Geochemistry Geophysics Geosystems G3

Article
Volume 14, Number 9
23 September 2013
doi: 10.1002/ggge.20230
ISSN: 1525-2027

Published by AGU and the Geochemical Society

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

Ed C. Hathorne
GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstrasse 1–3, Kiel DE-24148, Germany

MARUM-Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany (ehathorne@geomar.de)

Alex Gagnon
Division of Chemistry, California Institute of Technology, Pasadena, California, USA

Now at School of Oceanography, University of Washington, Seattle, Washington, USA

Thomas Felis
MARUM-Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany

Jess Adkins
Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA

Ryuji Asami
Trans-disciplinary Research Organization Subtropical Island Studies, University of the Ryukyus, Okinawa, Japan

Wim Boer
Royal Netherlands Institute for Sea Research, Den Hoorn, Netherlands

Nicolas Caillon
LSCE/IPSL, UMR-8212 CNRS-CEA-UVSQ, Domaine du CNRS, Gif-sur-Yvette, France

David Case
Department of Chemistry, Washington University, St. Louis, Missouri, USA

Now at Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA

Kim M. Cobb
School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA

Eric Douville
LSCE/IPSL, UMR-8212 CNRS-CEA-UVSQ, Domaine du CNRS, Gif-sur-Yvette, France

Peter deMenocal
Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, USA

Anton Eisenhauer
GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

Dieter Garbe-Schönberg
Institute of Geosciences, Christian-Albrechts University Kiel, Kiel, Germany

© 2013. American Geophysical Union. All Rights Reserved.

Walter Geibert
School of GeoSciences, University of Edinburgh, Edinburgh, UK

Steven Goldstein
Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, USA

Konrad Hughen
Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA

Mayuri Inoue and Hodaka Kawahata
Atmosphere and Ocean Research Institute, University of Tokyo, Kashiwa, Japan

Martin Kölling
MARUM-Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany

Florence L. Cornec
LOCEAN—PALEOPROXUS (UMR7159), IPSL/UPMC/CNRS/IRD/MNHN Centre IRD France Nord, Bondy, France

Braddock K. Linsley
Department of Atmospheric and Environmental Sciences, University at Albany-State University of New York, Albany, New York, USA

Now at Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, USA

Helen V. McGregor
School of Earth and Environmental Sciences, University of Wollongong, Wollongong, New South Wales, Australia

Paolo Montagna
Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, USA

Intan S. Nurhati
School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA

Singapore-MIT Alliance for Research and Technology, Singapore

Center for Oceanography and Marine Technology, Surya University, Indonesia

Terrence M. Quinn
Department of Geological Sciences, Jackson School of Geosciences, University of Texas at Austin, Austin, Texas, USA

Jacek Raddatz
GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

Hélène Rebaubier
LSCE/IPSL, UMR-8212 CNRS-CEA-UVSQ, Domaine du CNRS, Gif-sur-Yvette, France

Laura Robinson
Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA

Aleksey Sadekov
School of GeoSciences, University of Edinburgh, Edinburgh, UK

Now at Department of Earth Sciences, Cambridge University, Cambridge, UK

Rob Sherrell and Dan Sinclair
Institute of Marine and Coastal Sciences, and Department of Earth and Planetary Sciences, Rutgers University, New Brunswick, New Jersey, USA

Alexander W. Tudhope
School of GeoSciences, University of Edinburgh, Edinburgh, UK

Gangjian Wei
State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangdong, China

Henri Wong
Institute for Environmental Research, Australian Nuclear Science and Technology Organisation, Sydney, New South Wales, Australia

Henry C. Wu
Department of Atmospheric and Environmental Sciences, University at Albany-State University of New York, Albany, New York, USA

Now at MARUM-Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany

Chen-Feng You
Department of Earth Sciences, National Cheng Kung University, Tainan, Taiwan

[1] The Sr/Ca ratio of coral aragonite is used to reconstruct past sea surface temperature (SST). Twenty-one laboratories took part in an interlaboratory study of coral Sr/Ca measurements. Results show interlaboratory bias can be significant, and in the extreme case could result in a range in SST estimates of 7°C. However, most of the data fall within a narrower range and the *Porites* coral reference material JCp-1 is now characterized well enough to have a certified Sr/Ca value of 8.838 mmol/mol with an expanded uncertainty of 0.089 mmol/mol following International Association of Geoanalysts (IAG) guidelines. This uncertainty, at the 95% confidence level, equates to 1.5°C for SST estimates using *Porites*, so is approaching fitness for purpose. The comparable median within laboratory error is <0.5°C. This difference in uncertainties illustrates the interlaboratory bias component that should be reduced through the use of reference materials like the JCp-1. There are many potential sources contributing to biases in comparative methods but traces of Sr in Ca standards and uncertainties in reference solution composition can account for half of the combined uncertainty. Consensus values that fulfil 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 in both reference materials. In future, studies reporting coral element/Ca data should also report the average value obtained for a reference material such as the JCp-1.

Components: 11,363 words, 8 figures, 3 tables.

Keywords: coral Sr/Ca ratios.

Index Terms: 1094 Instruments and techniques: Geochemistry; 1065 Major and trace element geochemistry: Geochemistry; 4954 Sea surface temperature: Paleoceanography; 4916 Corals: Paleoceanography; 4220 Coral reef systems: Oceanography: General.

Received 27 March 2013; **Revised** 3 July 2013; **Accepted** 19 July 2013; **Published** 23 September 2013.

Hathorne, E. C., et al. (2013), Interlaboratory study for coral Sr/Ca and other element/Ca ratio measurements, *Geochem. Geophys. Geosyst.*, *14*, 3730–3750, doi:10.1002/ggge.20230.

1. Introduction

[2] 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; *Mitsuguchi 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 Cornec 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.

[3] 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 laboratories is desirable. The current study grew out of the Integrated Ocean Drilling Program (IODP) Expedition 310 "Tahiti Sea Level" [e.g., *Camoin et al*., 2007] where palaeoclimate reconstructions were carried out by international collaboration. Initial work sharing standards between a few laboratories found significant offsets between the Sr/Ca ratios measured in different laboratories [*Asami et al*., 2009; *DeLong et al*., 2010; *Hathorne et al*., 2011; *Felis et al*., 2012]. This highlighted the need for a reference material to allow comparison between laboratories and facilitate compilation projects such as PAGES - Past Global Changes Ocean2k. This study has three main purposes: (1) to characterize reference materials for the quality control (assessment of precision and accuracy) of coral element/Ca ratio measurements, (2) to quantify any systematic bias that may exist between the element/Ca ratios measured in different laboratories with different techniques, and (3) to identify reasons for such systematic biases and provide guidance to minimize any biases in the future.

2. Materials and Methods

2.1. Suitability and Homogeneity of Reference Materials

[4] 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.

[5] 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, Na_2O, 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].

[6] It is normal and recommended practice [e.g., *Kane et al*., 2003] in such interlaboratory studies to analyze at least two different materials. These materials should have a similar matrix ($CaCO_3$) but a different elemental composition. In the absence of another internationally available coral reference material, we chose a biogenic aragonite reference material from the GSJ made from a Holocene age fossil giant clam shell (*Tridacna gigas*) called "JCt-1" [*Inoue et al*., 2004] as the second material for this study. Both these materials have been previously characterized for many elements [*Okai et al*., 2002, 2004; *Inoue et al*., 2004]. The *Okai et al*. [2004] paper is in Japanese, but the data are presented in English and these data will be referred to as Ok'04 herein. Initial studies in Expedition 310 laboratories suggested the JCp-1 Sr/Ca ratio was distinctly higher than the provisional Ok'04 value of 8.66 mmol/mol. Therefore, we thought it desirable to characterize the JCp-1 reference material specifically for the purpose of coral Sr/Ca measurements, through an interlaboratory study involving experienced coral element/Ca analysts. This would also be an opportunity to better characterize the JCp-1 for elements where Ok'04 only provides information values.

