



Precise multielemental ratios in small foraminiferal samples determined by sector field ICP-MS

Thomas M. Marchitto

Department of Geological Sciences and Institute of Arctic and Alpine Research, University of Colorado, Campus Box 450, Boulder, Colorado 80309, USA (tom.marchitto@colorado.edu)

[1] Inductively coupled plasma mass spectrometry (ICP-MS) holds two main advantages over other techniques for the measurement of foraminiferal elemental ratios: (1) numerous trace metals may be precisely and simultaneously measured, and (2) smaller samples may theoretically be used. Methods are presented for the precise determination of Mg/Ca, Sr/Ca, Cd/Ca, Zn/Ca, Li/Ca, U/Ca, Mn/Ca, and Fe/Ca by sector field ICP-MS. Analytical precision is largely independent of sample size over the range of ~5 to 125 $\mu\text{g CaCO}_3$, eliminating the need for narrow target dilutions. Long-term 1σ precisions are as follows: Mg/Ca = 0.54%, Sr/Ca = 0.57%, Cd/Ca = 1.8%, Zn/Ca = 3.2%, Li/Ca = 0.88%, U/Ca = 1.9%, Mn/Ca = 0.97%, and Fe/Ca = 1.4%. For Mg/Ca, actual foraminiferal samples appear to give reliable results below 10 $\mu\text{g CaCO}_3$ (postcleaning mass).

Components: 5761 words, 4 figures, 2 tables.

Keywords: cadmium; foraminifera; magnesium; strontium.

Index Terms: 4924 Paleooceanography: Geochemical tracers; 4994 Paleooceanography: Instruments and techniques.

Received 13 May 2005; **Revised** 27 November 2005; **Accepted** 22 March 2006; **Published** 25 May 2006.

Marchitto, T. M. (2006), Precise multielemental ratios in small foraminiferal samples determined by sector field ICP-MS, *Geochem. Geophys. Geosyst.*, 7, Q05P13, doi:10.1029/2005GC001018.

Theme: Development of the Foraminiferal Mg/Ca Proxy for Paleooceanography
Guest Editor: Pamela Martin

1. Introduction

[2] Trace and minor elemental compositions of foraminiferal tests are widely employed to reconstruct paleoceanographic conditions. In recent years, Mg/Ca has received particularly keen attention as a paleotemperature indicator [e.g., Nurnberg *et al.*, 1996; Rosenthal *et al.*, 1997]. Cd/Ca [Boyle and Keigwin, 1982] and Zn/Ca [Marchitto *et al.*, 2000] are useful paleonutrient tracers and are therefore employed to reconstruct past circulation patterns. U/Ca in cultured planktonic foraminifera decreases systematically as seawater CO_3^{2-} concentration increases, making it a promising proxy for past carbonate system

chemistry [Russell *et al.*, 2004]. Li/Ca may hold similar promise [Hall and Chan, 2004]. Foraminiferal Sr/Ca may record long term changes in seawater Sr/Ca, though other environmental factors are clearly important [Martin *et al.*, 1999; Elderfield *et al.*, 2000]. Mn/Ca [Boyle, 1983] and Fe/Ca [Barker *et al.*, 2003] are routinely monitored to assess authigenic or detrital contamination.

[3] Among these various proxies, Mg/Ca is by far the most widely measured and applied. Because Mg is present in foraminiferal CaCO_3 at relatively high concentrations, it may be rapidly and precisely measured using ICP atomic emission spectrometry (AES) or ICP optical emission spectrometry

(OES) techniques [Schrage, 1999; de Villiers *et al.*, 2002; Green *et al.*, 2003]. While Sr/Ca is also routinely measured by these techniques, Cd/Ca, Zn/Ca, Li/Ca, and U/Ca are below detection limits. Cd/Ca and Zn/Ca were developed using atomic absorption spectrophotometry (AAS) [Boyle and Keigwin, 1982; Marchitto *et al.*, 2000], but sample-intensive analysis procedures preclude the measurement of many additional elements. ICP-MS offers higher sensitivities than AES and OES, enabling not only the measurement of more elements, but theoretically smaller sample sizes. Using isotope dilution and a quadrupole ICP-MS, Lea and Martin [1996] reported Cd/Ca and Ba/Ca precision of $\sim 2\text{--}3\%$ in standards as small as 25 μg CaCO_3 equivalent, and Martin *et al.* [2002] likewise accepted Mg/Ca data from foraminiferal samples as small as 25 μg postcleaning mass. Using sector field ICP-MS, Rosenthal *et al.* [1999] reported good (but not quantified) multielement precision for standards as small as 25 μg CaCO_3 equivalent.

[4] Methods are presented here for the simultaneous determination of Mg/Ca, Sr/Ca, Cd/Ca, Zn/Ca, Li/Ca, U/Ca, Mn/Ca, and Fe/Ca by sector field single-collector ICP-MS. These methods are largely based on those developed by Rosenthal *et al.* [1999] for Mg/Ca, Sr/Ca, Cd/Ca, Ba/Ca, U/Ca, and Mn/Ca using the Finnigan MAT Element sector field ICP-MS. A notable advance over that study is that high precision is shown to be maintained well below 25 μg CaCO_3 . Combined with linear matrix effects, this independence from sample size allows for greater flexibility during sample preparation and dilution. Potentially important spectral interferences on ^{24}Mg and ^{46}Ca are also discussed.

2. Methods

2.1. Instrumentation

[5] Methods were developed on a Thermo Finnigan Element2 sector field ICP-MS, interfaced to a CETAC ASX-100 autosampler with a 24-position sample tray. Sample injection is via an Elemental Scientific PFA-ST self-aspirating micronebulizer, with a flow rate of 100 $\mu\text{L min}^{-1}$. An Elemental Scientific quartz cyclonic spray chamber is used to minimize memory effects due to sample washout. The quartz torch is fitted with a Pt guard electrode, which was not originally used by Rosenthal *et al.* [1999] but was later added [Lear *et al.*, 2002] to increase sensitivity. Standard Ni cones are used.

