



# Application of secondary ion mass spectrometry to the determination of Mg/Ca in rare, delicate, or altered planktonic foraminifera: Examples from the Holocene, Paleogene, and Cretaceous

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[1] Secondary ion mass spectrometry (SIMS) is useful for measuring Mg/Ca in both primary calcite and diagenetic minerals in planktonic foraminifera. The excellent spatial resolution ( $<10\ \mu\text{m}$ ) and small amount of material removed ( $<2\ \text{ng}$ ) makes it easy to avoid targets that include obvious embedding material and encrusting or infilling minerals such as secondary calcite and authigenic clays in diagenetically altered samples. Because analyses can be performed on individuals, SIMS is also a viable technique for generating Mg/Ca values from sediment samples in which foraminifera are rare or have low mass. For clean primary calcite samples, Mg/Ca ratios from SIMS compare well to those obtained using inductively coupled plasma mass spectrometry (ICP-MS), while maintaining information regarding the true variability of elemental ratios within individual tests. For samples with secondary calcite or stubbornly adhering clays, SIMS enables us to accurately measure primary calcite compositions and to assess and reconcile contamination problems in bulk samples analyzed by solution-based ICP-MS. We have observed that SIMS is an invaluable and reliable tool for the identification and avoidance of problems of diagenesis and the analysis of rare or delicate planktonic foraminifera. However, because of operator time required to properly target delicate (thin-walled) or contaminated planktonic foraminifera, SIMS may not be feasible for Mg/Ca studies where large numbers (hundreds) of samples must be processed and bulk measurements on multiple individuals will suffice.

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## 1. Introduction

[2] In culture and sediment studies, the Mg/Ca ratio in various foraminifera has been shown to exhibit an exponential relationship to water temperature

[Nürnberg *et al.*, 1996; Rosenthal *et al.*, 1997; Lea *et al.*, 1999; Elderfield and Ganssen, 2000; Lear *et al.*, 2002]. Several methods are used to determine Mg/Ca in foraminifera for paleotemperature estimates, the most common being inductively coupled

plasma mass spectrometry (ICP-MS). ICP-MS generally begins with approximately 200–300  $\mu\text{g}$  of material (multiple individuals) for a single analysis. A series of cleaning procedures [e.g., *Boyle and Rosenthal*, 1996] is designed to remove clays, oxides and reduced metals. Dissolution also removes some primary calcite, preferentially that high in Mg [*Hecht et al.*, 1975; *Lorens et al.*, 1977; *Brown and Elderfield*, 1996; *Benway et al.*, 2003]. Whether it occurs naturally or in laboratory processing, preferential removal of Mg would tend to bias paleotemperature estimates toward values lower than actual water temperatures, unless compensated for using an appropriate calibration [e.g., *Rosenthal and Lohmann*, 2002]. At the same time, diagenetic calcitic contaminants not removed during standard dissolution cleaning techniques can be difficult to detect in ICP-MS results. ICP-MS therefore may not typically be suitable for analysis of samples in which individuals of a desired species are very rare or small, or which contain secondary calcite (as infilling or encrusting material), trace amounts of recrystallized calcite, or stubbornly adhering secondary authigenic clays.

[3] Secondary Ion Mass Spectrometry (SIMS) provides a unique capability for both high spatial resolution and precision in measuring metal/Ca ratios in marine carbonates. In the procedure we have developed, SIMS removes  $<2$  ng of material for an individual analysis. This capability, when carefully applied, enables the accurate determination of elemental ratios in discrete subvolumes of the complex skeleton of any given individual, which may reveal variations due to short-term climate cycles and ontogenetic changes. The SIMS technique has proven useful with corals [*Allison*, 1996; *Cohen et al.*, 2001; *Layne and Cohen*, 2002] and relatively large (diameter  $\sim 500$   $\mu\text{m}$ ) modern benthic foraminifera [*Allison and Austin*, 2003]. Apart from the obvious potential for the measurement of elemental ratios when only very small amounts of calcite are available and the potential to track changes in Mg/Ca during individual life cycles, the microsampling nature of SIMS allows the avoidance of diagenetic alteration or inclusions within the skeletal material, which would otherwise corrupt measurements. Further, it enables the characterization of the Mg/Ca of the contaminants themselves, allowing us to reconcile problems in the analyses of larger samples by more conventional solution-based techniques such as ICP-MS.

[4] Here, we examine SIMS as a tool for measuring Mg/Ca in several species of Cretaceous, Pa-

leogene and Holocene planktonic foraminifera. Results are compared to those obtained on the same species and samples with ICP-MS. The study examines both sediments believed to be free of diagenetic minerals and those observed to include secondary calcite and clays.

## 2. Methodology

### 2.1. Sample Preparation

[5] Whole specimens of apparently well-preserved *Morozovella aragonensis* and *Morozovella velascoensis* were picked from the 250–300  $\mu\text{m}$  sieve fraction of washed sediments from ODP Holes 1257A, 1257C and 1258B on Demerara Rise, in the tropical Atlantic. These foraminifer nannofossil chalks are late Paleocene and early Eocene in age [*Erbacher et al.*, 2004, available at [http://www-odp.tamu.edu/publications/207\\_IR/207ir.htm](http://www-odp.tamu.edu/publications/207_IR/207ir.htm)]. Whole specimens of *Hedbergella delrioensis* were picked from the 150–250  $\mu\text{m}$  sieve fraction of one Cenomanian laminated carbonaceous claystone (black shale) from ODP Hole 1260B, also on Demerara Rise. The Cretaceous black shale sample had been washed using an undiluted bleach procedure [*Bice and Norris*, 2005], which has been shown to be an efficient way to remove remnant organic matter that might otherwise bias results toward high Mg/Ca values [*Martin and Lea*, 2002]. Holocene samples were taken from several cores throughout the Arabian Sea (IOE-KK143 and IOE-KK114, Somali Margin; SO42-36KL, Eastern Arabian Sea; TN41-10JPC and TN47-6GGC, Oman Margin). Holocene *Globigerinoides ruber* and *Globigerina bulloides* were picked from 212–300  $\mu\text{m}$  and 250–350  $\mu\text{m}$  washed sediment size fractions, respectively. Picked samples were sonicated briefly in distilled water in order to remove material adhering to the outside of the tests. The Cretaceous and Holocene foraminifera are generally thin-walled species, requiring a sampling spot diameter of 10  $\mu\text{m}$  or less. The planktonic foraminifera chosen for this study are believed to be shallow mixed layer-dwelling species and are used frequently in paleoceanographic studies to estimate upper ocean water temperatures.

