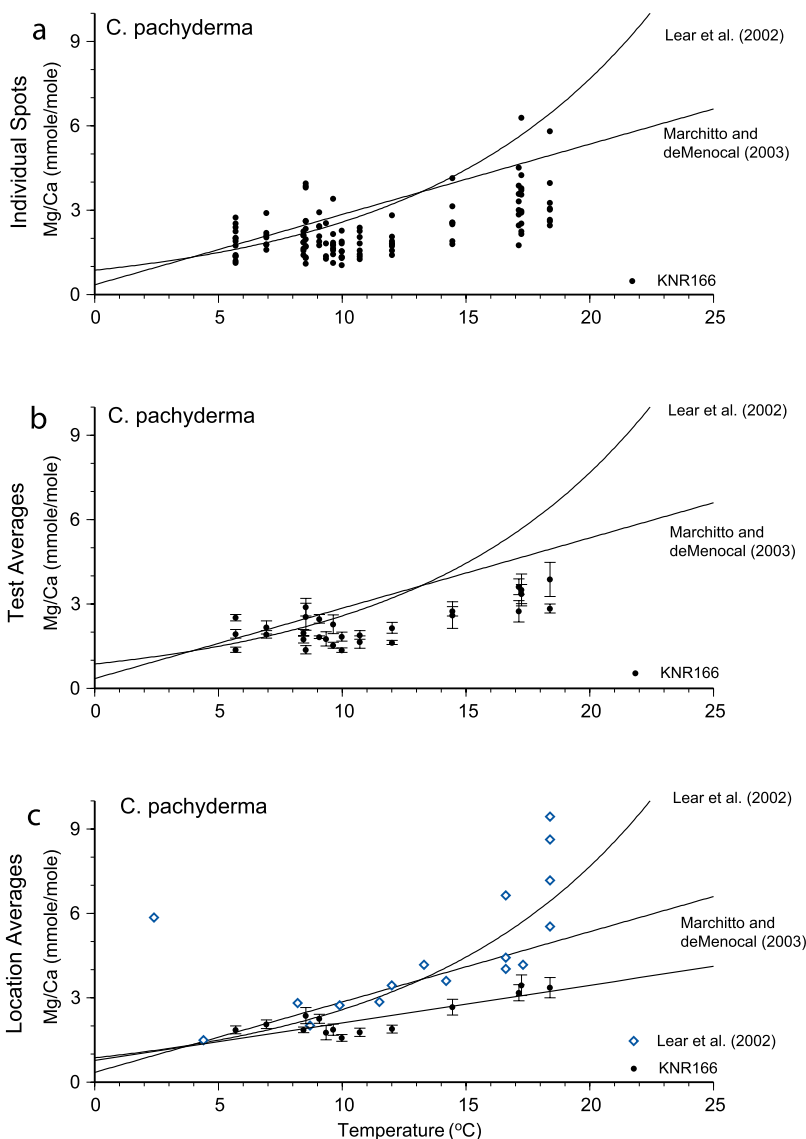
[20] The variability in Mg/Ca within each *C. pachyderma* test, presented as a percentage ( $1\sigma/\mu \cdot 100$  where  $\sigma$  is the standard deviation and  $\mu$  is the mean), is plotted as a histogram in Figure 6. The mean of the variability within each test is  $\sim \pm 20\%$ , and there is a small increase in variability (expressed as percent) with higher mean values ( $r = 0.37$ ,  $p < 0.05$ ). Although there are generally small numbers of measurements within each *C. pachyderma* test, the distribution of the Mg/Ca measurements appears to be normal (Gaussian). We have tested this possibility two different ways: for the individual foraminiferal tests and for composite Mg/Ca populations for each multicore location. The Mg/Ca in 23 of 24 *C. pachyderma* tests passes a Lilliefors test for

Gaussian distribution at the 95% confidence level. The Lilliefors test (here we used Matlab function `lillietest.m`) is used to test the null hypothesis that a data set is normally distributed. It compares the observed data to a cumulative distribution function with normal distribution and the same mean and variance as the data. (Only 24 were tested because a minimum of 4 values is needed to perform the test.) For the combined Mg/Ca values within each multicore top, 13 of 14 locations passes the same test for Gaussian distribution. One multicore location (KNR166-13MC, with the oldest measured radiocarbon age) fails this test for normality even at the 80% confidence level. If there were two different phases of calcite present in these tests (one primary and one diagenetic, for instance), we might expect to see non-Gaussian distributions within the data. So far we have not found evidence for this in the large majority of tests and core locations, although a more rigorous result would be obtained if we had many more measurements in each sample. It is also important to remember that we applied the SIMS approach in a way that would not easily measure overgrowths on the surface or interior walls of the foraminiferal tests. Rather, only heterogeneity within test walls is being detected.

