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A new methodology for precise cadmium isotope analyses of seawater

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Abstract Previous studies have revealed considerable Cd isotope fractionations in seawater, which can be used to study the marine cycling of this micronutrient element. The low Cd concentrations that are commonly encountered in nutrient-depleted surface seawater, however, pose a particular challenge for precise Cd stable isotope analyses. In this study, we have developed a new procedure for Cd isotope analyses of seawater, which is suitable for samples as large as 20 L and Cd concentrations as low as 1 pmol/L. The procedure involves the use of a ^{111}Cd–^{113}Cd double spike, co-precipitation of Cd from seawater using $Al(OH)_3$, and subsequent Cd purification by column chromatography. To save time, seawater samples with higher Cd contents can be processed without co-precipitation. The Cd isotope analyses are carried out by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The performance of this technique was verified by analyzing multiple aliquots of a large seawater sample that was collected from the English Channel, the SAFe D1 seawater reference material, and several samples from the GEOTRACES Atlantic intercalibration exercise. The overall Cd yield of the procedure is consistently better than 85% and the methodology can routinely provide $\varepsilon^{114/110}$Cd data with a precision of about ±0.5 ε (2sd, standard deviation) when at least 20–30 ng of natural Cd is available for analysis. However, even seawater samples with Cd contents of only 1–3 ng can be analyzed with a reproducibility of about ±3 to ±5 ε. A number of experiments were furthermore conducted to verify that the isotopic results are accurate to within the quoted uncertainty.

Keywords Isotopes · Stable isotopes · Mass fractionation · Geochemistry · Marine geochemistry · Chemical oceanography

Introduction

A number of previous studies have identified considerable mass-dependent variations in the Cd isotope compositions of both terrestrial and extraterrestrial samples [1, 2]. On Earth, stable isotope effects for Cd are particularly prominent in the oceans, and the largest natural terrestrial Cd isotope fractionations of about 4‰ have been reported for Cd-depleted surface seawater [3–5]. These effects have generally been attributed to reflect isotope fractionation of Cd that occurs during biological uptake and utilization of dissolved seawater Cd. This finding confirms studies which identified Cd as an essential marine micronutrient. This was first inferred from the phosphate-like distribution of the metal in the oceans [6] and more recently demonstrated by work which confirmed that Cd can act as catalytic metal ion in carbonic anhydrase, an enzyme which plays a central role in inorganic carbon acquisition by phytoplankton in the oceans [7, 8]. The marine Cd isotope fractionations are thus of interest as they can be used to study the cycling of the

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micronutrient Cd as well as its impact on ocean productivity and the global carbon cycle.

A number of recent studies have applied a double spike technique in combination with either multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) [9] or thermal ionization mass spectrometry (TIMS) [10] for Cd stable isotope measurements, as this procedure can provide more accurate results that are less prone to analytical artifacts from matrix effects than analyses which utilize other methods of instrumental mass bias correction, such as standard-sample bracketing or “external normalization” of the Cd isotope data to the ^{107}Ag/^{109}Ag ratio of admixed Ag [4, 11–13]. The data quality that is generated with a double spike methodology is, however, critically dependent on the application of an optimized spike composition and spike sample ratio [1].

Another key factor for obtaining high-quality Cd isotope data is the use of an appropriate separation procedure which can achieve both high yields and purified Cd samples that are free from contaminants that generate matrix effects or spectral interferences. An efficient pre-concentration technique is particularly critical for seawater Cd isotope analyses, because Cd contents of less than 0.05 nmol/L are common in the surface ocean. This implies that Cd must be isolated from several liters of seawater in order to obtain a sufficient quantity of the element (ideally, more than 10–20 ng) for precise isotopic analyses. The presently published methods, however, are not suitable or untested for the isolation of Cd at high yield from seawater samples larger than about 2 L and at a purity that is sufficient for accurate isotopic measurements.

The present study addresses these shortcomings through the development and validation of a novel technique for the isolation of Cd from seawater samples as large as 20 L, prior to stable isotope analysis. The methodology is able to process large samples by co-precipitation of Cd with Al(OH)$_3$, and achieves excellent yields and high elemental purity for Cd. The isotopic analyses of Cd were carried out using a double spike technique in conjunction with MC-ICP-MS. A new ^{111}Cd–^{113}Cd double spike was used, which is more suitable than other previously employed double spikes for MC-ICP-MS analyses, as it is less subject to spectral interferences whilst providing isotopic and concentration data of excellent precision and accuracy.

Experimental

Samples and reference materials

The method development required access to a large volume of seawater and hence a 180-L sample was collected from onboard the R/V Bill Conway in the Solent close to the English Channel (at 50.9°N, 1.4°W) in February 2008. The water was obtained with a trace metal clean pumping system that utilized a boom to allow sampling at a distance of about 3 m from the boat to minimize contamination from the ship. The seawater was initially stored in pre-cleaned low density polyethylene (LDPE) vessels, then transported to Imperial College London and filtered through 0.45-μm Millipore cellulose filters with the aid of a peristaltic pump into cleaned 10-L and 20-L LDPE containers. For storage, the samples were subsequently acidified with distilled 6 M HCl to pH 2. Growth of plankton was observed in all vessels holding Solent seawater prior to filtration. The filtration (and thereby removal of plankton) was a slow process that was only completed after 5 days for the 180-L sample as a result of frequent clogging of the filters by organic material. To distinguish between seawater that was filtered at different times (and which hence supported plankton growth for different time periods), the various 10- to 20-L subsamples of filtered Solent seawater (SSW) are denoted by distinct letters, whereby SSW-A was filtered within 24 h of collection, whilst SSW-E was treated last (about 4 days later).

