

# Simultaneous analysis of Ba and Sr to Ca ratios in scleractinian corals by inductively coupled plasma optical emissions spectrometry

Cantarero, Sebastian I.; Tanzil, Jani Thuaibah Isa; Goodkin, Nathalie Fairbank

2016

Cantarero, S. I., Tanzil, J. T. I., & Goodkin, N. F. (2017). Simultaneous analysis of Ba and Sr to Ca ratios in scleractinian corals by inductively coupled plasma optical emissions spectrometry. *Limnology and Oceanography: Methods*, 15(1), 116-123.

<https://hdl.handle.net/10356/86310>

<https://doi.org/10.1002/lom3.10152>

---

© 2016 The Authors. *Limnology and Oceanography: Methods* published by Wiley Periodicals, Inc. on behalf of Association for the Sciences of Limnology and Oceanography. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

*Downloaded on 27 Jan 2022 05:31:54 SGT*

## Simultaneous analysis of Ba and Sr to Ca ratios in scleractinian corals by inductively coupled plasma optical emissions spectrometry

Sebastian I. Cantarero,<sup>1,2</sup> Jani T. I. Tanzil,<sup>1,2</sup> Nathalie F. Goodkin<sup>1,2\*</sup>

<sup>1</sup>Asian School of the Environment, Nanyang Technological University, Singapore, Singapore

<sup>2</sup>Earth Observatory of Singapore, Nanyang Technological University, Singapore, Singapore

### Abstract

Chemical analyses of coral skeletons are useful for reconstructing past ocean conditions. Simultaneous measurements of Ba and Sr to Ca ratios in coral samples have predominantly been achieved by inductively coupled plasma mass spectrometry (ICP-MS). We demonstrate a method that expands the application of the inductively coupled plasma optical emissions spectrometry (ICP-OES) technique to precisely analyze Ba, Sr, and Ca simultaneously. Analytical drift and matrix interferences at a range of Ba/Ca ratios (3–10  $\mu\text{mol}/\text{mol}$ ) were explored to determine the efficacy of standardized corrections. Minor disparity in drift and matrix interferences between standards of varying Ba/Ca ratios indicate that standardized corrections can be applied. Comparative analysis between ICP-OES and an established ICP-MS technique in a Singapore coral and international coral standard JCP-1 were utilized to validate the proposed ICP-OES technique. ICP-MS and ICP-OES techniques showed a consistent offset, which was correctible with the use of an internal lab standard and resulted in only minor differences between techniques. ICP-OES showed comparable accuracy and precision to the ICP-MS, as evaluated by analysis of JCP-1 which averaged values within one standard deviation of established concentrations (accurate to within 0.38  $\mu\text{mol Ba}/\text{mol Ca}$  and 0.014  $\text{mmol Sr}/\text{mol Ca}$ ). We have demonstrated a sufficiently precise and accurate method for simultaneous analysis of Ba and Sr to Ca ratios in coral samples on an ICP-OES system. Expanding the application of ICP-OES in coral geochemical analysis provides a lower cost alternative to ICP-MS, while maintaining a high sample throughput.

Inductively coupled plasma optical emission spectrometry (ICP-OES) is a technique for measuring elemental concentrations based on exciting electrons in the outer valence shell and measuring the emitted radiation as they decay. Compared to inductively coupled plasma mass spectrometry (ICP-MS), the ICP-OES offers a relatively low cost, high-throughput analysis technique that is generally used to analyze elements with concentrations in the 10s of  $\mu\text{g}/\text{L}$  and above (Olesik 1991). ICP-OES is commonly used to measure the elemental composition of coral exoskeletons to be used as geochemical tracers of past ocean conditions.

Application of ICP-OES in the analysis of Sr/Ca content in marine carbonates was first introduced by Schrag (1999). Sr/Ca is inversely related to sea surface temperatures in marine carbonates (Smith et al. 1979) and is commonly used

in bivalve, foraminifera, and coral samples to generate records of sea surface temperature (SST) (De Villiers et al. 2002; Rosenthal et al. 2004; Goodkin et al. 2007; Mitsuguchi et al. 2008; Schöne et al. 2010; Yan et al. 2013). Analysis of coral skeletal Sr/Ca content for paleoclimate interpretation often produces long records of SST at monthly resolution requiring a high sample through-put (Beck et al. 1992; McCulloch et al. 1994; Shen et al. 1996; Hendy et al. 2002). Using the ICP-OES to make these measurements requires corrections to both the drift of the instrument and to the matrix interactions of Sr and Ca at varying concentrations of Ca. However, it greatly improves the cost and time per analysis compared to ICP-MS techniques.

Ba/Ca measurements in coral are commonly analyzed via ICP-MS (including sector field and laser ablation) and provide useful indications of changes in the Ba content of seawater related to fluvial or upwelling sources (Lea et al. 1989; Quinn and Sampson 2002; McCulloch et al. 2003; Montagnoni et al. 2006; Alibert and Kinsley 2008). Historically, the ICP-OES has not been utilized for simultaneously measuring Sr, Ca, and Ba content of untreated coral samples due to the inferior limits of detection compared to ICP-MS and to a

\*Correspondence: Nathalie@ntu.edu.sg

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

potentially large range of Ba/Ca concentrations in coral records compounding the difficulties to constrain matrix and drift affects simultaneously. While three studies have reported the use of ICP-OES for analyzing Ba/Ca in corals, none investigated the impact of varying ratios on either drift or matrix corrections nor do they simultaneously measure Sr/Ca (Carriquiry and Horta-Puga 2010; Chen et al. 2011; Horta-Puga and Carriquiry 2012).

We demonstrate the development of a method that expands the application of ICP-OES in coral geochemistry to precisely measure Sr, Ca, and Ba simultaneously while retaining a high sample throughput. This study also investigated the analytical implications of a potential 10-fold temporal increase in the ratio of Ba/Ca in coastal corals.

