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High-sensitivity determination of Cd isotopes in low-Cd geological samples by double spike MC-ICP-MS

This paper demonstrates the high-sensitivity measurement of Cd isotopes by double spike MC-ICP-MS. Through an improved Cd purification scheme specifically designed for low-Cd samples, sample size containing as low as 5 ng Cd is enough to achieve at least 0.08 ‰ analytical precision, which is a reduction in sample size of a factor of 2-5 compared to previous methods.

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High-sensitivity determination of Cd isotopes in low-Cd geological samples by double spike MC-ICP-MS†

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With new advancements in MC-ICP-MS technology, small Cd isotope fractionations in geological processes have attracted more interest in recent years. However, challenges remain in obtaining high-precision Cd isotope data for geological samples with low Cd concentrations and complex matrices. By an improved Cd purification and cleaning resin scheme for low-Cd samples using AGMP-1M resin with >90% Cd recovery, the ratios of trace elements Sn, Mo, Zr, etc. to Cd in the samples, which could potentially jeopardize the accuracy and precision of Cd isotope analysis under a high-sensitivity setup, were less than 0.001 after purification, and the total procedure blank is ≤ 0.1 ng. Hence, a sample containing 20–30 ng Cd can be employed for purification and subsequent isotope measurement. Cadmium isotope fractionation (expressed in $\delta^{114/110}\text{Cd}$ relative to NIST 3108) during column separation and instrument mass bias was corrected for by a ^{111}Cd – ^{113}Cd double spike. NIST 3108 was determined at a concentration of 5–25 ng mL⁻¹ on a Neptune Plus (^{112}Cd signal intensity: ~ 640 V ppm⁻¹) and 25–50 ng mL⁻¹ on a Nu plasma III (^{112}Cd signal intensity: ~ 280 V ppm⁻¹) MC-ICP-MS equipped with an Aridus II/III desolvator for more than one year, with a total external analytical precision of 0.034‰ (2SD, $n = 181$). NIST SRM 2711a, NOD-P-1 and GSS-1 were measured at 5, 10, 20, 25 and 50 ng mL⁻¹ levels to be $0.532 \pm 0.038\text{‰}$, $0.133 \pm 0.038\text{‰}$ and $0.098 \pm 0.027\text{‰}$, respectively, indicating that good accuracy and precision of Cd isotope analysis can be achieved with an injecting sample size as low as 5 ng Cd. Our method can be reliably applied to various geological reference materials (GRMs). The $\delta^{114/110}\text{Cd}$ values of GRMs with relatively high and low Cd concentrations are consistent with previous studies: NOD-A-1 ($0.124 \pm 0.067\text{‰}$), GSD-11 ($-0.274 \pm 0.037\text{‰}$) and BCR-2 ($-0.030 \pm 0.063\text{‰}$). SGR-1b ($0.069 \pm 0.049\text{‰}$), GSH-1 ($-0.337 \pm 0.077\text{‰}$) and others are reported for the first time in this paper. The $\delta^{114/110}\text{Cd}$ in basalt and stream sediments is relatively homogeneous and overlaps with that of the bulk silicate earth (BSE). The $\delta^{114/110}\text{Cd}$ in shale and soils varies greatly from -0.694 to 0.532‰ . Human hair and other animal organs are enriched in light isotopes relative to BSE, whereas terrestrial plants are enriched in heavy isotopes.

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1. Introduction

Cadmium (Cd) is a typical chalcophile element with an average abundance of approximately $0.13 \mu\text{g g}^{-1}$ in the earth's crust,¹ and its geochemical properties are similar to those of zinc.² During magmatic fractional crystallization, zinc is easily

replaced by Cd *via* anisomorphism in zinc-bearing minerals such as sphalerite and lead–zinc ore.³ In earth's surface environments, Cd is easily oxidatively mobilized from Cd-containing sulfides to form CdO, CdCO₃, and CdSO₄, and then enters the aquatic environment in which Cd can be biomagnified through the food chain, causing adverse effects on human health.^{4,5}

Cadmium has eight stable isotopes in nature: ^{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%). The earliest work on Cd isotope analysis goes back to the 1970s.^{6–10} The stable isotope composition of cadmium is typically expressed as the deviation of $^{114}\text{Cd}/^{110}\text{Cd}$ from a standard with a ‰ unit (parts per 1000). The external precision of Cd isotope composition determined by single focus thermal ionization mass spectrometry (TIMS) was greater than 1.6‰ (2SD).^{7,9} This

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precision was insufficient to distinguish Cd isotope fractionations in most geological and environmental samples.⁷ The study of Cd isotopes was therefore limited to extraterrestrial samples with large isotope fractionations.^{6,40} With the development of multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), Wombacher *et al.* (2003)⁴¹ previously carried out high-precision Cd isotope measurement. For samples with low levels of Cd (*e.g.*, 5 ng), the analytical precision of $\delta^{114/110}\text{Cd}$ was 0.4‰ (2SD).⁴¹ With a double spike technique, the analytical precision of Cd isotope measurements reached $\leq 0.15\%$.^{12–21}