Low-resolution sensitivity is typically $\sim 1 \times 10^6$ cps for 1 ppb of ^{115}In .

2.2. Standards and Blanks

[6] External standards were prepared gravimetrically using $1000 \pm 3 \text{ mg L}^{-1}$ stock solutions from High-Purity Standards and SPEX CertiPrep. Five mother solutions (S0–S4) were made at $\sim 5 \text{ mM}$ (200 ppm) Ca in 2% (v/v) HNO_3 (Fisher Optima), with minor and trace element concentrations that mimic the typical oceanic ranges of foraminifera. Elemental ratios for S1 through S4 are shown in Figure 3. Trace element impurities in the Ca solution (High-Purity Standards, made from CaCO_3) are significant relative to foraminiferal concentrations, so all elements of interest were determined by standard addition and included in the standard calculations. Calculated impurities are at least five times higher than the lot assay, except for Fe and U which are below assay. Relative to the elemental concentrations in the highest mother solution (S4), the contribution from the Ca stock solution ranges from $\sim 0.02\%$ for Mn to $\sim 15\%$ for Cd. The high impurity levels for elements like Cd are not problematic as long as they are well constrained. This is confirmed by linear standard curves that pass through the origin after accounting for impurities.

[7] For each sample run, standards are diluted to 2 mM (80 ppm) Ca using 2% HNO_3 . Sample elemental ratios are calculated offline using five-point linear standard curves interspersed between every eight samples. As discussed in section 3.4, five-point standard curves may be considered overkill, since two-point curves result in comparable precisions; Rosenthal *et al.* [1999] used a single standard. A blank consisting of the same 2% HNO_3 used to dilute the standards and samples is also run between every eight samples. Relative to S4, blank intensities are well below 1% for all elements except Li ($\sim 1\%$) and Zn ($\sim 2\%$). ^{46}Ca also has a high blank level ($\sim 2\%$) due to a spectral interference, discussed in section 3.1. All raw intensities (including standards) are blank-subtracted and then ratioed to Ca intensities.

[8] Standard curves are calculated using metal/Ca ratios, which minimizes errors due to dilution and evaporation [Rosenthal *et al.*, 1999] (see Figure 1 for Mg/Ca). Coefficients of determination (r^2) are always >0.999 and typically >0.9999 for all elemental ratios. Calculations are weighted according to position in run using linear interpolation between standards and blanks. There is usually a very

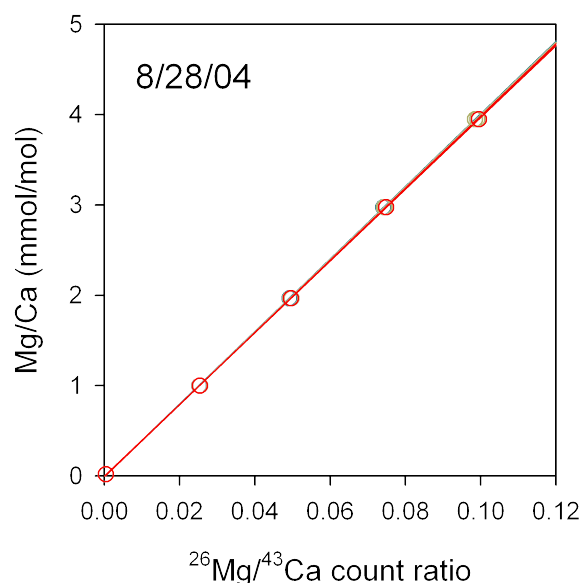


Figure 1. Four linear standard curves for Mg/Ca measured during the course of a single run. Curves 1 through 4 are shown in blue, green, yellow, and red, respectively. Intensity ratios are blank-corrected, and all fits are $r^2 > 0.9999$.

slight drift in the standard curves over the course of a run, suggesting small variations in mass discrimination with time (Figure 1).

2.3. Detection Modes

[9] The Element2 uses two detection modes depending on signal intensity. Counting mode is used for intensities below $\sim 5 \times 10^6$ cps. To avoid damaging the secondary electron multiplier (SEM), higher intensities are measured in analog mode. “Both” mode begins each measurement in count-

ing and then switches to analog if necessary. A cross-calibration is automatically performed by the Element2 software, so that samples measured in counting mode are directly comparable to those measured in analog. However, this cross-calibration is subject to error, especially if a sample is just at the edge of the analog switch. Precision is significantly improved if trace metals (Li, Zn, Cd, and U) are ratioed to the rarest Ca isotope (^{46}Ca , 0.004% abundance), since all signals may theoretically be collected in counting mode [Rosenthal *et al.*, 1999]. Minor elements (Mg, Mn, Sr, and Fe) are ratioed to ^{43}Ca (0.14% abundance), all measured in analog mode. In counting mode, the safety shutoff for ^{46}Ca occurs for samples as low as 2 mM Ca, but in “both” mode the shutoff is closer to $\sim 4\text{--}5$ mM Ca. For these reasons ^{46}Ca is run in “both” mode, samples are diluted to a target concentration ≤ 2 mM Ca, and standards are run at 2 mM Ca. These dilutions ensure that ^{46}Ca does not switch to analog.

