

1 **A SIMS Calibration of *Cibicidoides pachyderma* Mg/Ca with temperature**

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14

15 **Abstract**

16

17 An evaluation of *C. pachyderma* Mg/Ca using a new suite of warm water multicores  
18 from Florida Straits shows that the slope of Mg/Ca with temperature is shallower than  
19 previously thought. Using Secondary Ionization Mass Spectrometry we have  
20 documented that the distribution of magnesium within the foraminiferal tests is Gaussian  
21 suggesting that the Mg/Ca in these samples is not affected by the addition of a secondary  
22 high magnesium calcite overgrowth. The Mg/Ca within a typical *C. pachyderma* test  
23 varies by about  $\pm 20\%$  ( $1\sigma/\mu \cdot 100$ ) and the variability increases in tests with higher  
24 Mg/Ca. The regression of *C. pachyderma* Mg/Ca with temperature has a slope of 0.13  
25  $\text{mmole mole}^{-1}$  per  $^{\circ}\text{C}$ , indistinguishable from the slope observed in ICP-MS  
26 measurements from a different subset of the same multicores, but about one half the slope  
27 of previously published calibrations. The largest differences between the calibrations  
28 comes at the warm water end of the regression where previously published *C.*  
29 *pachyderma* Mg/Ca values from Little Bahama Bank are at least 3  $\text{mmole mole}^{-1}$  higher  
30 than observed in these new cores. The reasons for this difference are not fully known,

31 but are most likely related to diagenesis at Little Bahama Bank rather than down slope  
32 reworking.

33

### 34 **Introduction**

35

36 The use of paired measurements of foraminiferal metal/calcium ratios (Mg/Ca)  
37 and  $\delta^{18}\text{O}$  has been growing quickly because the combined proxies have the potential to  
38 quantify the contribution that salinity has on foraminiferal  $\delta^{18}\text{O}$ . For many planktonic  
39 foraminiferal species, Mg/Ca calibrations with temperature are quite robust [Nurnberg *et al.*,  
40 *1996*; Dekens *et al.*, 2002; Rosenthal and Lohmann, 2002; Anand *et al.*, 2003], but  
41 for benthic foraminifera the calibrations pose some significant problems [Rosenthal *et al.*,  
42 1997; Martin *et al.* 2002; Lear *et al.*, 2002; Marchitto and deMenocal, 2003]. In addition,  
43 sample preparation procedures may theoretically affect the metal/calcium ratio [Barker *et al.*,  
44 *2003*] since sample cleaning procedures include partial dissolution of the  
45 foraminiferal test and the potential loss of soluble mineral phases high in metal  
46 concentration.

47

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

60

61 Bice *et al.* [2005] produced Mg/Ca for planktonic foraminifera in Holocene,  
62 Cenozoic and Cretaceous age sediments in various states of preservation, including  
63 samples with obvious calcite spar cements. They compared SIMS measurements of the  
64 primary and secondary calcite with chemically-treated bulk samples measured by  
65 Inductively Couple Plasma Mass Spectrometry (ICP-MS). Bice *et al.* demonstrated that  
66 in unaltered samples, the SIMS and ICP-MS methodologies produced the same mean  
67 Mg/Ca values for the samples and that in contaminated or altered samples, the primary  
68 calcite could be measured by SIMS, while the bulk samples were biased by the higher  
69 Mg/Ca values of the contaminants or overgrowths.

70

71 In this paper we develop a modern calibration of the benthic foraminiferal species  
72 *Cibicidoides pachyderma* using the SIMS approach and compare the results with  
73 traditional ICP-MS measurements from the same samples [Marchitto *et al.*, 2007]. We  
74 are using a new suite of well-dated multicores from the Florida and Bahamas margins of  
75 the Florida Straits. Our goal is to document the reliability of the SIMS approach and to  
76 evaluate previous calibrations of *C. pachyderma* Mg/Ca with *in situ* water temperature.

77

## 78 **Rationale**

79

80 Several recent developments link large scale changes in ocean hydrology with  
81 changes in ocean circulation and climate. The most important and direct observation is  
82 by Adkins *et al.* [2002], who showed that the salinity gradients between glacial deep  
83 water masses were reversed during the last glacial period. Southern ocean deep waters  
84 were much saltier than deep waters produced in the North Atlantic, opposite the pattern  
85 observed today. This is an indication that the freshwater budget of the southern ocean  
86 was very different from today, perhaps due to brine rejection during sea ice formation  
87 and enhanced export of sea ice from the southern ocean [Adkins *et al.*, 2002]. Deep  
88 waters near the freezing point of sea water and large geographic gradients in water mass  
89 salinity imply that the glacial deep water density differences were dominated by the salt  
90 distribution. These changes in deep ocean circulation were accompanied by large changes  
91 in surface salinity. During periods of reduced North Atlantic overturning, surface

92 salinities increased in tropical regions of the Atlantic and Pacific Oceans on both orbital  
93 and millennial time scales [Stott *et al.*, 2002, 2004; Schmidt *et al.*, 2004], while surface  
94 waters in the subpolar North Atlantic experienced significantly lower salinities. These  
95 large changes in salinity (and hydrological cycle) must have played a major role in  
96 creating the different deep water mass geometry observed during the glacial period  
97 [Curry and Oppo, 2005].

98  
99         Unfortunately, the direct observation of past changes in deep water salinity is  
100 limited to a few locations where pore water chlorinity has been measured. A rapidly  
101 growing research strategy, however, supplements these direct observations with  
102 calculated salinities based on paired measurements of foraminiferal  $\delta^{18}\text{O}_c$  and Mg/Ca.  
103 This is particularly true for studies of surface water hydrography [*e.g.*, Stott *et al.*, 2002,  
104 2004; Schmidt *et al.*, 2004] where the calibrations of planktonic foraminiferal Mg/Ca  
105 *versus* sea surface temperature are well documented and apparently robust [Nurnberg *et al.*,  
106 1996; Dekens *et al.*, 2002; Rosenthal and Lohmann, 2002; Anand *et al.*, 2003].  
107 Using a similar research strategy for benthic foraminifera, calibrations have been  
108 developed for several species [Rosenthal *et al.*, 1997; Martin *et al.* 2002; Lear *et al.*,  
109 2002; Marchitto and deMenocal, 2003], although the calibrations are more difficult to  
110 apply because the slope of Mg/Ca *versus* temperature is low at low temperatures (< 5 °C)  
111 where most benthic foraminifera live. At higher temperatures, the slopes increase, but  
112 high variability within samples has made interpretation of the calibrations difficult.  
113 Marchitto and deMenocal [2003] pointed out these difficulties by showing that an  
114 exponential calibration and a linear calibration, both equally valid interpretations of the  
115 calibration data, leading to two different interpretations of the history of deep water  
116 temperatures for Labrador Sea Water in the North Atlantic. Differences in sample  
117 cleaning procedures, the existence of surface contamination with high magnesium, and  
118 possible high magnesium phases in the primary foraminiferal calcite also pose difficulties  
119 in applying this approach.

