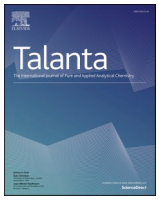
Talanta 285 (2025) 127296

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta



Efficient Cd separation protocols for high-precision cadmium isotope analyses of diverse samples by double spike MC-ICP-MS

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ARTICLE INFO

Handling Editor: Kin-ichi Tsunoda

Keywords:
Cadmium isotopes
Ion exchange chromatography
Meteorites
Rocks
Soil
Seawater

ABSTRACT

Cadmium isotope analyses are applied for research in planetary, Earth, environmental and life sciences. However, there is still a lack of efficient methods for the separation of the trace element Cd from the different types of samples that are of interest for isotopic analyses. This study presents new and improved Cd separation and purification techniques for meteorite, diverse terrestrial and seawater samples prior to Cd isotope measurements by multiple collector ICP-MS using the double spike approach for mass bias correction. The first separation stage for meteorites and terrestrial samples employs an existing anion exchange chromatography method that uses AG MP-1M resin, whilst AG 1-X8 and Nobias Chelate PA-1 resins were applied for the initial isolation of Cd from small and large seawater samples, respectively. Teflon microcolumns and AG MP-1M anion exchange resin was then employed for further Cd purification of all sample types. The methods consistently isolate Cd from matrix elements more efficiently than previous protocols, whilst achieving consistently high Cd recoveries, of >95 % for meteorite and terrestrial samples and >80 % for seawater samples, combined with low procedural blanks of <0.08 ng. The performance of the new protocols is demonstrated by repeated Cd isotope analyses of well-characterized geological and biological reference materials, which produced data that are in excellent agreement with results that were obtained with previous, more laborious separation methods. Furthermore, precise Cd isotope compositions (δ^{114}Cd) are presented for the Murchison meteorite and, for the first time, the ordinary chondrite GRO 95504. Finally, analyses of seven seawater samples, with Cd concentrations between 0.25 and 0.91 nmol kg^{-1} using sample volumes of up to 2 L, generated results consistent with those of previous studies. Overall, the new methods thus enable unbiased δ^{114}Cd measurements for diverse sample types with a 2SD precision of better than ±0.07 ‰, even for samples with 10 ng or less of natural Cd.

1. Introduction

Cadmium has eight naturally occurring stable isotopes: ^{106}Cd (1.25 %), ^{108}Cd (0.89 %), ^{110}Cd (12.47 %), ^{111}Cd (12.80 %), ^{112}Cd (24.11 %), ^{113}Cd (12.23 %), ^{114}Cd (28.74 %), and ^{116}Cd (7.51 %). Chemically, Cd is a group 12 element alongside Zn and in many environments, both elements have similar distributions, but with Cd abundances typically about three orders of magnitude lower. Both Zn and Cd are volatile elements in a cosmochemical sense [1,2] and hence isotope data for both elements have been used to study the origin of volatile depletion in meteorites and terrestrial planets [3–7]. In terrestrial environments, Cd is enriched in Zn-ores and typically recovered as a by-product of Zn production. In contrast to Zn, however, Cd is normally not an essential element for life but is highly toxic to most organisms. As such, Cd isotope studies have analyzed ores, industrial products and emissions, to investigate whether the release of the element from mining and production can be traced by isotopic fingerprinting [8–13]. In the oceans, Cd isotope investigations have focused on the biogeochemical cycling of the element and its nutrient-like marine distribution [14–19]. Furthermore, isotope data for marine sediments have been used to study past and present marine processes and conditions [20–22]. Cadmium isotope analyses of plants have been applied to determine why Cd is enriched in many crops to undesirable levels and whether hyperaccumulator plants can be used to clean contaminated soils [23–26].

Highly purified Cd sample solutions are a prerequisite for accurate isotope measurements to avoid analytical artifacts generated by matrix

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https://doi.org/10.1016/j.talanta.2024.127296
Received 1 July 2024; Received in revised form 22 November 2024; Accepted 25 November 2024
Available online 27 November 2024

effects and spectral interferences. Separation of Cd from the sample matrix prior to the mass spectrometry is therefore essential to Cd isotope studies. Since the first precise Cd stable isotope data were determined for various natural and anthropogenic materials using multiple collector (MC-) ICP-MS [5,8,14], various studies have presented high-precision Cd isotope compositions for meteorites [6,27,28], biological and geological materials [7,25,29,30] and seawater samples [15–18,31,32]. Importantly, recent studies that used modern double-spike techniques can routinely achieve a precision of better than ±0.1 ‰ for δ^{114}Cd (which denotes the deviation of the ^{114}Cd/^{110}Cd ratio of a sample from a pure Cd standard in parts per 1000). Such precision can reveal small variations in Cd isotope compositions between different planetary materials and different terrestrial samples (e.g., soil-plants system and marine systems). However, owing to the limited sample masses available and/or low Cd concentrations in such samples, high recovery of Cd and blank control for the separation of Cd are crucial to the measurements of Cd isotopes.

A common method for Cd separation utilizes anion exchange resin AG1-X8 (100–200 mesh or 200–400 mesh) followed by TRU Spec resin, with the latter used for the removal of Mo and Sn [5,33–35]. However, it was shown that organic reagents released from the TRU Spec resin can produce isotopic shifts during Cd isotope measurements [34,36]. A liquid-liquid extraction of the aqueous Cd fraction with heptane was hence added to remove any organic residues [36]. Together this yielded an effective but more complicated and time-consuming procedure. Alternative Cd separation methods, which use AG MP-1M resin and do not require an additional TRU Spec step, were initially proposed by Cloquet et al. [37] and have since been modified in subsequent studies [9,38,39].

Recent work by Tan et al. [40] improved the AG MP-1M method by utilizing a larger volume (2.8 mL) of the resin (100–200 mesh) and by adding an elution step for the removal of Mo and In. Furthermore, to fully eliminate residual Sn and other matrix elements present in the Cd fraction, the entire column procedure was repeated in their study using the same volume of resin and eluents [40]. This separation protocol was shown to achieve high Cd recoveries, but it is time-consuming because it requires relatively large volumes of eluent as two large-volume resin columns are applied, even when small samples are processed. An alternative method with only a single-stage of column chromatography using AG MP-1M resin (100–200 mesh) was successfully applied to separate Cd from geological samples [41]. This procedure, however, employs HF throughout the elution procedure, as HF–HCl mixtures with different HF concentrations are used to remove major matrix elements and limit the tailing of isobaric Sn into the Cd fraction. The use of HF is, notably, associated with significant safety concerns and this limits the applicability of the latter procedure. The performance of the available AG MP-1M resin methods for the separation of Cd [40,41] has, furthermore, only been validated for geological samples and they are hence currently not suitable for isolating Cd from seawater samples for subsequent isotopic analyses.

In the following, we present new and efficient procedures for the separation of Cd from matrix components and elements that produce problematic spectral interferences. Compared to previous AG MP-1M resin methods [40,41], the methodology improves sample throughput and does not require the use of dangerous reagents. The new protocols are also more straightforward and faster than previous procedures that applied AG1-X8 resin [5,33–35]. Finally, the techniques are suitable for all sample types that are currently of interest for Cd isotope investigations, including meteorites, terrestrial rocks and soils, biological materials, and seawater. The performance of the new methods is demonstrated by analyses of well-characterized reference materials and seawater samples.

2. Materials and methods

2.1. Samples

Solutions of NIST SRM 3108 Cd (termed SRM 3108 Cd in the following) were used as the primary Cd isotope reference material in this study, whilst BAM-I012 Cd solutions (BAM, Federal Institute for Materials Research and Testing, Germany) were analyzed as secondary reference material. Four aliquots of SRM 3108 Cd and two aliquots of BAM-I012 Cd were processed alongside samples for quality control. An ICP-MS Sn standard solution (Alfa Aesar) was diluted to 0.1 μg mL^{-1} and variable volumes of this were doped into SRM 3108 Cd to prepare matrix-free solutions with different Sn/Cd ratios.

