



Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates

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Abstract. A method for rapid determination of high-precision Sr/Ca ratios in scleractinian corals is presented. Using an inductively coupled plasma atomic emission spectrophotometer, samples are corrected for instrument drift using a reference solution, similar to the approach used for analysis of stable isotopes using gas-source mass spectrometry. Further correction for variation of the Sr/Ca ratio with Ca concentration is accomplished using internal standards. The precision, once all corrections have been made, is better than 0.1% (relative standard deviation, 1σ) for samples of similar Ca concentration and better than 0.2% for samples with variable Ca concentrations. This method increases the sample throughput by approximately a factor of 20 relative to thermal ionization mass spectrometry and significantly reduces instrument and per sample costs. Comparison of Sr/Ca data for a coral from the Galapagos Islands with an instrumental temperature record shows excellent agreement and demonstrates the potential for application of this technique to samples of modern and fossil scleractinian corals and other marine carbonates, including foraminifera.

1. Introduction

Reconstructing how sea surface temperatures (SSTs) have varied over geologic time is an essential component of paleoceanographic research. Since the 1950s, analysis of oxygen isotopes in marine carbonates has been a primary source of information on SST variability. More recently, this technique has been applied to skeletons of scleractinian corals to study seasonal and interannual variability [e.g., *Fairbanks and Dodge, 1979; Cole and Fairbanks, 1990*]. Massive coral colonies have growth rates typically of the order of 1 cm yr^{-1} so that oxygen isotope records with approximately monthly resolution can be generated by sampling at 1-mm intervals.

A complication in the interpretation of high-resolution coral oxygen isotope records is that the oxygen isotopic composition of the coral skeleton depends not only on temperature but also on the isotopic composition of the seawater in which the coral grows. The oxygen isotopic composition of seawater is affected by evaporation and precipitation and covaries with salinity. To circumvent this ambiguity, *Beck et al. [1992]* demonstrated that high precision Sr/Ca ratios in the coral aragonite could be used as a proxy for sea surface temperature independent from salinity, following the work of *Smith et al. [1979]*. Subsequent work by *Guilderson et al. [1994]* applied this technique to fossil corals from Barbados, concluding that tropical SSTs were 5-6°C colder than present during the Last Glacial Maximum. Other workers have applied this technique to modern corals to reconstruct the El Niño/Southern Oscillation (ENSO) [*McCulloch et al., 1994; Alibert and McCulloch, 1997*].

Recently, *Mitsuguchi et al. [1996]* suggested that high precision Mg/Ca ratios could also be used as a proxy for temperature, although some studies have suggested that other factors may also influence the Mg/Ca in corals [e.g., *Shen et al., 1992*].

One limitation of the Sr/Ca method is that the dependence of the Sr/Ca ratio in corals on temperature is small ($\sim 0.06 \text{ mmol/mol}$ ($\sim 0.7\%$) per degree) so that high-precision analysis by isotope dilution using thermal ionization mass spectrometry (TIMS) is required. Because this technique is labor and time intensive, it has been difficult for workers to produce longer time series (i.e., >100 years) and to collect adequate data to assess biological sources of variability and other complications with the method [e.g., *DeVilliers et al., 1994, 1995*]. Analysis of Sr/Ca ratios by inductively coupled plasma mass spectrometer (ICP-MS) can reach precision of ± 0.2 to 0.3% [*Le Cornec and Corregge, 1997*], but errors are more typically in the range of 1.0% [*Shen et al., 1992; Lea and Martin, 1996*] and cannot match the precision of TIMS analysis (as good as $\pm 0.03\%$ 2σ , *Beck et al., 1992*) and more typically $\pm 0.2\%$ ($\sim 0.3^\circ\text{C}$, 2σ) [e.g., *Alibert and McCulloch, 1997*]. *Hart and Cohen [1996]* used an ion microprobe to sample at higher resolution, producing records with precision of $\pm 0.5\%$.

