A precise, high-throughput method for determining Sr/Ca, Sr/Ba, and Ca/Ba ratios in marine barite

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[1] Recent evidence suggests that marine barite, an inorganic phase preserved in oxic, deep-sea sediments, may record seawater Sr and Ca concentrations. Here we describe a novel method for determining Sr/Ca, Sr/Ba, and Ca/Ba ratios of discrete marine barite separates. Marine barite, separated from deep-sea sediments, is dissolved in a basic, ethylene diamine tetra acetic acid (EDTA) solution and subsequently analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES). Since dissolution occurs within 2–5 days, and >15 samples can be analyzed on the ICP-OES per hour, data acquisition is rapid compared with other procedures. The method yields precisions of <0.7% (Sr/Ca), <0.6% (Sr/Ba), and <1.0% (Ca/Ba), which are reproducible within 1.7% (Sr/Ca), 1.7% (Sr/Ba), and 2.5% (Ca/Ba). Precise determination of trace element incorporation in marine barite has implications for paleoceanography (development of seawater Sr and Ca concentration curves) and calculation of barite solubility in both the modern and ancient ocean.

1. Introduction

[2] Marine barite, shown in Figure 1, precipitates in microenvironments in which saturation with respect to barite is achieved by the release of labile Ba associated with decaying organic matter (R. Ganeshram et al., An experimental investigation of barite formation in seawater, submitted to *Geochimica et Cosmochimica Acta*, 2003). Barite is thus ubiquitous in pelagic sediments, particularly underlying areas of high biological productivity (0.2–2% wt, $CaCO_3$ free [*Bostrom et al.*, 1973]). Approximately 30% of barite flux is pre-served at depth in oxic marine sediments [*Dymond et al.*, 1992; *Paytan and Kastner*, 1996], and the crystals behave as a closed system, thus barite is not prone to diagenetic alteration after burial in oxic conditions [*Paytan et al.*, 1993, 1996b, 1998]. For these reasons, isotopic ratios preserved in marine barite (S, Sr, Ra) have been successfully applied as monitors of paleoceanographic conditions, [*Paytan et al.*, 1993, 1996a, 1998; *Van Beek and Reyss*, 2001; *Van Beek et al.*, 2002; *Mearon et al.*, 2002]. Thus far, trace element ratios in barite (i.e., Sr/Ba, Sr/Ca, and Ca/Ba) have not been utilized as paleo-proxies.
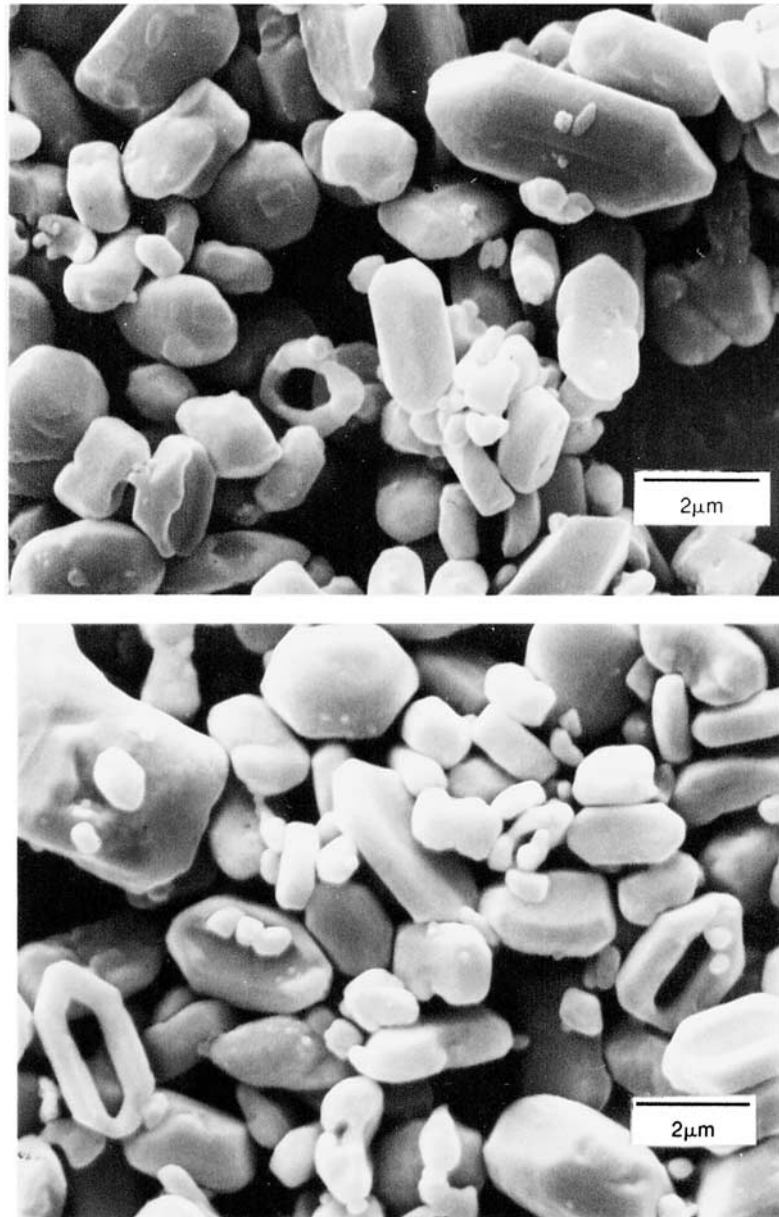
Figure 1. SEM micrographs of marine barite separates from deep-sea sediment. The morphology of these precipitates is typical of biologically produced barite. (Top: core top separate from PLDS 77BX; Bottom: downcore separate from DSDP site 575).

