Cadmium Isotope Analysis of Environmental Reference Materials via Microwave Digestion–Resin Purification–Double-Spike MC-ICP-MS

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ABSTRACT: Cadmium isotope fractionation is a promising indicator for tracing the source, transport, and transformation of Cd in the environment; therefore, a high-precision method for the Cd isotope analysis of environmental samples is urgently required. In this study, eight environmental reference materials (NIST 2711a, GSS-1, GSS-4, GSS-5, GSD-11, GSD-12, GSD-30, and BCR-679) with different matrices were digested under microwave irradiation and purified via anion exchange. Thereafter, their Cd isotope ratios were analyzed using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) with double-spike correction. The samples digested under microwave irradiation exhibited high Cd recovery (> 96%). One step of anion-exchange-based purification can remove most interfering elements without any detectable loss of Cd. If the purified solution contained Zn/Cd > 0.04, Zr/Cd > 0.01, Mo/Cd > 0.2, Pd/Cd > 4×10^{-5} , In/Cd > 0.02, or Sn/Cd > 0.1, a secondary step using the same purification procedure would be necessary. The measured $\delta^{114/110}\text{Cd}$ values of reference materials (from -0.558 to 0.550‰) were in adequate agreement with those of previous studies, suggesting that this method can be used to analyze the Cd isotope ratios in soil, sediment, and plant samples. In addition, the large variation in the Cd isotope ratios of these reference materials implies that the Cd isotope ratio is promising for identifying pollution sources and the biogeochemical cycle of Cd.

INTRODUCTION

Cadmium (Cd) is a heavy metal physiologically toxic to plants, animals, and humans. Cd in the environment is derived from both natural and anthropogenic sources.¹ The major natural sources of Cd include volcanic eruptions and rock weathering.² With industrialization, large amounts of Cd have been released into the environment via anthropogenic activities, such as the production

of Ni-Cd batteries, waste incineration, coal combustion, and fertilizer application.³ Soil suffers from severe Cd pollution because it is the main contaminant sink.⁴ When entering the soil, Cd can be adsorbed or immobilized by different soil components, internalized by plant roots, and eventually translocated to different plant tissues.^{5, 6} The complexities of the pollution sources and biogeochemical cycles of Cd in soil significantly restrict the solution to environmental Cd pollution.

Cd has eight stable isotopes with mass numbers in the range of 106–116. Cd isotope fractionation has been shown to occur during the evaporation/condensation and biological cycling of Cd.^{7, 8} Recent studies have reported a significantly large degree of Cd isotope fractionation among the products and waste produced during coal combustion, metal smelting/refining, and metal coating,^{9–12} which implies that isotope fractionation can be used to identify Cd pollution sources.¹³ Researchers have identified the main Cd sources and their contribution to Cd pollution by determining the Cd isotope ratios of various sources and contaminated receptors (*e.g.*, soil and sediments).^{14–17} Cd isotope fractionation also occurs during its adsorption-desorption between the solid and liquid phases^{18–20} and translocation to different plant tissues (*e.g.*, roots, shoots, and grains).^{21, 22} These observations have demonstrated that Cd isotope analysis is a promising tool for tracing the sources of Cd in contaminated sites and can also be used as an indicator for probing the behavior of Cd in the environment.

In early research, Cd isotope analysis was typically accomplished using thermal ionization mass spectroscopy.²³ With improvements in mass spectroscopy, the use of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) for metal isotope analysis became practical.²⁴ Since MC-ICP-MS can easily overcome the first ionization potential of Cd via plasma ionization, it is currently the dominant technique for Cd isotope analysis.²³ To accurately determine Cd isotope ratios, possible interfering substances must be removed from samples, which requires the samples to be completely digested, purified, and recovered. For environmental sample digestion, the most widely used protocol is to sequentially add sample and mineral acids (*e.g.*, HNO₃ and HF) to high-pressure bombs or perfluoroalkoxy (PFA) vials. Digestion is then performed using an oven or a hot plate for tens of hours.^{25–28} Although these methods can completely digest samples, they are time-consuming and exhibit poor organic matter removal performance due to the incomplete oxidation of carbon. Unfortunately, most environmental samples, such as agricultural soils and plants, contain large amounts of organic matter that can significantly affect the analytical accuracy of Cd isotope ratios.¹¹ Due to the increasing use of Cd isotope fractionation in environmental research, establishing an effective and efficient digestion method for environmental samples has become necessary. In addition, most soil samples contain interfering elements (*e.g.*, Zn, Zr, Mo, In, and Sn) in amounts that are 1–2 orders of magnitude higher than that of Cd. Thus, it also becomes necessary to evaluate whether current purification processes can effectively remove the matrix and interfering elements in a single operation, and if not, whether the content of interfering elements in the Cd sample solution can meet the requirements for Cd isotope analysis. Furthermore, if the Cd sample solution does not meet the test requirements, the performance of the secondary purification procedure needs to be evaluated.

