A highly sensitive MC-ICPMS method for Cd/Ca analyses of foraminiferal tests

Sonja Ripperger*[a] and Mark Rehkämper[ab]

Received 21st March 2007, Accepted 19th June 2007
First published as an Advance Article on the web 6th July 2007
DOI: 10.1039/b704267a

A new, highly sensitive technique for the precise and accurate determination of Cd/Ca ratios in foraminiferal shells is presented and validated. The excellent accuracy and precision of the method reflects the application of an isotope dilution (ID) protocol for both Cd and Ca, and isotopic analysis by multiple collector inductively coupled plasma mass spectrometry. The determination of the Cd abundances involves simultaneous measurements of ^{110}Cd and ^{111}Cd with a dual ion counting system, whereas the ID analyses for the major element Ca were carried out by multiple collection with Faraday cups. The performance of the method was verified by analyzing multiple samples of the planktonic foraminifer *Orbulina universa* that were handpicked from a sediment core taken in the North Atlantic. Analyses of unspiked samples that consumed as little as ~200 ng Ca, indicate that the Ca ID measurements are accurate to about ±0.2% (all errors are 1 RSD). For the Cd ID analyses, the accuracy and precision is about ±1.3% and ±3% for measurements that consumed 3–12 pg and 0.5–1.5 pg of Cd, respectively. Repeated analyses of spiked *O. universa* tests yielded a reproducibility of ±0.7% for the Cd/Ca ratio, based on measurements that each consumed about 5 pg and 700 ng of natural Cd and Ca, respectively. The method is characterized by a total procedural Cd blank of 112 ± 44 fg (1 s.d.), which results in a detection limit of 131 fg (3 s.d.). This demonstrates that the new technique is superior to published methods for the determination of foraminiferal Cd/Ca ratios, particularly with regard to the acquisition of precise data for samples of limited size.

Introduction

The trace element composition of calcite foraminiferal shells has become an important tool to reconstruct past oceanic conditions. This is based on the observation that trace elements are incorporated directly from seawater into foraminiferal tests, and therefore reflect the seawater conditions present during shell precipitation. Foraminiferal Cd has attracted particular attention over the past 25 years. This interest is based on the nutrient-type distribution of Cd in the oceans, which resembles that of the major nutrient phosphorus.[1,2] Hence, foraminiferal Cd/Ca ratios have been used in numerous paleoceanographic studies to assess past nutrient utilization.

In the last decades, studies of Cd/Ca ratios of foraminifers have focused mainly on the analysis of benthic species, primarily for methodical reasons. The advantage of using benthic species is that they have larger shells with a higher Cd content (up to 0.25 μmol per mol Ca) than the tests of planktonic foraminifers,[3,4] and therefore the number of specimens needed for analysis is smaller. Because of improved analytical techniques (*e.g.*, sector field inductively coupled plasma mass spectrometry)[5,6] more recent studies have extended the application of Cd/Ca to planktonic foraminifers. Such measurements are of particular interest, because the Cd in planktonic foraminifera is believed to be a proxy for surface water phosphate utilization, which in turn is linked to productivity.[7,8]

The precise determination of Cd/Ca ratios in planktonic foraminifers is a challenging task, however, because Cd abundances can be as low as 0.002 μmol per mol Ca.[4] This becomes critical, especially in cases where sample material is limited, for example for *in-situ* collected planktonic foraminifers. Such measurements are of particular interest because they can address concerns regarding the reliability of the Cd/Ca proxy.[9,10]

Therefore, the general goal of this study was to develop techniques, which are routinely able to provide Cd/Ca ratios for foraminiferal tests with a precision and accuracy of better than 5%, even for samples with as little as 1–5 pg of Cd. This goal was achieved by the application of the isotope dilution technique in conjunction with a multiple collector inductively coupled plasma mass spectrometer (MC-ICPMS) that was equipped with a multiple ion counting system. This instrumental setup is ideally suited for precise isotope dilution measurements of trace elemental quantities, because it provides superior sensitivity and more efficient sample utilization during the analyses compared to quadrupole inductively coupled plasma mass spectrometry (Q-ICPMS) and single collector magnetic-sector ICP mass spectrometry.

[a] *Institute of Isotope Geochemistry and Mineral Resources, ETH Zürich, Clausiusstrasse 25, 8092 Zürich, Switzerland. E-mail: ripperger@erdw.ethz.ch; Fax: +41 44 632 1827; Tel: +41 44 632 3833*
[b] *Department of Earth Science and Engineering, Imperial College, London, UK SW7 2AZ. E-mail: markrehk@imperial.ac.uk*

Table 1 Average Cd isotope compositions determined for the JMC Cd Zürich standard and the ^{110}Cd-Spike-B. The uncertainties given in the parentheses denote 2 standard deviations (and refer to the last significant digits). n = number of measurements

Solution	n	$^{110}Cd/^{111}Cd$	$^{112}Cd/^{111}Cd$	$^{113}Cd/^{111}Cd$	$^{114}Cd/^{111}Cd$
JMC Cd Zürich[a]	56	0.977047 (122)	1.878769 (126)	0.950117 (69)	2.22783 (278)
^{110}Cd-Spike-B[b]	4	72.7346 (3860)	1.14095 (396)	0.432102 (2712)	0.915444 (6861)

[a] The isotope data for the JMC Cd Zürich standard were obtained over a period of 11 months by internal normalization relative to $^{110}Cd/^{114}Cd$ = 0.438564 (ref. 13) with the exponential law. [b] The isotopic data for the spike were obtained on four separate measurement days by external normalization to admixed Ag, relative to a value of $^{110}Cd/^{114}Cd$ = 0.438564 for natural Cd.

Laboratory methods and reagents

Laboratory methods

All blank-critical laboratory work was carried out in Class 10 laminar flow workbenches within a Class 10 000 clean room facility. Hydrazine and its solutions were only handled in conventional exhaust hoods, however, due to the toxicity of this reagent.[11] The mineral acids were purified once by sub-boiling distillation in quartz stills (6 M HCl, 14 M HNO_3) and the water was 18 MΩ-grade from a Millipore purification system. All reagents used for foraminiferal cleaning were of ultra pure quality. The reductive and oxidative cleaning solutions were freshly prepared on the day of use.[12]

Standard solutions

Cd isotope standard. A gravimetric "JMC Cd Zürich" solution[13] with a concentration of 1224.01 μg g^{-1} was prepared from 99.999% pure Cd metal pellets (Alfa Aesar Puratronic grade) that had been leached with 0.1 M HNO_3 and cleaned with water and ethanol to remove oxide coatings, prior to dissolution in 2 M HNO_3 (Table 1). Further dilutions of this primary solution were used for the calibration of Cd tracer solutions and as Cd isotope standards for MC-ICPMS analyses.

