Interlaboratory study for coral Sr/Ca and other element/Ca ratio measurements

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1. Introduction

The geochemical analysis of annually banded coral skeletons provides the opportunity to extend the instrumental record of tropical sea surface conditions. Elements such as Mn, Cu, Zn, Ba, and Pb in coral skeletons are useful indicators of marine pollution and sediment input [e.g., Fallon et al., 2002; Sinclair and McCulloch, 2004; Prouty et al., 2008], while the Li, B, Mg, Sr, and U content of tropical corals are related to water temperature at various locations [e.g., Beck et al., 1992; McCulloch et al., 1994; Min et al., 1995; Matsu- guchi et al., 1996; Gagan et al., 1998; Sinclair et al., 1998; Quinn and Sampson, 2002; Felis et al., 2009; Hathorne et al., 2013]. The Sr/Ca ratio is by far the most utilized elemental proxy for water temperature in corals and has been shown to be robust across a range of salinities [e.g., Gagan et al., 1998]. High-precision measurements of Sr/Ca are required to reconstruct SST since Sr/Ca changes by only 0.06 mmol/mol or 0.67% with every degree Celcius [e.g., Corrège, 2006]. In the early studies of coral Sr/Ca, isotope dilution (ID) Thermal Ionization Mass Spectrometry (TIMS) was used to obtain very precise ratios (e.g., ±0.03% (2 SD)) [Beck et al., 1992]. However, TIMS is a very time consuming method, and the advent of Inductively Coupled Plasma (ICP) sources combined with Mass Spectrometry (ICP-MS) or Optical Emission Spectroscopy (ICP-OES, note that Atomic Emission Spectroscopy (AES) is synonymous with OES) has greatly increased sample throughput and reduced costs. While ICP techniques can approach the precision of TIMS [e.g., Schrag, 1999], especially if ID techniques are employed [Fernandez et al., 2011], the precision is generally between 0.2 and 1% at the 2σ (95% confidence) level [e.g., Le Corneè and Corrège, 1997; Rosenthal et al., 1999; Ourbak et al., 2006; Nurhati et al., 2011]. A well-characterized reference material, with the appropriate matrix, is required to improve accuracy and ensure quality data are reported [Jochum and Nohl, 2008]. Progress has been made with this for analyses of other marine biogenic carbonates namely fish Otoliths [Sturgeon et al., 2005] and Foraminifera [Greaves et al., 2008] but those standards are not appropriate for the high Sr content of coral skeletons and only approximate the coral matrix.

Initial studies of coral Sr/Ca palaeothermometry conducted both the measurements for the modern calibration of the proxy thermometer and the reconstruction of past seawater temperatures in the same laboratory. The growth of the coral geochemistry field in recent years has meant the direct comparison of data generated in different laborato-

2. Materials and Methods

2.1. Suitability and Homogeneity of Reference Materials

The first consideration when choosing a reference material is that the matrix is similar to that of the samples and that the concentrations of the elements of interest are similar to those found in the samples. The reference material best suited to coral element/Ca measurements is a coral sample with a matrix virtually identical to that of the samples, including residual organics. The second consideration is finding a suitably homogenous reference material that can be analyzed many thousands of times. Coral skeletons are chemically heterogeneous on a variety of length scales [e.g., Sinclair et al., 1998; Meibom et al., 2008] making the preparation of a suitably homogenous reference material from a coral skeleton difficult. Even so, many laboratories have in-house coral powder reference materials they employ for quality control purposes, although there is not likely to be enough material to share with laboratories around the world.

The Geological Survey of Japan (GSJ) prepared a coral powder reference material from a Porites sp. coral collected on the northeast coast of Ishigaki Island, Ryukyu Islands, Japan (24°33'30"N, 124°20'00"E). The coral was cleaned, cut, crushed, sieved to >420 μm, washed...
again, mixed in a ball mill for 4 days, and finally sieved to <250 μm to prepare the “JCp-1” powder reference material (see Okai et al. [2002] for more details). The coral was not bleached during processing. The resulting 15 kg of reference material passed homogeneity tests for MgO, CaO, Na₂O, and Sr using 100 mg test portions [Okai et al., 2002]. This makes JCp-1 an ideal candidate for an international coral reference material but unfortunately since the completion of this study the JCp-1 powder is no longer commercially available because of export restrictions on corals. All the JCp-1 powder used in this study was obtained free of charge for collaborative research purposes and many laboratories throughout the world now have enough powder to last many years. It should also be possible for such labs to send small aliquots of their JCp-1 powder to other laboratories for noncommercial quality control purposes. Although the commercial unavailability of the JCp-1 powder hinders its use as an international reference material it is now the best characterized coral reference material and should play a critical role in the traceability [e.g., Kane and Potts, 2002] of any future characterization of new coral reference materials. Powdered reference materials are preferred over solutions because of the long-term stability of such geological materials as demonstrated by reference materials like G-1 and W-1 being used for over 50 years [Kane, 2004].