[3] Attempts to reconstruct $[Sr/Ca]_{SW}$ using marine carbonates [*Graham et al.*, 1982; *Delaney et al.*, 1985; *Stoll and Schrag*, 2001; *Lear et al.*, 2003] are complicated by diagenetic and vital effects [*Stoll and Schrag*, 2001]. In addition, fluctuations in $[Ca]_{SW}$ cannot be determined from $[Sr/Ca]_{SW}$ curves constructed using carbonate sources; therefore, it is unknown whether $[Sr/Ca]_{SW}$ oscillations are driven by changes in $[Sr]_{SW}$, $[Ca]_{SW}$, or both. Thus, a reliable record of seawater Sr and Ca concentrations from marine barite would provide independent confirmation of existing carbonate Sr/Ca records, in addition to a seawater Ca concentration curve.

[4] Significant analytical challenges must be addressed to determine precise Sr/Ba, Ca/Ba, and Sr/Ca ratios of natural marine barite, including the concomitant measurement of ions of widely vary-

ing concentrations. Direct analysis of solid $BaSO_4$ samples has been attempted using ion microprobe technologies (A. Paytan and A. Meibom, unpublished data, 2001). Microprobe techniques, however, are complicated because marine barite crystals are smaller than the focused diameter of the instrument ion beam. Consequently, for our purposes, solution analyses are preferable. Preparation of analyte solutions with dissolved barite is not as straightforward as with other minerals used for paleoceanographic work (e.g., $CaCO_3$) since the solubility product (K_{sp}) of barite is $\sim10^{-10}$ (25°C, 1 atm [*Church and Wolgemuth*, 1972]). Barite can be dissolved via resin exchange techniques, reflux with sodium carbonate or lithium borate, or via ligand-promoted dissolution [*Church*, 1970; *Bosbach et al.*, 1998; *Wang et al.*, 2000]. Of these, resin exchange techniques did not recover 100% of Ba from dissolved barite; such incongruent stripping of cations (Ba, Sr, Ca) from resin is acceptable for isotope analyses (e.g., $^{87}Sr/^{86}Sr$), but not for elemental ratio studies. Dissolution using reflux was not attempted since the high Ca content of the fluxing reagents would pose a significant blank. Accordingly, samples prepared using chelating ligands (i.e., ethylene diamine tetra acetic acid, EDTA) in a basic solution (pH 13) proved the most efficient and effective procedure. Ligand-mediated dissolution is advantageous over other methods because dissolution occurs within hours, and incomplete dissolution should not affect relative concentration ratios, since barite crystals are typically 0.5 to 5 µm [*Dehairs et al.*, 1980; *Bishop*, 1988] and are thus expected to be homogenous in composition. Moreover, electron microprobe analyses imply that the Sr/Ca variability in a natural barite separate is in the range of 6% (A. Paytan and A. Meibom, unpublished data, 2001), thus incomplete dissolution is not expected to result in significant variability.