[6] For SIMS analyses, foraminifera were mounted in ethyl cyanoacrylate instant adhesive (Henkel Technologies Loctite 416™ or Loctite 430™) and low viscosity epoxy resin (Buehler Epothin™). The cured mount was polished with 16  $\mu\text{m}$  (600 grit) silicon carbide paper then sonicated in distilled water for 5 min, rinsed with isopropanol and dried.

**Table 1.** Theoretical Precision Error Limits for  $X^{+}/^{40}\text{Ca}^{+}$  Ratio Measurements, Based on Peak Counting Times and Switching Cycles Described in Text<sup>a</sup>

Ion Ratio to $^{40}\text{Ca}^{+}$	Counting Time, s/cycle	Average Count Rate, cps, in OKA-C	Theoretical Error, %, for OKA-C	Theoretical Error, %, for foraminifera
$^{23}\text{Na}^{+}$	20	320	0.6	0.3
$^{24}\text{Mg}^{+}$	20	1181	0.5	0.5
$^{25}\text{Mg}^{+}$	20	155	0.9	1.0
$^{26}\text{Mg}^{+}$	20	154	0.9	1.0
$^{88}\text{Sr}^{+}$	20	12377	0.1	0.4

<sup>a</sup>The  $^{40}\text{Ca}^{+}$  was counted for 2 seconds s in each cycle. The average count rate for  $^{40}\text{Ca}^{+}$  in the OKA-C standard was 762,000 counts per second (cps).

Cavities in the rough ground surface of individual foraminifera, if present, were filled with ethyl cyanoacrylate instant adhesive and cured again. Mounts were then reground with 600 grit carbide, polished with 6  $\mu\text{m}$  diamond suspension, and finally polished with 0.3  $\mu\text{m}$  deagglomerated alumina suspension. (In subsequent experiments, we found more rapid satisfactory results using 1200 grit paper for grinding, followed by polishing with 1  $\mu\text{m}$  diamond suspension and 0.3  $\mu\text{m}$  deagglomerated alumina suspension.) Between each grinding or polishing stage, mounts were sonicated for at least 10 min in each of two consecutive distilled water baths. Each sectioned foraminifer was photographed and examined using high power reflected light microscopy to assess the quality of the carbonate and to assist the choice of targets for microprobe analyses.

[7] For Paleogene and Holocene samples, all carbonate samples appear to be composed of primary calcite with preservation characterized as good, very good or excellent. Paleogene foraminifera tests are opaque, but there is no evidence of mineral infilling or overgrowths. Some dry Paleogene tests exhibit a chalky appearance. Dry Holocene foraminifera tests are translucent and glassy in appearance. In both cases, fine laminar structure and pores (now filled with embedding media) are visible through much of the shell. However, because of the wide variety of test cross sections available on the mount surface, these pores are easily avoided when positioning the ion beam for analysis. Several samples (discussed below, see Figure 5a) had clay linings visible in some chambers. No obvious secondary calcite infilling or overgrowths were observed in Paleogene or Holocene samples. Some diagenetic dissolution may have occurred in early Paleogene foraminifera with a chalky appearance. If secondary calcite is present in these specimens, it is impossible to distinguish it optically from primary calcite in the sectioned individuals.

[8] In the Cretaceous *H. delrioensis*, the primary calcite is pristine in appearance and no clay was observed. However, the outermost one or two chambers of some individuals were filled with individual calcite spar crystals (one per chamber). In Holocene specimens, clay linings were observed in some chambers. These secondary materials were avoided with the microprobe when analyzing primary calcite, and were intentionally targeted in other cases in order to characterize the composition of contaminant material that might be measured during ICP-MS analyses of specimens from the same core samples. Following SIMS analyses, all mounts were again examined using reflected light microscopy to assure that sputtered areas did not include obvious regions filled with embedding material.

## 2.2. Secondary Ion Mass Spectrometry

[9] Metal/Ca ratio analyses were performed using a Cameca IMS 3f ion microprobe at the Northeast National Ion Microprobe Facility (NENIMF) at Woods Hole Oceanographic Institution (WHOI). Each mount was first coated with 300Å of Au. Foraminifera were bombarded with 1 nA of  $\text{O}^{-}$  primary ions produced in a Duoplasmatron, accelerated through an 8 kV nominal potential, and focused to a spot diameter of less than 10  $\mu\text{m}$ . The positive secondary ions were extracted through a nominal potential of 4500 V and subjected to energy filtering using a sample offset voltage of  $-70$  V and a 40 eV energy window. This energy filtering suppresses isobaric interferences (e.g.,  $^{23}\text{NaH}^{+}$  or  $^{48}\text{Ca}^{++}$  on  $^{24}\text{Mg}^{+}$ ) that would potentially affect the accuracy of the ratios measured. Secondary ions were detected using an electron multiplier in pulse counting mode. Individual analyte peaks were detected through magnetic switching. A cycle of six analyte peaks (Table 1) and a background counting position (10 s) were repeated 4 times in each spot for a total data accumulation time of 408 s. The sampled craters are 10  $\mu\text{m}$  in diameter and less

**Table 2.** Average Element Counts From SIMS in One Microprobe Sample Mount<sup>a</sup>

Ion	Average Count per Spot Measurement			
	Foram Calcite	Epothin	Loctite	Clay
<sup>23</sup> Na <sup>+</sup>	135868	25169	7979	361163
<sup>24</sup> Mg <sup>+</sup>	70530	4252	3176	577347
<sup>25</sup> Mg <sup>+</sup>	8952	367	309	73827
<sup>26</sup> Mg <sup>+</sup>	9371	333	319	80412
<sup>40</sup> Ca <sup>+</sup>	5987012	2476	775	147167
<sup>88</sup> Sr <sup>+</sup>	62695	13	7	14247

<sup>a</sup>The foraminifer calcite and clay measurements are from Paleocene *M. aragonensis* and *M. velascoensis* individuals from Sites 1257 and 1258.

than 5  $\mu\text{m}$  deep, thus consuming less than 2 ng of material per measurement. Our reference standard is a calcite from the Oka Carbonatite Complex, Quebec (OKA-C). In OKA-C, and in typical foraminiferal carbonate, counting statistics for our routine dictate the theoretical error limits for individual analyses shown in Table 1. Average elemental count rates for OKA-C are also given in Table 1.

[10] Each spot was presputtered with the beam rastered over a 25  $\mu\text{m}$  square for at least 3 min. The <sup>40</sup>Ca<sup>+</sup> distribution was monitored in ion microscope mode during presputtering to detect the presence of any obvious low calcium material, including embedding media filling pore space or defects in the test. (This check was repeated at the end of each analysis.) If such material was detected, the primary beam was repositioned. Samples were then presputtered in spot mode (less than 10  $\mu\text{m}$ ) for an additional 3 min before data collection began.