[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 HNO_3 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 ^{7}Li, ^{11}B, ^{25}Mg, ^{43}Ca, ^{55}Mn, ^{88}Sr, ^{137}Ba, and ^{238}U with a sector field ICP-MS (Element 2) in low-resolution mode. Element/Ca ratios were calculated directly from the $X/^{43}Ca$ 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 the IODP 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

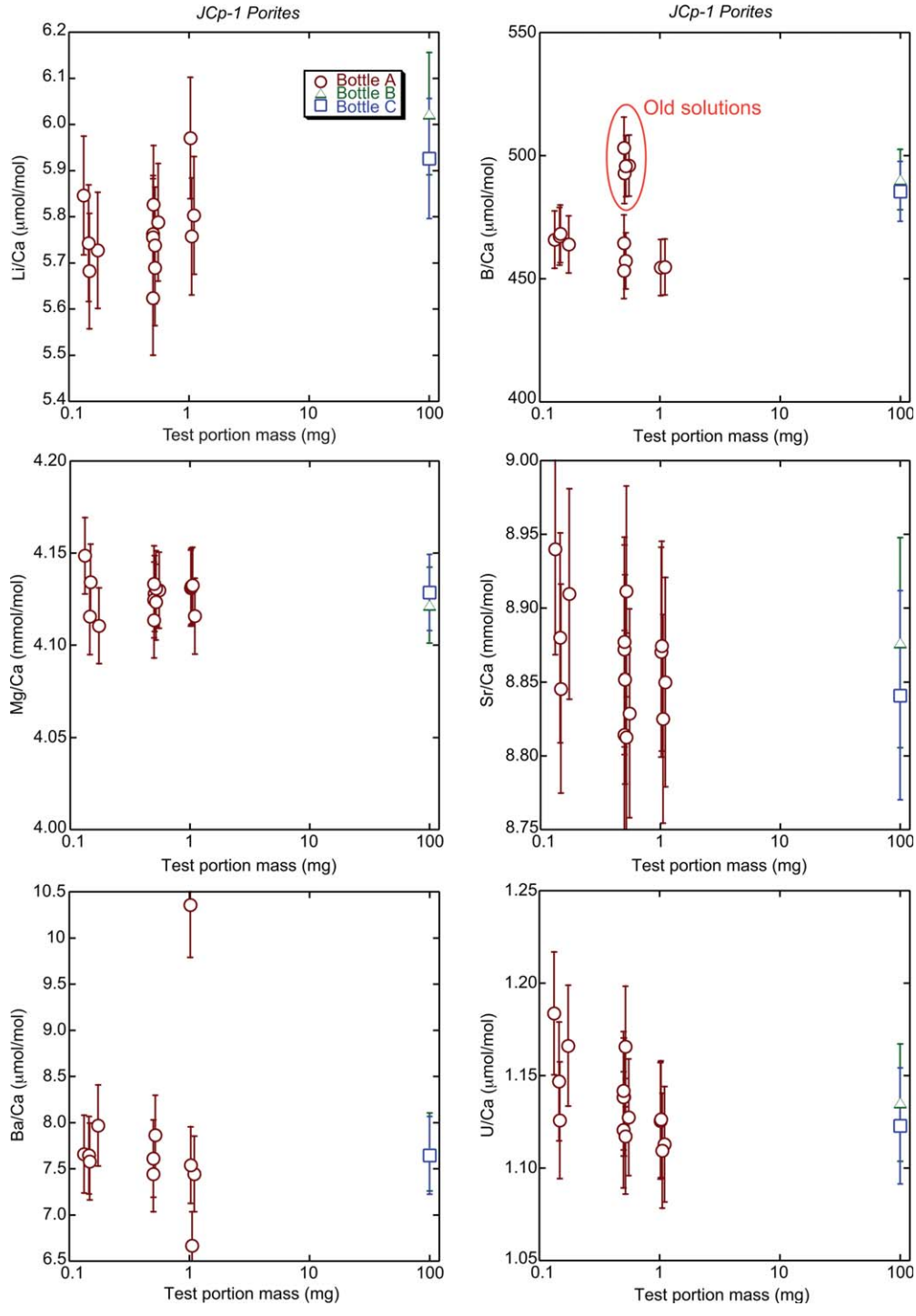


Figure 1. Homogeneity test results for JCp-1. Error bars represent two standard deviations of the mean for the 0.5 mg test portion dissolutions. The 2σ uncertainty of the measurements of the JCp-1 material is 2.3% for Li/Ca, 2.5% for B/Ca, 0.3% for Mg/Ca, 41% for Mn/Ca, 0.8% for Sr/Ca, 5.5% for Ba/Ca, and 2.9% for U/Ca.

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).