Ca isotope standard. A gravimetric Ca solution (288.73 μg g^{-1}) was prepared from NIST SRM 915a Ca, which is a 99.97% pure $CaCO_3$ powder purchased from the National Institute of Standards & Technology (Table 2). Prior to dissolution in 2 M HNO_3, the Ca powder had been dried in an oven at 70 °C for four hours and then stored in a desiccator to remove chemically bound water. The calibration of the Ca tracer and further MC-ICPMS analyses utilized solutions that were prepared from this primary stock solution.

Spike solutions

^{110}Cd spike preparation. About 50 mg of ^{110}Cd-enriched metal (95.6% purity, Isoflex Corp., USA) was dissolved in 200 ml of 2 M HNO_3 and the isotope composition and concentration of this solution (hereafter referred to as ^{110}Cd-Spike-A) were determined by mass spectrometry. These results were used to plan the preparation of a more dilute ^{110}Cd-Spike-B solution, which was made up from a suitable volume (~60 μl) of ^{110}Cd-Spike-A that was weighed, dried, and redissolved in ~1000 ml of 2 M HNO_3. Repeated analyses were conducted on four separate days to define the Cd isotope composition of the ^{110}Cd-Spike-B (Table 1) relative to the natural reference ratio of $^{110}Cd/^{114}Cd$ = 0.438564.[14] These analyses used external normalization to added Ag with the exponential law for mass bias correction.[13] The Cd concentration of the ^{110}Cd-Spike-B was determined by reverse isotope dilution using the gravimetric JMC Cd Zürich solution that was prepared in our laboratory. This solution is ideally suited for the calibration because its Cd concentration is known to within about ±0.02%. Repeated analyses of four separate spike–standard mixtures yielded a Cd concentration of 13.189 ± 0.026 ng g^{-1} (2 s.d.) for the tracer.

Finally, a very dilute ^{110}Cd-Spike-C solution was prepared for the spiking of small samples of foraminiferal tests. To this end, ~10 ml of the ^{110}Cd-Spike-B was weighed and diluted with 2 M HNO_3 to obtain one litre of tracer solution with a Cd concentration of 153.90 pg g^{-1}.

^{43}Ca spike preparation. About 6 mg of $CaCO_3$, isotopically enriched in ^{43}Ca (49.5% purity, Isoflex Corp., USA) was dissolved in 150 ml of 2 M HNO_3. The isotopic composition and concentration of this solution (hereafter referred to as ^{43}Ca-Spike-A) were then roughly determined by MC-ICPMS. Further dilution of this concentrated stock solution served to produce ^{43}Ca-Spike-B. The Ca isotope composition of this solution (Table 2) was determined by repeated analyses on 3 separate days, relative to the natural reference ratio of $^{42}Ca/^{44}Ca$ = 0.31221.[15] The spike analyses used an optimised fractionation factor that was based on the mean of instrumental mass fractionation factors determined for multiple analyses of a NIST SRM 915a Ca solution conducted on the same day. A Ca concentration of 0.6582 ng g^{-1} ± 0.0021 (2 s.d.) was determined by reverse isotope dilution for

Table 2 Average Ca isotope compositions determined for the NIST SRM 915a Ca standard and the ^{43}Ca-Spike-B. The uncertainties given in the parentheses denote 2 standard deviations (and refer to the last significant digits). n = number of measurements

Solution	n	$^{42}Ca/^{44}Ca$	$^{43}Ca/^{44}Ca$
NIST SRM 915a Ca[a]	88	0.312210	0.064800 (63)
^{43}Ca-Spike-B[b]	11	0.062563 (3228)	4.69550 (1549)

[a] The isotopic data for the NIST SRM 915a Ca standard were obtained over a period of 4 months by internal normalization to $^{42}Ca/^{44}Ca$ = 0.312210 (ref. 15) with the exponential law. [b] The isotope data for the ^{43}Ca-Spike-B were acquired over a period of 2 months. The spike was measured relative to NIST SRM 915a Ca using an empirically optimized fractionation factor (see section Spike solutions).

^{43}Ca-Spike-B, based on replicate analyses of 4 individual spike–standard mixtures.

Samples and sample handling

Samples

Planktonic foraminifers of the species *Orbulina universa* were used throughout this study for method validation. The specimens were picked from the >500 μm size fraction of homogenized sediment material from the Azores Front core KL 88 (34.78° N and 27.66° W, 2060 m water depth).[16]

A number of analyses were carried out on unspiked foraminiferal tests. In this case, sample size ranged from a maximum of about 15 specimens (equivalent to an initial weight of ~900 μg $CaCO_3$) down to only 4 specimens (equivalent to ~240 μg $CaCO_3$). In addition, we performed analyses of 1 and 2 specimens (equivalent to ~60–120 μg $CaCO_3$), that were first leached and dissolved according to the standard sample preparation protocol (see below), and then split into 2 or 3 approximately equal aliquots.

The analyses of spiked foraminiferal shells utilized a large homogenized sample of 46 *O. universa* tests. The tests were first leached and dissolved according to the standard sample preparation protocol (see below) and the solution was split into 4 approximately equal fractions. These fractions were then spiked and further processed and analyzed as four individual samples.

Cleaning of foraminiferal tests

Following picking, the foraminiferal tests were crushed with a Teflon needle, homogenized, and transferred to precleaned 1.5 ml centrifuge vials using a moistened brush. A cleaning procedure modified after Boyle and Keigwin,[17] Boyle and Rosenthal,[18] Martin and Lea,[12] and Weldeab *et al.*[19] was then applied (Table 3). The minor modifications pertain to the volumes of cleaning solution that were used (which were adapted to the sample size) and the exact duration of the ultrasonication periods. It is possible, albeit unlikely, that the applied procedure will slightly alter the Cd/Ca ratios of the residual carbonate material.[12,19] Any small alterations will not be problematic, however, as most laboratories now apply very similar leaching techniques. This ensures that the Cd/Ca data from various sources are comparable, even if the absolute ratios are slightly offset from the native values. Rigorously cleaned tests that are completely free of potentially contaminating phases (such as adhering detrital particles, Fe–Mn oxyhydroxide coatings or residues of organic tissue) are furthermore essential for paleoceanographic studies, which utilize the foraminiferal Cd/Ca ratios as a proxy of seawater nutrient utilization. Without such cleaning, residual contaminants can readily obscure the native Cd/Ca signal of the foraminiferal calcite and produce serious analytical artefacts and erroneous interpretations (*e.g.*, ref. 20 and 21).