Six concentration-certified reference materials and one meteorite were selected to evaluate the performance of the new Cd purification procedure for meteorites, geological and biological materials. These encompassed a continental flood basalt (BCR-2), an ocean island basalt (BHVO-2) and an andesite (AGV-2) from the United States Geological Survey (USGS), and San Joaquin soil (NIST SRM 2709a), spinach leaves (NIST SRM 1570a) and baking chocolate (NIST SRM 2384). The meteorites analyzed were Murchison and GRO 95504, which are classified as CM2 carbonaceous chondrite and L3.2 ordinary chondrite, respectively. For the soil and baking chocolate reference materials, separate aliquots were processed as part of this study using established methods [25,35,36], to support thorough validation of the new separation protocols.

Seven seawater samples, for which the Cd concentrations and isotope compositions had been determined in a previous study [32], were again analyzed in this study. These samples were collected in the Atlantic Ocean sector of the Southern Ocean during GEOTRACES expedition ANT XXIV/3 aboard the RV Polarstern [32]. These encompassed five samples from depths between 100 and 500 m from a depth profile at Station 198 (65.61°S, 36.40°W) and surface water samples collected with a FISH at depths of 2–5 m at Stations 142 (62.23°S, 0.00°) and 148 (64.21°S, 0.01°E). All seawater samples were collected using ultraclean techniques, immediately filtered to 0.2–0.45 μm, acidified to pH 2 with distilled 6 M HCl and then stored in pre-cleaned PE containers.

2.2. Reagents and materials

Sample preparation and the Cd isotope measurements were carried out in the MAGIC Laboratories at the Department of Earth Science and Engineering of Imperial College London. Sample digestion and Cd purification were performed in ISO Class 4 laminar flow hoods within an ISO Class 6 clean room. All acids used in the procedures were purified by sub-boiling distillation in Teflon or quartz glass stills (15.6 M HNO_3, 6 M HCl, 11.2 M HCl, 28 M HF). All water used was of ≥18.2 MΩ cm^{-1} quality from a Millipore purification system and Suprapure 30–32 % H_2O_2 was from Merck. A 5 M ammonium acetate (NH_4OAc) solution was prepared from Optima grade acetic acid (HAc) and aqueous NH_3, obtained from Fisher Scientific. The anion exchange resins AG MP-1M (100–200 mesh) and AG 1-X8 (100–200 mesh) were purchased from Bio-Rad Laboratories, whilst the Nobias Chelate PA-1 resin (Hitachi High Technologies) was purchased from VWR.

The double spike method is capable of correcting for any isotope fractionation incurred during Cd purification and isotopic analyses by MC-ICP-MS [33,35,42,43]. A^{111} Cd–^{113}Cd double spike solution, featuring a ratio of ^{111}Cd/^{113}Cd ≈ 1.7, was used for this purpose throughout the study. This ratio is in accord with the optimal spike composition, with ^{111}Cd/^{113}Cd ratio of 1.56 suggested by error propagation models [43]. The double spike solution was prepared and calibrated using techniques previously described by Ripperger and Rehkämper [33]. Optimal or near-optimal ratios of double spike-derived to natural Cd (termed S/N ratios in the following) of 1–3 were used for the double spiking of samples. This helps to reduce error propagation during data reduction and improve the accuracy of the Cd isotope compositions.

2.3. Sample preparation for terrestrial samples and meteorites

2.3.1. Digestion and double spiking

Between 0.5 and 1 g of meteorite and silicate rock samples were first digested in Teflon vials with 8–16 mL of a 1 to 2–3 mixture of 15.6 M HNO_3 to 28 M HF at 130 °C for at least three days. Following this, the samples were evaporated to complete dryness and further digested with 8–16 mL of a 1 : 1 mixture of 15.6 M HNO_3: 6 M HCl at 120 °C for 48 h.

Samples of the other three reference materials (~100 mg for SRM 2709a soil; ~250 mg for SRM 1570a spinach leaves and SRM 2384 baking chocolate) were digested using a Milestone Ethos EZ microwave fitted with an SK-10 high pressure rotor and 100 mL PFA vessels. A mixture of 8 mL 15.6 M HNO_3 and 2 mL 30–32 % H_2O_2 was added to each sample. The samples were left at room temperature for 12 h for initial digestion before being placed in the microwave oven. The samples were heated to 90 °C for 15 min, then to 180 °C for 60 min. After cooling, the sample solutions were transferred into Savillex Teflon vials and evaporated to dryness on a hotplate. To dissolve silicates and any residual organics, an 8 : 1: 1 mixture of 15.6 M HNO_3: H_2O_2: 28 M HF was added to these samples, to a total of 2 mL for soil and 1 mL for the spinach leaves and baking chocolate, and refluxed first at 90 °C for 30 min, then 130 °C for up to 48 h.

For all samples, during the silicate digestion stage, an ultrasonic bath was used for 20 min at least twice. Once fully digested, the sample solutions were evaporated to dryness and refluxed in 3–10 mL 6 M HCl for two days at 120 °C, to break down any residual fluorides. The sample solutions were then mixed with an appropriate weighed amount of the ^{111}Cd–^{113}Cd double spike solution to achieve an S/N ratio of 1–3. To ensure that full equilibration was achieved between the double spike-derived and sample Cd, the spiked samples were placed on a hotplate at 120 °C overnight, before being evaporated to dryness and re-dissolved in 3 M HCl for column chromatography.

2.3.2. Anion exchange chromatography

An improved purification procedure was applied to separate Cd from meteorites and terrestrial samples using a two-step anion exchange chromatography protocol (Table 1). The method utilizes the anion exchange resin AG MP-1M (100–200 mesh) and different molarities of hydrochloric acid to initially elute most matrix elements from the resin whilst retaining Cd, which is then stripped from the column in purified form.

The first stage is modified from the method of Tan et al. [40], using quartz glass columns with 50 mL acid reservoirs and 2.8 mL AG MP-1M resin (100–200 mesh) in beds with a diameter of 6 mm (Table 1). After cleaning and conditioning of the resin using 15 mL 2 M HNO_3, 5 mL MQ water, and 20 mL 6 M HCl, followed by 10 mL 3 M HCl, the spiked samples were loaded in 3 M HCl. The exact volume of the solutions that were used for sample loading depended on sample mass and type but loading volumes of up to 20 mL 3 M HCl were found to be unproblematic. Elution of Pb, Mo, Zn, and Sn were achieved with 10 mL 2 M HCl and 10 mL 1 M HCl, followed by 20 mL 0.3 M HCl, 20 mL 0.06 M HCl and 10 mL 0.012 M HCl. Finally, Cd was collected with 20 mL of 0.0012 M HCl (Table 1).

The second chromatography stage was carried out in PTFE shrink-fit microcolumns with resin bed dimensions of 22 × 3 mm and a reservoir volume of 2 mL, loaded with 150 µl AG MP-1M resin (100–200 mesh). This clean-up column procedure is approximately the same elution procedure as the first stage but with scaled-down eluent volumes, roughly in proportion to the size of the respective beds. In addition, the resin was cleaned in the same manner, before equilibrating with 550 µL 2 M HCl. Samples were loaded in 1000 µL 2 M HCl (Table 1). The elution scheme was then repeated with reduced acid volumes to elute residual matrix elements and purified Cd (Table 1).

2.4. Sample preparation for seawater samples

A new, simplified chemistry scheme was developed to separate Cd from seawater samples. This scheme encompasses two different first stages, for the initial pre-concentration of Cd from seawater. For seawater samples with Cd concentrations exceeding 0.3 nmol kg^{-1}, smaller volumes, of less than 0.5–1 L, are sufficient for isotope analysis and such samples can be directly processed with anion exchange column chromatography for the separation of Cd (Seawater Method 1). In contrast, a batch-extraction of Cd with Nobias Chelate PA-1 resin (Seawater Method 2) is employed for larger seawater samples with lower Cd contents, where larger volumes of more than 0.5–1 L are needed for precise Cd analysis.

2.4.1. Seawater method 1 (less than 0.5–1 L seawater)

Seawater samples of approximately 800 mL from Station 198 of the ANT XXIV/3 cruise were weighed and 11.2 M HCl was added to ensure final HCl concentrations of 0.7 M [33]. This acidic medium helps release

Table 1
Column chromatography procedure for separation of Cd from terrestrial samples and meteorites.