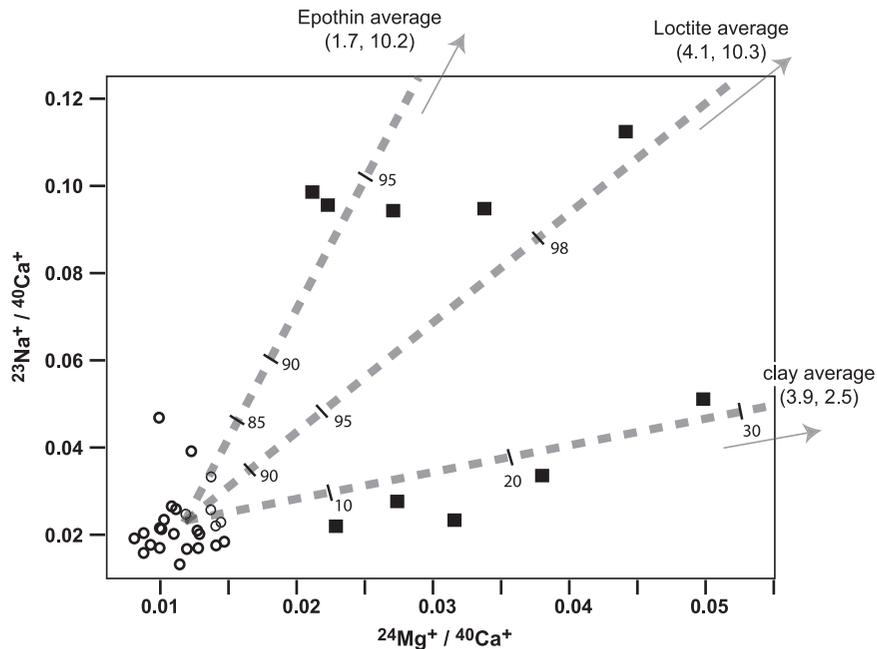
[11] The OKA-C calcite standard was used to convert measured Mg/Ca count ratios to mmol/mol quantities by direct comparison of the ratios measured in each sample spot. OKA-C was analyzed in replicate at the beginning and end of each SIMS session using the same presputter and 4 cycle measurement procedure used for unknowns. On the basis of the standard deviation of 48 replicate analyses, it appears that OKA-C is homogeneous to better than 3% for Mg/Ca, and replicate analyses within each analytical session reduced this uncertainty to less than 1%. For each spot, each of the three Mg<sup>+</sup>/<sup>40</sup>Ca<sup>+</sup> isotope ratio counts was normalized to the corresponding average OKA Mg<sup>+</sup>/<sup>40</sup>Ca<sup>+</sup> ratio for that session, then the three Mg isotope ratios were averaged. Finally, the average and standard deviation of all spot analyses for a single species in a single sediment sample were calculated and the result was multiplied by

4.55 ( $\pm 0.03$  1 $\sigma$ ) mmol/mol, the OKA-C Mg/Ca ratio determined from five replicate analyses of splits of single crystals performed on the WHOI Finnigan Element2 ICP-MS (using the same technique as that used for foraminiferal unknowns; section 2.3). The accepted values for OKA-C Sr/Ca and Na/Ca (based on commercial lab ICP-MS analysis) are 19.3 and 1.94 mmol/mol, respectively.

[12] We attempted to make multiple measurements within each individual foraminifer and, when possible, to target both inner and outer chamber walls. Chamber wall triple junctions tended to provide some of the best targets for SIMS analyses. The approach used here, with measurements randomly distributed among good calcite targets, is representative of what is practical if SIMS is being used as a tool to discriminate between primary calcite Mg/Ca and that of diagenetic contaminants, such as clay and spar calcite. Because of higher sample throughput, ICP-MS is clearly the superior technique for processing the large numbers of samples (typically hundreds) needed in paleoceanographic studies, as long as contamination by secondary minerals is not present and sufficient foraminiferal material is available for replicate analyses of a sample.

[13] Several spots of 100% embedding media were analyzed in each mount in order to determine the apparent Na, Mg, and Sr compositions of epoxy and ethyl cyanoacrylate adhesive. These materials were found to have apparent Mg isotope ratios substantially different (<sup>24</sup>Mg/<sup>25</sup>Mg greater than 8.5) from those expected for naturally occurring terrestrial materials ( $\sim 7.9$  [Copen *et al.*, 2002]). The Sr/Ca ratios in epoxy and ethyl cyanoacrylate adhesive were near or below the detection limit of about 5 ppm. Epoxy and ethyl cyanoacrylate adhesive Mg/Ca values (apparent mmol/mol concentrations, or isotope count ratios) were two orders of magnitude higher than that of primary foraminiferal calcite but because actual counts on these elements were very low (Table 2) relative to biogenic calcite, a substantial amount of embedding material must be present in a spot in order to significantly bias that measurement (Figure 1). Still, it was important that we avoid measuring spots that were part calcite, part embedding material and that we eliminate any measurements potentially biased by such contamination.

[14] In order to accurately target clay inclusions for analysis, the primary ion beam was positioned on the sample so as to produce high observed signals for <sup>27</sup>Al<sup>+</sup> and <sup>28</sup>Si<sup>+</sup> before analysis was begun.