In this paper, a new method is presented for rapid analysis of high precision Sr/Ca analyses in scleractinian corals and other marine carbonates using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES). The method has the advantages of employing an instrument that is inexpensive relative to ICP-MS or TIMS technologies, with small per sample costs and minimal sample preparation. The technique is capable of producing over 180 analyses of samples per day, at least a 20-fold improvement over TIMS methods with a small fraction of the labor required. The external precision on measurements of Sr/Ca ratios can be as good as $\pm 0.05\%$ (1σ) and typically better than $\pm 0.2\%$ ($\sim 0.3^\circ\text{C}$),

which is adequate for most paleoceanographic applications. Although the emphasis here is on analysis of Sr/Ca ratios, the instrument is capable of simultaneously making high-precision analyses of Mg/Ca, as well as a variety of other elemental ratios, on corals and other marine carbonates.

2. Methods

Samples are analyzed using an ICP-AES made by Jobin-Yvon (Model JY-46). The instrument is equipped with 21 photomultiplier tubes for simultaneous collection of 21 spectral lines. For this study, only three lines were used: Sr (407.77 nm), Ca (393.37 nm), and Mg (285.21 nm). Samples are introduced to the plasma using a Gilson autosampler and a peristaltic pump, with a Meinhard TR-50 C1 nebulizer and Scott spray chamber. Flow rate for the sample introduction is 1 mL min⁻¹. The optical portion of the instrument is maintained at constant temperature and purged with a nitrogen stream to improve instrumental stability. Voltages for individual photomultiplier tubes are optimized to achieve greatest stability for the range of concentrations of elements in our samples, rather than optimizing simply for sensitivity as detection limits for Ca, Sr, and Mg are several orders of magnitude smaller than the concentrations in the sample solutions. Consumables in this technique include polypropylene tubes, acid, nitrogen gas and liquid argon. Because the sample throughput is high (at least 180 samples plus reference solution and standards per day), the cost per sample, excluding labor, is extremely low compared with similar analytical methods.

Samples for this study include both synthetic solutions containing mixtures of pure SrCO₃, CaCO₃, and Mg (metal), as well as a coral from the Galapagos Islands, which was collected from Urvina Bay by G. Wellington in 1990 and supplied by R. Dunbar. This same coral core was used to study radiocarbon variability in the eastern tropical Pacific by *Guilderson and Schrag* [1998]. The growth rate of this colony is ~1 cm yr⁻¹. Samples were drilled from a 1-cm-thick slab at 1-mm intervals using a low-speed drill press. For each sample, ~0.6 mg of coral powder dissolved in 3 mL of 2% nitric acid (prepared with high-purity 70% nitric acid) and deionized water. Smaller samples (i.e., <50 µg) could be measured easily without significantly adjusting the method. Blanks of acid and deionized water are routinely monitored for contamination.

3. Results and Discussion

3.1. Instrument Stability and Corrections

Overall stability of the instrument, given by the relative standard deviation (RSD) of multiple analyses of Sr or Ca in a gravimetrically prepared solution measured over a 10-hour period, is better than 1% (Figures 1a and 1b). Most of this scatter is due to short-term variability in the plasma and in the sample introduction system, with some component due to longer-term drift. Because the collection of multiple elements is simultaneous, high-frequency variability in the plasma and

in the sample introduction will affect all spectral lines in similar ways and can be removed by taking an elemental ratio. Precision of the Sr/Ca ratio over the same ten hour period is 0.3% (RSD) (Figure 1c) but varies between runs from 0.1% to 0.5% and is limited by low frequency drift in the ratios.