## Materials and procedures

### Coral samples

A ~ 7 mm thick coral slab was obtained from a massive *Porites* sp. colony sampled from Kusu Island, Singapore (1°13'32"N, 103°51'35"E) and cleaned (mild oxidative treatment) for 24–48 h in a 1 : 5 mix of commercially available household bleach solution (NaOCl, 3–7% reactive chlorine) and water to remove surficial organic contaminants (Grove et al. 2015). The coral slab was sonicated in deionized water for a total of 30 min (water changed every 10 min). The slab was photographed under ultraviolet (UV) light (365 nm wavelength) and the position of annual luminescent bands were used to reconstruct the annual chronology of the coral (Tanzil et al. 2013). In equatorial corals, subject to wet and dry seasons with limited temperature variability, luminescence is a more accurate way to develop an age model than X-radiographs (Brown et al. 1986). A 5-yr period was identified and the slab was drilled/milled at every 0.5 mm along the maximum growth axis starting from the top of the colony to give a total of 127 powdered coral samples.

Powdered coral samples with weights of 253–378  $\mu\text{g}$  were transferred to new, non-acid cleaned 15 mL Greiner centrifuge tubes and digested in 5 mL of 5% (~ 1.2M) trace metal grade  $\text{HNO}_3$  (Fisher Chemical) < 15 h before start of analyses, corresponding to approximate Ca concentrations of 20–40 mg/L. Sample tubes were not acid-cleaned as preliminary tests showed that these 15 mL tubes gave comparable blanks with or without acid-cleaning when analyzed within 48 h of preparation.

Digested solutions were split into 4 mL and 1 mL volumes just prior to analyses, 4 mL were used for the ICP-OES analysis. The additional 1 mL was further diluted with 3.5 mL of deionized water to produce 4.5 mL solutions containing Ca concentrations of 4 mg/L dissolved in ~ 1.1%  $\text{HNO}_3$  for analysis on the ICP-MS. All samples were analyzed in triplicates and method blanks were prepared and split for analysis on both machines in the same manner.

### Coral standards

All analyses were conducted with regular measurements of international coral standard JCp-1 and an internal lab standard, Bunaken. Bunaken is comprised of a crushed, homogenized coral passed through < 250  $\mu\text{m}$  sieve, which was collected off Bunaken Island, Indonesia by K. Hughen and was previously used as a homogenous coral standard (e.g., Goodkin et al. 2007). JCp-1 is a coral powder reference material produced by the Geological Survey of Japan. Material collected from a *Porites* sp. coral near the northeast coast of Ishigaki Island, Japan (24°33'30"N, 124°20'00"E) was repeatedly cleaned, crushed, and sieved (< 250  $\mu\text{m}$ ) and has passed homogeneity tests for  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , and Sr (Okai et al. 2002). Further inter-laboratory calibration exercises on ICP-MS indicate the suitability of JCp-1 to serve as a Ba reference material (Hathorne et al. 2013).

Coral standards prepared for comparative analyses between the ICP-MS and ICP-OES systems were split in the same manner as the coral samples described previously. Additional tests to replicate measurements of JCp-1 and Bunaken via the ICP-OES alone were conducted using the same preparatory procedures.

### ICP-OES analysis and parameters

Samples were analyzed using an iCap 6000 series ICP-OES made by Thermo Electron Corporation. A peristaltic pump supplies samples dissolved in 5%  $\text{HNO}_3$  to a glass capillary nebulizer. Argon gas entering a side arm of the nebulizer provided a low-pressure region at the sample capillary and diffuses the sample as an aerosol into a Pyrex cyclonic spray chamber (non-baffled), Thermo iCAP6x00. The sample's solvent was removed and its atoms excited via a 10,000°K plasma discharge produced by a 27.12 Mhz solid-state radio frequency generator. The radiofrequency (RF) generator that maintained plasma stability and regulated plasma temperature was set to 1150W RF power. Pressurized argon gas entered the side arm of the nebulizer at 0.6 L/min with an auxiliary gas flow of 0.5 L/min. The peristaltic pump flow rate was approximately 1 L/min and sample triplicates were integrated for 25 s each.

In this study, the light energies of spectral lines Ca (317.9 nm), Sr (421.5 nm), and Ba (455.4 nm) were converted into an electrical charge by the CID detector, the intensity of which was proportional to the concentration of the sample. An axial torch view was used for the detection of Ba to maximize the signal sensitivity, while the more stable but less sensitive radial view was used for the analysis of Sr and Ca. Ba 455.4 nm has the highest intensity and was chosen to maximize the Ba detection limit of the method. Ca and Sr are considerably more abundant in coral exoskeletons, and lower intensity spectral lines were chosen so as not to saturate the detector.

The intensity of each spectral line was calibrated via solution standards containing a range of known Ca, Sr, and Ba

**Table 1.** Preparation of drift solution standards at four different Ba/Ca ratios, but constant Sr/Ca and Ca concentrations.

| Drift standard                | 3 : 1 | 5 : 1 | 7 : 1 | 10 : 1 |
|-------------------------------|-------|-------|-------|--------|
| Ba/Ca ( $\mu\text{mol/mol}$ ) | 3.73  | 4.95  | 6.86  | 9.97   |
| Sr/Ca (mmol/mol)              | 9.16  | 9.16  | 9.16  | 9.16   |
| [Ca] (mg/L)                   | 30    | 30    | 30    | 30     |

concentrations and a linear regression between concentration and intensity was calculated daily for each new sample batch. Calibration standards were prepared by a dilution and mixture of two solution standards produced by SCP Science. The first was comprised of 9950 mg/L Ca, 199.4 mg/L Sr, and (ratio of 9.16 mmol Sr/mol Ca) the second was comprised of 10 mg/L Ba. Calibration standards were produced as a mixture of these two standards at a fixed Ba/Ca ratio of 7.18  $\mu\text{mol/mol}$ . The mixed solution was then diluted with trace metal grade 5%  $\text{HNO}_3$  to produce calibration standards containing 5 mg/L, 10 mg/L, 20 mg/L, 50 mg/L, and 80 mg/L Ca and a calibration blank of 5%  $\text{HNO}_3$ . Sample triplicates with a %RSD > 3% were removed as they indicated short-term variability in the sample entry, count detection, or plasma stability.