In recent years, with increasingly wide application of the Cd isotope system, small Cd isotope fractionations have attracted more attention. Cadmium isotopes are an emerging geochemical proxy and widely used to study the evolution of celestial objects,^{20,22–24} to investigate the cycling of Cd and nutrient elements such as P and Zn,^{18,25–27} to estimate ocean primary productivity^{21,28,29} and to trace the source of Cd pollutants in surface environments.^{30–34} However, obtaining highly precise and accurate Cd isotope data depends on effective separation of Cd from sample matrices, and a robust method to correct for artificial isotope fractionations related to sample preparation and instrument mass bias. Cadmium purification methods can be roughly classified into two categories (Table S1†): (1) a two-column purification scheme that relies on the anion exchange resin AG1-X8 (100–200 mesh or 200–400 mesh) is used to remove most matrix elements, followed by a TRU Spec resin (Eichrom, USA) to separate Sn from Cd;^{11,12,15,19,23,24,35} (2) a single-column scheme using AGMP-1M (100–200 mesh) resin with different concentrations of HCl.^{36–39} Both methods, having their own advantages, can obtain high Cd recoveries (>85%) and low Cd blanks (<0.02 ng) (Table S1†), and are now commonly utilized.^{16,19,38,40–46}

Although several Cd purification methods using AGMP-1M have been described for sediments, soils and organisms, most of these methods were designed for samples with high Cd concentrations (>1 $\mu\text{g g}^{-1}$; Table S1†).^{30,36–40} Methods specifically for low-Cd samples with complex matrices are still lacking. In addition, previous methods^{36–38} could not completely remove Mo and Zr in low-Cd samples such as BCR-2 (Mo/Cd = 873) and soil GSS-4 (Zr/Cd > 1000), leading to the formation of polyatomic interferences (MoO^+ and ZrO^+) that adversely affect the high-precision determination of Cd isotope compositions.³⁸ For this reason, high-precision $\delta^{114/110}\text{Cd}$ data for low-Cd geological reference materials are still scarce. Since the Cd blank from purification procedures has been reduced to less than 0.02 ng (Table S1†), improving the instrumental sensitivity and reducing the sample size for purification and measurement are the best ways to obtain precise Cd isotope composition for extremely low-Cd samples. Some studies have attempted to measure Cd isotopes at the 1–5 ng level by enhancing the sensitivity (~ 280 V ppm^{-1}) and using double spike MC-ICP-MS.^{13–15,35} But the precision of the measured $\delta^{114/110}\text{Cd}$ values was generally poor with $\geq 0.20\%$,^{13–15,35} and the highest was 0.60%.¹³ These precisions were insufficient to identify the smaller Cd isotope variations that are often found in various biogeochemical processes. Therefore, we improved the

instrument sensitivity to 600–680 V ppm^{-1} (for ^{112}Cd), which is much higher than that of previous studies and allows us to determine precise Cd isotope compositions at the 5–10 ng levels. Compared with the previous analysis of low Cd samples with complex matrices,^{13–15,18,20,35} the analytical precision of the $\delta^{114/110}\text{Cd}$ values has been greatly improved up to 0.030–0.083‰ even when the required Cd mass for a single measurement has reduced to 2.5 ng (2711a, 2SD = 0.067‰). Besides, owing to the high-sensitivity setup (600–680 V ppm^{-1} for ^{112}Cd) for MC-ICP-MS, the interference and matrix effects might be different from those for wet plasma and dry plasma with general sensitivity. The magnitudes of these effects on the high-sensitivity measurement of Cd isotopes at the 10 and 25 ng levels were systematically evaluated.

To ensure the high-sensitivity determination of Cd isotopes, we present an improved purification method initially proposed by Cloquet *et al.* (2005)³⁶ to separate Cd effectively from large amounts of matrix elements in low-Cd samples. A step was designed to eliminate Mo, In and trace Zr using 1 M HCl, which ensured that the ratios of Mo/Cd, In/Cd and Zr/Cd in purified samples were less than 0.001. We also report, for the first time, the $\delta^{114/110}\text{Cd}$ values of different types of geological reference materials (GRMs) with low Cd contents such as GSH-1 (human hair: 0.1 $\mu\text{g g}^{-1}$) and GSS-14 (soil: 0.19 $\mu\text{g g}^{-1}$). Replicate analyses of standard solutions and natural samples with a Cd concentration down to 5 ng mL^{-1} yielded an external precision better than 0.083‰ (2SD).

2. Experimental methods

2.1 Apparatus and reagents

Optima-grade HCl, HNO_3 , and HF were purchased from the Beijing Institute of Chemical Reagents, China. Hydrochloric acid (HCl) and nitric acid (HNO_3) were distilled twice using the Savillex™ DST-1500 sub-boiling acid system, while HF was distilled only once. The experimental water (MQ, 18.2 M Ω cm^{-1}) was prepared using a Milli-Q Element System. The strong alkaline anion exchange resin AGMP-1M (100–200 mesh) was purchased from Bio-Rad Company, USA. The Cd standard solution NIST SRM 3108 (lot no. 130116; hereafter named as NIST 3108) was bought from the National Institute of Standards and Technology (NIST), USA. All the Savillex™ PFA (15 and 22 mL) beakers were sequentially cleaned with HNO_3 (1 : 1), HCl (1 : 1) and MQ water, and pipette tips were also washed sequentially with 10% HNO_3 (v/v), 4 M HCl, and MQ water before use.

In order to test if there are differences in Cd isotope compositions between different batches of NIST 3108, another NIST 3108 (lot no. 060531) and Münster Cd with a known Cd isotope composition were generously provided by Dr Rehkämper at Imperial College London (ICL) and Dr Wombacher at University of Cologne. Other standard solutions BAM-I012 and Spex-Cd were obtained from the German Bundesanstalt für Materialforschung und-prüfung (BAM) and Merck (China), respectively. ICP-MS standard solutions (1000 $\mu\text{g mL}^{-1}$) of Sn, Zn, Mo, Zr, *etc.* were obtained from Alfa Aesar Co. Ltd in China. These standard solutions were diluted to 10 $\mu\text{g mL}^{-1}$ with 2% HNO_3 .

