Click Here for Full Article

Cadmium measurements in coral skeleton using isotope dilution−inductively coupled plasma−mass spectrometry

Kathryn A. Matthews
Department of Earth and Environmental Science, University of Pennsylvania, 240 South 33rd Street, Philadelphia, Pennsylvania 19104–6316, USA (kam2@sas.upenn.edu)

William F. McDonough
Department of Geology, University of Maryland, College Park, Maryland 20742–4211, USA

Andréa G. Grottoli
School of Earth Sciences, Ohio State University, Columbus, Ohio 43210–1398, USA

[1] Here a method for the precise analysis of Cd/Ca in coral skeleton using inductively coupled plasma–mass spectrometry (ICP-MS) is presented. Isotope dilution and gravimetric standards with internal standardization were used for Cd and Ca determination, respectively. Separation of alkaline earth metals from Cd using ion chromatography reduced the high total dissolved solids while maintaining a strong Cd signal. Repeated Cd/Ca measurements of a coral standard yielded a precision of ±2.2% (one standard deviation as a fraction of signal). Analyses of reference materials (BCR-1, BHVO-1, W-2, GSR-3, GSR-6, CACB-1, JCp-1, and JCt-1) fell within established ranges, with a precision comparable to other ICP-MS measurements. Advantages of this approach over existing methods for corals are as follows: (1) reduced introduction of high-concentration elements into the mass spectrometer, (2) sample requirements as low as 15 mg (i.e., $\geq$1 pmol Cd/sample), and (3) determination of multiple element ratios on the same sample aliquot with a precision of ±7% or better.

1. Introduction

[2] Paleoceanographers require accurate measurements of cadmium present in reef-building coral skeleton to construct records of the frequency and intensity of oceanic upwelling. During upwelling, cadmium-rich deep water is brought to the surface and that increase in concentration is reflected in a coral's skeletal aragonite. A direct relationship between the Cd concentrations of seawater and coral skeleton has been observed, with a distribution coefficient of ∼1 [*Shen et al.*, 1987]. Pub-

Table 1. Reported Coral Skeletal Cd/Ca Ranges in Seasonally Upwelling Regions[a]

Cd/Ca Range, nmol Cd/mol Ca	Reported Error, % RSD	Definition of Error as Reported in the Publication	Cleaned Sample Mass, mg	Method	Species	Location	Source
1.5–7.0	±6–27	1 SD of triplicate analyses of samples	100	1	Pavona clavus	Galápagos	Shen et al. [1987]
1.0–5.0	±2–10	1 SD of duplicate analyses of samples	30	1	Montastrea annularis	Isla Tortuga, Venezuela	Reuer et al. [2003]
1.7–16.5	±9.8	percent relative error of duplicate samples	100	1	Pavona clavus	Galápagos	Shen et al. [1992]
1–8	±13	average relative SD of individual samples from du/triplicate samples	100	1	Pavona clavus	Galápagos	Linn et al. [1990]
9–20	±5	overall measurement reproducibility	100	1	Pavona gigantea	Gulf of Panamá	Shen and Sanford [1990]
1–7	±5	overall measurement reproducibility	100	1	Pavona clavus	Galápagos	Shen and Sanford [1990]
5.98	±2.2	1 SD of replicate analyses (n = 7)	15	2	Pavona clavus (PPC-1)	Gulf of Panamá	this study

[a] Relative standard deviation (RSD) is one standard deviation (SD) divided by the Cd/Ca value. Method 1 is Cd via GFAAS, Ca via FAAS; method 2 is Cd via ID-ICP-MS, Ca via ICP-MS.