[5] While most instrumental methods described for paleoceanographic studies focus on resolving precise Sr/Ca ratios of carbonate minerals [*Rosenthal et al.*, 1999; *Schrag*, 1999; *de Villiers et al.*, 2002], limited data are available for instrumental analyses of Ca/Ba [e.g., *Lea and Boyle*, 1993] and Sr/Ba [e.g., *Bernstein et al.*, 1991] ratios of natural samples.

Isotope dilution thermal ionization mass spectrometry (ID-TIMS) yields excellent precision for Sr/Ca ratio analyses (0.03 to 0.2% RSD, 2σ [*Beck et al.*, 1992; *Alibert and McColloch*, 1997]), yet sample throughput is on the order of 10 samples/day. Inductively coupled plasma using a mass spectrometer detector (ICP-MS) has also been widely employed for paleoceanographic analyses of samples with varied solution matrices, yielding precisions from 0.06 to 2% RSD, 1σ (Sr/Ca [*Lea and Martin*, 1996; *Rosenthal et al.*, 1999]). Application of ICP-MS to our samples resulted in interference with each isotope of Ca, a likely consequence of the relatively high concentration of salts in the sample matrix. Despite minimal analytical errors associated with ID-TIMS and ICP-MS, both instruments are impractical for this study, which requires analysis of hundreds of samples, and compatibility with a high-salt, high-pH, analyte matrix. The most promising instrument for developing a method for trace metal analyses of barite, with maximized throughput and adequate precision, is inductively coupled plasma optical emission spectrometry (ICP-OES).

[6] Here we report a newly developed, high-throughput method for determining Sr/Ba, Ca/Ba, and Sr/Ca ratios in marine barite, which will later be used to develop a record of seawater Sr and Ca concentrations. Such a data set, along with other paleoceanographic data (Sr isotope composition, sea level, spreading rates), may be able to constrain the relative influence of silicate weathering, carbonate and sulfate sedimentation, and hydrothermal processes on the long-term carbon cycle.

2. Method Development

[7] Methods for constructing extensive paleoceanographic records using ICP-OES, reporting Sr/Ca precisions <0.3% RSD (1σ), have been described for Sr/Ca and Ba/Ca ratios of marine carbonates [*Schrag*, 1999; *de Villiers et al.*, 2002]. However, compared with barite, carbonate Sr concentrations are similar, Ca concentrations are higher (corals: 7500 ppm Sr and 40% Ca, barite: 7000 ppm Sr and 400 ppm Ca), and Ba concentrations are lower (carbonate: 1–30 ppm Ba, barite: 60% Ba). The sample matrix for dissolved carbonates and barite

also differs. Carbonate samples (e.g., coral, fora-minifera, mollusks) are prepared in acidic solutions, whereas the barite sample matrix is highly alkaline. Consequently, the analytical challenges (concentration ranges, detection wavelengths, common-ion effects) for carbonate processing are significantly different than those related to analyzing barite samples. Accordingly, the analytical procedures, corrections, and associated errors reported here are not comparable with published methods for determining Sr/Ca and Ba/Ca ratios of biogenic carbonates.

2.1. Reagents, Standards, and Reference Solutions

[8] Initial ICP-OES analyses of reagents prepared in general laboratory conditions showed significant Ca contamination, causing inadequate precision between both sample and blank replicates. Consequently, all reagents, standards, reference solutions, and analytes (subsequent to barite separation) should be prepared in a clean room to improve the precision of blank and sample replicates, and all equipment acid-cleaned prior to use.

[9] Materials and reagents required for barite separations are described by *Paytan et al.* [1993]. For dissolution of barite samples, a bulk (10 L) 10 mM EDTA solution adjusted to pH > 13 using KOH is prepared.

[10] Trace metal grade HNO_3 (2%) is used to prepare standards. A bulk, mixed standard solution (2 L) should be gravimetrically prepared with Sr (1 ppm), Ca (1 ppm), and Ba (200 ppm). This standard solution is used to calibrate the ICP-OES.

[11] An internal standard is prepared by adding Sr, Ca, and Ba to EDTA-KOH in the appropriate concentration (approximately 2 ppm Sr, 0.08 ppm Ca, 200 ppm Ba). This final barite reference solution is calibrated using the gravimetrically prepared quality control standard solution (1 ppm Sr, 1 ppm Ca, 200 ppm Ba).