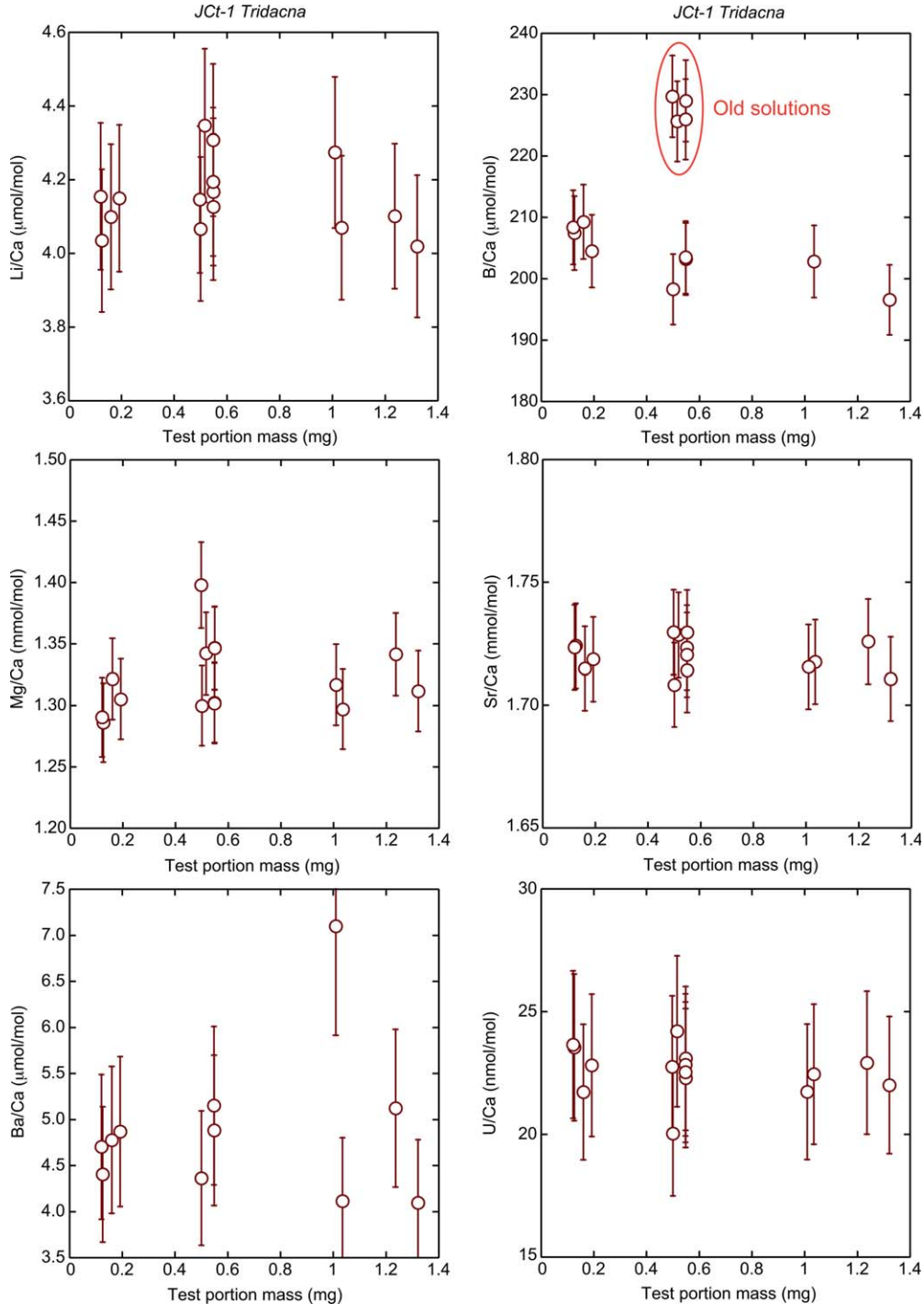


Figure 2. Homogeneity test results for JCt-1. Error bars represent two standard deviations of the mean for the 0.5 mg test portion dissolutions. The 2σ measurement uncertainty of the JCt-1 material is 4.8% for Li/Ca, 2.9% for B/Ca, 2.5% for Mg/Ca, 91% for Mn/Ca, 1.0% for Sr/Ca, 17% for Ba/Ca, and 13% for U/Ca.

2.3. Isotope Dilution (ID) as the Definitive Method

[9] 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 1. Details of Sample Treatment and Analysis Provided by the Participating Laboratories

Lab	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10	Lab 11	Lab 12	Lab 13	Lab 14	Lab 15	Lab 16	Lab 17	Lab 18	Lab 19	Lab 20	Lab 21
Test Portion Mass (mg)	2	13	50	5.5	100	14	173	1.3	4.3	0.5	1	20	0.25	25	0.5		208	0.3	3	5	2.5
Dissolution Acid: Pure HNO_3 in >18.2 MΩ Water	0.5 M	0.1 M	0.3 M	2 % wt.	4 N	5% vol.	2% vol.	1.1 M	3%	0.075 M	0.1M	0.1M	1.95% vol.	0.5 M	1% v/v		2% v/v	0.3 M	8.9 %wt.	0.3 M	5% vol
Volume of Dissolution Acid (mL)	15	25	20	30	10	15	2.07–2.56	1.1	13.6–15	2	4	100	7	10	5		100	30	0.375	10	20
Dissolution Vessel	15 mL PP	30 mL LDPE	15 mL PFA	30 mL PP	Teflon	LDPE	1000 mL LDPE	microcentri	15 mL PE not cleaned	2 mL microcentri	FEP	LDPE 125	PolyStyrol 11 mL	50 mL PP	10 mL PP		HDPE	LDPE	HDPE microcentri	Teflon	30 mL HDPE
Samples Centrifuged		5000 rpm, 10 min	7000 rpm		11,000 rpm, 20 min																
Other Treatment			One part cleaned by 10% NaOCl and 0.0075 N HNO_3					ID spike added		Sonicated for 30 min			Shaken				Ultrasonic				
Time Between Dissolution and Analysis	>24 h	1 or 15 day	<3 day		7 day	1 day	12–24 h	1 day	<1 day	1–2 h	1 day	30 day	>48 h	3 h	7 day		<3 day	>1 day	3 day	>1 day	1–2 day
Storage Vessel (if Different)	PFA or PP bottle		15 mL PFA		15 mL PE	2 mL PP	3 mL														
Analysis Vessel (if Different)		10 mL PE	7 mL PFA							0.5 mL microcentri		0,5 mL		15 mL PP			PP	PP		PP	10 mL poly-carbonate
ppm Ca Analyzed	40–60	15	20	40–110	80–90	61–63	28–30	16	35–200	~100	90–110	40	10–20	100	35–40		8	10	160	20	39–49
Dilution Acid Strength (if Different)					2%														4.2 %wt.		
Internal Standard Elements (if Any)	Y			Sc, Y, and In	Be, Sc, In	In							Sc						Y or In		
Instrument Type	ICP-AES	ICP-OES	SF-ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-OES	MC-ICP-MS	ICP-OES	ICP-OES	SF-ICP-MS	ICP-OES	ICP-OES	ICP-MS	ICP-AES	ICP-OES	ICP-OES	SF-ICP-MS	ICP-OES or MS	ICP-MS	ICP-AES

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 $^{86}Sr^{2+}$ on $^{43}Ca^{+}$ and $^{88}Sr^{2+}$ on $^{44}Ca^{+}$ 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 and 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 2σ, $n = 113$) and 1.2% Mg/Ca (relative standard deviation 2σ, $n = 98$). 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 $0.59 \cdot n$ replicates can be included in

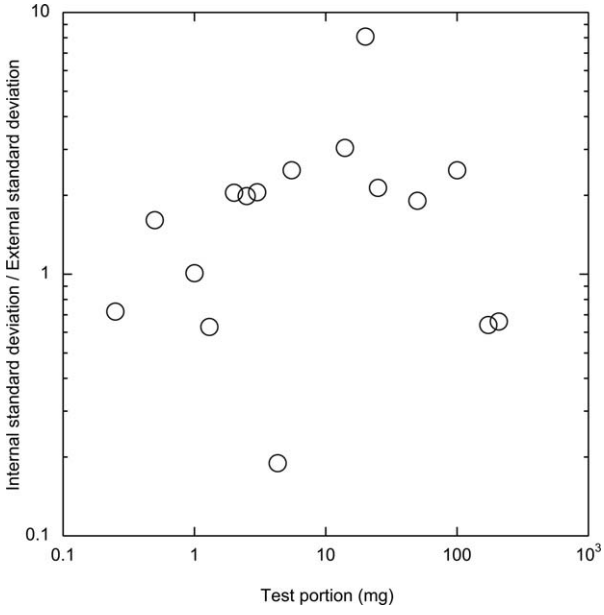


Figure 3. The ratio of the average standard deviation of measurements of a single dissolution (internal) to the standard deviation of the different dissolutions (external) reported by each lab. Each data point represents the results from a single laboratory plotted against the test portion sized used 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.

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 Zbíral*, 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 ≥0.25 mg.