[7] Before the international interlaboratory study could be conducted, it was necessary to conduct additional homogeneity tests as such information has not been published for the JCt-1 powder and the previous homogeneity tests for JCp-1 were performed on relatively large test portions (100 mg). It is routine for coral element/Ca analyses to consume 1 mg or less of coral powder, so homogeneity tests were conducted with test portions of approximately 150 μg, 500 μg, and 1 mg of JCp-1 and JCt-1 powders. Weighed powder was transferred to acid cleaned high-density polyethylene (HDPE) bottles and dissolved in 0.3 M HNO₃ overnight. Additional samples of JCp-1 were obtained from two different bottles of JCp-1 powder meaning three different bottles or batches were investigated. Solutions were diluted to have a Ca concentration of 10 ppm and were analyzed for 7Li, 11B, 25Mg, 43Ca, 55Mn, 88Sr, 137Ba, and 238U with a sector field JCP-MS (Element 2) in low-resolution mode. Element/Ca ratios were calculated directly from the X/43Ca intensity ratios following a method adapted from Rosenthal et al. [1999]. The results suggest Li, B, Mg, Sr, and U are all homogenously distributed using test portions ≥150 μg (Figures 1 and 2). It is interesting to note that dissolutions of both reference materials prepared in the same manner a few months previously exhibited higher B/Ca ratios (“Old solutions” labeled in Figures 1 and 2), suggesting either B leaching from the acid-cleaned bottles or some other aging process affecting B only. Besides occasional outliers, the Ba results suggest the material may be suitable as a reference material as there is no clear trend with test portion size (Figures 1 and 2). The results for Mn on the other hand (not shown), with relative standard deviations of more than 20% and 40%, clearly demonstrate Mn is heterogeneously distributed in both materials at all the test portion sizes investigated.

2.2. Outline of Interlab Study

[8] An invitation letter detailing the initial results of the interlaboratory study from theIODP Expedition 310 participants and the results of homogeneity tests described above was sent to authors who had published coral element/Ca ratio data in recent years. Interested parties then replied with a postal address, and laboratories across four continents were sent approximately 1 g aliquots of JCp-1 and JCt-1 powders. Participants were asked to analyze the powders in the same manner as coral samples in their laboratories. Participants were
requested to analyze multiple dissolutions of both JCp-1 and JCT-1 for as many elements as routinely acquired in their laboratory and to report averages and standard deviations for each dissolution analyzed. These data and some general information concerning the procedures followed were reported to an independent data collector to ensure the data remained anonymous. The lead author was given unidentified data files and a list of participants who had returned data. Participants are expected to identify themselves based on the general information they provided (Table 1).
2.3. Isotope Dilution (ID) as the Definitive Method

For certification of reference materials a definitive measurement method is required, as defined by International Organization for Standardization (ISO) Guide 35 [e.g., Kane et al., 2003]. ID analysis is considered a definitive method as, although ultimately dependent on the spike calibration, the result stems from measurements directly related to
<table>
<thead>
<tr>
<th>Lab</th>
<th>Lab 1</th>
<th>Lab 2</th>
<th>Lab 3</th>
<th>Lab 4</th>
<th>Lab 5</th>
<th>Lab 6</th>
<th>Lab 7</th>
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<th>Lab 18</th>
<th>Lab 19</th>
<th>Lab 20</th>
<th>Lab 21</th>
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<tbody>
<tr>
<td>Test Portion Mass (mg)</td>
<td>2</td>
<td>13</td>
<td>50</td>
<td>5.5</td>
<td>100</td>
<td>14</td>
<td>173</td>
<td>1.3</td>
<td>4.3</td>
<td>0.5</td>
<td>1</td>
<td>20</td>
<td>0.25</td>
<td>25</td>
<td>0.5</td>
<td>208</td>
<td>0.3</td>
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<td>5</td>
<td>2.5</td>
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<tr>
<td>Dissolution Acid: Pure HNO₃ m &gt;18.2 M Water Volume of Dissolution Acid (mL)</td>
<td>0.5 M</td>
<td>0.1 M</td>
<td>0.3 M</td>
<td>2 % vol.</td>
<td>4 N</td>
<td>5% vol.</td>
<td>2% vol.</td>
<td>1.1 M</td>
<td>3%</td>
<td>0.075 M</td>
<td>0.1M</td>
<td>0.1M</td>
<td>1.95% vol.</td>
<td>0.5 M</td>
<td>1% v/v</td>
<td>2% v/v</td>
<td>0.3 M</td>
<td>8.9% w/w</td>
<td>0.3 M</td>
<td>5% vol</td>
<td></td>
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<tr>
<td>Dissolution Vessel Samples Centrifuged</td>
<td>15 mL PP</td>
<td>30 mL LDPE 5000 rpm, 10 mm</td>
<td>7000 rpm</td>
<td>30 mL PP</td>
<td>Teflon 11,000 rpm, 20 mm</td>
<td>LDPE 1000 mL LDPE</td>
<td>microcentrifuge</td>
<td>15 mL PE microcentrifuge</td>
<td>2 mL microcentrifuge</td>
<td>FEP</td>
<td>LDPE 125</td>
<td>PolyStyrol 11 mL</td>
<td>0.5 mL PP</td>
<td>10 mL PP</td>
<td>HDPE</td>
<td>HDPE microcentrifuge</td>
<td>Teflon</td>
<td>30 mL HDPE</td>
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<td>Other Treatment</td>
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<td>Dissolution and Analysis Storage Vessel (if Different)</td>
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<td>Analysis Vessel (if Different)</td>
<td>10 mL PE</td>
<td>7 mL PFA</td>
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<tr>
<td>ppm Ca Analyzed Dilution Acid Strength (if Different)</td>
<td>40-60</td>
<td>15</td>
<td>20</td>
<td>40-110</td>
<td>80-90</td>
<td>2%</td>
<td>61-63</td>
<td>28-30</td>
<td>16</td>
<td>35-200</td>
<td>~100</td>
<td>90-110</td>
<td>40</td>
<td>10-20</td>
<td>100</td>
<td>35-40</td>
<td>8</td>
<td>10</td>
<td>160</td>
<td>4.2% w/w</td>
<td>20</td>
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<tr>
<td>Internal Standard Elements (if Any)</td>
<td>Y</td>
<td>Sc, Y, and In</td>
<td>Be, Sc, In</td>
<td>ln</td>
<td>ln</td>
<td>Sc</td>
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<tr>
<td>Instrument Type</td>
<td>ICP-AES</td>
<td>ICP-OES</td>
<td>SF-ICP-MS</td>
<td>KPM</td>
<td>KPM</td>
<td>ICP-MS</td>
<td>KPM</td>
<td>KCP-MS</td>
<td>KPM</td>
<td>ICP-MS</td>
<td>ICP-MS</td>
<td>ICP-MS</td>
<td>SF-ICP-MS</td>
<td>ICP-OES</td>
<td>KPM</td>
<td>ICP-MS</td>
<td>ICP-AES</td>
<td>ICP-OES</td>
<td>ICP-OES</td>
<td>SF-ICP-MS</td>
<td>ICP-OES or MS</td>
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</table>
the SI units kilograms and moles [e.g., Watters et al., 1997]. In this study, one laboratory measured Mg/Ca and Sr/Ca ratios using an improved version of the ID method described in Fernandez et al. [2011]. The main improvements involved adapting the method to use a Neptune multicollector (MC) ICP-MS (ThermoFinnigan) to analyze the isotope ratios of dissolved and spiked coral samples. Specifically, instrumental methods for Ca and Sr on the MC-ICP-MS were adapted from Wieser et al. [2004] and Ramos et al. [2004], respectively. As indicated in Fernandez et al. [2011], significant offline corrections are made for the isobaric interferences of $^{86}\text{Sr}^{2+}$ on $^{43}\text{Ca}^{+}$ and $^{88}\text{Sr}^{2+}$ on $^{44}\text{Ca}^{+}$ by monitoring double charge formation at masses 21.5 and 43.5. In this ID method, instrumental mass fractionation was corrected through sample-standard bracketing using an isotopically enriched matrix-matched dissolved coral standard [Fernandez et al., 2011].