lished Cd values (reported as a ratio with respect to calcium) range from 1 to >20 nmol Cd/mol Ca (i.e., 1 to >22 ppb Cd) for corals from seasonally upwelling regions (Table 1). To date, all coral Cd analyses have been conducted using graphite furnace atomic adsorption spectroscopy (GFAAS) with relative standard deviations (1 standard deviation as a percent of signal; RSD) ranging from ~2% to ~20% (Table 1). It should be noted that the sample size requirement for GFAAS (30 – 100 mg coral) has made elucidating the full range and variability of the upwelling record as recorded in coral skeleton difficult, since previous studies were only able to take bulk samples (i.e., ≥3 months growth) that yielded average values over that time. Coral skeletal Cd has also been measured as a tracer of pollution in corals growing near industrial/urban sites where Cd concentrations can be 10 times higher than those found in pristine areas, and are usually reported as a dry weight concentration. Pollution levels of Cd are typically measured by atomic adsorption spectroscopy (33.7% RSD of duplicates [*Hanna and Muir*, 1990]), anodic stripping voltametry (7.2% RSD of duplicates with a detection limit of 50 ppb [*McConchie and Harriot*, 1992]) and standard addition inductively coupled plasma–mass spectrometry (ICP-MS) (no error reported [*Scott*, 1990]). In general, large sample requirements, higher detection limits and/or lower precisions render these methods difficult to use for paleoceanographic reconstructions.

[3] Previously published methods using ICP-MS to analyze Cd in carbonates were developed using foraminifera [e.g., *Lea and Martin*, 1996; *Mashiotta et al.*, 1997; *Rosenthal et al.*, 1999; *Yu et al.*, 2005; *Harding et al.*, 2006]. Although the trace metal concentrations in foraminifera and corals are often similar, the Cd/Ca ratios in forams (50–250 nmol Cd/mol Ca) are substantially higher than those in corals (1–30 nmol/mol). Since Cd background levels become large relative to signal below ~15 nmol/mol, foram-based ICP-MS methods are difficult to adapt for high-precision Cd analysis of pristine corals. For example, a recently published method for ICP-MS analysis of forams by *Rosenthal et al.* [1999] scanned a single isotope of Cd, and ratios were calculated using direct measurements of signal intensity. While suitable for Cd/Ca ratio determination as long as the signal is sufficient, this method does not yield Cd concentration determinations in a sample. In addition, due to the high total dissolved solids (TDS) in the solutions used, that method

produced a large buildup of solids in the MS source during the course of the run, requiring frequent cleaning of skimmer and sample cones, adding peripheral cost and time to the analyses. Indeed, large throughput of high Ca and Mg TDS poses a substantial blank memory problem for the mass spectrometer. Isotope dilution (ID) ICP-MS yields more precise results (e.g., for forams in the work of *Lea and Martin* [1996]), and when combined with chromatographic separation to scrub out unnecessary dissolved solids [*Strelow et al.*, 1978], improves measurements of Cd and substantially reduces the negative consequences for the mass spectrometer. This is the approach used here for coral Cd/Ca analyses.

[4] The application of ID-ICP-MS results in highly accurate and precise data, without the need for a full recovery of the element during preconcentration or separation steps. Comprehensive reviews of this technique are presented elsewhere [*Fasset and Paulsen*, 1989; *Smith*, 2000]. Briefly, ID-ICP-MS involves the addition of a known amount of an enriched isotope of the element of interest (the spike) to the sample. This addition is made prior to sample dissolution so that any subsequent sample loss does not influence the isotopic ratio. The sample concentration is determined by measuring the isotopic composition of the mixture (sample and spike), and knowing the sample and spike weights, and the isotopic ratios of the sample and spike. Since the results are based on the mixture ratio, dilution errors, instrumental drift and other related matrix effects do not affect the outcome. This technique is considered a definitive method and is well suited for the certification of reference materials and other measurements that require a high degree of accuracy and precision.

[5] Here a novel approach is described for the determination of Cd/Ca and Cd concentration in coral skeleton. An anion exchange resin was used to separate the alkaline earth metals (Mg, Ca, Sr, Ba) from Cd to reduce the high TDS while maintaining a strong Cd signal. Each sample was processed as a pair, once for Ca and once for Cd. This method was tested using an in-house coral standard (PPC-1) in addition to existing silicate and carbonate standard materials. Cd concentration data are reported for the following certified reference materials: BCR-1 (basalt), W-2 (andesite), BHVO-1 (basalt), GSR-3 (basalt), GSR-6 (argillaceous limestone), CACB-1 (calcium carbonate), as well as two new carbonate reference materials from

Japan's Geologic Survey, JCt-1 (giant clam) and JCp-1 (coral).
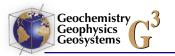
2. Experimental Procedures

[6] Coral and other carbonate samples were spiked, dissolved and passed through an anionic chromatographic column to remove alkaline earth elements. The Cd-bearing elutant was then reconstituted in 2% HNO_3 and analyzed using a single-collector ICP-MS with dry desolvation introduction. Full details on the sample preparation, solution chemistry and the ICP-MS analyses are given below.