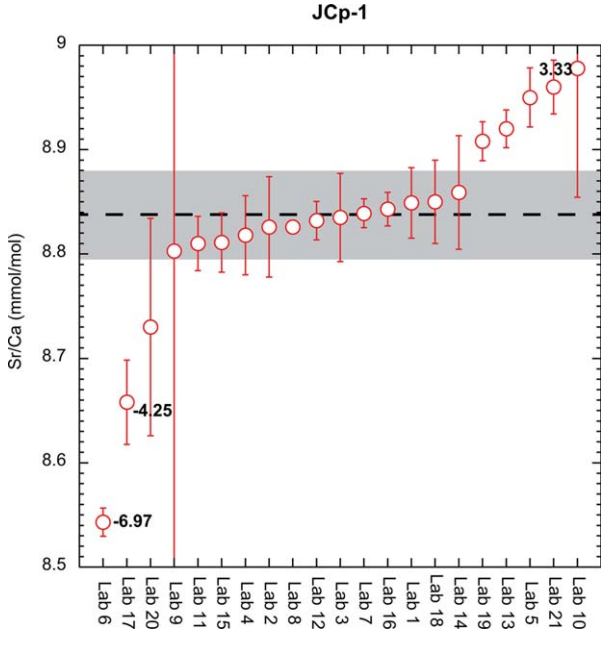


Figure 4. Ranked average Sr/Ca values for each laboratory with error bars representing two standard deviations of the mean (95% confidence level). For lab 9, the error bars are ±0.48 mmol/mol. The dashed line is the robust average and the gray area denotes the robust standard deviation of all the data. Z-scores calculated using the robust average and standard deviation that require action, >3 or <−3, are shown next to the appropriate data point.

Table 2. Summary of Results for JCp-1[a]

Laboratory	Sr/Ca (mmol/mol)	Mg/Ca (mmol/mol)	U/Ca (μmol/mol)	Ba/Ca (μmol/mol)	B/Ca (μmol/mol)	Li/Ca (μmol/mol)
Lab 1	8.849	4.213				
Lab 2	8.826	4.258				
Lab 3	8.835	4.114	1.229	8.830	448.3	
Lab 4	8.818	4.203	1.177		484.5	4.459
Lab 5	8.950	4.145	1.140	7.180		
Lab 6	8.543	4.102		7.130		6.227
Lab 7	8.839	4.270				
Lab 8	8.826	4.157				
Lab 9	8.803	3.990		1.284	150.3	
Lab 10	8.978	4.247				
Lab 11	8.810	4.219	1.450	8.284		
Lab 12	8.832	4.222		7.421		
Lab 13	8.920	4.275				
Lab 14	8.859	4.208	1.190	7.413	459.3	6.007
Lab 15	8.811	4.266		5.446		
Lab 16	8.843					
Lab 17	8.658	4.189				
Lab 18	8.850	4.140	1.090		469.0	6.290
Lab 19	8.908	4.239	1.203	7.947	436.6	
Lab 20	8.730	4.210	1.204	7.047		6.240
Lab 21	8.960					
Robust average	8.838	4.199	1.192	7.465	459.6	6.185
Robust standard deviation	0.042	0.065	0.045	0.655	22.7	0.107
Number of Labs (n)	21	19	8	10	6	5
Median within-Lab standard deviation	0.0129	0.0127	0.0116	0.0903	4.7	0.0718
u	0.0443	0.0659	0.0469	0.6616	23.2	0.1287
U	0.089	0.132	0.094	1.323	59.6	0.357
Two-sided t at 95% for $n-1$	2	2	2	2	2.571	2.776
Ok'04 provisional value (info value)	8.660	4.192	1.277	7.862	462.5	5.738
Combined Ok'04 U95%	0.095	0.041		0.384		

[a]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 0.3σ (where σ 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 σ is the interlab robust standard deviation. There may be better ways to estimate σ 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

Table 3. Summary of Results for JCt-1[a]

Laboratory	Sr/Ca (mmol/mol)	Mg/Ca (mmol/mol)	U/Ca (nmol/mol)	Ba/Ca (μmol/mol)	B/Ca (μmol/mol)	Li/Ca (μmol/mol)
Lab 1						
Lab 2	1.693	1.292				
Lab 3	1.698	1.291	25.00	4.540	184.0	
Lab 4	1.669	1.280	20.90		206.2	3.008
Lab 5	1.740	1.320	22.00			
Lab 6	1.619	1.253		4.355		4.165
Lab 7						
Lab 8	1.676	1.257				
Lab 9	1.710	1.368		2.517		
Lab 10	1.596	1.082				
Lab 11	1.677	1.290	31.17	4.938		
Lab 12	1.681	1.286		4.490		
Lab 13	1.666	1.244				
Lab 14	1.667	1.261	22.36	4.325	189.0	4.046
Lab 15						
Lab 16	1.678					
Lab 17	1.702	1.336				
Lab 18						
Lab 19	1.681	1.805		4.018		
Lab 20	1.720	1.288	20.44	4.352		4.584
Lab 21	1.624					
Robust average	1.680	1.289	22.71	4.348	191.0	4.076
Robust standard deviation	0.026	0.045	2.40	0.280	9.3	0.503
Number of Labs (n)	17	15	6	8	3	4
Median within-Lab standard deviation	0.00693	0.00939	0.6775	0.1016	1.747	0.0294
u	0.0273	0.0459	2.4895	0.2976	9.4582	0.5037
$\boldsymbol{U}$	0.055	0.092	6.40	0.595	40.7	1.603
Two-sided t at 95% for $n-1$	2	2	2.571	2	4.303	3.182
Ok'04 provisional value (info value)	1.651	1.245	21.12	4.557	184.1	3.104
Combined Ok'04 U95%	0.059	0.017		0.299		

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

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 [*Corrège*, 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 2σ.

[20] It is more appropriate to consider the precision desired for the application of different element/Ca ratios when determining the "fitness for

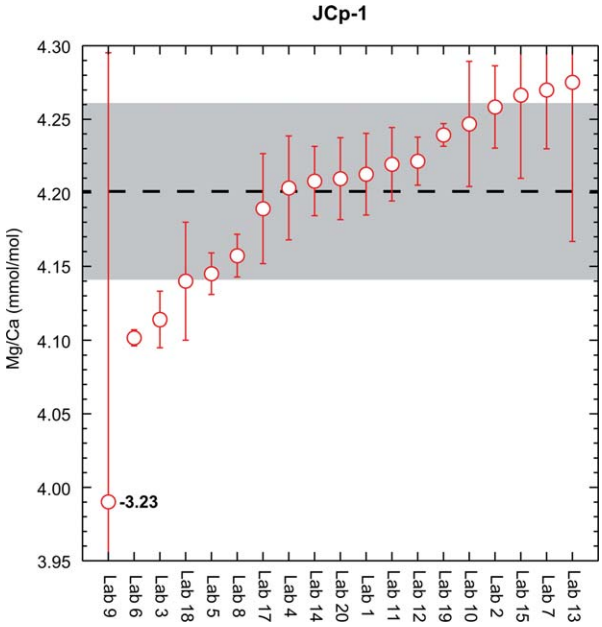


Figure 5. Ranked average Mg/Ca values for each laboratory with error bars representing two standard deviations of the mean (95% confidence level). For lab 9, the error bars are ±0.3 mmol/mol. The dashed line is the robust average and the gray area denotes the robust standard deviation of all the data. Z-scores calculated using the robust average and standard deviation that require action, >3 or <−3, are shown next to the appropriate data point.