2.4. Isotopes and Acquisition Parameters

[10] Measured isotopes and acquisition parameters are listed in Table 1. Possible spectral interferences are discussed in section 3.1. All elements are measured in low resolution ($m/\Delta m = 300$) except for ^{56}Fe , which must be measured in medium resolution ($m/\Delta m = 4000$) to avoid the large interference from $^{40}\text{Ar}^{16}\text{O}$ (all Fe isotopes have large argide interferences in low resolution). During most of the matrix effect analyses presented here, ^{56}Fe intensities were ratioed to low-resolution ^{43}Ca intensities. It has since been determined that Fe/Ca precision is markedly improved if ^{43}Ca is also measured in medium resolution. Therefore

Table 1. ICP-MS Measurement Parameters

Isotope	Mass Window	Settling Time, s	Sample Time, s	Samples per Peak	Search Window	Integration Window	Detection Mode
<i>Low Resolution: 3 Runs \times 20 Passes</i>							
^7Li	5	0.300	0.02	200	0	5	Counting
^{26}Mg	5	0.050	0.01	200	0	5	Analog
^{43}Ca	5	0.025	0.01	200	0	5	Analog
^{46}Ca	5	0.001	0.01	200	0	5	Both
^{55}Mn	5	0.001	0.01	200	0	5	Analog
^{66}Zn	5	0.025	0.02	200	0	5	Counting
^{88}Sr	5	0.019	0.01	200	0	5	Analog
^{111}Cd	5	0.100	0.03	200	0	5	Counting
^{238}U	5	0.084	0.03	200	0	5	Counting
<i>Medium Resolution: 3 Runs \times 6 Passes</i>							
^{43}Ca	50	0.300	0.01	100	50	10	Analog
^{56}Fe	50	0.040	0.01	100	50	10	Analog

Fe/Ca matrix effects are not discussed below. The revised acquisition parameters (Table 1) only affect Fe/Ca since the low-resolution parameters were unchanged.

[11] Drift of the mass calibration is automatically corrected by the Element2 software by monitoring the drift of $^{40}\text{Ar}/^{40}\text{Ar}$. This correction, combined with the flat-topped peaks produced in low resolution, means no search windows are required to keep 5% mass integration windows well centered [Rosenthal *et al.*, 1999]. In contrast, the medium-resolution ^{56}Fe and ^{43}Ca peaks may drift significantly during a run, so a 50% search window is applied. The suite of low-resolution isotopes is measured in 60 replicate passes (^7Li to ^{238}U) for each analysis, followed by 18 passes over the medium-resolution ^{43}Ca and ^{56}Fe . Magnet settling times between isotopes are as suggested by the Element2 software except for Cd, which is set to 0.1 s. ^{88}Sr counts are several orders of magnitude higher than ^{111}Cd counts in typical foraminiferal samples, leading to a significant bleed-over of the Sr signal into the Cd signal if settling times are too short. Sample times (the duration of discrete mass measurements) are longer for rarer elements, to improve signal-to-noise ratios (Table 1).

[12] Each measurement requires 500 μL of solution and takes ~ 5 min, including 2 min of uptake time. In addition, the spray chamber is washed for 2 min between each measurement. Including standards and blanks, a run of 24 samples takes about 6 hr. Prospects for reducing this time are discussed in section 3.4.

2.5. Foraminiferal Sample Preparation

[13] Monospecific foraminiferal samples are gently crushed between glass slides and loaded into 500 μL BioRad polypropylene microcentrifuge vials, preleached in hot 0.5N HCl. Samples are chemically cleaned using the “trace metal” technique developed by Boyle and Keigwin [1985/1986] and modified by Boyle and Rosenthal [1996]. This consists of four main steps: (1) clay removal by repeated ultrasonication in ultra-pure water and methanol; (2) reduction of authigenic ferromanganese oxides by anhydrous hydrazine (NH_2NH_2) in a buffered citric acid- NH_4OH solution; (3) oxidation of organic matter by H_2O_2 in a NaOH solution; and (4) surface leaching with 0.001N HNO_3 . The concentration of 30% H_2O_2 in the oxidizing reagent may range from 0.4% to 5%, depending on the organic matter content of the sediments. Much of the cleaning process is per-

formed in HEPA class 100 laminar flow benches, and the entire procedure takes place in a class 1000 clean room (the ICP-MS is in a separate room). The clean room significantly reduces the frequency of sample contamination, particularly for Zn.

[14] Cleaned foraminiferal samples are dissolved in 100 μL of 0.5% (0.075 N) HNO_3 . A fraction of this volume is then diluted with 2% HNO_3 to bring the sample to ≤ 2 mM Ca in 500 μL . The dilution is done in a PTFE autosampler cup, preleached in cool 10% HNO_3 . With a little experience, a technician can visually estimate the necessary dilution on the basis of postcleaning sample size. Either 30, 50, or 100 μL of the dissolved sample is used. Poorly estimated dilutions have no effect on results unless Ca is so high (> 4 –5 mM) that ^{46}Ca switches to analog (section 2.3), a scenario that has not yet been encountered in over 400 foraminiferal measurements. The resulting small variation in final HNO_3 concentration (1.7–1.9%) has no significant effect on measured elemental ratios.

3. Results and Discussion

3.1. Spectral Interferences

[15] A multitude of spectral interferences may combine with analyte isotope peaks in low resolution, especially due to polyatomic species. In most cases these interferences may be identified by moving to medium or high resolution. As mentioned above, ^{56}Fe must be measured in medium resolution to avoid interference from $^{40}\text{Ar}^{16}\text{O}$. Other plasma/acid related polyatomics were ruled out for all isotopes except ^{46}Ca , which has a small interference due to $^{14}\text{N}^{16}\text{O}^{16}\text{O}$. This probably accounts for the stable (within a run) $\sim 2\%$ background in acid blanks relative to standards. In theory this interference should be roughly constant across blanks, standards, and samples, and is therefore correctable.

[16] Interferences that may vary with sample composition are more troublesome. ^{24}Mg was rejected because of a minor (order 1%) interference due to $^{48}\text{Ca}^{2+}$. ^{46}Ca has an interference due to ^{46}Ti , which is not separable even in high resolution. Since ^{46}Ca is so rare (0.004% abundance), a theoretical sedimentary Ti/Ca contamination of 100 $\mu\text{mol mol}^{-1}$ could produce a 20% interference. To evaluate this possibility, the blank-corrected ratio of ^{46}Ca to ^{43}Ca was examined for standards and foraminiferal samples from several regions (Figure 2). If the samples contain enough Ti to affect ^{46}Ca counts, this should show up as anomalous Ca ratios.