2.2. Sample Preparation

[12] Marine barite is separated from deep-sea sediments using previously described methods [*Paytan et al.*, 1993; *Eagle et al.*, 2003]. Samples are screened for diagenesis and contamination using

SEM with EDAX [*Paytan et al.*, 1993; *Eagle et al.*, 2003], and Raman spectra are collected on most samples to check for contaminants [*Averyt et al.*, 2001]. If SEM observations or Raman data indicate that a sample is not pure (i.e., contains detectable Sr or Ca bearing phases other than barite), the sample is deemed unreliable and is not used.

[13] Between 1–3 mg of sample (barite separation residue) and 7 mL of the EDTA-KOH solution are added directly to ICP tubes. The addition of more barite resulted in incomplete sample dissolution and clogging of the ICP introduction system. Increasing the concentration of the EDTA-KOH solution allowed for more effective dissolution [*Wang et al.*, 2000]; however, ICP analyses of barite samples dissolved in a 50 mM EDTA solution caused detector saturation at several of the detection wavelengths. Dilute acid samples with similar Sr and Ca concentrations, run under the same instrumental conditions, did not exhibit saturation, implying that the saturation was a consequence of the increased salt content of the analyte solution. Therefore, concentrations and quantities of barite and ligand (as specified above) minimize matrix interferences and plasma instability, and provide sufficient Sr, Ca, and Ba signals for quantification.

[14] After preparation, the ICP tubes are tightly covered, sonicated periodically, and analyzed using ICP-OES within 2–5 days. Repeated analyses of a single sample suggest that the Sr/Ca ratio of a single sample is stable for about 5 days. Before and after this interval, the within-run precision of the Sr/Ca ratio is diminished, possibly due to variable dissolution and a decrease in pH caused by equilibration with atmospheric CO_2 for samples kept more than 5 days.

[15] Aliquots (7 ml) of both the barite reference solution and the EDTA-KOH bulk solution (blank) are added directly from their respective bulk samples to ICP tubes. Samples and reference solutions are analyzed by ICP-OES in batches totaling <120, but typically 75, total samples.

2.3. Analysis Using Inductively Coupled Plasma-Optical Emission Spectrometry

[16] An inductively coupled plasma optical emission spectrophotometer (ICP-OES) equipped with

Table 1. Operating Conditions for TJA IRIS ICP-OES

Parameter	Optimum	Parameters Tested (If Applicable)		
Radio-frequency (RF) Power	750 W	750−1150 W		
Auxiliary Gas Flow Rate	Low			
Nebulizer Flow Rate	0.55 L min.$^{-1}$	0.55−0.63 L min.$^{-1}$		
Peristaltic Pump Flow Rate	Self-aspiration (∼2.5 ml min^{-1})	1.48−2.20 ml min.$^{-1}$, Self-aspiration		
Integration Time	3 seconds	1−10 seconds		
Background Correction	Dynamic			

			Detection Limit	
		Wavelength, nm	Lower, ppb	Upper, ppm
Ca Detection Wavelengths	393.3 (085) nm	315.8	17.4	400
		317.9	6.0	400
		393.3	6.0	1
Sr Detection Wavelengths	407.7 (082) nm	346.4	10.0	400
		407.7	0.2	3
Ba Detection Wavelengths	233.5 (144) nm	233.5	0.6	300

the IRIS Advantage ICAP (Inductively Coupled Argon Plasma) Spectrometer from Thermo Elemental (Franklin, MA) is used to measure Sr, Ca, and Ba concentrations in solutions. This instrument has a radial plasma for flexibility and high sensitivity, and a charge injection device (CID) solid-state detector, which provides the flexibility of selecting wavelengths for the specific element with minimized interferences.

[17] The instrument is cleaned before all analyses to minimize contamination. Prior to each run, the torch unit is removed and cleaned thoroughly, and the tubing between the peristaltic pump and the auto-sampler sipper replaced. Before initiating the analysis, the system is warmed up for >1.5 hours, after which 250 mL of EDTA-KOH solution are used to flush the system for an additional 30 to 40 minutes.