In a first step (Table 3), clays and fine-grained carbonates were removed by rinsing the shell fragments with distilled water and methanol. Each rinse included 30 s of ultrasonication before the supernatant was siphoned off. The shell fragments were then treated with a reductive cleaning solution containing 1 M buffered hydrazine to remove Mn-rich coatings. Following addition of this solution, the samples were placed in a warm (50 °C) water bath for 30 min and ultrasonicated and flipped briefly every 5 min. Organic material, as well as any surface organics, were removed with an oxidative cleaning solution that was made up from 50 μl H_2O_2 (25%) and 5 ml NaOH (0.1 M). The treatment consisted of two oxidative cleaning steps, each including the addition of 250 μl cleaning solution, heating of the samples in a warm (50 °C) water bath for 10 min, as well as ultrasonication and a brief flipping of the centrifuge vials.

Table 3 Procedure used for the cleaning of foraminiferal tests

Initial rinse	3 rinses with distilled water (500 μl), ultrasonicate for 30 s each time and pipette off supernatant 3 rinses with methanol (500 μl), ultrasonicate for 30 s each time and pipette off supernatant 2 rinses with distilled water (500 μl), ultrasonicate for 30 s each time and pipette off supernatant
Reductive treatment	Reductive cleaning solution ("RCS"): 93.75 μl of 98.5% anhydrous hydrazine added to a mixture of 1.25 ml, 0.25 M citric acid monohydrate and 1.5 ml, 25% aqueous ammonium (freshly prepared on the day of use) Add 100 μl RCS, place samples in subboiling water bath (~50 °C) for 30 min, flip and briefly ultrasonicate every 5 min for 30 s and open caps Pipette off RCS 3 rinses with distilled water where vial and cap are filled completely, pipette off supernatant 2 rinses with distilled water (500 μl), ultrasonicate for 30 s each time and pipette off supernatant
Oxidative treatment	Oxidative cleaning solution ("OCS"): 50 μl of 25% H_2O_2 to 5 ml, 0.1 M NaOH solution (freshly prepared on the day of use) Carry out twice: add 250 μl OCS and heat for 10 min, flip and ultrasonicate twice for 30 s and pipette off supernatant 3 rinses with distilled water where vial and cap are filled completely, pipette off supernatant 2 rinses with distilled water (500 μl), ultrasonicate for 30 s each time and pipette off supernatant
Sample transfer	Carry out 3 times: add 100 μl distilled water and immediately transfer suspension to a new vial Pipette off excess water from sample in new vial
Weak acid leach	Add 250 μl of 0.001 M HNO_3, ultrasonicate for 30 s and pipette off supernatant 2 rinses with distilled water (500 μl), ultrasonicate for 30 s each time, and pipette off supernatant Carefully remove any remaining water
Dissolution	Dissolve test fragments in 500 μl of 0.075 M HNO_3 Ultrasonicate as long as CO_2 production increases Centrifuge for 5 min at 10 000 *g* and remove residual particles

Multiple water rinses were employed after the reductive and oxidative treatment to remove any suspended impurities and remaining reagents. After transferring the shell fragments to a fresh vial, any remaining organic material and contaminants adsorbed to the shell surfaces were removed by leaching the tests briefly with 0.001 M HNO_3. In a final step, the shell fragments were rinsed with distilled water and dissolved in 500 µl of 0.075 M HNO_3.

The leaching procedure was typically associated with about 50% of the sample material being lost during cleaning, which is similar to the loss reported in a previous study of benthic foraminifers.[22] This is most likely due to partial dissolution of shell fragments during the reductive treatment and weak acid leach, as well as the loss of small shell particles during solution transfers.

Spiking of samples

The sample solutions in 0.075 M HNO_3 were transferred to 2.5 ml Savillex beakers and split in two parts, whereby the minor aliquot (5%) was spiked with ^{43}Ca-Spike-B and the major aliquot (95%) with ^{110}Cd-Spike-C. To this end, a suitable mass of the ^{43}Ca tracer ($\sim$350 mg) was weighed into an empty Savillex beaker and 25 µl of the sample solution was added. The remaining 475 µl of solution was then spiked with a suitable volume ($\sim$80 mg) of the ^{110}Cd tracer. The spiked samples were then left on a hot plate to equilibrate for one day prior to evaporation to dryness.

The Ca aliquot did not require further processing and the residue was simply redissolved in $\sim$30 µl of 14 M HNO_3 for storage. Just prior to use, the Ca fraction was evaporated to near complete dryness and redissolved in an appropriate volume of 0.1 M HNO_3 to obtain a solution suitable for mass spectrometric analysis. The Cd aliquot was dried with a few drops of 10 M HCl to convert the residue into the chloride form, dried again with one drop 1 M HCl, and finally taken up in 50 µl of 1 M HCl for column chemistry.

Column chemistry

An ion-exchange chromatography procedure, modified after Rickaby *et al.*[3] was used to isolate Cd from the major element Ca as well as from minor matrix elements, such as Na, K, Mg, Sr, and others. Biorad AG 50W-X8, 200–400 mesh cation-exchange resin was used in Teflon columns, with 250 µl resin beds and 3.5 ml sample reservoir volumes (Table 4). Following loading of the sample solutions, Cd was eluted from the resin with 1 M HCl. The Cd eluates were then evaporated to dryness, dried again with one drop of 14 M HNO_3 to remove any residual chloride and finally taken up in $\sim$30 µl of 14 M HNO_3 for storage. Just prior to use, the solutions were evaporated to near complete dryness and dissolved in an appropriate volume of 0.1 M HNO_3 to obtain the desired Cd concentration for mass spectrometric analysis. This separation method typically achieved yields of >90% for Cd.

Table 4 Column chemistry procedure for the separation of Cd from the calcite matrix

Bio Rad AG 50W-X8 resin, 200–400 mesh, 250 µl resin in shrink-fit Teflon columns	
14 ml, 6 M HCl	Resin cleaning
1 ml, 1 M HCl	Equilibration
50 µl sample solution in 1 M HCl	Sample loading and Cd collection
150 µl, 1 M HCl	Cd collection
150 µl, 1 M HCl	Cd collection

Mass spectrometry

All mass spectrometric analyses were carried out with Nu Plasma MC-ICPMS instruments at the ETH Zürich. The isotope dilution (ID) concentration measurements were performed using a multiple ion counting system for Cd and multiple Faraday collectors equipped with 10^{11} Ω resistors for Ca. All analyses employed a CETAC MCN 6000 desolvator for sample introduction, in conjunction with T1H nebulizers (CETAC) that operated at flow rates of about 100–120 µl min^{-1}.

Cd concentration measurements. The Cd ID measurements utilized 2 data acquisition cycles (Table 5). In the first cycle, the ^{105}Pd ion beam was monitored to correct for the isobaric interference from ^{110}Pd. The second cycle served to simultaneously determine the ion currents of ^{110}Cd and ^{111}Cd. Data collection for both cycles comprised 20 integrations of 5 s each. Each Cd analysis was preceded by an on-peak zero determination. This involved an ion beam intensity measurement with the data acquisition routine described above, whilst 0.1 M HNO_3 was aspirated. The Cd analyses were followed by a thorough (5–10 min) washout, whereby the sample introduction system was flushed first with 1 M HNO_3 and then with 0.1 M HNO_3.