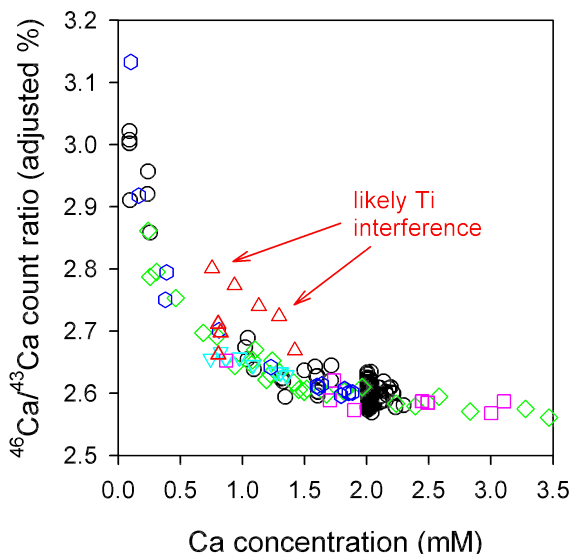


Figure 2. Ratios of low-resolution, blank-corrected ^{46}Ca counts to ^{43}Ca counts for various standards (black circles) and foraminiferal samples across six runs. Count ratios from each run were slightly normalized to bring the average of external standards S0–S4 (black circles near 2 mM Ca) to 2.6 (observed averages were 2.5–2.7). Samples are from ODP 658 off northwestern Africa (green diamonds), KNR166-2 multicores from the Florida Straits (cyan triangles), OMZ01-PC14 off southern Baja California (blue hexagons), various Mid-Atlantic Ridge cores (pink squares), and B997-330PC off northern Iceland (red triangles). The Iceland core exhibits some elevated $^{46}\text{Ca}/^{43}\text{Ca}$ ratios suggestive of a slight ^{46}Ti interference.

Standard $^{46}\text{Ca}/^{43}\text{Ca}$ ratios are close to the theoretical value of 2.6% and vary nonlinearly with Ca concentration. This nonlinearity is not related to any spectral interferences, but rather appears to result from some poorly understood mass bias (matrix) effect which is implicitly included in the matrix effects discussed below. Foraminifera from ODP 658 (off northwestern Africa), KNR166-2 multicores (Florida Straits), OMZ01-PC14 (off southern Baja California), and various Mid-Atlantic Ridge cores all exhibit good agreement with standards, indicating no significant Ti interference. The only exception is B997-330PC (off northern Iceland), in which several samples show $^{46}\text{Ca}/^{43}\text{Ca}$ enhanced by $\sim 0.1\%$, suggesting a Ti interference of several percent. This core is by far the “dirtiest” of the group, featuring dark specks of either volcanic ash or pyrite that survived the cleaning process. Fe/Ca was also elevated, at $\sim 100\text{--}250\ \mu\text{mol mol}^{-1}$. The slight interference may be corrected by either using the $^{46}\text{Ca}/^{43}\text{Ca}$ data or by measuring another isotope of Ti. However, such high Ti concentrations

are a warning that elemental ratios of interest may also be affected by silicate contamination [Barker *et al.*, 2003; Greaves *et al.*, 2005].

3.2. Matrix Effects

[17] ICP-MS ion transmission varies with sample matrix. In the case of CaCO_3 analyses, the matrix effect may be determined by comparing measured elemental ratios to Ca concentrations in known standards. Figure 3 shows deviations in measured metal/Ca ratios (expressed as fractional difference from known ratios) versus measured Ca concentration (expressed as difference from 2.02 mM Ca external standards), based on various dilutions of mother solutions S1 through S4. Mg/Ca, Mn/Ca, Zn/Ca, Cd/Ca, and U/Ca show significant ($\geq 99\%$ level) signal suppression with increasing Ca concentration over the range 0.1 to 2.5 mM. Li/Ca exhibits significant ($>99\%$ level) signal enhancement with Ca concentration, and Sr/Ca shows no effect. For all ratios except Sr/Ca and Fe/Ca, linear corrections based on these data are applied to all foraminiferal samples. To ensure accuracy in these equations, 2σ outliers (triangles in Figure 3) are rejected and linear fits are forced through the origin. For each element, the matrix effect (expressed as percentages) also appears to be independent of metal/Ca ratio, consistent with the findings of Lear *et al.* [2002] for Mg/Ca. Since matrix effects may vary with instrument geometry, the slopes in Figure 3 should not be applied to other Element2 laboratories without independent verification.

[18] There is no strong indication of non-linearity in these matrix effects over the Ca range investigated. Rosenthal *et al.* [1999] reported apparently linear effects over a wider Ca range of 2 to 24.5 mM, but with considerably lower slopes due to the absence of a guard electrode [Lear *et al.*, 2002]. Rosenthal *et al.* [1999] diluted their samples to match the Ca concentration of standards within a factor of two to three ($\sim 2\text{--}7$ mM), and applied matrix corrections to samples differing from standards by more than a factor of three to four. With the addition of a guard electrode to improve sensitivity, Lear *et al.* [2002] found a matrix effect for Mg/Ca comparable to that reported here, but with a strong nonlinearity at low Ca. This led Lear *et al.* [2002] to dilute their samples to a target concentration of 3 ± 1 mM Ca; samples smaller than ~ 0.5 mM ($< 25\ \mu\text{g CaCO}_3$ equivalent) required additional standards closely matched to sample Ca concentrations. Subsequent work at Rutgers University (D. H. Andreasen *et al.*,