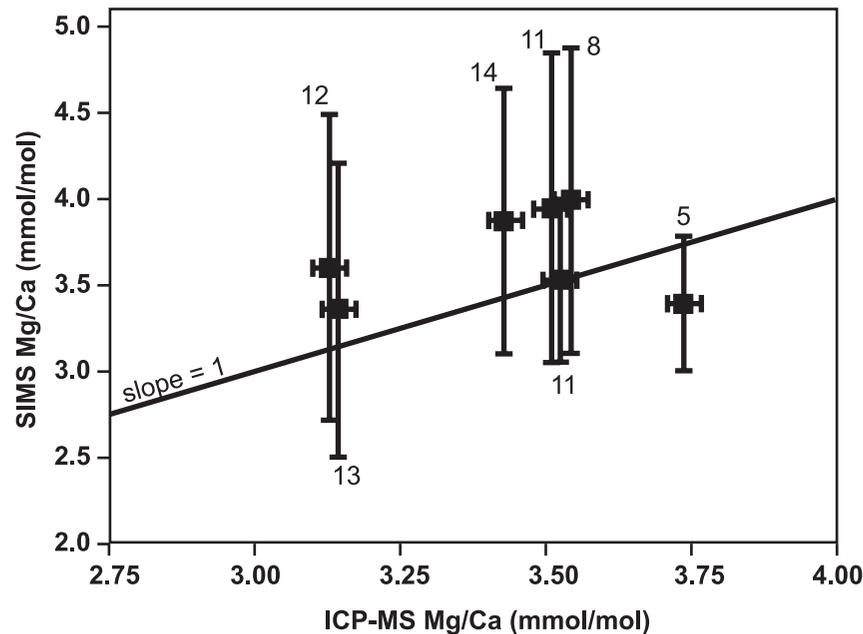


**Figure 1.** Cross plot of raw count ratios for  $^{23}\text{Na}^+ / ^{40}\text{Ca}^+$  and  $^{24}\text{Mg}^+ / ^{40}\text{Ca}^+$  for individual spot measurements in one SIMS mount. The data consist of Paleocene *M. aragonensis* and *M. velascoensis* analyses from Sites 1257 and 1258. The dashed lines indicate the mixing lines between average foraminiferal calcite with no apparent contamination and average apparent ratios in intentionally targeted clay, Loctite and Epothin. Labeled tick marks on the apparent mixing ratio lines indicate the estimated percentage of contaminant present in a spot falling at that point on the dashed line. Because we lack a well-characterized standard for Na/Ca and Mg/Ca in clays and embedding media, these tick marks indicate only approximate relative proportion of contaminant in foram calcite. Data points indicated by the solid black squares are those eliminated based on the likelihood of contamination of the primary foraminiferal calcite target with clay or embedding media. Open circles indicate data points retained as apparently uncontaminated with respect to Mg/Ca.

Intentionally targeted clays in Paleogene and Holocene samples were characterized by apparent Sr/Ca values 7 to 9 times higher than primary calcite. On average, adhering clays had apparent Na/Ca and Mg/Ca values 2 orders of magnitude greater than that of foraminiferal calcite and, because sodium and magnesium ion counts in clays were higher than those in biogenic calcite and calcium counts were low (Table 2), small amounts of clay contamination in a spot introduced an obvious bias (Figure 1). Most of our spot measurements in clays probably include at least some embedding media contamination, due to the porous grain structure of the materials. This, combined with the fact that we do not currently have a well-characterized clay mineral standard for Mg/Ca, prevents us from being able to accurately estimate the composition and relative amounts of clay or other contaminant using SIMS.

[15] Data quality control involved several steps to eliminate primary calcite measurements that might have been contaminated with embedding material or highly heterogeneous Mg-rich silicates (clays).

First, we eliminated any individual cycle ratio measurements that lay more than  $3\sigma$  from the mean for all cycles, which reflect sputtering through highly heterogeneous material or pore space. Next, we eliminated any point with an anomalously high Na/Ca ratio (greater than 15), which would suggest the presence of embedding material or clay. Finally, we eliminated any point in which the  $^{24}\text{Mg}^+ / ^{25}\text{Mg}^+$  ratio deviated from the expected natural abundance (7.9) [Copen *et al.*, 2002] by more than 0.6, indicating the likely effect of embedding material. A  $\pm 0.6$  deviation allows for the expected mass-dependent instrumental fractionation and is far in excess of the natural variations in  $^{24}\text{Mg}^+ / ^{25}\text{Mg}^+$  expected in foraminifera, which would be within 0.03 of 7.9 [Chang *et al.*, 2002]. Cross plots of  $^{88}\text{Sr}^+ / ^{40}\text{Ca}^+$  or  $^{23}\text{Na}^+ / ^{40}\text{Ca}^+$  versus  $^{24}\text{Mg}^+ / ^{40}\text{Ca}^+$  for individual mounts show that eliminated data points fall along mixing lines between good primary calcite values and embedding media and/or intentionally targeted clays (Figure 1). In this study, of the 110 spot measurements made in what was believed to be primary calcite in Paleogene *Moro-*



**Figure 2.** Comparison of Mg/Ca ratios (mmol/mol) from SIMS and ICP-MS for Paleogene samples (Table 2). The SIMS values are averages of multiple spots within *Morozovella* calcite. Vertical bars indicate one standard deviation for SIMS values, and the corresponding number of individual spot measurements (N) is given near the top or bottom of each bar. Each ICP-MS value is the result of one analysis of an initial 200–300  $\mu\text{g}$  “bulk” sample of several *Morozovella* individuals. The bar on each ICP-MS value (N = 1) is the  $\pm 0.03$  mmol/mol instrumental external precision based on replicate analyses of a standard, *not* discrete foraminifer sample measurements. The diagonal line indicates a 1:1 correspondence.

*zovella*, only six data points were eliminated owing to possible contamination from embedding media, and 12 points were eliminated owing to possible contamination from minor clay.

### 2.3. ICP-MS

[16] Samples for ICP-MS were weighed and crushed gently between two glass slides in order to open the individual chambers for more effective cleaning. Samples were then subjected to a series of cleaning treatments designed to remove clays, metal oxides, and organic matter from the shells. Our cleaning procedure followed that of *Boyle and Keigwin* [1985] and subsequent revisions [*Rosenthal et al.*, 1995; *Boyle and Rosenthal*, 1996]. Following cleaning, samples were dissolved in 2% nitric acid prior to running on the ICP-MS. Initial sample weights were between 200 and 300  $\mu\text{g}$ , or 20–40 individual *G. ruber* or *G. bulloides*, 10–15 individual *Morozovella*, and 30–80 individuals for the Cretaceous planktonics we have measured, including *H. delrioensis*. On the basis of comparison of sample calcium peak intensities with those of the standards, it is estimated that as much as 50% of the sample mass was lost in the cleaning procedure. Most of this loss is believed