Therefore, eight environmental reference materials, including soil, sediments, and plants, were tested to evaluate the use of microwave digestion and anion-exchange-based chemical purification procedures using double-spike MC-ICP-MS for Cd isotope analysis. In addition, the effects of isobaric (Pd, In, and Sn) and polyatomic (Zn, Zr, and Mo) interferences on Cd isotope analysis were evaluated and discussed.

EXPERIMENTAL

Reagents, standard solutions, and samples. TraceMetal™ grade HNO₃ and hydrochloric acid (HCl) were procured from Thermo Fisher Scientific (Waltham, MA). Analytical-grade HF and hydrogen peroxide (H₂O₂) were procured from Beijing Chemicals (Beijing, China). HNO₃ and HCl were distilled twice using a Savillex™ DST-1000 sub-boiling acid system. The ¹¹¹Cd-¹¹³Cd double-spike solution used in this study was prepared using the enriched ¹¹¹Cd (purity of 96.00%) and ¹¹³Cd isotopes (purity of 94.90%) from Isotopes for Science, Medicine, and Industry (San Francisco, CA). Briefly, the enriched ¹¹¹Cd and ¹¹³Cd isotopes were individually dissolved in 2 mol L⁻¹ HNO₃, and suitable volumes of the individual isotope solutions were weighed and mixed to obtain a double-spike solution with a ¹¹¹Cd-to-¹¹³Cd ratio ≈ 1, which could then provide high precision for the double-spike method.^{25, 29} Finally, after the double-spike solution was stabilized for 12 h, it was diluted to 10 µg g⁻¹. An AG-MP-1M ion-exchange resin (100–200 dry mesh size, Bio-Rad Laboratories AB, Solna, Sweden) was used for sample purification. Milli-Q water (18.2 MΩ cm⁻¹) was used in all experimental procedures.

Four mono-elemental Cd solutions were used to validate the method: (1) an NIST SRM3108 Cd solution, a common reference material for Cd isotope studies (Lot 130116);³⁰ (2) AAS-Cd, a commercial ICP standard solution (Lot 1797541);²⁵ (3) Thermo-Cd, a commercial ICP standard solution (Lot 9158147) (Alfa Aesar, Thermo Fisher Scientific, Leicestershire, United Kingdom); and (4) GSB-Cd, a mono-elemental Cd standard solution (GSB 04-1721-2004) (Iron and Steel Research Institute, Beijing, China). Other mono-elemental (Mg, Ca, Mn, Cu, Zn, Zr, Mo, Pd, In, Sn, and Pb) standard solutions used in this study were also procured from the Iron and Steel Research Institute (Beijing, China).

Eight environmental reference materials with certified Cd concentrations and isotopic compositions were used to evaluate treatment processes, including four soil reference materials (NIST 2711a, GSS-1, GSS-4, and GSS-5), three stream sediment reference materials (GSD-11, GSD-12, and GSD-30), and one plant reference material (BCR-679).

