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## **Fidelity of radially viewed ICP-OES and magnetic-sector ICP-MS measurement of Mg/Ca and Sr/Ca ratios in marine biogenic carbonates: Are they trustworthy together?**

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[1] Improving interlaboratory reproducibility (in both precision and accuracy) of Mg/Ca and Sr/Ca determination in marine biogenic carbonates is critical in optimizing their utility as paleothermometers. Coupled with a need for uniform sample cleaning practices, there is a need for more exacting methods and procedures across laboratories using varied instrumentation. Here we employ an intensity ratio/matrix-effect correction methodology to a suite of solution standards and biogenic carbonates (foraminifera tests and a gastropod shell) to investigate short-term and long-term Mg/Ca and Sr/Ca precision and accuracy by different instruments: a magnetic-sector inductively coupled plasma-mass spectrometer (ICP-MS) and a radially viewed inductively coupled plasma-optical emission spectrophotometer (ICP-OES). Over an extended 1.0–24.5 mM Ca concentration range, both instruments have significant Ca matrix effects for Mg/Ca and somewhat less for Sr/Ca. Over our working Ca range (1–8 mM Ca), Mg/Ca matrix effects are significant, requiring correction, and Sr/Ca matrix effects are small to negligible, occasionally requiring correction (linear or logarithmic fit) using a suite of matrix standards for both instruments. The short-term (intran) precision for a suite of solution standards is <0.2% (1 $\sigma$  %RSD) for Mg/Ca and Sr/Ca for both instruments. A long-term (interrun) precision of <0.9% is demonstrated for Mg/Ca and <0.6% for Sr/Ca on both instruments. The accuracy of measured Mg/Ca and Sr/Ca values for short- and long-term standards is similar on both instruments at better than  $1 \pm 0.5\%$ , on par with our long-term precision. An interinstrument comparison of the same measured suite of biogenic carbonates demonstrates that after accounting for matrix effects, data generated on either instrument are essentially interchangeable (within analytical precision) to a high degree of fidelity.

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**Theme:** Developmental of the Foraminiferal Mg/Ca Proxy for Paleoceanography

**Guest Editor:** Pamela Martin

## 1. Introduction

[2] Estimating paleo-sea surface temperature (SST) is a vital component to understanding mechanisms of paleoceanographic variability [*Climate: Long-Range Investigation Mapping Prediction (CLIMAP) Project Members*, 1976, 1981; *Herbert et al.*, 2001; *Lea et al.*, 2000, 2003]. Over the past decade, researchers have increasingly recognized that minor element constituents, Mg/Ca in foraminifera calcite [*Nürnberg et al.*, 1996; *Rosenthal et al.*, 1997; *Hastings et al.*, 1998; *Elderfield and Ganssen*, 2000], and Sr/Ca in aragonitic corals [*Beck et al.*, 1992; *Guilderson et al.*, 1994], are sensitive to ambient ocean temperatures. Furthermore, paired measurement of Mg/Ca and  $\delta^{18}\text{O}$  in foraminifera tests allows for partitioning of the temperature component of foraminifera  $\delta^{18}\text{O}$  leaving a residual seawater  $\delta^{18}\text{O}$  signal [*Mashiotta et al.*, 1999; *Lea et al.*, 2000; *Rosenthal et al.*, 2003]. Likewise, knowledge of seawater Sr/Ca, measured in planktonic foraminifera, may help in partitioning whole ocean Sr/Ca changes from temperature effects in corals [*Martin and Lea*, 1999; *Stoll and Schrag*, 2000]. These promising advances have precipitated widespread use of foraminiferal Mg/Ca and coral Sr/Ca paleothermometry in climate study [*Guilderson et al.*, 1994; *Lea et al.*, 2000].

[3] Several analytical advances have enhanced the ability of the scientific community to rapidly and simultaneously generate precise and accurate data of Ca and minor to trace chemical constituents in marine biogenic carbonates whose concentrations range many orders of magnitude [*Lea and Martin*, 1996; *Rosenthal et al.*, 1999; *Schrag*, 1999]. Attendant to the growing paleoceanographic utility of

these geochemical data, is a need to examine intralaboratory and interlaboratory integrity, with respect to both methodology and instrumentation [*Rosenthal et al.*, 2004].

[4] Among several instruments capable of measuring minor-element to calcium ratios in marine biogenic carbonates, either inductively coupled plasma–mass spectrometry (ICP-MS) or inductively coupled plasma–optical emission spectrophotometry (ICP-OES) is used in most cases [*Rosenthal et al.*, 2004]. Magnetic sector ICP-MS offers a versatile combination of very high sensitivity simultaneously across a wide isotopic range. ICP-MS is mainly used by researchers who are also measuring trace metals in foraminifera (e.g., Cd/Ca and Zn/Ca) and need its very high resolution and sensitivity. However, because of their relative economy, streamlined operation, and relative ease of use, less sensitive ICP-OES instruments have gained favor for routine minor element analysis of marine biogenic carbonates.

[5] As the application of Mg/Ca-thermometry in paleoceanographic studies broadens, questions about interlaboratory consistency become critical. Some of the issues associated with interlaboratory consistency in minor elemental analyses of carbonate samples may be related to differences in the precision and accuracy among the various instruments used for these measurements. In this paper, we assess the potential sources of interinstrumental variability and quantify their magnitude. We also examine the contribution of matrix effect corrections, specific to each instrument, to the inaccuracies of measurements generated by both instruments. The results show interinstrument accuracy of about 1.0%, which is not significantly

different than the long-term precision of each individual instrument supporting the argument of *Rosenthal et al.* [2004] that the choice of instrument is a not a critical factor in the accuracy of Mg/Ca-based sea surface temperature reconstructions. Although the study of *Rosenthal et al.* [2004] has shown similar short term precision of the different instruments, to date there is no study that compares the results of Mg/Ca and Sr/Ca analyses on the same samples and solutions under identical experimental conditions.

## 2. Methods

### 2.1. Instrumentation

[6] We compare measurement characteristics and fidelity of two instruments that use inductively coupled plasma (ICP) technology to ionize a solution containing minor element chemical constituents, Mg and Sr, within a Ca matrix. In mass spectrometry, plasma generated ions are accelerated, mass separated via Lorentz forces, and relative intensities are counted in a detector. In OES, spectral intensities of atomic and ionic constituents emitted from within the plasma are measured optically. Both approaches share complexities associated with plasma optimization and unique instrument specific complexities. Another major difference between our two instruments that may affect the precision is the mode of data acquisition: our ICP-MS is a sequential instrument, whereas the ICP-OES is a simultaneous instrument.

#### 2.1.1. ICP-MS

[7] Many of the salient issues and parameters of the Finnigan MAT Element magnetic sector field ICP-MS operation have been documented [*Rosenthal et al.*, 1999]. However, since then, Element instruments have been fitted with a “guard electrode,” a platinum shield inserted between the load coil and the torch, that substantially improves detection limits. Torch shielding allows operation under “cold plasma” conditions (reduced forward RF power) as well as under typical hot plasma conditions. Sensitivity improves by an order of magnitude (1 to 2 million ions per second for 1ppb Indium solution). A cost of adding the guard electrode is a significant increase in matrix-induced mass-dependent discrimination for the Mg/Ca [*Lear et al.*, 2002] and Sr/Ca (this study). As we show below, however, a similar precision to that obtained by *Rosenthal et al.* [1999], can be

achieved with the guard electrode, provided proper matrix corrections are implemented.

#### 2.1.2. ICP-OES

[8] In May, 2003 a new Vista-Pro CCD simultaneous radially viewed inductively coupled plasma–optical emission spectrophotometer (ICP-OES, Varian, Inc; <http://www.varianinc.com>) was installed in the inorganic geochemistry laboratory at Rutgers University. Ease of use for routine high-volume minor element analysis of the ICP-OES instrument were chosen to augment the existing laboratory ICP-MS. Furthermore, ICP-OES instruments in radial configuration was anticipated to have minor matrix effects specifically for easily ionized elements [*Brenner and Zander*, 2000].