2.1. Solutions, Resin, and Standards

[7] All solutions were made with MilliQ water (18 mΩ; Millipore, MA) and ultrapure reagents unless otherwise noted. All labware was precleaned prior to sample handling in a Class 100 clean room. Teflon vials (Savillex, MN) were leached in 6M HCl at 90°C for 24 h and then rinsed 5 times with MillliQ water. Column tubes, pipette tips, polycarbonate autosampler cups and HDPE vials were leached for at least 24 h in 1M HCl and then rinsed thoroughly with MilliQ water.

[8] The strongly basic anion exchange resin AG1-X8 (Bio-Rad Laboratories, CA) was used in this method. This is a low-porosity analytical grade resin (100–200 mesh size, Cl^- form) with quaternary ammonium functional groups attached to the styrene divinylbenzene copolymer lattice. Further details about the application of this resin to trace metal separations can be found elsewhere [*Strelow et al.*, 1978]. The resin was batch-rinsed with MilliQ water three times and then stored as a slurry in MilliQ water.

[9] An in-house carbonate coral standard (PPC-1) was made from a coral fragment (see preparation details below) and measured repeatedly to test the development of the chemical separation and analytical measurement methodologies (Figure 1, step 1). Gravimetric standards were used to make calibrations curves for Ca, Sr and Ba determination. A custom standard (SPEX Certi-Prep, NJ) was prepared from high-purity calcite. (Note that if additional elements are to be determined (e.g., Mg), then the Ca standard can be doped with appropriate amounts of those elements and multiple calibration curves can be derived from the same set of standards.) Stock standard solutions were diluted with ultrapure 2% HNO_3 (v/v) to concentrations that matched expected sample concentrations. For Ca
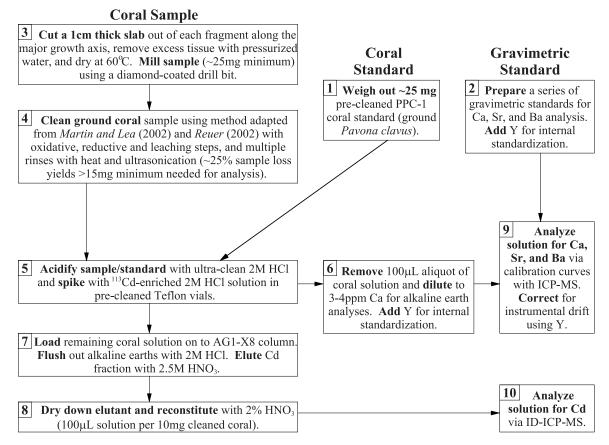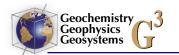
Coral Sample

3 **Cut a 1cm thick slab** out of each fragment along the major growth axis, remove excess tissue with pressurized water, and dry at 60°C. **Mill sample** (~25mg minimum) using a diamond-coated drill bit.

Coral Standard

1 **Weigh out ~25 mg** pre-cleaned PPC-1 coral standard (ground *Pavona clavus*).

Gravimetric Standard

2 **Prepare** a series of gravimetric standards for Ca, Sr, and Ba analysis. **Add** Y for internal standardization.

4 **Clean ground coral** sample using method adapted from *Martin and Lea* (2002) and *Reuer* (2002) with oxidative, reductive and leaching steps, and multiple rinses with heat and ultrasonication (~25% sample loss yields >15mg minimum needed for analysis).

5 **Acidify sample/standard** with ultra-clean 2M HCl and **spike** with ^{113}Cd-enriched 2M HCl solution in pre-cleaned Teflon vials.

6 **Remove** 100μL aliquot of coral solution and **dilute** to 3-4ppm Ca for alkaline earth analyses. **Add** Y for internal standardization.

9 **Analyze solution for Ca, Sr, and Ba** via calibration curves with ICP-MS. **Correct** for instrumental drift using Y.

7 **Load** remaining coral solution on to AG1-X8 column. **Flush** out alkaline earths with 2M HCl. **Elute** Cd fraction with 2.5M HNO_3.