Sample digestion. Samples were digested using microwaves. For

Table 1 Microwave digestion procedure

Temperature (°C)	Ramping time (min)	Holding time (min)	Power (W)
120	10	10	1800
150	15	20	1800
190	15	30	1800

Table 2 Chemical purification procedure for Cd separation

Reagent	Volume (mL)	Aim
2 mol L ⁻¹ HCl	10	Balance resin
Sample solution	2	Load sample
2 mol L ⁻¹ HCl	10	Elute matrix element
0.3 mol L ⁻¹ HCl	30	Elute Zr, Pb, In, Mo
0.06 mol L ⁻¹ HCl	20	Elute Zn and Sn
0.012 mol L ⁻¹ HCl	6	Elute Sn
0.0012 mol L ⁻¹ HCl	20	Collect Cd

Table 3 Instrumental parameters for Cd isotope measurement

MC-ICP-MS conditions	Settings
RF power, W	1200–1300
Cooling Ar, L min ⁻¹	16
Auxiliary Ar, L min ⁻¹	~0.90 (optimized daily)
Nebulizer Ar, L min ⁻¹	~0.95 (optimized daily)
Sample introduction	Aridus II
Cone	Ni Jet cone, H-skimmer cone
Spray chamber temperature, °C	110
Membrane temperature, °C	160
Number of cycles	one block with 30 cycles
Integration time, s	4.194
Typical ¹¹⁴ Cd sensitivity, V per mg kg ⁻¹	130

soil or sediment samples, 100 ± 0.1 mg of the sample was placed in a 60 mL Teflon tube, and HCl-HNO₃-HF mixtures (10 mL, 6: 2: 2, v/v) were added into the tube. For plant samples, 250 ± 0.1 mg of the plant sample was placed in a 60 mL Teflon tube, and HNO₃-H₂O₂-HF mixtures (8.5 mL, 6: 2: 0.5, v/v) were added into the tube. Following the microwave digestion procedure (Table 1), the Teflon tubes were put on a hot plate at 140 °C to reduce the acid concentration until the solution volume reached ~0.5 mL, which was done to prevent the possible loss of Cd. The residue was transferred into a pre-cleaned centrifuge tube, and 2% (w/w) HNO₃ was added until the volume reached 15 mL. Thereafter, 0.5 mL of the digested solution was diluted, and the Cd concentration was measured using inductively coupled plasma mass spectrometry (ICP-MS). The rest of the digested solution was transferred into a pre-cleaned PFA screw-cap beaker (15 mL) and a double-spike (¹¹¹Cd/¹¹³Cd ≈ 0.98, ¹¹⁰Cd/¹¹⁴Cd ≈ 0.097, ¹¹¹Cd/¹¹⁴Cd ≈ 17.66, and ¹¹³Cd/¹¹⁴Cd ≈ 18.08) solution was added to achieve a double-spike-to-sample ratio of approximately 0.5 (the ratio was determined using the double-spike software toolbox developed by Rudge et al.).²⁹ The PFA screw-cap beaker was then placed on a hot plate at 145 °C until the solution was evaporated to near dryness, and the residue was then dissolved in 2 mL of 2 M HCl for chemical purification.

Chemical purification. The one-step chemical purification procedure using the AG-MP-1M anionic exchange resin is widely

used to remove matrix elements and purify Cd.^{10, 31–33} The chemical purification procedure used herein was modified from the procedures reported by Wen et al.³² and Wei et al.³⁴ The steps in the purification procedure are listed in Table 2. Briefly, a micro-column was filled with 3 mL pre-cleaned resin (10% (w/w) HNO₃ and Milli-Q water), and the resin column was then sequentially cleaned with Milli-Q water (10 mL) and 2% (w/w) HNO₃ (10 mL). The sample in 2 M HCl (2 mL) was loaded onto a column equilibrated with 2 M HCl (10 mL). Thereafter, matrix elements were eluted by 2 M HCl (10 mL), 0.3 M HCl (30 mL), 0.06 M HCl (20 mL), and 0.012 M HCl (6 mL). The Cd fraction was then collected with 0.0012 M HCl (20 mL) in a 25 mL PFA beaker, after which it was evaporated to dryness on a hot plate at 145 °C. During heating, 0.2 mL of concentrated HNO₃ was added into the beaker to remove possible organic matter from the resin.^{34, 35} The residue remaining in the beaker after evaporation was then dissolved in 2 mL of 2% HNO₃ (w/w). To evaluate the extent of purification, 0.5 mL of this solution was then taken and the concentration of Cd and interfering elements measured. The entire procedural blank of Cd was below 0.1 ng, which was negligible.