### 2.2. Solutions and Standards

[9] Solutions were prepared from distilled deionized water (ddH<sub>2</sub>O) and ultrapure 16N HNO<sub>3</sub> (SEASTAR<sup>®</sup>). All plasticware used for sample handling was leached in 1N HCl (reagent grade in ddH<sub>2</sub>O) at 60°C for 12 hrs, then rinsed thoroughly (5x) with ddH<sub>2</sub>O. Primary standards (1000 ± 3 μg mL<sup>-1</sup> in 3% HNO<sub>3</sub> V/V; HIGH-PURITY<sup>®</sup> Standards, Charleston, SC) were used to prepare multi-elemental stock standard mixtures by gravimetrically spiking 500 mL of 1000 μg mL<sup>-1</sup> Ca standard with appropriate concentrations of Mg, Sr and Mn to match the typical elemental composition of foraminiferal shells. Cross contamination was negligible for all the mono-elemental standards except calcium. Therefore we used the standard additions method to quantify Mg and Sr concentrations in the primary calcium standard and included these small contributions in the calculation of the multi-element standard concentrations. In addition, we prepared three primary consistency standards (CS1, CS2, CS3) with identical calcium matrix but different element-to-calcium ratios, in the range typical of foraminiferal samples. Working standards were made by diluting the stock standard solution to 2-7 mM calcium concentration to match the average sample calcium concentration. An aliquot of this primary spiked solution was additionally spiked with Al, Ti, and Fe in appropriate concentrations and is used to monitor for sample contamination due to refractory residues or insufficient sample cleaning.

### 2.3. Sample Preparation

[10] Real sample analyses included same sample measurement of two different marine biogenic

carbonate bearing organisms: foraminifera and gastropoda. For foraminifera, we used mixed layer dwelling spinose species *Globogerinoides sacculifer* samples from the Sulu Sea that span the last glacial-to-interglacial transition (Termination I). For gastropoda, we used powders drilled from an aragonitic shell of species *Conus ermineus* collected from the seafloor at 20–30 m depth in the Flower Garden Banks National Marine Sanctuary on the U.S. Gulf Coast [Sosdian *et al.*, 2006]. Foraminifera samples contained 5–10 individual shells totaling 100 to 200  $\mu\text{g}$  prepared for analysis following the procedure outlined by Barker *et al.* [2003]. To prevent any contamination in the laboratory after cleaning, all sample handling was performed in a HEPA class 100 laminar flow hood. The gastropod shell was cleaned and polished with medium sandpaper prior to drilling to remove the periostracum, surface contamination, and encrusting organisms. We milled linear sample grooves parallel to growth banding using a 0.3 mm Brasseler carbide drill bit to obtain  $>200 \mu\text{g}$  of carbonate powder. Both cleaned foraminiferal shells and gastropod powders were progressively dissolved in trace metal clean 0.065N  $\text{HNO}_3$  (OPTIMA<sup>®</sup>). After 10 minutes centrifugation to remove any remaining clays, 100  $\mu\text{l}$  of the supernatant solution was diluted with 300  $\mu\text{l}$  trace 1 trace metal clean 0.5N  $\text{HNO}_3$  to obtain a Ca concentration of  $4 \pm 1 \text{ mmol L}^{-1}$ . This progressive dissolution procedure assures that the sample solution Ca concentration range will not vary by much and will be close to that of the standard in order to minimize matrix effects (see below). Our preferred Ca concentration of  $4 \pm 1 \text{ mmol L}^{-1}$  is significantly higher than reported by other ICP-OES users [Green *et al.*, 2003; Wara *et al.*, 2003]. While higher concentration enhances Ca matrix effects, it improves the signal to noise ratio and thus reduces the effects of potential interferences and contaminants. We think that the latter is more important since it is easier to correct for Ca matrix effects (as shown below) than for interferences or contamination.

## 2.4. Methodology

[11] Elemental ratios were determined directly from the intensity ratios following the method outlined by Rosenthal *et al.* [1999] for the ICP-MS, and modified here for application to ICP-OES operation. In both instruments, samples were introduced into the plasma using a CETAC ASX-100 autosampler in free aspiration mode to

minimize noise introduced by the peristaltic pump. We used a PFA microflow 100 (nominal 100  $\mu\text{l}/\text{min}$ ) nebulizer (Elemental Scientific, Inc, Omaha, Nebraska).

### 2.4.1. ICP-MS

[12] Samples were analyzed by Finnigan MAT Element Sector Field inductively coupled plasma–mass spectrometer (ICP-MS) operated in low resolution ( $m/\Delta m = 300$ ). All isotopes were measured in analog detection mode, except Fe, which was monitored in medium-resolution pulse counting mode.  $^{43}\text{Ca}$ ,  $^{48}\text{Ca}$ ,  $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$ ,  $^{87}\text{Sr}$ , and  $^{88}\text{Sr}$  are the major isotopes in biogenic carbonate monitored during each sample ICP-MS analysis. In addition,  $^{55}\text{Mn}$ ,  $^{56}\text{Fe}$ ,  $^{47}\text{Ti}$ , and  $^{27}\text{Al}$  isotopes were also measured to monitor authigenic oxides overgrowth and clay mineral contamination and to check for consistent sample batch cleaning [e.g., Boyle, 1983]. We prefer using the  $^{25}\text{Mg}/^{43}\text{Ca}$  ratio, instead of  $^{24}\text{Mg}/^{43}\text{Ca}$  ratio, because doubly charged  $^{48}\text{Ca}$  ions superimpose upon the  $^{24}\text{Mg}$  measured intensities resulting in a tendency toward relatively higher  $^{24}\text{Mg}/^{43}\text{Ca}$  compared to  $^{25}\text{Mg}/^{43}\text{Ca}$ . However, we use  $^{24}\text{Mg}/^{43}\text{Ca}$  to  $^{25}\text{Mg}/^{43}\text{Ca}$  differences as an indicator for plasma stability and its effects on Mg/Ca measurements. Experience has shown  $^{88}\text{Sr}/^{43}\text{Ca}$  to have smaller matrix effects and give better precision on standards than  $^{87}\text{Sr}/^{43}\text{Ca}$ , hence we report data using the  $^{88}\text{Sr}/^{43}\text{Ca}$  ratio. Doubly ionized  $^{87}\text{Sr}^{++}$  is used to monitor the production of  $^{86}\text{Sr}^{++}$  and its isobaric interference on  $^{43}\text{Ca}$ .

### 2.4.2. ICP-OES

[13] The analytical method for measuring Mg/Ca and Sr/Ca is based on the method outlined by Rosenthal *et al.* [1999] and adapted for use on our ICP-OES. Optimum operating conditions for parameters (gas flow rates within the plasma, plasma viewing height, and RF power) for Mg/Ca and Sr/Ca reproducibility were set after extended tests. Operating conditions and preferred emission lines for the ICP-OES were established primarily on the basis of two criteria: (1) plasma robustness (evaluated as a measure of the Mg ionic/atomic ratio  $\text{MgII}_{280.270 \text{ nm}}/\text{MgI}_{285.213 \text{ nm}}$ ) [Brenner and Zander, 2000] and (2) the reproducibility of the matrix effects, which is important for correction. On the basis of our tests we use RF Power of 1.3–1.5kW, nebulizer gas flow rate of 0.75–0.85 L/min, and viewing height of  $10 \pm 1 \text{ mm}$ . The preferred emission lines and Element/Ca ratios are  $\text{Mg}_{280}/\text{Ca}_{315}$  and  $\text{Sr}_{407}/\text{Ca}_{318}$ .

**Table 1.** Summary Statistics Intercomparing ICP-MS and ICP-OES Short-Term Precision Within a Single Analytical Run<sup>a</sup>