The low-frequency drift in the data is due to several factors including temperature changes in the room, drift in the conditions of the plasma, and drift in the electronics. To correct for these types of variability, an approach is used similar to that in gas-source mass spectrometry for analysis of high-precision isotopic ratios. A reference solution of Sr, Mg, and Ca in proportions similar to the coral skeleton is prepared gravimetrically. The reference solution is measured between each sample, and a correction factor for each sample is calculated using the average value of the reference measurements bracketing the sample, normalized to the actual value of the reference solution. Through this procedure, the precision is improved to between 0.05% and 0.1% (RSD) (Figure 1c), with accuracy dependent on reliability of the reference solution. If there is high-frequency variability in the reference measurements, as seen in Figure 1, this can introduce some scatter in the sample data that was not in the uncorrected analysis. However, the overall result of this reference correction is to improve the precision to a level comparable with analysis by TIMS. Because all analyses are made relative to the reference solution, long-term error in the analysis depends on careful maintenance of reference solutions like any laboratory standard. For this purpose, concentrated stocks of reference solutions are sealed and archived for future analysis and comparison. Long-term reproducibility of analysis of synthetic standards (i.e. over several months) is better than 0.1%.

A further source of error results from the non linear response of the intensity of the 393.37-nm Ca line (and less significantly the 407.77-nm Sr line) with concentration (Figure 2a). At the start of each run, the instrument is calibrated using gravimetric standards, and a calibration line is calculated using software supplied by Jobin-Yvon which is limited to a second-order polynomial. For Ca this yields an inexact fit to the calibration data, leaving a residual error in calibration that is polynomial in form (Figure 2a). If solutions have identical Ca concentrations to the reference solution (within 5%), this calibration error can be ignored, and the error of the analysis is better than 0.1% (RSD). If samples have variable Ca concentrations, the error can be corrected by measuring standard solutions with identical Sr/Ca ratios but different Sr and Ca concentrations spaced throughout the run. Figures 2b and 2c illustrate the correction procedure with data from three synthetic solutions measured at five different concentrations before and after the correction. The polynomial fit through the concentration standard (solution 1) is used to normalize analyses of the other samples (solutions 2 and 3) to the same Ca concentration as the reference solution (77.5 ppm). This fit does not change with time during a run but must be recalculated every time a new calibration of the instrument is performed.

If the variation of the Sr/Ca ratio with Ca concentration for each sample parallels that of the concentration standard, the correction will not introduce additional error. In practice, as the Sr/Ca ratio of the sample deviates from the Sr/Ca ratio of