[10] The external precision of the method was assessed by the regular analysis of a deep-sea coral consistency standard with a Sr/Ca of 10.264 mmol/mol and a Mg/Ca of 3.062 mmol/mol. Long-term external reproducibility of consistency standard measurements over 4 years was 0.1% for Sr/Ca (relative standard deviation $2\sigma$, $n = 113$) and 1.2% Mg/Ca (relative standard deviation $2\sigma$, $n = 98$). External precision is worse for Mg/Ca than for Sr/Ca due to a small but variable and persistent magnesium blank associated with the mass spectrometer front end. The external precision for Sr/Ca using the ID MC-ICP-MS method is nearly as good as the 0.03% external error reported for the more time consuming ID-TIMS methods [Beck et al., 1992]. Within run precision is typically better than long-term reproducibility, matching that reported for TIMS. Furthermore, the ID MC-ICP-MS method has an additional advantage in that both Mg/Ca and Sr/Ca ratios can be measured simultaneously with high precision.

[11] Much like ID-TIMS, the accuracy of the ID MC-ICP-MS method is controlled by ID spike calibration. Additionally, a matrix-matched isotope ratio standard must be calibrated to correct for mass fractionation during MC-ICP-MS analysis. Both the spike and the standard used in this study were calibrated as described in detail by Fernandez et al. [2011]. Briefly, the abundances of magnesium, calcium, and strontium isotopes in the ID spike were established using gravimetric mixtures between the ID spike and pure elemental standards, followed by isotope ratio analysis. While a solid certified standard of both known elemental concentration and known isotopic abundances exists for strontium, National Institute of Standards and Technology Standard Reference Material (NIST SRM) 987, the isotopic composition of the solid elemental standards used for both magnesium and for calcium had to be independently established. For these near-natural abundance elemental standards, isotope ratios were measured repeatedly using certified reference materials of known and closely matched isotope ratios as standards (NIST SRM 980 for Mg and the CaF$_2$ reference material used by Russell et al. [1978] for calcium). Similar measurements were used to determine the isotope ratios of the instrumental mass-fractionation standard, which was diluted to reduce matrix effects. Together with accurate weighing of solid samples, the precise measurement of isotope ratios lead to an accurate calibration of the ID spike, and consequently, into accurate Sr/Ca and Mg/Ca measurements.

3. Results and Statistical Analysis

3.1. JCp-1

[12] Twenty-one laboratories anonymously returned Sr/Ca data for JCp-1 and the average value from a single laboratory ranges from 8.54 to 8.98 mmol/mol (Table 2). The mean value of all data is 8.831 mmol/mol with a standard deviation of 0.098 mmol/mol. Most laboratories reported the repeatability of a single dissolution as well as values for different dissolutions enabling both the internal and external reproducibility to be estimated for each lab. The internal reproducibility represents how well the measurement technique reproduces while the external reproducibility includes the dissolution technique and any heterogeneity at the test portion size.