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 μmol/mol per °C [e.g., *Sinclair et al*., 1998; *Quinn and Sampson*, 2002; *Felis et al*., 2009] while a change of 0.21 μmol/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 μmol/mol for the U/Ca ratio of JCp-1 is fit for purpose for determining changes of 0.5 pH units or about 2° of temperature. Similar considerations suggest the *U* of 60 μmol/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° 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° 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 μmol/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 JCt-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 JCt-1 agree well with the isotope dilution measurements suggests that although the JCt-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 [*Corrège*, 2006]. In contrast, the robust average Sr/Ca value for the JCt-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 JCt-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 JCt-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 JCt-1 suggesting a systematic offset.

[23] The values from Ok'04 were all measured as weight units (ug/g or wt%) and as such may have

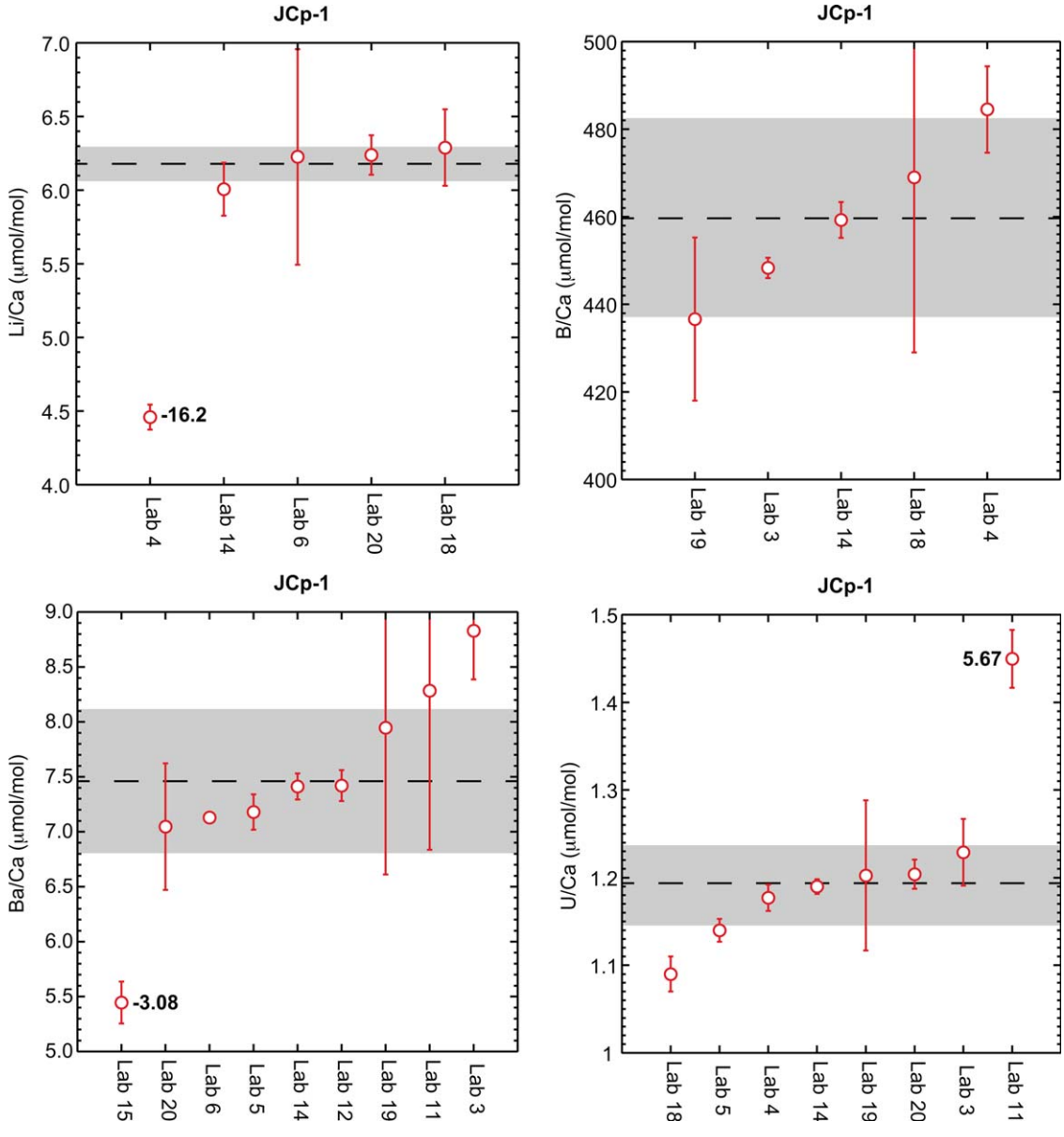


Figure 6. Ranked average Li/Ca, B/Ca, Ba/Ca, and U/Ca values for each laboratory with error bars representing two standard deviations of the mean (95% confidence level). The dashed line is the robust average and the gray area denotes the robust standard deviation of all the data. Z-scores calculated using the robust average and standard deviation that require action, >3 or <−3, are shown next to the appropriate data point.