Procedure	Stage 1		Stage 2	
	Quartz glass columns[a] with 2.8 mL AG MP-1M, 100–200 mesh resin		Teflon columns[b] with 150 µL AG MP-1M, 100–200 mesh resin	
Clean resin	15 mL	2 M HNO_3	2000 µL	2 M HNO_3
Wash resin to neutral	5 mL	H_2O	1000 µL	H_2O
Clean resin, convert to Cl^- form	20 mL	6 M HCl	2000 µL	6 M HCl
Column equilibration	10 mL	3 M HCl	550 µL	2 M HCl
Load sample	up to 20 mL[c]	3 M HCl	1000 µL	2 M HCl
Matrix elution	10 mL	2 M HCl	550 µL	2 M HCl
Matrix elution (In, Mo, Pb)	10 mL	1 M HCl	550 µL	1 M HCl
Elution of Pb, Mo	20 mL	0.3 M HCl	1100 µL	0.3 M HCl
Elution of Zn, Sn	20 mL	0.06 M HCl	1100 µL	0.06 M HCl
Elution Sn	10 mL	0.012 M HCl	550 µL	0.012 M HCl
Collect Cd	20 mL	0.0012 M HCl	1100 µL	0.0012 M HCl

[a] Quartz glass columns with 50 mL acid reservoirs and a bed diameter of 6 mm.
[b] Teflon columns with a reservoir volume of 2 mL and resin bed height and diameter of about 22 mm and 3 mm.
[c] The volume of sample solutions depends on the mass and type of samples.

Table 2
Stage 1 column chromatography procedure for separation of Cd from small seawater samples (≤0.5–1 L).

Procedure	Reagent	Volume
Quartz glass columns[a] with 1.7 mL AG1-X8 resin, 100–200 mesh		
Clean resin	2 M HNO_3	11 mL
Wash resin to neutral	H_2O	3 mL
Clean resin, convert to Cl^- form	6 M HCl	25 mL
Column equilibration	0.7 M HCl	11 mL
Load sample	0.7 M HCl	up to 1 L
Matrix elution	0.7 M HCl	23 mL
Matrix elution	1 M HCl	10 mL
Matrix elution	2 M HCl	10 mL
Elution of Ag	8 M HCl	10 mL
Elution of Zn	0.5 M HNO_3 – 0.1 M HBr	10 mL
Matrix elution	2 M HNO_3	2 mL
Collect Cd	2 M HNO_3	10 mL

[a] Quartz glass columns with 100 mL acid reservoirs and a bed diameter of 6 mm.

Table 3
Instrumental operating conditions and protocol for Cd isotope measurements.

MC-ICP-MS	Nu Instruments NuPlasma II
RF Power	1300 W
Sampler cone	Ni
Skimmer cone	Ni
Coolant airflow	13 min^{-1}
Auxiliary airflow	0.9 min^{-1}
Sample introduction system	CETAC Aridus II or Nu Instruments DSN-100
Nebulizer	PFA MicroMist or glass pneumatic nebulizer
Nominal uptake rate	100 μL min^{-1}
Spray chamber temperature	110 °C
Desolvator temperature	160 °C
Cd isotope measurements	
Number of blocks per run	3
Number of cycles per block	20
Integration time per cycle	5 s
Baseline measurement	15 s

Cd from organic ligands and aids in the formation of Cd chloro-complexes that are strongly bound to the anion exchange resin which is used in the subsequent Cd separation. An appropriate weighed amount of the ^{111}Cd–^{113}Cd double spike solution was added to obtain an S/N ratio of about 1.2. The spiked-seawater samples were then left at room temperature for at least 3 days to ensure full equilibration between the double spike and sample Cd. During this stage, the sample bottles were shaken 3 times a day.

A two-stage anion exchange column chromatography procedure was employed to separate Cd from small seawater samples of less than 0.5–1 L volume. The first stage is modified from the first step of Ripperger and Rehkämper [33] and it employs 1.7 mL AG 1-X8 resin (100–200 mesh) in quartz glass columns with 100 mL reservoir and 6 mm diameter resin beds (Table 2). The purified Cd fractions that were eluted with 2 M HNO_3 from the first stage columns were evaporated to dryness and then dried down twice with a few drops of 6 M HCl to convert to chloride form. After redissolution in 2 M HCl, the Cd fractions were further purified by applying twice the Stage 2 clean-up chemistry used for meteorites and solid terrestrial samples (Table 1).

2.4.2. Seawater method 2 (more than 0.5–1 L seawater)

Seawater samples with a volume of about 1 L from ANT XXIV/3 Station 198 as well as surface waters of about 2 L from ANT XXIV/3 Stations 142 and 148 were acidified with 6 M HCl to a pH of 1.5–1.9 to release any Cd adsorbed to the inside of the container. After spiking with the ^{111}Cd–^{113}Cd double spike solution to an S/N ratio of 1–3, all samples were left for at least 3 days with occasional shaking for full equilibration of the spike-derived and seawater Cd.

Cadmium was first preconcentrated by solid-phase extraction with Nobias Chelate PA-1 resin via a batch procedure as described in Conway et al. [38] and Packman et al. [44]. This procedure can process up to 1 L of seawater per batch and it can be repeated if larger seawater samples are required due to low Cd concentrations. In detail, 2 mL 0.01 M H_2O_2 was added per litre of seawater and the samples were left to stand for at least 24 h to break down organic compounds. Following this, 2 mL 5 M ammonium acetate (NH_4OAc) was added per litre of seawater, before aqueous NH_3 solution was added to buffer the pH at 4.8 ± 0.2 [44]. About 10 g of the Nobias Chelate resin was used for each seawater sample and cleaned by vacuum filtration of 30 mL 3 M HNO_3 and 150 mL H_2O via a filtration rig system. The pre-cleaned Nobias Chelate resin was then added to the seawater in 1 L PE bottles which were then placed on a shaking table for 2 h at 200 rpm. The seawater-resin mixture was subsequently transferred into the filtration rig system and the seawater was removed by vacuum filtration. The resin with the chelated Cd was rinsed with 150 mL water to remove remaining seawater salts and organic ligands. Finally, Cd together with other trace metals was eluted from the resin with 5 × 5 mL 3 M HNO_3. After evaporation, the sample residues were refluxed with a mixture of 180 μL 15.6 M HNO_3 and 20 μL 30 % H_2O_2 at 140 °C for at least 2 h. Following this, the sample solutions were evaporated to dryness and redissolved in 2 M HCl for further purification using the Stage 2 clean-up chemistry (Table 1).

2.5. Mass spectrometry

2.5.1. Measurement techniques

To prepare the samples for mass spectrometry, the purified Cd fractions were evaporated to dryness, dried down twice with a few drops of 15.6 M HNO_3 and then redissolved in 0.1 M HNO_3.

The Cd isotope compositions were determined with a Nu Instruments Nu Plasma II MC-ICP-MS instrument (Table 3). Four Cd isotopes, ^{111}Cd, ^{112}Cd, ^{113}Cd, and ^{114}Cd were used to determine the Cd isotope compositions of samples. To monitor and correct for isobaric interferences from ^{112}Sn, ^{113}In, and ^{114}Sn, the ion beams of ^{115}In and ^{117}Sn were simultaneously measured during the Cd isotope analyses. Faraday collectors equipped with 10^{11} Ω resistors were used for all ion beams.

Samples and Cd standard solutions dissolved in 0.1 M HNO_3 were introduced into the plasma via a Cetac ASX-112FR autosampler and either a Nu Instruments DSN-100 or a Cetac Aridus II desolvating nebulizer system that employed either glass or PFA nebulizers with nominal uptake rates of about 100 μL min^{-1} (Table 3). The sensitivities achieved for Cd isotope measurement were about 400–900 V/(μg mL^{-1}) using the DSN-100 or 600–1000 V/(μg mL^{-1}) with the Aridus II system. Based on these sensitivities, the sample solutions were diluted to total Cd concentrations between 30 ng mL^{-1} and 60 ng mL^{-1}.