#### 4.3. Mg/Ca:Temperature Calibration

[21] Using Conductivity-Temperature-Depth (CTD) profiles taken during KNR166 and Niskin bottle samples of the near-bottom seawater at each location, Marchitto *et al.* [2007] developed a complete set of hydrographic properties for the seawater immediately above each multicore location. From the data we have produced the local calibration of Mg/Ca versus temperature for *C. pachyderma* (Figure 7) and compare the results with previous calibrations for *C. pachyderma* [Lear *et al.*, 2002; Marchitto and deMenocal, 2003]. For the SIMS data, the minimum Mg/Ca spot value is  $1.05 \text{ mmol mol}^{-1}$  and the maximum Mg/Ca spot value exceeds  $6 \text{ mmol mol}^{-1}$  (only 2 of 126 Mg/Ca measurements exceed  $5 \text{ mmol mol}^{-1}$ ). The large majority of the Mg/Ca values fall well below the previous calibration lines in water temperatures above about  $10^\circ\text{C}$ . In the warmest waters, the differences approach  $3 \text{ mmol mol}^{-1}$  and no individual spot measurements approach the  $9 \text{ mmol mol}^{-1}$  values observed by Lear *et al.* [2002]. Below  $10^\circ\text{C}$ , the Mg/Ca values are the same in each study. The differences in Mg/Ca values at high temperatures are too large to explain by methodological differences since we have documented that both SIMS and ICP-MS methods appear to give





**Figure 7.** *C. pachyderma* Mg/Ca versus bottom temperature for multicore tops from the Florida Straits (KNR166): (a) 126 individual spot measurements of Mg/Ca from 29 tests of *C. pachyderma*; (b) test averages ( $\pm 1$  standard error); and (c) mean values for each multicore top along with the Lear et al. [2002] *C. pachyderma* values from Little Bahama Bank (OCE205) and three samples from Hawaii. Mean Mg/Ca values ( $\pm 1$  standard error) for each test and location are plotted on the basis of multiple spot measurements using SIMS techniques. The three lines on the plot are three different calibration equations: (1) the Lear et al. [2002] exponential equation based on a global data set of *C. pachyderma*; (2) the Marchitto and deMenocal [2003] linear equation based on a subset of the Lear et al. [2002] data; and (3) a regression equation using the plotted measurements from KNR166. At high temperatures, the observed Mg/Ca values are significantly lower in this study than in previous studies. The differences are not the result of analytical problems since chemical cleaning and ICP-MS analysis produce similar values in the same core tops (see Figure 5).

the same values (within about  $0.3\text{--}0.4\text{ mmol mol}^{-1}$ ) in the Florida Straits samples.

[22] The slope of Mg/Ca versus temperature in warm waters is much shallower in this data set than in previously published calibrations using *C. pachyderma* [Rosenthal et al., 1997; Lear et al., 2002; Marchitto and deMenocal, 2003]. Using the

average values for each individual test (Figure 7b), the equation is

$$\text{Mg/Ca} = (0.126 \pm 0.048) \cdot T + (0.886 \pm 0.560)$$

( $n = 29, r = 0.72, 95\% \text{ CI}$ )

where Mg/Ca is expressed in  $\text{mmol mol}^{-1}$  and T is temperature in  $^{\circ}\text{C}$ .

[23] For the core top averages, the equation is

$$\text{Mg/Ca} = (0.134 \pm 0.053) \cdot T + (0.767 \pm 0.634)$$

(n = 14, r = 0.85, 95% CI)

In each case the slope is about one half of the linear slope calculated by *Marchitto and deMenocal* [2003] and, at higher temperatures, much lower than the exponential slope determined by *Lear et al.* [2002]. The slope observed in these data,  $\sim 0.13$  mmol mol<sup>-1</sup> per °C, is indistinguishable from the slope observed by *Marchitto et al.* [2007] using 29 core tops,  $0.116 \pm 0.028$  ( $2\sigma$ ) mmol mol<sup>-1</sup> per °C. This is not surprising since we have analyzed a subset of the same multicores and since we can show that both SIMS and ICP-MS produce the same Mg/Ca values to within about 0.3–0.4 mmol mol<sup>-1</sup> (Figure 5).