8 **Dry down elutant and reconstitute** with 2% HNO_3 (100μL solution per 10mg cleaned coral).

10 **Analyze solution for Cd** via ID-ICP-MS.

Figure 1. Schematic flow diagram of sample preparation and analysis. Each step is numbered in the top left corner.

analyses, the 2% HNO_3 used for blank and sample solutions was spiked with yttrium (SPEX Certi-Prep, NJ) for internal standardization purposes (Figure 1, step 2).

2.2. Coral Sample and Ca Fraction Preparation

[10] The in-house coral standard, PPC-1, was made from a *Pavona clavus* fragment collected from the Gulf of Chiriqui, Panamá (Pacific) in July 2002. The fragment was cleaned of surface tissue using pressurized seawater and then frozen for shipment to the University of Pennsylvania. Upon arrival the fragment was cleaned of remaining tissue using pressurized MilliQ water, and dried for 5 days at 60°C. A large (~10 cm^3) section of the fragment was homogenized in an agate mortar (precleaned in weak acid and MilliQ water), sieved to include the $300-700$ μm range grain sizes, and stored in a cleaned HDPE bottle.

[11] All sample handling after this step occurred in a Class 100 clean room at the University of Maryland. Coral samples of approximately 25 mg were precleaned for elemental analysis following a

method adapted from the works of *Martin and Lea* [2002] and *Reuer* [2002], which ensured the removal of both organics and metal oxides such that only lattice-bound elements were measured (Figure 1, steps 3–4). Samples were ultrasonicated in MilliQ water, oxidized in a solution of 50:50 0.2M NaOH and 30% H_2O_2, reduced using hydrazine buffered in 50:50 mixture of 30% NH_4OH and 0.25M $(NH_4)_2C_6H_6O_7$, and leached in 0.001M HNO_3, with subboiling heat baths and ultrasonication, and multiple MilliQ water rinses between steps. This cleaning usually resulted in a ~25% loss of mass, although species with a coarser skeletal structure (e.g., *Pavona gigantea*) retained more sample than species with a finer structure (e.g., *Porites lobata*). After careful weighing, the coral standard was then spiked with ^{113}Cd and acidified in 2M HCl (in a ratio of 100 mg coral/mL soln) in a Teflon vial (Figure 1, step 5). The ^{113}Cd spike (Oak Ridge National Laboratory, TN) solution was prepared and characterized in house. For Ca, Sr and Ba analysis, 100 μL of the spiked solution was added to 9.9 mL of Y-spiked 2% HNO_3 (Ca = 3–4 ppm) and set aside (Figure 1, step 6). (Note that if needed, this diluted solution

could also be used for additional minor and trace element analyses such as Mg and U.)

2.3. Silicate Standard Preparation

[12] The silicate-bearing reference materials (i.e., BCR-1, BHVO-1, W-2, GSR-3, and GSR-6) were digested on a hotplate at 120°C for 2 hours with ultrapure, concentrated HNO_3 and HF. That solution was then dried down, reconstituted in HNO_3 alone to remove fluorine, and then evaporated to dryness. The residue was reconstituted in 2M HCl to match the chemistry of the carbonate standards and then processed in parallel with them for Cd analysis.

2.4. Column Preparation and Cadmium Separation

[13] Using a pipette, 0.4 mL of wet resin was added to a 10-mL Poly Prep column (Bio-Rad, CA). The resin was flushed with 10 mL MilliQ water, 4 mL 12M HCl, 5 mL MilliQ water and then conditioned with 4 mL 2M HCl. The remaining 9.9 mL 2M HCl carbonate solution was slowly added to the resin bed, and the alkaline earth metals were eluted with 10 mL 2M HCl and discarded. Using 10 mL 2.5M HNO_3, Cd was eluted from the resin (Figure 1, step 7) and dried down on a warm hotplate ($\sim$20 h at 80°C) in a laminar flow fume hood. The sample residue (often not visible to the naked eye) was reconstituted with 2% HNO_3, capped, ultrasonicated for 5 minutes and set on the hot plate for 30 minutes at 80°C. The samples were then removed, ultrasonicated again and allowed to cool to room temperature (Figure 1, step 8).