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

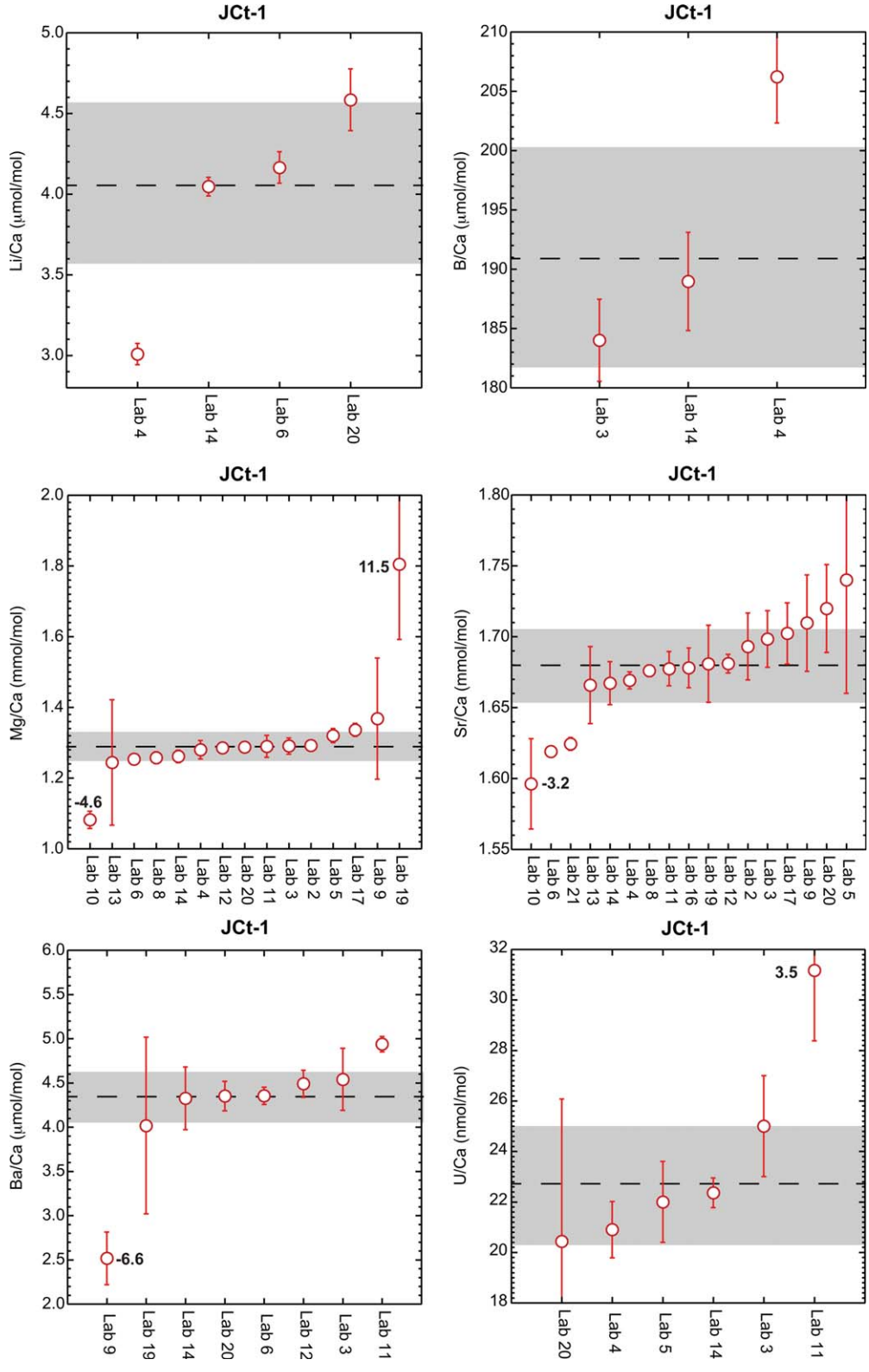


Figure 7. Ranked average Li/Ca, B/Ca, Mg/Ca, Sr/Ca, Ba/Ca, and U/Ca values for the JCt-1 reference material. Error bars represent two standard deviations of the mean (95% confidence level) for each laboratory. The dashed line is the robust average and the gray area denotes the robust standard deviation 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.

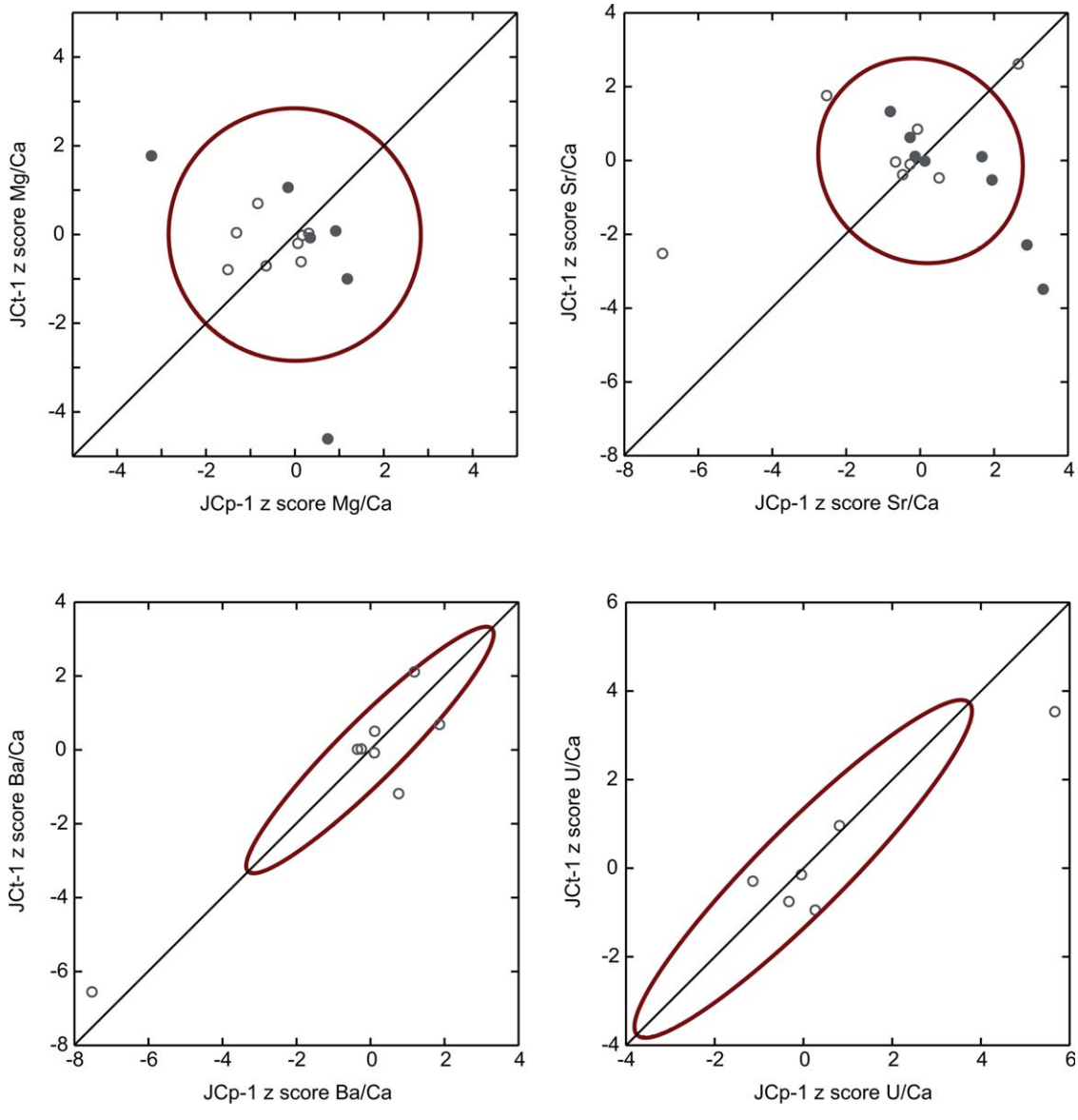


Figure 8. Youden plots of z-scores for both JCp-1 and JCt-1 from the different laboratories. Confidence ellipses were calculated following *ISO 13528* [2005]. For Mg/Ca and Sr/Ca, open points represent labs employing ICP-MS while filled points are from labs using ICP-OES.

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.

[25] 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.

[26] 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

[27] 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]:

$$y = (rs/rm)x$$

where y is $X/Ca_{sample\ actual}$, 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 $Sr/Ca_{standard\ actual}$

[28] 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.

[29] 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) HNO_3 with a density of 1.000 g/mL while the more concentrated Ca solution is in 2% (v/v) HNO_3 with a density of 1.038 g/mL. Not accounting for the 3.8% difference in density results in a calculated Sr/Ca ratio that is 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 HNO_3 matrix, from the same manufacturer at least, would have the same acid content.

[30] Another source of uncertainty for the Sr/Ca ratio of the standard solution is the variable amount of Sr impurity in the Ca standard solution. 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 $^{86}Sr^{2+}$ ion formation of 3% in their mass spectrometer and when 3% of the ^{86}Sr intensity was subtracted from the ^{43}Ca 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

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

[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 [*Corrège*, 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. This is common practice in isotope geochemistry where, for example, Sr isotope data are always accompanied by the average values obtained for the NBS 987 during the study. Reference materials are proliferating, and with tools like the GeoREM database [*Jochum and Nohl*, 2008] hopefully soon all geochemical data will be traceable to some degree.