120  
121         The calibrations are only as good as the suite of samples they are based on and  
122 nearly every calibration of benthic foraminiferal Mg/Ca *versus* temperature is very

123 dependent on a suite of samples collected in Northwest Providence Channel on the  
124 southern margin of Little Bahama Bank (OCE205: Slowey and Curry, [1995]). This  
125 cruise was the first dedicated coring program of thermocline water depths and it  
126 recovered a suite of high-quality box cores that spanned water column temperatures from  
127 < 5 °C to > 18 °C. Samples from this cruise have been used in many benthic  
128 foraminiferal element ratio calibrations since. Rosenthal *et al.* [1997] published an early  
129 calibration of Mg/Ca (as well as other elements) for benthic foraminifera using the  
130 OCE205 suite of cores. Martin *et al.* [2002] used some of the Rosenthal *et al.* [1997]  
131 Bahamas data in their calibration of *Cibicidoides*. Lear *et al.* [2002] used the same  
132 samples with an improved cleaning technique to reevaluate the calibration for several  
133 benthic foraminiferal species. Marchitto and deMenocal (2003) used several of the  
134 OCE205 core top measurements in their reevaluation of the *C. pachyderma*  
135 Mg/Ca:temperature calibration. These benthic foraminiferal calibrations are dependent  
136 on the Bahamas suite of samples to the extent that in the Lear *et al.* [2002] calibration, 9  
137 of 11 measurements of *C. pachyderma* Mg/Ca in cores at 12° C or higher come from  
138 OCE205 cores from the Bahamas. The other two come from shallow cores collected near  
139 Hawaii. Lear *et al.* [2002] noted that at higher temperatures, the Mg/Ca values for the *C.*  
140 *pachyderma* were very scattered at the Bahamas and suggested that the variability may  
141 result from diagenetic alteration of the primary elemental signal or down-slope  
142 movement of foraminiferal tests, leading them to reject some high Mg/Ca measurements  
143 in their calibration.

144

145         Given the doubts about the quality of the OCE205 samples, a reevaluation of the  
146 *C. pachyderma* Mg/Ca:temperature calibration seems justified. In this paper, we address  
147 this calibration issue using a new suite of cores which provide many well-dated multicore  
148 samples in high temperature thermocline waters.

149

## 150 **Methods**

151

152         *Study Area.* The multicores for this study were collected from the western and  
153 eastern sides of the Florida Straits (Figure 1) on RV Knorr 166-2 as part of a study to

154 reconstruct past density gradients and geostrophic flow through the straits [Lynch-  
155 Stieglitz et al., 1999; Lund *et al.*, 2006]. The cores are from shallow water depths (200 to  
156 800 m) and sample large gradients in upper water column physical properties  
157 (temperatures from 5 to 20 °C and salinities 34.9 to 36.7 psu: Marchitto *et al.*, 2007).  
158 The multicores from the southern Florida margin intersect lower salinity waters with an  
159 equatorial Atlantic origin and the multicores from the western margin of Great Bahamas  
160 Bank intersect higher salinity waters with a subtropical North Atlantic origin [Schmitz  
161 and Richardson, 1991]. AMS radiocarbon dates were produced for many of the  
162 multicores [Lund and Curry, 2004, 2006; Marchitto *et al.*, 2007]. Sedimentation rates are  
163 higher on the Bahamas side of the straits (20 to several hundred cm kyr<sup>-1</sup>) than on the  
164 southern Florida margin (10 to 50 cm kyr<sup>-1</sup>). AMS <sup>14</sup>C measurements in the core tops  
165 record the effects of atmospheric nuclear weapons testing and as a result many have  
166  $F_{modern} > 1$ . The hydrographic data for the bottom waters immediately above each core  
167 site have been presented in Marchitto *et al.* [2007]. The supplementary data table for this  
168 paper includes bottom water temperature, salinity, as well as other core location  
169 information.

170

171 *SIMS approach.* We are following the same methodology as outlined in Bice *et*  
172 *al.* [2005]. We produced polished sections of the benthic foraminiferal taxon *C.*  
173 *pachyderma* and measured a variety of metal/Ca ratios using a Cameca IMS 3f ion  
174 microprobe at the Woods Hole Oceanographic Institution. The process involves  
175 sputtering a polished surface of a mineral (in this case CaCO<sub>3</sub>, but best known and  
176 evaluated for a variety of silicates) using a negatively charged primary beam (O<sup>-</sup>) 10 μm  
177 in diameter and accelerating the sputtered positively charged ions through a double-  
178 focusing mass spectrometer system for direct ion counting. For our procedure, we began  
179 each analysis by cleaning an area of the test wall with a 25 μm rasterized beam, and then  
180 reduced the beam size to 10 μm and measured the middle of the cleaned area. We  
181 measured five isotopes (<sup>23</sup>Na<sup>+</sup>, <sup>24</sup>Mg<sup>+</sup>, <sup>25</sup>Mg<sup>+</sup>, <sup>26</sup>Mg<sup>+</sup>, <sup>40</sup>Ca<sup>+</sup> and <sup>88</sup>Sr<sup>+</sup>) in four sets of scans  
182 with counting times of 20 seconds each (except for <sup>40</sup>Ca<sup>+</sup> which requires only 2 seconds  
183 of counting to achieve stable measurements in counts per second). Isobaric interferences  
184 (such as <sup>24</sup>Mg<sup>16</sup>O<sup>+</sup> on <sup>40</sup>Ca<sup>+</sup> and <sup>44</sup>Ca<sup>+2</sup> on <sup>88</sup>Sr<sup>+</sup>) were suppressed by energy filtering by

185 applying a small acceleration offset of -70V to the secondary ion beam [Shimizu and  
186 Hart, 1982; Swart, 1990].

187

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

192

193 Ratios of metal/ $^{40}\text{Ca}^+$  in unknowns were then compared with the Mg/Ca ratio in  
194 standards (OKA carbonatite, Carrara marble), which have been measured independently  
195 by ICP-MS. The measured  $^{24}\text{Mg}^+ / ^{40}\text{Ca}^+$  using SIMS and measured Mg/Ca concentrations  
196 using ICP-MS for the two  $\text{CaCO}_3$  samples used as primary standards for calibration are  
197 presented in Figure 2. For this instrument to make accurate Mg (or Sr) measurements the  
198 relationship should be linear and the intercept must go through the origin. With only two  
199 calibration points, it is not possible to document a linear response using these data alone.  
200 However, the linear response of SIMS system is well documented for silicate minerals at  
201 a variety of trace element concentration levels as long as the same mineral substrate is  
202 being analyzed [Shimizu, 1997]. The sputtering process fractionates the sputtered ions  
203 relative to the original substrate, a process generally termed “matrix effects”. Thus it is  
204 not possible to use a calibration curve for a silicate mineral to constrain elemental  
205 variations in different silicate or carbonate minerals. Here we use the calibration curve in  
206 Figure 2 to document the performance of the Cameca IMS 3f. Conversion of the  
207  $(^{24,25,26})\text{Mg}/^{40}\text{Ca}$  isotopic ratio data to Mg/Ca ratios (in mmole mole<sup>-1</sup>) was made using the  
208 measured values for OKA.