[13] Further statistical analysis follows ISO 13528 [2005] “Statistical methods for use in proficiency testing by interlaboratory comparisons.” These statistical techniques were designed for data sets with the same number of replicate measurements for every laboratory. However, given the large number of replicate measurements ($\geq 3$ except for two laboratories), the different number of replicate measurements (dissolutions) contributing to a laboratory mean has an insignificant effect. This was tested by performing the same statistical analysis using only the first three Sr/Ca values reported and also with the first five Sr/Ca values reported. For missing data the ISO 13528 [2005] suggests data with at least 0.59-$n$ replicates can be included in
the analysis meaning labs reporting two different dissolutions can be considered in the $n = 3$ analysis and labs reporting three different dissolutions can be included in the $n = 5$ analysis. Unfortunately, one laboratory only reported the average value of 20 dissolutions so the data from that laboratory were omitted from the $n = 3$ and $n = 5$ analyses. The assigned value is calculated as the robust average following the iterative approach of algorithm A [ISO 5725-5, 1998]. Robust statistical approaches avoid the rejection of outliers and are considered best practice [e.g., Srnková and Zbiral, 2009] although different robust methods exist [e.g., Wilrich, 2007]. The Sr/Ca robust average (robust standard deviation) determined for the entire data set is 8.838 (0.042) mmol/mol, while it is 8.850 (0.074) and 8.834 (0.048) for the $n = 3$ and $n = 5$ data sets, respectively. Laboratory number 9 returned Sr/Ca values for five different dissolutions that differed much more than for any of the 20 other laboratories and had an external standard deviation four times that of any other laboratory. Although the mean of the five Sr/Ca values from lab 9 is close to the assigned value, the mean of the first three values is $>0.1$ mmol/mol higher, thus explaining the slight difference between the $n = 3$ and $n = 5$ data sets. No weighting is given to average values from different laboratories and no differences were found using different numbers of replicates, so all further statistical analyses are made using all the available data.

[14] In total, Sr/Ca values were reported for 179 separate dissolutions of the JCP-1 powder. Twelve laboratories used ICP-OES and nine laboratories used an ICP-MS instrument of some kind; no difference between the different techniques can be detected (ICP-OES average (standard deviation) is 8.852 (0.085) mmol/mol and the ICP-MS average (standard deviation) is 8.802 (0.113) mmol/mol). The mean value obtained by ID MC-ICP-MS was 8.826 mmol/mol.

[15] Any heterogeneity at the test portion size would be revealed if the external reproducibility is detectably larger than the internal reproducibility. However, in all but one case the internal/external reproducibility ratio is $>0.5$ and in many instances is $>1$ (where the external is more reproducible than the internal). This and the fact there is no trend in the internal/external reproducibility ratio with test portion size (Figure 3) clearly demonstrates the JCP-1 powder distributed from a single bottle is effectively homogenous for Sr/Ca at test portions $\geq 0.25$ mg.

Figure 3. The ratio of the average standard deviation of measurements of a single dissolution (internal) to the standard deviation of the different dissolutions (external) reported by each lab. Each data point represents the results from a single laboratory plotted against the test portion sized used by that lab. Heterogeneity would be revealed if more points plotted in the lower half and the internal/external reproducibility ratio increased with test portion size.

Figure 4. Ranked average Sr/Ca values for each laboratory with error bars representing two standard deviations of the mean (95% confidence level). For lab 9, the error bars are $\pm 0.48$ mmol/mol. The dashed line is the robust average and the gray area denotes the robust standard deviation of all the data. Z-scores calculated using the robust average and standard deviation that require action, $>3$ or $<-3$, are shown next to the appropriate data point.
The ISO 13528 [2005] describes the sample as suitably homogenous if the between sample standard deviation is less than or equal to $0.3/C_{27}$ (where $C_{27}$ is the standard deviation for proficiency testing). The between sample deviation is the median of the external reproducibility for the different labs, 0.0129 mmol/mol, and $0.3/C_{27} = 0.0127$ mmol/mol, if $C_{27}$ is the interlab robust standard deviation. There may be better ways to estimate $C_{27}$ so the robust $S_n$ matrix method was also used [Wilrich, 2007, and references therein]. The $S_n$ for all Sr/Ca data is 0.0476 mmol/mol so in this case $0.3/S_n = 0.0143$ mmol/mol, and the homogeneity criterion is satisfied. The $S_n$ was also calculated for the $n = 3$ and the $n = 5$ data sets and is similar to the robust standard deviation from algorithm A [ISO 5725-5, 1998].

As the assigned value used in the estimation of laboratory bias was obtained from the results of participants the appropriate performance statistic is the “z-score.” Figure 4 shows the Sr/Ca results with z-scores higher than 3 or less than $-3$ labeled as these values require action. This means 3 laboratories out of 21 (or 14%) have not performed satisfactory and have results that are biased for some reason. The fact that all error bars estimated from two external standard deviations (95% confidence level) for each laboratory do not always overlap with the robust standard deviation (gray area in Figure 4) suggests that there is also some bias component not accounted for in those uncertainty estimates. A full assessment of uncertainty components will be made in the discussion below.

The results for other elements in the JCp-1 are presented in Table 2 and the results for JCt-1 are presented in Table 3. The ranked results for other elements in JCp-1 are presented in Figures 5 and 6 and the results for JCt-1 in Figure 7.