5. Conclusions

[36] The Sr/Ca results from 21 different laboratories show interlaboratory bias can be significant and in the extreme case could result in a range in SST estimates of 7°C. Three laboratories achieved unsatisfactory z-scores for Sr/Ca ratios that require action meaning 85% of participating laboratories preformed well compared to the robust average and standard deviation. The *Porites* coral reference material JCp-1 is now characterized well enough to have a certified Sr/Ca value of 8.838 mmol/mol with an expanded uncertainty of 0.089 mmol/mol following International Association of Geoanalysts (IAG) guidelines. This uncertainty, at the 95% confidence level, equates to 1.5°C for SST estimates so is approaching fitness for purpose, but the comparable median within laboratory error is <0.5°C. Following QUAM guidelines and using the simplest analytical model as an example results in a combined expanded uncertainty of 0.098 mmol/mol, which equates to 1.6°C. The uncertainty component resulting from Sr impurities in the Ca standard is estimated to contribute 0.3°C. The combined expanded uncertainty could be reduced to 0.8°C if the standard Sr/Ca ratio is known precisely. This reveals the interlaboratory bias component that should be reduced in the future through the use of reference materials like the JCp-1. 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.

Acknowledgments

[37] Thanks, Danke and Merci to all participants and laboratories. E.C.H. (MARUM Fellowship) and T.F. were supported by the DFG-Research Center/Excellence Cluster "The Ocean in the Earth System," University of Bremen. The Geological Survey of Japan prepared the reference materials and kindly supplied them for this study. Christina Gnade (MARUM) helped distribute reference powders and collected the data. HVM was supported by an AINSE Research Fellowship.

References

Allison, N., A. A. Finch, and EIMF (2010), δ^{11}B, Sr, Mg and B in a modern Porites coral: The relationship between calcification site pH and skeletal chemistry, *Geochim. Cosmochim. Acta*, *74*(6), 1790–1800.

Andreasen, D. H., S. Sosdian, S. Perron-Cashman, C. H. Lear, T. deGaridel-Thoron, P. Field, and Y. Rosenthal (2006), Fidelity of radially viewed ICP-OES and magnetic-sector ICP-MS measurement of Mg/Ca and Sr/Ca ratios in marine biogenic carbonates: Are they trustworthy together?, *Geochem. Geophys. Geosyst.*, *7*, Q10P18, doi:10.1029/2005GC001124.

Asami, R., T. Felis, P. Deschamps, K. Hanawa, Y. Iryu, E. Bard, N. Durand, and M. Murayama (2009), Evidence for tropical South Pacific climate change during the Younger Dryas and the Bølling-Allerød from geochemical records of fossil Tahiti corals, *Earth Planet. Sci. Lett.*, *288*(1-2), 96–107.

Beck, J. W., R. L. Edwards, 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*(5070), 644–647.

Camoin, G. F., Y. Iryu, D. B. McInroy, and the Expedition 310 Scientists (2007), *Proc. IODP*, 310: Washington, DC

(Integrated Ocean Drilling Program Management International, Inc.). doi:10.2204/ iodp.proc.310.2007.

Coadic, R., F. Bassinot, D. Dissard, E. Douville, M. Greaves, and E. Michel (2013), A core-top study of dissolution effect on B/Ca in Globigerinoides sacculifer from the tropical Atlantic: Potential bias for paleo-reconstruction of seawater carbonate chemistry, *Geochem. Geophys. Geosyst.*, doi:10.1029/2012GC004296, in press.

Corrège, T. (2006), Sea surface temperature and salinity reconstruction from coral geochemical tracers, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *232*(2-4), 408–428.

DeLong, K. L., T. M. Quinn, C.-C. Shen, and K. Lin (2010), A snapshot of climate variability at Tahiti at 9.5 ka using a fossil coral from IODP Expedition 310, *Geochem. Geophys. Geosyst.*, *11*, Q06005, doi:10.1029/2009GC002758.

Ellison, S. L. R., and A. Williams (Eds). Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition (2012), ISBN 978-0-948926-30-3. [Available from www.eurachem.org].

Fallon, S. J., J. C. White, and M. T. McCulloch (2002), Porites corals as recorders of mining and environmental impacts: Misima Island, Papua New Guinea, *Geochim. Cosmochim. Acta*, *66*(1), 45–62.

Felis, T., A. Suzuki, H. Kuhnert, M. Dima, G. Lohmann, and H. Kawahata (2009), Subtropical coral reveals abrupt early-twentieth-century freshening in the western North Pacific Ocean, *Geology*, *37*(6), 527–530.

Felis, T., et al. (2012), Pronounced interannual variability in tropical South Pacific temperatures during Heinrich Stadial 1, *Nat. Commun.*, *3*(965), doi:10.1038/ncomms1973.

Fernandez, D. P., A. C. Gagnon, and J. F. Adkins (2011), An isotope dilution ICP-MS method for the determination of Mg/Ca and Sr/Ca ratios in calcium carbonate, *Geostand. Geoanal. Res.*, *35*(1), 23–37.

Gagan, M. K., L. K. Ayliffe, D. Hopley, J. A. Cali, G. E. Mortimer, J. Chappell, M. T. McCulloch, and M. J. Head (1998), Temperature and surface-ocean water balance of the mid-Holocene tropical western Pacific, *Science*, *279*, 1014–1018.

Greaves, M., et al. (2008), Interlaboratory comparison study of calibration standards for foraminiferal Mg/Ca thermometry, *Geochem. Geophys. Geosyst.*, *9*, Q08010, doi:08010.01029/02008GC001974.

Hathorne, E. C., T. Felis, R. H. James, and A. Thomas (2011), Laser ablation ICP-MS screening of corals for diagenetically affected areas applied to Tahiti corals from the last deglaciation, *Geochim. Cosmochim. Acta*, *75*(6), 1490–1506.

Hathorne, E. C., T. Felis, A. Suzuki, H. Kawahata, and G. Cabioch (2013), Lithium in the aragonite skeletons of massive Porites corals: A new tool to reconstruct tropical sea surface temperatures, *Paleoceanography*, *28*, 143–152, doi:10.1029/2012PA002311.

Inoue, M., M. Nohara, T. Okai, A. Suzuki, and H. Kawahata (2004), Concentrations of trace elements in carbonate reference materials coral JCp-1 and giant clam JCt-1 by inductively coupled plasma-mass spectrometry, *Geostand. Geoanal. Res.*, *28*(3), 411–416.

Inoue, M., R. Suwa, A. Suzuki, K. Sakai, and H. Kawahata (2011), Effects of seawater pH on growth and skeletal U/Ca ratios of Acropora digitifera coral polyps, *Geophys. Res. Lett.*, *38*, L12809, doi:10.1029/2011GL047786.

ISO 5725-5 (1998), *Accuracy (trueness and precision) of measurement methods and results—Part 5: Alternative methods for the determination of the precision of a standard measurement method*, Int. Organ. for Stand., Geneva.

ISO 13528 (2005), *Statistical methods for use in proficiency testing by interlaboratory comparisons*, Int. Organ. for Stand., Geneva.

Jochum, K. P., and U. Nohl (2008), Reference materials in geochemistry and environmental research and the GeoReM database, *Chem. Geol.*, *253*, 50–53.

Kane, J. S. (2002), Fitness-for-purpose of reference material reference values in relation to traceability of measurement, as illustrated by USGS BCR-1, NIST SRM 610 and IAEA NBS28, *Geostand. Newsl.*, *26*(1), 7–29.

Kane, J. S. (2004), Report of the International Association of Geoanalysts on the certification of Penrhyn slate, OU-6, *Geostand. Geoanal. Res.*, *28*(1), 53–80.

Kane, J. S., and P. J. Potts (2002), Traceability in geochemical analysis, *Geostand. Newsl.*, *26*(2), 171–180.