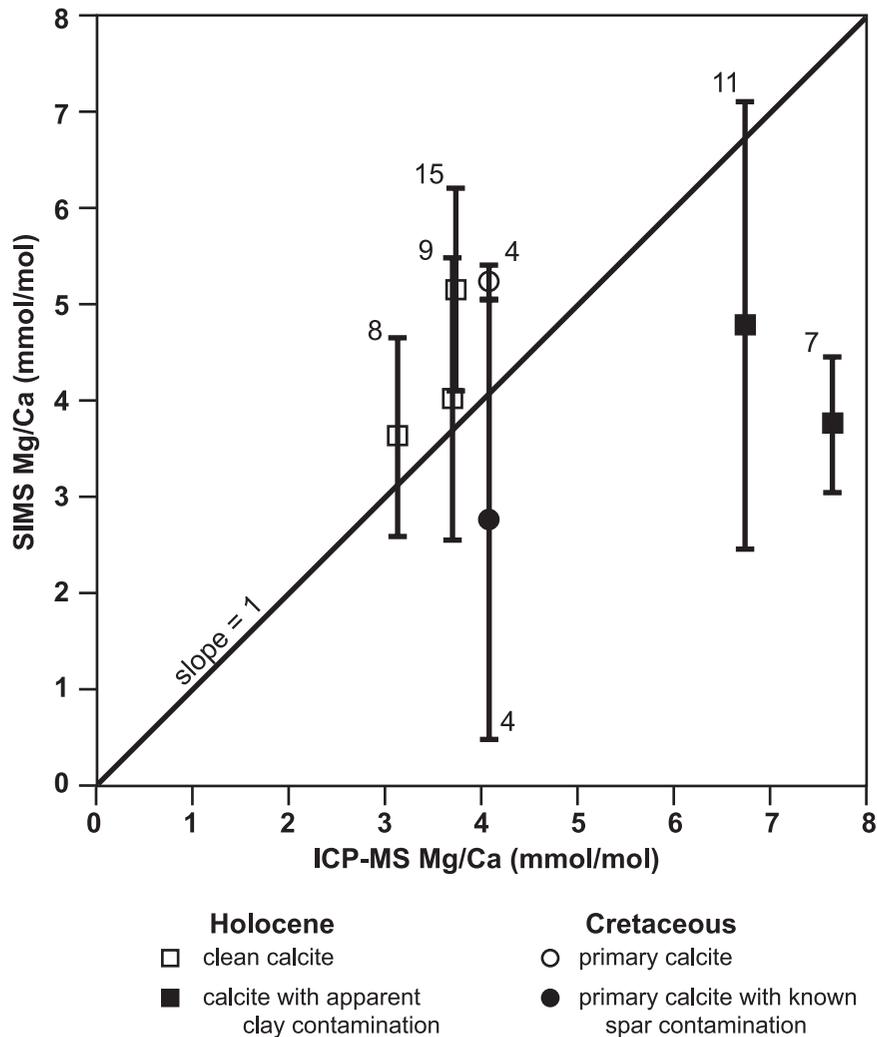
to be due to the physical removal of small fragments during siphoning designed to remove clays.

[17] Mg/Ca ratios were measured with a high-resolution sector-field inductively coupled plasma mass spectrometer (ICP-MS, Finnigan Element2) at WHOI. Mg and Ca concentrations were determined in low-resolution mode by averaging measurements from 74 scans. Ions were counted in analog mode. A standard containing high-purity elements in ratios consistent with those observed in foraminifera and a blank of 2% nitric acid were run between every four samples. Instrumental external precision for Mg/Ca, based on repeated measurements of a series of standards, is 0.03 mmol/mol, or less than 1%.

## 3. Results and Discussion

### 3.1. Comparison of the Two Techniques for Mg/Ca

[18] The comparison of single ICP-MS and average SIMS Mg/Ca values for OPD Leg 207 late Paleocene and early Eocene *Morozovella* is shown in Figure 2. Results for Arabian Sea Holocene



**Figure 3.** Comparison of Mg/Ca ratios (mmol/mol) from SIMS and ICP-MS for Holocene (squares) and Cretaceous (circles) samples. The values and error bars are as described for Figure 2. The  $\pm 0.03$  mmol/mol error bar for ICP-MS values here is the width of the symbols used. The diagonal line indicates a 1:1 correspondence. Solid squares indicate data for which the ICP-MS cleaning procedure likely did not remove all clays, resulting in unreasonably high Mg/Ca measurements. The solid circle shows the comparison of ICP-MS Mg/Ca for bulk *H. delrioensis* with known spar infilling and the average SIMS Mg/Ca value for the spar calcite alone. The open circle shows the comparison of ICP-MS Mg/Ca for bulk *H. delrioensis* with known spar infilling and the average SIMS Mg/Ca value for primary calcite alone.

*G. ruber* and *G. bulloides*, and one Cenomanian *H. delrioensis* are shown in Figure 3. Note that, in Figures 2 and 3, the bars shown on SIMS values indicate the standard deviation about the mean for  $N$  measurements made.  $N$ , the number of individual spot measurements for each sample, is given near the top or bottom of the vertical bars. In contrast, the error given on each ICP-MS value ( $N = 1$ ) is the instrumental external precision ( $\pm 0.03$  mmol/mol) based on typical replicate analyses of a standard, not multiple discrete foraminifera sample measurements. It would be incorrect to assume from

Figures 2 and 3 that ICP-MS yields a more accurate measurement of Mg/Ca. For both machines, the instrumental precision for an individual measurement of foraminiferal Mg/Ca is less than 1%. For SIMS, the relatively large standard deviations shown arise from true compositional variance among the multiple spots analyzed. Such intratest variability can currently only be examined accurately using high-resolution techniques such as SIMS (this study), laser ablation ICP-MS [e.g., Hathorne *et al.*, 2003] or electron microprobe [Puechmaille, 1994; Brown and Elderfield, 1996].

This variance is averaged out in ICP-MS measurements of multiple (or single) individuals.

[19] Where multiple SIMS measurements were made within an individual, we saw no clear systematic differences between early and late primary calcite Mg/Ca. However, we stress that we did not attempt to make a series of systematic, sequential measurements to characterize the spectrum of intratest variations. This type of study has been performed for various species by others using laser ablation ICP-MS and electron microprobe analysis (references above). While such work could be performed quite well using the SIMS technique outlined here, this was not the objective of the current study. As explained in section 2.2, we tried simply to make multiple measurements within each individual and, when possible, to target both inner and outer chambers.

[20] Taken together, the two techniques yield Mg/Ca ratios for Paleogene samples ranging from 3.1 to 4.0 mmol/mol. In five of seven samples, the average SIMS Mg/Ca is higher than that from ICP-MS but is still within one standard deviation (Figure 2). Minor clay was observed within foraminifera chambers in three Paleogene samples (Table 3) and was targeted using the ion microprobe. Apparent Mg/Ca in the clay ranged from 731–1564 mmol/mol, if referenced against the calcite standard OKA-C. These three samples yielded the lowest ICP-MS Mg/Ca values shown in Figure 2. It therefore appears that the cleaning steps used to remove clays before ICP-MS analysis was largely efficient for these *Morozovella* samples, if clay was also originally present in individuals selected for ICP-MS. The large size of *Morozovella* individuals (diameter >250  $\mu\text{m}$ ) and chambers is likely to have facilitated removal of clay infillings during crushing and rinsing.