Several measurements of a JMC Cd Zürich standard solution were conducted at the beginning of each analytical session, to confirm that the instrument was performing properly. In addition, a mixed Cd–Pd standard solution, which yielded a ^{110}Pd/^{110}Cd ratio of about 0.05 was analyzed, to optimise the parameters of the Pd interference correction (see section Data processing).

A Cd ID analysis with 40 data acquisition cycles required about 4 min, during which about 400–500 µl of sample solution were consumed. The analyses of spiked samples utilized solutions with total Cd concentrations of $\sim$16 pg ml^{-1} (ppt), and thus they consumed about 5 pg of foraminiferal Cd. Such solutions generally yielded ion beam intensities of about 56×10^3 and 13×10^3 cps for ^{110}Cd and ^{111}Cd, respectively.

Ca concentration measurements. The Ca ID analyses were modified from techniques established for high-precision Ca isotope composition measurements by MC-ICPMS.[23] The acquisition of the Ca ID data (”main run”) comprised 20 integrations of 5 s each, whereby the ion beam intensities of ^{42}Ca, ^{43}Ca, and ^{44}Ca were measured simultaneously with the Faraday cups of the instrument (Table 5). Additionally, $^{87}Sr^{2+}$ was monitored at 43.5 u to enable interference corrections for the doubly charged ions $^{84}Sr^{2+}$, $^{86}Sr^{2+}$ and $^{88}Sr^{2+}$, which have nearly the same mass/charge ratios as $^{42}Ca^{+}$, $^{43}Ca^{+}$ and $^{44}Ca^{+}$, respectively.

For each sample, the main run was immediately followed by a second measurement (“Mn run”) that comprised two data

Table 5 Collector configurations and major molecular interferences for the Cd and Ca isotope dilution analyses

Mass	42	43	43.5	44	55	105	110	111
Cd analyses								
Cycle 1						IC1		
Cycle 2							IC1	IC0
Ca–Mn analyses								
Main run	L4	L1	H1	H4				
Mn run, cycle 1					Ax			
Mn run cycle 2	L4	L1	H1	H4				
Abundances of Cd, Ca and Mn isotopes and isobaric nuclides (in %)								
Cd							12.49	12.80
Pd						22.33	11.72	
Ca (and Mn)	0.647	0.135		2.086	(100)			
Major molecular interferences for Ca, Pd and Cd								
$M^{40}Ar^+$						^{65}Cu	^{70}Zn ^{70}Ge	^{71}Ga
$M^{16}O^+$	^{26}Mg	^{27}Al		^{28}Si		^{89}Y	^{94}Zr ^{94}Mo	^{95}Mo
$M^{14}N^+$	^{28}Si	^{29}Si		^{30}Si		^{91}Zr	^{96}Zr ^{96}Mo ^{96}Ru	^{97}Mo

acquisition cycles for the determination of Mn/Ca ratios (see section on Mn/Ca ratios below). The first cycle served to measure the ion current of ^{55}Mn, whereas the second cycle was used to monitor the ion beam intensities at positions corresponding to 42 u, 43 u, 43.5 u, and 44 u (Table 5). The data acquisition sequence comprised 4 integrations of 15 s each for both cycles.

Prior to each main run, on-peak zeros were measured at mass positions 42 u, 43 u, 43.5 u, 44 u and 55 u, whilst 0.1 M HNO_3 was aspirated ("acid run"). These on-peak zero measurements were necessary to correct for baseline aberrations from scattered $^{40}Ar^+$ and $^{40}Ca^+$ ions. Electronic baselines were furthermore determined for 15 s at the beginning of each measurement (main run, Mn run, acid run), whilst the ion beam was deflected in the electrostatic analyzer. Each Mn run was followed by a thorough ($\sim$10 min) washout, whereby the sample introduction system was flushed first with 1 M HNO_3 and then with 0.1 M HNO_3.

A complete analysis (including Ca main run and Mn run) required about 6.5 min, during which $\sim$650 µl of sample solution were aspirated, whilst a Ca measurement alone needed only 3 min and $\sim$300 µl of solution. The foraminiferal samples were generally analyzed as solutions with total Ca concentrations of about 1–3 µg ml^{-1} (ppm). Calcium solutions with concentrations of $\sim$2 ppm generally yielded total ion beam intensities of about 300×10^{-11} A.

Data processing

Cd isotope dilution data. The raw uncorrected Cd intensity data were processed by an off-line data reduction scheme. First, the measured on-peak zero values were subtracted from the ion beam intensities of ^{105}Pd, ^{110}Cd and ^{111}Cd. This yielded background-corrected $^{110}Cd/^{111}Cd$ ratios that were then adjusted to account for the isobaric interference from ^{110}Pd. The correction involved the use of the ^{105}Pd intensities to calculate $^{110}Pd/^{111}Cd$ ratios, which were corrected for mass discrimination with a power law technique[24] and an empirically optimised mass fractionation factor of $\sim$1.5% per amu mass difference.

A gain correction factor was then applied to all $^{110}Cd/^{111}Cd$ data. This factor was based on the mean $^{110}Cd/^{111}Cd$ ratio obtained for analyses of the JMC Cd Zürich solution during each measurement session, relative to the reference value of $^{110}Cd/^{111}Cd = 0.977047$ (Table 1). In a last step, the mass fractionation factor of the Pd interference correction was optimised, such that the Pd-doped Cd standard yielded gain-corrected $^{110}Cd/^{111}Cd$ data that were indistinguishable from those obtained for the essentially Pd-free JMC Cd Zürich standard.

As long as the $^{110}Pd/^{110}Cd$ ratios obtained for samples are smaller than those of the Pd-doped Cd standards, it can be assumed that the $^{110}Cd/^{111}Cd$ ratios were properly corrected for contributions from ^{110}Pd. This was the case for all spiked foraminiferal samples, as they yielded $^{110}Pd/^{110}Cd$ ratios that were approximately three times lower (at $\sim$0.015) compared to the Pd-doped Cd standards ($\sim$0.04–0.05).

Ca isotope dilution data. The raw Ca isotope data from the mass spectrometric analyses were also processed with an off-line data reduction scheme. This involved the following steps: (1) subtraction of the electronic baselines from the raw ion beam intensities determined during the acid run and the main run; (2) subtraction of the on-peak zero values obtained during the acid run from the Ca ion beam intensities determined in the main run; (3) this set of raw intensity data was used to obtain Ca isotope ratios for standards that were corrected for interferences from doubly charged ions ($^{84}Sr^{2+}$, $^{86}Sr^{2+}$ and $^{88}Sr^{2+}$) and (4) instrumental mass fractionation. For standards, the latter utilized an exponential law normalization relative to $^{42}Ca/^{44}Ca = 0.312210$ (Table 2). An optimised fractionation factor was used for the instrumental mass bias correction of samples. This factor corresponds to the mean of the instrumental mass fractionation determined for multiple analyses of a NIST SRM 915a Ca solution measured on the same day.