To assess the purification procedure, an artificial mixed solution (Cd: Mg: Ca: Mn: Cu: Zn: Zr: Mo: Pd: In: Sn: Pb = 1: 200: 300: 100: 100: 10: 10: 2.5: 1: 2: 2.5: 5) was purified using the same procedure. The composition and proportion of the artificial mixed solution were designed to simulate the soil composition.²⁵ The concentrations of Mg, Ca, Cu, Mn, and Pb in the eluent were measured using inductively coupled plasma-optical emission spectrometry (ICP-OES), and the concentrations of Zn, Sn, In, Pd, Zr, Mo, and Cd were measured using ICP-MS.

Measurement using MC-ICP-MS. Cd isotope ratios were measured using MC-ICP-MS (Neptune Plus, Thermo Fisher Scientific, Bremen, Germany) at Jiangnan University (Wuhan, China). Instrumental parameters are presented in Table 3. The ion currents of ¹¹⁰Cd, ¹¹¹Cd, ¹¹³Cd, and ¹¹⁴Cd were collected using L2, L1, C, and H1 Faraday cups, respectively. To investigate and correct the isobaric interference of ¹¹⁰Pd on ¹¹⁰Cd, ¹¹³In on ¹¹³Cd, and ¹¹⁴Sn on ¹¹⁴Cd, the ion currents of ¹⁰⁵Pd, ¹¹⁵In, and ¹¹⁸Sn were simultaneously collected using L4, H2, and H4 Faraday cups, respectively. For MC-ICP-MS measurements, an Aridus II membrane desolvation system was used for sample introduction. Parameters (gas flow, torch position, lens settings, and zoom optics) were optimized to obtain a ¹¹⁴Cd (100 µg kg⁻¹) signal over 13 V. Before each measurement, the sample introduction system was rinsed with 5% HNO₃ (w/w) for 1 min and 2% HNO₃ (w/w) for 2 min.

Data correction. MC-ICP-MS data were corrected in three steps. First, the instrumental mass bias was corrected using the generalized power law^{36, 37}:

$$f = \ln(R/r) / \ln(m_2/m_1) \quad (1)$$

Table 4 Cd concentration and isotopic compositions of the environmental reference materials used in this study and references

Reference materials	Zn or Sn/Cd (Before purification)	Zn or Sn/Cd (After purification)	Reference value (mg kg ⁻¹)	Measured value (mg kg ⁻¹)	$\delta^{114/110}\text{Cd}$ (‰) in this study	$\delta^{114/110}\text{Cd}$ (‰) in references
Soil NIST 2711a	Zn/Cd > 7 Sn/Cd > 3	Zn/Cd < 0.01 Sn/Cd < 0.005	54.1 ± 0.5	53.8 ± 0.6	0.550 ± 0.046	0.532 ± 0.038 ²⁶
						0.57 ± 0.07 ²⁷
						0.58 ± 0.08 ²⁷
						0.551 ± 0.051 ²⁵
						0.57 ± 0.04 ⁴³
Soil GSS-1	Zn/Cd > 158 Sn/Cd > 1	Zn/Cd < 0.01 Sn/Cd < 0.1	4.3 ± 0.4	4.23 ± 0.08	0.099 ± 0.054	0.62 ± 0.03 ²⁸
						0.10 ± 0.23 ¹⁰
						0.11 ± 0.06 ²⁷
Soil GSS-4	Zn/Cd > 600 Sn/Cd > 16	Zn/Cd ≈ 0.01 Sn/Cd ≈ 1	0.35 ± 0.06	0.34 ± 0.01	-0.303 ± 0.044	0.098 ± 0.027 ²⁶
						-0.308 ± 0.016 ²⁶
Soil GSS-5	Zn/Cd > 1000 Sn/Cd > 40	Zn/Cd < 0.2 Sn/Cd < 10	0.45 ± 0.06	0.45 ± 0.01	-0.558 ± 0.046	-0.23 ± 0.09 ²⁸
						-0.694 ± 0.010 ²⁶
Sediment GSD-11	Zn/Cd > 160 Sn/Cd > 160	Zn/Cd < 0.05 Sn/Cd < 0.05	2.3 ± 0.2	2.28 ± 0.05	-0.320 ± 0.067	-0.54 ± 0.06 ²⁸
						-0.274 ± 0.037 ²⁶
						-0.305 ± 0.054 ⁴³
Sediment GSD-12	Zn/Cd > 120 Sn/Cd > 13	Zn/Cd < 0.04 Sn/Cd < 0.001	4.0 ± 0.4	3.86 ± 0.01	-0.041 ± 0.030	-0.34 ± 0.06 ²⁸
						-0.071 ± 0.060 ²⁶
						-0.020 ± 0.095 ²⁷
						0.290 ± 0.030 ¹⁴
Sediment GSD-30	Zn/Cd > 21 Sn/Cd > 0.7	Zn/Cd ≈ 0 Sn/Cd ≈ 0	4.3 ± 0.3	4.25 ± 0.04	0.289 ± 0.042	0.00 ± 0.13 ²⁷
						-0.10 ± 0.06 ²⁸
Plant BCR-679	Zn/Cd > 48	Zn/Cd ≈ 0	1.66 ± 0.07	1.68 ± 0.06	0.203 ± 0.012	0.22 ± 0.02 ⁴⁴