## 5. Discussion

[24] Previous calibrations of *C. pachyderma* Mg/Ca versus temperature have rejected some unusually high Mg/Ca measurements from Little Bahama Bank because of suspicions about down-slope reworking of foraminiferal tests or because of the possibility of diagenetic alteration of the tests with secondary high magnesium calcite overgrowths [*Lear et al.*, 2002; *Marchitto and deMenocal*, 2003]. Yet even after culling these suspect values, many high Mg/Ca measurements remain in the calibrations. These high values are not found in waters of similar temperature at the nearby Florida Straits. Of the two proposed reasons for the high values, secondary diagenetic overgrowths are much more likely than down slope reworking.

[25] Carbonate diagenesis in surface and down-core sediments is well documented at the Bahamas [*Neumann et al.*, 1977; *Mullins et al.*, 1985; *Morse*, 2003]. *Neumann et al.* [1977] observed carbonate hardgrounds on DSRV *Alvin* dives in surface sediments along the western margin of Little Bahama Bank at depths of about 600 m, and at shallow depths in some but not all locations within Northwest Providence Channel. It was not observed in deeper locations in the channel. Carbonate diagenetic horizons have also been found in subsurface sediments often concentrated at glacial-interglacial transitions [*Slowey et al.*, 1989]. High magnesium calcites are a common component of the diagenetic overprint, and if these calcites are affecting the core top benthic foraminiferal chemistry, Mg/Ca calibrations with temperature may be very misleading. *Marchitto et al.* [2007] measured one subsurface

diagenetic hard ground from Little Bahama Bank and observed a very high Mg/Ca value of  $\sim 150$  mmol mol<sup>-1</sup>. Only a small overprint of such a high Mg/Ca value would bias the Little Bahama Bank foraminiferal tests.

[26] Although we have no direct evidence for diagenetic alteration of the Mg/Ca signal at Little Bahama Bank, this is the more likely explanation for the high Mg/Ca values observed there. Down slope reworking can be eliminated as the primary cause of high Mg/Ca values at Little Bahama Bank. If the low slopes of Mg/Ca versus temperature observed in this paper and by *Marchitto et al.* [2007] are correct, the highest measured Mg/Ca values at Little Bahama Bank require the presence of very high seawater temperatures, much greater than are observed in the oceans. Thus the simple downward displacement of *C. pachyderma* with high Mg/Ca could not be the reason for such discrepancies in the previous calibration studies.

[27] Other possible explanations are much more speculative. For instance the interactions of groundwaters and the carbonate banks may produce locally high Mg/Ca waters, which may in turn affect the primary calcite of living *C. pachyderma*. Thus the proximity of cores to land may explain why the Little Bahama Bank location is affected but the far western margin of Great Bahama Bank is not.

[28] Unfortunately the low slope of Mg/Ca versus temperature appears to limit its usefulness as a proxy for reconstructions of past deep and intermediate water temperature changes. Small temperature changes at any given core location may not be resolvable using *C. pachyderma* Mg/Ca. It is possible, however, that our measured Mg/Ca:temperature slope is being suppressed by an additional environmental factor, such as carbonate ion concentration [*Marchitto et al.*, 2007]. Indeed temperature explains only about 72–73% of the Mg/Ca variance in both this study and that of *Marchitto et al.* [2007]. Downcore Holocene *C. pachyderma* Mg/Ca data from the Laurentian margin require a greater slope and/or an additional environmental impact on Mg/Ca to result in oceanographically reasonable paleotemperatures [*Marchitto and deMenocal*, 2003]. Additional measurements from other regions are required to investigate the possibility of ancillary environmental effects on *C. pachyderma* Mg/Ca.