Calculation of Cd and Ca concentrations and Cd/Ca ratios. The Cd and Ca concentrations were determined using a spreadsheet-based ID calculation. For Ca, these calculations were based on the $^{43}Ca/^{44}Ca$ ratio, and the $^{42}Ca/^{44}Ca$ ratio was used to correct for minor offsets of the data from the spike-sample mixing line by application of a secondary mass fractionation correction. The Cd ID calculation utilized the $^{110}Cd/^{111}Cd$ isotope ratio and the data were corrected for the contribution of the procedural blank (see section Procedural blanks and detection limit).

The final Cd/Ca results are reported in units of μmol mol^{-1}, with a "total uncertainty" that was determined by propagating the individual uncertainties:

$$\text{total uncertainty} = R\sqrt{\sigma_B^2 + \sigma_{Cd}^2 + \sigma_{43Ca}^2 + \sigma_{42Ca}^2} \quad (1)$$

where R is the Cd/Ca ratio of the spiked sample in μmol mol^{-1} and σ_B, σ_{Cd}, σ_{43Ca}, and σ_{42Ca} denote the relative errors from the uncertainty of the Cd blank correction, and from the uncertainties of the Cd and Ca concentrations, based on the within-run statistics of the measured $^{110}Cd/^{111}Cd$, $^{43}Ca/^{44}Ca$ and $^{42}Ca/^{44}Ca$ isotope ratios. The uncertainties of the weights, isotope compositions and concentrations of the isotopically enriched Cd and Ca tracer solutions can be neglected in this error propagation because they generally have only a very minor (1 to 10%) effect on the total uncertainty of the Cd/Ca data obtained for samples.

Mn/Ca ratios. The Mn/Ca ratios of cleaned foraminifera shells are determined on a routine basis in most Cd/Ca studies, to detect samples with high residual Mn contents from incomplete removal of ferromanganese oxyhydroxides (*e.g.*, ref. 3, 20 and 25). In our study, the Mn/Ca ratios of the samples were quantified relative to a calibration line defined by three Ca standard solutions doped with different amounts of Mn. The calculations utilized the measured and known $^{55}Mn/^{44}Ca$ ratios of the standards and the measured $^{55}Mn/^{44}Ca$ ratios of samples, following subtraction of spike-derived ^{44}Ca.

Generally, Mn/Ca values below 100 μmol mol^{-1} are considered indicative of sufficient removal of secondary Mn-oxide overgrowth.[20,25] In this study, Mn/Ca ratios of less than 8 μmol mol^{-1} were determined for all analysed foraminiferal samples, and this demonstrates that our methods are sufficiently effective in removing Mn-rich phases from the carbonate shells.

Results

Procedural blanks and detection limit

Blank samples (that initially consisted only of distilled acid) were routinely processed alongside real samples through the complete procedure that was used to prepare foraminiferal tests for analysis (including cleaning, spiking and column chemistry). The blank samples were then analyzed by ID-MC-ICPMS with the same (or very similar) techniques that were applied for samples. Repeated measurements indicate that the procedural Cd blank of the method was about 112 ± 44 fg (1 s.d., $n = 12$) and all concentration data were corrected for this contribution. For samples with 1 pg of Cd, a blank correction of this magnitude generates an uncertainty of about ±4% (1 RSD) for the Cd concentration. The uncertainty of the Cd blank furthermore yields a detection limit of 131 fg (3 s.d.).

The Ca blank, which comprises 17 ± 6 ng (1 s.d., $n = 3$) has a negligible effect on the measured Ca contents because it constitutes only ~0.2% of the indigenous Ca present in spiked sample solutions. The uncertainty of the blank provides a method detection limit of 18 ng (3 s.d.) for Ca.

Analyses of standard solutions

Multiple analyses of Cd and Ca standard solutions were carried out on each measurement session prior to the actual ID analyses. The within-day reproducibility obtained for these standard measurements provide an estimate of the precision that can be achieved for sample measurements that are conducted at similar conditions. Note that all quoted uncertainties are 1 RSD, unless otherwise stated.

Results for JMC Cd Zürich standards. For solutions with Cd concentrations of 30 to 70 ppt, the standard analyses yielded within-day reproducibilities of about ±0.1 to ±0.3% for the $^{110}Cd/^{111}Cd$ ratio (Table 6). In this case, a single measurement consumed about 11 to 30 pg of Cd. To evaluate the precision for samples with extremely low Cd contents, we performed analyses of standard solutions with Cd concentrations of about 1 and 5 ppt. The within-day reproducibility for such solutions was somewhat worse at about 1 and 0.4%, but these measurements consumed only about 0.5 and 2 pg of Cd, respectively (Table 6).

Results for NIST SRM 915a Ca standards. The majority of the analyses utilized Ca solutions with concentrations of about 2 to 3 ppm, such that the measurements consumed about 600–900 ng Ca. These analyses yielded within-day reproducibilities of about 0.05 to 0.10% for $^{43}Ca/^{44}Ca$. The precision of the $^{42}Ca/^{44}Ca$ data was slightly worse at about 0.2 to 0.4%, because the baseline is significantly noisier at mass 42.

Accuracy of isotopic data—analyses of unspiked foraminiferal tests

The accuracy of the analytical technique was verified by analyzing multiple samples of unspiked *O. universa* tests that were individually processed in the laboratory. Such measurements constitute a rigorous test for the accuracy of the method

Table 6 Within-day reproducibility of the $^{110}Cd/^{111}Cd$ ratio obtained for multiple analyses of a JMC Cd Zürich standard solution at various concentration levels

Concentration (ppt)	n	Range of reproducibility (RSD %)	Natural Cd consumed per analysis/pg
70	3	~0.12 ± 0.08	~25–30
50	2	~0.21 ± 0.05	~20
30	9	~0.25 ± 0.07	~12
5	1	~0.4	~2
1	1	~1.0	~0.5

n = number of independent measurement sessions.