Various other seawater reference samples were analyzed to validate and document the performance of the new analytical method. This includes aliquots of SAFe D1 seawater and a number of samples from the 2008 GEOTRACES Atlantic intercalibration exercise. The SAFe D1 seawater was collected in the western Pacific Ocean (30°N, 140°W) at 1,000-m depth during the Sampling and Analysis of Fe (SAFe) research cruise in October/November 2004 [14]. Following collection, this water was filtered using 0.2-μm Poretics cartridge filters, homogenized, acidified to pH 1.8 using distilled HCl, and filled into 500-mL LDPE bottles [14].

The 2008 GEOTRACES Atlantic intercalibration cruise obtained seawater from the BATS (Bermuda Atlantic Time Series) station at 31.8°N, 64.1°W. The seawater samples, which were transferred to and stored in pre-cleaned LDPE containers following collection, are (i) GSI (GEOTRACES surface intercalibration) collected from near the surface by a towed underway fish; (ii) GDI (GEOTRACES deep intercalibration) obtained at 2,000-m depth by multiple casts of the GEOTRACES Go-Flo rosette; and (iii) an intercalibration depth profile (GPrI) covering 75–3,000 m that was collected with the same device.

A number of different Cd isotope standards, for which previously published reference values are available, were analyzed to test the performance of the new ^{111}Cd–^{113}Cd double spike. These included JMC Cd Münster and Münster Cd, Alfa Cd Zurich, BAM-I012 Cd (from the German Bundesanstalt für Materialwissenschaft und -prüfung), and NIST SRM 3108, which is a new proposed Cd isotope reference material [1, 15].

Reagents and general laboratory procedures

All critical sample preparation work was carried out in Class 10 laminar flow workbenches within the Class 1,000 MAGIC clean room facility at Imperial College London. Mineral acids were purified once by sub-boiling distillation in either quartz (6 M HCl, 15 M HNO_3) or Teflon (12 M HCl) stills. A purified about 8 M NH_3 solution was prepared by isopiestic distillation of commercially available 28% NH_3 solution in a Savillex Teflon elbow. All water used was of better than 18 MΩ grade from a Millipore purification system. The HNO_3/HBr mixture that is required for the anion-exchange chemistry was prepared freshly on the day of use.

Two different ^{111}Cd–^{113}Cd double spike solutions with Cd concentrations of approximately 100 ng/g in 0.7 M HCl were used during the course of this work. Both featured ^{111}Cd/^{113}Cd ratios of approximately 1.5–2.0, in accordance with error propagation models, which suggest that a spike with ^{111}Cd/^{113}Cd ratio of 1.56 is the best composition for precise double spike stable Cd isotope analyses that do not require measurement of ^{106}Cd, ^{108}Cd, ^{110}Cd, and ^{116}Cd [16]. These isotopes were avoided for the MC-ICP-MS analyses, as they may involve the monitoring of ion beams that have an unsuitably large mass dispersion or which feature problematic spectral interferences, particularly from Pd and Sn. In comparison with a previously used ^{110}Cd–^{111}Cd double spike, the new spike composition is thus superior as it provides more favorable error propagation [16] and does not suffer from Pd interferences, which are not straightforward to correct [9]. The preparation and calibration of both double spike solutions followed techniques previously outlined [9].

A purified, Cd-free solution of Al at a concentration of about 0.23 mol/L (or 0.63% w/v) in 0.7 M HCl (which yields the stoichiometry of $AlCl_3$) was used to produce insoluble $Al(OH)_3$ for the co-precipitation of Cd. This solution was prepared as follows. About 0.5 g of Al slug (99.9999% purity; Alfa Aesar Puratronic) was dissolved in 15 mL 6 M HCl at 90 °C on a hotplate. Following digestion of the metal, the solution was diluted with Milli-Q water to obtain 0.7 M HCl. Purification of the Al solution (particularly for the removal of Cd) was then achieved by anion-exchange chromatography, using a variant of the procedure that is applied for Cd separation from seawater (see below).

Sample preparation for Cd isotope analysis

Rationale

A commonly employed procedure for the separation of Cd and other trace metals from seawater for concentration analyses involves co-precipitation with $Mg(OH)_2$, which forms on addition of aqueous NH_3 to seawater [17, 18]. In principle, such a technique is also adaptable to the much larger seawater volumes that are needed for Cd isotope measurements, but there are a number of drawbacks. These include the relatively large volumes of aqueous NH_3 needed to precipitate Mg hydroxide, poor Cd yields, and co-precipitation of other elements (such as Mo, Sn), which can introduce problematic spectral interferences. The results of this study demonstrate that the disadvantages of $Mg(OH)_2$ can be avoided if Cd is precipitated from seawater using $Al(OH)_3$, following which the samples are further purified prior to isotopic analysis by column chromatography. Sample volumes of less than 1–2 L are sufficient for seawater with higher Cd contents (of approximately greater than 0.05 nmol/kg) and such samples can be processed directly with the column chemistry [9], without use of co-precipitation.

Preliminary Cd concentration measurements

Prior to preparing seawater samples for Cd isotope analyses, it is helpful if the Cd concentrations are known to within a factor of 2–5, or better. This is to (i) determine whether use of the co-precipitation technique is necessary for the processing of samples with low Cd contents (less than 0.05 nmol/kg) and (ii) achieve optimum spiking of samples with a (molar) ratio of spike-derived Cd to natural Cd (S/N ratio) of about 1, relevant for our particular double spike composition [16].