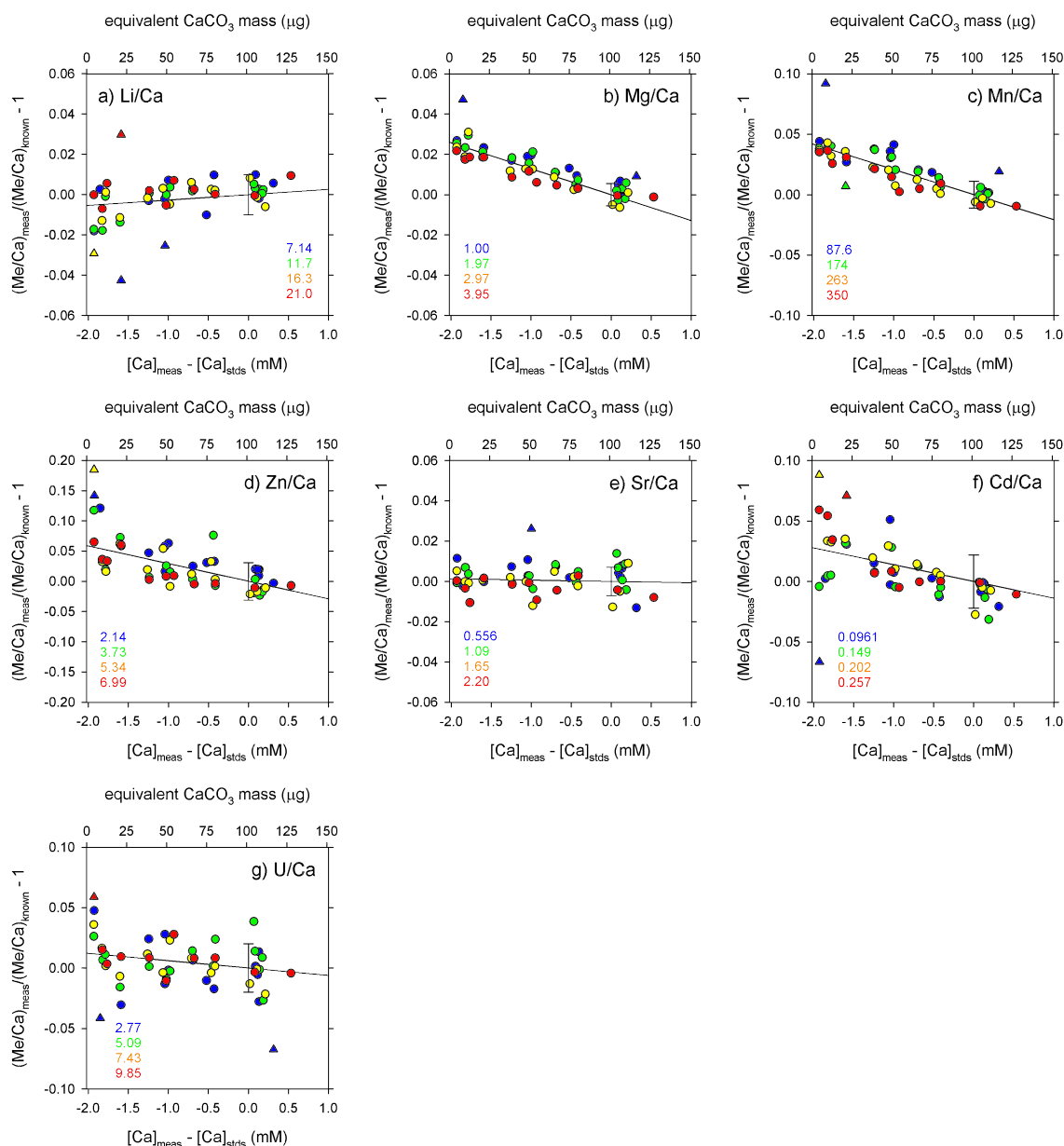


Figure 3. Measured metal/Ca ratios in various dilutions of standards S1–S4 (expressed as fractional deviation from known ratios) versus measured Ca concentrations (expressed as deviation from Ca concentration of external standards (2.02 mM)). Top axes show equivalent mass of CaCO_3 . S1, S2, S3, and S4 are shown in blue, green, yellow, and red, respectively, and metal/Ca ratios for each are listed (all in $\mu\text{mol mol}^{-1}$ except Mg/Ca and Sr/Ca in mmol mol^{-1} , and U/Ca in nmol mol^{-1}). Significance levels noted in section 3.3 are for linear fits through all data, but 2σ outliers (triangles) are excluded from the plotted fits, which are used for the matrix effect corrections. Slopes and r^2 are as follows: Li/Ca = 0.00268, 0.27; Mg/Ca = -0.0129 , 0.81; Mn/Ca = -0.0208 , 0.82; Zn/Ca = -0.0292 , 0.44; Sr/Ca = -0.000641 , 0.00; Cd/Ca = -0.0139 , 0.50; and U/Ca = -0.00612 , 0.10. The Sr/Ca fit is insignificant. Error bars at the origin show $\pm 1\sigma$ spread around the trends including outliers, a measure of analytical precision.

Fidelity of radial-viewed ICP-OES and magnetic-sector ICP-MS measurement of Mg/Ca and Sr/Ca ratios in marine biogenic carbonates: Are they trustworthy together?, submitted to *Geochemistry, Geophysics, Geosystems*, 2006) indicates that the

Mg/Ca matrix effect is linear if Ca is limited to a relatively narrow range of 1 to 8 mM. Linear matrix effects as reported here allow for greater flexibility in sample dilution, with simple corrections relative to a single set of standards.