where f is the mass fractionation factor of the instrument; R and r correspond to the measured and true Cd isotope ratios, respectively; and m_1 and m_2 are the masses of the two Cd isotopes. Before each sample measurement sequence, a pure NIST 3108 solution was tested, and the isotope ratio of ^{114}Cd to ^{110}Cd was used to calculate the mass fractionation factor f . The f cannot be ignored, otherwise, it will produce percent-level bias in the measured isotopic composition from the true isotopic composition of sample.³⁸

Second, the isobaric interferences of ^{110}Pd on ^{110}Cd , ^{113}In on ^{113}Cd , and ^{114}Sn on ^{114}Cd were corrected as follows: (1) using the ion current of ^{105}Pd to calculate the ion current of ^{110}Pd ; (2) using the ion current of ^{118}Sn to calculate the ion current of ^{115}Sn , and then using the ion current of ^{115}In (corrected ion current of ^{115}Sn) to calculate the ion current of ^{113}In ; and (3) using the ion current of ^{118}Sn to calculate the ion current of ^{114}Sn . Thereafter, the measured ion currents of ^{110}Cd , ^{113}Cd , and ^{114}Cd were corrected using the calculated ion currents of ^{110}Pd , ^{113}In , and ^{114}Sn , respectively, to obtain the true ion currents of ^{110}Cd , ^{113}Cd , and ^{114}Cd . The interferences of ^{110}Pd , ^{113}In , and ^{114}Sn were calculated as follows²⁵:

$$^{110}\text{Pd}_m = ^{105}\text{Pd}_m \times (^{110}\text{Pd} / ^{105}\text{Pd})_n \times (110 / 105)^f \quad (2)$$

$$^{113}\text{In}_m = (^{115}\text{In}_m - ^{115}\text{Sn}_m) \times (^{113}\text{In} / ^{115}\text{In})_n \times (113 / 115)^f \quad (3)$$

$$^{115}\text{Sn}_m = ^{118}\text{Sn}_m \times (^{115}\text{Sn} / ^{118}\text{Sn})_n \times (115 / 118)^f \quad (4)$$

$$^{114}\text{Sn}_m = ^{118}\text{Sn}_m \times (^{114}\text{Sn} / ^{118}\text{Sn})_n \times (114 / 118)^f \quad (5)$$

where m and n correspond to the measured signal and the

corresponding isotope natural abundance ratio, respectively; and f is the mass fractionation factor of the instrument. Considering similar mass number of Pd, In, and Sn to that of Cd, the same f was used here.²⁵

Third, the three measured isotope ratios, ^{111}Cd -to- ^{110}Cd , ^{113}Cd -to- ^{110}Cd , and ^{114}Cd -to- ^{110}Cd , were inserted into three simultaneous nonlinear equations that can be iteratively solved to obtain the true isotopic composition of the sample after infinitely excluding the double-spike composition based on a mathematical algorithm.^{29,39}

Cd isotopic compositions were reported in δ -notation relative to the NIST SRM3108 Cd solution, which is defined as follows:

$$\delta = \left(\frac{(^{114}\text{Cd} / ^{110}\text{Cd})_{\text{sample}}}{(^{114}\text{Cd} / ^{110}\text{Cd})_{\text{SRM 3108}}} - 1 \right) \times 1000 \quad (6)$$