The Cd isotope measurement procedures were identical to the established methods outlined by Ripperger and Rehkämper [33] and Xue et al. [35]. Ion beam intensities were collected for three blocks with each block comprised of 20 cycles with an integration time of 5 s each. At the beginning of each measurement run, a peak centering routine was carried out and the baselines of the cups were measured for 15 s whilst the ion beam was detected in the electrostatic analyzer of the instrument. After each measurement, the sample introduction system was cleaned using 0.1 M HNO_3 for 3 min to eliminate Cd memory signals.

The samples were analyzed relative to and interspersed between

double-spiked solutions of SRM 3108 Cd, which matched the S/N ratios and Cd concentrations of the bracketed samples to within 10 %. This monitors the stability of the measurement conditions and helps to minimize systematic errors during data reduction. Furthermore, the secondary BAM-I012 Cd isotope reference standard was routinely analyzed to ensure the analyses were not biased by systematic errors.

2.5.2. Data reduction and uncertainties

The yields of the Cd separation procedure were determined by comparing the expected and measured Cd ion beam intensities during the isotope measurements. During the determination of Cd isotope compositions, instrumental mass bias and isobaric interferences were corrected with an offline iterative procedure [33,35]. The Sn interferences on ^{112}Cd and ^{114}Cd were monitored using ^{117}Sn and corrected using Sn isotope ratios of ^{112}Sn/^{117}Sn = 0.12676 and ^{114}Sn/^{117}Sn = 0.08585 [45]. The In interference on ^{113}Cd was corrected using ^{115}Sn/^{117}Sn = 0.04416 and ^{113}In/^{115}In = 0.04480 [45,46]. When samples were analyzed only once, the quoted uncertainties for δ^{114}Cd correspond to the 2SD between-run precision determined from repeated analyses of bracketing standard solutions within a single measurement session. For samples analyzed more than once, the 2SD values were normally calculated from all individual measurement results, whilst the average within-run (internal) 2SE precision (for 60 data acquisition cycles) was quoted when the latter was worse than the former.

Cadmium concentrations were obtained via the isotope dilution technique, using the mass bias corrected ^{111}Cd/^{114}Cd ratio of the spike-sample mixture, which is obtained as a by-product of the analyses of the double spiked samples for the determination of the δ^{114}Cd values. This procedure produces robust and very precise Cd abundance data, which is unaffected by any loss of Cd once the spike and sample are equilibrated. As such, any Cd loss during the anion exchange chromatography will have no impact on the measured Cd concentrations. Furthermore, once spike-sample equilibration is obtained, any loss of Cd that is associated with isotope fractionation will also have no impact on the measured δ^{114}Cd values. The excellent quality of the Cd abundance is underlined by the results of repeat analyses of single sample digest aliquots, which yielded Cd concentrations that were identical to within ±0.2 % or better. In the following, uncertainties are therefore not presented for the Cd concentrations of individual sample aliquots. The mean Cd concentrations of samples for which several digests were analyzed are, however, quoted with the 1SD precision.

3. Results and discussion

3.1. Results for Cd standard solutions

Individual measurements of samples and double-spiked Cd standard solutions with total Cd concentrations of 30 ng mL^{-1} to 60 ng mL^{-1} typically produced within-run precisions (2SE) of between ±0.03 and ± 0.06 ‰ for δ^{114}Cd. Each measurement session typically encompassed 30–60 Cd isotope runs of about 7–12 h. The between-run precision (2SD) within a single measurement session was ±0.03 to ±0.07 ‰.

The secondary BAM-I012 Cd reference material was analyzed routinely alongside samples from February 2022 to August 2023. These analyses of BAM-I012 Cd yield a long-term mean precision and δ^{114}Cd value, relative to NIST SRM 3108 Cd standard, of −1.33 ± 0.06 ‰ (2SD, n = 19), in excellent agreement with the results of previous studies [7,35,47].

The δ^{114}Cd values determined for SRM 3108 Cd and BAM I012 Cd aliquots that were processed through columns at yields of ~100 % are −0.02 ± 0.04 ‰ (2SD, n = 5) and −1.31 ± 0.07 ‰ (2SD, n = 4), respectively. As expected, these values are identical, within analytical precision, to those of the unprocessed standard solutions.

3.2. Evaluation of spectral interferences

In this study, the δ^{114}Cd data were determined from the measured ^{112}Cd/^{111}Cd, ^{113}Cd/^{111}Cd, and ^{114}Cd/^{111}Cd ratios. The acquisition of accurate isotope ratios requires the avoidance of spectral interferences from polyatomic ions, in particular ^{72,73,74}Ge^{40}Ar$^+$, ^{71}Ga^{40}Ar$^+$, ^{96}Zr^{16}O$^+$, and ^{95,96,97,98}Mo^{16}O$^+$, as well as low, correctable levels of the isobars ^{113}In and ^{112,114}Sn.

Tan et al. [40] demonstrated with three different MC-ICP-MS instruments that δ^{114}Cd values are not significantly affected by spectral interferences from Mo oxides when the purified samples have Mo/Cd ratios of less than 1×10^{-1}. In the current study, the Mo/Cd ratio of the samples after purification were significantly lower, at 1×10^{-4} to 8×10^{-4}, with a mean of 4×10^{-4}, and are similar to the Mo/Cd ratios reported by Tan et al. [40] for their purified Cd fractions. Similarly, the Ge/Cd and Ga/Cd ratios of the samples after purification were $<2 \times 10^{-4}$, again in accord with the sample results reported by Tan et al. [40]. At this level, the polyatomic interferences formed by ^{40}Ar with Ge and Ga hence have no impact on the measured Cd isotope compositions. Tan et al. [40] also quoted a maximum tolerable Zr/Cd ratio of 1×10^{-2} at which ^{96}Zr^{16}O$^+$ ions have no effect on the Cd isotope data [40] and the purified samples of this study had much lower Zr/Cd ratios of less than 2×10^{-4}. These results indicate that the new purification methods remove interfering elements to levels that are readily sufficient to ensure they have no detrimental impact on the measured δ^{114}Cd values.

The isotope measurements of the samples revealed that the contributions of ^{113}In to the total ion beam at mass number 113 were indistinguishable from those of the NIST SRM 3108 Cd standard solutions at $<1 \times 10^{-6}$. Such levels were essentially negligible and had no significant effect on the measurements of ^{113}Cd. Conversely, the contributions of

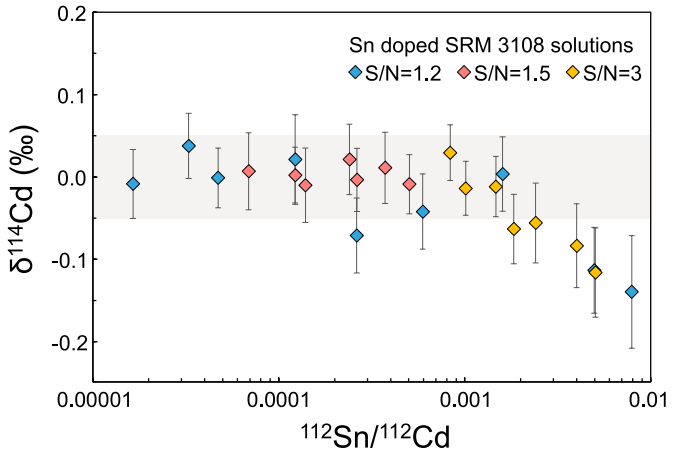

Fig. 1. Effect of isobaric interferences from Sn on Cd isotope measurements. Error bars for single measurements of Sn doped SRM 3108 Cd solutions (with total Cd concentrations of 30 ng g^{-1} to 50 ng g^{-1}) represent the within-run 2SE uncertainties. The grey band indicates the reproducibility (±0.05 ‰, 2SD) of δ^{114}Cd measurements, as determined from repeated analyses of bracketing SRM 3108 Cd solutions within the measurement sessions. The S/N ratio refers to the ratio of spike-derived to natural Cd in a sample.

Table 4
Cadmium concentrations and isotope compositions of terrestrial samples and meteorites.