[18] The general operating conditions for the ICP-OES are described in Table 1. Several of these parameters had to be considered and tested experimentally to define optimal operating conditions for determining precise elemental ratios.

2.3.1. Detection Wavelength

[19] To obtain the most precise elemental ratios, Sr, Ca, and Ba analyte concentrations should lie within the linear range of the detection wavelengths, and the sensitivity of the lines to high-frequency perturbations (variability in plasma, sample introduction) should be similar. Concentrations of Sr and

Ca in modern marine barite are approximately 7000−10000 ppm Sr and 300−400 ppm Ca. Therefore, 1−3 mg of marine barite in 7 mL of solution should result in analyte concentrations of 1.4−2.0 ppm Sr, 0.06−0.08 ppm Ca, and 100−300 ppm Ba. Preliminary analyses of samples of different ages (0−65 million years) define the expected ranges as 0.8 to 8.0 ppm for Sr, 0.04 to 0.30 ppm for Ca, and 85 to 200 ppm Ba. These concentrations fall within the dynamic linear range for several wavelengths for Ca (315.8 nm, 317.9 nm, 393.3 nm), and Sr (407.7 nm, 346.4 nm); only one wavelength (233.5 nm) can be used for Ba measurements.

[20] To determine the optimal wavelengths for precise elemental ratios, the covariance of the Sr/Ca signals was evaluated for the detection wavelengths above. The most accurate and precise (1.2% RSD, 1σ) ratios are obtained using the 393.3 nm and 407.7 nm lines for Ca and Sr, respectively (Figure 2). The covariance of these two lines demonstrates their sensitivity, and implies that perturbations in the signal due to instrument interference are minimized. The 233.5 nm line is used for Ba.

2.3.2. Radiofrequency (RF) Power

[21] The RF power regulates the temperature of the flame and the stability of the argon plasma, and thus regulates the sensitivity and precision of the instrument. Samples with high salt concentra-
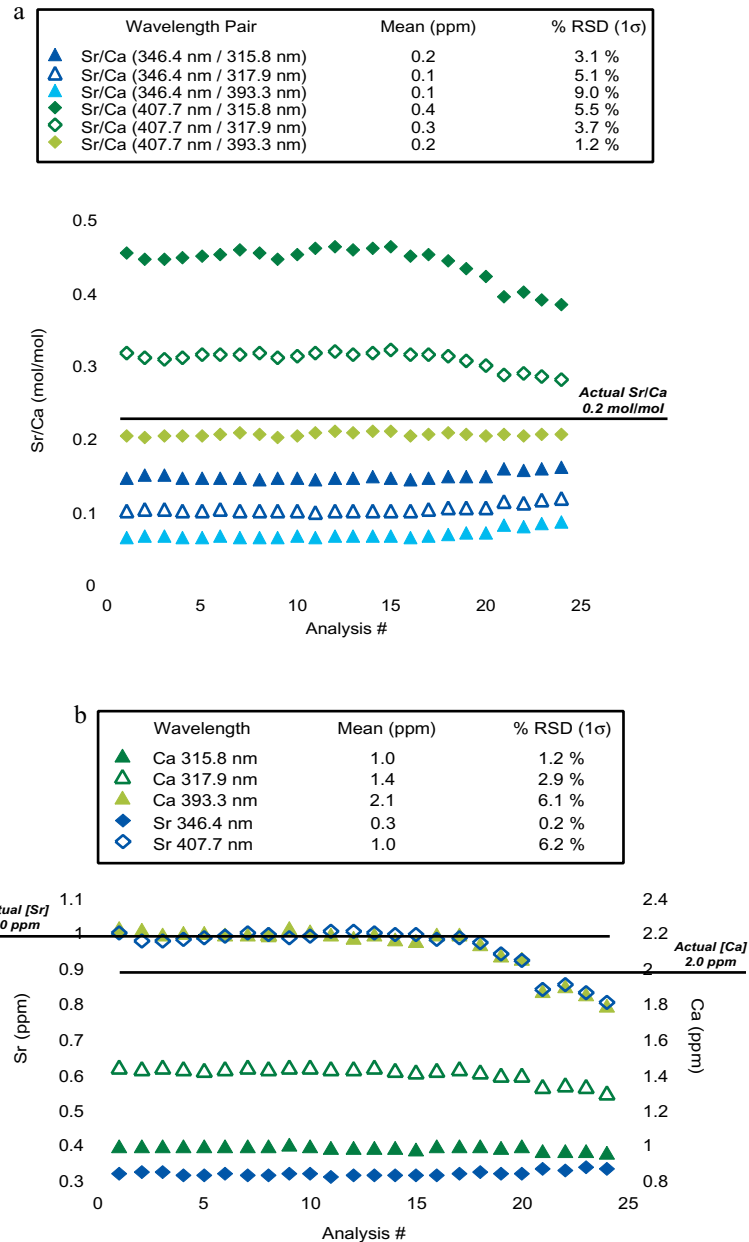
Figure 2. (a) Comparison of [Sr] and [Ca] (ppm) for a standard solution at different Sr and Ca detection wavelengths over a single ICP run. The most accurate Sr data are given by the 407.7 nm wavelength, although significant drift occurs (6.0% RSD) relative to the 346.4 nm line (0.2% RSD). The results are similar for Ca. The [Ca] in the standard solution is 2 ppm, for which the 393.3 nm line gives the most accurate, yet imprecise, results. (b) Sr/Ca ratios (mol/mol) determined using different wavelengths combinations. The most accurate and precise Sr/Ca ratio data result from comparison of the 407.7 nm (Sr) and 393.3 nm (Ca) lines (0.2 mol/mol, 1.2% RSD, 1σ). The improvement in the RSD of the Sr/Ca ratios implies that the Sr 407.7 and Ca 393.3 lines are of similar sensitivity, therefore responses of the individual lines to short-term variability (e.g., plasma perturbations), are eliminated by comparing the data (Sr/Ca ratios).