RESULTS AND DISCUSSION

Efficiency of the microwave digestion procedure. The reference and measured Cd concentrations of the eight reference materials are listed in Table 4. According to these results, microwave digestion completely digested the samples and did not cause a significant loss of Cd, which is indicated by the Cd recoveries of 99.5%, 98.7%, 98.0%, 99.7%, 99.1%, 96.4%, 98.9%, and 101% for NIST 2711a, GSS-1, GSS-4, GSS-5, GSD-11, GSD-12, GSD-30, and BCR-679, respectively. Compared to the time required for hot plate digestion or high-pressure bombs, significantly lesser

Fig. 1 Elution curves of the artificial mixed standard solution (Cd: Mg: Ca: Mn: Cu: Zn: Zr: Mo: Pd: In: Sn: Pb = 1: 200: 300: 100: 100: 10: 10: 2.5: 1: 2: 2.5: 5).

time (~3 h) was required for microwave digestion, including sample weighing, reagent addition, digestion, and cooling. Although microwave digestion consumed a large volume of acid mixtures (10 mL), and the acid mixtures must be evaporated after digestion (approximately 2 h), the overall time requirement was still significantly lower than that of other digestion methods. In addition, microwave digestion effectively destroyed the organic matrix in the samples,^{40,41} as supported by the changes in the color of the digestion solution (transparent or pale yellow) and the subsequent chemical purification performance. Microwave digestion simultaneously digested 40 samples (including blanks), and the digestion performance was highly parallel. Therefore, microwave irradiation can be efficiently used to digest environmental samples for the subsequent Cd isotope analysis.

Performance of the chemical purification procedure. Cd isotope analysis is marred by a variety of interferences that must be removed, including the matrix effect, isobaric interference, and polyatomic interference. First, interference removal was attempted using an anion-exchange-based resin purification procedure with an artificial mixed standard solution. As shown in Fig. 1, the matrix elements (Mg, Ca, Mn, and Cu) were almost completely leached from the column in the first stage (2 M HCl), and the interfering elements (Zn, Zr, and Mo), which can form polyatomic molecules, were completely leached out of the column before the fourth stage (0.012 M HCl). Pd was immobilized on the column and was not detected in any eluents, while In was eluted out of the column in the second stage (0.3 M HCl). Most Sn was eluted out of the column in the third (0.06 M HCl) and fourth stages (0.012 M HCl), and a small fraction of Sn was observed together with Cd in the last stage (0.0012 M HCl). Elution curves were in adequate agreement with those of other studies.^{10, 33, 42}

In addition, the incomplete recovery of Cd during chemical purification may produce significant isotope fractionation.^{10, 24}

However, previous studies have indicated that Cd isotopes are not significantly fractionated when the recovery after chemical purification is higher than 95%.^{10, 31} The recovery of Cd in the procedure used in this study, monitored using a mixed standard solution, was >98%, which guarantees data quality. The above results suggest that this chemical purification procedure can efficiently separate the matrix and interference elements from Cd without causing any loss of Cd.

To further verify the performance of the purification procedure, the digestion solutions of the eight environmental reference materials were purified after evaporation and re-dissolution. The Cd recoveries for all eight samples after purification exceeded 98%, as determined using ICP-MS analysis. In addition, interference elements, including Zr, Mo, Pd, and In, were not detected after purification, but small amounts of Zn and Sn remained in some analyte solutions (Table 4). This may be related to the matrix composition of the sample and the relative content of the interference elements in the sample. For example, the matrices of NIST 2711a, GSD-12, GSD-30, and BCR-679 are relatively simple (Table 4), and the concentration ratios of Zn to Cd and Sn to Cd in the analyte solution after purification were extremely low. However, for GSS-1, GSS-4, GSS-5, and GSD-11, the concentration ratios of Zn to Cd and Sn to Cd after purification were higher.

These results demonstrate that the above procedure can effectively purify the samples. However, in some samples with high concentrations of interference elements, the interference elements were not completely removed. Thus, it is necessary to evaluate whether the concentration of the interference elements in the analyte solution after purification can cause bias during MC-ICP-MS measurements, and whether secondary chemical purification is required for subsequent MC-ICP-MS analysis.