Standard	ICP-MS			ICP-OES				
	$R_{43Ca}$ $\left(\frac{I_{sample}}{I_{standard}}\right)$	$\frac{^{25}Mg}{^{43}Ca}$ $\left(\frac{mmol}{mol}\right)$	$\frac{^{88}Sr}{^{43}Ca}$ $\left(\frac{mmol}{mol}\right)$	$RCa_{315}$ $\left(\frac{I_{sample}}{I_{standard}}\right)$	$\frac{Mg_{280}}{Ca_{315}}$ $\left(\frac{mmol}{mol}\right)$	$\frac{Sr_{407}}{Ca_{315}}$ $\left(\frac{mmol}{mol}\right)$	$RCa_{318}$ $\left(\frac{I_{sample}}{I_{standard}}\right)$	$\frac{Sr_{407}}{Ca_{318}}$ $\left(\frac{mmol}{mol}\right)$
CS1								
Expected		1.246	0.459		1.246	0.459		0.459
Mean	0.997	1.239	0.455	1.000	1.231	0.459	1.000	0.459
±1s	0.005	0.001	0.001	0.001	0.002	0.000	0.004	0.000
%RSD	0.95%	0.11%	0.17%	0.45%	0.14%	0.06%	0.42%	0.09%
Δ(meas-exp) %		-0.59%	-0.89%		-1.18%	0.02%		-0.05%
CS2								
Expected		3.318	0.918		3.318	0.918		0.918
Mean	0.992	3.304	0.900	0.997	3.312	0.900	0.997	0.900
±1s	0.003	0.004	0.001	0.004	0.005	0.001	0.004	0.000
%RSD	1.20%	0.13%	0.09%	0.31%	0.14%	0.12%	0.27%	0.04%
Δ(meas-exp) %		-0.43%	-1.94%		-0.19%	-1.99%		-1.98%
CS3								
Expected		7.504	1.843		7.504	1.843		1.843
Mean	0.994	7.457	1.790	0.984	7.507	1.797	0.983	1.798
±1s	0.008	0.008	0.003	0.008	0.007	0.001	0.004	0.001
%RSD	0.91%	0.10%	0.18%	0.77%	0.09%	0.07%	0.81%	0.08%
Δ(meas-exp) %		-0.63%	-2.89%		0.03%	-2.50%		-2.41%
S1								
Expected		1.856	1.011		1.856	1.011		1.011
Mean	0.963	1.827	0.998	0.962	1.818	0.995	0.96	0.996
±1s	0.005	0.004	0.002	0.005	0.003	0.001	0.005	0.000
%RSD	0.93%	0.24%	0.22%	0.54%	0.16%	0.08%	0.50%	0.04%
Δ(meas-exp) %		-1.59%	-1.26%		-2.06%	-1.54%		-1.45%
S2								
Expected	3.682	2.025		3.682	2.025		2.025	
Mean	0.987	3.600	1.973	0.967	3.619	1.978	0.967	1.978
±1s	0.009	0.007	0.006	0.007	0.010	0.002	0.009	0.002
%RSD	1.84%	0.19%	0.31%	0.90%	0.27%	0.10%	0.97%	0.12%
Δ(meas-exp) %		-2.24%	-2.57%		-1.72%	-2.32%		-2.31%

<sup>a</sup> Mean values are from ten consecutive determinations of each standard. RCa is calculated as the ratio between the sample and standard intensities.

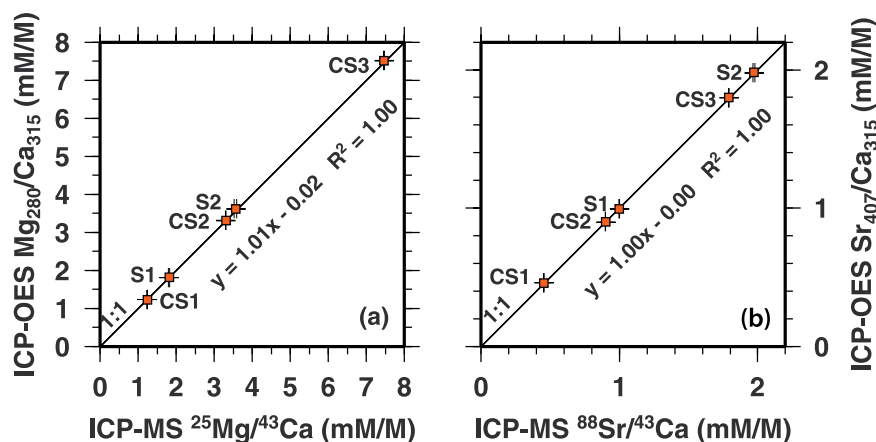
[14] Supporting data for all data and figures presented herein are available from the authors upon request.

### 3. Results

#### 3.1. Short-Term Precision and Internal Accuracy

[15] Short-term precision of both instruments measuring five different standard solutions over a wide range of Mg/Ca ratios was excellent, about <0.2%RSD or better for both instruments (Table 1). For Sr/Ca, ICP-OES precision was 0.1%RSD or better, and the ICP-MS precision was 0.2%RSD or better (Table 1). Interinstrument consistency in the measured values of the same standard was gener-

ally <1% for Mg/Ca and <0.6% for Sr/Ca (derived from Table 1, Figure 1). The Mg/Ca and Sr/Ca precisions and between-instrument consistency are within the range of, or even better than, the results reported for community wide inter laboratory comparison study [Rosenthal et al., 2004]. Rosenthal et al. [1999] reported Mg/Ca and Sr/Ca precision of 0.45% when using a multi-ratio method (6 elemental ratios) and a Sr/Ca precision of 0.06% (1σ) when acquired in a single elemental ratio mode using the same ICP-MS instrument as used here but without a guard electrode (measured on solutions with similar elemental concentrations to those used in this study). The difference reflects the fact that the Element 1 is a single collector instrument, which acquires data in a sequential mode. As a result, the larger the number of elemental ratios acquired in



**Figure 1.** Short-term intercomparison of internal consistency standards (CS1, CS2, CS3) and interlaboratory intercalibration standard (S1, S2) [Rosenthal *et al.*, 2004] as measured by the ICP-MS and ICP-OES (mean and standard deviation results from Table 1). (a) Mg/Ca ICP-MS/ICP-OES instrument intercomparison and (b) same for Sr/Ca intercomparison.

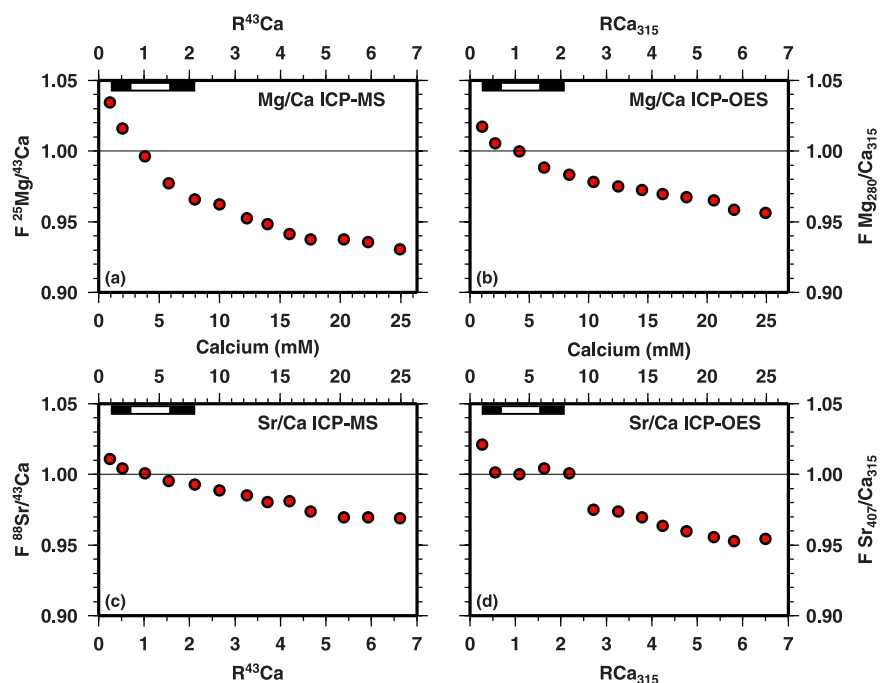
each analysis the worse the precision gets due to the decreased ratio between time required to cycle the magnet and time spent acquiring data [Rosenthal *et al.*, 1999]. In this study we measured only three elemental ratios, and hence the precision on the ICP-MS is slightly better than that reported in multi-element mode in 1999. As our ICP-OES acquires data simultaneously, the number of measured elemental ratios is not an issue. As pointed out above, comparing our low concentration Sr/Ca precision, on both instruments, with precision for analysis of higher concentration coral is somewhat misleading because magnitude of %RSD is also dependent on the Sr concentration of the sample. Because Sr/Ca in coral aragonite are about eight times higher than in foraminifera, in principle, significantly better short-term precision for coral Sr/Ca analysis than presented herein might be achievable.

[16] Measured Mg/Ca ratios were accurate relative to the gravimetrically determined ratios within 1% or better for the internal standards (CS1–CS3). For both instruments measured standard ratios (S1 and S2) used in the study of Rosenthal *et al.* [2004] were low by 1.5–3.3% relative to the gravimetric ratios and the mean value determination by multiple laboratories [Rosenthal *et al.*, 2004]. This maximum offset from expected Mg/Ca values translates into a temperature offset of 0.2°C (using the paleotemperature equation of Anand *et al.* [2003]). Measured Sr/Ca standard ratios were lower than expected in the standard solution (gravimetric) ratios by up to 2.6%; however, interinstrument offsets in measured values of the same standard agree within 1% (derived from Table 1, Figure 1b). The overall consistency (<1%) between

the two instruments, both for Mg/Ca and Sr/Ca measurements, suggests that the offsets from the expected values is probably due to our limitation in accurately determining the gravimetric values. Thus we conclude that our accuracy is likely better than 1%.