209

210 A constraint on the quality of the measurement comes from analysis of the three  
211 isotopes of magnesium ( $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$ ) which occur in nature with specific  
212 abundance ratios. For our standard measurements, the  $^{24}\text{Mg}/^{25}\text{Mg}$  is  $7.9 \pm 0.2$  and the  
213  $^{24}\text{Mg}/^{26}\text{Mg}$  is  $7.4 \pm 0.2$ , about the same as the abundance ratios seen in nature (7.77 and  
214 7.05, respectively) (Figure 3). Fractionation in the SIMS systems preferentially biases  
215 the observed ratios toward higher  $^{24}\text{Mg}$  by fractionating  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$  in an

216 approximate 1:2 ratio. Magnesium isotope variations within foraminifera at the per mil  
217 (‰) level are not resolvable by this methodology or instrument. Drift in the isotopic  
218 ratios is a sign of poor mass spectrometer tuning and surface contamination. For this  
219 work, we rejected  $^{24}\text{Mg}/^{25}\text{Mg}$  greater than 8.5 and less than 7.3, following Bice *et al.*  
220 [2005]. In addition, we removed from consideration any data with Na/Ca ratios higher  
221 than 22 mmole mole<sup>-1</sup> because of the observed high Na/Ca in the mounting medium [Bice  
222 *et al.*, 2005].

223

224 Using this approach, external analytical precisions for standards average  $\pm 3.5\%$   
225 ( $1\sigma$  Relative Standard Deviation, RSD) for Mg/Ca (and  $\pm 1.7\%$  for Sr/Ca). Internal  
226 precisions are better (generally  $< \pm 2\%$ ), while replicate measurements of spots from *C.*  
227 *pachyderma* have greater variability ( $\pm 10\%$  for Mg/Ca), probably reflecting  
228 heterogeneity within the foraminiferal test wall itself.

229

## 230 **Results**

231

232 The complete data set is listed in the supplemental information. We measured 29  
233 foraminiferal tests in 14 multicore tops from the Florida Straits. For each foraminiferal  
234 test we measured four to eight individual spots (Figure 4) and produced a total of 133  
235 individual measurements of Mg/Ca (and Sr/Ca), after culling the data for quality and  
236 contamination. Using these data we compare the SIMS measurements with chemically-  
237 cleaned ICP-MS measurements made from the same multicores; we evaluate the internal  
238 variability of Mg/Ca in the *C. pachyderma* tests; and we determine the relationship of  
239 Mg/Ca to the temperature of the overlying sea water at each location.

240

241 *Intercomparison with ICP-MS.* In Figure 5, we present paired values of Mg/Ca  
242 produced independently using SIMS and ICP-MS. The ICP-MS measurements were  
243 produced from cleaned *C. pachyderma* using standard cleaning protocols [Boyle and  
244 Rosenthal, 1996] and are presented in Marchitto *et al.* [2007]. The values for SIMS are  
245 the averages ( $\pm 1$  standard error) for all spots measured at a location (usually from two or  
246 three tests – see the Supplementary Information for a complete listing of spot

247 measurements at each location). Thirteen pairs of measurements are included in Figure 5  
248 and seven measurements fall within about 0.3 mmole mole<sup>-1</sup> of the 1:1 concordance line.  
249 Five others fall off the 1:1 line with values about 0.5 to 0.7 mmole mole<sup>-1</sup> higher for the  
250 ICP-MS measurements. For the full comparison, the average difference between the  
251 SIMS and ICP-MS data is 0.33 mmole mole<sup>-1</sup> and the root mean squared (rms) deviation  
252 is 0.42 mmole mole<sup>-1</sup>. Seven of the multicore tops contain significant bomb radiocarbon,  
253 and all but one of them falls very close to the 1:1 concordance line for the paired  
254 measurements. For the five multicores where the measurements diverge, each falls  
255 within a fairly narrow water temperature range of 9 to 12 °C and most of these multicores  
256 come from the Florida margin side of the straits. At this time we cannot be sure why  
257 these measurements differ by so much. That they fall within a limited temperature range  
258 and are from a restricted geographic region suggests that the differences may be related to  
259 sediment lithology, difficulties in cleaning these samples and/or the existence of  
260 secondary calcite with a slightly higher Mg/Ca value. Marchitto *et al.* [2007] provide  
261 evidence that secondary crusts near Little Bahama Bank are extremely elevated in Mg.  
262 High magnesium cements are common to many carbonate bank facies, but so far there is  
263 no evidence for contamination or diagenetic alteration of the Florida Straits core top  
264 samples. All of the ICP-MS data pass standard data quality evaluation [Marchitto *et al.*,  
265 2007]. Thus the reason for the small but seemingly systematic difference between the  
266 SIMS and ICP-MS measurements remains unresolved.

267

268 *Internal Variability.* The variability in Mg/Ca within each *C. pachyderma* test,  
269 presented as a percentage ( $1\sigma/\mu \cdot 100$ ), is plotted as a histogram in Figure 6. The mean  
270 variability in this data set is  $\pm 20\%$ , and there is a small increase in variability (expressed  
271 as percent) with higher mean values ( $r = 0.37$ ,  $p < .05$ ). Although there are generally  
272 small numbers of measurements within each *C. pachyderma* test, the distribution of the  
273 Mg/Ca measurements within each core top appears to be normal (Gaussian). The  
274 statistical distribution of Mg/Ca in thirteen of fourteen multicores passes a Lilliefors test  
275 for Gaussian distribution at the 95% confidence level. One multicore (KNR166-13MC,  
276 with the oldest measured radiocarbon age) fails this test for normality even at the 80%  
277 confidence level. If there were two different phases of calcite present in these tests (one

278 primary and one diagenetic, for instance), we would expect to see non-Gaussian  
279 distributions within the data. So far we have not found evidence for this in the large  
280 majority of core locations.

281

282 *Mg/Ca: Temperature Calibration.* Using Conductivity-Temperature-Depth (CTD)  
283 profiles taken during KNR166 and Niskin bottle samples of the near-bottom sea water at  
284 each location, Marchitto *et al.* [2007] developed a complete set of hydrographic  
285 properties for the sea water immediately above each multicore location. From the data  
286 we have produced the local calibration of Mg/Ca *versus* temperature for *C. pachyderma*  
287 (Figure 7) and compare the results with previous calibrations for *C. pachyderma* [Lear *et*  
288 *al.*, 2002; Marchitto and deMenocal, 2003]. For the SIMS data, the minimum Mg/Ca  
289 spot value is 1.05 mmole mole<sup>-1</sup> and the maximum Mg/Ca spot value exceeds 6 mmole  
290 mole<sup>-1</sup> (only 2 of 126 Mg/Ca measurements exceed 5 mmole mole<sup>-1</sup>). The large majority  
291 of the Mg/Ca values fall well below the previous calibration lines in water temperatures  
292 above about 10 °C. In the warmest waters, the differences approach 3 mmole mole<sup>-1</sup> and  
293 no individual spot measurements approach the 9 mmole mole<sup>-1</sup> values observed by Lear  
294 *et al.* [2002]. Below 10 °C, the Mg/Ca values are the same in each study. The  
295 differences in Mg/Ca values at high temperatures are too large to explain by  
296 methodological differences since we have documented that both SIMS and ICP-MS  
297 methods appear to give the same values (within about 0.3-0.4 mmole mole<sup>-1</sup>) in the  
298 Florida Straits samples.

299

300 The slope of Mg/Ca *versus* temperature in warm waters is much shallower in this  
301 data set than in previously published calibrations using *C. pachyderma* [Rosenthal *et al.*,  
302 1997; Lear *et al.*, 2002; Marchitto and deMenocal, 2003]. Using the average values for  
303 each individual test (Figure 7b), the equation is:

304

$$305 \quad \text{Mg/Ca} = (0.126 \pm 0.048) \cdot T + (0.886 \pm 0.560) \quad (n = 29, r = 0.72, 95\% \text{ CI})$$

306

307 where Mg/Ca is expressed in mmole mole<sup>-1</sup> and T is temperature in °C.