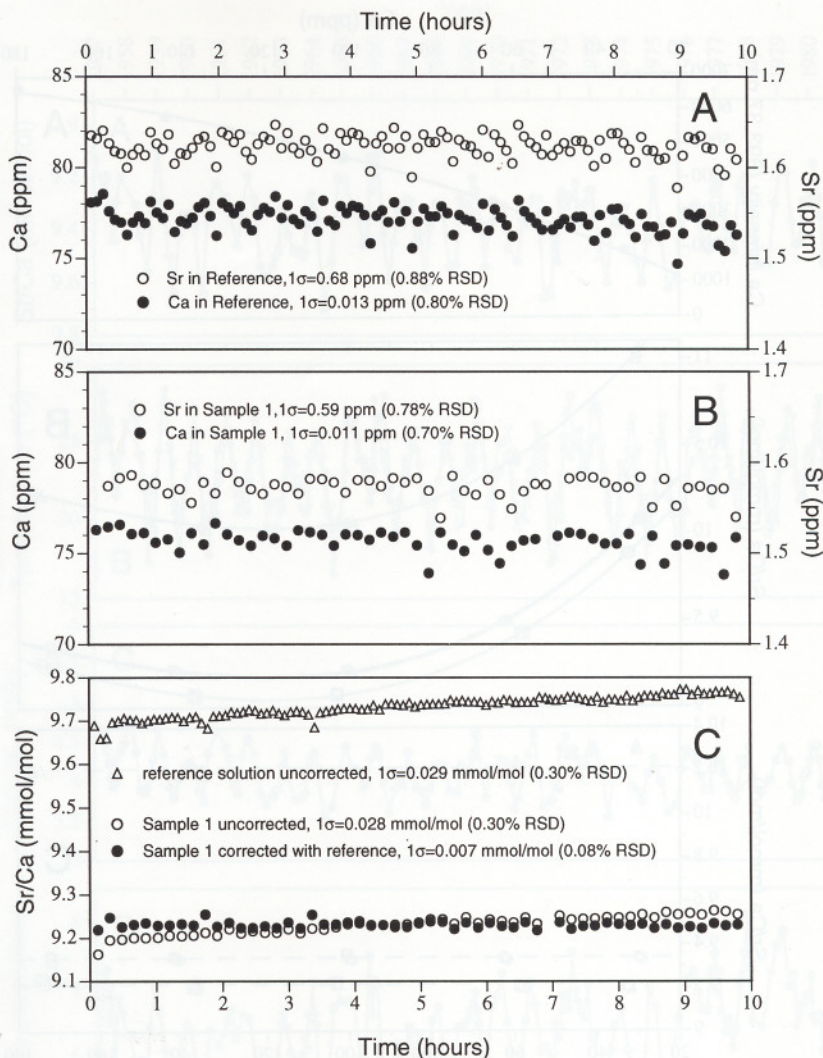


Figure 1. (a) Sr (open circles) and Ca (solid circles) in the reference solution measured between each sample. (b) Sr (open circles) and Ca (solid circles) in sample 1, a synthetic sample with similar Sr/Ca ratio to the reference solution. (c) Sr/Ca ratio of reference solution (triangles) and sample 1 before (open circles) and after (solid circles) correcting for drift with the reference solution. Calculating the elemental ratio accomplishes most of the reduction in high-frequency variability, while the reference correction removes the lower-frequency drift.

the concentration standard, the lines become less parallel and the correction becomes less accurate. For example, the standard deviation of the corrected values for solution 2, which differs in Sr/Ca ratio from the concentration standard (solution 1) by only 1.3%, is 0.015 mmol/mol (0.16%). The standard deviation for solution 3, which differs by 9.6%, is 0.040 mmol/mol (0.39%). If the data at lowest Ca concentration (30 ppm) are excluded, the standard deviation for solution 3 improves to 0.019 mmol/mol (0.19%). By preparing samples so that the Ca concentration varies by less than a factor of 4 about the reference solution, and if the samples have Sr/Ca ratios varying by $\sim 10\%$, the precision after making the concentration correction is better than 0.2% (RSD) (Figure 2).

Scleractinian corals exhibit a very narrow range of variability in Sr/Ca ratios ($<10\%$), so that analysis at precision $\pm 0.2\%$ without careful weighing of each sample is routine. Other marine carbonates, such as foraminifera tests, exhibit a larger range of variability in Sr/Ca ratio, so that the

concentration corrections may be inaccurate. In this case, a set of concentration standards can be measured during the run that cover the range of concentrations and Sr/Ca ratios of the samples [Stoll, 1998]. The concentration corrections can then be made using the concentration standard with the closest Sr/Ca ratio as the sample. Alternatively, samples solutions can be prepared with identical Ca concentrations so no corrections are necessary.

3.2. Temperature From a Galapagos Coral

The Sr/Ca data for the Galapagos coral (Figure 3a) use an age model constructed by comparing COADS SST data from the $2^\circ \times 2^\circ$ area around the Galapagos Islands with oxygen isotope measurements of splits of the same samples used for Sr/Ca analysis [Guilderson and Schrag, 1998]. The time series extends from 1957 through 1982, when the coral died during