[29] Nevertheless, even our low Mg/Ca:temperature sensitivity may be large enough to record the



gradients of temperature within the thermocline and across the Florida Straits. Along the Bahamas side of the Florida Straits, the existing multicore samples a 10°C vertical gradient in temperature while along the Florida margin side they sample a 7°C vertical gradient. Changes in temperature gradient at this scale should be resolved by *C. pachyderma* Mg/Ca, since they correspond to gradients in Mg/Ca of 0.8 mmol mol<sup>-1</sup> or more, which can be easily detected by ICP-MS analysis. Of course the standard error of estimate for our regression based on core top averages is large (the equivalent of ±2.6°C (1σ)), so multiple measurements may be needed to reduce the uncertainty at any individual core in a depth transect. Accurate determination of temperature using benthic foraminifera would enhance the possibility of reconstructing past density gradients and calculating the component of Florida Current transport that is in geostrophic balance. So far, the application of the geostrophic method in this region has depended on the empirical correlation of benthic foraminiferal δ<sup>18</sup>O and density [Lynch-Stieglitz *et al.*, 1999; Lund *et al.*, 2006]. Adding information about temperature gradients would make these calculations much more robust.

[30] The Mg/Ca values in *C. pachyderma* from the Florida Straits multicore locations appear to be normally (Gaussian) distributed, suggesting that Mg/Ca in each test is from a single population with a typical test variability of about ±20%. This within-test range is too large to be caused simply by water temperature fluctuations within the individual's lifetime. The weak positive correlation of this internal variability with higher mean Mg/Ca suggests that the variability may be caused by the biology of the benthic species, perhaps related to growth rate differences in higher temperature water. The observation of normally distributed values at each location makes it less likely Mg/Ca in *C. pachyderma* from the Florida Straits are biased by secondary high magnesium calcite cements, at least within foraminiferal test walls. Using this method we have not tested for the possibility of surface overgrowths, which remain a possible source of high Mg/Ca values in the Florida Straits and at other shallow water carbonate margins. Our work also implies that polished test walls of this species are clean enough to avoid the biasing effects of clay contamination and that the test walls are not so porous that the mounting medium affects the ion probe measurement, as was first demonstrated by Bice *et al.* [2005] for planktonic foraminiferal samples. The SIMS technique appears to be a

viable approach for producing high-quality Mg/Ca data. Data production rates are low, however, so the SIMS approach may be of limited usefulness for producing long, high-resolution time series of Mg/Ca. Manual data acquisition and long integration times for each spot measurement may limit the SIMS approach to focused research activities related to shell calcification and the incorporation of Mg into fossil tests and testing for the presence of alteration or contamination of the primary Mg/Ca signal.

## 6. Conclusions

[31] 1. Secondary ionization mass spectrometry appears to be a viable approach to measure the distribution of metals in late Quaternary benthic foraminifera. The precision of the measurements is about ±3.5% for Mg/Ca and with appropriately calibrated standards, mean values of multiple spot measurements in test walls generally produce the same results as standard chemical cleaning and ICP-MS. Measurements for the same multicores using the SIMS and ICP-MS methods yield an average difference of 0.33 mmol mol<sup>-1</sup> (equivalent to 2.6°C) and a root mean squared deviation of 0.42 mmol mol<sup>-1</sup>. Most paired measurements agree with a much smaller deviation, while cores in 9 to 12°C waters of the Florida Straits differ by more, with the ICP-MS data consistently higher.

[32] 2. Multiple measurements of Mg/Ca from 29 individual tests of *C. pachyderma* document an average internal variability of Mg/Ca of ~±20% (1σ/μ ·100). There is a small but significant increase in internal variability in tests with higher Mg/Ca ( $r = 0.37$   $p < 0.05$ ). Higher Mg/Ca occurs in warmer waters, so the higher variability may result from a growth rate effect on magnesium incorporation into the foraminiferal calcite. Marchitto *et al.* [2007] point out that temperature and CO<sub>3</sub><sup>2-</sup> covary in the Florida Straits, which may impact both the measured values of Mg/Ca as well as the variability in the foraminiferal tests. The probability distribution of Mg/Ca in foraminiferal tests appears to be Gaussian for thirteen of fourteen core locations, which suggests that the foraminiferal Mg/Ca in these cores is not affected by the addition of one or more secondary sources of high magnesium calcite.

[33] 3. The observed slope of *C. pachyderma* Mg/Ca with temperature is much lower than in previous calibrations especially in warm waters. The slope observed here (0.13 mmol mol<sup>-1</sup> per °C) is





indistinguishable from the slope ( $0.12 \text{ mmol mol}^{-1}$  per  $^{\circ}\text{C}$ ) observed by Marchitto *et al.* [2007], which was measured on a larger set of the same multicores.

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