Sample/data source	[Cd] ± 1SD (ng g^{-1})[a]			δ^{114}Cd ± 2SD (‰)[b]			n[c]	Cd Yield (%)	^{112}Sn/^{112}Cd after purification
BCR-2 (Basalt)									
Digestion 1	221			0.05	±	0.05	2	96	9×10^{-5}
Digestion 2	212			0.05	±	0.03	3	100	1×10^{-4}
This study (Mean)	**217**	**±**	**6**	**0.05**	**±**	**0.04**	**5**		
Liu et al. [48]	209			0.02	±	0.07	14		
Tan et al. [40]	220			−0.03	±	0.06	4		
Pickard et al. [7]	207	±	4	0.01	±	0.04	10		
BHVO-2 (Basalt)									
Digestion 1	93.9			0.03	±	0.06	2	98	1×10^{-4}
Digestion 2	95.0			0.07	±	0.03	2	100	1×10^{-4}
This study (Mean)	**94.5**	**±**	**0.8**	**0.05**	**±**	**0.04**	**4**		
Liu et al. [48]	88			0.04	±	0.05	8		
Tan et al. [40]	200			−0.03	±	0.08	4		
Pickard et al. [7]	88.5	±	2.8	0.09	±	0.08	6		
AGV-2 (Andesite)									
Digestion 1	69.6			0.13	±	0.04	2	100	2×10^{-4}
Digestion 2	70.9			0.12	±	0.03	2	100	2×10^{-4}
This study (Mean)	**70.2**	**±**	**1.0**	**0.12**	**±**	**0.04**	**4**		
Palk et al. [28]	67.7			0.15	±	0.08	–		
Liu et al. [48]	70.0			0.09	±	0.04	8		
Pickard et al. [7]	67.7			0.14	±	0.05	3		
Murchison (CM2 chondrite)									
This study	**387**			**0.34**	**±**	**0.03**	**2**	97	6×10^{-6}
Xiao and Lipschutz [49]	398	±	12						
Baker et al. [27]	387	±	8	0.35	±	0.12	–		
GRO 95504 (L3.2 chondrite)									
Digestion 1	20.4			7.51	±	0.04	2	98	2×10^{-5}
Digestion 2	21.1			7.59	±	0.05	1	100	5×10^{-5}
This study (Mean)	**20.7**	**±**	**0.5**	**7.55**	**±**	**0.08**	**3**		
SRM 2709a (San Joaquin Soil)									
Digestion 1	363			−0.21	±	0.05	1	100	1×10^{-5}
Digestion 2	352			−0.20	±	0.05	1	97	1×10^{-5}
Digestion 3	362			−0.23	±	0.06	1	100	2×10^{-5}
Digestion 4	379			−0.21	±	0.06	1	100	2×10^{-5}
This study (Mean)	**364**	**±**	**11**	**−0.21**	**±**	**0.03**	**4**		
This study (Previous method)	346	±	19	−0.17	±	0.04	3		
Wiggenhauser et al. [23]	356	±	10	−0.22	±	0.02	2		
Imseng et al. [24]	343	±	4	−0.17	±	0.04	3		
Liu et al. [48]	–			−0.22	±	0.05	8		
Certificate[d]	371	±	2						
SRM 2384 (Baking chocolate)									
Digestion 1	70.7			−0.13	±	0.06	1	99	2×10^{-4}
Digestion 2	69.8			−0.17	±	0.06	1	100	3×10^{-4}
Digestion 3	69.4			−0.18	±	0.05	1	100	1×10^{-4}
Digestion 4	70.8			−0.12	±	0.05	1	100	1×10^{-4}
This study (Mean)	**70.2**	**±**	**0.7**	**−0.15**	**±**	**0.05**	**4**		
This study (Previous method)	70.0	±	1.0	−0.14	±	0.05	6		
Barraza et al. [30]	64.5	±	1.1	−0.26	±	0.10	2		
Certificate[d]	73.4	±	7.7						
SRM 1570a (Spinach leaves)									
Digestion 1	–			0.43	±	0.06	2	–	2×10^{-5}
Digestion 2	–			0.46	±	0.04	2	–	5×10^{-5}
This study (Mean)	–			**0.45**	**±**	**0.06**	**4**		
Moore et al. [25]	2709	±	10	0.44	±	0.06	4		
Borovička et al. [51]	2872	±	10	0.45	±	0.05	5		
Zhou et al. [26]	2739	±	34	0.48	±	0.04	6		
Certificate[d]	2876	±	58						

[a] Reported uncertainties for Cd concentration are 1SD based on n individual runs for the different digestions of each sample.
[b] Reported uncertainties with δ^{114}Cd values for sample digests that were measured only once represent the between-run 2SD precision of bracketing standard. For samples analyzed more than once, the 2SD uncertainties were calculated from n individual measurements or represent the average 2SE precisions, see text for details. Uncertainties for literature concentrations and Cd isotope data are quoted from original sources.
[c] Total number of measurements for one or several digests.
[d] Concentration data with uncertainties from National Institute of Standards & Technology.

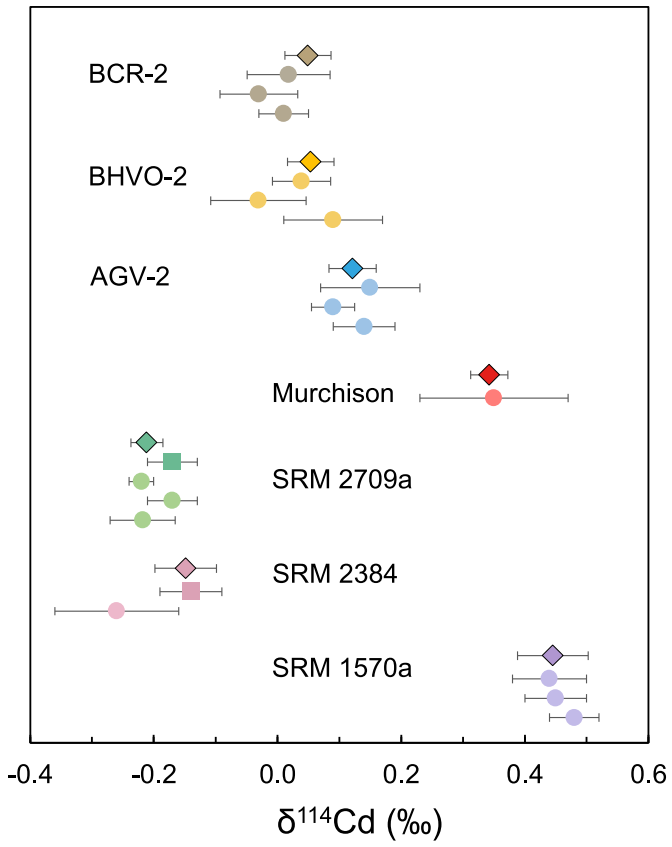

Fig. 2. Cadmium isotope compositions of terrestrial reference materials and the Murchison CM2 chondrite analyzed in this study, with literature values plotted for comparison. For clarity, data for the L3.2 ordinary chondrite GRO 95504 are not plotted due to the high δ^{114}Cd value (7.55 ± 0.08 ‰). Data obtained in this study with the new separation protocol are shown as diamonds, while data for SRM 2709a and SRM 2384 acquired using a previously published separation method are shown as squares. Literature results are shown as circles. All data are compiled in Table 4.

^{112}Sn to the total ion beam at mass number 112 varied between 3 × 10^{-6} and 3 × 10^{-4} in the purified Cd fractions of samples (Tables 4 and 5), with slightly smaller ^{114}Sn contributions to the total ion beam at mass number 114. Given that NIST SRM 3108 Cd standard solutions consistently had ^{112}Sn/^{112}Cd ratios of less than 3 × 10^{-5}, some sample data required correction for isobaric interferences from ^{112}Sn and ^{114}Sn to obtain unbiased Cd isotope results.