### Table 2. Summary of Results for JCp-1

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Sr/Ca (mmol/mol)</th>
<th>Mg/Ca (mmol/mol)</th>
<th>U/Ca (μmol/mol)</th>
<th>Ba/Ca (μmol/mol)</th>
<th>B/Ca (μmol/mol)</th>
<th>Li/Ca (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab 1</td>
<td>8.849</td>
<td>4.213</td>
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<tr>
<td>Lab 2</td>
<td>8.826</td>
<td>4.258</td>
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<td>0.045</td>
<td>0.655</td>
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<td>6</td>
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<td>Median within-Lab standard deviation</td>
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<td>0.0127</td>
<td>0.0116</td>
<td>0.0903</td>
<td>4.7</td>
<td>0.0718</td>
</tr>
</tbody>
</table>

*Only the median within-lab standard deviation is given to avoid a precision contest.*

[16] The ISO 13528 [2005] describes the sample as suitably homogenous if the between sample standard deviation is less than or equal to $0.3\sigma$ (where $\sigma$ is the standard deviation for proficiency testing). The between sample deviation is the median of the external reproducibility for the different labs, 0.0129 mmol/mol, and $0.3\sigma = 0.0127$ mmol/mol, if $\sigma$ is the interlab robust standard deviation. There may be better ways to estimate $\sigma$ so the robust $S_n$ matrix method was also used [Wilrich, 2007, and references therein]. The $S_n$ for all Sr/Ca data is 0.0476 mmol/mol so in this case $0.3\sigma = 0.0143$ mmol/mol, and the homogeneity criterion is satisfied. The $S_n$ was also calculated for the $n = 3$ and the $n = 5$ data sets and is similar to the robust standard deviation from algorithm A [ISO 5725-5, 1998].

[17] As the assigned value used in the estimation of laboratory bias was obtained from the results of participants the appropriate performance statistic is the “z-score.” Figure 4 shows the Sr/Ca results with z-scores higher than 3 or less than $-3$ labeled as these values require action. This means 3 laboratories out of 21 (or 14%) have not performed satisfactory and have results that are biased for some reason. The fact that all error bars estimated from two external standard deviations (95% confidence level) for each laboratory do not always overlap with the robust standard deviation (gray area in Figure 4) suggests that there is also some bias component not accounted for in those uncertainty estimates. A full assessment of uncertainty components will be made in the discussion below.

[18] The results for other elements in the JCp-1 are presented in Table 2 and the results for JCt-1 are presented in Table 3. The ranked results for other elements in JCp-1 are presented in Figures 5 and 6 and the results for JCt-1 in Figure 7.

### 4. Discussion

#### 4.1. Assigned Value Uncertainty and Fitness for Purpose

[19] An example of the full assessment of uncertainty for Sr/Ca ratio determination following the Quantifying Uncertainty in Analytical...
Measurement (QUAM) guidelines [EURACHEM/CITAC, 2012] will be presented below. For practical reasons the International Association of Geoanalysts (IAG) recommends the expanded uncertainty of reference values be calculated in a different way [Kane et al., 2003]. The IAG protocol combines the interlaboratory standard deviation with variability relating to homogeneity and uncertainty in the dry weight of powder. The homogeneity tests did not reveal any Sr/Ca heterogeneity for the recommended sample size detectable above the standard deviation of the technique. As we are interested in element/Ca ratios measured on the same solution the dry weight uncertainty is not considered. To estimate the uncertainty, here we combine the median of the within laboratory standard deviation with the robust interlaboratory standard deviation and expand by a coverage factor of 2, unless \( n \leq 6 \), as recommended by QUAM [EURACHEM/CITAC, 2012]. The expanded uncertainties \( U \) at the 95% confidence level calculated in this way are given in Tables 2 and 3. The \( U \) for the Sr/Ca ratio of the JCP-1 reference material is 0.089 mmol/mol, equating to 1.5°C using a compiled average Sr/Ca-temperature slope [Corrèje, 2006], and is clearly dominated by the interlaboratory uncertainty. This \( U \) approaches fitness for purpose for equatorial seas where the annual SST cycle is only 3°C or less and where the glacial-interglacial change in SST is estimated to be around 3°C [e.g., Stott et al., 2007]. Ideally \( U \) would equate to \(<1°C\) but \( U \) is comparable to the average external measurement precision routinely obtained [e.g., Schrag, 1999] if given at the 95% confidence level. However, it is often noted that the desired level of characterization of a reference material has confidence limits less than one third of the routine laboratory measurement uncertainty [e.g., Kane, 2002]. The laboratory bias component will need to be significantly reduced for this to be achieved. The same can be said for all the other elements measured as \( U \) is always much larger than the median within laboratory standard deviation expanded to 2\( \sigma \).

Table 3. Summary of Results for JCt-1a

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Sr/Ca (mmol/mol)</th>
<th>Mg/Ca (mmol/mol)</th>
<th>U/Ca (mmol/mol)</th>
<th>Ba/Ca (µmol/mol)</th>
<th>B/Ca (µmol/mol)</th>
<th>Li/Ca (µmol/mol)</th>
</tr>
</thead>
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<tr>
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<td>1.693</td>
<td>1.292</td>
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<td>25.00</td>
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<td>4.348</td>
<td>191.0</td>
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<td>4</td>
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<td>( U )</td>
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<tr>
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<td>2</td>
<td>4.303</td>
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<td>4.557</td>
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<td>0.017</td>
<td>0.299</td>
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*Only the median within-lab standard deviation is given to avoid a precision contest.
purpose” of the current characterizations. For example, variations in coral U/Ca attributed to a degree of temperature change range from 0.084 to 0.029 m mol/mol per 14C14C [e.g., Sinclair et al., 1998; Quinn and Sampson, 2002; Felis et al., 2009] while a change of 0.21 m mol/mol was observed for a pH change from 7.2 to 8.2 in cultured Acropora corals [Inoue et al., 2011]. Therefore, the U of 0.094 m mol/mol for the U/Ca ratio of JCp-1 is fit for purpose for determining changes of 0.5 pH units or about 2°C of temperature. Similar considerations suggest the U of 60 m mol/mol for the B/Ca ratio of JCp-1 is fit for purpose for determining pH changes of 0.2 pH units [Allison and Finch, 2010] or 0.3°C of temperature [Sinclair et al., 1998]. The U for the Mg/Ca ratio (0.13 mmol/mol) of JCp-1 equates to a little less than 1°C of temperature [e.g., Mitsuguchi et al., 1996; Sinclair et al., 1998; Quinn and Sampson, 2002] while the U for the Li/Ca ratio (0.36 m mol/mol) of JCp-1 equates to between 1 and 2°C [Hathorne et al., 2013]. It is important to note that the U for element/Ca ratios with few labs reporting data are expanded by larger coverage factors (Tables 2 and 3) to account for the lack of data and hopefully future studies can improve this situation. Ba/Ca variations in corals resulting from flood events or sediment remobilization are normally large, on the order of 5–10 µmol/mol [e.g., McCulloch et al., 2003; Sinclair and McCulloch, 2004; Prouty et al., 2010], so the U for the Ba/Ca ratio of JCp-1 of 1.3 µmol/mol is fit for purpose.