2.2 Sample preparation and digestion

In order to better evaluate our improved Cd purification procedure and high-sensitivity Cd isotope measurement method, some international GRMs were selected, including basalt (BCR-2 and BHVO-2), shale (SGR-1b), Manganese nodule (NOD-A-1 and NOD-P-1), soil (NIST SRM 2711a, GSS-1, GSS-4, GSS-5, and GSS-14), stream sediments (GSD-5a, GSD-6, GSD-7a, GSD-10, GSD-11, GSD-12, GSD-17, GSD-21, and GSD-23), human hair (GSH-1) and plant (GSV-2) samples. The above GRMs were individually purchased from the United States Geological Survey (USGS), NIST (USA), and the Institute of Geophysical and Geochemical Exploration (IGGE) of the Chinese Academy of Geological Sciences (CAGS). Details of these samples are given in Table S2.†

In this work, sample digestion followed procedures described in Zhu *et al.* (2014, 2018).^{47,48} For basalt samples, 50 ± 1 mg powders were accurately weighed into 15 mL PFA vials, and then 1 mL HNO₃ (15.8 M) and 2 mL HF (23 M) were added. Intermittent ultrasonic treatment was conducted during heating on a hot plate at 140 °C for 8 h until samples were digested completely. Samples were then evaporated to 0.5–1 mL at 150 °C, and the remainder evaporated to dryness at 110 °C. After that, 4 mL *aqua regia* (HNO₃ : HCl = 1 : 3) was added into the PFA vials. With vials sealed tightly, the samples were heated on a hot plate at 140 °C for 8 h to completely decompose the residual solids. After evaporating to incipient dryness on a hot plate at 110 °C, the samples were then dissolved and stored in 1 mL 2 M HNO₃.

For soil, sediment, shale, human hair and plants, 100 ± 1 mg powders (200 mg for human hair) were accurately weighed into 30 mL Teflon (PTFE) liner vials. 1–2 drops of MQ water were added to wet the samples, and then 2.5 mL HNO₃ (15.8 M) and 0.8 mL HF (23 M) were added sequentially. After degassing for at least 1 h, the samples were sealed in bombs and placed in a pre-heated oven at 185 ± 5 °C for 36–48 h. After cooling, 1 mL of

30% H₂O₂ was added into the PTFE liners, and heated on a hot plate at 110 °C to evaporate the sample solution to incipient dryness. After that, 3 mL HNO₃ was added to PTFE liners and continuously heated (sealed) for 12–16 h in an oven at 185 ± 5 °C. In this step, 0.3 mL of HF was added if residual solid remained from the first digestion. Finally, the samples were evaporated to incipient dryness on a hot plate at 110 °C, and dissolved in 1 mL of 2 M HNO₃.

For manganese nodules, 100 ± 1 mg powders were firstly dissolved in 1 mL of 6 M HCl, dried down, and then re-dissolved in 3.2 mL concentrated HNO₃ contained in 30 mL Teflon liner vials. The sealed vials were then placed into a pre-heated oven at 185 ± 5 °C for 24 h. After digestion, the samples were transferred to 15 mL PFA vials, with 1 mL 30% H₂O₂ added, and then heated to incipient dryness on a hot plate at 110 °C. Dried samples were dissolved in 1 mL of 2 M HNO₃. We noted that these samples always contained a small amount of residual solids, and centrifugation was used to extract the supernatant, from which Cd was purified.

2.3 Chromatographic separation of Cd

All sample purification steps were carried out in a class 100 hood at the Isotope Geochemistry Laboratory of China University of Geosciences (Beijing). In order to obtain high-precision and high-accuracy Cd isotope data, the elements responsible for isobaric (Pd, In, Sn, *etc.*) and polyatomic (Zn, Ge, Zr, Mo, *etc.* with the Ar/O) interference,^{38,49,50} and some matrix elements such as Mg and Fe must be eliminated. Here, a modified purification scheme was employed for Cd separation using the strong alkaline anion exchange resin AGMP-1M (Table 1), which was originally proposed by Cloquet *et al.* (2005)³⁶ and used in many later studies.^{37–42} Our improvement was the quantitative removal of interference elements Mo, Zr and In.

Before purification, samples containing 20–100 ng Cd, occasionally 200 ng for long-term monitoring, were mixed with

Table 1 Cadmium purification scheme of geological samples using AGMP-1M resin

Separation stage	Reagent	Volume(mL)
Step I		
<i>Column I: anion exchange resin (AGMP-1M, 100–200 mesh, 2.8mL)</i>		
Condition	2 M HCl	10
Load sample	2 M HCl	2
Elute matrix (Mg, Ca, Fe, Ni, Ga, Ge, Zr, <i>etc.</i>)	2 M HCl	10
Elute Mo, In	1 M HCl	10
Elute Pb, Mo	0.3 M HCl	20
Elute Zn, Sn	0.06 M HCl	20
Elute Sn	0.012 M HCl	10
Collect Cd	0.0012 M HCl	20
Step II		
<i>Column II: anion exchange resin (AGMP-1M, 100–200 mesh, 2.8mL)</i>		
Washing	3.5 M HNO ₃	12
Washing	2 M HCl + 8 M HF	10
Washing	6 N HCl	10
Wash to near neutral	Milli-Q water	10
Condition	2 M HCl	10
Redo step I		

an appropriate amount of the ^{111}Cd - ^{113}Cd double spike (DS) in 15 mL PFA beakers so that the ratio of $^{111}\text{Cd}_{\text{spike}}$ to $^{112}\text{Cd}_{\text{sample}}$ was ~ 2 . The PFA beakers were tightly sealed and placed on a hot plate at 100 °C overnight to ensure that the sample and spike were mixed homogeneously. Then the spiked samples were evaporated to dryness and dissolved in 2 mL of 2 M HCl.