tions often require a higher RF power in order to combat salt interference. However, within-run precision for Sr/Ca ratios using a high RF power (1150 W) was 0.4%, as compared with 0.3% at a reduced power (750 W), since the high RF power also enhances the interferences on the measuring element. Given these results, an RF power of 750 W is optimal.
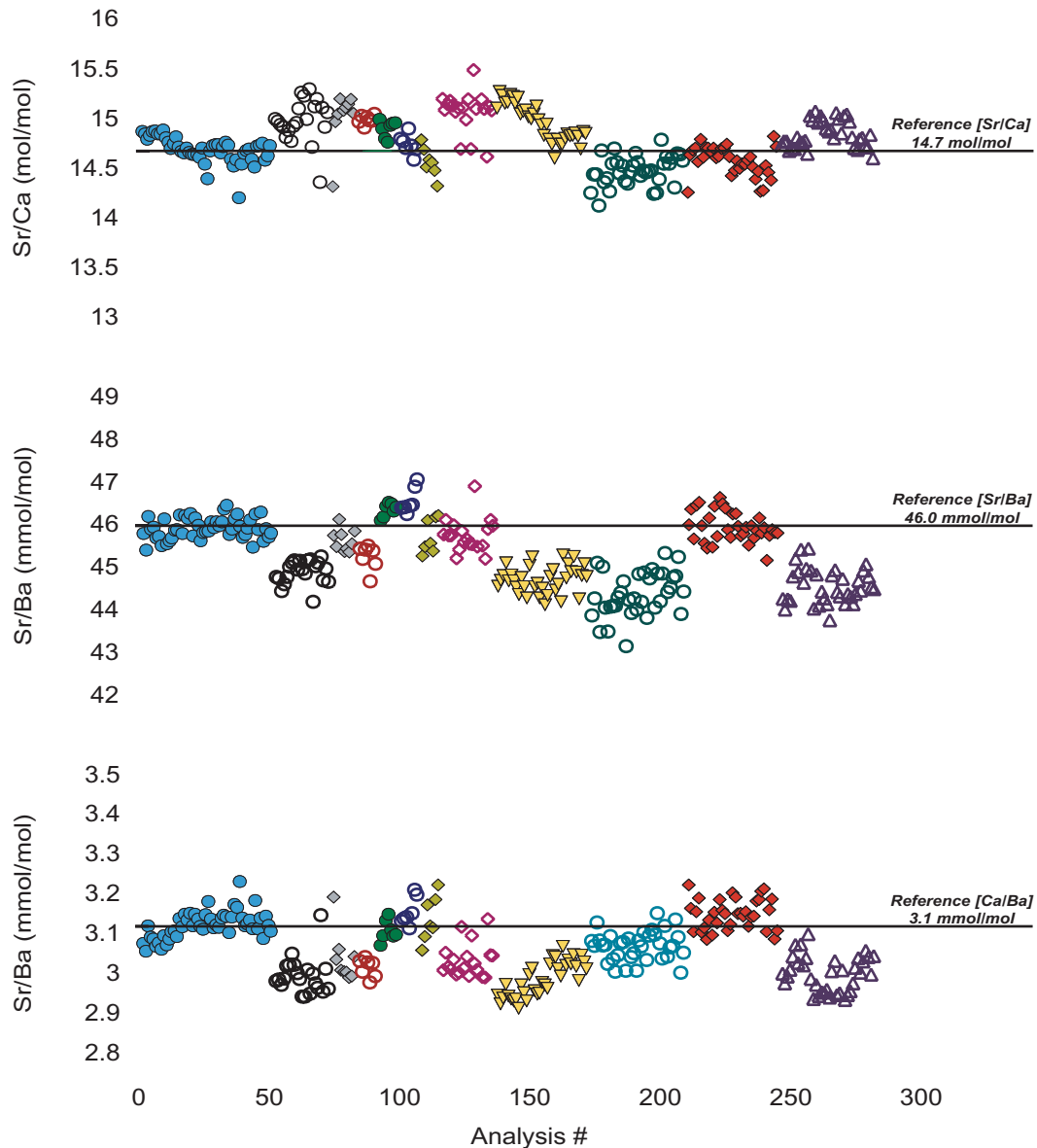
Figure 3. Long-Term Precision and Accuracy. Different groups of symbols represent individual batch runs processed on the ICP; the statistical data for each batch are shown in Table 2. The analysis number does not account for the number of samples processed between each barite reference solution. Data are not drift corrected.