In order to maintain the highest possible precision and stability during ICP-OES analysis, several solution standards were periodically measured to correct for both analytical drift and potential optical interferences between elements detected simultaneously. Instrumental drift results from minor variability in the power source to the plasma, variability in the sample introduction system, and external conditions in the laboratory (De Villiers et al. 2002), but can be mitigated by preceding and following each sample with a standard solution containing constant Sr, Ca, and Ba concentrations. Standards for correcting analytical drift were prepared with the same certified SCP Science standard solutions and a correction factor was calculated from the average of the drift measurements before and after each sample, normalized to the known value in the prepared standard. In order to determine the validity of using a single drift standard to correct for such a large potential range of Ba/Ca values, four drift solutions were compared at different Ba/Ca ratios (3.73  $\mu\text{mol/mol}$ , 4.95  $\mu\text{mol/mol}$ , 6.86  $\mu\text{mol/mol}$ , and 9.97  $\mu\text{mol/mol}$  referred to as Drift Standards 3 : 1, 5 : 1, 7 : 1, and 10 : 1 henceforth,) but constant Sr/Ca (9.16 mmol Sr/mol Ca; see Table 1). The tests comprised of analyzing each drift solution measured in succession over a  $\sim 13$  h analysis period and a comparison of each time series to determine if the analytical drift varies consistently between the four solutions.

Matrix interferences between elemental lines can significantly affect the accuracy and precision of ICP-OES analyses. As the concentration of Sr, Ca, and Ba change, the detected

**Table 2.** Preparation of matrix standard sets at three different Ba/Ca ratios and a constant Sr/Ca ratio.

| Matrix standard set           | 3 : 1                 | 7 : 1                 | 10 : 1                |
|-------------------------------|-----------------------|-----------------------|-----------------------|
| Ba/Ca ( $\mu\text{mol/mol}$ ) | 3.06                  | 7.19                  | 10.27                 |
| Sr/Ca (mmol/mol)              | 9.16                  | 9.16                  | 9.16                  |
| [Ca] mg/L*                    | 10, 20, 30,<br>45, 55 | 10, 20, 30,<br>45, 55 | 10, 20, 30,<br>45, 55 |

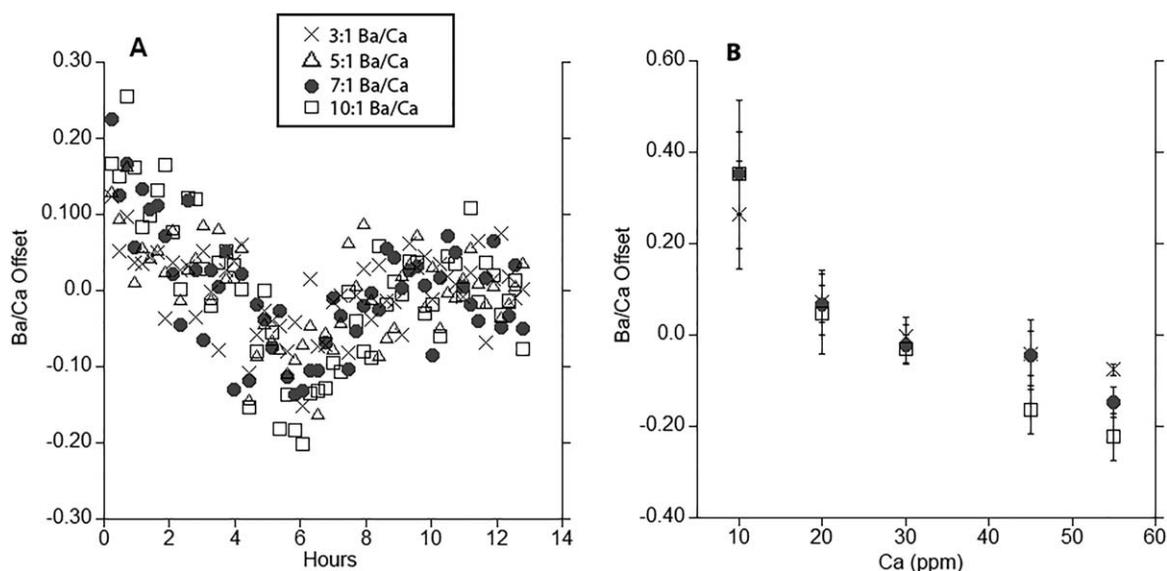
\*Note: each matrix standard set is comprised of five different solutions ranging in Ca concentration but with constant Ba/Ca and Sr/Ca.

counts of Sr/Ca and Ba/Ca can be inflated/deflated as a result of line coincidence, formation of molecules, or ionization and evaporation effects (Olesik 1991, 1996). A correction is necessary to address these effects and is accomplished by periodically measuring a set of prepared solutions that contain constant Sr/Ca and Ba/Ca ratios, but stepped Ca concentrations. One set of matrix standards consists of five solutions with constant Ba/Ca and Sr/Ca ratios, but stepped Ca concentrations (10, 20, 30, 45, and 55 mg/L Ca;) produced by diluting the same certified SCP Science solution standards as all previous standards. Matrix effects were corrected by fitting a polynomial regression that adjusts Ba/Ca values based on the concentration of Ca, to the known concentration in the standards and improves the precision and accuracy of measurements potentially affected by variability in sample weight.

In order to evaluate whether or not matrix interferences varied consistently across a large range of Ba/Ca concentrations, three sets of matrix standards were produced at the same stepped Ca concentrations but with varying Ba/Ca (3.06, 7.19, and 10.27  $\mu\text{mol Ba/mol Ca}$ : referred to as Matrix Standards 3 : 1, 7 : 1, and 10 : 1 henceforth), all with a fixed Sr/Ca of 9.16 mmol/mol (see Table 2). Matrix effects were corrected by fitting a polynomial regression that adjusted Ba/Ca values based on the concentration of Ca, to the known concentration in the standards and improved the precision and accuracy of measurements potentially affected by variability in sample weight.