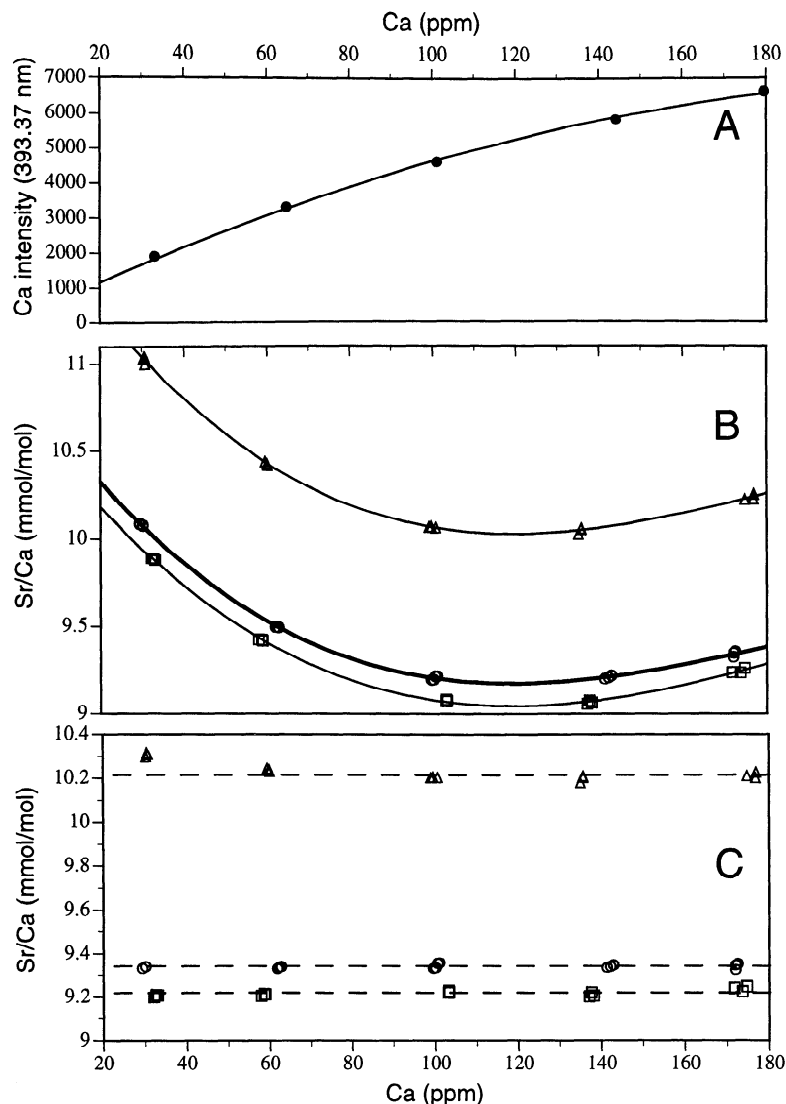


Figure 2. (a) Calibration curve for instrument showing intensity of Ca line (393.37 nm) as a function of Ca concentration of gravimetric standard. The curve is a second-order polynomial fit, which leaves a polynomial dependence of the elemental ratios with Ca concentration. (b) Sr/Ca versus Ca concentration for the "concentration standard" (circles) and two synthetic solutions (squares and triangles). Variation in Sr/Ca ratio with Ca concentration for all samples is corrected using a parabolic fit through the concentration standard (bold line). (c) Sr/Ca ratio corrected for Ca concentration yield excellent precision ($\pm 0.2\%$), although the correction is less accurate for the sample with Sr/Ca ratio most different from the concentration standard (triangles), particularly at the lowest Ca concentrations. Dashed curves show the gravimetrically determined Sr/Ca ratios of each solution.

the large El Niño event. Such a data set would take several months to collect using TIMS, whereas with ICP-AES, these measurements required slightly more than 1 day of instrument time. Replicate samples of this coral measured several months after the initial data were collected yield reproducibility better than 0.2% demonstrating the long-term error of this method.

The Sr/Ca data show excellent agreement with the Comprehensive Ocean-Atmosphere Data Set (COADS) SST (Figure 3b), with high correlation between annually averaged values of SST and Sr/Ca ($r=0.7$). The results are compelling, particularly considering that the coral is a point measurement while COADS integrates shipboard measurements from a 10,000 km² area. Converting the Sr/Ca measurements to temperature using the calibration by Shen *et al.* [1996] for

Porites lobata and *Porites lutea* ($\text{Sr/Ca} \times 10^3 = 10.286 - 0.0514 \times T$ (°C)) yields an appropriate amplitude of seasonal and interannual variability but a mean value that is too low by 3°C. A better fit is achieved if the intercept is increased slightly to 10.55 (Figure 3b) (see Alibert and McCulloch [1997] for a review of differences in Sr/Ca paleothermometer calibrations).