[21] For Paleogene samples, it is not clear if any secondary calcite influenced Mg/Ca values from either SIMS or ICP-MS. Prior to cleaning and sonication, many dry *Morozovella* individuals exhibited a chalky appearance using a binocular microscope. The microgranular texture of these individuals may be the result of partial dissolution (minor etching) of primary calcite during diagenesis, but we cannot rule out the presence of microgranular secondary diagenetic calcite. Future work with the scanning electron microscope may answer this question. For now, we can say only that, if secondary calcite is present in the late Paleocene and early Eocene *Morozovellids*, its effect is present in both SIMS and ICP-MS Mg/Ca measure-

ments, or its Mg/Ca composition is very similar to that of well-preserved primary calcite targeted using SIMS.

[22] The Cenomanian *H. delrioensis* (circle symbols in Figure 3) analyzed using both SIMS and ICP-MS clearly demonstrates the effect of the secondary spar calcite in biasing Mg/Ca from ICP-MS toward low values. In sample 207-1260B-37R-1, 10–16 cm, *H. delrioensis* is a small (diameter <250  $\mu\text{m}$ ), thin-walled (generally <20  $\mu\text{m}$  thick) planktonic (Figures 4a and 4b). *H. delrioensis* is also relatively rare in this sample, as it is in many Cretaceous black shales we have examined from ODP Leg 207. From the original 40  $\text{cm}^3$  black shale sample obtained shipboard on ODP Leg 207, we were able to pick enough clean (spar free) *H. delrioensis* for two oxygen and carbon stable isotope analyses (15 individuals each) [Bice and Norris, 2005]. To get ~70 individuals from the remaining sample for one ICP-MS analysis in this experiment, we had to include ~10 individuals in which spar calcite was visible in the outermost chamber. Five additional individuals were mounted for SIMS; three of these contain spar calcite. Spar calcite targeted using SIMS had an average Mg/Ca ratio of 2.8 mmol/mol, while primary calcite was 5.2 mmol/mol. The ICP-MS Mg/Ca analysis, which we know includes some secondary spar calcite infillings, is 4.1 mmol/mol, likely reflecting a mixture of primary and spar calcite. The values reported in Figure 4 show that there is large variability both within and among different spar crystals in this sample, but this observation is based on only two individuals. Subsequent high-resolution transect measurements made using SIMS in three different *H. delrioensis* individuals from our Site 1260 sample indicate that 4–6 mmol/mol ranges in Mg/Ca values is typical of these particular spar crystals and suggest that the spar is zoned with respect to Mg/Ca. Although the temperature and kinetic controls on Mg/Ca ratios in abiotic marine calcite are only just beginning to be understood [Gaetani and Cohen, 2004, available at [http://www.icp8.cnrs.fr/poster\\_abstracts.pdf](http://www.icp8.cnrs.fr/poster_abstracts.pdf)], spar infillings such as those observed in the Leg 207 black shale planktonics might one day yield seafloor paleoceanographic information using fine resolution techniques such as SIMS.

[23] Two of the five Holocene planktonics analyzed (solid square symbols in Figure 3) suggest likely contamination of ICP-MS Mg/Ca analyses by clays. *G. bulloides* in sample TN41-10JPC and *G. ruber* in sample TN47-6GGC yielded unreasonably high

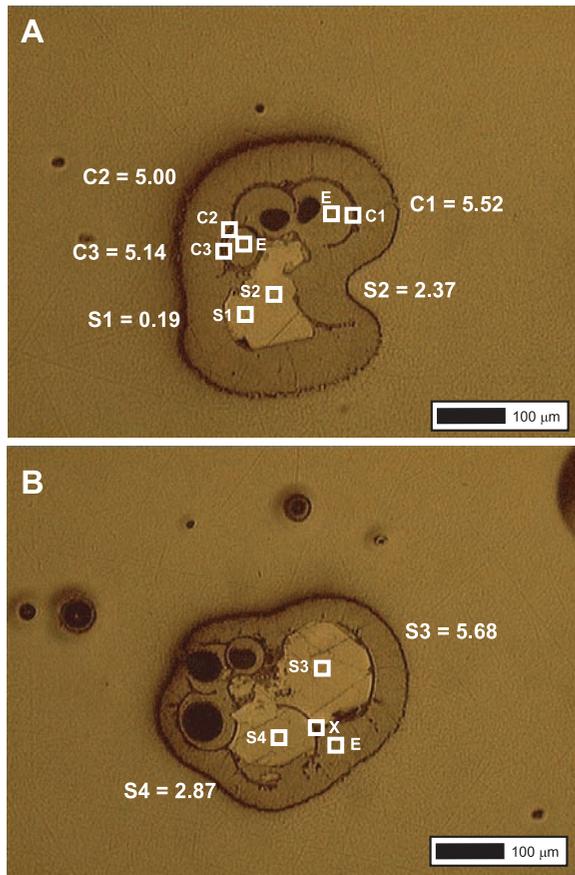
**Table 3.** Mg/Ca Ratios From ICP-MS and SIMS<sup>a</sup>

Sample Name and Foraminifer Species	ICP-MS	SIMS		
	Mg/Ca	Mg/Ca	s.d.	No. Spots (No. Ind.)
207-1257A-11X-2, 15-cm, <i>M. velascoensis</i> , Eoc. primary calcite bulk foraminifera	3.51	3.95	0.90	11 (5)
207-1257A-12X-3, 62–64 cm, <i>M. velascoensis</i> , Pal. primary calcite bulk foraminifera	3.53	3.54	0.48	11 (4)
207-1257A-14X-3, 38–40 cm, <i>M. velascoensis</i> , Pal. primary calcite clay in <i>M. velascoensis</i> bulk foraminifera	3.43	3.88 731.3	0.78 57.9	14 (5) 1 (1)
207-1257C-3R-3, 130–150 cm, <i>M. velascoensis</i> , Pal. primary calcite bulk foraminifera	3.74	3.40	0.38	5 (2)
207-1257C-5R-2, 130–150 cm, <i>M. velascoensis</i> , Pal. primary calcite clay in <i>M. velascoensis</i> bulk foraminifera	3.13	3.61 1563.7	0.90 56.0	12 (3) 1 (1)
207-1258A-6R-2, 40–42 cm, <i>M. aragonensis</i> , Eoc. primary calcite bulk foraminifera	3.55	3.99	0.90	8 (3)
207-1258A-25R-2, 20–22 cm, <i>M. aragonensis</i> , Pal. primary calcite clay in <i>M. aragonensis</i> bulk foraminifera	3.14	3.36 1215.4	0.86 347.1	13 (3) 2 (2)
207-1260B-37R-1, 10–16 cm, <i>H. delrioensis</i> , Cen. primary calcite spar calcite in <i>H. delrioensis</i> bulk foraminifera (including spar <sup>b</sup> )	4.06	5.24 2.78	0.15 2.26	4 (2) 4 (2)
IOE-KK143, <i>G. ruber</i> , core top primary calcite bulk foraminifera	3.72	5.17	1.04	15 (4)
IOE-KK114, <i>G. ruber</i> , 20 kyr primary calcite clay in <i>G. ruber</i> bulk foraminifera	3.12	3.65 123.3	1.01 87.8	8 (3) 5 (2)
SO42-36KL, <i>G. ruber</i> , 20 kyr primary calcite clay in <i>G. ruber</i> bulk foraminifera	3.69	4.03 90.6	1.45 123.4	9 (3) 4 (2)
TN41-10JPC, <i>G. bulloides</i> , 20 kyr primary calcite clay in <i>G. bulloides</i> bulk foraminifera	7.63	3.78 243.5	0.69 244.9	7 (4) 7 (2)
TN47-6GGC, <i>G. ruber</i> , core top primary calcite bulk foraminifera	6.73 <sup>c</sup>	4.79	2.30	11 (4)