To quantitatively evaluate the impact of the Sn correction on Cd isotope compositions, different amounts of Sn were added to double-spiked SRM 3108 Cd standard solutions in 0.1 M HNO_3. As shown in Fig. 1, for solutions with ^{112}Sn/^{112}Cd ≤ 2 × 10^{-3}, the Sn-corrected δ^{114}Cd values are identical to that of the pure Cd standard, within uncertainty (±0.05 ‰, 2SD). For solutions with ^{112}Sn/^{112}Cd > 2 × 10^{-3}, the Cd isotope compositions show gradually lighter Cd isotope compositions with increasing ^{112}Sn/^{112}Cd ratios. In detail, for Sn-doped Cd solutions with ^{112}Sn/^{112}Cd ratios between 5 × 10^{-3} and 8 × 10^{-3}, the Sn corrected δ^{114}Cd values ranged from −0.11 ± 0.05 ‰ (2SE) to −0.14 ± 0.07 ‰ (2SE). These deviations indicate that the Sn corrections for samples with such high Sn levels generate biased δ^{114}Cd data (Fig. 1) and, to have a margin of safety, Cd isotope data obtained for solutions with ^{112}Sn/^{112}Cd > 2 × 10^{-3} are therefore best disregarded.

Due to the efficiency of the Cd separation chemistry that was developed for and applied in this study, the ^{112}Sn/^{112}Cd ratios of all analyzed samples were lower than 3 × 10^{-4} (Table 4 and 5). At this level, the isobaric interferences from Sn had no uncorrectable impact on the accuracy of the δ^{114}Cd results.

3.3. Terrestrial samples and meteorites

3.3.1. Yields and blanks

The Cd recoveries for the analyzed terrestrial and meteorite samples were consistently better than 95 % (Table 4; the yields for the SRM 1570a spinach leaves samples are unknown due to some solution loss during the digestion procedure). The mean total procedural Cd blank, as assessed from the sample preparation to the isotope measurements, was 52 ± 17 pg (1SD, n = 4) for the terrestrial silicate rocks and the meteorites, and 13 ± 6 pg (1SD, n = 4) for the remaining terrestrial samples. The measured Cd concentrations of samples were corrected for the corresponding blank contributions. No blank corrections were applied to the Cd isotope compositions as the blanks corresponded to ≤ 0.1 % of the natural Cd present in all samples, except for the GRO 95504 ordinary chondrite, where the blank contribution was ~0.5 %. At these levels, the impact of the blank on the δ^{114}Cd results is very limited. In detail, for a sample with a δ^{114}Cd that differs by a large value of 8 ‰ from the blank, and whereby the latter contributes 0.1 % or 0.5 % to the total natural Cd present, the blank will alter the measured δ^{114}Cd by 0.008 ‰ or 0.04 ‰. Even in the most extreme case, the blank impact is hence not resolvable given the typical analytical precision of ~0.05 ‰.

3.3.2. Cd concentrations

The Cd concentrations determined for five terrestrial samples and the Murchison CM2 meteorite agree to within 5 % with the official certified values and/or published results (Table 4; Cd concentrations are not available for SRM 1570a spinach leaves due to loss of solution during digestion).

Repeat analyses of two independent digestions of basalt BCR-2 yielded a mean Cd concentration of 217 ± 6 ng g^{-1} (1SD, n = 2), in line with the results of three previous studies which range from 207 ± 4 ng g^{-1} (1SD) to 220 ng g^{-1} (Table 4) [7,40,48]. For the ocean island basalt BHVO-2, a mean Cd concentration of 94.5 ± 0.8 ng g^{-1} (1SD, n = 2) was determined. This result is marginally higher than the concentrations of 88 ng g^{-1} and 88.5 ± 2.8 ng g^{-1} (1SD) that were determined by Liu et al. [48] and Pickard et al. [7], respectively. Notably, all of these BHVO-2 results are significantly lower than the Cd concentration of 200 ng g^{-1} published by Tan et al. [40]. The observed differences in Cd abundances most likely reflect sample heterogeneity between different batches of the powdered rock. The andesite AGV-2 displays the lowest Cd concentration of the rock samples analyzed in this study, with a mean of 70.2 ± 1.0 ng g^{-1} (1SD, n = 2) for two digestions. This result is identical to the Cd concentration of 70 ng g^{-1} reported by Liu et al. [48] and within 4 % of the data obtained in previous studies conducted in our laboratory (Table 4) [7,28].

The Murchison CM2 chondrite has a higher Cd concentration than the terrestrial rocks, with 387 ng g^{-1}, from repeat analyses of a single digestion (Table 4). This result agrees well with literature data of 398 ± 12 ng g^{-1} (1SD) and 387 ± 8 ng g^{-1} that were determined by radiochemical neutron activation analysis (RNAA) and isotope dilution technique, respectively [27,49]. The limited variabilities in the Cd concentrations observed for Murchison and other CM2 chondrites indicate homogeneous distribution of Cd in meteorites of this group [6]. A much lower Cd concentration, with a mean of 20.7 ± 0.5 ng g^{-1} (1SD, n = 2) was determined for the L3.2 ordinary chondrite GRO 95504, based on two independent digestions (Table 4). Notably, ordinary chondrites commonly feature much lower Cd abundances than volatile-rich carbonaceous chondrites such as Murchison [6].

Considering the remaining terrestrial samples, analyses of four digestions of the soil reference material SRM 2709a yielded a mean Cd concentration of 364 ± 11 ng g^{-1} (1SD, n = 4). This result is within uncertainty of the certified value of 371 ± 2 ng g^{-1} (1SD) and the concentration published by Wiggenhauser et al. [23] but slightly higher than the result of 343 ± 4 ng g^{-1} (1SD) reported by Imseng et al. [24].

Table 5
Cadmium concentrations and isotope compositions for seawater samples from Station 198, 142, and 148 obtained on RV Polarstern cruise ANT XXIV/3.

Sample/data source	Mass (g)	[Cd] (nmol kg^{-1})	δ^{114}Cd ± 2SD (‰)[a]			n[b]	Cd Yield (%)	^{112}Sn/^{112}Cd after purification
St. 198, 100m								
Seawater Method 1	846	0.730	0.23	±	0.04	1	81	1×10^{-4}
Seawater Method 2	907	0.723	0.25	±	0.05	2	91	3×10^{-6}
Xue et al. [32]		0.719	0.26	±	0.04			
St. 198, 200m								
Seawater Method 1	878	0.892	0.19	±	0.05	3	80–98	5×10^{-5}
Seawater Method 2	894	0.913	0.18	±	0.03	2	82	3×10^{-6}
Xue et al. [32]		0.890	0.17	±	0.04			
St. 198, 300m								
Seawater Method 1	870	0.893	0.20	±	0.07	1	88	4×10^{-5}
Seawater Method 2	912	0.904	0.16	±	0.03	2	86	3×10^{-6}
Xue et al. [32]		0.888	0.14	±	0.04			
St. 198, 400m								
Seawater Method 1	881	0.892	0.16	±	0.05	1	80	6×10^{-5}
Seawater Method 2	915	0.898	0.18	±	0.05	2	87	3×10^{-6}
Xue et al. [32]		0.882	0.10	±	0.04			
St. 198, 500m								
Seawater Method 1	864	0.872	0.19	±	0.07	1	81	6×10^{-5}
Seawater Method 2	902	0.878	0.18	±	0.03	2	85	3×10^{-6}
Xue et al. [32]		0.863	0.25	±	0.02			
St. 142, 2-5m								
Seawater Method 2	1955	0.271	0.71	±	0.08	5	84	3×10^{-5}
Xue et al. [32]		0.270	0.68	±	0.05			
St. 148, 2-5m								
Seawater Method 2	2151	0.249	0.71	±	0.07	5	90	3×10^{-5}
Xue et al. [32]		0.247	0.74	±	0.05			

[a] Reported uncertainties with δ^{114}Cd values for sample digests that were measured only once represent the between-run 2SD precision of bracketing standard. For samples analyzed more than once, the 2SD uncertainties were calculated from n individual measurements or represent the average 2SE precisions, see text for details. Uncertainties for literature data are quoted from original sources.
[b] Total number of measurements for one or several digests.