Table 2. Standard Precision and Internal Accuracy^a

	Li/Ca	Mg/Ca	Mn/Ca	Zn/Ca	Sr/Ca	Cd/Ca	U/Ca	Fe/Ca
Matrix RSD	1.0	0.55	1.1	3.1	0.70	2.2	2.0	n/a
CS1–4 RSD	0.88	0.54	0.97	3.2	0.57	1.8	1.9	1.4
CS1 (n = 25)								
Mean	7.14	1.00	88.4	2.19	0.56	0.0962	2.79	62.7
RSD	0.90	0.32	0.97	4.8	0.43	1.4	2.5	1.5
Accuracy	0.01	0.49	0.90	2.2	0.56	0.05	0.76	0.39
CS2 (n = 32)								
Mean	11.7	1.97	174	3.70	1.10	0.149	5.09	121
RSD	1.0	0.48	0.97	1.7	0.46	1.9	1.7	1.4
Accuracy	0.06	0.42	0.34	−0.67	0.35	−0.10	0.14	0.38
CS3 (n = 31)								
Mean	16.3	2.98	263	5.29	1.65	0.202	7.41	181
RSD	0.72	0.62	0.82	1.6	0.65	1.8	1.3	1.5
Accuracy	−0.10	0.18	0.07	−0.93	0.01	−0.09	−0.36	0.44
CS4 (n = 6)								
Mean	20.9	3.93	349	7.08	2.20	0.260	9.83	241
RSD	0.63	0.36	0.88	1.2	0.58	2.7	0.99	1.2
Accuracy	−0.45	−0.52	−0.18	1.3	0.07	1.2	−0.14	0.84

^aMatrix relative standard deviations (RSDs, 1σ) are calculated from scatter about the matrix effect trend lines, including outliers, measured between August 2004 and February 2005 (Figure 3). Consistency standard (CS) parameters are calculated from ~ 0.5 – 2 mM Ca dilutions of mother solutions S1–S4 (CS1–CS4) run as samples between February and November 2005. Means are in mmol mol^{-1} for Mg/Ca and Sr/Ca; $\mu\text{mol mol}^{-1}$ for Li/Ca, Mn/Ca, Zn/Ca, Cd/Ca, and Fe/Ca; and nmol mol^{-1} for U/Ca. CS RSDs are given as percent of means, and accuracies are percent deviations from known gravimetric values. Of 752 CS metal/Ca measurements, 7 clearly contaminated values are excluded from the above calculations: 2 Mg/Ca (CS2, CS3); 4 Zn/Ca (CS1, CS2, 2 CS3); and 1 U/Ca (CS3). If included, CS1–4 RSDs would increase to 1.9%, 7.7%, and 4.1% for these three ratios, respectively, but individual accuracies would remain below 1% except for Zn/Ca CS1, which would increase to 3.7%.

3.3. Precision, Accuracy, and Sample Size

[19] The standard data shown in Figure 3 were measured over the course of seven months, both in standard-only runs and as consistency standards within foraminiferal runs. The scatter about the matrix effect trends is therefore one measure of long-term analytical precision. Treating all dilutions of all standards S1 through S4 together, and including the 2σ outliers, analytical precisions are as follows (1σ): Li/Ca = 1.0%, Mg/Ca = 0.55%, Mn/Ca = 1.1%, Zn/Ca = 3.1%, Sr/Ca = 0.70%, Cd/Ca = 2.2%, and U/Ca = 2.0%. Perhaps a better measure of precision is based on the analysis of four gravimetric consistency standards at ~ 0.5 – 2.0 mM Ca over the subsequent ten months. If several obviously contaminated values are omitted (representing $<1\%$ of all measurements), 1σ analytical precisions are consistent with the above estimates: Li/Ca = 0.88%, Mg/Ca = 0.54%, Mn/Ca = 0.97%, Zn/Ca = 3.2%, Sr/Ca = 0.57%, Cd/Ca = 1.8%, U/Ca = 1.9%, and Fe/Ca = 1.4% (Table 2).

[20] *Rosenthal et al.* [1999] reported marginally better precisions for Mg/Ca, Mn/Ca, Sr/Ca, Cd/Ca, and U/Ca based on a single standard measured at 4 mM Ca in two runs four months apart. *Lear et al.* [2002], using *Rosenthal et al.*'s [1999] methods with the addition of a guard electrode, reported

long-term Mg/Ca precision at 3.7% for $1.10 \text{ mmol mol}^{-1}$ and 1.5% for $2.40 \text{ mmol mol}^{-1}$. *Lea et al.* [2000], using isotope dilution and a quadrupole ICP-MS, estimated long-term Mg/Ca precision at 2.1% for $1.56 \text{ mmol mol}^{-1}$. ICP-AES and ICP-OES techniques optimized for Mg/Ca and Sr/Ca have produced precisions of $<0.3\%$ [*Schrag*, 1999; *de Villiers et al.*, 2002; *Green et al.*, 2003]. *Marchitto et al.* [2002] reported AAS long-term precisions of 2–3% for Zn/Ca, 3–6% for Cd/Ca, and 8–9% for Mn/Ca.

[21] Accuracy is somewhat more difficult to assess than precision. Internal accuracy, based on the analysis of gravimetric consistency standards, assumes that stock solution compositions are perfectly known and that gravimetric standards (made from synthetic CaCO_3) exhibit the same matrix effects as natural CaCO_3 . On this basis, accuracies for consistency standards CS1–CS4 are all better than 1% except for Zn/Ca CS1 (2.2%) and CS4 (1.3%), and Cd/Ca CS4 (1.2%) (Table 2). External accuracy may be estimated through analysis of a community standard with agreed upon trace metal concentrations, preferably a solid CaCO_3 . One such standard is ECRM 752-1, a commercially available powdered limestone certified reference material [*Greaves et al.*, 2005]. Measurements on 6 separate ~ 50 mg powder aliquots of ECRM 752-1 agree with the range of values measured by