In our initial tests, we aimed to evaluate each effect. The three different matrix standard sets (3 : 1, 7 : 1, 10 : 1) were placed at the beginning, middle and end of a run to evaluate optical interferences (matrix standards were replicated on three separate days). The matrix standards bracketed four Ba/Ca drift standards run at a constant Ca ppm of 30 mg/L (Table 1). The four ratios were run in sequence (3 : 1, 5 : 1, 7 : 1, 10 : 1) for a total of 55 analysis at each ratio. These runs allowed us to evaluate the behavior of both matrix and drift standards at varying Ba/Ca ratios.

Once a proper drift and matrix method correction was established, we ran the international standard JCP-1 and internal standard Bunaken as unknowns using this method.



**Fig. 1.** Solution standards prepared with 3 : 1, 5 : 1, 7 : 1, and 10 : 1  $\mu\text{mols Ba/mol Ca}$  normalized to 0 by subtracting the average concentration from each drift standard and the known concentration from each matrix standard. Each standard contains the same Sr/Ca concentration. **(A)** Ba/Ca deviation ( $\mu\text{mol/mol}$ ) in multiple drift solution standards (test replicated three times). **(B)** Deviation of Ba/Ca ( $\mu\text{mol/mol}$ ) in stepped matrix standards ranging in Ca concentration. Bars indicate range of variability between three separate days of testing.

**Table 3.** Ba/Ca of drift solution standards ( $\mu\text{mol Ba/mol Ca}$ ) and their variability ( $n = 55$ ) over  $\sim 13$  h analysis period. Correlation coefficients for 5-point running averages are defined relative to the 7 : 1 drift trend.

| Drift standard          | 3 : 1 | 5 : 1 | 7 : 1 | 10 : 1 |
|-------------------------|-------|-------|-------|--------|
| Average                 | 3.74  | 4.95  | 6.86  | 9.97   |
| Minimum                 | 3.58  | 4.78  | 6.72  | 9.76   |
| Maximum                 | 3.86  | 5.11  | 7.08  | 10.22  |
| Correlation coefficient | 0.90  | 0.85  | —     | 0.96   |

The values measured for JcP-1 and Bunaken were compared to established values for JcP-1 and to measurements made on the same solutions using ICP-MS. Finally, the method was employed to analyze Ba/Ca measurement from a coral collected off of Kusu Island, Singapore. The samples were prepared as above and split after dissolution for analysis on both an ICP-OES and ICP-MS.

#### ICP-MS analysis and parameters

Solutions were analyzed for  $^{137}\text{Ba}$ ,  $^{138}\text{Ba}$ , and  $^{43}\text{Ca}$  with a Thermo Scientific iCAP Q ICP-MS. The ICP-MS was run in standard mode and samples were introduced into the system with a pump speed of 40 rpm. The sample was converted into an aerosol via an argon carrier gas and a quartz glass peltier-cool cyclonic spray chamber with a 2.5 mm ID quartz injector. The RF power was set at 1550W, with cool, auxiliary, and nebulizer gas flows set at 14 L/min, 0.8 L/min, and 1.015 L/min, respectively. Sample order

was randomized and drift and blanks ran every  $\sim 10$  samples. Element concentrations and molar ratios were calculated from calibration curves derived from the same solution standards that were used for the ICP-OES. Solution standards were further diluted to Ca concentrations ranging from 1 to 5 mg/L and Ba concentrations ranging from 0.05 to 1  $\mu\text{g/L}$  and used to calculate linear calibration regressions.

#### Assessment

##### Instrumental drift corrections

Tests analyzing drift standards showed that over a course of an  $\sim 13$  h run Ba/Ca ratios can vary by up to 0.25  $\mu\text{mol Ba/mol Ca}$  (Fig. 1A) relative to the average measured value in each respective solution; a small amount considering the range of Ba/Ca typically measured in unknowns, e.g., ranging from 1 to 10  $\mu\text{mol Ba/mol Ca}$  in a single coral record (Hart and Cohen 1996; Montaggioni et al. 2006; Moyer et al. 2012). Some minor variability occurred between Drift Standards 3 : 1, 5 : 1, 7 : 1, and 10 : 1, however in this test the standards are temporally spaced much further apart than in a normal analysis where a single drift standard would be run between samples instead of once every fourth sample as performed in this experiment. In this analysis, we aimed to determine whether all ratios covaried over the large changes due to drift. Drift standards 3 : 1, 5 : 1, and 10 : 1 varied closely and correlated significantly with the 7 : 1 standard when 5-point running averages were considered ( $r = 0.90$ , 0.85, and 0.96 respectively, Table 3). Therefore, we propose that a single solution standard with constant Sr, Ca, and Ba

**Table 4.** Average Ba/Ca of matrix solution standards ( $\mu\text{mol Ba/mol Ca}$ ) across 3 d at stepped Ca concentrations (10–55 mg/L). Correlation coefficient is defined relative to the 7 : 1 matrix trend. Coefficient of determination ( $R^2$ ),  $p$ -value ( $\rho$ ), and number of samples ( $N$ ) are reported for the best fit polynomial used to apply matrix corrections at each ratio.

| Matrix standards                                | 3 : 1  | 7 : 1  | 10 : 1 |
|---|--------|--------|--------|
| Actual Ba/Ca                                    | 3.06   | 7.19   | 10.27  |
| 10 mg/L   | 3.34   | 7.55   | 10.63  |
| 20 mg/L   | 3.15   | 7.26   | 10.32  |
| 30 mg/L   | 3.08   | 7.17   | 10.24  |
| 45 mg/L   | 3.04   | 7.15   | 10.11  |
| 55 mg/L   | 3.01   | 7.05   | 10.05  |
| $R^2$ of best fit polynomial within each ratio  | 0.75   | 0.90   | 0.82   |
| $\rho$ of best fit polynomial within each ratio | <0.001 | <0.001 | <0.001 |
| $N$   | 49     | 50     | 74     |
| Correlation coefficient of comparisons to 7 : 1 | 0.99   | —      | 0.98   |

is sufficient to correct for instrumental drift in Ba/Ca as previously used (Carriquiry and Horta-Puga 2010; Chen et al. 2011; Horta-Puga and Carriquiry 2012).