The SRM 2709a soil was also analyzed in this study using our previous Cd separation procedure [35,36] and this provided a Cd content, of 346 ± 19 ng g^{-1} (1SD, n = 3), which is slightly lower than but within error identical to the result obtained with the new Cd separation technique.

For the SRM 2384 baking chocolate, separate sample aliquots from which Cd was separated using the present method and the previous procedure applied in our laboratory [35,36] yielded identical Cd concentrations of 70.2 ± 0.7 ng g^{-1} (1SD, n = 4) and 70.0 ± 1.0 ng g^{-1} (1SD, n = 3), respectively (Table 4). These results are consistent with the official certified value of 73.4 ± 7.7 ng g^{-1} (1SD). A slightly lower Cd content of 64.5 ± 1.1 ng g^{-1} was reported by Barraza et al. [30].

3.3.3. Cd isotope compositions

Overall, the δ^{114}Cd values determined in this study are consistent with published results within 2SD uncertainties for all samples (Fig. 2 and Table 4). The isotope compositions measured for the two basalts are identical to each other, with mean δ^{114}Cd values of 0.05 ± 0.04 ‰ (2SD, n = 5) for BCR-2 and 0.05 ± 0.04 ‰ (2SD, n = 4) for BHVO-2. These values are within uncertainties indistinguishable from the Pickard et al. [7] data for BCR-2 (0.01 ± 0.04 ‰) and BHVO-2 (0.09 ± 0.08 ‰), which were previously determined in our laboratory, and further literature results [40,48]. Repeated analyses of two independent digestions of andesite AGV-2 yielded a mean δ^{114}Cd value of 0.12 ± 0.04 ‰ (2SD, n = 4), in line with published data that range from 0.09 ± 0.04 ‰ to 0.15 ± 0.08 ‰ (Fig. 2 and Table 4). The analyzed terrestrial rocks are slightly enriched in heavy Cd isotopes relative to the bulk silicate Earth with a δ^{114}Cd of −0.06 ± 0.03 ‰ (2SD), based on data for spinel lherzolites. Pickard et al. [7] concluded that the marginal enrichment of igneous rocks from the continental crust and oceanic basalts reflects minor isotope fractionation of Cd during partial melting and melt differentiation.

Repeat analyses of a single digestion of the CM2 chondrite Murchison revealed a heavier Cd isotope composition than found for the terrestrial rocks analyzed in this study (Fig. 2 and Table 4), with a mean δ^{114}Cd of 0.34 ± 0.03 ‰ (2SD, n = 2). This is in accord with a less precise literature value of 0.35 ± 0.12 ‰ (2SD) published by Baker et al. [27]. Of interest is the observation that two further CM2 chondrites have similar isotope compositions, with δ^{114}Cd values of 0.53 ± 0.18 ‰ (2SD) for Cold Bokkeveld [27] and 0.29 ± 0.04 ‰ (2SD) for Winchcombe [50]. Precise isotope data are hence required to investigate the homogeneity of Cd isotope compositions within the CM2 group and variabilities between different groups of carbonaceous chondrites. Repeat analyses of two separate digestions of the GRO 95504 L3.2 ordinary chondrite yielded a mean δ^{114}Cd of 7.55 ± 0.08 ‰ (2SD, n = 3; Table 4). Notably, this is the first precise Cd isotope composition determined with the double spike technique for an ordinary chondrite. In contrast, previously published mass-dependent Cd isotope data for ordinary chondrites have much larger errors of up to ±0.43 ‰ for δ^{114}Cd [6].

The soil reference material SRM 2709a was analyzed in this study following the application of two different Cd separation methods. The average δ^{114}Cd of −0.21 ± 0.03 ‰ (2SD, n = 4) determined using the new separation technique is indistinguishable from the value of −0.17 ± 0.04 ‰ (2SD, n = 3) obtained with the previous chromatographic methods [35,36], and results of other published studies (Fig. 2 and Table 4). Similarly, repeat analyses of four separate digestions for baking chocolate SRM 2384 that were processed with the new Cd separation scheme produced a mean δ^{114}Cd of −0.15 ± 0.05 ‰ (2SD, n = 4) that is within error identical to the result of −0.14 ± 0.05 ‰ (2SD, n = 6) that was obtained for a repeatedly analyzed digest from which Cd was isolated using an older protocol [35,36]. The Cd isotope compositions determined for this sample in this study are slightly heavier but still in agreement with the result of −0.26 ± 0.10 ‰ (2SD, n = 2) previously

determined by Barraza et al. [30]. The δ^{114}Cd value measured here for SRM 1570a spinach leaves is 0.45 ± 0.06 ‰ (2SD, n = 4). This closely aligns with the data of 0.44 ± 0.06 ‰ (2SD, n = 4) by Moore et al. [25] and 0.48 ± 0.04 ‰ (2SD, n = 6) by Zhou et al. [26] measured in our laboratory, as well as with a further published result of 0.45 ± 0.05 ‰ (2SD, n = 5) from a different laboratory [51] (Fig. 2 and Table 4). As small amounts of the spinach leaf sample solutions were lost at the beginning of the digestion procedure, the Cd contents of the remaining solutions were determined to enable addition of appropriate amounts of double spike. The final δ^{114}Cd results confirm that sample loss during digestion had no observable impact on the measured Cd isotope compositions, and no such effect is expected as bulk losses are not associated with changes in isotope compositions.

3.4. Seawater samples

3.4.1. Yields and blanks

The Cd yields for small seawater samples (less than 0.5–1 L) that are purified with Seawater Method 1 using solely anion exchange column chromatography ranged from 80 % to 98 % (Table 5). Similar yields of between 82 % and 91 % were observed for larger seawater samples (more than 0.5–1 L) that were processed with Seawater Method 2 (Table 5), which first employs batch-extraction of Cd with Nobias Chelate PA-1 resin.

The total procedural Cd blanks for seawater sample preparation were 58 ± 20 pg (1SD, n = 3) and 30 ± 8 pg (1SD, n = 3) for Seawater Method 1 and 2, respectively. These blanks represent ⟨ < 0.1 % of the natural Cd for all samples. The measured Cd concentrations of seawater samples were corrected for the small blank contribution. No blank corrections were applied to the measured δ^{114}Cd values as the impact of such minor blank contributions is very limited (see Section 3.3.1).

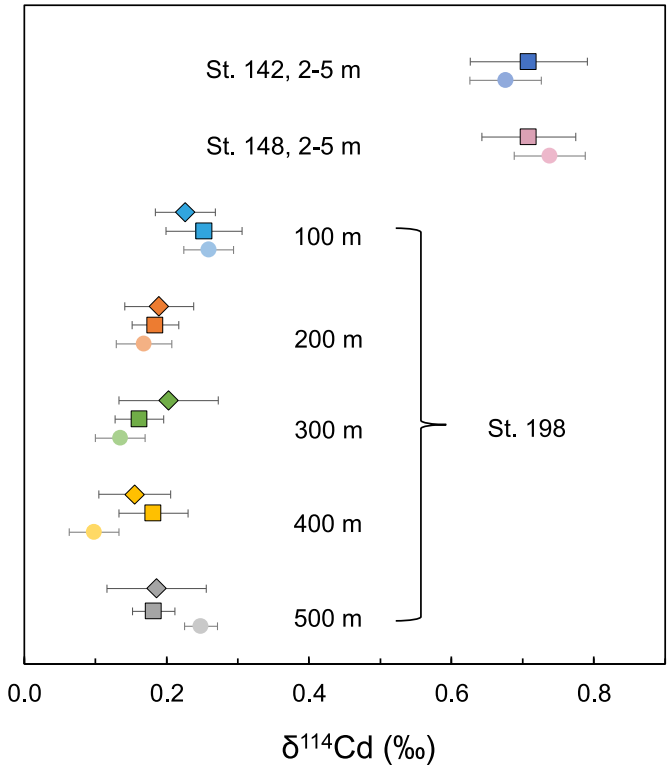

Fig. 3. Cadmium isotope compositions for seawater samples from Station 198, 142, and 148 obtained on RV Polarstern cruise ANT XXIV/3 analyzed in this and previous studies. Data obtained using Seawater Method 1 and Seawater Method 2 are shown as diamonds and squares, respectively. The literature results of Xue et al. [32] are shown as circles. All data are compiled in Table 5.