Kane, J. S., P. J. Potts, M. Wiedenbeck, J. Carignan, and S. Wilson (2003), International Association of Geoanalysts' protocol for the certification of geological and environmental reference materials, *Geostand. Newsl.*, *27*(3), 227–244.

Le Cornec, F., and T. Corrège (1997), Determination of uranium to calcium and strontium to calcium ratios in corals by inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.*, *12*(9), 969–973.

Marchitto, T. M. (2006), Precise multielemental ratios in small foraminiferal samples determined by sector field ICP-MS, *Geochem. Geophys. Geosyst.*, *7*, Q05P13, doi:10.1029/2005GC001018.

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*(6924), 727–730.

McCulloch, M. T., M. K. Gagan, G. E. Mortimer, A. R. Chivas, and P. J. Isdale (1994), A high-resolution Sr/Ca and δ^{18}O coral record from the Great Barrier Reef, Australia, and the 1982–1983 El Nino, *Geochim. Cosmochim. Acta*, *58*(12), 2747–2754.

Meibom, A., J.-P. Cuif, F. Houlbreque, S. Mostefaoui, Y. Dauphin, K. L. Meibom, and R. Dunbar (2008), Compositional variations at ultra-structure length scales in coral skeleton, *Geochim. Cosmochim. Acta*, *72*, 1555–1569.

Min, G. R., L. R. Edwards, F. W. Taylor, J. Recy, C. Gallup, and J. W. Beck (1995), Annual cycles of U/Ca in coral skeletons and U/Ca thermometry, *Geochim. Cosmochim. Acta*, *59*, 2025–2042.

Mitsuguchi, T., E. Matsumoto, O. Abe, T. Uchida, and P. J. Isdale (1996), Mg/Ca Thermometry in coral skeletons, *Science*, *274*(5289), 961–963.

Nurhati, I. S., K. M. Cobb, and E. Di Lorenzo (2011), Decadal-scale SST and salinity variations in the central tropical Pacific: Signatures of natural and anthropogenic climate change, *J. Clim.*, *24*(13), 3294–3308.

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. Newsl.*, *26*, 95–99.

Okai, T., A. Suzuki, S. Terashima, M. Inoue, M. Nohara, H. Kawahata, and N. Imai (2004), Collaborative analysis of GSJ/AIST geochemical reference materials JCp-1 (Coral) and JCt-1 (Giant Clam), *Chikyu Kagaku*, *38*, 281–286.

Ourbak, T., T. Corrège, B. Malaizē, F. Le Cornec, K. Charlier, and J. P. Peypouquet (2006), A high-resolution investigation of temperature, salinity, and upwelling activity proxies in corals, *Geochem. Geophys. Geosyst.*, *7*, Q03013, doi:10.1029/2005GC001064.

Prouty, N., K. Hughen, and J. Carilli (2008), Geochemical signature of land-based activities in Caribbean coral surface samples, *Coral Reefs*, *27*(4), 727–742.

Prouty, N. G., M. E. Field, J. D. Stock, S. D. Jupiter, and M. McCulloch (2010), Coral Ba/Ca records of sediment input to the fringing reef of the southshore of Molokai, Hawaii, over the last several decades, *Mar. Pollut. Bull.*, *60*(10), 1822–1835.

Quinn, T. M., and D. E. Sampson (2002), A multiproxy approach to reconstructing sea surface conditions using coral skeleton geochemistry, *Paleoceanography*, *17*(4), 1062, doi:1010.1029/2000PA000528.

Raitzsch, M., E. C. Hathorne, H. Kuhnert, J. Groeneveld, and T. Bickert (2011a), Modern and late Pleistocene B/Ca ratios of the benthic foraminifer Planulina wuellerstorfi determined with laser ablation ICP-MS, *Geology*, *39*(11), 1039–1042.

Raitzsch, M., H. Kuhnert, E. C. Hathorne, J. Groeneveld, and T. Bickert (2011b), U/Ca in benthic foraminifers: A proxy for the deep-sea carbonate saturation, *Geochem. Geophys. Geosyst.*, *12*, Q06019, doi:10.1029/2010GC003344.

Ramos, F. C., J. A. Wolff, and D. L. Tollstrup (2004), Measuring 87Sr/86Sr variations in minerals and groundmass from basalts using LA-MC-ICPMS, *Chem. Geol.*, *211*, 135–158.

Rosenthal, Y., M. P. Field, and R. M. Sherrell (1999), Precise determination of element/calcium ratios in calcareous samples using sector field inductively coupled plasma mass spectrometry, *Anal. Chem.*, *71*, 3248–3253.

Russell, W. A., D. A. Papanastassiou, and T. A. Tombrello (1978), Ca isotope fractionation on Earth and other solar-system materials, *Geochim. Cosmochim. Acta*, *42*, 1075–1090.

Schrag, D. P. (1999), Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates, *Paleoceanography*, *14*(2), 97–102.

Shen, C.-C., H.-Y. Chiu, H.-W. Chiang, M.-F. Chu, K.-Y. Wei, S. Steinke, M.-T. Chen, Y.-S. Lin, and L. Lo (2007), High precision measurements of Mg/Ca and Sr/Ca ratios in carbonates by cold plasma inductively coupled plasma quadrupole mass spectrometry, *Chem. Geol.*, *236*, 339–349.

Sinclair, D. J., and M. T. McCulloch (2004), Corals record low mobile barium concentrations in the Burdekin River during the 1974 flood: Evidence for limited Ba supply to rivers?, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *214*, 155–174.

Sinclair, D. J., L. P. J. Kinsley, and M. T. McCulloch (1998), High resolution analysis of trace elements in corals by laser ablation ICP-MS, *Geochim. Cosmochim. Acta*, *62*(11), 1889–1901.

Srnková, J., and J. Zbíral (2009), Comparison of different approaches to the statistical evaluation of proficiency tests, *Accreditation Qual. Assurance*, *14*(8), 467–471.

Stott, L., A. Timmermann, and R. Thunell (2007), Southern hemisphere and deep-sea warming led deglacial atmospheric CO2 rise and tropical warming, *Science*, *318*, 435–438.

Sturgeon, R. E., S. N. Willie, L. Yang, R. Greenberg, R. O. Spatz, Z. Chen, C. Scriver, V. Clancy, J. W. Lam, and S. Thorrold (2005), Certification of a fish otolith reference material in support of quality assurance for trace element analysis, *J. Anal. At. Spectrom.*, *20*(10), 1067–1071.

Watters, R. L., Jr., K. R. Eberhardt, E. S. Beary, and J. D. Fassett (1997), Protocol for isotope dilution using inductively coupled plasma-mass spectrometry (ICP-MS) for the determination of inorganic elements, *Metrologia*, *34*(1), 87–96.

Wieser, M. E., D. Buhl, C. Bouman, and J. Schwieters (2004), High precision calcium isotope ratio measurements using a magnetic sector multiple collector inductively coupled plasma mass spectrometer, *J. Anal. At. Spectrom.*, *19*(7), 844–851.

Wilrich, P.-T. (2007), Robust estimates of the theoretical standard deviation to be used in interlaboratory precision experiments, *Accreditation Qual. Assurance*, *12*(5), 231–240.

Yu, J., J. Day, M. Greaves, and H. Elderfield (2005), Determination of multiple element/calcium ratios in foraminiferal calcite by quadrupole ICP-MS, *Geochem. Geophys. Geosyst.*, *6*, Q08P01, doi:10.1029/2005GC000964.