<sup>a</sup> Mg/Ca in mmol/mol. For SIMS analyses, the standard deviation (s.d.), number of spot measurements and number of different individuals measured are given. Ratios reported for clay are apparent ratios based on comparison against the OKA standard concentration, not a clay standard.

<sup>b</sup> Approximately 15% of the *H. delrioensis* individuals picked for ICP-MS analysis had visible clear spar calcite infilling the outermost chambers.

<sup>c</sup> Clay infilling was observed in this sample but was not measured using SIMS.



**Figure 4.** Photomicrographs of Cretaceous *H. delrioensis* from ODP sample 207-1260B-37R-1, 10–16 cm, with calcite spar crystals visible in the outermost chambers. Open squares indicate the areas within which spot measurements of primary calcite (C1–C3), spar calcite (S1–S4), and embedding material (E) were made using SIMS. The spot labeled X was one eliminated owing to obvious contamination from embedding material. Spot Mg/Ca values (mmol/mol) are reported adjacent to labels. The in-run precision ( $1\sigma$ ) for individual SIMS analyses is  $\sim 0.1$  mmol/mol for foraminiferal calcite and 0.05 mmol/mol or less for spar calcite.

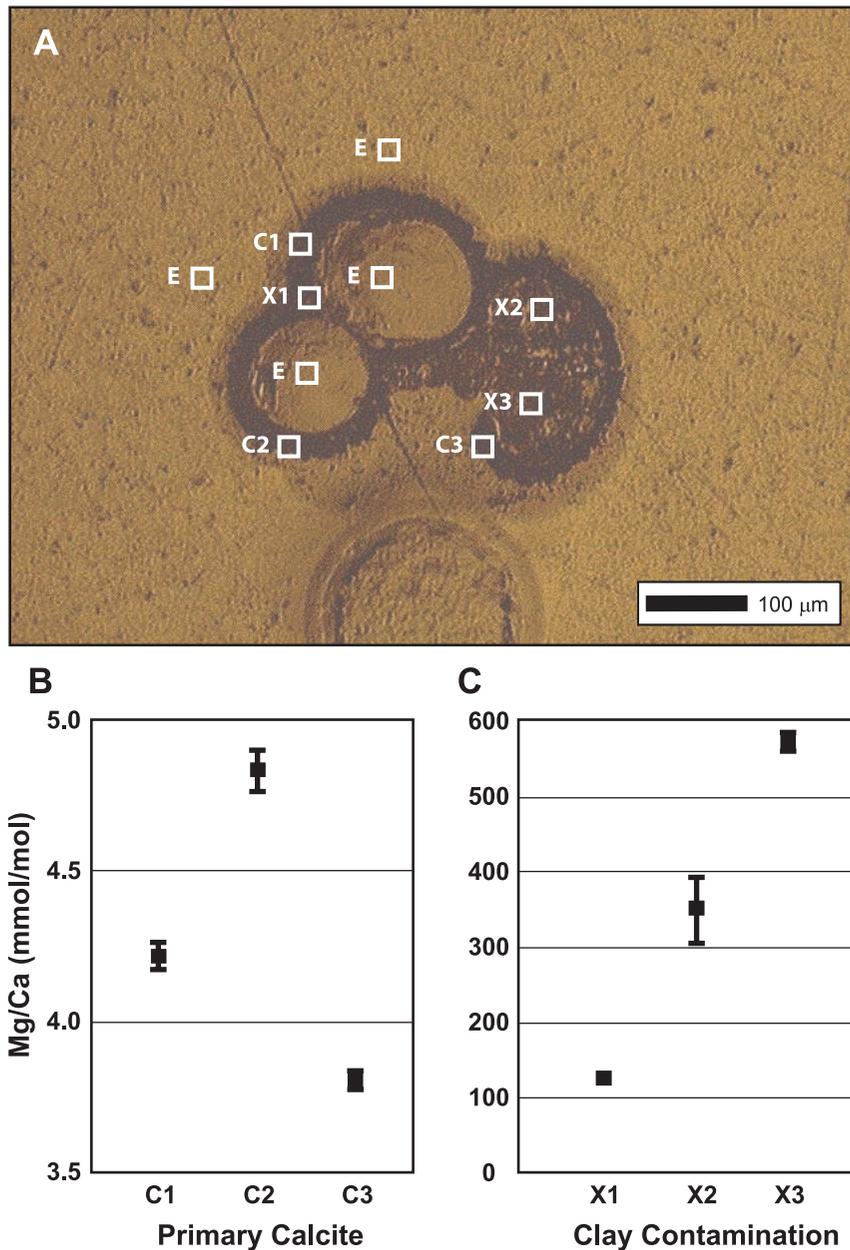
Mg/Ca ratios from ICP-MS (Table 3), given the current understanding of 0–20 ka upper ocean water temperatures in the Arabian Sea [Schulte and Müller, 2001] combined with a plausible temperature-Mg/Ca relationship for these species [Anand et al., 2003]. The presence of an abundant aluminosilicate mineral was confirmed by high observed signals for  $^{27}\text{Al}^+$  and  $^{28}\text{Si}^+$  during SIMS analysis of these samples. When analyzed using SIMS, primary calcite in these samples averaged 3.8–4.8 mmol/mol, consistent with that expected for the temperature relationship and with other primary calcite samples from the region. An example of clay lining targeted

using SIMS in one chamber in TN41-10JPC (Figure 5) revealed apparent Mg/Ca values greater than 300 mmol/mol. It appears likely that, for the TN41 and TN47 samples, the cleaning technique used before ICP-MS did not successfully remove what must be stubbornly adhering clays. The clays shown in Figure 5a were not removed even when the foraminifera chamber was opened during grinding and subjected to sonication during preparation and cleaning of the SIMS mount.