#### Matrix corrections

Averages of matrix standards (3 : 1, 10 : 1) at stepped Ca concentrations establish matrix interferences of similar magnitude and were correlated closely to the 7 : 1 standard ( $r = 0.99$  and  $0.98$  respectively, Table 4). The averages were normalized to 0 by subtracting the known Ba/Ca for each solution standard (Fig. 1B) to compare the offsets between Ba/Ca ratios. Statistically robust polynomial best fits were applied at each ratio to evaluate matrix interferences (see Table 4). For each standard the largest spectral interferences occur at Ca ppm extremes ( $< 15$  mg/L Ca and  $> 45$  mg/L Ca) as does the greatest variability between the different matrix standard ratios. This indicated that in order to minimize matrix interferences, analysis of unknowns should not extend below 15 mg/L or above 45 mg/L Ca. However the variability (one standard deviation) within any single matrix standard was comparable to the variability between standards of differing Ba/Ca ratios, demonstrating that only one molar ratio (7 : 1) is necessary to correct matrix interferences for a range of unknowns (3–10  $\mu\text{mol Ba/mol Ca}$ ).

#### Accuracy and precision of analysis

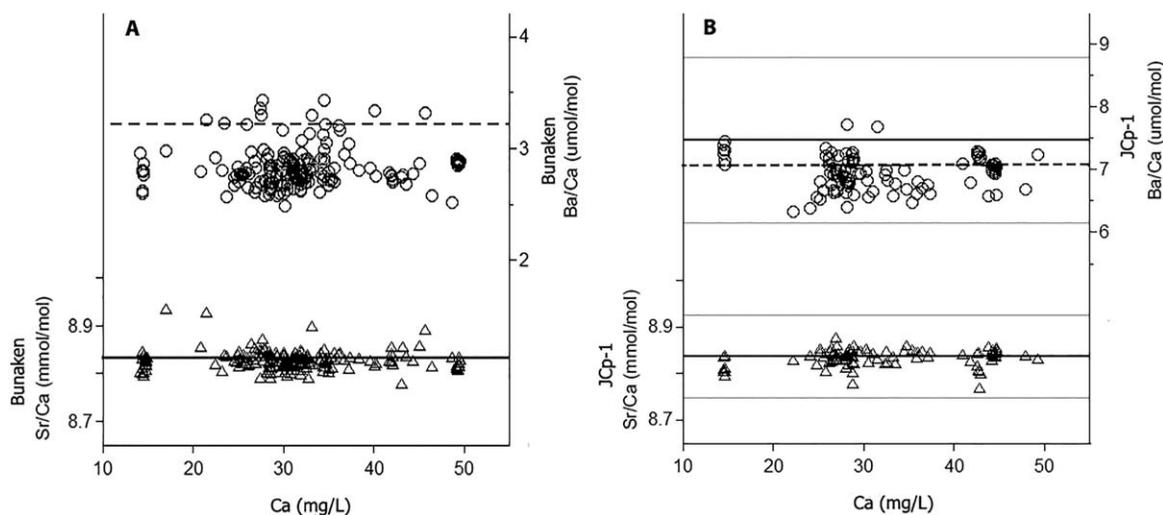
The ICP-MS returned an average Ba/Ca ratio of  $7.06 \pm 0.33$   $\mu\text{mol/mol}$  (precision defined by one standard deviation, where  $n = 28$ ) for JCp-1, well within one standard deviation of the established value ( $7.465 \pm 0.655$   $\mu\text{mol/mol}$ ) (Hathorne et al. 2013), indicating robust results. Measured values for internal lab standard Bunaken exhibited a

consistent offset between the ICP-MS and ICP-OES analyses (Fig. 2A). An offset factor of 1.14 was defined by the ratio between the averaged Bunaken values measured by the ICP-MS (3.22  $\mu\text{mol Ba/mol Ca}$ ,  $n = 28$ ) divided by the averaged Bunaken values measured by the ICP-OES (2.82  $\mu\text{mol Ba/mol Ca}$ ,  $n = 174$ ). The offset between the two machines may be a result of spectral interferences on the ICP-OES with other elements contained in the coral lattice. Complex matrices, which are expected in coral samples, are capable of affecting the relative magnitudes of the signal and background noise (Olesik 1991). This offset did not occur within solution standards, which only consisted of Ca, Sr, Mg, and Ba. By multiplying the ICP-OES results with the offset factor defined above (1.14), we corrected the ICP-OES measurements of the international standard JCp-1 (Fig. 2B), yielding an average of  $6.92 \pm 0.38$   $\mu\text{mol Ba/mol Ca}$  (precision defined by one standard deviation, where  $n = 166$ ), within one standard deviation of the established multi-lab average.