Comparison of the Sr/Ca ratios with $\delta^{18}\text{O}$ measurements (Figure 3c) shows high correlation ($r=0.7$) as expected. However, the amplitude of the oxygen isotope variability ($\sim 0.7\text{‰}$) is less than half of the expected range if the variability is only affected by changes in SST. This indicates either that variation in $\delta^{18}\text{O}$ of seawater in Urvina Bay accounts for approximately half of the $\delta^{18}\text{O}$ variability in the coral and is out of phase with seasonal variability in SST or that the $\delta^{18}\text{O}$

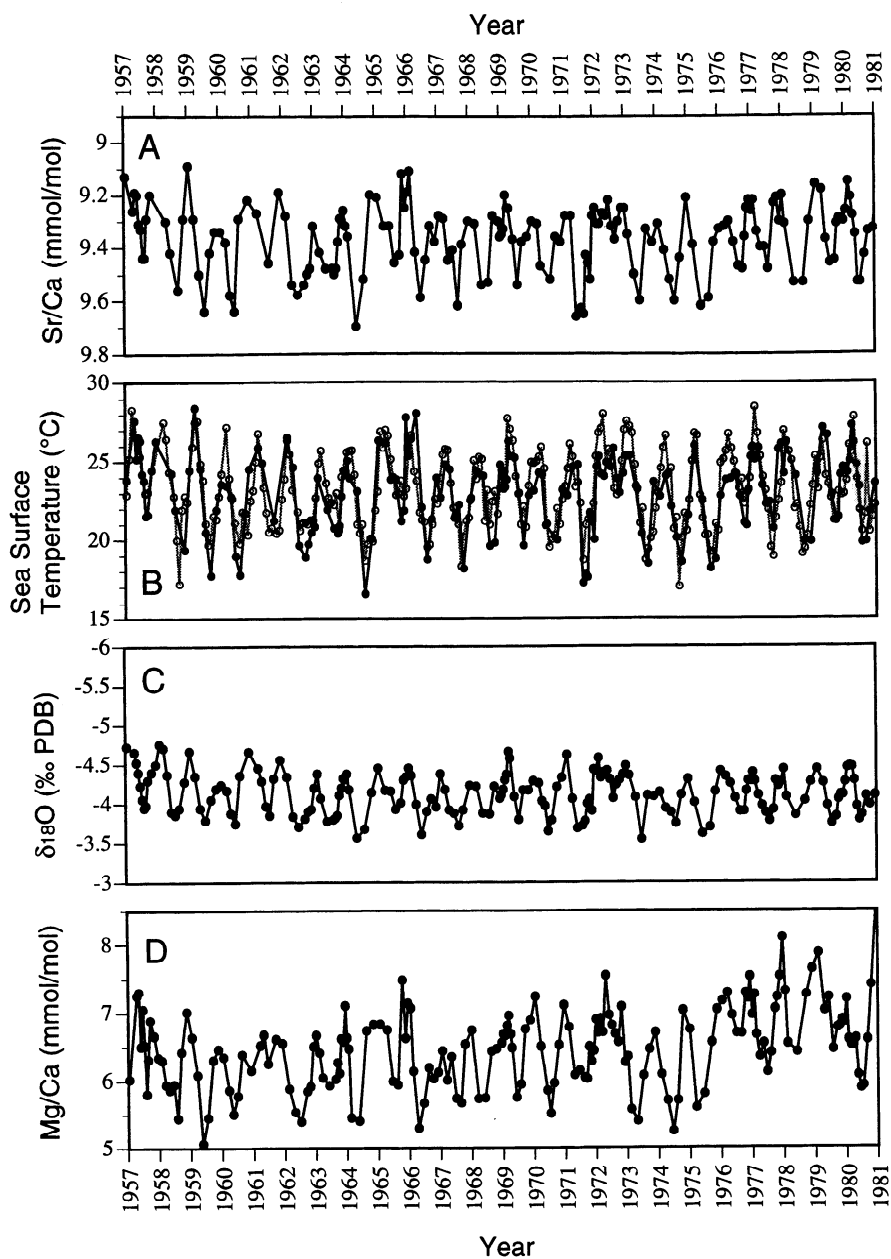


Figure 3. (a) Sr/Ca ratio for a *Porites lutea* coral collected from Urvina Bay in the Galapagos islands in 1990. The coral died in 1982 during the large El Niño event. (b) SSTs calculated from Sr/Ca ratios ($Sr/Ca \text{ (mmol/mol)} = 10.55 - 0.0514 \times T(^{\circ}C)$) (solid circles) compared with instrumental measurements of SST from COADS (open circles). Annual average values, with the seasonal cycle removed, show high correlation ($r=0.7$). (c) Oxygen isotope data for the same coral. The vertical scale reflects an equivalent temperature dependence as the scale for the Sr/Ca data. (d) Mg/Ca data, corrected using an identical method as for the Sr/Ca data. Precision of the Mg/Ca data is ± 0.035 mmol/mol (0.5%). Correlation of the Mg/Ca data with SST ($r=0.52$) is lower than Sr/Ca data.

dependence on temperature in this coral is much smaller than seen in other locations. Combining Sr/Ca and oxygen isotope data can yield an estimate of salinity variability, assuming that the relationship between $\delta^{18}O$ of seawater and salinity of seawater is constant, but this is outside the scope of this study.

3.3. Mg/Ca and Other Elemental Ratios in Corals and Other Marine Carbonates

The ICP-AES technique can collect high-precision Mg/Ca data as well as a wide variety of other elements provided that