### 3.2. Calcium Interference: Matrix Effects

[17] Intraplasma interferences between Ca cations and minor elements are a common concern when operating ICP interfaced instruments. This issue is not a major concern when applying an isotope dilution technique for determining the elemental ratios [Lea and Martin, 1996]. Whereas isotope dilution is a good solution for the matrix effect problem for ICP-MS, albeit not a cheap one, it is not applicable for optical instruments. Thus a variety of strategies have been employed to address these effects. For some instruments Ca matrix interferences on measured minor element intensities are small enough that they do not require correction [Wara *et al.*, 2003]. However, where Ca matrix interferences are nonnegligible, mitigating approaches include careful weighing or pre-screening samples prior to dilution in order to run in a narrow Ca concentration range [Koutavas *et al.*, 2002; Green *et al.*, 2003] and a variety of standardization techniques to minimize or characterize and correct for Ca matrix effects [e.g., Rosenthal *et al.*, 1999; Schrag, 1999; de Villiers *et al.*, 2002]. Our method combines both approaches. First, as mentioned above, we constrain the Ca concentrations of our samples to within a narrow range from that of the standard. Additionally, for each batch run we characterize a



**Figure 2.** Normalized minor element (Mg, Sr)/Ca ratios ( $F$ , relative to gravimetric values nominally at 4 mM Ca) over a range of calcium concentrations (1–24.5 mM Ca). Data are also presented on a normalized Ca concentration scale ( $R$ , relative to 4 mM Ca). Black bars at the top of each plot mark the operational range of internal laboratory “matrix” standards incorporated into each analytical run, with the internal white bar marking the typical (target) range of sample Ca concentrations. (a) ICP-MS Mg/Ca, (b) ICP-OES Mg/Ca, (c) ICP-MS Sr/Ca, and (d) ICP-OES Sr/Ca.

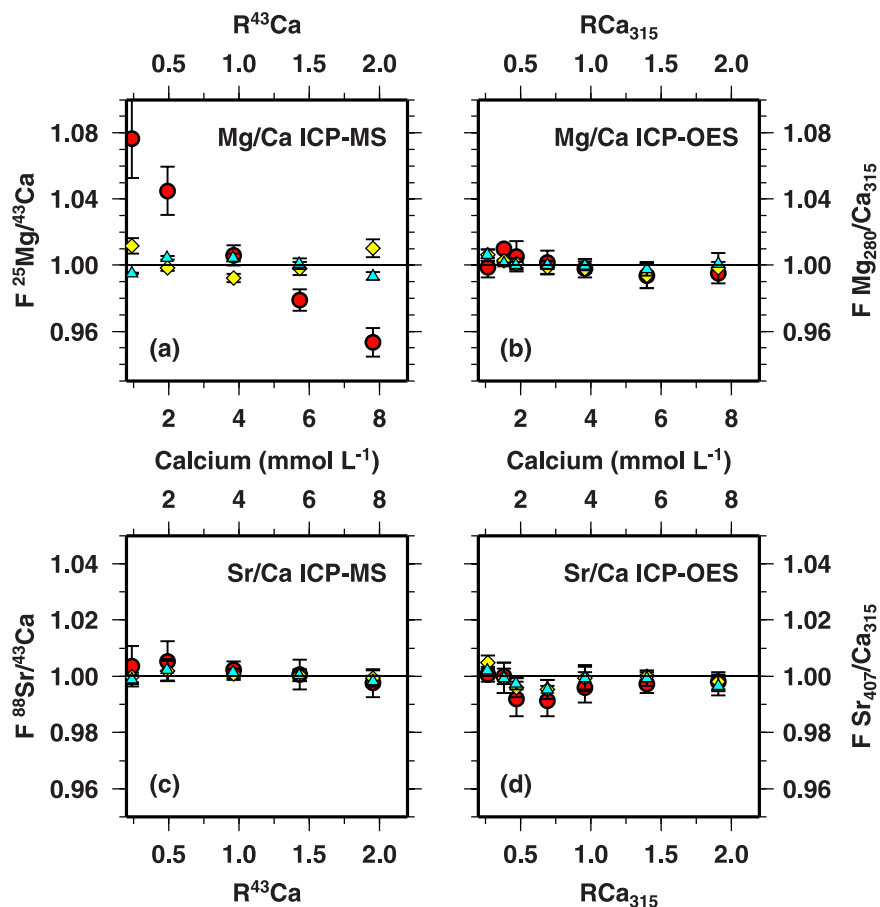
suite of standard solutions having a range of Ca concentrations that exceed the sample range. Samples are then corrected for any significant Ca concentration bias. Note, however, that an improvement has been made in our matrix mass discrimination correction methodology. Previously, a quadratic correction was made from a fit of the measured Mg/Ca and the Ca intensity difference between standards having a range of calcium concentrations (typically 1–8 mmol L<sup>-1</sup> relative to the 4 mmol L<sup>-1</sup> standard (denoted  $\Delta\text{Ca}$ )). Further analysis indicated  $\Delta\text{Ca}$  was not unique, and varied with instrument sensitivity. For example, a 20% change in Ca sensitivity could lead to a change as large as 0.3% in the matrix corrected Mg/Ca value, under typical operating conditions. If needed, we may now apply either a linear or logarithmic matrix correction calculated from a fit of the measured Ca intensity ratio relative to a 4 mmol L<sup>-1</sup> Ca standard solution (denoted  $R^{43}\text{Ca} = (I_{\text{sample}}/I_{\text{standard}})$ , where  $I$  is intensity per second). This  $R^{43}\text{Ca}$  normalization is insensitive to day-to-day changes in ICP-MS Ca sensitivity.

[18] For Mg/Ca, Ca matrix effects are appreciable for both ICP-MS, and to a lesser extent, for ICP-OES instruments used in this study (Figures 2a and 2b).

To test for instrument mass dependence across a wide Ca concentration range (1.0–24.6 mM) we prepared a suite of thirteen dilutions of our in-house laboratory spike gravimetric standard (SGS, 24.6 mM Ca). For the ICP-MS, Mg/Ca values range by nearly 8% between 1–10 mM Ca, and about 3% between 10–24 mM Ca. For ICP-OES, the Mg/Ca range was significantly smaller, with values varying less than 4% between 1–10 mM Ca, and about 2% from 10–24 mM Ca. A larger range for the ICP-MS is attributed to the guard electrode, as mentioned earlier. For Sr/Ca, Ca matrix effects are appreciable for both ICP-MS and ICP-OES instruments used in this study (Figures 2c and 2d). Over the full Ca range (1–24.6 mM), ICP-MS Sr/Ca varied by 4% and ICP-OES varied by 7%.

[19] The matrix described above covers a large range of Ca concentrations. However, when analyzing real samples we match the Ca concentrations of the samples and standard to less than factor of two. The Ca content of our standard is 4 mM, whereas sample Ca concentrations vary between 2 and 6 mM. The Ca matrix effects on Mg/Ca and Sr/Ca ratios, are significantly smaller within this limited range (Figure 3). Within this range, the day-to-day Mg/Ca matrix effects generally are





**Figure 3.** Normalized minor elemental (Mg,Sr)/Ca ratios ( $F$ , relative to gravimetric values nominally at 4 mM Ca) over a narrow working range of Ca concentrations. Data are also presented on a normalized Ca concentration scale ( $R$ , relative to 4 mM Ca). A suite of five dilutions of our laboratory spiked gravimetric standard (SGS) were run. These had Ca concentrations which exceed the sample Ca concentration range, typically by a factor of two. Individual data points (red circles) reflect the mean and standard deviation ( $\pm 1\sigma$ ) of matrix standards from multiple runs ( $N = 7$  for the ICP-OES and  $N = 9$  for the ICP-MS). In practice, intrarun matrix corrections were derived from either a linear or logarithmic regression of normalized elemental ratios relative to the calcium intensity ratio ( $RCa$ ) relative to the 4 mmol L<sup>-1</sup> Ca SGS standard intensity. Yellow diamonds and green triangles reflect the mean and standard deviation of corrected matrix standards for linear and logarithmic corrections, respectively. (a) ICP-MS Mg/Ca, (b) ICP-OES Mg/Ca, (c) ICP-MS Sr/Ca, and (d) ICP-OES Sr/Ca.

more pronounced for the ICP-MS, and less so for ICP-OES (Figures 3a and 3b). Matrix effects on Sr/Ca ratios are very small on both instruments and often do not require any correction (Figures 3c and 3d).