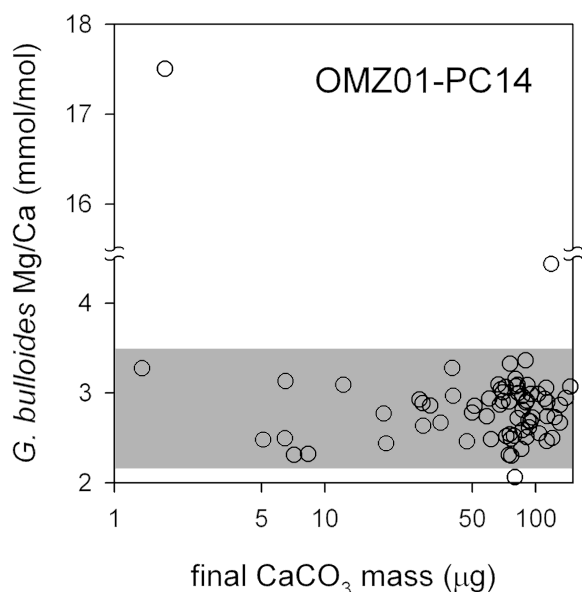


Figure 4. Mg/Ca in *G. bulloides* from Baja California margin core OMZ01-PC14, plotted versus postcleaning sample size. Gray band indicates the $\pm 2\sigma$ range of the Mg/Ca data from samples larger than 10 μg . Reproducibility of 10 sample split pairs is almost exactly the symbol size ($\pm 1\sigma$). Note the log scale of the x axis and the broken scale of the y axis.

Greaves *et al.* [2005] by ICP-AES within 1σ for Mg/Ca ($0\text{--}0.001\text{ mmol mol}^{-1}$ mean offset), Sr/Ca ($0.007\text{--}0.010\text{ mmol mol}^{-1}$ mean offset), and Fe/Ca ($5\text{--}6\text{ }\mu\text{mol mol}^{-1}$ mean offset); and within 2σ for Mn/Ca ($9\text{--}10\text{ }\mu\text{mol mol}^{-1}$ mean offset). 1σ precision on the 6 aliquots is $<1\%$ except for Fe/Ca (3.5%). ECRM 752-1 is part of an ongoing inter-laboratory calibration study, so additional assays will soon be available.

[22] Equivalent CaCO_3 masses for the various matrix effect standard dilutions are shown on the top axis of each panel in Figure 3. The most dilute standards are equivalent to just 5 μg CaCO_3 dissolved in 500 μL HNO_3 . For Mg/Ca, Mn/Ca, and Sr/Ca, there is no apparent loss of precision at such low concentrations. Li/Ca, Zn/Ca, Cd/Ca, and U/Ca may show somewhat increased scatter at or below $\sim 10\text{ }\mu\text{g}$ CaCO_3 , but values are still quite reasonable. This is believed to be the first demonstration of reliable multielemental ratios for samples smaller than 25 μg CaCO_3 .

[23] Regardless of sample size, reproducibility of foraminiferal sample splits is typically several times poorer than analytical precision, presumably due to sample heterogeneity and the combined

risks of sedimentary and laboratory contamination. Therefore although measurements on very small standards are shown to be reliable, application to very small foraminiferal samples might be impractical because of contamination. To test this possibility, samples of *Globigerinoides bulloides* (250–355 μm) from Baja California margin core OMZ01-PC14 were examined across a wide range of sample sizes. Samples consisted of between 23 and 68 individuals, with additional spread in final sizes resulting from variable loss of CaCO_3 during cleaning. Average Mg/Ca reproducibility of 10 sample split pairs was 2.8%, or about 5 times larger than analytical precision. For Mg/Ca, if one extreme outlier is excluded, there is no obvious increase in inter-sample scatter below 10 μg post-cleaning mass (Figure 4). Sr/Ca also shows only one 2σ outlier below 10 μg . Among the other elemental ratios, Zn/Ca and Mn/Ca show the greatest increase in scatter, each with four 2σ outliers below 10 μg .

[24] Reliable measurement of Mg/Ca on very small foraminiferal samples holds two potential advantages. First, as in the above experiment, samples that are initially large often lose much of their mass during the cleaning process, due to either fragile tests or human error. As long as this loss does not introduce significant bias (for example, preferential dissolution of delicate chambers formed in warm waters), samples previously considered to be lost may now be salvaged. Second, reliable analysis of single tests, both benthic and planktonic, may allow for improved understanding of variability within a population. If individual planktonic foraminifera prove to be precise recorders of water temperature, estimates of past interannual variability may be possible through discrete analyses that each represent several weeks, instead of the usual pooling of multiple individuals formed in different years.

3.4. Standard Curves and Analysis Time

[25] Relative to the methods of Rosenthal *et al.* [1999], several of the above modifications combine to markedly increase the time required for analyses, notably: the addition of Li, Zn, and Fe, and removal of Ba; the use of five-point standard curves instead of a single standard; and increased wash and uptake times. Rosenthal *et al.* [1999] noted that a run consisting of 30 samples and 3 consistency standards requires ~ 2.5 hr. Using the methods presented here, a run of 21 samples and 3 consistency standards takes ~ 6 hr. The objective

was to optimize precision given sample volumes of 500 μL , and no effort was made to minimize the analysis time. Some considerations regarding analysis time are detailed below.

[26] Considerable time may be saved by omitting some standards. Recalculation of the data in Figure 3 using two-point standard curves (S0 and S4) increases relative standard deviations by only 0.1% or less (e.g., Mg/Ca becomes 0.62%), and observations regarding small sample sizes remain valid. Five-point standard curves were employed to guard against undue influence from occasional bad standard analyses, but reproducibility of standards is generally excellent. Reducing the standard curves to two points would save ~ 1.4 hrs from a 6 hr run. Alternatively, one standard curve could be omitted, giving 12 samples between calibrations. A relatively long wash time of 2 min is used to thoroughly rinse out the spray chamber between samples and avoid memory effects, but this duration could possibly be reduced to ~ 1 min. The 2 min uptake time cannot be greatly reduced unless a shorter autosampler capillary is used, since ~ 1.5 min is required for the initial sample uptake to reach the detector and additional time is needed for the signal to plateau.