concentrations are well above the detection limits. ICP-AES was used in the study of Mg/Ca in corals by *Mitsuguchi et al.* [1996], although they did not employ the methods of correction described here and their precision was only $\pm 1.0\%$. If the approach described here for Sr/Ca is applied to Mg/Ca in coral samples, the precision after normalizing to the reference solution is slightly lower than for Sr/Ca (0.02 mmol/mol, 0.3% RSD), although the sensitivity of Mg/Ca in corals on temperature, as suggested by *Mitsuguchi et al.* [1996], is 4 times higher. As with Sr/Ca analysis, concentration

correction reduces the precision by a factor of 2 (0.035 mmol/mol, 0.5% RSD). Mg/Ca data from the Galapagos coral are shown in Figure 3d. Correlation of annual average values with Sr/Ca ($r=-0.56$) and with SST ($r=0.52$) suggests that the Mg/Ca ratio in corals does not appear to be as accurate a proxy for SST as Sr/Ca. This is consistent with previous studies on Galapagos corals suggesting that widespread utility of Mg/Ca ratios in scleractinian corals as a thermometer is limited, although it may still be effective in some locations [Shen *et al.*, 1992].

Recently, studies have proposed that the Mg/Ca ratio in foraminifera may be a proxy for temperature [Nürnberg *et al.*, 1996; Hastings *et al.*, 1998; Lea *et al.*, 1997]. ICP-AES, using the correction methods described here, may represent an inexpensive and convenient alternative to isotope dilution with ICP-MS, the method employed in several recent studies. Precision for small samples has not yet been tested. However, with sample introduction systems for highest sensitivity (e.g., low-flow nebulizer), analysis of individual foraminifera should be possible.

4. Conclusions

The application of ICP-AES technology to marine carbonates is an ideal technique for producing high-precision

analyses of elemental ratios with extremely high sample throughput. Both the instrument and per sample costs are inexpensive, and the method requires a minimum of sample preparation. Precision of Sr/Ca ratio in scleractinian corals is better than $\pm 0.1\%$ (RSD) if samples are carefully weighed out. For more efficient sample preparation without weighing samples, routine analysis of 180 samples per day produces errors less than $\pm 0.2\%$, adequate for most studies of coral paleothermometry.

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