[21] The JCl-1 has a generally lower trace element content compared to a coral and as such is more appropriate as a reference material for other biogenic carbonates such as Foraminifera [e.g., Raitzsch et al., 2011a, 2011b; Coadic et al., 2013] or giant clams. The fact that the new data for the JCl-1 agree well with the isotope dilution measurements suggests that although the JCl-1 powder was analyzed with methods optimized for coral element/Ca ratios, this had a minimal impact on the data. The new data also agree well with the previous published values for this reference material (see below).

[22] Ok’04 report Sr concentrations in ppm and Ca concentrations in percentage for the JCp-1 powder from 10 laboratories. Accounting for the uncertainty reported for both Sr and Ca concentrations gives a range of Sr/Ca ratios of 8.47–9.26 mmol/mol with the average value of all data being 8.86 mmol/mol. This value agrees with the robust average from this study but following outlier rejection the Ok’04 provisional value for the Sr/Ca ratio of JCp-1 is 8.66 mmol/mol. Combining the reported uncertainty for both Sr and Ca concentrations following QUAM the Ok’04 95% confidence limits overlap with U from this study by only 0.006 mmol/mol (Table 2). The average values differ by 0.17 mmol/mol, which equates to almost 3°C using an average Sr/Ca-temperature slope [Corrèze, 2006]. In contrast, the robust average Sr/Ca value for the JCl-1 powder of this study agrees to the second decimal place with the Ok’04 provisional value. Of the other elements studied, Ok’04 report provisional “certified” values for Mg and Ba in the JCp-1 and JCl-1 powders. In both cases, the robust average values for Mg/Ca and Ba/Ca values agree with the Ok’04 values within the limits of U and the robust standard deviation (Tables 2 and 3). Ok’04 also report information values for Li/Ca, B/Ca and U/Ca for the JCp-1 and JCl-1. In the case of B/Ca and U/Ca, the values obtained here agree well with the Ok’04 values. However, the Ok’04 Li/Ca values are somewhat lower than the robust average of this study for both JCp-1 and JCl-1 suggesting a systematic offset.

[23] The values from Ok’04 were all measured as weight units (µg/g or wt%) and as such may have
additional uncertainty relating to the dry weight uncertainty of the powder. Additionally, it seems in all cases the Ca content was measured with a different technique (X-ray fluorescence), and therefore not simultaneously with the minor and trace elements. Ok’04 aimed to characterize the material for a wide range of elements and accomplished that goal but as the end user wishes to know the element/Ca ratios as precisely as possible it is more appropriate to characterize the material with direct measurements of element/Ca ratios.

4.2. Reasons for Interlaboratory Bias

[24] To see if there is a significant relationship between the JCP-1 and JCT-1 values reported by labs, a rank correlation test was conducted for all element/Ca ratios where there is data for both JCP-1 and JCT-1 from six or more labs. In all cases, the rank correlation coefficient was below the critical value [ISO 13528, 2005] suggesting there is no relationship between the JCP-1 and JCT-1 values reported by the different labs. This is clear in the Youden plots (Figure 8) where the lack of a

Figure 6. Ranked average Li/Ca, B/Ca, Ba/Ca, and U/Ca values for each laboratory with error bars representing two standard deviations of the mean (95% confidence level). The dashed line is the robust average and the gray area denotes the robust standard deviation of all the data. Z-scores calculated using the robust average and standard deviation that require action, >3 or <−3, are shown next to the appropriate data point.
Figure 7. Ranked average Li/Ca, B/Ca, Mg/Ca, Sr/Ca, Ba/Ca, and U/Ca values for the JCt-1 reference material. Error bars represent two standard deviations of the mean (95% confidence level) for each laboratory. The dashed line is the robust average and the gray area denotes the robust standard deviation of all the data. Z-scores calculated using the robust average and standard deviation that require action, >3 or <−3, are shown next to the appropriate data point.
correlation between the JCp-1 and JCt-1 Mg/Ca and Sr/Ca values causes the confidence ellipse to be virtually circular. A similar result was found by Greaves et al. [2008] when the element/Ca ratios of the reference materials were too different. The relationship between the JCp-1 and JCt-1 Ba/Ca and U/Ca values was stronger but not significant at the 95% level. The Youden plots show that the laboratory biases are not simply the result of a calibration bias applied to both JCp-1 and JCt-1 measurements. Points plotting outside the confidence ellipse are biased and although not systematic, i.e., falling along the 1:1 line, generally laboratories that obtained unsatisfactory z-scores for one material also had high or low z-scores for the other material. Interestingly, it appears that the ICP-OES Sr/Ca z-scores are negatively correlated suggesting a positive bias for the JCp-1 is related to a negative bias for the JCt-1. This is difficult to explain but is probably related to the different Sr/Ca ratios of the two materials. Although laboratories were asked to analyze both powders in the same way as coral samples, it was clear that JCt-1 has a much lower Sr/Ca ratio than typical coral samples so some labs may have used different calibration standards for the different materials.