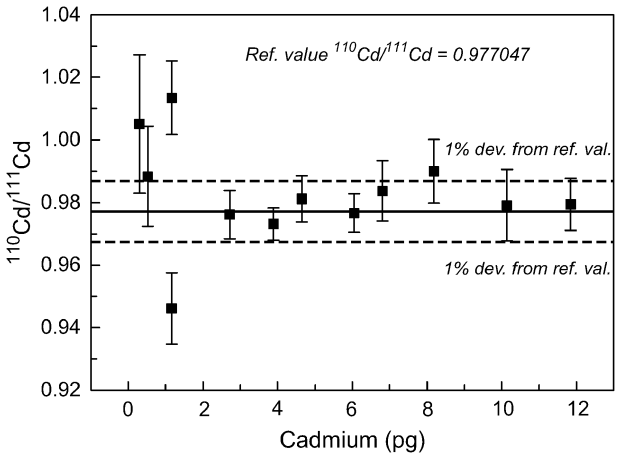

Fig. 1 $^{110}Cd/^{111}Cd$ ratios obtained for unspiked samples of *O. universa versus* the amount of Cd consumed during analysis. The results show that most measurements which utilized ~3 to 12 pg Cd yielded offsets of less than 0.7% from the reference value (solid line). Deviations of up to 3% were only observed for analyses that consumed less than 1 pg of Cd. The error bars denote the 1σ mean within-run statistics of the isotopic measurements. The dashed lines denote a 1% deviation from the reference value $^{110}Cd/^{111}Cd$ = 0.977047 (Table 1).

because the isotopic analyses of such samples should yield the (known) natural isotope ratios for $^{110}Cd/^{111}Cd$, $^{43}Ca/^{44}Ca$ and $^{42}Ca/^{44}Ca$, whereas any systematic deviation would indicate the presence of analytical artefacts, for example from spectral interferences.[26]

Results for cadmium. Cadmium isotope data ($^{110}Cd/^{111}Cd$) were acquired for 12 unspiked samples of *O. universa* (Fig. 1). Measurements that consumed about 3–12 pg Cd showed deviations from the reference value (Table 1) of less than 1.3% and the $^{110}Cd/^{111}Cd$ ratios displayed a precision of ±0.5%. In addition, we also analyzed samples with only ~0.5 to 1.5 pg Cd and found that even such small amounts can be analyzed with an accuracy of better than about ±3% (Fig. 1). Most of these low-Cd samples featured $^{110}Cd/^{111}Cd$ ratios that were slightly higher than the reference value. This indicates that the deviations are probably due to small residual spectral interferences on the ^{110}Cd ion beam. Further evidence for this conclusion is provided by the observation that the low-Cd samples required relatively large Pd corrections of 20–45% (equivalent to $^{110}Pd/^{110}Cd$ ratios of 0.20–0.45), due to decreased Cd contents in relation to the approximately constant levels of Pd present in the sample solutions. In contrast, Pd corrections of only 1–8% were observed for the samples with 3–12 pg of Cd.

Analyses of real (spiked) samples will be less affected by these problems. Such samples typically have $^{110}Cd/^{111}Cd$ ratios of between 5 and 30, and the latter are significantly larger than the natural value of $^{110}Cd/^{111}Cd \approx 1$ due to the addition of the ^{110}Cd tracer (Table 1). Measurements of sub-picogram quantities of Cd for real samples will thus exhibit ^{110}Cd ion beam intensities that are similar to those which are obtained for unspiked samples with more than ~3 pg Cd.

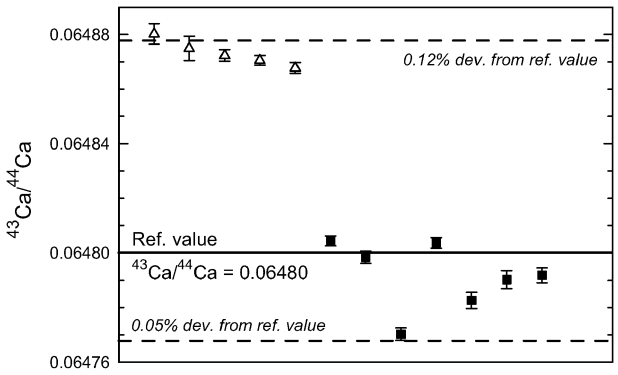

Fig. 2 $^{43}Ca/^{44}Ca$ ratios acquired for unspiked foraminiferal tests of *O. universa*. The samples were treated and analysed using the standard analytical protocol for Ca but without addition of the ^{43}Ca tracer. The results show that samples display deviations of less than 0.05% from the reference value for analyses, which consumed ~900 ng of Ca (filled squares). Deviations of about 0.12% were observed for measurements that consumed only about 200 ng Ca (open triangles). The error bars denote the 1σ mean within-run statistics of the isotope analyses.

Over a wide range of spike-sample ratios ($^{110}Cd/^{111}Cd \approx$ 5–30), the error magnification factor[27,28] of the Cd ID data reduction is less than 2. This means that an uncertainty of about ±1% on the $^{110}Cd/^{111}Cd$ ratio translates into an error of about ±1–2% for the Cd concentration. This demonstrates that the accuracy and precision of the analytical data for small spiked samples, with ≤1 pg Cd, is governed primarily by the uncertainty of the Cd blank correction.

Results for calcium. For Ca, we determined the $^{43}Ca/^{44}Ca$ and $^{42}Ca/^{44}Ca$ ratios of 12 individually processed unspiked samples of *O. universa*. The isotope data were obtained in measurements that utilized sample solutions with Ca concentrations of 0.7 ppm and 3 ppm, such that the analyses consumed about 200 ng and 900 ng of Ca, respectively.

The $^{43}Ca/^{44}Ca$ ratios obtained for 3 ppm Ca solutions indicate a maximum deviation from the reference value (Table 2) of less than 0.05% and the individual data are characterized by a precision of ±0.02% (Fig. 2). For analyses of solutions with concentrations of 0.7 ppm Ca, the deviation from the reference value was somewhat larger at about 0.12%, but the RSD value was similar at ±0.01% (Fig. 2). The majority of the measured $^{42}Ca/^{44}Ca$ ratios showed deviations of less than 0.5% from the reference value and the data provided a RSD of ±0.1%.

Over a wide range of spike–sample ratios (that yield $^{43}Ca/^{44}Ca \approx$ 0.2–2.4 for samples), errors of ±0.1% and ±0.5% on $^{43}Ca/^{44}Ca$ and $^{42}Ca/^{44}Ca$, respectively, yielded Ca concentrations that are erroneous by about ±0.2%. This indicates that the Ca ID abundance data are also expected to have an accuracy of about ±0.2%.

Evaluation of molecular interferences

Repeated mass scans of sample solution aliquots were performed to identify elements that were able to generate diatomic oxide-, nitride- or argide-based molecular ions that could interfere with the Ca and Cd ID measurements

Table 7 Reproducibility of Cd/Ca ratios obtained for multiple analyses of *O. universa* tests from the sediment core KL 88

Sub-sample	*n*	Cd/Ca in μmol mol^{-1}	Uncertainty/ μmol mol^{-1}
1/1	1	0.0270	0.0003
1/2	1	0.0269	0.0003
1/3	1	0.0271	0.0003
1/4	1	0.0274	0.0003
Average	4	0.0271 ± 0.0002 (RSD = 0.7%)	

The average value was calculated as unweighted mean of *n* independent measurements and the quoted uncertainty denotes 1 standard deviation. The uncertainty of the individual results was calculated as described in the section Calculation of Cd and Ca concentrations and Cd/Ca ratios.