If the Cd concentration of a sample is not known or cannot be estimated to the desired level of accuracy (e.g., based on published phosphate data), it is useful to carry out a preliminary concentration analysis using a small aliquot of the available sample. Such measurements can utilize published techniques that employ either quadrupole or high resolution ICP-MS [17, 18] but in this study we used an abbreviated version of the methodology that is applied for the Cd isotope analyses. To this end, a small aliquot (about 50–100 mL) of the seawater sample was removed, spiked (with the Cd double spike), and acidified to 0.7 M HCl. Following this, the Cd was separated from the matrix with a simplified version of the column chemistry described below (this involved use of only the 1st stage anion-exchange and the 3rd stage Eichrom TRU-spec resin columns [9]). Finally, the Cd concentration was determined by an isotope dilution analysis with the MC-ICP-MS, in a manner similar to that employed for the stable isotope measurements. It is conceivable that a simpler procedure, using only the 1st stage anion-exchange columns with or even without double spiking, could also be used for the preliminary concentration measurements by MC-ICPMS, but this was not tested during the course of this study.

Weighing and spiking of samples

The Cd isotope analyses of this study utilized seawater samples with volumes of about 0.25–20 L. These samples were first weighed and for each, a suitable volume of ^{111}Cd–^{113}Cd double spike solution was then weighed into a 15-mL Savillex Teflon beaker, to obtain an optimal S/N ratio of about 1. Large seawater samples (greater than 2 L), which required Cd co-precipitation, were checked to have pH no greater than 1.6, prior to the addition of the Cd double spike. For smaller samples, which were processed without co-precipitation, the double spike solution was added directly and the samples were then made up to 0.7 M HCl by addition of 6 M HCl. All samples were then left to stand for at least 3 days [9] prior to further processing.

Co-precipitation of Cd with Al(OH)$_3$

Following spike–sample equilibration, a suitable volume of the about 0.23 M $AlCl_3$ solution was added to the seawater samples, to obtain an Al^{3+} concentration of 50 mg/L. The solutions were first left to stand for 48 h and $Al(OH)_3$ was then precipitated by addition of aqueous NH_3 solution, to obtain a final pH of 8.5. The samples were thoroughly shaken and left to stand for at least 3 days to allow the precipitate to fully form, coagulate, and sink to the bottom of the containers. Next, the supernatant was decanted as far as possible in several steps. In general, 90–95% of the supernatant could be decanted without significant entrainment of precipitate. Subsequently, the precipitate was dissolved in 6 M HCl and the volume of acid added was adjusted, on the basis of the volume of (i) NH_3 used and (ii) remaining sample solution, to obtain a final HCl molarity of about 0.7 M. This solution was left to stand for at least 24 h, following which it was ready for the separation of Cd by column chromatography.

Cd separation by column chromatography

The three-stage column chemistry procedure that was used for the purification of Cd is essentially identical to that previously employed by [9] and hence this is only briefly summarized here. The first separation stage employed 1.5 mL anion-exchange resin in large quartz glass columns with 100-mL reservoirs and two modifications were made in comparison to the methods employed [9]: (i) Biorad AG 1X8 100–200 mesh anion-exchange resin was employed in this study (instead of AG 1X8 with 200–400 mesh beads) because this provides higher elution rates; and (ii) the initial conversion of the resin to the Cl^- form was accomplished using 25 mL 6 M HCl instead of 16 mL 8 M HCl. The remaining two stages of the separation chemistry were identical to those described by Ripperger and Rehkämper [9]. Both were carried out in small shrink-fit Teflon columns that featured 100-μL beds of (i) Biorad AG 1X8 200–400 mesh anion-exchange resin (2nd stage) and (ii) Eichrom TRU Spec resin (3rd stage), respectively.

Following separation, the purified Cd fractions were evaporated to dryness, dried twice with a drop (about 30 μL) of 15 M HNO_3, and a further drop of 15 M HNO_3 was then added for sample storage. Prior to Cd isotope analysis, these solutions were evaporated to near complete dryness, redissolved in an appropriate volume of 0.1 M HNO_3 to obtain the desired Cd concentration, and ultrasonicated for 5–15 min to ensure complete dissolution.

Cd isotope measurements

Mass spectrometry

The double spike isotope measurements were carried out with a Nu Instruments Nu Plasma MC-ICP-MS at the MAGIC Laboratories, Imperial College London. The instrument was operated using an acceleration potential of 6 kV and is fitted with a large capacity (80 L/min) rotary pump for evacuation of the expansion chamber. Sample introduction was achieved with a Nu Instruments DSN desolvator and Micromist glass nebulizers with flow rates of about 100–120 μL/min. For the isotopic analyses, the ion currents at masses 111 (Cd), 112 (Cd + Sn), 113 (Cd + In), 114 (Cd + Sn), 115 (In), and 117 (Sn) were measured simultaneously with Faraday cups, which are equipped with 10^{11}-Ω resistors. The ion beams of ^{115}In and ^{117}Sn were monitored to achieve precise interference corrections. The measurement and washout procedures are otherwise identical to those described by Ripperger and Rehkämper [9]. Most seawater samples were analyzed as solutions with total Cd concentrations of about 40–60 ng/mL and typically these samples were spiked to obtain an S/N ratio of about 1, such that each analysis consumed only about 20–30 ng of natural (seawater-derived) Cd. In general, these measurements were carried out at sensitivities of about 250–350 V/ppm, equivalent to a transmission efficiency of up to about 0.25%.