Figure 8. Youden plots of z-scores for both JCp-1 and JCt-1 from the different laboratories. Confidence ellipses were calculated following ISO 13528 [2005]. For Mg/Ca and Sr/Ca, open points represent labs employing ICP-MS while filled points are from labs using ICP-OES.
The different sample preparations and the analytical techniques used (Table 1) seem to have little effect with all laboratories (with the notable exception of lab 9) returning values with comparable and good within laboratory precision (median is given in Tables 2 and 3). Differences in sample preparation include variations in the strength of the dissolution acid used, the dissolution vessels used and whether centrifugation was performed following dissolution. Most laboratories reported a single value or narrow range for the Ca concentration at which the measurements were conducted (Table 1). This implies most laboratories were conducting active matrix matching of samples and standards to avoid or minimize matrix effects.

It seems that all the measurement methods used are capable of producing precise results for coral element/Ca ratios (except lab number 9). Various techniques have been published for obtaining element/Ca ratios with ICP-OES and ICP-MS instruments [e.g., Schrag, 1999; Rosenthal et al., 1999; Yu et al., 2005; Andreasen et al., 2006; Marchitto, 2006; Shen et al., 2007] and it is down to the experience of the analyst to know what approach works best with their own instrument. Instead of pointing to techniques that work better than others, the results of this study highlight the inaccuracies that can occur when calibrating Sr/Ca measurements and the need for an international standard to ensure results from different labs can be compared directly.

4.3. Calculation of Combined Uncertainty Following QUAM

The QUAM [EURACHEM/CITAC, 2012] details how all sources of uncertainty should be propagated in the way defined by the analytical model. Here, we will consider the simplest case of determining ratios directly from measured intensity ratios [Rosenthal et al., 1999]:

\[ y = \frac{rs}{rm}x \]

where \( y \) is X/Ca_{sample measured}, \( rs \) is X/Ca_{standard actual}, \( rm \) is X/Ca_{standard measured}, and \( x \) is X/Ca_{sample measured}. Using this model, the uncertainties associated with X/Ca_{standard actual} X/Ca_{standard measured} and X/Ca_{sample measured} must be considered. Comparable uncertainties must be considered with other comparative analytical methods whether using a calibration curve of intensity ratios or single mass/wavelength intensities [e.g., Schrag, 1999; Marchitto, 2006]. The analytical model of isotope dilution is distinct in that uncertainties mostly stem from spike calibration, the degree of over or under spiking, and a relatively small contribution from instrumental uncertainty during isotope ratio measurements.

4.3.1. Uncertainty of Sr/Ca_{standard actual}

For standards made gravimetrically from high-purity single-element solutions, the uncertainty of Sr/Ca_{standard actual} includes components of uncertainty from the certified values given by the manufacturer and the uncertainty of the weighing. For example, when making a Sr/Ca standard using a Sr solution with a certified concentration of 1002 ± 3 μg/mL and a Ca solution with a certified concentration of 10,007 ± 25 μg/mL the combined uncertainty (QUAM section 8.2) including weighing errors (at 95% confidence level) is 0.033 mmol/mol for a standard with a Sr/Ca ratio of 8.573 mmol/mol. This uncertainty is dominated by the uncertainty provided by the solution manufacturer as weighing errors taken from the calibration report for the five decimal place balance used are only 0.006% for 500 mg and 0.012% for 90 mg. In both cases, this equates to uncertainty on the last decimal place of the balance reading only and is negligible compared to the standard solution concentration uncertainties. Buoyancy corrections would also be negligible in such circumstances where the densities of the standard solutions are so similar.

When the standard solution concentration is given in microgram per milliliter units, the density of the solution needs to be accounted for when calculating the mass of an element contained in a weighed aliquot of standard solution. In this particular case, the Sr solution is in 0.1% (v/v) HNO3 with a density of 1.000 g/mL while the more concentrated Ca solution is in 0.313 mmol/mol lower and it is clear that this could be a very significant source of bias. Not all manufacturers supply such detailed information and one could be forgiven for assuming all standards in a weak HNO3 matrix, from the same manufacturer at least, would have the same acid content.

Another source of uncertainty for the Sr/Ca ratio of the standard solution is the variable amount of Sr impurity in the Ca standards. Some workers have highlighted the presence of such impurities and quantify them [Yu et al., 2005; Andreasen et al., 2006; Marchitto, 2006] while others do not mention the impurities or...
suggest the effect is insignificant [Shen et al., 2007]. Although manufacturers provide information regarding impurity concentrations on the certificate of analysis experience has demonstrated, especially for Sr, determining the contribution from impurities in the Ca standard can be important. Often detailed certificates of analysis are only supplied with the most expensive products and it is only possible to find out the impurity content once a solution has been purchased. The Sr impurity varies widely, even between different batches from the same manufacturer. To demonstrate this, we conducted a five point standard addition analysis of four different Ca solutions from three different manufacturers. The results vary from 0.31 to 2.06 μg/mL Sr in a 10,000 μg/mL Ca solution with different batches from the same manufacturer having values of 0.31 and 0.80 μg/mL Sr. This does not seem like much but a standard with a Sr/Ca ratio of about 9 mmol/mol will have around 200 μg/mL Sr in a 10,000 μg/mL Ca solution. Therefore, a bias of up to 1% could be introduced by not accounting for impurities in the Ca standard but a bias of approximately 0.3% or 0.03 mmol/mol is likely. [31] In summary, assuming differences in the density of standard solutions has been accounted for, the uncertainty associated with Sr/Ca standard ratios is on the order of 0.033 mmol/mol (2σ) and the bias introduced by the Sr impurity in the Ca solution is estimated at 0.03 mmol/mol. Adding these two sources of uncertainty following QUAM and allocating the Sr impurity uncertainty a 1σ confidence limit gives a combined standard uncertainty (1σ) of 0.035 mmol/mol to propagate for the Sr/Ca standard actual.