[14] For final sample reconstitution after the column elution, it was determined that a ratio of 100 μL 2% HNO_3 per 10 mg of coral powder was most suitable (i.e., 25 mg of sample yields a final solution volume of 250 μL). A more concentrated solution delivered excess Ca, and in a less concentrated solution the Cd signal had an unacceptably low signal-to-noise ratio for the mass spectrometer. If sample material is unlimited or the determination of bulk samples is desired, cleaned coral masses of up to $\sim$100 mg can be handled with the resin and solution quantities given above. However, if sample size is limited the cleaned sample mass can be reduced to as little as 15 mg, as a minimum of 150 μL is necessary for sample analysis.

[15] Repeated tests using both dissolved carbonate samples and gravimetric cadmium standards

Table 2. Instrumental Settings[a]

Instrument	Parameter	Setting
Element 2	rf power (W)	1220
Element 2	cool gas (L/min)	16
Element 2	sample gas (L/min)	0.90–1.10
Element 2	auxiliary gas (L/min)	1.00–1.20
Aridus	spray chamber (°C)	100
Aridus	desolvator (°C)	150
Aridus	sweep gas (L/min)	2.50–3.50
Aridus	N_2 (mL/min)	0.08–0.14

[a] Lenses, stage, and gas flows (except cool gas) were tuned to maximum sensitivity and stability before every run.

showed a 98–99% recovery rate of Cd from the resin. Calcium content of the cadmium elution was reduced by >500-fold (with a similar reduction in the concentration of other earth alkaline elements). This reduction of Ca allowed for the analysis of Cd without the problems associated with high TDS such as cone fouling and signal suppression due to matrix effects.

2.5. Instrumentation

[16] Measurements were carried out on a Finnigan Element 2 magnetic sector field ICP-MS (Thermo Electron Corp., Bremen, Germany), using low resolution (300), operated in E-scan mode (a combination of magnet jumps and electrostatic peak hopping). The large dynamic range of the detector allowed for the simultaneous measurement of Ca, Sr and Ba, which differ in concentration by six orders of magnitude. The sample introduction system consisted of an Aridus (CETAC Technologies, NE) with an efficient membrane desolvation system, coupled to a PTFE spray chamber and low flow (50 μL/min) nebulizer (Elemental Scientific Inc., NE). The system also included N_2 addition for signal enhancement. Operating conditions are outlined in Table 2 and the acquisition method is detailed in Table 3. Prepared sample solutions (Figure 1, steps 9 and 10) were introduced to the Aridus using a ASX-100 Micro Autosampler (CETAC Technologies, NE). Analysis time for 15 samples including instrument and procedural blanks, internal standards, gravimetric standards, reference materials, duplicates and between-sample washes, was approximately 3 hours.

2.6. Sample Analyses

[17] Ca, Sr, and Ba data were all normalized to Y to correct for signal drift over the course of the run, blank corrected and then concentrations calculated using the calibration curves of the gravimetric

Table 3. Acquisition Methods for Cd, Sr, Ba and Ca[a]

Isotope	Mass Window, %	Magnet Settling Time, s	Sample Time, s	Samples per Peak
Cd Method (40 Runs, 1 Pass)				
Cd-111	120	0.275	0.0150	15
Cd-113	150	0.001	0.0150	10
In-115	100	0.001	0.0050	7
Sn-117	100	0.001	0.0050	7
Sn-118	100	0.001	0.0050	7
Ca Method (40 Runs, 1 Pass)				
Ca-43	120	0.275	0.0050	10
Ca-48	120	0.001	0.0050	10
Sr-86	120	0.080	0.0050	10
Sr-87	120	0.001	0.0050	10
Y-89	100	0.001	0.0050	8
Ba-135	100	0.071	0.0150	15
Ba-137	100	0.001	0.0150	15
Ba-138	100	0.001	0.0150	15

[a] The acquisition mode for all isotopes was E-scan, with counting detection mode in low resolution (300). Analysis times for Cd and Ca (plus Sr and Ba) methods were 36 s and 61 s, respectively.