Data reduction and reporting

The Cd isotope data collected during the mass spectrometric analyses were further processed to calculate the “true” isotope compositions of the unspiked samples that were corrected for both instrumental mass bias and isobaric interferences. These data were then used to determine the reported $\varepsilon^{114/110}$Cd values of the samples relative to an isotopic standard (std):

$$\varepsilon^{114/110}\mathrm{Cd} = \left[\frac{\left({}^{114}\mathrm{Cd}/{}^{110}\mathrm{Cd}\right)_{\mathrm{sample}}}{\left({}^{114}\mathrm{Cd}/{}^{110}\mathrm{Cd}\right)_{\mathrm{std}}} - 1\right] \text{ x } 10,000$$

In this study, the $\varepsilon^{114/110}$Cd data were determined and are reported relative to the JMC Cd Münster solution, which has been used in a number of previous investigations [1, 15]. The reduction of the isotopic data was carried out offline, using a modified version of the spreadsheet-based methods described by Ripperger and Rehkämper [9]. In brief, our calculations utilized the measured ^{112}Cd/^{111}Cd, ^{113}Cd/^{111}Cd, and ^{114}Cd/^{111}Cd isotope ratios. These were first corrected for isobaric interferences and the double spike equations were then solved to determine $\varepsilon^{114/113}$Cd values relative to the JMC Cd Münster standard. These calculations utilized the iterative procedures of Siebert et al. [19], which were modified to allow use of the general power law [20], as this permits mass fractionation effects to be described by any desired non-linear function. In this study, the instrumental and natural mass fractionation was assumed to follow the general power law with an exponent of $n\approx 0.2$ [21] and the exponential law, respectively. Finally, the $\varepsilon^{114/113}$Cd data were translated into $\varepsilon^{114/110}$Cd using the relationship

$$\varepsilon^{k/m}\mathrm{Cd} = \left\{\left[\left(\mathrm{e}^{l/m}\mathrm{Cd}/10,000\right)+1\right]^{\beta}-1\right\}\times 10,000$$

For the kinetic law, β is defined as

$$\beta = \ln(m_k/m_m)/\ln(m_l/m_m)$$

where m_k, m_l, and m_m refer to the exact atomic masses of the Cd isotopes k, l, and m [1, 15].

As a by-product, the Cd double spike measurements also yield precise Cd concentration data. To this end, the mass-bias-corrected ^{114}Cd/^{111}Cd isotope ratios of the spiked samples were evaluated using a conventional isotope dilution equation. All concentration data were corrected for blanks of 20–30 pg Cd, which were determined by processing total procedural blanks alongside each batch of 6–12 samples. No blank corrections were applied to the $\varepsilon^{114/110}$Cd results, as the blank raised the Cd concentrations of the three most highly Cd-depleted samples (from the GEOTRACES intercalibration cruise) by only about 1.0–1.5% and amounted to less than 0.25% of the indigenous Cd for the remainder of the seawater samples.

Results and discussion

Results for the JMC Cd Münster zero-epsilon standard

Mixtures of the ^{111}Cd–^{113}Cd double spike and the zero-epsilon standard with a near-optimal S/N ratio of about 1 were analyzed at least 5–7 times during each measurement session. Such analyses typically achieved within-day reproducibilities (2sd, standard deviation) of about ±0.5 $\varepsilon^{114/110}$Cd, when spiked standard solutions with total Cd concentrations of about 60 ng/mL were used (Table 1). Higher total Cd contents of up to 120 ng/mL did not significantly improve the precision, presumably because this is primarily limited by uncertainties of the data reduction scheme rather than counting statistics. These analyses consumed about 30–60 ng of natural Cd, but smaller samples can also be analyzed with good precision (Table 1). For example, measurements of spiked Cd solutions with concentrations of 40 and 20 ng/mL showed within-day reproducibilities of about ±0.7 and ±1.4 $\varepsilon^{114/110}$Cd, respectively. Even isotopic measurements of only 0.5–1.5 ng of natural Cd are possible, as solutions with total Cd at 1–3 ng/mL, but such analyses typically feature uncertainties of ±2 to ±5 ε (Table 1). In summary, this demonstrates that sample analyses with solutions containing 60 ng/mL Cd are ideal and these only require 30 ng of natural Cd for a solution volume of 1 mL. Importantly, no deviations in $\varepsilon^{114/110}$Cd values were found when solutions with Cd concentrations of between 20 and 120 ng/ml were analyzed relative to one another.

As in a previous Cd isotope investigation [9], which utilized a ^{110}Cd–^{111}Cd double spike, our analyses of double spike/zero-epsilon standard mixtures generally yielded small but non-negligible offsets (typically ±0.5 to ±3 $\varepsilon^{114/110}$Cd) from the correct result of $\varepsilon^{114/110}\mathrm{Cd}=0$. These deviations are interpreted to reflect day-to-day variations in the mass bias behavior of the instrument and sample introduction system [9, 21]. To account for this variability, the $\varepsilon^{114/110}$Cd data of samples are given relative to the mean result obtained for multiple analyses of double spike/zero-epsilon standard mixtures in the same measurement session, an approach that was previously shown to be reliable [9].