3.4.2. Cd concentrations

The Cd concentrations that were determined for the five seawater samples from the depth profile at Station 198 following processing with Seawater Methods 1 and 2 agree to within ~2 % or better (Table 5). In detail, the lowest Cd concentrations of 0.730 nmol kg^{-1} (Seawater Method 1) and 0.723 nmol kg^{-1} (Seawater Method 2) were determined for the sample from 100 m depth. Nearly constant Cd concentrations of about 0.89–0.90 nmol kg^{-1} were obtained for the seawater sampled at depths of 200–400 m, whilst slightly lower concentrations of 0.872 and 0.878 nmol kg^{-1} were determined for the sample from 500 m depth (Table 5). Aside from showing excellent agreement with one another, the Seawater Methods 1 and 2 results are also fully in accord with published data for the same samples, with a deviation of less than 3 % [32].

For two surface waters from depths of 2–5 m, processing with Seawater Method 2, yielded Cd concentrations of 0.271 and 0.249 nmol kg^{-1} for the samples for Station 142 and 148, respectively. These results differ by less than 1 % from the published data of Xue et al. [32] for the same samples that were processed with a different method [33,35]. Together, these results demonstrate that the two seawater methods can provide accurate Cd concentration data.

3.4.3. Cd isotope compositions

The accuracy of the Cd isotope data is evaluated in the following by comparing the results obtained with the two seawater methods with one another and to literature results. For the five seawater samples from the Station 198 depth profile, the δ^{114}Cd values that were determined using Seawater Methods 1 and 2 are identical, within 2SD uncertainties (Fig. 3 and Table 5). Furthermore, both methods produced results that are identical, within error, to the published Cd isotope data of Xue et al. [32] for the samples from depths of 100–400 m. For 500 m sample, the average δ^{114}Cd value of 0.18 ± 0.03 ‰ (2SD, n = 2) determined in this study using Seawater Method 2 is slightly lower than the value of 0.25 ± 0.02 ‰ reported by Xue et al. [32]. Considering the long-term δ^{114}Cd reproducibility of 0.06 ‰ reported by Xue et al. [32], the results overlap within uncertainty.

The validation of Seawater Method 2 for the processing of samples with volumes exceeding 1 L is achieved by Cd isotope analyses of the two surface waters from Stations 142 and 148. In detail, repeat analyses of the Station 142 sample produced a mean δ^{114}Cd of 0.71 ± 0.08 ‰ (2SD, n = 5), in excellent agreement with the value of 0.68 ± 0.05 ‰ from Xue et al. [32]. Furthermore, the average δ^{114}Cd of 0.71 ± 0.07 ‰ (2SD, n = 5) determined in this study for the Station 148 surface water, is identical, within error, to the δ^{114}Cd value of 0.74 ± 0.05 ‰ reported by Xue et al. [32].

Based on the above comparisons, the Cd isotope compositions of seawater samples processed using Seawater Methods 1 and 2, show excellent agreement with each other and published data. This indicates that our new separation scheme is suitable for accurate Cd isotope analyses of seawater samples with volumes that are relatively small (less than 0.5–1 L; Seawater Method 1) and those exceeding 0.5–1 L (Seawater Method 2), depending on the Cd concentrations of the waters.

3.5. Method performance for analyses of low-Cd samples

The consistent agreement between the Cd isotope data of this study with published results that were obtained with different methods in various laboratories demonstrates the excellent performance of the new Cd separation protocols for meteorites, diverse terrestrial samples, including silicate rocks, soils, and different biological materials, as well as seawater. The new procedure applies Teflon microcolumns for the second separation stage, rather than repeating the use of the large columns that are employed for the initial Cd isolation. This change significantly speeds up the overall separation process and requires lower quantities of consumables compared to the procedure of Tan et al. [40], which will inevitably reduce the procedural Cd blank. In detail, the

modified Stage 2 separation employs only 5 % of the AG MP-1M resin and mineral acid volumes required for the procedure of Tan et al. [40]. Consequently, the microcolumn chemistry can be completed in half the time (~5 h). In addition, the performance of the method for isolating Cd from matrix components, and in particular from elements that produce spectral interferences, is equivalent or better than that of published techniques (e.g., for Sn; Tables 4 and 5). Given the low blank and high Cd recovery, the new separation method is particularly suitable for samples with low Cd concentrations, for which only limited natural Cd is available for analysis. This is demonstrated by the analyses of two aliquots of the ordinary chondrite GRO 95504, which produced consistent δ^{114}Cd values with a 2SD precision of ±0.08 ‰, even though one digest had only ~10 ng of natural Cd. Furthermore, the column chemistry with AG MP-1M resin was, for the first time, also employed to separate Cd from seawater samples. Following initial pre-concentration of Cd from the seawater matrix, the new method is more efficient in isolating Cd than a published protocol for low-Cd seawater samples [33], because the additional purification steps, which use TRU Spec resin and liquid-liquid extraction of the Cd fraction, are not required.

4. Conclusions

This study presents new Cd purification methodologies for the accurate determination of Cd isotope compositions of a wide range of sample types. For meteorites and diverse terrestrial samples, we modified the column chemistry procedure of Tan et al. [40], using Teflon microcolumns for the second stage. The modified method uses considerably less resin and lower acid volumes and is faster than previous protocols, without compromising matrix element removal and Cd extraction efficiency. The clean-up column was also applied for processing of seawater samples, following a Cd pre-concentration protocol with a different anion exchange column chemistry (for less than 0.5–1 L seawater) or a batch-extraction with chelating resin (for more than 0.5–1 L seawater). As such, our methods allow the processing of all sample types which are currently being studied for Cd isotope compositions.

The between-run reproducibility (2SD) of δ^{114}Cd values for repeated sample and SRM 3108 Cd runs within a single measurement session is typically better than ±0.07 ‰, for total Cd concentrations of 30 ng g^{-1} to 60 ng g^{-1}. Given the high recovery achieved for both seawater (>80 %) and all other sample types (>95 %), the present method allows unbiased and highly precise Cd isotope measurements for samples containing as little as ~10 ng natural Cd.

The data that were obtained with this improved method for four geological and two biological reference materials show excellent agreement with results that were produced using previous Cd separation protocols as part of the current study or in previous, published investigations. A precise δ^{114}Cd value of 0.34 ± 0.03 ‰ is reported for the Murchison CM2 chondrite, and this is also in accord with literature data. In addition, this study reports the first precise Cd isotope composition for the L3.2 ordinary chondrite GRO 95504, obtained with the double spike technique on sample aliquots with as little as ~10 ng Cd. Finally, the δ^{114}Cd values determined for seawater samples with volumes of up to about 2 L show excellent agreement with published results that were acquired with previously validated but more time- and reagent-consuming Cd separation methods.

CRediT authorship contribution statement

Yihang Huang: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Zijian Jia:** Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **Hui Xu:** Validation, Methodology. **Katharina Kreissig:** Writing – review & editing, Resources, Methodology. **Barry J. Coles:** Resources, Methodology. **Mark Rehkämper:** Writing – review & editing, Resources, Methodology, Funding acquisition, Conceptualization. **Rebekah E.T. Moore:** Writing – review & editing, Validation, Resources, Methodology, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was partly supported by UKRI STFC grant ST/W001179/1 to M. Rehkämper. The authors would like to acknowledge Fiorella Barraza for providing the baking chocolate SRM 2384, and P. Heck and J.L. Holstein from the Field Museum in Chicago for providing the Murchison meteorite. The US Antarctic meteorite sample is from the Antarctic Search for Meteorites (ANSMET) program; ANSMET samples are curated by the Dept. of Mineral Sciences of the Smithsonian Institution and the Astromaterials Curation Office at NASA Johnson Space Center. The authors are grateful to the scientists and crew on the 2008 GEOTRACES expedition ANT XXIV/3 aboard the RV Polarstern for collecting the seawater samples employed in this study and to Hein de Baar and Rob Middag for making them available for analysis.

Data availability

Data will be made available on request.

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