4.3.2. Uncertainty of Sr/Ca standard measured

[32] Despite the great advance of multielement quantification brought about with the introduction and development of ICP-OES and ICP-MS instruments, there are many spectral and molecular interferences which can influence analyte signal intensities. The added complexity of matrix effects, in this case the relatively high levels of Ca introduced to the plasma, provides plenty of scope for significant interlaboratory bias to be generated during measurement. Although different schemes are used to minimize or correct for matrix effects [e.g., Schrag, 1999; Yu et al., 2005] these are instrument specific and even vary with the hardware setup of similar instruments. For example, the use of a shielded torch significantly changes the mass bias [e.g., Andreasen et al., 2006] and different instrument types exhibit different Ca matrix effects for some elements (compare Yu et al. [2005] and Marchitto [2006]). The uncertainty resulting from such corrections is difficult to isolate but Schrag [1999] suggests by limiting the Ca concentration variations to less than a factor of 4 the precision after correction is around 0.2% or 0.02 mmol/mol. Shen et al. [2007] report a 86Sr/Ca ion formation of 3% in their mass spectrometer and when 3% of the 86Sr intensity was subtracted from the 43Ca intensity for a 15 h run of various coral Sr/Ca standard solutions the maximum difference between the corrected and uncorrected Sr/Ca values was 0.02 mmol/mol. Therefore, we estimate the standard uncertainty of Sr/Ca standard measured to be propagated to be 0.02 mmol/mol.

4.3.3. Uncertainty of Sr/Ca sample measured

[33] The uncertainty of the element/Ca ratio measured for the sample solutions also depends on the same factors that influence the standards such as matrix effects and interferences. There is scope for a larger uncertainty to be associated with sample element/Ca measurements as the calibration standards are likely to be more pure, for example, not containing residual organics, and therefore have a more narrow matrix composition. Here, we estimate the external analytical precision for Sr/Ca measurements using within lab reproducibility as reported by the participating labs. The median within laboratory standard deviation for JCp-1 Sr/Ca ratios was 0.013 mmol/mol (Table 2), which is only 0.15% relative to the average value. In one laboratory, the average relative standard deviation of 17 different coral Sr/Ca standards (including dissolutions of JCp-1 and JCT-1) run at 10 or 20 ppm Ca, over a 15 h run, was 0.32%. Therefore, the conservative standard uncertainty of Sr/Ca sample measured to be propagated is estimated to be 0.026 mmol/mol.

4.3.4. Combined Expanded Uncertainty and Implications for Sr/Ca Temperature Reconstructions

[34] Following QUAM the combined uncertainty \( u(y) \) of \( y \) will be

\[
 u(y) = \sqrt{\left( \frac{u(rs)}{rs} \right)^2 + \left( \frac{u(rm)}{rm} \right)^2 + \left( \frac{u(x)}{x} \right)^2}
\]

[35] Using the conservative estimates of the standard uncertainty discussed above, the combined uncertainty is 0.049 mmol/mol or 0.098 mmol/mol when expanded by the coverage factor 2 to obtain a 95% confidence level. This is comparable to the \( U \) obtained for the assigned value following IAG
guidelines and equates to 1.6°C using the compiled mean slope between SST and the Sr/Ca ratio of *Porites* corals [Corrêge, 2006]. Assuming the Sr impurity in the Ca standard has been corrected for or is insignificant the *u(rs)* term reduces to 0.017 mmol/mol and then the combined expanded uncertainty is 0.076 mmol/mol which equates to 1.3°C. If the uncertainty of the Sr/Ca ratio of the standard could be negated by using a reference material with an agreed set value, that is the *u(rs)* term is zero, and using the best case estimates of 0.02 mmol/mol for *u(rm)* and 0.013 for *u(x)*, then the combined expanded uncertainty could be reduced to 0.049 mmol/mol or 0.8°C. Such a 95% confidence interval would be fit for the purpose of discerning small changes in tropical SST on seasonal and interannual time scales. However, to obtain such refined expanded uncertainties will require the better characterization of reference materials than obtained in the current study. Studies characterizing new coral reference materials should employ ID measurements from multiple laboratories and use the well-characterized JCP-1 to ensure traceability. In the meantime, it is suggested that studies reporting coral element/Ca ratio data report the average value obtained for a reference material such as the JCP-1. Consensus values that fulfill the requirements to be certified values were also obtained for Mg/Ca in JCP-1 and for Sr/Ca and Mg/Ca ratios in the JCT-1 giant clam reference material. Reference values with variable fitness for purpose have also been obtained for Li/Ca, B/Ca, Ba/Ca, and U/Ca ratios in both reference materials.

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### References