The Muromac complete polypropylene mini columns (7.4 mm in diameter, Japan) were packed with 2.8 mL of AGMP-1M resin (100–200 mesh). The columns were cleaned with 10 mL ($10 \times 1\text{ mL}$) of 3.5 M HNO_3 , 10 mL ($10 \times 1\text{ mL}$) of 2 M HCl–8 M HF, 10 mL ($10 \times 1\text{ mL}$) of 6 M HCl, and MQ water, and conditioned with 10 mL of 2 M HCl. The spiked samples were loaded onto the columns in a manner of $2 \times 1\text{ mL}$. Then, 10 mL ($10 \times 1\text{ mL}$) of 2 M HCl was added to remove K, Ca, Mg, Fe, Ni, Zr, Ga and other matrix elements. After that, 10 mL ($10 \times 1\text{ mL}$) of 1 M HCl was used to elute Mo and In and further remove matrix elements such as K, Na, Zr and Ga. Subsequently, 20 mL ($20 \times 1\text{ mL}$) of 0.3 M HCl, 20 mL ($20 \times 1\text{ mL}$) of 0.06 M HCl and 10 mL ($10 \times 1\text{ mL}$) of 0.012 M HCl were sequentially added to elute Pb, Zn and Sn. Finally, Cd was eluted with 20 mL ($20 \times 1\text{ mL}$) of 0.0012 M HCl. The collected Cd solutions were put on a hot plate at 130 °C overnight to evaporate to dryness. To avoid the isobaric interference of residual Sn on Cd in the high-sensitivity setup, dried samples were dissolved in 2 mL of 2 M HCl and the same column procedure was repeated to further purify Cd. After purification, Cd samples were dissolved in 1 mL of 2% HNO_3 as the stock solution for isotope determination on an MC-ICP-MS.

2.4 Analysis of Cd isotopes

2.4.1 Cd double spike. Following previous studies,^{13,17} the ^{111}Cd - ^{113}Cd DS was implemented to correct for Cd isotope fractionation during chemical purification and mass spectrometry. High purity ^{111}Cd (97.23%) and ^{113}Cd (93.35%) single isotope spikes were purchased from ISOFLEX (USA). In order to minimize error propagation during data reduction, we combined the Monte Carlo and nest iteration to optimize the ratios of $^{111}\text{Cd}_{\text{spike}}/^{113}\text{Cd}_{\text{spike}}$ in DS and $^{111}\text{Cd}_{\text{spike}}/^{112}\text{Cd}_{\text{sample}}$ in mixed DS-sample solutions.^{51–55} The optimal mixing range of $^{111}\text{Cd}_{\text{spike}}/^{112}\text{Cd}_{\text{sample}}$ we obtained was 0.8 to 6 (Fig. 1), whereas the optimal ratio of $^{111}\text{Cd}_{\text{spike}}/^{113}\text{Cd}_{\text{spike}}$ was 1.5. Hence, the ^{111}Cd - ^{113}Cd double spike solution was calibrated to be 1.549727 using $^{107}\text{Ag}/^{109}\text{Ag} = 1.076378$ on a Nu Plasma II MC-ICP-MS, following a similar calibration method used by Ripperger and Rehkämper (2007).³⁵ We also used this Ag method to calibrate the isotopic ratios of NIST 3108 (lot no. 130116) (Table S3†). The isotope composition of NIST 3108 was consistent with the data reported by Abouchami *et al.* (2012).⁵⁰ Thus, these ratios were used as the starting values in the iterative data reduction algorithm for samples. We spiked the standard solution NIST 3108 with different amounts of DS (under-, normal- and over-spiked, with the $^{111}\text{Cd}_{\text{spike}}/^{112}\text{Cd}_{\text{sample}}$ ratio ranging from 0.8 to 6) and measured on a Nu Plasma II/III MC-ICP-MS; we found that the optimal ratio was 2, consistent with the theoretical simulation (Fig. 1). For real samples, $^{111}\text{Cd}_{\text{spike}}/^{112}\text{Cd}_{\text{sample}}$ values may be >2 or <2 owing to occasionally incorrect estimates of Cd concentrations, but the accuracy and precision of $\delta^{114/110}\text{Cd}$

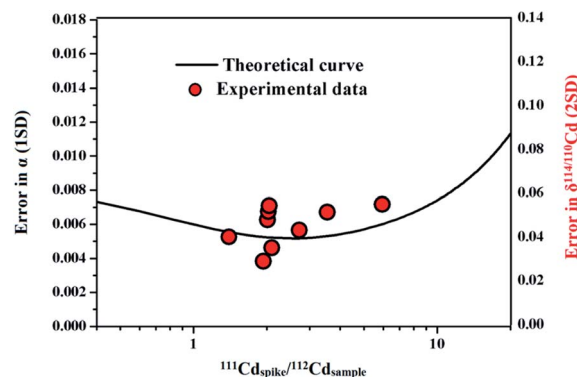


Fig. 1 The best mixing ratio of spike to sample by theoretical simulation (black curve) and experimental determination (red circles). The left and right y-axes show the variation of the theoretical error in α (fractionation factor of natural samples relative to SRM 3018) and the measured error in $\delta^{114/110}\text{Cd}$, respectively.

measurement would not be greatly affected as long as the ratio of $^{111}\text{Cd}_{\text{spike}}/^{112}\text{Cd}_{\text{sample}}$ is within the range of 0.8–6.