4. Conclusions

[27] Mg/Ca, Sr/Ca, Cd/Ca, Zn/Ca, Li/Ca, U/Ca, Mn/Ca, and Fe/Ca may be measured by sector field ICP-MS with long-term precisions comparable to or better than previous methods. All ratios except Sr/Ca exhibit significant linear matrix effects that are stable through time and therefore correctable. For each ratio, analytical precision is largely independent of both the magnitude of the ratio and the sample size. Reliable results may be obtained on samples smaller than 10 μg CaCO_3 , especially for Mg/Ca and Sr/Ca. These methods were not specifically optimized for very small sample sizes, so even smaller samples could theoretically be analyzed for at least a subset of elemental ratios.

Acknowledgments

[28] Thanks to J. Bauer and D. Lopez for assistance with foraminifera picking; C. Wolak for laboratory assistance; D. Lea for helpful advice; and M. Greaves, P. Martin, and an anonymous reviewer for comments that improved this manuscript. This work was supported by Marchitto's startup funds at INSTAAR and by NSF grants OCE-0214221, OCE-0221979, and OCE-0425522.

References

- Barker, S., M. Greaves, and H. Elderfield (2003), A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry, *Geochem. Geophys. Geosyst.*, 4(9), 8407, doi:10.1029/2003GC000559.
- Boyle, E. A. (1983), Manganese carbonate overgrowths on foraminifera tests, *Geochim. Cosmochim. Acta*, 47, 1815–1819.
- Boyle, E. A., and L. D. Keigwin (1982), Deep circulation of the North Atlantic over the last 200,000 years: Geochemical evidence, *Science*, 218, 784–787.
- Boyle, E. A., and L. D. Keigwin (1985/1986), Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: Changes in deep ocean circulation and chemical inventories, *Earth Planet. Sci. Lett.*, 76, 135–150.
- 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 et al., pp. 423–443, Springer, New York.
- de Villiers, S., M. Greaves, and H. Elderfield (2002), An intensity ratio calibration method for the accurate determination of Mg/Ca and Sr/Ca of marine carbonates by ICP-AES, *Geochem. Geophys. Geosyst.*, 3(1), 1001, doi:10.1029/2001GC000169.
- Elderfield, H., M. Cooper, and G. Ganssen (2000), Sr/Ca in multiple species of planktonic foraminifera: Implications for reconstructions of seawater Sr/Ca, *Geochem. Geophys. Geosyst.*, 1(11), doi:10.1029/1999GC000031.
- Greaves, M., S. Barker, C. Daunt, and H. Elderfield (2005), Accuracy, standardization, and interlaboratory calibration standards for foraminiferal Mg/Ca thermometry, *Geochem. Geophys. Geosyst.*, 6, Q02D13, doi:10.1029/2004GC000790.
- Green, D. R. H., M. J. Cooper, C. R. German, and P. A. Wilson (2003), Optimization of an inductively coupled plasma–optical emission spectrometry method for the rapid determination of high-precision Mg/Ca and Sr/Ca in foraminiferal calcite, *Geochem. Geophys. Geosyst.*, 4(6), 8404, doi:10.1029/2002GC000488.
- Hall, J. M., and L.-H. Chan (2004), Li/Ca in multiple species of benthic and planktonic foraminifera: Thermocline, latitudinal, and glacial-interglacial variation, *Geochim. Cosmochim. Acta*, 68, 529–545.
- Lea, D. W., and P. A. Martin (1996), A rapid mass spectrometric method for the simultaneous analysis of barium, cadmium, and strontium in foraminifera shells, *Geochim. Cosmochim. Acta*, 60, 3143–3149.
- Lea, D. W., D. K. Pak, and H. J. Spero (2000), Climate impact of Late Quaternary equatorial Pacific sea surface temperature variations, *Science*, 289, 1719–1724.
- Lear, C. H., Y. Rosenthal, and N. Slowey (2002), Benthic foraminiferal Mg/Ca-paleothermometry: A revised core-top calibration, *Geochim. Cosmochim. Acta*, 66, 3375–3387.
- Marchitto, T. M., W. B. Curry, and D. W. Oppo (2000), Zinc concentrations in benthic foraminifera reflect seawater chemistry, *Paleoceanography*, 15, 299–306.
- Marchitto, T. M., Jr., D. W. Oppo, and W. B. Curry (2002), Paired benthic foraminiferal Cd/Ca and Zn/Ca evidence for a greatly increased presence of Southern Ocean Water in the glacial North Atlantic, *Paleoceanography*, 17(3), 1038, doi:10.1029/2000PA000598.

- Martin, P. A., D. W. Lea, T. A. Mashiotta, T. Papenfuss, and M. Sarnthein (1999), Variation of foraminiferal Sr/Ca over Quaternary glacial-interglacial cycles: evidence for changes in mean ocean Sr/Ca?, *Geochim. Geophys. Geosyst.*, *1*(1), doi:10.1029/1999GC000006.
- 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 Planet. Sci. Lett.*, *198*, 193–209.
- Nurnberg, D., J. Bijma, and C. Hemleben (1996), Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures, *Geochim. 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 foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography, *Geochim. Cosmochim. Acta*, *61*, 3633–3643.
- Rosenthal, Y., M. P. Field, and R. M. Sherrell (1999), Precise determination of element/calcium ratios in calcareous samples using sector field inductively coupled plasma mass spectrometry, *Anal. Chem.*, *71*, 3248–3253.
- Russell, A. D., B. Honisch, H. J. Spero, and D. W. Lea (2004), Effects of seawater carbonate ion concentration and temperature on shell U, Mg, and Sr in cultured planktonic foraminifera, *Geochim. Cosmochim. Acta*, *68*, 4347–4361.
- Schrag, D. P. (1999), Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates, *Paleoceanography*, *14*, 97–102.