[24] In *G. ruber* from Holocene samples IOE-KK114 (Figure 3,  $N = 8$ ) and SO42-36KL (Figure 3,  $N = 9$ ), clay was noted in the SIMS mount samples, but Mg/Ca values from ICP-MS suggest no contamination from Mg-rich clays. Mg/Ca from ICP-MS and average SIMS Mg/Ca are within  $\sim 0.5$  mmol/mol. In these samples, the standard ICP-MS cleaning procedure appears to have removed clays, if they were present in the individuals crushed for ICP-MS analysis. No clays or other secondary mineralization were noted in *G. ruber* from sample IOE-KK143 (Figure 3,  $N = 15$ ), but average Mg/Ca from SIMS is  $\sim 1.5$  mmol/mol greater than that from the single ICP-MS analysis performed. We currently have no unequivocal explanation for this discrepancy in values. It may be the result of some sampling bias in the individuals randomly selected for SIMS and ICP-MS analyses. Individual spot Mg/Ca values from SIMS range from 3.4 to 7.7 mmol/mol for this sample. Replicate ICP-MS analyses are warranted for this sample, but the 3.7 mmol/mol value obtained from ICP-MS is more reasonable than the 5.2 mmol/mol average from 15 SIMS analyses.

### 3.2. Optimization of the SIMS Techniques for Mg/Ca

[25] This study has allowed us to verify and refine the techniques being used to produce Mg/Ca measurements using SIMS at WHOI. Our 3-min presputter cleaning time appears to be optimal. In preliminary measurements of foraminiferal calcite using a 2-min presputtering routine, the ratio  $^{24}\text{Mg}^+ / ^{40}\text{Ca}^+$  had a tendency to drift downward during the four cycles of peak analysis. This implied interferences present in surficial material, an interpretation supported by a concomitant systematic decrease in  $^{23}\text{Na}^+$  counts. We increased the surface cleaning presputter time to 3 min and saw no further shift in  $^{24}\text{Mg}^+ / ^{40}\text{Ca}^+$ . Allison and Austin [2003] used exclusively  $^{26}\text{Mg}^+$  as an analyte peak for Mg, did not energy filter secondary ions and did not use an explicit presputter cleaning step. In comparing analyses using 0.5 and 10 nA primary



**Figure 5.** (a) Photomicrograph of Holocene *G. bulloides* from Arabian Sea core TN41-10JPC, with obvious clay lining in the rightmost chamber. Open squares indicate the locations of spot measurements of primary calcite (C1–C3), clay contamination (X1–X3) and embedding material (E) made using SIMS. (b) Plot of SIMS Mg/Ca ratios (mmol/mol) for primary calcite (C1–C3). (c) Plot of SIMS Mg/Ca ratios (mmol/mol) for calcite contaminated with clay (X1) and intentionally targeted clay (X2–X3). Note the difference in Y-axis scale for Figures 5b and 5c. The in-run precision ( $1\sigma$ ) on individual SIMS analyses is indicated by bars when the value is larger than the symbol used.

currents, they found that the latter produced more reliable results. This probably reflects the influence of surface contamination more rapidly removed by a 20-fold increase in primary beam current. However, the 10 nA current used reduced lateral resolution to only 40  $\mu\text{m}$ , which would be insufficient to target primary calcite in delicate planktonics such as *H. delrioensis*, *G. ruber*, and *G. bulloides*.

Newer SIMS instruments allow the preprogramming of coincident, higher current primary beams for presputtering, which would allow our 3-min presputtering time to be easily reduced to 1 min or less without consumption of additional material.

[26] In this study, the redundant measurement of all three isotopes of Mg ( $^{24}\text{Mg}^+$ ,  $^{25}\text{Mg}^+$ , and  $^{26}\text{Mg}^+$ )

was retained in order to verify the lack of interferences on these three analyte peaks. The observation that Mg isotope ratios for biogenic calcite analyses are consistent with natural abundance ratios [Coplen *et al.*, 2002] shows that the energy filtering we have used is effectively removing any substantial isobaric interferences. We conclude that, using a combination of modest energy filtering and sufficient presputtering,  $^{24}\text{Mg}^+$  can be used as an exclusive analyte peak for Mg. Counting only  $^{23}\text{Na}^+$  for 10 s (for contamination monitoring) and  $^{24}\text{Mg}^+$  for 40 s (thus improving counting statistic precision twofold over the Table 1 value) would require only 250 s for data accumulation, while yielding very accurate Mg/Ca determinations.

[27] Work is underway at WHOI to examine the potential calibration of water temperature with Mg/Ca determined in modern benthic foraminifera using SIMS. This study is designed to provide quantitative proof of the utility of Mg/Ca sample averages from distributed spot measurements in foraminifera for paleotemperature reconstructions. We are also participants in a current interlaboratory Mg/Ca intercalibration study, a follow-up to Rosenthal *et al.* [2004]. The establishment of an internationally accepted standard for Mg/Ca analyses using ICP-MS, and cross-calibration of the OKA-C standard, will be an important step in the establishment of a SIMS-based Mg/Ca-temperature calibrations for benthic and planktonic foraminifera.

#### 4. Conclusions

[28] 1. In samples free of visible diagenetic material, the agreement of Mg/Ca ratios from SIMS and ICP-MS is very good. In only one out of 10 such samples examined here did the average Mg/Ca from SIMS differ from ICP-MS Mg/Ca by more than one standard deviation in the data.

[29] 2. SIMS is an accurate and effective tool for microsampling even delicate planktonic foraminifera for Mg/Ca analysis.

[30] 3. SIMS allows accurate targeting of primary calcite, as well as characterization of the apparent Mg/Ca of any visible contaminants present. It therefore enables the reconciliation of contamination problems in the analyses of larger mass samples by more conventional solution-based techniques. When suspect Mg/Ca ratios from ICP-MS are caused by incomplete removal of stubbornly adhering diagenetic clays, or secondary calcite that cannot be removed by standard cleaning procedures, the high-resolution capabilities and accuracy

of SIMS for Mg/Ca analyses are unique and invaluable.

[31] 4. SIMS is superior to solution-based techniques such as ICP-MS when multiple analyses of rare, or very low mass, species are required.

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