[20] For the ICP-OES,  $Sr_{407}/Ca_{315}$  and  $Sr_{407}/Ca_{318}$  (not shown) exhibit a perplexing response as a function of Ca concentration (e.g., Figure 2d). For a suite of five matrix standards over a Ca concentration range, our experience is often that one Sr/Ca determination does not vary smoothly with the other four, and hence is “erratic.” To test whether this effect was specific to our particular instrument or endemic to this ICP-OES model in general, we had the same batch of standard solutions (13 stand-

ards between 1–24.5 mmol Ca) analyzed on an identical instrument in a different laboratory. Both instruments exhibited the same effect, suggesting that some physical limitation of the torch/plasma/detector system has been reached. Extensive tests have yet to isolate the component of the system driving this erratic behavior. Practically speaking, for ICP-OES within the range of our sample Ca concentrations, Ca matrix effects on Sr/Ca ratios are quite small, 0.35% or better, as suggested from the long term RSD precision (Table 2).

[21] By characterizing day-to-day instrumental changes in Ca matrix effects, sample values may be adjusted for instrument performance. Typically, Mg/Ca shows appreciable effects (Figures 3a

**Table 2.** Effect of Solution Ca Concentration on Mg/Ca and Sr/Ca Over the Long Term From Seven ICP-OES Runs<sup>a</sup>

Date	$\frac{Mg_{280}}{Ca_{315}}$			$\frac{Sr_{407}}{Ca_{315}}$			$\frac{Sr_{407}}{Ca_{318}}$		
	uncorr	corr-lin	corr-log	uncorr	corr-lin	corr-log	uncorr	corr-lin	corr-log
10/22/03									
Expected	5.405	5.405	5.405	1.483	1.483	1.483	1.483	1.483	1.483
Mean	5.422	5.410	5.408	1.473	1.481	1.479	1.482	1.484	1.484
±1s	0.058	0.024	0.013	0.009	0.009	0.007	0.003	0.003	0.003
%RSD	1.06%	0.44%	0.24%	0.60%	0.60%	0.46%	0.23%	0.23%	0.23%
Δ(meas-exp) %	0.32%	0.09%	0.05%	-0.67%	-0.16%	-0.25%	-0.05%	0.04%	0.04%
10/22/03									
Expected	5.405	5.405	5.405	1.483	1.483	1.483	1.483	1.483	1.483
Mean	5.420	5.408	5.407	1.475	1.479	1.480	1.482	1.483	1.483
±1s	0.035	0.015	0.014	0.010	0.006	0.004	0.003	0.003	0.003
%RSD	0.64%	0.28%	0.27%	0.71%	0.38%	0.30%	0.23%	0.23%	0.23%
Δ(meas-exp) %	0.28%	0.06%	0.04%	-0.55%	-0.25%	-0.22%	-0.05%	0.01%	0.01%
12/15/03									
Expected	5.405	5.405	5.405	1.483	1.483	1.483	1.483	1.483	1.483
Mean	5.417	5.347	5.407	1.469	1.478	1.479	1.481	1.483	1.483
±1s	0.034	0.033	0.014	0.005	0.002	0.003	0.006	0.006	0.006
%RSD	0.62%	0.62%	0.26%	0.37%	0.15%	0.19%	0.42%	0.42%	0.42%
Δ(meas-exp) %	0.22%	-1.07%	0.03%	-0.97%	-0.31%	-0.30%	-0.15%	-0.02%	-0.02%
12/15/03									
Expected	5.405	5.405	5.405	1.483	1.483	1.483	1.483	1.483	1.483
Mean	5.421	5.407	5.406	1.484	1.481	1.481	1.488	1.488	1.489
±1s	0.023	0.007	0.003	0.002	0.002	0.002	0.008	0.008	0.009
%RSD	0.42%	0.13%	0.06%	0.15%	0.15%	0.15%	0.52%	0.52%	0.59%
Δ(meas-exp) %	0.29%	0.04%	0.02%	0.05%	-0.16%	-0.16%	0.37%	0.37%	0.38%
12/16/03									
Expected	5.405	5.405	5.405	1.483	1.483	1.483	1.483	1.483	1.483
Mean	5.424	5.407	5.406	1.479	1.481	1.481	1.493	1.493	1.493
±1s	0.034	0.012	0.005	0.009	0.009	0.009	0.010	0.010	0.010
%RSD	0.63%	0.22%	0.09%	0.63%	0.63%	0.63%	0.67%	0.67%	0.67%
Δ(meas-exp) %	0.35%	0.04%	0.01%	-0.28%	-0.16%	-0.16%	0.65%	0.65%	0.65%
2/3/04									
Expected	5.405	5.405	5.405	1.483	1.483	1.483	1.483	1.483	1.483
Mean	5.356	5.405	5.405	1.476	1.480	1.481	1.494	1.494	1.494
±1s	0.026	0.026	0.026	0.005	0.005	0.005	0.007	0.009	0.007
%RSD	0.48%	0.48%	0.48%	0.35%	0.34%	0.35%	0.50%	0.57%	0.50%
Δ(meas-exp) %	-0.91%	0.00%	0.00%	-0.45%	-0.19%	-0.16%	0.74%	0.76%	0.74%
2/3/04									
Expected	5.405	5.405	5.405	1.483	1.483	1.483	1.483	1.483	1.483
Mean	5.375	5.405	5.405	1.475	1.481	1.479	1.492	1.493	1.493
±1s	0.026	0.026	0.026	0.008	0.008	0.004	0.011	0.011	0.009
%RSD	0.48%	0.48%	0.48%	0.51%	0.51%	0.29%	0.72%	0.72%	0.61%
Δ(meas-exp) %	-0.56%	0.00%	0.00%	-0.57%	-0.16%	-0.28%	0.59%	0.70%	0.66%
Statistics for seven runs									
Mean	5.405	5.399	5.406	1.476	1.480	1.480	1.487	1.488	1.488
±1s	0.012	0.009	0.009	0.003	0.003	0.002	0.003	0.003	0.003
%RSD	0.22%	0.17%	0.16%	0.20%	0.20%	0.16%	0.20%	0.20%	0.18%
Δ(meas-exp) %	0.00%	-0.12%	0.02%	-0.49%	-0.20%	-0.22%	0.30%	0.36%	0.35%

<sup>a</sup> All concentration data in mmol/mol.

and 3b, Tables 2 and 3), whereas Sr/Ca matrix behavior (Figures 3c and 3d, Tables 2 and 3) often does not warrant a matrix correction, which is not applied if the matrix standard-RCa correlation (R) is <0.5. Sample sizes are targeted for a nominal Ca concentration of 4 mM and typically range between 2–6 mM Ca. This range is centered within

the matrix standard suite. Either linear or logarithmic line fits of the matrix standard are then used to adjust the samples as a function of Ca concentration (RCa). Calcium matrix effects are substantially more pronounced in ICP-MS than in ICP-OES. Measuring Mg/Ca on the ICP-MS, the %RSD on the analysis of five samples with Ca concentration