2.4.2 Mass spectrometry. Cadmium isotope composition was measured on three instruments (Table 2): a Nu Plasma II MC-ICP-MS (Nu II) housed in the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (IGCAS), a Nu Plasma III MC-ICP-MS (Nu III) in the Laboratory of Surficial Environmental Geochemistry, Institute of Earth Sciences, and a Neptune Plus MC-ICP-MS (NP) in the Isotope Geochemistry Laboratory, China University of Geosciences (Beijing) (CUGB). Nu II/III instruments are equipped with 16 Faraday cups connected to $10^{11}\ \Omega$ standard amplifiers, and the cup configuration is listed in Table 2. Each measurement consists of 3 blocks, each block with 10 cycles, with each cycle lasting for 10 s for the Nu II and 15 s for the Nu III. Before the measurement of each block, baseline was measured *via* ESA deflection for 10 s (Nu II) and 15 s (Nu III). The ESA deflection voltages were set to 10 V for the Nu II and 20 V for the Nu III. The Neptune Plus is equipped with 9 Faraday cups connected with $10^{11}\ \Omega$ amplifiers. Measurement was conducted in static mode using 9 Faraday cups (Table 2). Signals were collected for 3 blocks, each block with 15 (for $\geq 20\text{ ng mL}^{-1}$) or 20 (for 10 and 5 ng mL^{-1}) measurement cycles, each cycle with 4.194 s integration time. The on-peak blank was measured in 2% HNO_3 or 2% HNO_3 -0.1% HF (v/v) and subtracted from subsequent sample signals. ^{118}Sn (Nu II/III) or ^{117}Sn (NP) was detected to monitor and correct for the isobaric interference of ^{112}Sn on ^{112}Cd and ^{114}Sn on ^{114}Cd .

Purified samples dissolved in 2% HNO_3 or 2% HNO_3 -0.1% HF were introduced into the plasma through an Aridus II desolvator (Teledyne CETAC Technologies Omaha, NE, USA) equipped with a $100\ \mu\text{L min}^{-1}$ PFA nebulizer *via* a Cetac ASX-112FR auto-sampler. The signal intensity of ^{112}Cd was approximately 5–6 V on the Nu II with a Cd concentration of 100 ng mL^{-1} . In contrast, the ^{112}Cd signal was 6–8 V for the Nu III and 15–17 V for the NP with only 25 ng mL^{-1} . After each measurement, the sample introduction system was cleaned with 2% HNO_3 -0.1% HF for 8–10 minutes until the ^{111}Cd signal was $<5\text{ mV}$. The spiked NIST

Table 2 Instrumental operating parameters for Cd isotope measurements

Parameters	Settings for the NP	Settings for the Nu II/III
Cup configuration	L4(¹⁰⁷ Ag), L3(¹⁰⁸ Cd, ¹⁰⁸ Pd), L2(¹⁰⁹ Ag) L1(¹¹⁰ Cd), C(¹¹¹ Cd), H1(¹¹² Cd, ¹¹² Sn), H2(¹¹³ Cd), H3(¹¹⁴ Cd, ¹¹⁴ Sn), H4(¹¹⁷ Sn)	L5(¹⁰⁴ Pd), L4(¹⁰⁶ Cd), L2(¹⁰⁸ Cd), Ax(¹¹⁰ Cd), H1(¹¹¹ Cd) H2(¹¹² Cd, ¹¹² Sn), H3(¹¹³ Cd, ¹¹³ In), H4(¹¹⁴ Cd, ¹¹⁴ Sn) H5(¹¹⁵ In), H6(¹¹⁶ Cd, ¹¹⁶ Sn), H7(¹¹⁸ Sn)
RF power	1250 W	1300 W
Sampler cone	H cone	541B (1.15mm)/dry cone (0.9 mm)
Skimmer cone	X cone	540 (0.6 mm orifice)/dry cone
Cooling Ar flow rate	15 L min ⁻¹	15 L min ⁻¹
Auxiliary Ar flow rate	0.8 L min ⁻¹	0.8 L min ⁻¹
Nebulizer Ar flow rate	30–35 psi	25–33 psi
Sweep gas flow rate	4.5–5.8 L min ⁻¹ (II)	3.0–3.9 L min ⁻¹ (II)/3.5–5 L min ⁻¹ (III)
T of the spray chamber ^a	110 °C	110 °C
T of the desolator	160 °C	160 °C
Sample uptake rate	110 µL min ⁻¹	100 µL min ⁻¹
Cycle integration time	4.194 s	10/15 s
Number of cycles	45 for 25 ng/60 for 5–20 ng	30
Sensitivity of ¹¹² Cd	640 V ppm ⁻¹	60/280 V ppm ⁻¹

^a T represents the temperature.

3108 standard solution was measured every 3–5 samples to monitor the stability of the instrument, and it was also used to normalize the sample data. Meanwhile, in the case of BAM-I012 and SPEX Cd-CUGB every 5 or 10 samples were measured to ensure the accuracy of measured values.

On the Nu II/III, measured Cd isotope data such as $\delta^{114/110}\text{Cd}$ and $\delta^{112/110}\text{Cd}$ were reduced *via* an online DS program built into

the executive software of the instrument (*i.e.* *.crf), while data collected from the NP required offline calculation using an EXCEL worksheet. The Cd isotope composition is typically expressed using either the δ (parts per thousand, or ‰) or ϵ (parts per ten thousand) notation.^{6–10,13,14,16,50} In this paper, the international NIST 3108 (lot no. 130116) is used as the Cd isotope reference standard, and the expression is presented in