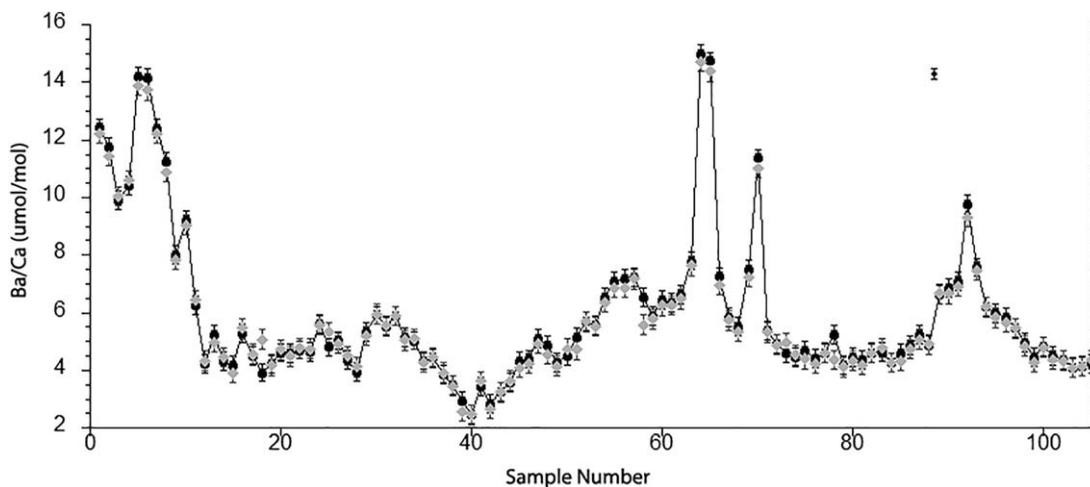
Kusu Island coral samples split for analysis on both the ICP-OES and ICP-MS systems and treated as described above demonstrated minor differences relative to the overall variability of Ba/Ca in the coral (Fig. 3), with a root mean square of the residuals (RMSR) between the two techniques of 0.18  $\mu\text{mol Ba/mol Ca}$  (less than the 0.38 analytical error of the ICP-OES as determined by the precision of JCp-1 measurements). In addition, measurements of the coral tissue layer demonstrate the offset is consistent across a large range of Ba/Ca ratios ( $\sim 2$ –95  $\mu\text{mol Ba/mol Ca}$ , Table 5) and is correctable with comparative analyses of our internal coral standard. The %RSD of Ba/Ca per run on the ICP-OES can range from  $\sim 3\%$  to  $8\%$  (as defined by the precision of JCp-1 measurements). However, this variability is relatively minor compared to the potential range of Ba/Ca found in coral skeletons and thus does not preclude the identification of changes in oceanographic conditions reflected in the coral chemistry.

#### Effect on Sr/Ca analysis

A potential concern for adding Ba to a multi-element analysis of coral skeletons via ICP-OES is an effect on the established methodology for measuring Sr/Ca to produce sea surface temperature reconstructions. No adverse effects on the precision or accuracy of analysis on international standard JCp-1 were detected (Fig. 2A), with an average value of 8.83 mmol Sr/mol Ca and a %RSD of less than 0.2% ( $n = 191$ ) in excellent agreement with the established multi-lab values (Hathorne et al. 2013). Rather, the increased integration times and broader calibration ranges necessary for measuring Ba in this method are likely to expand the detection limits of Sr and Ca. However, the length of time required to analyze a sample roughly doubled. These results indicate that Ba can be added to a multi-elemental analysis of Sr and Ca without reducing the accuracy or precision of SST reconstructions while still maintaining a relatively high



**Fig. 2.** Measured values of Ba/Ca and Sr/Ca on the ICP-OES are denoted as open circles and triangles respectively. **(A)** Internal lab coral standard Bunaken measurements ( $n = 174$ ) with dashed line indicating average Ba/Ca value obtained via the ICP-MS system ( $n = 28$ ) and solid line indicating long term lab average Sr/Ca ( $n = 947$ ). **(B)** International standard JCP-1 measurements ( $n = 166$ ) with dashed lines indicating the average Ba/Ca value obtained via the ICP-MS system ( $n = 28$ ). The solid lines denote the established values of Ba/Ca and Sr/Ca, while the gray lines denote the range of uncertainty determined for JCP-1 (Hathorne et al. 2013).



**Fig. 3.** Ba/Ca measurements on *Porites* sp. colony sampled from Kusu Island, Singapore via ICP-OES (closed circles) and ICP-MS (gray diamonds) with RMSR plotted (closed diamond, =  $0.18 \mu\text{mol Ba/mol Ca}$ , top right corner). Bars indicate analytical error defined by SD of JCP-1 measurements on the ICP-OES and MS systems ( $0.38$  and  $0.33 \mu\text{mol/mol}$  respectively).

throughput of samples compared to other analytical instruments such as ICP-MS.

### Implications for coral geochemistry

We have demonstrated the first viable technique for simultaneously measuring Ba and Sr to Ca ratios via ICP-OES while maintaining the precision necessary for oceanographic interpretations (within  $0.38 \mu\text{mol/mol}$  and  $0.014 \text{ mmol/mol}$ , respectively). This investigation has determined that analytical drift and matrix interferences, inherent to ICP-OES analyses, do not significantly vary within a large range of Ba/Ca concentrations ( $\sim 2\text{--}95 \mu\text{mol/mol}$ ) and allow for the

continued use of conventional drift and matrix corrections. This method reduces the dependency on ICP-MS techniques for measuring Ba/Ca in coral crystal lattices.

### Discussion

ICP-OES is ideal for coral records that often require the analysis of thousands of samples. Due to low cost, high sample throughput, and simple operation, ICP-OES has developed into a useful tool for marine carbonate chemistry. Adding the ability to analyze Ba in conjunction with Sr and Ca, greatly expands the ability of researchers to produce

**Table 5.** Ba/Ca ( $\mu\text{mol/mol}$ ) for coral tissue layer samples. % Difference is defined by  $([\text{Ba/Ca}]_{\text{MS}} - [\text{Ba/Ca}]_{\text{OES}}) \div [\text{Ba/Ca}]_{\text{MS}}$ .

| ICP-MS | ICP-OES | % Difference |
|--------|---------|--------------|
| 95.53  | 95.00   | 0.55         |
| 17.46  | 17.28   | 1.06         |
| 24.97  | 24.88   | 0.35         |
| 19.93  | 19.95   | -0.10        |
| 32.43  | 31.85   | 1.78         |
| 23.36  | 23.35   | 0.03         |
| 27.95  | 27.74   | 0.74         |
| 22.25  | 22.43   | -0.81        |
| 23.42  | 23.72   | -1.25        |
| 14.72  | 14.87   | -1.02        |
| 14.13  | 14.30   | -1.18        |
| 13.51  | 13.85   | -2.55        |
| 14.53  | 15.13   | -4.11        |

meaningful oceanographic reconstructions. This provides a solution for laboratories and research groups attempting to produce both SST and fluvial/upwelling records concurrently without the use of the considerably more expensive ICP-MS systems. We believe the oceanographic community will benefit from the development of a more affordable analytical technique.