Evaluation of polyatomic and isobaric interferences. During instrumental detection, the non-target elements in analyte solutions can cause spectral interference during Cd isotope measurements, including polyatomic and isobaric interferences. Polyatomic interferences include $^{94}\text{Zr}^{16}\text{O}^+$, $^{94}\text{Mo}^{16}\text{O}^+$, $^{70}\text{Zn}^{40}\text{Ar}^+$ on ^{110}Cd , $^{95}\text{Mo}^{16}\text{O}^+$ on ^{111}Cd , $^{97}\text{Mo}^{16}\text{O}^+$ on ^{113}Cd , and $^{98}\text{Mo}^{16}\text{O}^+$ on ^{114}Cd .³⁶ Isobaric interferences include ^{110}Pd on ^{110}Cd , ^{113}In on ^{113}Cd , and ^{114}Sn on ^{114}Cd .³⁶ Therefore, the thresholds for these interferences must be evaluated. Cd isotopes were measured in a series of NIST SRM3108 solutions ($100\text{ }\mu\text{g L}^{-1}$) doped with different concentrations of Zn, Zr, Mo, Pd, In, and Sn. As shown in Fig. 2, $\text{Zn}/\text{Cd} > 0.04$, $\text{Zr}/\text{Cd} > 0.01$, and $\text{Mo}/\text{Cd} > 0.2$ in the analyte solution result in significant Cd isotopic deviation. Isobaric interferences can theoretically be corrected using mathematical calculations, but their correction is difficult when the concentration ratios of these elements to Cd exceed a certain range.²⁵ In this study, isotopic deviations could not be corrected when the ratios of Pd to Cd $> 4 \times 10^{-5}$, In to Cd > 0.02 , and Sn to Cd > 0.1 (Fig. 3). These

Fig.2 Doping experiments for evaluating the effects of polyatomic interferences on Cd isotope measurements.

Fig. 3 Doping experiments for evaluating the effects of isobaric interferences on Cd isotope measurements.

observations differ from those of some previous studies.^{10,25,26} The threshold ratios of polyatomic interference elements as reported elsewhere ranged from 0.01 to 0.1 for Zn, 0.001 to 0.005 for Zr, and 0.1 to 1 for Mo.^{10,25,26} In this study, the results for Zn, Zr, and Mo adhered to those ranges. In addition, the threshold ratios of isobaric interference elements varied among the studies. Insufficient information is available about the threshold ratio of Pd because of the low levels in environmental and geological samples.

However, our results for Pd were similar to those reported by Liu *et al.*²⁵ For In, previously reported threshold ratios ranged from 10^{-3} to 0.02,^{25,28} and our result for In was similar to that reported by Peng *et al.*²⁸ For Sn, different levels (0.02 to 0.5) of Sn-to-Cd ratios were reported by different laboratories,²⁶⁻²⁸ and our result for Sn fell within that range. However, the interference trends of In and Sn in this study were different from those reported previously.²⁵⁻²⁷ For In, the test range far exceeded that reported by Liu *et al.*,²⁵ and $\delta^{114/110}\text{Cd}$ values decreased when the ratio of In to Cd increased from 0.02 to 0.05 and increased when the ratio of In to Cd exceeded 0.05. This may be due to the fact that a high ^{113}In signal, produced from high In content, can disrupt the data correction of Cd.²⁸ For Sn, $\delta^{114/110}\text{Cd}$ values decreased when the ratio of Sn to Cd increased, but the decrease was small. As mentioned earlier, the threshold ratios of Sn were different among different studies.²⁶⁻²⁸ In addition, Liu *et al.*²⁵ reported that the interference of Sn can be corrected. Therefore, the threshold ratios of interference may be related to different instruments and experimental conditions that may produce different mass discrimination,^{26,28} as well as the difference in the trend of interference.

As mentioned above, when the concentration ratio of any interfering element to Cd after the first purification exceeds its corresponding threshold, a second chemical purification procedure is required. According to the interfering elements in the solution after the first purification, the reference materials GSS-4, GSS-5, GSD-11, and GSD-12 needed to be purified for a second time. After the secondary chemical purification procedure, the concentrations of the interfering elements in the purified solution decreased to their corresponding threshold without a loss of Cd, and the Cd isotopic ratios were consistent with those reported in previous studies (Table 4).