Table 3 Reported sensitivity of instruments for Cd isotope analysis

References	Instrument	Sample introduction system	Analyzed concentration (ng mL ⁻¹)	Uptake ratio (µL min ⁻¹)	Sample/skimmer cones	¹¹² Cd signal (V ppm ⁻¹)
Wombacher <i>et al.</i> (2003) ⁴¹	Nu plasma	MCN 6000	200	~100	—	7.2–24
	IsoProbe	MCN 6000	—	~100	—	2.4–27
Cloquet <i>et al.</i> (2005) ³⁶	IsoProbe	Wet plasma	500	100	—	4.83
Lacan <i>et al.</i> (2006) ²⁵	Neptune	Wet plasma	—	~60	—	7.24
Pallavicini <i>et al.</i> (2014) ³⁸	Neptune plus	Wet plasma	200	50	H/H	22
Wei <i>et al.</i> (2015) ³⁹	Nu plasma HR	Wet plasma	400	100	285A/497	13
Li <i>et al.</i> (2018) ⁴²	Neptune plus	Wet plasma	100	~100	Jet/X	11
Zhang <i>et al.</i> (2018) ⁴¹	Neptune plus	Wet plasma	100	50	Pt jet/X	14–17
Ripperger <i>et al.</i> (2007) ²⁸	Nu plasma	Aridus	30–50	100	—	—
Shiel <i>et al.</i> (2009) ⁵⁹	Nu plasma	DSN-100	60	—	541B/540	47–76
Gault-Ringold <i>et al.</i> (2012) ¹⁴	Nu plasma	DSN-100	~10	50	—	—
Xue <i>et al.</i> (2012) ¹³	Nu plasma	DSN-100	40–60	100–120	—	60–84
Lambelet <i>et al.</i> (2013) ¹⁷	Nu plasma HR	DSN-100	20–60	100–120	—	72–104
Yang <i>et al.</i> (2012) ¹⁵	Nu plasma	Aridus I	—	—	—	—
Conway <i>et al.</i> (2013) ¹⁶	Neptune	Apex-Q	—	~100–150	Pt jet/Al- X	270
Zhu <i>et al.</i> (2016) ⁶⁸	Neptune plus	Aridus II	—	~100	—	21
Bridgestock <i>et al.</i> (2017) ⁶⁹	Nu plasma	Aridus II	—	110–115	—	48–72
Fouskas <i>et al.</i> (2018) ⁴⁵	Nu plasma HR	—	25	—	—	39
Kruijjer <i>et al.</i> (2013) ⁴³	Neptune plus	Aridus II	—	100	—	290
Pallavicini <i>et al.</i> (2014) ³⁸	Neptune plus	Aridus II	20	40–100	Jet/X	517
		Aridus II	20	40–100	H/H	172
Liu <i>et al.</i> (2019) ⁴⁶	Neptune plus	Aridus II	50–100	50	Jet/H	103
This study	Nu plasma II	Aridus II	50–100	100	541B/540	60
	Nu plasma III	Aridus III	25	100	Dry/Dry	280
	Neptune plus	Aridus II	5–25	100	H/X	640

the delta (δ) notation as per mil deviation (‰) relative to NIST 3108: $\delta^{114/110}\text{Cd}$ (‰) = $\left(\frac{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{sample}}}{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{NIST 3108}}}-1\right) \times 1000$.

3. Results and discussion

3.1 Sensitivity and data validation

The sensitivity of the ^{112}Cd signal on the Nu II and Nu III using an Aridus II/III desolvator falls within the range of those reported in previous studies (Table 3). In contrast, our sensitivities (600–680 V ppm $^{-1}$ for ^{112}Cd) on the NP are much higher than previously published sensitivities except for Pallavicini *et al.* (2014)³⁸ who used Jet and X cones (517 V ppm $^{-1}$ for ^{112}Cd). This means that the signal of ^{112}Cd is at least 3 V with a 5 ng mL $^{-1}$ solution. However, higher sensitivity has unwanted side effects such as memories and interferences. To minimize the memory effects of Cd, Mo, and Sn in the Aridus II, 2% HNO $_3$ –0.1% HF was used to rinse the sample introduction system for 10 minutes on the NP. Schmitt *et al.* (2009)³⁶ found that $\delta^{114/110}\text{Cd}$ values were often shifted drastically within one analytical session and irreproducible between sessions for the Nu plasma MC-ICP-MS. Pallavicini *et al.* (2014)³⁸ proposed that the stability of instrumental mass bias using the Aridus was remarkably lower than that of the standard introduction system (SIS) for the NP. However, we only occasionally observed these phenomena when analyzing 10 ng mL $^{-1}$ Cd solutions on the Nu III (Aridus III). On the NP, we routinely achieved high stability with the relative standard deviation of the ^{112}Cd signal intensity varying $\leq 5\%$ over 8 hours, even in 5 ng mL $^{-1}$ solution. The $\delta^{114/110}\text{Cd}$ values obtained from the three instruments agree very well (Fig. 2) at different sensitivities.

3.2 Performance of separation procedures

Several schemes have been proposed in the past years for purifying Cd from rock, soil, sediment, plant, seawater and blood samples.^{11–14,16,19,30,31,36–42,44,57} Cadmium recoveries obtained by the previous single-column^{36–42} and double-column

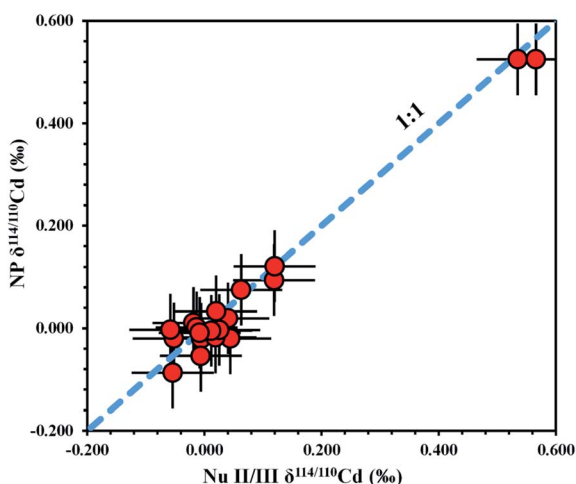


Fig. 2 Comparison of Cd isotope data measured on the NP versus Nu II/III.

methods^{11–14,19,26} varied but mostly higher than 90% (Table S1†). In order to eliminate the tailing Mo during chromatography,³⁸ we present a modified method (Table 2) for purifying Cd from samples with widely ranging matrix/Cd ratios with consistently >90% recoveries (Table 4).