Analyses were also carried out to ascertain that the ^{111}Cd–^{113}Cd double spike can provide accurate results over a wide range of spike to sample (S/N) ratios. In these experiments, the $\varepsilon^{114/110}$Cd values of double spike/zero-epsilon standard mixtures characterized by S/N ratios of

Table 1 Typical within-day reproducibility of Cd isotope data (reported as $\varepsilon^{114/110}$Cd) for multiple analyses of Cd double spike/natural Cd mixtures at different concentrations and S/N≈1

Total Cd concentration of spike + std. solution (ppb)	±2sd uncertainty for $\varepsilon^{114/110}$Cd	Natural Cd consumed per analysis (ng)
120	0.4–0.7	~60
60	0.4–0.7	~30
40	0.5–0.8	~20
20	1.0–1.4	~10
3	~2–3	~1.5
1	~5	~0.5

between 0.2 and 20 were analyzed relative to a mixture with S/N=1 (Fig. 1). These measurements showed that accurate results, with $\varepsilon^{114/110}$Cd values that are identical within uncertainty to $\varepsilon^{114/110}$Cd=0, were obtained over a relatively wide range of S/N, from about 0.6 to 6 (Fig. 1). Despite this excellent dynamic range, the actual seawater analyses were typically carried out relative to double spike/standard mixtures, which had S/N ratios and total Cd contents that were matched to within better than a factor of 2. This procedure was adopted to optimize the accuracy of the results and ensure that the uncertainty of the sample data could be determined from multiple analyses of a comparable standard solution.

Results for other Cd isotope reference materials

A number of different Cd isotope reference materials, which have been used in previous studies, were analyzed as part of this study (Table 2). Such analyses are vital (i) to document the accuracy of the data and (ii) to facilitate the comparison of Cd isotope results acquired in different laboratories, with different zero-epsilon standards. The data summarized in Table 2 show that the analyses with the new ^{111}Cd–^{113}Cd double spike yielded results that are identical, within uncertainty, to previously published data. Of particular importance in this regard are the fractionated BAM-I012 and Münster Cd reference materials, as data are available for these samples from a large number of different laboratories and studies. The results acquired for the SRM NIST 3108 Cd solution, which is only marginally fractionated relative to the JMC Cd Münster solution with $\varepsilon^{114/110}$Cd=1.0±0.3, are of interest because this material has been proposed as a possible international zero-epsilon standard for future Cd isotope studies [1, 3].

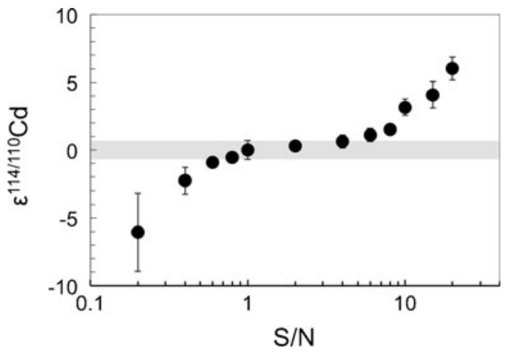

Fig. 1 Plot of Cd isotope data (as $\varepsilon^{114/110}$Cd) for mixtures of the Cd double spike with the JMC Cd Münster standard, obtained at various S/N ratios (molar ratio of Cd from spike vs. natural Cd from the standard). The $\varepsilon^{114/110}$Cd values were determined and calculated relative to a Cd double spike/JMC Cd Münster mixture with S/N=1. The *error bars* denote the 2sd uncertainties determined from the results of multiple analyses

Results for Solent seawater

Five different subsamples of Solent seawater from separate containers, denoted SSW-A through SSW-E, were analyzed (Table 3). Initial co-precipitation experiments with SSW-A3 and SSW-A4 utilized additions of 40 and 100 mg/L Al^{3+}, respectively, and both experiments provided essentially identical Cd yields of about 90%. On the basis of this, the co-precipitation experiments for SSW-D3 and SSW-E3 (and all other samples; see Table 4) utilized Al^{3+} additions of 50 mg/L and Cd yields of better than 85% were achieved in all cases. Similar measurements were carried out for samples that only utilized column chromatography for the Cd separation, and these also consistently showed yields of greater than 90%. Overall, these results demonstrate that the present methods can provide nearly quantitative Cd separation yields on a routine basis.

Three of the SSW subsamples, SSW-A, SSW-D, and SSW-E, were analyzed multiple times, with and without the application of co-precipitation for Cd separation (Table 3). Importantly, the different separation methods provide data that are identical, within uncertainty, for all analyzed aliquots. This suggests that the Cd separation and data acquisition are robust and can routinely provide reliable results. The uncertainties quoted for the individual SSW aliquots (Table 3) are based on the reproducibility of the matching double spike/zero-epsilon standard analyses, which is typically about 0.5–1.0 ε (±2sd, Table 3). For a few samples, the uncertainties are larger as a result of instabilities in the instrumental mass bias that were tolerated during the early stages of method validation.

For the Cd concentration data, the results obtained for individual aliquots deviate from the mean value by less than ±0.1% for subsamples SSW-D and SSW-E, whilst larger deviations of up to about ±0.5% were observed for SSW-A (Table 3). On the basis of these results, the Cd concentrations are estimated to have an accuracy and precision of better than 0.5% (±2sd), in accordance with the data of a study that utilized similar methods [9].

Of interest is the observation that the five SSW subsamples (A–E) display resolvable and systematic variations in Cd concentrations from 147.2 to 195.8 pmol/kg. This variability is unlikely to reflect original differences in the Cd content of the sampled seawater because all bottles were filled at the same location within a time span of 1.5 h. Rather, it is more plausible that the differences in dissolved [Cd] are due to biological uptake within the bottles prior to filtration and subsequent acidification. This interpretation is reasonable because the time period between collection and filtration varied from about 3 h for SSW-A to about 96 h for SSW-E.