**Table 3.** Effect of Solution Ca Concentration on Mg/Ca and Sr/Ca Over the Long Term From Five ICP-MS Runs<sup>a</sup>

Date	$\frac{^{24}\text{Mg}}{^{43}\text{Ca}}$			$\frac{^{25}\text{Mg}}{^{43}\text{Ca}}$			$\frac{^{88}\text{Sr}}{^{43}\text{Ca}}$		
	uncorr	corr-lin	corr-log	uncorr	corr-lin	corr-log	uncorr	corr-lin	corr-log
4/6/03									
Expected	5.405	5.405	5.405	5.405	5.405	5.405	1.483	1.483	1.483
Mean	5.456	5.414	5.402	5.467	5.416	5.403	1.49	1.484	1.484
±1s	0.249	0.041	0.036	0.256	0.046	0.038	0.008	0.007	0.007
%RSD	4.57%	0.76%	0.67%	4.68%	0.85%	0.70%	0.51%	0.51%	0.51%
Δ(mes-exp) %	0.94%	0.17%	-0.06%	1.14%	0.20%	-0.04%	0.47%	0.07%	0.07%
6/11/03									
Expected	5.405	5.405	5.405	5.405	5.405	5.405	1.483	1.483	1.483
Mean	5.427	5.409	5.402	5.42	5.408	5.4	1.479	1.482	1.482
±1s	0.154	0.016	0.029	0.163	0.018	0.029	0.003	0.001	0.001
%RSD	2.84%	0.29%	0.54%	3.01%	0.33%	0.54%	0.23%	0.06%	0.07%
Δ(meas-exp) %	0.41%	0.07%	-0.06%	0.28%	0.06%	-0.09%	-0.27%	-0.07%	-0.07%
6/12/03									
Expected	5.405	5.405	5.405	5.405	5.405	5.405	1.483	1.483	1.483
Mean	5.46	5.416	5.401	5.447	5.414	5.399	1.485	1.483	1.484
±1s	0.31	0.056	0.03	0.313	0.058	0.029	0.01	0.004	0.003
%RSD	5.68%	1.03%	0.55%	5.74%	1.07%	0.54%	0.67%	0.28%	0.17%
Δ(meas-exp) %	1.01%	0.20%	-0.07%	0.77%	0.17%	-0.11%	0.13%	0.00%	0.07%
6/16/03									
Expected	5.405	5.405	5.405	5.405	5.405	5.405	1.483	1.483	1.483
Mean	5.458	5.415	5.403	5.469	5.417	5.405	1.487	1.484	1.483
±1s	0.239	0.037	0.031	0.249	0.04	0.029	0.01	0.003	0.001
%RSD	4.37%	0.68%	0.57%	4.54%	0.74%	0.53%	0.65%	0.17%	0.09%
Δ(meas-exp) %	0.98%	0.18%	-0.04%	1.18%	0.22%	0.00%	0.27%	0.07%	0.00%
6/17/03									
Expected	5.405	5.405	5.405	5.405	5.405	5.405	1.483	1.483	1.483
Mean	5.538	5.427	5.409	5.544	5.428	5.41	1.487	1.484	1.483
±1s	0.355	0.08	0.027	0.362	0.075	0.029	0.014	0.004	0.005
%RSD	6.42%	1.47%	0.50%	6.52%	1.38%	0.53%	0.94%	0.26%	0.37%
Δ(meas-exp) %	2.43%	0.41%	0.07%	2.54%	0.42%	0.09%	0.27%	0.07%	0.00%
Statistics for five runs									
Mean	5.468	5.416	5.403	5.469	5.416	5.403	1.486	1.483	1.483
±1s	0.25	0.047	0.028	0.256	0.047	0.029	0.01	0.004	0.004
%RSD	4.57%	0.86%	0.52%	4.68%	0.87%	0.53%	0.64%	0.27%	0.27%
Δ(meas-exp)	1.16%	0.21%	-0.03%	1.19%	0.21%	-0.03%	0.18%	0.03%	0.02%

<sup>a</sup> All concentration data in mmol/mol.

varying from 1 to 8 mM is about 5%. After correction, the long-term precision on these samples is about 0.9%, and 0.5% for linear and logarithmic corrections, respectively (Table 3). For Sr/Ca, the %RSD on the raw measurements is 0.6%, and the corrected values yield precision of 0.3% for both the linear and logarithmic corrections. For ICP-OES, the Ca matrix effects are minimal. For Mg/Ca, the %RSD on the raw measurements is 0.6%, and the corrected values yield precision of 0.4% and 0.3% for the linear and logarithmic corrections, respectively. For Sr/Ca, we examined two lines, 407/315 nm and 407/318 nm. For both ratios, the %RSD on the raw measurements is <0.5%, and the precision of the corrected values is ~0.4% or better for both the linear and logarithmic corrections. These corrections can

potentially introduce slight biases in the data. For example, the matrix correction for the ICP-MS Mg/Ca data would produce artificially high Mg/Ca values for samples at 4 mM Ca, on order 0.8% (Figure 3a), and relatively low values around 1 and 8 mM Ca. Logarithmic correction biases would tend to be smaller and of the opposite sense than a linear fit for ICP-MS Mg/Ca (Figure 3a). These biases tend to smaller for ICP-MS Sr/Ca ratios and on the ICP-OES (Figures 3b, 3c, and 3d) but may be exacerbated if, for example, sample sizes in measuring Sr/Ca on the ICP-MS are distributed in the 0.3–0.7 RCa<sub>315</sub> range (Figure 3d). In sum, by careful accounting for instrumental Ca mass dependence, samples across a range of Ca concentrations can be reliably corrected with precision and accuracy better than 1%.

**Table 4.** Long-Term ICP-MS Analytical Precision of Laboratory Internal Consistency Standards

Consistency Standard	Statistic	$\frac{^{24}\text{Mg}}{^{43}\text{Ca}}$	$\frac{^{25}\text{Mg}}{^{43}\text{Ca}}$	$\frac{^{88}\text{Sr}}{^{43}\text{Ca}}$
		( $\frac{\text{mmol}}{\text{mol}}$ )	( $\frac{\text{mmol}}{\text{mol}}$ )	( $\frac{\text{mmol}}{\text{mol}}$ )
CS1	Expected	1.246	1.246	0.459
	Mean	1.268	1.227	0.453
	$\pm 1s$	0.016	0.011	0.003
	%RSD	1.27%	0.90%	0.59%
CS2	$\Delta(\text{meas-exp})$ %	1.76%	-1.52%	-1.27%
	Expected	3.318	3.318	0.918
	Mean	3.294	3.272	0.899
	$\pm 1s$	0.025	0.026	0.004
CS3	%RSD	0.76%	0.78%	0.46%
	$\Delta(\text{meas-exp})$ %	-0.74%	-1.42%	-2.13%
	Expected	7.504	7.504	1.843
	Mean	7.378	7.406	1.796
	$\pm 1s$	0.07	0.06	0.01
	%RSD	0.91%	0.82%	0.53%
	$\Delta(\text{meas-exp})$ %	-1.71%	-1.32%	-2.60%

### 3.3. Long-Term Precision and Internal Accuracy

[22] Long-term precision for Mg/Ca and Sr/Ca were evaluated by incorporating three internal consistency standards (CS1–CS3) run as samples at the beginning and end of each batch run. Consistency standards receive the same post-run data processing treatment as samples and are reported as corrected values, even though the matrix standards may not warrant correction, especially for Sr/Ca (see Tables 4 and 5). This approach ensures that the consistency standards and samples are treated identically. Data for long-term precision span 10 and 4 months of analyses, respectively, for the ICP-MS and ICP-OES. Precision for the ICP-OES and ICP-MS was better than 0.6% and 0.9% for Mg/Ca, and 0.3% and 0.6% for Sr/Ca, respectively (Tables 4 and 5, Figure 4). Interinstrument offsets of measured values of the same standard agree within  $1 \pm 0.5\%$  (derived from Tables 4 and 5, Figure 5). For Sr/Ca, interinstrument offsets of measured values of the same standard agree within 0.8%. Direct comparison of ICP-MS and ICP-OES standards for Mg/Ca and Sr/Ca ratios over their full range demonstrates high long-term fidelity of both instruments (Figure 5), as also seen in the short-term run.