308

309 For the core top averages, the equation is:

310

$$311 \quad \text{Mg/Ca} = (0.134 \pm 0.053) \cdot T + (0.767 \pm 0.634) \quad (n = 14, r = 0.85, 95\% \text{ CI})$$

312

313 In each case the slope is about one half of the linear slope calculated by Marchitto and  
314 deMenocal [2003] and, at higher temperatures, much lower than the exponential slope  
315 determined by Lear *et al.* [2002]. The slope observed in these data,  $\sim 0.13$  mmole mole<sup>-1</sup>  
316 per °C, is indistinguishable from the slope observed by Marchitto *et al.* [2007] using 29  
317 core tops,  $0.116 \pm 0.014$  mmole mole<sup>-1</sup> per °C. This is not surprising since we have  
318 analyzed a subset of the same multicores and since we can show that both SIMS and ICP-  
319 MS produce the same Mg/Ca values to within about 0.3-0.4 mmole mole<sup>-1</sup> (Figure 5).

320

## 321 **Discussion**

322

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

332

333 Carbonate diagenesis in surface and down-core sediments is well documented at  
334 the Bahamas [Neumann, *et al.*, 1977; Mullins *et al.*, 1985; Morse, 2003]. Neumann *et*  
335 *al.*, [1977] observed carbonate hardgrounds on DSRV Alvin dives in surface sediments  
336 along the western margin of Little Bahama Bank at depths of about 600 m, and at shallow  
337 depths in some but not all locations within Northwest Providence Channel. It was not  
338 observed in deeper locations in the channel. Carbonate diagenetic horizons have also  
339 been found in subsurface sediments often concentrated at glacial-interglacial transitions

340 [Slowey *et al.*, 1989]. High magnesium calcites are a common component of the  
341 diagenetic overprint, and if these calcites are affecting the core top benthic foraminiferal  
342 chemistry, Mg/Ca calibrations with temperature may be very misleading. Marchitto *et al.*  
343 [2007] measured one subsurface diagenetic hard ground from Little Bahama Bank and  
344 observed very high Mg/Ca values of  $\sim 150$  mmole mole<sup>-1</sup>. Only a small overprint of such  
345 a high Mg/Ca values would bias the Little Bahama Bank foraminiferal tests.

346

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

356

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

362

363         Unfortunately the low slope of Mg/Ca versus temperature limits its usefulness as  
364 a proxy for reconstructions of past deep and intermediate water temperature changes.  
365 Small temperature changes at any given core location may not be resolvable using *C.*  
366 *pachyderma* Mg/Ca. However, the Mg/Ca:temperature sensitivity is large enough to  
367 record the gradients of temperature within the thermocline and across Florida Straits.  
368 Along the Bahamas side of Florida Straits, the existing multicores sample a 10 °C vertical  
369 gradient in temperature while along the Florida margin side they sample a 7 °C vertical  
370 gradient. Changes in temperature gradient at this scale should be resolved by *C.*

371 *pachyderma* Mg/Ca, thus enhancing the possibility of reconstructing past density  
372 gradients and calculating the component of Florida Current transport that is in  
373 geostrophic balance. So far, the application of the geostrophic method in this region has  
374 depended on the empirical correlation of benthic foraminiferal  $\delta^{18}\text{O}$  and density [Lynch-  
375 Stieglitz *et al.*, 1999; Lund *et al.*, 2006]. Adding information about temperature gradients  
376 would make these calculations much more robust.

377

378         The Mg/Ca values in *C. pachyderma* tests from the Florida Straits appear to be  
379 normally (Gaussian) distributed, suggesting that Mg/Ca in each test is from a single  
380 population with a typical test variability of about  $\pm 20\%$ . The weak positive correlation of  
381 this internal variability with higher mean Mg/Ca suggests that the variability is caused by  
382 the biology of the benthic species perhaps related to growth rate differences in higher  
383 temperature water. The observation of normally distributed values in the tests makes it  
384 unlikely Mg/Ca in *C. pachyderma* from Florida Straits are biased by secondary high  
385 magnesium calcite cements, as they may be in Northwest Providence Channel near Little  
386 Bahama Bank. It also implies that polished test walls of this species are clean enough to  
387 avoid the biasing effects of clay contamination and that the test walls are not so porous  
388 that the mounting medium affects the ion probe measurement. The SIMS technique for  
389 at least this species appears to be a viable approach for producing high quality Mg/Ca  
390 data. Data production rates are low, however, so the SIMS approach may be of limited  
391 usefulness for producing long, high resolution time series of Mg/Ca. Manual data  
392 acquisition and long integration times for each spot measurement may limit the SIMS  
393 approach to focused research activities related to shell calcification and the incorporation  
394 of Mg into fossil tests and testing for the presence of alteration or contamination of the  
395 primary Mg/Ca signal.

396

## 397 **Conclusions**

398

399 1. Secondary Ionization Mass Spectrometry appears to be a viable approach to measure  
400 the distribution of metals in late Quaternary benthic foraminifera. The precision of the  
401 measurements is about  $\pm 3.5\%$  for Mg/Ca and with appropriately calibrated standards,

402 mean values of multiple spot measurements in test walls produce the same results as  
403 standard chemical cleaning and ICP-MS. Measurements for the same multicores using  
404 the SIMS and ICP-MS methods yield an average difference of 0.33 mmole mole<sup>-1</sup> and a  
405 root mean squared deviation of 0.42 mmole mole<sup>-1</sup>. Most of the paired measurements  
406 agree with a smaller deviation. Paired measurements from cores in 9 to 12 °C waters of  
407 Florida Straits differ by more, with the ICP-MS data consistently higher

408

409 2. Multiple measurements of Mg/Ca from 29 individual tests of *C. pachyderma* document  
410 an average internal variability of Mg/Ca of ±20% ( $1\sigma/\mu \cdot 100$ ). There is a small but  
411 significant increase in internal variability in tests with higher Mg/Ca ( $r = 0.37$   $p < .05$ ).  
412 Higher Mg/Ca occurs in warmer waters, so the higher variability may result from a  
413 growth rate effect on magnesium incorporation into the foraminiferal calcite. Marchitto  
414 et al. [2007] point out that temperature and CO<sub>3</sub><sup>=</sup> covary in the Florida Straits, which may  
415 impact both the measured values of Mg/Ca as well as the variability in the foraminiferal  
416 tests. The probability distribution of Mg/Ca in foraminiferal tests appears to be Gaussian  
417 for thirteen of fourteen core locations, which suggests that the foraminiferal Mg/Ca in  
418 these cores is not affected by the addition of one or more secondary sources of high  
419 magnesium calcite.

420

421 3. The observed slope of *C. pachyderma* Mg/Ca with temperature is much lower than in  
422 previous calibrations especially in warm waters. The slope observed here (0.13 mmole  
423 mole<sup>-1</sup> per °C) is indistinguishable from the slope (0.12 mmole mole<sup>-1</sup> per °C) observed  
424 by Marchitto *et al.* [2007], which was measured on a larger set of the same multicores.