Further support for this explanation is provided by the observation that the SSW data are in accordance with a

Table 2 Summary of Cd isotope data (as $\varepsilon^{114/110}$Cd) from this study and the literature, for various standards and reported relative to the JMC Cd Münster zero-epsilon isotope reference material

Cd standard	Method	Alfa Cd Zurich	BAM-I012 Cd	Münster Cd	NIST 3108 Cd
This study	DS, MC-ICP-MS	0.5±0.3	−12.4±0.8	46.2±0.5	1.0±0.3
Wombacher and Rehkämper (2004) [15]	Ag norm, MC-ICP-MS		−10.8±1.5	46.5±0.5	
Ripperger and Rehkämper (2007) [9]	DS, MC-ICP-MS	0.0±0.5	−12.4±1.1	46.4±1.2	
Ripperger and Rehkämper (2007) [9]	Ag norm, MC-ICP-MS		−11.4±1.5	46.0±1.5	
Schmitt et al. (2009) [10]	DS, TIMS		−12.3±0.3	44.8±0.2	
Gao et al. (2008) [24]	SSB, MC-ICP-MS		−12.0±1.2	45.9±1.2	
Shiel et al. (2009) [12]	Ag norm, MC-ICP-MS		−13.7±2.5	45.0±0.3	

All results are reported with ±2sd uncertainties. For the data of this study, the uncertainties are based on the results of multiple sample analyses except for Münster Cd, where the uncertainty is based on multiple analyses of a matching standard. For the published results, the uncertainties are reported as given

Ag norm external normalization using admixed Ag, *DS* double spike

logarithmic trend in a diagram of $\varepsilon^{114/110}$Cd vs. Cd content (Fig. 2), equivalent to a linear trend in a plot of $\varepsilon^{114/110}$Cd vs. ln[Cd]. The slope of the latter correlation (m) was used to determine the isotope fractionation factor α for biological uptake and utilization of Cd [5]:

$$\alpha = \left(\frac{m}{10,000} + 1\right)^{-1}$$

The observed slope of $m=-5.0\pm2.7$, determined with the software package Isoplot [22], thus yields a fractionation factor of $\alpha\approx1.0005\pm0.0003$. This value is identical to the fractionation factors of $\alpha\approx1.0002$–1.0006 that were previously inferred to characterize biological Cd isotope fractionation in the oceans [3–5]. The agreement thus supports the conclusion that the observed variations in Cd concentration amongst different subsamples of SSW (Table 3) reflect in situ uptake of Cd by plankton prior to filtration.

Results for SAFe D1 seawater

A 1-L aliquot of SAFe D1 was analyzed using co-precipitation for the pre-concentration of Cd, whilst three further analyses utilized only the column chemistry for the

Table 3 Cd concentrations and isotope compositions for five subsamples of Solent seawater (SSW) that were analyzed with and without the aid of $Al(OH)_3$ co-precipitation

Subsample	Aliquot	Sample weight (g)	Co-precipitation	Cd concentration (pmol/kg)	$\varepsilon^{114/110}$Cd ± 2sd[b]
SSW-A	1	932	–	196.7	2.5±0.6
	2	926	–	195.1	2.0±0.6
	3	928	Yes	195.8	1.9±0.6
	4	928	Yes	195.8	2.6±0.6
	Average SSW-A[a]			195.8±0.9	2.3±0.4
SSW-B	1	931	–	158.6	3.1±0.9
SSW-C	1	931	–	149.7	4.2±0.7
SSW-D	1	906	–	148.5	5.2±0.8
	2	3,624	–	148.6	3.3±1.4
	3	3,624	Yes	148.6	4.2±0.7
	Average SSW-D[a]			148.6±0.1	4.2±1.0
SSW-E	E-1	914	–	147.1	3.7±0.8
	E-2	3,655	–	147.2	3.7±1.4
	E-3	3,655	Yes	147.2	3.3±0.7
	Average SSW-E[a]			147.2±0.1	3.6±0.3

[a] To account for the small number of replicates, the uncertainties given for average values encompass the total range of the data

[b] The uncertainties of the individual sample analyses are based on the 2sd uncertainties of the $\varepsilon^{114/110}$Cd values obtained for matching standard solutions that were analyzed before and after sample measurements

Table 4 Cd concentrations and isotope compositions for seawater reference material SAFe D1 and the GEOTRACES intercalibration samples GDI, GSI, and GPrI

Sample	Aliquot/bottle	Water depth (m)	Sample weight (g)	Co-precipitation	Cd concentration (pmol/kg)	$\varepsilon^{114/110}$Cd ± 2sd[b]
SAFe D1	256-1	2,000	255	–	1,011	4.2±1.1
	256-2	2,000	252	–	1,014	4.1±0.5
	257-1	2,000	256	–	1,012	4.3±0.5
	255-2, 257–2, 258	2,000	1,025	Yes	1,010	4.2±0.5
	Average SAFe D1[a]				1,012±2	4.2±0.1
GDI	49	2,000	931	–	270.6	6.1±0.4
	50	2,000	931	–	272.1	6.0±0.4
	51	2,000	938	–	270.8	5.5±0.4
	Average GDI[a]				271.2±0.9	5.8±0.3
GSI	74, 75	5	20,393	Yes	1.2	23.1±5.3
GPrI	49	75	8,859	Yes	2.2	14.5±5.3
GPrI	41	125	7,932	Yes	1.7	12.8±5.3
GPrI	33	250	150	–	34.8	–[c]
GPrI	27	500	927	–	138.4	6.7±0.6
GPrI	21	1,000	937	–	293.8	6.6±0.6
GPrI	9	2,500	931	–	293.1	5.2±0.6
GPrI	4	3,500	934	–	295.1	5.5±0.6