(Table 5). The mass scans focused on the mass ranges 23 to 45 u (for Ca) and 60 to 120 u (for Cd). These analyses revealed only traces of Mg, Al, Si, Cu, Zn, Ge, Zr, Mo, and Ru. In a previous study, Ripperger and Rehkämper[13] evaluated the formation rates of these diatomic ions for a wide range of elements at instrumental operating conditions that were nearly identical to those of the present study. They found that the formation rates were generally less than 4×10^{-3} for oxide ions (including the refractory oxides YO^+ and ZrO^+), less than 3×10^{-5} for nitrides and other oxides, and less than 5×10^{-4} for argides. No data are presently available for Mg, Si, and Al but it is not unreasonable to assume that the oxide, nitride, and argide formation rates of these elements are also adequately described by the maximum values determined for the suite of elements previously investigated by Ripperger and Rehkämper.[13]

The severity of a molecular interference for a particular analysis can be described by the interference ratio R_I, which is defined as:

$$R_I = \frac{I_x \alpha}{I_y} \quad (2)$$

where I_x refers to the ion beam intensity of an isotope that forms a molecular interference, α is the formation rate of the molecular ion, and I_y is the intensity of the corresponding Ca, Cd, or Pd ion beam, which is affected by the interference. For all analyzed foraminiferal samples, R_I was found to be less than 10^{-4} for $I_y = {}^{42}Ca$ and ${}^{110}Cd$, less than 10^{-5} for $I_y = {}^{43}Ca$, ${}^{44}Ca$ and ${}^{111}Cd$ and less than 10^{-2} for $I_y = {}^{105}Pd$. At this level, the interferences are far too insignificant to alter the measured Ca and Cd concentrations by more than 0.1%. These results, and the previously discussed measurements of unspiked *O. universa* shells, thus demonstrate that our sample preparation techniques yield solutions, which enable essentially interference-free (and hence accurate) ID concentration analyses of foraminiferal Cd/Ca ratios.

Reproducibility of Cd/Ca ratios

The reproducibility of the method was evaluated by analyses of four individually spiked aliquots of a single dissolution of *O. universa* tests. The data that were acquired in these measurements, which each utilized about 5 pg and 700 ng of natural Cd and Ca, respectively, are summarized in Table 7. The analyses yielded an average Cd/Ca ratio of 0.0271 μmol mol^{-1} and a reproducibility of about ±0.0002 μmol mol^{-1} (1 s.d.), which is equivalent to an uncertainty of ±0.7%. This result demonstrates that our method can provide Cd/Ca ratios that have a precision of better than 1%, even for foraminiferal samples with low Cd contents of less than 10 pg.

Discussion

Previously published methods for the determination of element/Ca ratios by various ICPMS techniques and TIMS (thermal ionization mass spectrometry) are summarized in Table 8. Sector field and quadrupole ICPMS instruments have rapid mass scanning capabilities and they are thus well suited for the simultaneous determination of several element/Ca ratios, including Li/Ca, Mg/Ca, Sr/Ca, Ba/Ca, Zn/Ca, Cd/Ca, U/Ca and others (Table 8). Hence, they have become an important and routine tool for paleoceanographic studies, which utilize and interpret the element/Ca ratios of foraminiferal calcite, corals, and other carbonate samples. These techniques typically achieve a precision of about 2% for Cd/Ca when more than 15 to 20 pg of Cd are available for analysis (Table 8).

Table 8 Comparison of various methods used for the determination of Cd/Ca ratios

	Method[a] and metal/Ca ratios determined for:	Cd/Ca in μmol mol^{-1}	RSD[b] (%)	Sample[c]	Cd/pg[d]
This study	ID-MC-ICPMS	0.027	0.7	Plankt. F.	~5
	Cd, Mn	~0.005	~4	Cd, Ca Std	~1
Marchitto[6]	SF-ICPMS				
	Li, Mg, Sr, Mn, Fe, Zn, Cd, U	0.096–0.26	1.4–2.7	ME-Std	~13–72
Rosenthal *et al.*[5]	SF-ICPMS				
	Mg, Sr, Mn, Cd, U	~0.14	1.7	ME-Std	~16
Lea and Martin[29]	ID-Q-ICPMS				
	Sr, Ba, Cd	~0.15	~2	ME-Std	~4–30
Harding *et al.*[31]	Q-ICPMS				
	Mg, Sr, Mn, Zn, Cd, U	~0.14	1.7	ME-Std	~20
Yu *et al.*[30]	Q-ICPMS				
	Li, B, Mg, Sr, Al, Mn, Zn, Cd, U	0.01–0.07	4.8	ME-Std	1–4
		0.07–0.24	2.4		4–15
Rickaby *et al.*[3]	ID-TIMS (Cd), AAS (Ca)				
	Cd		~0.5–1	Cd, Ca Std	~50

[a] AAS: atomic absorption spectrometry, ID: isotope dilution, MC: multiple collector, Q: quadrupole, SF: sector field. [b] Precision of the Cd/Ca analyses. [c] Plankt. F.: planktonic foraminifers, ME-Std: multi-element standard. [d] Natural Cd consumed for an individual analysis.

Both Lea and Martin[29] and Yu *et al.*[30] also carried out Cd/Ca analyses with only ~5 pg of Cd and quoted reproducibilities of about 2 to 5% for these measurements. In comparison, our technique yields data that are precise to about 1% at similar conditions (Tables 7 and 8). Our methods are slightly less precise (but still superior to other techniques) when even smaller amounts of Cd (~1 pg or less) are analyzed (Table 8) because the reproducibility is then essentially limited by the uncertainty of the blank correction, which is ±44 fg (1 s.d.).

Our total procedural blank is non-negligible because Cd is separated from the calcite matrix by ion-exchange chromatography. This separation also has advantages, however, because it eliminates elements that can generate molecular interferences during mass spectrometry (Table 5) and such interferences are likely to be most problematic for samples with low Cd contents. As a result, we have been able to demonstrate that our analyses generate accurate Cd isotope dilution data even for natural calcite samples with <1 pg Cd (Fig. 1), but such rigorous tests have yet to be carried out for the other methods summarized in Table 8. This lack of documentation demonstrates that there is a need to establish well-characterized and widely available reference materials that can be used to validate the accuracy (and precision) of element/Ca ratio measurements for natural carbonates.