Another point that should be emphasized is the selection of laboratory equipment. A heating plate with an anti-rust coating was initially used in this laboratory, and no abnormalities were observed during the initial period of use. However, over time, rusting occurred around the plate, leading to a significant increase in the Zn concentration in the analyte solution. Therefore, a graphite-coated heating plate was used to avoid Zn contamination.

Precision, accuracy, and Cd isotope ratios of environmental reference materials. To evaluate the precision and accuracy of this method, three types of samples were measured: (1) four pure Cd solutions; (2) a synthetic solution containing matrix elements in three pure Cd solutions (NIST SRM3108, Thermo-Cd, and GSB-Cd); and (3) eight environmental reference materials.

The long-term precision of NIST 3108 was $\pm 0.05\text{‰}$ (2SD, $n = 28$). The $\delta^{114/110}\text{Cd}$ value of AAS-Cd in this study ($-0.699 \pm 0.048\text{‰}$, 2SD, $n = 21$) was in adequate agreement with that reported by Liu *et al.*²⁵ The average $\delta^{114/110}\text{Cd}$ values for Thermo-

Fig. 4 Long-term measurement results of standard solutions relative to NIST SRM 3108.

Cd and GSB-Cd (two commercial mono-elemental standard solutions) were -1.208 ± 0.049 (2SD, n = 20) and $4.441 \pm 0.053\text{‰}$ (2SD, n = 22), respectively (Fig. 4). To verify that the purification process did not change the true Cd isotope ratios of the samples, synthetic solutions (with double-spike) were purified and analyzed. Their $\delta^{114/110}\text{Cd}$ values were -0.028 ± 0.056 (NIST SRM3108, 2SD, n = 3), -1.218 ± 0.043 (Thermo-Cd, 2SD, n = 3), and $4.437 \pm 0.063\text{‰}$ (GSB-Cd, 2SD, n = 3), which is in adequate agreement with those of pure solutions. These results demonstrate that the chemical purification procedure did not change the true Cd isotope ratios of the samples. In addition, the Cd isotope ratios of the eight environmental reference materials were measured. Samples were digested under microwave irradiation, a double-spike solution was added before purification, and the ratios were then measured using MC-ICP-MS. $\delta^{114/110}\text{Cd}$ values were $0.550 \pm 0.046\text{‰}$ (2SD, n = 7) for NIST 2711a, $0.099 \pm 0.054\text{‰}$ (2SD, n = 3) for GSS-1, $-0.303 \pm 0.044\text{‰}$ (2SD, n = 3) for GSS-4, $-0.558 \pm 0.046\text{‰}$ (2SD, n = 7) for GSS-5, $-0.320 \pm 0.067\text{‰}$ (2SD, n = 5) for GSD-11, $-0.041 \pm 0.030\text{‰}$ for GSD-12 (2SD, n = 5), $0.289 \pm 0.042\text{‰}$ (2SD, n = 5) for GSD-30, and $0.203 \pm 0.012\text{‰}$ (2SD, n = 3) for BCR-679, in adequate agreement with those reported in previous studies (Table 4).

CONCLUSIONS

In this study, microwave digestion was conducted to prepare environmental samples for high-precision Cd isotope analysis. Compared with the digestion efficiency of traditional digestion methods (hot plate or high-pressure bombs), that achieved herein was significantly higher. Typically, the chemical purification procedure using an anion exchange resin effectively removed matrix elements without the loss of Cd. However, a secondary purification step was required for the analyte solutions with high concentrations of interference elements ($\text{Zn/Cd} > 0.04$, $\text{Zr/Cd} > 0.01$, $\text{Mo/Cd} > 0.2$, $\text{Pd/Cd} > 4 \times 10^{-5}$, $\text{In/Cd} > 0.02$, or $\text{Sn/Cd} > 0.1$). The $\delta^{114/110}\text{Cd}$ values of the eight environmental reference materials with different matrices varied from -0.558 to 0.550‰ , with Cd concentrations from 0.45 to 54.1 mg kg^{-1} , which was in adequate agreement with that reported in previous studies. The developed microwave digestion–resin purification–double-spike MC-ICP-MS method is useful for the Cd isotope analysis of environmental matrices and can improve the understanding of the source, transportation, and transformation of Cd in the environment.

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Notes

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