standards ($r^2 \geq 0.985$). For quantification, ^{48}Ca, ^{87}Sr, and ^{138}Ba were used. At least one additional isotope of each element was monitored to check for interferences. Although not exhaustive, tests for a Ca matrix effect were performed. Using multielement standards where Ca concentrations ranged from 100 ppb to 20 ppm, it was determined that Ba and Sr signal intensities varied by ~5%. Since all samples were diluted to approximately the same concentration (3.6–4.1 ppm Ca), and the values fell well within the range of gravimetric standards used (1–5 ppm Ca), the matrix effect was likely indistinguishable from other errors given the analytical precision of the described method. For the Cd analyses, corrections for column blanks and interferences (<1.5%) were determined and the

$^{111}Cd/^{113}Cd$ ratio was used to calculate the Cd concentration (for calculation method details, see *Smith* [2000]). As there was potential for an ^{113}In interference on ^{113}Cd, ^{115}In was monitored (as was Sn for interference on ^{115}In); in all instances, the correction was minor (<0.30%).

2.7. Alternative Semiquantitative Method: A Non-ID Approach for Lower-Precision Analyses

[18] If high-precision Cd analyses are not required for a particular application or study, the same method can be run without the ID step. Using this simpler method, both Cd and Ca were determined using a series of gravimetric standards with Y internal standardization to correct for instrumental drift. Within-day reproducibility of Cd for a dissolved coral solution (PPC-2) was very high (e.g., 3.24 ± 0.04 nmol Cd/mol Ca ± 1SD, n = 8). However, long-term reproducibility was much lower (4.05 ± 0.29 nmol/mol, n = 56). Nevertheless, this simple and rapid method is ideal for initial, semiquantitative determinations, such as would be needed before accurate spiking of a sample of unknown composition, or for studies where the expected Cd range is large and a very small standard deviation is not required.

3. Results and Discussion

[19] Cd concentrations of eight geologic reference materials and of the in-house PPC-1 standard were measured (Table 4). The experimental uncertainties associated with these results, where given, are at ±1 standard deviation. This incorporates the uncertainties in sample and tracer weights, spike calibration, blank corrections and mass spectrometric

Table 4. Cd Measurements of Reference Materials[a]

Reference Material	Composition	Published Values Average ± 1SD (n), ppb	This Study Average ± 1SD (n), ppb
BCR-1	basalt	132 ± 7 (6)[b]	132.4 ± 10.6 (3)
BHVO-1	basalt	94 ± 6 (3)[b]	98 (1)
W-2	andesite	76.8 ± 2.3 (3)[b]	75 (1)
GSR-3	basalt	67[c]	69 (1)
GSR-6	argillaceous limestone	69[c]	65.5 ± 4.7 (4)
CACB-1	calcium carbonate	7.6 ± 1.1[d]	8.0 ± 0.3 (3)
JCp-1	coral (*Porites spp.*)	32 ± 2 (8)[e]	33.2 ± 2.6 (3)
JCt-1	giant clam	2.8 ± 0.6 (7)[e]	2.34 ± 0.37 (3)
PPC-1	coral (*Pavona clavus*)	n/a	4.82 ± 0.11 (7)

[a] Definitions are as follows: ppb, parts per billion; n, number of samples analyzed; Average = $(X_1 + X_2 + \ldots X_n)/n$; SD, standard deviation of the average.
[b] *Sands and Rosman* [1997, and references therein].
[c] *Govindaraju* [1994].
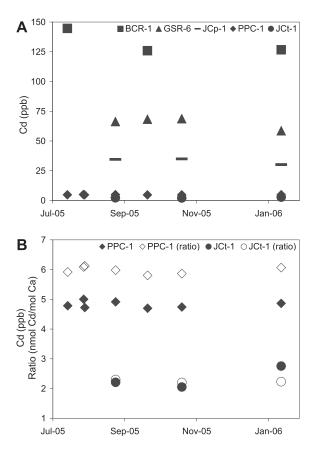[d] National Research Council of Canada.
[e] *Inoue et al.* [2004].

measurements. Although the inhomogeneity of the standards could not be directly assessed, with the exception of JCp-1, JCt-1 and PPC-1, the materials have been well studied and their uniformity has been well documented. In addition, it should be noted that over the course of several months, the results of repeated analyses showed no major variations or trends (Figure 2).