Similar to previous studies,^{36–41} for the selected samples in our study, >95% major (K, Ca, Mg, Fe, Ti, Mn, *etc.*) and trace (Co, Ni, Cu, Ga, Ge, *etc.*) matrix elements can be washed out from the column during sample loading (2 mL) and the subsequent rinsing with 10 mL of 2 M HCl (Fig. S1†). However, the elution behavior of Mo and Sn changes remarkably with the different sample matrices (Fig. S2†), similar observations were reported by Pallavicini *et al.* (2014).³⁸ Mo, Zr and Sn contents are generally higher than that of Cd in geological samples, especially igneous rocks, shale and soils (Table S4†). Therefore, effectively removing Mo, Sn and Zr is key for high-sensitivity Cd isotope measurement for these low-Cd samples. 10 mL of 2 M HCl can elute >99% Zr, but only $\leq 0.1\%$ Mo and Sn (Fig. S1†). Pallavicini *et al.* (2014)³⁸ observed that 50–60% of Mo can elute together with Pb and Zn (12 mL of 0.3 M HCl and 12 mL of 0.012 M HCl) with the rest eluted together with the Cd cut. This observation is similar to our test experiment, even using 30 mL of 0.3 M HCl to wash but it is not demonstrated in Li *et al.* (2018)⁴² and Liu *et al.* (2019)⁴⁶ Since 1 M HCl was a better choice to elute Mo for AG1-X8 and AGMP-1M resin,³⁸ we added a special step (1 \times 10 mL 1 M HCl) to eliminate >95% Mo and 99% In (Fig. S1†). Following this 1 M HCl step, an additional 20 mL of 0.3 M HCl removes >99% residual Mo for SGR-1b (original Mo/Cd = 53.8) (Fig. S1†). Tests using BHVO-2 and BCR-2 showed that >97% Pb was also washed out and 100% Cd remained on the column. Wei *et al.* (2015)³⁹ showed that Zn and Sn can also be partially removed in 0.3 M HCl (Fig. S1†). Instead, we used 0.06 M HCl and 0.012 M HCl to elute Zn and Sn. Despite higher [Matrix]/Cd in samples analyzed here, >99% Zn and $\sim 50\%$ Sn can be removed, with the rest of the Sn remaining on the ion exchange column and tailing into the Cd cut. Some previous studies noted this phenomenon, but did not elaborate on how to eliminate the residual Sn.^{37,42,46} However, Wombacher *et al.* (2003)¹¹ and Kruijer *et al.* (2013)⁴³ used a second mini-column with 0.12 mL Eichrom TRU-Spec resin to remove Sn. Since we carried out high-sensitivity measurement of Cd isotopes at 5–25 ng mL $^{-1}$, column I procedures were repeated to reduce Sn/Cd further as well as other matrices (Fig. S2†). The entire procedure takes 2 days but can achieve high-purity Cd for high-precision and high-sensitivity isotope analysis.

3.3 Evaluation of isobaric and matrix interference

Determination of Cd isotopic ratios on a MC-ICPMS is susceptible to isobaric (^{110}Pd on ^{110}Cd , ^{113}In on ^{113}Cd , and ^{114}Sn on ^{114}Cd) and polyatomic (ZnAr^+ , GeAr^+ , ZrO^+ , MoO^+ , *etc.*) interference.^{38,50,59} In addition, matrix effects caused by Mg, Fe, and Pb can also negatively affect analytical results.^{46,59} An *et al.* (2014)⁶⁰ also reported that matrix effects on Mg isotope analyses vary among different instruments and laboratories. Therefore, by doping varying amounts of Sn, Zn, Zr, Mo, Ge, and Fe into NIST 3108 (Fig. 3), we thoroughly tested the effects of these

Table 4 Cd isotopic compositions of geological reference materials in this study and the literature