### 3.4. Contaminant Phase Detection

[23] For paleothermometry, one important aspect of evaluating data fidelity is the monitoring of contaminant phases, specifically Mg-rich aluminosilicates derived from clay minerals adsorbed onto

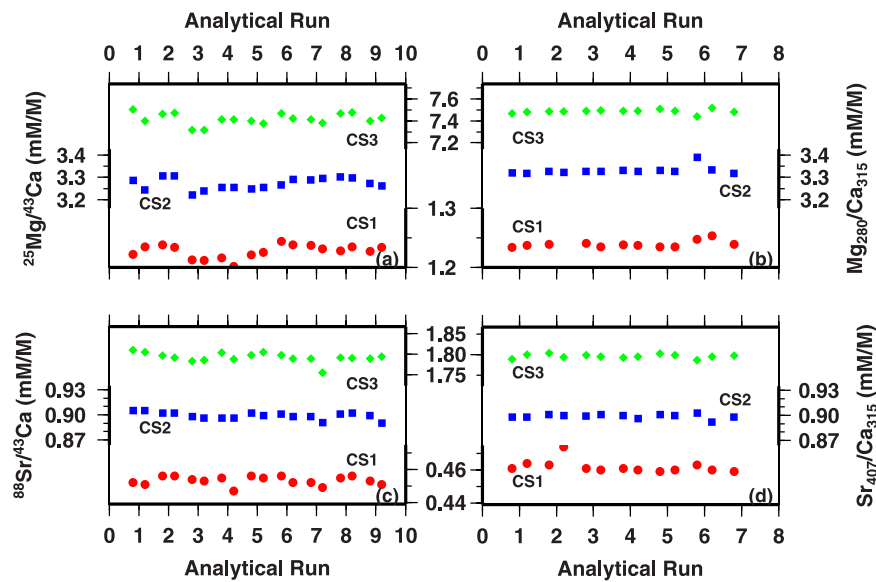
marine biogenic calcite and Mn-Fe oxyhydroxide coatings. These concerns are particularly true for foraminiferal tests. Historically Mn/Ca has been monitored [Boyle, 1983], and, more recently, Al, Ti, and Fe have been analyzed to quantify potential contaminant influences of clay minerals [Barker *et al.*, 2003; Lea *et al.*, 2005]. While well within ICP-MS detection limits, relatively low Al, Ti, and Mn concentrations in marine biogenic carbonates (Fe is in trace concentrations in foraminiferal tests) make detection via radial ICP-OES problematic for evaluating clay contamination. For the radial ICP-OES, we determined detection limits to average  $1.545 \pm 0.92$  ppb ( $1\sigma$ ;  $\pm 2.77$   $3\sigma$ ) for Al and  $0.324 \pm 0.10$  ppb ( $1\sigma$ ;  $\pm 0.30$   $3\sigma$ ) for Mn. In sum, the ICP-OES has marginally sufficient sensitivity for Mn to monitor for clay contamination, but insufficient sensitivity to detect Al in marine carbonates.

### 3.5. Marine Biogenic Carbonates

[24] Comparison of ICP-MS and ICP-OES instrument was tested by same sample Mg/Ca and Sr/Ca measurement of different marine biogenic carbonate bearing organisms: foraminifera and gastropoda. Measured *Conus ermineus* values ranged between 0.05–0.8 mM/M Mg/Ca and 1.1–2.8 mM/M Sr/Ca (Figure 6). *G. sacculifer* samples values ranged between 3–4 mM/M Mg/Ca and 1.27–1.31 mM/M Sr/Ca. In all cases paired interinstrument measurements plot very close to the 1:1 line (Figure 6). However, slight offsets in both the slope and absolute values are evident, particularly in the Sr/Ca foraminifera data (Figure 6b). Depending on the question at hand, these slight differences

**Table 5.** Long-Term ICP-OES Analytical Precision of Laboratory Internal Consistency Standards

Consistency Standard	Statistic	$\frac{\text{Mg}_{280}}{\text{Ca}_{315}}$	$\frac{\text{Sr}_{407}}{\text{Ca}_{315}}$	$\frac{\text{Sr}_{407}}{\text{Ca}_{318}}$
		( $\frac{\text{mmol}}{\text{mol}}$ )	( $\frac{\text{mmol}}{\text{mol}}$ )	( $\frac{\text{mmol}}{\text{mol}}$ )
CS1	Expected	1.246	0.459	0.459
	Mean	1.239	0.461	0.460
	$\pm 1s$	0.006	0.002	0.004
	%RSD	0.45%	0.35%	0.80%
CS2	$\Delta(\text{meas-exp})$ %	-0.55%	-0.42%	0.20%
	Expected	3.318	0.918	0.918
	Mean	3.330	0.899	0.898
	$\pm 1s$	0.019	0.003	0.002
CS3	%RSD	0.56%	0.31%	0.26%
	$\Delta(\text{meas-exp})$ %	0.37%	-2.13%	-2.18%
	Expected	7.504	1.843	1.843
	Mean	7.486	1.796	1.795
	$\pm 1s$	0.018	0.005	0.005
	%RSD	0.25%	0.27%	0.28%
	$\Delta(\text{meas-exp})$ %	-0.24%	-2.56%	-2.63%

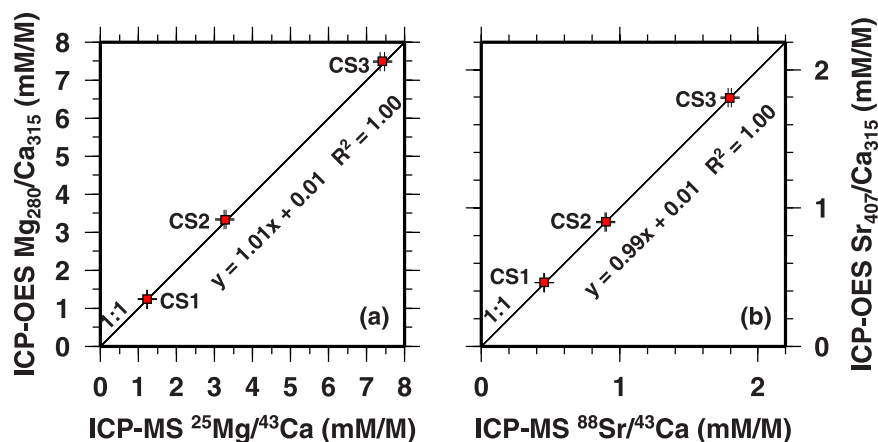


**Figure 4.** Long-term analytical precision of intralaboratory consistency solutions with a chemical composition covering the common range of marine biogenic carbonates. Internal laboratory consistency standards (CS1, CS2, CS3) are routinely analyzed at the beginning and end of each analytical run (Analysis #). Data that span 10 and 4 months of analyses for the ICP-MS and ICP-OES instruments, respectively, are presented. (a) ICP-MS Mg/Ca, (b) ICP-OES Mg/Ca, (c) ICP-MS Sr/Ca, and (d) ICP-OES Sr/Ca. Symbols for each standard are individually labeled on each plot and adjacent to the appropriate scale for each consistency standard. Note that the scale is adjusted at each concentration such that the total range reflects 8%RSD.

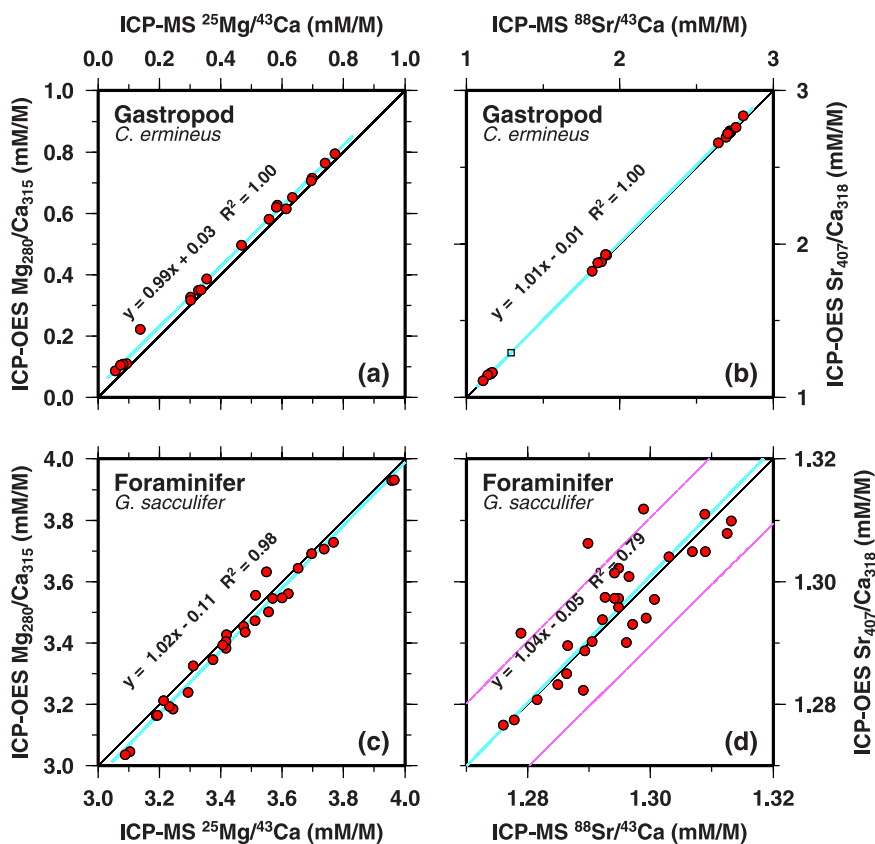
can be important when comparing data from different laboratories and equipment. For example, constraining late Pleistocene seawater Sr/Ca requires precise and accurate data because Sr/Ca varies by only 1–5% [Martin *et al.*, 1999; Stoll *et al.*, 1999; Elderfield *et al.*, 2000]. Our foraminifera Sr/Ca data span the last glacial-interglacial transition (Termination I) and exemplify the scatter endemic to measurements over this very narrow data range (Figure 6b). Yet examining differences

at this fine detail presents an ideal case study to investigate issues surrounding interinstrument data compatibility. In particular, we examine below the ramifications of matrix effects corrections on data fidelity.