This method does however require greater spectral peak integration times as well as greater rinsing and flush times compared to established Sr/Ca methods. Depending on the precision/accuracy of the analysis required, and the model of ICP-OES, analysis time can increase by as much as 100%. However, in general, the sample throughput is expected to be higher than that of most ICP-MS systems. It is important to note that this increase in integration and flush times may increase the amount of sample needed by twofold, depending on the concentration of Ba, potentially limiting its application to coral species of higher density or greater annual extension.

### Comments and recommendations

Application of this method requires an ICP-OES system with dual mode torch view capabilities. Fundamental to this method is the ability to analyze the spectral wavelengths of Ca (317.9 nm) and Sr (421.5 nm) on the radial view and Ba (455.4 nm) on the axial view. This allows for the large differences in analytical range to be overcome by maximizing the sensitivity of Ba detection without saturating the detector with the more abundant and/or sensitive wavelengths. Older ICP-OES instruments lacking this dual view functionality will not likely be able to apply this technique for measuring Ba/Ca.

If applying this method to other marine carbonates, it is important to test the matrix of the proposed samples and reconfigure parameters such as the radiofrequency power and the nebulizer flow rate to minimize background signals.

Lower detection limits might be attainable with the use of higher-grade nitric acid, however this would greatly increase the cost of analysis.

### References

- Alibert, C., and L. Kinsley. 2008. A 170-year Sr/Ca and Ba/Ca coral record from the western Pacific warm pool: 1. What can we learn from an unusual coral record? *J. Geophys. Res. Oceans* (1978–2012) **113**. doi:10.1029/2007JC004263
- Beck, J. W., E. R. Lawrence, E. Ito, F. W. Taylor, J. Recy, F. Rougerie, P. Joannot, and C. Henin. 1992. Sea-surface temperature from coral skeletal strontium/calcium ratios. *Science* **257**: 644–647. doi:10.1126/science.257.5070.644
- Brown, B., M. Le Tissier, L. Howard, M. Charuchinda, and J. Jackson. 1986. Asynchronous deposition of dense skeletal bands in *Porites lutea*. *Mar. Biol.* **93**: 83–89. doi:10.1007/BF00428657
- Carrquiry, J. D., and G. Horta-Puga. 2010. The Ba/Ca record of corals from the Southern Gulf of Mexico: Contributions from land-use changes, fluvial discharge and oil-drilling muds. *Mar. Pollut. Bull.* **60**: 1625–1630. doi:10.1016/j.marpolbul.2010.06.007
- Chen, T., K. Yu, S. Li, T. Chen, and Q. Shi. 2011. Anomalous Ba/Ca signals associated with low temperature stresses in *Porites* corals from Daya Bay, northern South China Sea. *J. Environ. Sci.* **23**: 1452–1459. doi:10.1016/S1001-0742(10)60606-7
- De Villiers, S., M. Greaves, and H. Elderfield. 2002. An intensity ratio calibration method for the accurate determination of Mg/Ca and Sr/Ca of marine carbonates by ICP-AES. *Geochem. Geophys. Geosyst.* **3**. doi:10.1029/2001GC000169
- Goodkin, N. F., K. A. Hughen, and A. L. Cohen. 2007. A multicolor calibration method to approximate a universal equation relating Sr/Ca and growth rate to sea surface temperature. *Paleoceanography* **22**. doi:10.1029/2006PA001312
- Grove, C. A., A. Rodriguez-Ramirez, G. Merschel, R. Tjallingii, J. Zinke, A. Macia, and G.-J. A. Brummer. 2015. UV-spectral luminescence scanning: Technical updates and calibration developments, p. 563–581. *In* I. W. Croudace, R. G. Rothwell, [eds.], *Micro-XRF studies of sediment cores*. Springer.
- Hart, S. R., and A. L. Cohen. 1996. An ion probe study of annual cycles of Sr/Ca and other trace elements in corals. *Geochim. Cosmochim. Acta* **60**: 3075–3084. doi:10.1016/0016-7037(96)00154-8
- Hathorne, E. C., and others. 2013. Interlaboratory study for coral Sr/Ca and other element/Ca ratio measurements. *Geochem. Geophys. Geosyst.* **14**: 3730–3750. doi:10.1002/ggge.20230
- Hendy, E. J., M. K. Gagan, C. A. Alibert, M. T. McCulloch, J. M. Lough, and P. J. Isdale. 2002. Abrupt decrease in tropical Pacific sea surface salinity at end of Little Ice Age. *Science* **295**: 1511–1514. doi:10.1126/science.1067693