The results of this study demonstrate that our technique provides particular advantages for the accurate and precise determination of Cd/Ca ratios for samples with very low Cd contents and/or which are available only in limited quantities. This includes, for example, planktonic foraminifera collected in sediment traps and tows. The methods will also be of interest to isotope laboratories that already have access to MC-ICPMS instrumentation but not to a quadrupole or sector field ICPMS instrument. The technique can furthermore be extended to additional elements, such as Li, Mg, Sr, Ba, Zn, and U, which can be (a) spiked with a suitable enriched tracer and (b) sequentially eluted at high yield from the cation-exchange columns that are used for the Cd separation.

Summary and conclusions

A new method for the determination of the Cd/Ca ratios of foraminiferal tests is presented and validated. The results demonstrate that our analytical techniques permit the determination of foraminiferal Cd/Ca with an accuracy and reproducibility of about ±1%, for samples with 3 to 12 pg of natural Cd. Even very small samples of foraminiferal tests with as little as 1 pg of natural Cd can be analysed. In this case, the accuracy and reproducibility is about ±4%, mainly due to the uncertainty of the Cd blank correction.

These performance characteristics demonstrate that our method is superior to previously published procedures for the determination of Cd/Ca ratios in foraminiferal tests, with respect to both the quantification limit and the accuracy and reproducibility of the results.[3,5,6,17,29–31] Our method is therefore the best available technique for determining Cd/Ca when only limited sample material with low Cd contents is available. This includes, for example, Cd/Ca analyses of *in-situ* sampled planktonic foraminifers.[32]

Acknowledgements

We are grateful to R. Schiebel for kindly sharing sample material and for help with the foraminiferal samples. H. Baur, U. Menet, D. Niederer, F. Oberli, C. Stirling, H. Williams and S. Woodland are thanked for keeping the clean labs and mass specs running. This project has profited from discussions with and the support of A. N. Halliday, J. McKenzie, R. Schiebel and D. Schmidt and the constructive comments of two anonymous reviewers. Financial aid for the study was provided by a grant from the Schweizerische Nationalfond (SNF).

References

1 E. A. Boyle, F. Sclater and J. M. Edmond, *Nature*, 1976, **263**, 42–44.
2 K. W. Bruland, *Earth Planet. Sci. Lett.*, 1980, **47**, 176–198.
3 R. E. M. Rickaby, M. J. Greaves and H. Elderfield, *Geochim. Cosmochim. Acta*, 2000, **64**, 1229–1236.
4 D. W. Lea, in *Modern Foraminifera*, ed. B. K. Sen Gupta, Kluwer, Dordrecht. 1999, pp. 259–277.
5 Y. Rosenthal, M. P. Field and R. M. Sherrell, *Anal. Chem.*, 1999, **71**, 3248–3253.
6 T. M. Marchitto, *Geochem. Geophys. Geosyst.*, 2006, **7**, Q05P13, DOI: 10.1029/2005GC001018.
7 R. E. M. Rickaby and H. Elderfield, *Paleoceanography*, 1999, **14**, 293–303.
8 H. Elderfield and R. E. M. Rickaby, *Nature*, 2000, **405**, 305–310.
9 D. C. McCorkle, P. A. Martin, D. W. Lea and G. P. Klinkhammer, *Paleoceanography*, 1995, **10**, 699–714.
10 E. A. Boyle, *Paleoceanography*, 1988, **3**, 471–489.
11 J. W. Mitchell, T. D. Harris and L. D. Blitzer, *Anal. Chem.*, 1980, **52**, 774–776.
12 P. A. Martin and D. W. Lea, *Geochem. Geophys. Geosyst.*, 2002, **3**, 8401, DOI: 10.1029/2001GC000280.
13 S. Ripperger and M. Rehkämper, *Geochim. Cosmochim. Acta*, 2007, **71**, 631–642.
14 F. Wombacher and M. Rehkämper, *Geostand. Geoanal. Res.*, 2004, **28**, 173–178.
15 W. A. Russell, D. A. Papanastassiou and T. A. Tombrello, *Geochim. Cosmochim. Acta*, 1978, **42**, 1075–1090.
16 R. Schiebel, U. Struck, G. Grimm, H. Hübner and S. Themann, in *North Atlantic 1999, Cruise No. 45. Meteor-Berichte 00-4*, eds. F. Schott, G. Meinecke, S. Neuer and E. Zenk, 2000, pp. 104–108.
17 E. A. Boyle and L. D. Keigwin, *Earth Planet. Sci. Lett.*, 1985, **76**, 135–150.
18 E. Boyle and Y. Rosenthal, in *The South Atlantic: Present and Past Circulation*, eds. G. Wefer, W. H. Berger, G. Siedler and D. J. Webb, Springer, Berlin, 1996, pp. 423-443.
19 S. Weldeab, R. R. Schneider and M. Kölling, *Geochem. Geophys. Geosyst.*, 2006, **7**, Q04P12, DOI: 10.1029/2005GC000990.
20 E. A. Boyle, *Geochim. Cosmochim. Acta*, 1983, **47**, 1815–1819.
21 E. A. Boyle, *Earth Planet. Sci. Lett.*, 1981, **53**, 11–35.
22 E. A. Boyle, *J. Foraminiferal Res.*, 1995, **25**, 4–13.
23 L. Halicz, A. Galy, N. S. Belshaw and R. K. O'Nions, *J. Anal. At. Spectrom.*, 1999, **14**, 1835–1838.
24 F. Wombacher and M. Rehkämper, *J. Anal. At. Spectrom.*, 2003, **18**, 1371–1375.
25 P. A. Martin and D. W. Lea, *Paleoceanography*, 1998, **13**, 572–585.
26 M. Rehkämper, M. Schönbächler and C. H. Stirling, *Geostand. Newsl.*, 2001, **25**, 23–40.
27 B. N. Colby, A. E. Rosecrance and M. E. Colby, *Anal. Chem.*, 1981, **53**, 1907–1911.
28 W. Riepe and H. Kaiser, *Fresenius' Z. Anal. Chem.*, 1966, **223**, 321–335.
29 D. W. Lea and P. A. Martin, *Geochim. Cosmochim. Acta*, 1996, **60**, 3143–3149.
30 J. Yu, J. Day, M. Greaves and H. Elderfield, *Geochem. Geophys. Geosyst.*, 2005, **6**, Q08P01, DOI: 10.1029/2005GC000964.
31 D. J. Harding, J. W. Arden and R. E. M. Rickaby, *Geochem. Geophys. Geosyst.*, 2006, **7**, Q06003, DOI: 10.1029/2005GC001093.
32 S. Wichtlhuber, M. Rehkämper, R. Schiebel and A. N. Halliday, *Geochim. Cosmochim. Acta*, 2004, **68**, A486.