[a] To account for the small number of replicates, the uncertainties given for mean values encompass the total range of the data

[b] The uncertainties quoted for the samples are based on the 2sd uncertainties determined for multiple analyses of matching standard solutions that were analyzed before and after each sample measurement

[c] Insufficient sample volume available for an isotopic measurement of comparable precision

isolation of Cd (Table 4). Notably, the Cd concentrations and $\varepsilon^{114/110}$Cd values of these four analyses deviate from the mean by less than 0.2% and 0.1 ε. The lack of any systematic offset between the results obtained with and without co-precipitation furthermore underlines the accuracy of the results. This conclusion is reinforced by the observation that SAFe D1, which was collected in the Pacific Ocean at 1,000-m depth [14], has an isotope composition of $\varepsilon^{114/110}$Cd=4.2±0.1 (Table 4), which is in accordance with previous results for Pacific seawater from depths of at least 1,500 m and the relatively constant $\varepsilon^{114/110}$Cd of +3.8±0.5 inferred for global deepwater (corrected for a 0.5-ε offset between JMC Cd Münster and Alfa Cd Zürich; Table 2) [3, 5].

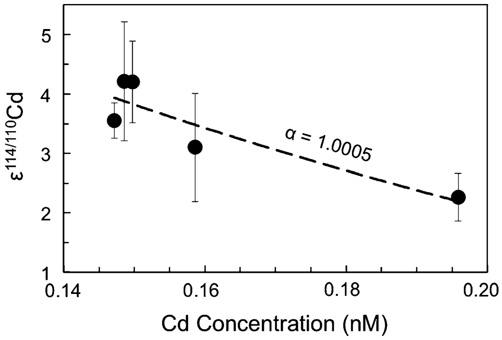

Fig. 2 Plot of $\varepsilon^{114/110}$Cd values vs. Cd concentrations for the five subsamples of Solent seawater SSW (SSW-A to SSW-E; see Table 3). A significant variability of Cd concentrations is correlated with smaller changes in $\varepsilon^{114/110}$Cd and the correlation is in accordance with Cd isotope fractionation by biological utilization and a fractionation factor of α=1.0005±0.0003 (*dashed line*). The uncertainties are taken from Table 3

Results for the 2008 GEOTRACES Atlantic intercalibration samples

Three of the GEOTRACES intercalibration samples, GSI and the GPrI seawater from 75-m and 125-m depth, have Cd contents of only about 1–2 pmol/kg (Table 4). For the isotope analyses, it was therefore necessary to isolate Cd from large seawater volumes of about 10–20 L by co-precipitation with $Al(OH)_3$ (Table 4). However, despite the large sample volumes, less than 2.5 ng of natural Cd was available for the isotopic analyses. Nonetheless, the measurements achieved reasonable uncertainties of about ±5 ε, and this was sufficient to identify and characterize the isotopically fractionated nature of these samples (Table 4; Figs. 3, 4)

The remaining GEOTRACES samples (with the exception of GPrI from 250-m depth, which was only analyzed for Cd content; Table 4) had Cd concentrations of greater

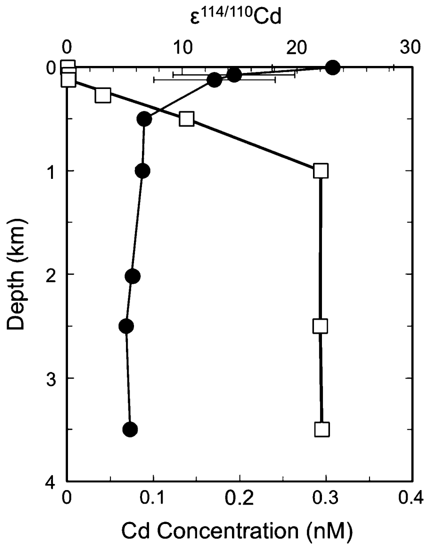

Fig. 3 Depth profiles of Cd concentrations (*open squares*) and isotope compositions (as $\varepsilon^{114/110}$Cd; *filled dots*) for the GEOTRACES intercalibration samples GSI and GDI (surface and deep water, respectively) as well as the GPrI depth profile samples from the BATS station in the North Atlantic (Table 4). Together, these samples provide the first full Cd isotope depth profile for the Atlantic Ocean, and this is similar to a published depth profile for the central Pacific (station 7 [5]). The Cd concentration of GDI is not plotted, as this deviates significantly from the essentially constant values of the GPrI samples at depths greater than 1,000 m (Table 4). This difference presumably reflects that the GDI and GPrI samples are from two different casts

than 0.1 nmol/kg, and the sample preparation thus required only column chemistry (Table 4). For these samples, about 10–30 ng of natural Cd was available and the analyses achieved uncertainties (2sd), based on multiple analyses of matching standards, of about ±0.5 $\varepsilon^{114/110}$Cd. Furthermore, three separate 1-L aliquots of the deepwater sample GDI were analyzed, and the individual results deviate from the mean value by less than ±0.5% for the Cd concentration and by less than ±0.3 ε for the isotope composition (Table 4). This indicates that the new analytical procedures can produce Cd isotope data with reproducibilities that approach those of the best double spike TIMS results [3, 10, 23].