- Horta-Puga, G., and J. D. Carriquiry. 2012. Coral Ba/Ca molar ratios as a proxy of precipitation in the northern Yucatan Peninsula, Mexico. *Appl. Geochem.* **27**: 1579–1586. doi:[10.1016/j.apgeochem.2012.05.008](https://doi.org/10.1016/j.apgeochem.2012.05.008)
- Lea, D. W., G. T. Shen, and E. A. Boyle. 1989. Coralline barium records temporal variability in equatorial Pacific upwelling. *Nature* **340**: 373–376. doi:[10.1038/340373a0](https://doi.org/10.1038/340373a0)
- McCulloch, M. T., M. K. Gagan, G. E. Mortimer, A. R. Chivas, and P. J. Isdale. 1994. A high-resolution Sr/Ca and  $\delta^{18}\text{O}$  coral record from the Great Barrier Reef, Australia, and the 1982–1983 El Niño. *Geochim. Cosmochim. Acta* **58**: 2747–2754. doi:[10.1016/0016-7037\(94\)90142-2](https://doi.org/10.1016/0016-7037(94)90142-2)
- McCulloch, M., S. Fallon, T. Wyndham, E. Hendy, J. Lough, and D. Barnes. 2003. Coral record of increased sediment flux to the inner Great Barrier Reef since European settlement. *Nature* **421**: 727–730. doi:[10.1038/nature01361](https://doi.org/10.1038/nature01361)
- Mitsuguchi, T., P. X. Dang, H. Kitagawa, T. Uchida, and Y. Shibata. 2008. Coral Sr/Ca and Mg/Ca records in Con Dao Island off the Mekong Delta: Assessment of their potential for monitoring ENSO and East Asian monsoon. *Glob. Planet. Change* **63**: 341–352. doi:[10.1016/j.gloplacha.2008.08.002](https://doi.org/10.1016/j.gloplacha.2008.08.002)
- Montaggioni, L. F., F. Le Cornec, T. Corrège, and G. Cabioch. 2006. Coral barium/calcium record of mid-Holocene upwelling activity in New Caledonia, South-West Pacific. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **237**: 436–455. doi:[10.1016/j.palaeo.2005.12.018](https://doi.org/10.1016/j.palaeo.2005.12.018)
- Moyer, R. P., A. G. Grottoli, and J. W. Olesik. 2012. A multiproxy record of terrestrial inputs to the coastal ocean using minor and trace elements (Ba/Ca, Mn/Ca, Y/Ca) and carbon isotopes ( $\delta^{13}\text{C}$ ,  $\Delta^{14}\text{C}$ ) in a nearshore coral from Puerto Rico. *Paleoceanography* **27**. doi:[10.1029/2011PA002249](https://doi.org/10.1029/2011PA002249)
- Okai, T., A. Suzuki, H. Kawahata, S. Terashima, and N. Imai. 2002. Preparation of a new Geological Survey of Japan geochemical reference material: Coral JCp-1. *Geostand. Newslett.* **26**: 95–99. doi:[10.1111/j.1751-908X.2002.tb00627.x](https://doi.org/10.1111/j.1751-908X.2002.tb00627.x)
- Olesik, J. W. 1991. Elemental analysis using ICP-OES and ICP/MS. *Anal. Chem.* **63**: 12A–21A. doi:[10.1021/ac00001a001](https://doi.org/10.1021/ac00001a001)
- Olesik, J. W. 1996. Peer reviewed: Fundamental research in ICP-OES and ICPMS. *Anal. Chem.* **68**: 469A–474A.
- Quinn, T. M., and D. E. Sampson. 2002. A multiproxy approach to reconstructing sea surface conditions using coral skeleton geochemistry. *Paleoceanography* **17**: 14–11–14–11. doi:[10.1029/2000PA000528](https://doi.org/10.1029/2000PA000528)
- Rosenthal, Y., and others. 2004. Interlaboratory comparison study of Mg/Ca and Sr/Ca measurements in planktonic foraminifera for paleoceanographic research. *Geochem. Geophys. Geosyst.* **5**. doi:[10.1029/2003GC000650](https://doi.org/10.1029/2003GC000650)
- Schöne, B. R., Z. Zhang, D. Jacob, D. P. Gillikin, T. Tütken, D. Garbe-Schönberg, and A. Soldati. 2010. Effect of organic matrices on the determination of the trace element chemistry (Mg, Sr, Mg/Ca, Sr/Ca) of aragonitic bivalve shells (*Arctica islandica*)—Comparison of ICP-OES and LA-ICP-MS data. *Geochem. J.* **44**: 23–37.
- Schrag, D. P. 1999. Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates. *Paleoceanography* **14**: 97–102. doi:[10.1029/1998PA900025](https://doi.org/10.1029/1998PA900025)
- Shen, C.-C., T. Lee, C.-Y. Chen, C.-H. Wang, C.-F. Dai, and L.-A. Li. 1996. The calibration of D [Sr/Ca] versus sea surface temperature relationship for *Porites* corals. *Geochim. Cosmochim. Acta* **60**: 3849–3858. doi:[10.1016/0016-7037\(96\)00205-0](https://doi.org/10.1016/0016-7037(96)00205-0)
- Smith, S. V., R. W. Buddemeier, R. C. Redalje, and J. E. Houck. 1979. Strontium-calcium thermometry in coral skeletons. *Science* **204**: 404–407. doi:[10.1126/science.204.4391.404](https://doi.org/10.1126/science.204.4391.404)
- Tanzil, J. T., B. E. Brown, R. P. Dunne, J. N. Lee, J. A. Kaandorp, and P. A. Todd. 2013. Regional decline in growth rates of massive *Porites* corals in Southeast Asia. *Glob. Chang. Biol.* **19**: 3011–3023. doi:[10.1111/gcb.12279](https://doi.org/10.1111/gcb.12279)
- Yan, H., D. Shao, Y. Wang, and L. Sun. 2013. Sr/Ca profile of long-lived *Tridacna gigas* bivalves from South China Sea: A new high-resolution SST proxy. *Geochim. Cosmochim. Acta* **112**: 52–65. doi:[10.1016/j.gca.2013.03.007](https://doi.org/10.1016/j.gca.2013.03.007)

#### Acknowledgments

We would like to thank Konrad Huguen for the development of the Bunaken coral standard. Fidel Costa and Garreth Fabbro for laboratory access and assistance in ICP-MS analysis. Taufiq Mohtar and Edwin Sia for helping with our laboratory experiments and sample preparation. K. Delong for discussions on ICP-OES methodologies. This project was funded by the National Research Foundation Singapore under its Singapore NRF Fellowship scheme awarded to N.F. Goodkin (National Research Fellow Award No. NRF-RF2012-03), as administered by the Earth Observatory of Singapore and the Singapore Ministry of Education under the Research Centres of Excellence initiative.

#### Conflict of Interest

None declared.

Submitted 04 April 2016

Revised 16 August 2016

Accepted 07 November 2016

Associate editor: Maeve Lohan