2.3.3. Sample Introduction

[22] The greatest source of analytical uncertainty is the sample introduction system. Assuming that sample introduction is not affecting the chemistry of the elements being analyzed, high-frequency perturbations should theoretically be eliminated when expressed as the ratio of the concentrations. Repeated analyses of barite reference solutions show that slower flow rates ($\sim$2.0 mL min^{-1}) result in significant drift in the Ca component of

the Sr/Ca and Ca/Ba ratios. Self-aspiration ($\sim$2.5 mL min^{-1}) of the analyte solutions minimizes this effect and improves instrumental noise.

2.3.4. Calibration and Blank Correction

[23] The system is calibrated using a standard solution prepared in 2% HNO$_3$. A matrix matched (EDTA-KOH) standard proved unreliable over time since the solution pH depended on exposure to air. Typically, 5–10 samples of the EDTA-KOH solu-

Table 2. Short-Term and Long-Term Precision Data[a]

	Batch (N)												All	Actual
	1 (50)	2 (20)	3 (9)	4 (7)	5 (7)	6 (7)	7 (7)	8 (20)	9 (36)	10 (36)	11 (35)	12 (36)		
Sr/Ca	14.70	14.99	15.03	15.00	14.91	14.75	14.58	15.02	14.97	14.49	14.59	14.85	14.8 ± 0.03	14.7
RSD	0.9%	1.4%	1.8%	0.3%	0.6%	0.7%	1.0%	2.4%	1.2%	1.0%	1.0%	0.9%	1.7%	
Sr/Ba	45.95	44.93	45.66	45.27	46.38	46.59	45.77	45.76	44.73	44.40	45.98	44.59	45.3 ± 0.8	46.0
RSD	0.5%	0.6%	0.6%	0.6%	0.3%	0.6%	0.9%	0.8%	0.7%	1.2%	0.8%	0.9%	1.6%	
Ca/Ba	3.13	3.00	3.04	3.02	3.11	3.16	3.14	3.05	2.99	3.07	3.15	3.00	3.1 ± 0.08	3.1
RSD	1.1%	1.5%	2.1%	0.8%	0.8%	1.1%	1.8%	2.4%	1.5%	1.2%	1.2%	1.5%	2.5%	

[a] Each batch number corresponds with the appropriate symbol in Figure 3. Values for each ratio are the mean of all data within a batch run; the number of samples analyzed in each batch is noted (N). Only a single datum was eliminated due to significant Ca contamination. The %RSD includes all data and is not confined to 1σ, since data are not corrected for drift.