[20] Replicate analyses of BCR-1, GSR-6, and CACB-1 fell within the range of all published values. Indeed, high-quality Cd values via ID–thermal ionization–MS for BCR-1 are 130 ppb [*Govindaraju*, 1994] and 134 ppb [*Sands and Rosman*, 1997], compared with 132.4 ppb using this ID-ICP-MS method. Single measurements for BHVO-1, W-2, and GSR-3 are also in agreement with published concentrations. Repeated ID-ICP-MS analyses of the modern marine carbonate standards JCt-1 (giant clam) and JCp-1 (*Porites* coral) also fell within the range of published values obtained by standard addition ICP-MS [*Inoue et al.*, 2004]. Using this method, Cd abundance and Cd/Ca values for JCt-1 (2.34 ± 0.37 ppb and 2.24 ± 0.05 nmol/mol, respectively) were more precisely determined. The high Cd content for JCp-1 (33.2 ± 2.6 ppb and 38.7 ± 2.0 nmol/mol, respectively) was unusual for a coral and is most likely due to the lack of a precleaning step as is often done to marine carbonates prior to elemental analyses [*Reuer et al.*, 2003, and references therein]. The lack of well-described and widely used coral standards makes it difficult to calibrate measurements among laboratories. As such, a well-defined coral standard would be a valuable tool for trace metal coral geochemists.

[21] Seven measurements of the in-house standard, PPC-1, yielded an average value of 4.82 ± 0.11 ppb (2.3%RSD). When combined with Ca concentration data, that produced a ratio of 5.98 ± 0.13 nmol Cd/mol Ca (2.2%RSD), which agrees with previously published values of *Pavona clavus* from comparable locations. Using this ID-ICP-MS method, which requires smaller samples and has a lower percent RSD than previously published methods (see Table 1), the high-resolution, high-precision coral Cd/Ca measurements needed for paleoreconstructions can be reliably produced.

[22] This method can also be readily modified to include other elements. Although not explored at this time, additional trace elements could be measured in the Cd sample, including zinc, manganese and copper, as those coelute. In the Ca fraction, other elements can be measured as well, providing

Figure 2. Results of Cd analyses over time. Figure 2a displays data for all standards that were measured on more than one date. Figure 2b shows the results of the two least concentrated Cd standards, PPC-1 and JCt-1, and their Cd/Ca ratios.

their concentrations are high enough. In PPC-1, Sr (9.12 ± 0.51 mmol Sr/mol Ca; n = 10) and Ba (8.60 ± 0.63 μmol Ba/mol Ca; n = 6) were measured. Although precision for those elements is not as high as reported elsewhere [*Lea and Martin*, 1996], this method does not require ID for Ba and a simple multielement gravimetric standard can be used for Ca, Sr, and Ba measurement. Indeed, the Ca fraction analysis can be quickly and easily adapted for the analysis of other minor elements (e.g., Mg) by the addition of those elements to the gravimetric stock standard.

4. Summary

[23] A new technique for the preparation and analysis of Cd in coral skeleton is presented in which both the elemental Cd concentration and the Cd/Ca ratio are determined. The use of ion chromatography allowed for the separation of Cd from alkaline earth elements, concentrating the Cd fraction and

diluting the Ca-bearing fraction. Using small samples, low-concentration Cd measurements with high analytical precision are possible with reduced matrix and machine memory effects, and negligible cone fouling issues associated with concentrated Ca solutions [cf. *Rosenthal et al.*, 1999]. The use of isotope dilution with a ^{113}Cd spike significantly reduced the uncertainty accompanying the recovery of the element from the column.

[24] The Cd concentrations of eight reference materials were measured using ID-ICP-MS. For the first time, Cd ID-ICP-MS values were reported for GSR-3, GSR-6, JCp-1, and JCt-1. All values agreed, within experimental uncertainty, with previously published results. For replicate measurements of PPC-1, the relative standard deviation was similar to or better than previously published results for coral skeleton using GFAAS while using half of the sample mass required for that method. The use of this technique for the measurement of Cd, particularly in coral skeleton where concentrations are low, generates reproducible results without the need for concentrated solutions. Such a technique would be very suitable for the construction of high-resolution coral Cd/Ca records.