425

## 426 **Acknowledgments**

427

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## References

- Adkins, J. F., K. McIntyre, and D. E. Schrag, 2002. The salinity, temperature and  $\delta^{18}\text{O}$  of glacial deep water. *Science*, 298, 1769-1773.
- Allison, N. and W. E. N. Austin, 2003. The potential of ion microprobe analysis in detecting geochemical variations across individual foraminifera test, *Geochemistry, Geophysics, Geosystems*, 4, doi:10.1029/2002GC000430.
- Anand, P., H. Elderfield, and M. H. Conte, 2003, Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series, *Paleoceanography*, 18(2), 1050, doi:10.1029/2002PA000846.
- Barker, S., M. Greaves, and H. Elderfield, 2003. A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry, *Geochemistry, Geophysics, Geosystems*, 4, doi:10.1029/2003GC000559.
- Bice, K. L., G. D. Layne, and K. Dahl, 2005. The application of SIMS for measuring Mg/Ca in rare, delicate, or altered planktonic foraminifera: Examples from the Holocene, Paleogene and Cretaceous. *Geochemistry, Geophysics, Geosystems*, 6, Q12P07, doi:10.1029/2005GC000974.
- Boyle, E. A., and Y. Rosenthal, 1996. Chemical hydrography of the South Atlantic during the last glacial maximum: Cd vs.  $\delta^{13}\text{C}$ , in *The South Atlantic: Present and Past Circulation*, edited by G. Wefer and et. al., pp. 423-443, Springer-Verlag, Berlin.
- Curry, W. B. and D. W. Oppo, 2005. Glacial water mass geometry and the distribution of  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$  in the western Atlantic Ocean. *Paleoceanography*, 20, doi:10.1029/2004PA001021.
- Dekens, P., D. W. Lea, D. K. Pak, and H. J. Spero, 2002. Core top calibration of Mg/Ca in tropical foraminifera: Refining paleotemperature estimation, *Geochemistry, Geophysics, Geosystems*, 3, doi:10.1029/2001GC000200.
- Lear, Caroline H., Yair Rosenthal, and Niall Slowey, 2002. Benthic foraminiferal Mg/Ca paleothermometry: A revised core-top calibration. *Geochimica et Cosmochimica Acta*, 66, 3375-3387.
- Lund, D. C., and W. B. Curry, 2004, Late Holocene variability in Florida Current surface density: Patterns and possible causes, *Paleoceanography*, 19, PA4001, doi:10.1029/2004PA001008.
- Lund, D. C. and W. B. Curry, 2006. Florida Current surface temperature and salinity variability during the last millennium. *Paleoceanography*, 21, PA2009, doi:10.1029/2005PA001218.

- Lund, D. C., J. Lynch-Stieglitz, and W. B. Curry, 2006. Gulf Stream density structure and transport during the last millennium. *Nature*, 444, 601-604, doi:10.1038/nature05277
- Lynch-Stieglitz, J., W. B. Curry, and N. C. Slowey, 1999. Geostrophic transport through the Florida Straits during the last glacial maximum. *Nature*, 402, 644-648.
- Marchitto, T. M., and P. B. deMenocal, 2003. Late Holocene variability of upper North Atlantic Deep Water temperature and salinity, *Geochemistry, Geophysics, and Geosystems*, 4, doi:10.1029/2003GC000598.
- Marchitto, T. M., S. W. Bryan, W. B. Curry, and D. C. McCorckle, 2007. Linear Mg/Ca temperature calibration for the benthic foraminifer *Cibicides pachyderma*. *Paleoceanography*.
- Martin, P. A. and D. W. Lea, 2002. A simple evaluation of cleaning procedures on fossil benthic foraminiferal Mg/Ca. *Geochemistry, Geophysics, and Geosystems*, 3, doi:10.1029/2001GC000280.
- Martin, P. A., D. W. Lea, Y. Rosenthal, N. J. Shackleton, M. Sarnthein, and T. Papenfuss, 2002. Quaternary deep sea temperature histories derived from benthic foraminiferal Mg/Ca. *Earth and Planetary Science Letters*, 198, 193-209.
- Morse, J. W., 2003. Formation and diagenesis of carbonate sediments, *Treatise on Geochemistry*, 7, 67-85.
- Mullins, H. T., S. H. Wise, J. A. F. Gardulski, E. J. Hincley, P. M. Masters, and D. I. Siegel, 1985. Shallow subsurface diagenesis of Pleistocene periplatform ooze: northern Bahamas, *Sedimentology*, 32, 473-494.
- Neumann, A. C., J. W. Kofoed, and G. H. Keller, 1977. Lithohermes in the Straits of Florida. *Geology*, 5, 4-10.
- Nurnberg, D., J. Björk, and C. Hemleben, 1996. Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures, *Geochim. et Cosmochim. Acta*, 60, 803-814.
- Rosenthal, Y., E. A. Boyle, and N. Slowey, 1997. Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminifera shells from Little Bahama Bank: Prospects for thermocline paleoceanography. *Geochimica et Cosmochimica Acta*, 61, 3363-3643.
- Rosenthal, Y. and G. Lohmann, 2002. Accurate estimation of sea surface temperatures using dissolution-corrected calibrations for Mg/Ca paleothermometry, *Paleoceanography*, 17, doi:10.1029/2001PA000749.

- Schmidt, M. W., H. J. Spero, and D. W. Lea, 2004, Links between salinity variation in the Caribbean and North Atlantic thermohaline circulation, *Nature*, 428, 160– 163.
- Schmitz, W. J., and P. Richardson, 1991. On the sources of the Florida Current, *Deep-Sea Research*, 38, s379-s409.
- Shimizu, N. 1997. Principles of SIMS and modern ion microprobes. In “Modern Analytical Geochemistry, An Introduction to Quantative Chemical Analysis Techniques for Earth, Environmental and Materials Scientists”, edited by Robin Gill, Addison Wesley Longman Limited, Essex, England, pp. 235-242.
- Shimizu, N and S. R. Hart, 1982. Applicaitoions of the ion micorprobe to geochemistry and cosmocemsitry. *Annual Reviews of Earth and planetary Science*, 10, 483-526.
- Slowey, N. C. and W. B. Curry, 1995. Glacial-interglacial differences in circulation and carbon cycling within the upper western North Atlantic. *Paleoceanography*, 10, 715-732.
- Slowey, N. C., A. C. Neumann, and K. C. Baldwin, 1989. Seismic expression of Quaternary cliamtic cycles in the peri-platform carbonate ooze of the northern Bahamas. *Geological Society of America Bulletin*, 101, 1563-1573.
- Stott, Lowell, Christopher J. Poulsen, Steve Lund, Robert Thunell, 2002. Super ENSO and global climate oscillations at millennial time scales. *Science*, 297(5579), 222-226
- Stott, L., K. Cannariato, R. Thunnell, G. H. Haug, A. Koutavas, and S. Lund, 2004, Decline of surface temperature and salinity in the western tropical Pacific Ocean in the Holocene epoch, *Nature*, 431, 56–59.
- Swart, P. K., 1990. Calibration of the ion microprobe for the quantitative determination of Strontium, Iron, Manganese, and Magnesium in carbonate minerals. *Anal. Chem.*, 62, 722-728.

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

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 measured independently by ICP-MS (Bice *et al.*, 2005; Marchitto, unpublished data). 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 based on standard measurements made during a session.

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.