[25] Table 6 compiles the average sample-to-sample offset between the ICP-MS ( $^{88}\text{Sr}/^{43}\text{Ca}$ ) and ICP-OES ( $\text{Sr}_{407}/\text{Ca}_{315}$  and  $\text{Sr}_{407}/\text{Ca}_{318}$ ) data, slope, intercept and correlation coefficient for matrix



**Figure 5.** Long-term intercomparison of internal consistency standards (CS1, CS2, CS3) as measured by the ICP-MS and ICP-OES over 10 and 4 months of individual runs, respectively (mean and standard deviation results from Tables 2 and 3). (a) Mg/Ca ICP-MS/ICP-OES instrument intercomparison and (b) Sr/Ca intercomparison.



**Figure 6.** Real sample-to-sample measurement intercomparison of ICP-MS and ICP-OES determined for gastropod *Conus ermineus*, (a) Mg/Ca and (b) Sr/Ca, and foraminifer *G. sacculifer*, (c) Mg/Ca and (d) Sr/Ca. Light black lines are 1:1 lines, and light blue-green lines are the Type II least squares linear regression lines through the data. Note in Figure 6d the very fine scale relative to Figure 6b. The small box in plotted in Figure 6b is the full scale of Figure 6d. Error bars (magenta lines in Figure 6d) are the  $\pm 1\sigma$  error bars of our long-term Sr/Ca precision of  $<0.8\%$ .

corrected and uncorrected cases. In most cases, differences between the two instruments fall within the long-term precision of both instruments, and certainly within the range of consistency obtained above. The analysis of Sr/Ca ratios in foraminiferal shells, presents an extreme case. As shown in

Figure 6d, the range of variability is very limited, about four times the %RSD of the long-term precision (we used the long-term rather than short-term precision because samples were run on different instruments and at different times). Most of the data fall within the range of  $\pm 1\sigma$ , which

**Table 6.** Sample-to-Sample Planktonic Foraminifer *G. sacculifer* Sr/Ca Differences, Slope, and Correlation as Measured by Both ICP-OES Relative to ICP-MS

ICP-OES	Correction Applied	ICP-MS $\left(\frac{^{88}\text{Sr}}{^{43}\text{Ca}}\right)_{\text{uncorr}}$				ICP-MS $\left(\frac{^{88}\text{Sr}}{^{43}\text{Ca}}\right)_{\text{lin-corr}}$				ICP-MS $\left(\frac{^{88}\text{Sr}}{^{43}\text{Ca}}\right)_{\text{log-corr}}$			
		%diff <sup>a</sup>	slope <sup>b</sup>	b <sup>c</sup>	R <sup>2</sup>	%diff	slope	b	R <sup>2</sup>	%diff	slope	b	R <sup>2</sup>
$\frac{\text{Sr}_{407}}{\text{Ca}_{315}}$	uncorr	-0.40	1.18	-0.24	0.75	-0.37	1.17	-0.22	0.68	-0.44	1.17	-0.22	0.66
	lin-corr	-0.48	1.17	-0.23	0.83	-0.45	1.15	-0.20	0.84	-0.52	1.15	-0.20	0.82
	log-corr	-0.26	1.13	-0.18	0.85	-0.22	1.11	-0.15	0.85	-0.30	1.11	-0.15	0.84
$\frac{\text{Sr}_{407}}{\text{Ca}_{318}}$	uncorr	-0.35	1.06	-0.08	0.78	-0.32	1.04	-0.06	0.72	-0.40	1.04	-0.04	0.77
	lin-corr	-0.03	1.00	-0.08	0.82	-0.00	1.04	-0.05	0.72	-0.07	1.04	-0.05	0.78
	log-corr	-0.04	1.06	-0.07	0.80	-0.08	1.04	-0.05	0.79	-0.01	1.03	0.04	0.76

<sup>a</sup> Average sample-to-sample percent ICP-OES minus ICP-MS difference. Positive % difference indicates ICP-OES Sr/Ca values are on average higher than ICP-MS Sr/Ca values.

<sup>b</sup> Based on Model II regression: Line is fit by minimizing both x- and y-residuals simultaneously.

<sup>c</sup> Intercept.

suggests a relatively tight fit between the two instruments. Given this narrow range of Sr/Ca variability, ICP-OES Sr<sub>407</sub>/Ca<sub>315</sub> correlations and the offset of the interinstrument regression from the 1:1 line are impressive. Nonetheless, the data in Figure 6d, clearly show that when assessing data with such a narrow range of variability, particular care should be taken when comparing results generated by two different instruments.

[26] Does applying Ca matrix corrections improve the interinstrument data fidelity? Comparing the uncorrected ICP-OES versus ICP-MS foraminifera Sr/Ca data shows that the R<sup>2</sup> correlation, slope and intercept lie within the expected errors from the long-term precision. Data offsets between the instruments also fall within  $\pm 1\sigma$  of the long term precision (Table 6). Comparing the uncorrected ICP-OES data to (linear or logarithmic) corrected ICP-MS data shows little change in both the slope and offset of ICP-MS Sr/Ca values relative to the ICP-OES values. This indicates, for this example, that the ICP-MS matrix corrections are very small. When correlating Sr/Ca values after ICP-OES data is matrix corrected the interinstrument offset is eliminated and both data sets agrees perfectly within our precision. Overall, the matrix correction methodology applied in this study brings short and long-term standards and marine biogenic carbonate data generated on independent instruments into agreement, within analytical uncertainties (Figures 1, 5, and 6), demonstrating an approach that can yield directly and accurately comparable data sets, independent of the instrumentation used to generate the data.

#### 4. Conclusions

[27] A coupled approach of calculating elemental ratios directly from simultaneous determination of Mg/Ca and Sr/Ca ratios and correcting for calcium matrix effects was tested on two instruments; magnetic sector ICP-MS and radially viewed ICP-OES. In documenting the performance of both instruments we show (1) over a broad range of Ca concentrations, a short-term precision of <0.2% and long-term precision <0.9% for Mg/Ca and Sr/Ca, regardless of the instrument used; (2) interinstrument short-term and long-term accuracy is about  $1 \pm 0.5\%$  for Mg/Ca, and better than 0.8% for Sr/Ca, or essentially the same as our long-term precision.

[28] When we apply a consistent paired ratio-intensity and matrix correction methodology to mea-

sure Mg/Ca and Sr/Ca in the same set of foraminifer and gastropod biogenic carbonate samples on two different instruments, we show that data can be reproduced to a high degree of fidelity, achieving accuracies consistent with our long-term precision. Correction for matrix effects is critical to achieve this fidelity in order to adjust for instrument biases that would otherwise impart offsets between the data sets.

[29] We are ambivalent about choosing radially viewed ICP-OES instrumentation as the lab primary tool for Mg/Ca and Sr/Ca measurement in marine biogenic carbonates. Advantages are that the ICP-OES is relatively inexpensive and simple to operate. In addition, both solutions and samples analyzed for Mg/Ca and Sr/Ca as part of this study were measured to the same precision and accuracy as on the ICP-MS, sometimes significantly better. Disadvantages include (1) an anticipated reduction of Ca matrix effects using ICP-OES in radial mode for easily ionized elements is only partially realized on this instrument; (2) the radial-viewed ICP-OES lacks the ability to monitor for Al and is marginally sensitive to Mn contamination in foraminifera samples. Fortunately, in our laboratory residual samples can be reanalyzed on the ICP-MS if clay mineral contamination is suspected. In retrospect, we recommend the more sensitive axially viewed ICP-OES to monitor trace elements from clays. Our study demonstrates that a very good short- and long-term precision of 0.1–0.3%, respectively, can be achieved for Sr/Ca ratios of about 1 mmol/mol. In principle, precision should be much better for the coral range (9 mmol/mol). Overall, ICP-OES disadvantages are minor and for most instances ICP-OES generated data are interchangeable to a high degree of precision and accuracy with ICP-MS data with this methodology.

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