Acknowledgments

References

Fasset, J. D., and P. J. Paulsen (1989), Isotope dilution mass spectrometry for accurate elemental analysis, *Anal. Chem.*, *61*, 643–649.

Govindaraju, K. (1994), 1994 compilation of working values and sample description for 383 geostandards, *Geostand. Newsl.*, *18*, 1–158.

Hanna, R. G., and G. L. Muir (1990), Red Sea corals as biomonitors of trace metal pollution, *Environ. Monit. Assess.*, *14*, 211–222.

Harding, D. J., J. W. Arden, and R. E. M. Rickaby (2006), A method for precise analysis of trace element/calcium ratios in carbonate samples using quadrupole inductively coupled plasma mass spectrometry, *Geochem. Geophys. Geosyst.*, *7*, Q06003, doi:10.1029/2005GC001093.

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*, 411–416.

Lea, D. W., and P. A. Martin (1996), A rapid mass spectrometric method for the simultaneous analysis of barium, cadmium and strontium in foraminifera shells, *Geochim. Cosmochim. Acta*, *60*, 3143–3149.

Linn, L., M. Delaney, and E. Druffel (1990), Trace metals in contemporary and seventeenth-century Galápagos coral: Records of seasonal and annual variations, *Geochim. Cosmochim. Acta*, *54*, 387–394.

Martin, P. A., and D. W. Lea (2002), A simple evaluation of cleaning procedures on fossil benthic foraminiferal Mg/Ca, *Geochem. Geophys. Geosyst.*, *3*(10), 8401, doi:10.1029/2001GC000280.

Mashiotta, T. A., D. W. Lea, and H. J. Spero (1997), Experimental determination of cadmium uptake in shells of the planktonic foraminifera *Orbulina universa* and *Globigerina bulloides*: Implications for surface water paleoreconstructions, *Geochim. Cosmochim. Acta*, *61*, 4053–4065.

McConchie, D., and V. J. Harriot (1992), The partitioning of metals between tissue and skeletal parts of corals: Application in pollution monitoring, *Proc. Int. Coral Reef Symp.*, *7th*(1), 97–103.

Reuer, M. K. (2002), Centennial-scale elemental and isotopic variability in the tropical and subtropical North Atlantic Ocean, Ph.D. thesis, 187 pp., Mass. Inst. of Technol., Cambridge.

Reuer, M. K., E. A. Boyle, and J. E. Cole (2003), A mid-twentieth century reduction in tropical upwelling inferred from coralline trace element proxies, *Earth Planet. Sci. Lett.*, *210*, 437–452.

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.

Sands, D. G., and K. J. R. Rosman (1997), Cd, Gd, and Sm concentrations in BCR-1, BHVO-1, BIR-1, DNC-1, MAG-1, PCC-1 and W-2 by isotope dilution thermal ionisation mass spectrometry, *Geostand. Newsl.*, *21*, 77–83.

Scott, P. J. B. (1990), Chronic pollution recorded in coral skeletons in Hong Kong, *J. Exp. Mar. Biol. Ecol.*, *139*, 51–64.

Shen, G. T., and C. L. Sanford (1990), Trace element indicators of climate variability in reef-building corals, in *Global Ecological Consequences of the 1982–83 El Niño–Southern Oscillation*, edited by P. W. Glynn, pp. 255–283, Elsevier, New York.

Shen, G. T., E. A. Boyle, and D. W. Lea (1987), Cadmium in corals as a tracer of historical upwelling and industrial fallout, *Nature*, *328*, 794–795.

Shen, G. T., J. E. Cole, D. W. Lea, L. J. Linn, T. A. McConnaughey, and R. G. Fairbanks (1992), Surface ocean variability at Galápagos from 1936–1982: Calibration of geochemical tracers in corals, *Paleoceanography*, *7*, 563–588.

Smith, D. H. (2000), Isotope dilution mass spectrometry, in *Inorganic Mass Spectrometry*, edited by C. M. Barshick, D. C. Duckworth, and D. H. Smith, pp. 223–240, CRC Press, Boca Raton, Fla.

Strelow, F. W. E., A. Victor, and C. H. S. W. Weinert (1978), Ion exchange chromatography applied to the separation and accurate determination of some trace elements in rocks, *Geostand. Newsl.*, *2*, 49–55.

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.