Figure 4. Within test variability for two *C. pachyderma* tests from KNR166-94MC, a multicore bathed in 18 °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  $3.36 \pm 0.36$  mmole/mole (1 standard error =  $1\sigma/\sqrt{n} = 1.03/\sqrt{8}$ ). The value measured by ICP-MS is 3.41 mmole/mole. The within test variability of  $\pm 1.03$  mmole/mole 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 ( $r = 0.37$   $p < .05$ ) – 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. It is still unclear the reason for this discrepancy.

Figure 6. Within test variability, expressed as a percent of the mean value, for 33 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 ( $r = 0.37$ ,  $p < .05$ ).

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 based on 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).

# KNR166-2 Multicore Stations

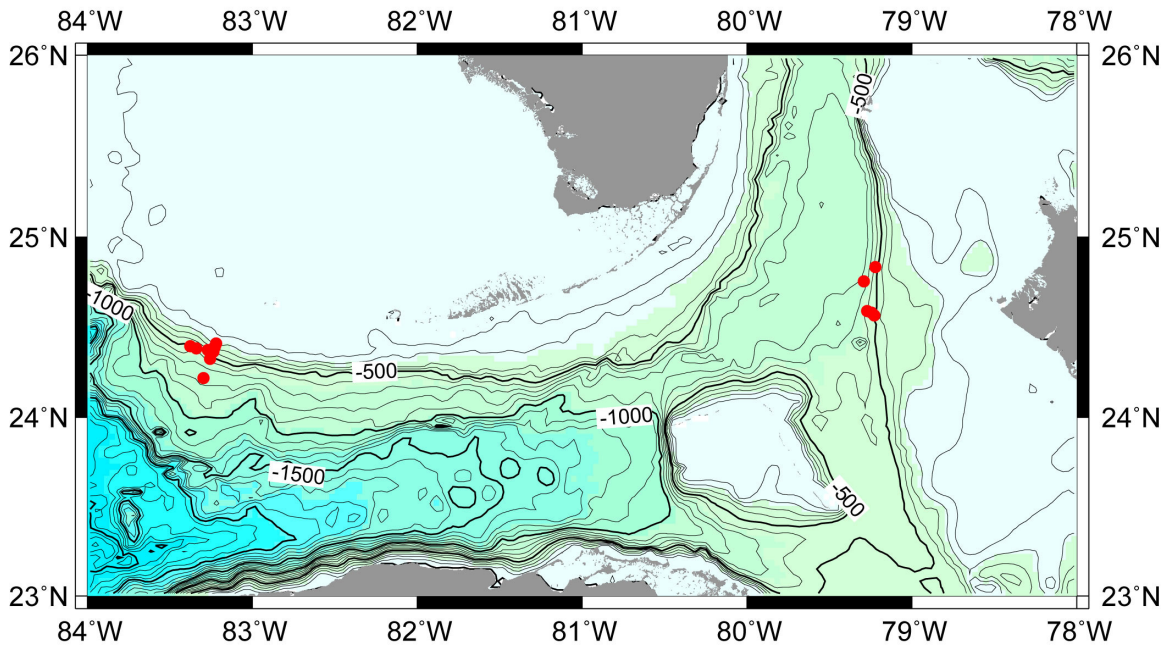
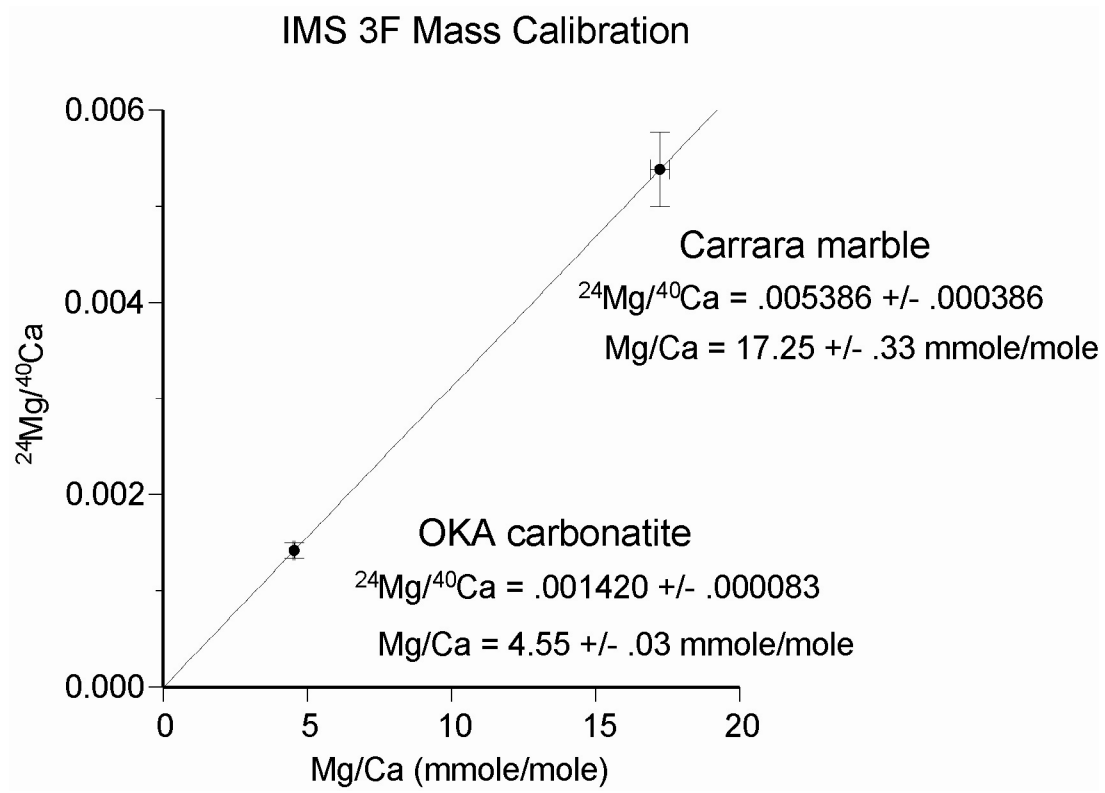