tion are used as blanks for each batch of samples processed. For Sr and Ba, blank concentrations are negligible compared with sample concentrations; the Ca blank is typically <10% of sample concentrations, but for smaller samples, is as great as 25%. However, when the solution pH remains >13, Ca concentrations in the EDTA-KOH solution are reproducible (1σ, RSD = 1.6%), suggesting that trace amounts of Ca present in the EDTA and KOH reagents are responsible for the blank. (The reagents used in these studies exhibited the lowest level of Ca contamination of those tested). The Ca blank in the matrix is a systematic error, therefore using non-matrix matched standards and a blank subtraction procedure should not significantly influence the precision among the data. Since relative fluctuations in the Sr/Ca, Sr/Ba, and Ca/Ba ratios are most important for paleoceanographic records, such systematic errors are not likely to appreciably affect the utility of this method.

2.3.5. Drift Correction

[24] To assess adequate performance of the instrument, approximately 5 samples of the internal barite reference solution are analyzed at the beginning of a given run, immediately following the EDTA-KOH blank solutions. Precision is monitored throughout the run using barite reference solutions interspersed among samples. Instrument drift is corrected by interpolating between each reference, and correcting to the known concentration of the internal reference. A higher frequency of interspersed barite reference solutions does not significantly improve drift correction. Interspersing

a reference every other sample, compared with every 5 samples, improves precision only slightly: 0.7% to 0.6% (Sr/Ca), 0.8% to 0.7% (Sr/Ba), and 1.0% to 0.9% (Ca/Ba). Accordingly, a barite internal standard solution was run every 5 samples to correct for drift.

2.4. Precision and Accuracy

[25] Precision is monitored throughout the run using barite reference solutions interspersed among samples. Depending on the degree of precision required, the frequency of interspersed barite reference solutions can be altered. To test this, a suite of 75 barite reference solutions was analyzed, and some reference solutions were arbitrarily assigned as samples, and then drift corrected. The most precise Sr/Ca and Ca/Ba data are obtained by analyzing a reference between each sample, although for Sr/Ba, the precision shows little or no improvement. Typical, uncorrected precisions (%RSD, N = 75) are 1.0% (Sr/Ca), 0.7% (Sr/Ba), and 1.5% (Ca/Ba). Treating every other reference as a "sample," and correcting for drift, the precision improves to <0.7%, <0.6%, and <1.0%, respectively. The precision is diminished only slightly (Sr/Ca: 0.8%, Sr/Ba: 0.8%, Ca/Ba: 1.3%) when data are treated as groups of 4 "samples," and corrected by interpolation between bracketing barite reference solutions. Therefore, barite reference sample data should be collected at most every fifth sample to assure adequate reproducibility.

[26] Both the long-term precision and accuracy of the method (Figure 3) are based on analyses of barite

reference solutions in consecutive ICP runs over a period of 12 months. The mean ratios and %RSD for each batch run are compared with long-term data in Table 2. None of the data are drift corrected, and only one datum from all the references analyzed was eliminated due to a high Ca blank. Based on the mean of all the reference solutions analyzed, the long-term precisions (%RSD among all data) are better than 1.7% (Sr/Ca), 1.7% (Sr/Ba), and 2.5% (Ca/Ba). Accuracy of the method is 0.7% (Sr/Ca), 1.5% (Sr/Ba), and 1.0% (Ca/Ba), based on the deviation of the barite reference solution values from a known concentration.

3. Conclusions

[27] Compared with other procedures designed for analyzing trace element content of minerals, the rate of data acquisition is significantly faster using ICP-OES, although precision is sacrificed. This methodology consistently yields precisions of <0.7% (Sr/Ca), <0.6% (Sr/Ba), and <1.0% (Ca/Ba), which are reproducible within 1.7% (Sr/Ca), 1.7% (Sr/Ba), and 2.5% (Ca/Ba). Since the natural variability for Sr/Ca, Sr/Ba, and Ca/Ba among core top marine barites is significantly greater (10.1%, 15.0%, and 16.3%, respectively [*Averyt and Paytan*, 2003]) than the analytical precision, this methodology is adequate for paleoceanographic analyses of the Sr and Ca content of marine barite.

Acknowledgments

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