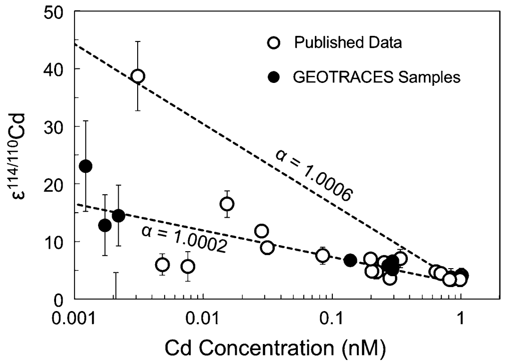

Fig. 4 Cadmium isotope compositions (as $\varepsilon^{114/110}$Cd) vs. Cd concentrations for the GEOTRACES intercalibration samples from the BATS station in the Atlantic Ocean (Table 4) and previous data from the literature [5]. The *dashed lines* denote calculated Rayleigh fractionation trends for fractionation factors of $\alpha \approx 1.0002$ and 1.0006

An important feature of the GEOTRACES intercalibration data is that they combine to provide the first comprehensive Cd isotope depth profile for the Atlantic Ocean (Fig. 3). Importantly, this isotopic profile is in accordance with published seawater results, in that large isotope fractionations, with $\varepsilon^{114/110}$Cd values of greater than +10 are only found in Cd-depleted samples from depths of less than 250 m [5]. In contrast, the GPrI samples from at least 1,000 m exhibit almost identical Cd concentrations of about 0.29 nmol/kg and only very limited variability in $\varepsilon^{114/110}$Cd, with values of between about +5.2 and +6.7 (Table 4, Fig. 3). However, the mean Cd content of GDI is slightly but significantly lower compared with the GPrI seawater from depths of 1,000–3,500 m. The origin of this difference is unclear but may reflect that the GDI and GPrI samples were collected on separate casts.

The observation that the GEOTRACES deepwater samples have a relatively constant $\varepsilon^{114/110}$Cd of approximately +5.5 (Table 4, Fig. 3) is significant, because previous analyses of deepwater from the Southern, Pacific, and Arctic Oceans defined an essentially constant isotope composition of $\varepsilon^{114/110}$Cd of +3.8±0.5 (1sd, n=7 [5]). It is conceivable, that the marginally more positive value determined here for the deep Atlantic Ocean reflects the young ventilation age of this water mass. This tentative interpretation is interesting, as it implies that Cd isotope data can be used for isotopic tracing of water masses, but will need to be confirmed by additional analyses of further suitable samples.

In a diagram of $\varepsilon^{114/110}$Cd vs. Cd concentrations, the GEOTRACES samples define a positive correlation, albeit with significant scatter (Fig. 4). This observation supports the interpretation that the positive $\varepsilon^{114/110}$Cd values of the surface and near-surface water samples are generated by isotope fractionation from biological utilization. In fact, all data are in accordance with a single, closed-system Rayleigh fractionation trend characterized by a fractionation factor of α=1.0002 (Fig. 4). This result is in general agreement with previous Cd isotope analyses of seawater, which suggest that marine biological utilization of Cd is associated with an isotope fractionation factor of about 1.0002–1.0006 [3–5]. However, the fractionations seen here for the most Cd-depleted samples are more moderate than the maximum effect, of $\varepsilon^{114/110}$Cd of approximately +40, that was previously determined for Pacific Ocean surface water. It is hence conceivable that the trend seen in Fig. 4 documents not only biological isotope fractionation during Cd uptake but also, at least in part, mixing of surface water with water masses that feature more moderate $\varepsilon^{114/110}$Cd values combined with higher Cd contents [5].

Conclusions

A new technique has been developed for Cd isotope analyses of seawater. The methodology employs a new ^{111}Cd–^{113}Cd double spike, co-precipitation of Cd with Al$(OH)_3$, Cd purification by column chromatography, and isotopic analysis by MC-ICP-MS. The method can routinely achieve Cd yields of better than 85%, whilst the co-precipitation step allows isolation of Cd from seawater samples with volumes of up to 20 L. Together, this enables isotopic analyses of highly nutrient-depleted seawater with dissolved Cd contents of less than 5 pmol/kg. Co-precipitation is not required, however, for samples with Cd concentrations that exceed 50–100 pmol/kg. In this case, the separation of Cd is best accomplished using column chromatography only.

The performance of the procedure was evaluated by multiple analyses of several Cd isotope reference materials and various seawater samples. The results of these measurements demonstrate that the Cd isotope composition of seawater can be determined with an accuracy and precision (±2sd) of 0.4–0.6 $\varepsilon^{114/110}$Cd at optimal analytical conditions, which require at least about 20 ng of natural Cd.

The methods were furthermore employed to obtain the first Cd isotope depth profile for the Atlantic Ocean. These measurements revealed extremely low Cd contents of 1–2 pmol/kg in the upper water column (0–125 m depth), and highly fractionated Cd isotope compositions with $\varepsilon^{114/110}$Cd values of up to about +20. The highly positive $\varepsilon^{114/110}$Cd data of the samples are in accordance with previous results obtained for nutrient-depleted surface seawater from the Pacific Ocean, and are thus likely to reflect isotope fractionation from biological utilization of Cd. The samples from depths of at least 2,000 m feature an essentially constant Cd isotope composition of $\varepsilon^{114/110}$Cd of approximately +5.5 that is slightly more positive than the previously inferred global Cd isotope deepwater value of +3.8±0.5, which is based primarily on results for Pacific, Southern, and Arctic Ocean samples [5]. It is conceivable that this small difference in $\varepsilon^{114/110}$Cd reflects the relatively young ventilation age of Atlantic deepwater.

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