Figure 1



**Figure 2**

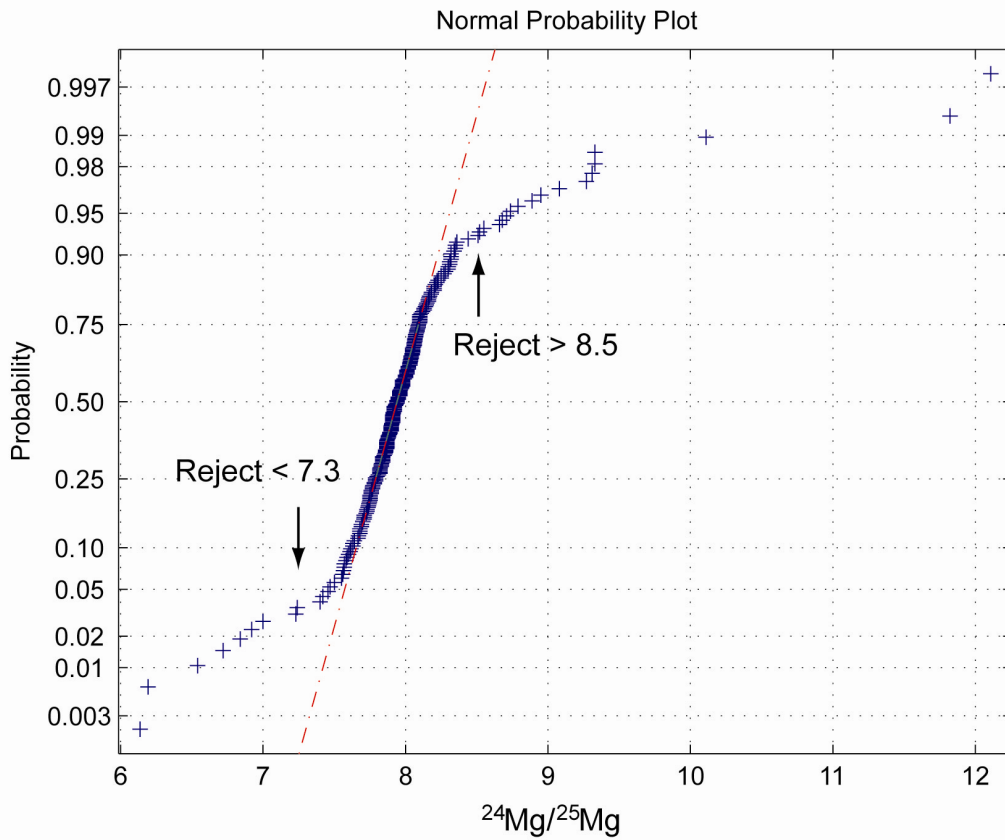
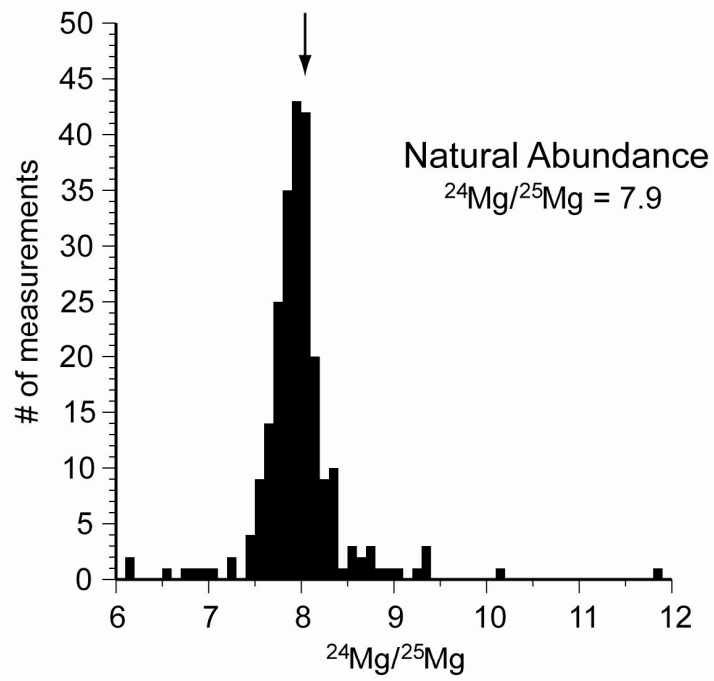
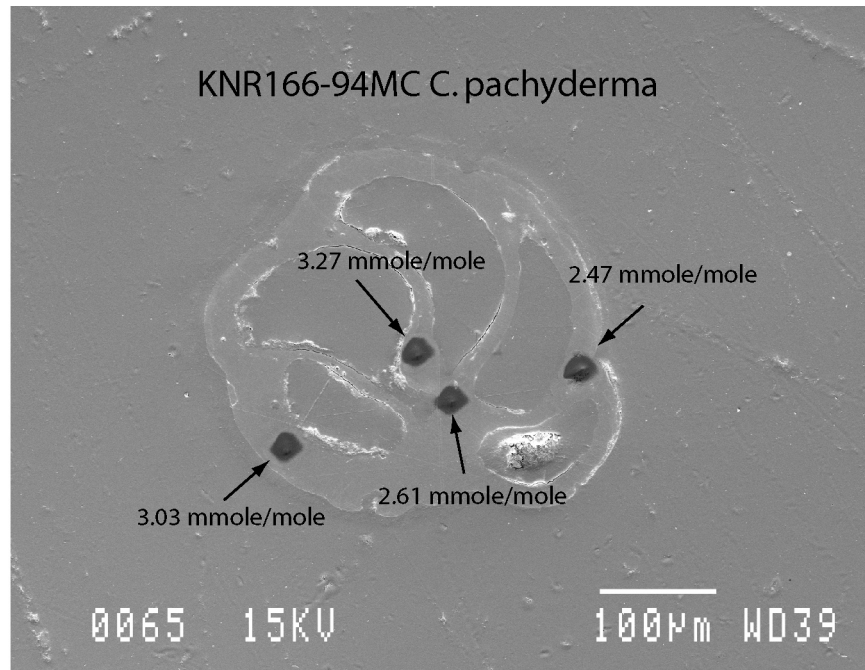
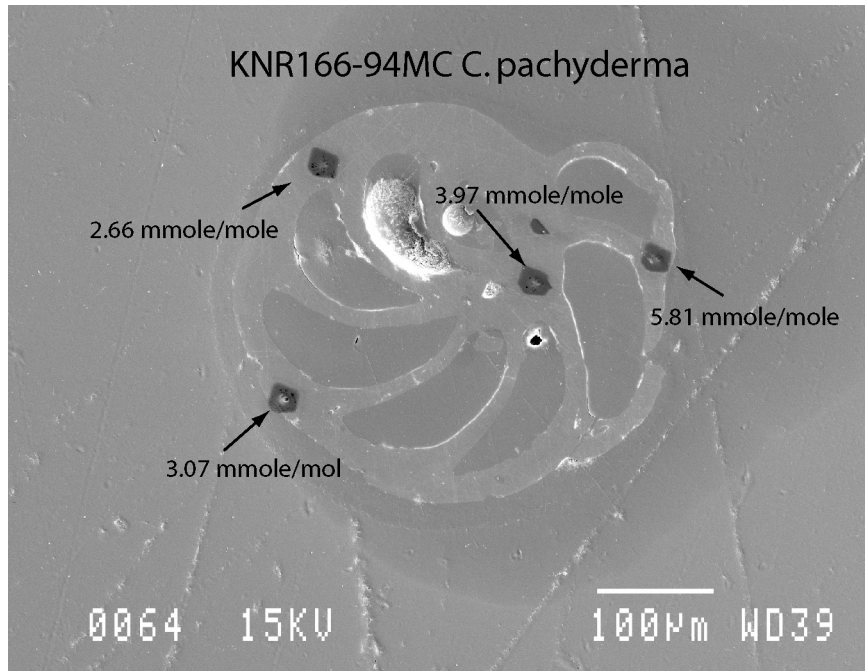
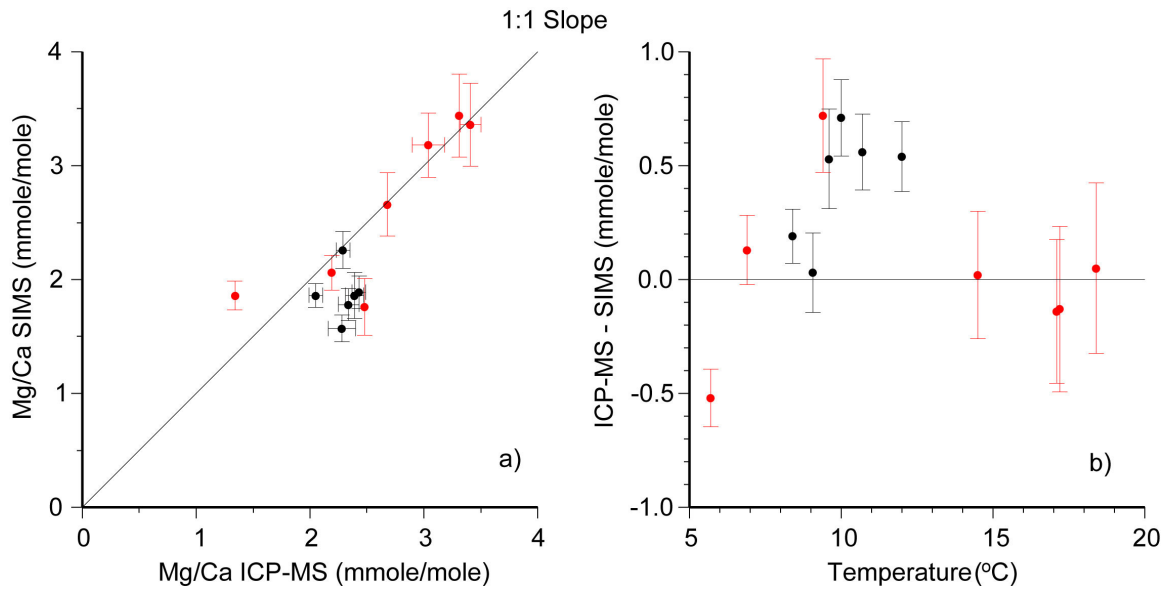


Figure 3



**Figure 4**



**Figure 5**

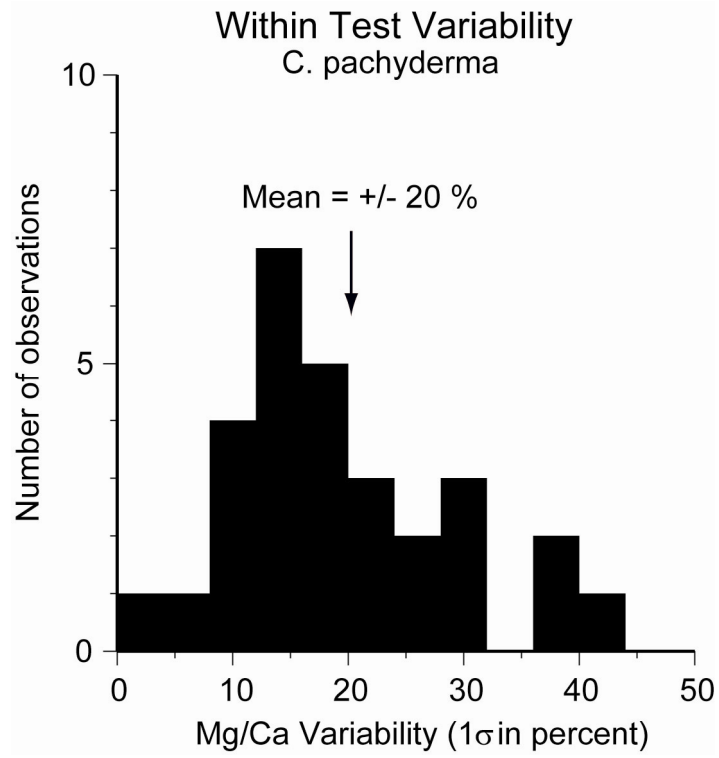


Figure 6

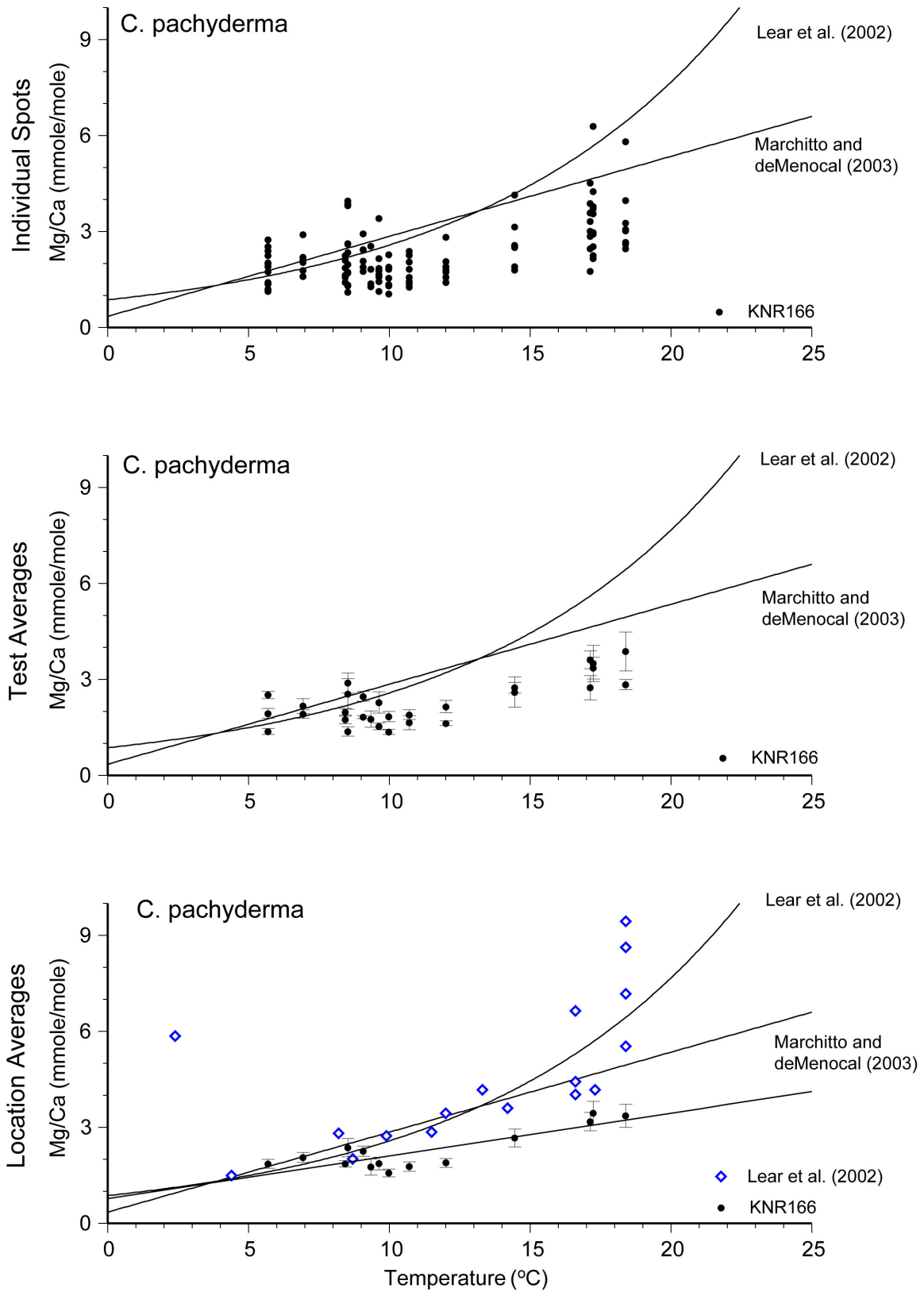


Figure 7