Sample name	Sample type	Reference	Cd ($\mu\text{g g}^{-1}$)	Sn/Cd	Sn/Cd after purification	$\delta^{114/110}$ Cd (‰)	2SD ^j	N ^{h,i}	Yield (%)
BCR-2	Basalt	This study ^a	0.22	7.13	0.002	-0.007 ^f	0.046	3	97.52
		This study ^b	0.22	7.13	0.001	-0.052	0.070	1	
		Average				-0.030	0.063	4	
BHVO-2	Basalt	Liu <i>et al.</i> (2019) ⁴⁶				0.031	0.067	6	
		This study ^a	0.2	8.07	0.001	-0.003 ^f	0.075	3	93.74
		This study ^b	0.2	8.07	0.003	-0.058	0.070	1	
		Average				-0.031	0.077	4	
NOD-A-1	Mn-nodule	Liu <i>et al.</i> (2019) ⁴⁶				0.039	0.047	8	
		This study ^a	6.13	—	<0.001	0.094	0.032	7	95.64
		This study ^a				0.160 ^f	0.024	4	
		This study ^c				0.119	0.083	3	
		Average				0.124	0.067	14	
NOD-P-1	Mn-nodule	Cloquet <i>et al.</i> (2005) ³⁶				-0.051 ^d	0.100		98.77
		Schmitt <i>et al.</i> (2009) ⁶²				0.129 ^d	0.008	2	
		Horner <i>et al.</i> (2010) ¹²				0.180 ^d	0.060	2	
		Pallavicini <i>et al.</i> (2014) ³⁸				0.086	0.031	4	>95
		Zhang <i>et al.</i> (2018) ⁴¹				0.040	0.060		>90
		Li <i>et al.</i> (2018) ⁴²				0.160	0.100	4	
		This study ^a	17.49	—	<0.001	0.121	0.029	7	90.86
		This study ^a				0.116 ^g	0.025	5	
		This study ^a				0.156 ^f	0.025	4	
		This study ^a				0.150 ^e	0.042	4	
		This study ^c			0.120	0.082	3		
		Average				0.133	0.038	23	
SGR-1b	Shale	Cloquet <i>et al.</i> (2005) ³⁶				0.149 ^d	0.100		95.3
		Schmitt <i>et al.</i> (2009) ⁶²				0.167 ^d	0.080	2	
		Horner <i>et al.</i> (2010) ¹²				0.150 ^d	0.060	3	
		Pallavicini <i>et al.</i> (2014) ³⁸				0.120	0.038	4	>95
		Zhang <i>et al.</i> (2018) ⁴¹				0.090	0.050		>90
		Li <i>et al.</i> (2018) ⁴²				0.160	0.080	4	
		Liu <i>et al.</i> (2019) ⁴⁶				0.163	0.040	8	
		This study ^a	0.65		<0.001	0.075	0.020	3	98.42
		This study ^b			0.063	0.077	3		
		Average				0.069	0.049	6	
NIST 2711a	Soil	This study ^a	45.43		<0.001	0.521	0.025	5	>95
		This study ^a				0.527 ^g	0.025	3	
		This study ^a				0.510 ^f	0.024	3	
		This study ^a				0.532 ^e	0.058	3	
		This study ^b			<0.001	0.535	0.067	5	>95
		This study ^c			0.005	0.566	0.082	7	>95
		This study ^a			0.574^h	0.068	3		
		Average				0.532	0.038	26	
NIST 2711		Li <i>et al.</i> (2018) ⁴²				0.570	0.070	5	
		Liu <i>et al.</i> (2019) ⁴⁶				0.551	0.051	8	
		Cloquet <i>et al.</i> (2005) ³⁶				0.529 ^d	0.020	4	>95
NIST 2711		Pallavicini <i>et al.</i> (2014) ³⁸			0.803	0.071	8	>95	
GSS-1		This study ^a	3.27	4.01	<0.001	0.084	0.030	5	93.44
		This study ^a				0.091 ^g	0.040	4	
		This study ^a				0.101 ^f	0.037	4	
		This study ^a				0.115 ^e	0.061	4	
		Average				0.098	0.027	17	
GSS-4	Stream sediment	Cloquet <i>et al.</i> (2005) ³⁶				0.099 ^d	0.230	2	99
		Li <i>et al.</i> (2018) ⁴²				0.080	0.080	4	
		Liu <i>et al.</i> (2019) ⁴⁶				0.110	0.050	8	
		This study ^a	0.32	17.5	0.003	-0.308	0.016	3	92.96
GSS-5		This study ^a	0.39	46.2	0.008	-0.694	0.010	2	92.62
GSS-14		This study ^a	0.19	16.3	0.002	-0.111	0.044	2	102.3
GSD-5a		This study ^a	1.31	4.03	<0.001	0.036	0.064	5	91.75
GSD-6		This study ^c	0.43	6.51	<0.001	0.018	0.063	2	—
GSD-7a		This study ^a	5.18	0.48	<0.001	-0.054	0.030	7	99.88
		This study ^b				-0.006	0.070	1	
		Average				-0.03	0.033	8	

Table 4 (Contd.)

Sample name	Sample type	Reference	Cd ($\mu\text{g g}^{-1}$)	Sn/Cd	Sn/Cd after purification	$\delta^{114/110}\text{Cd}$ (‰)	2SD ^j	N ^{h,i}	Yield (%)
GSD-10		This study ^a	0.76	1.84	<0.001	-0.046	0.028	3	99.97
GSD-11		This study ^a	0.74	500	<0.001	-0.274	0.037	3	99.81
GSD-12		Pallavicini <i>et al.</i> (2014) ³⁸	1.89	28.6	0.001	-0.305	0.054	4	>95
		This study ^a				-0.087	0.058	6	94.26
		This study ^c				-0.054	0.061	2	>95
		Average				-0.071	0.060	8	
		Cloquet <i>et al.</i> (2005) ³⁶				-0.361 ^d			95.94
		Li <i>et al.</i> (2018) ⁴²			-0.020	0.095	4		
		Yang <i>et al.</i> (2019) ⁴⁰			0.290	0.030		>97	
GSD-17		This study ^a	3.86	1.87	<0.001	0.043	0.023	7	102.4
GSD-21		This study ^a	0.71	2.82	<0.001	-0.009	0.009	4	98.1
GSD-23		This study ^a	4.09	1.64	<0.001	0.071	0.031	7	99.45
GSH-1	Human hair	This study ^a	0.1	—	<0.001	-0.377	0.043	2	103.7
GSV-2	Plant	This study ^a	0.52	0.52	<0.001	0.080	0.077	4	100.4

^a Samples were determined on NP. ^b Samples were determined on Nu III. ^c Samples were determined on Nu II. ^d The $\delta^{114/110}\text{Cd}$ values for previous studies were recalculated relative to NIST SRM 3108, according to Abouchami *et al.* (2012).⁵⁰ ^e The injected concentration of sample per analysis is 5 ng mL⁻¹. ^f The injected concentration of sample per analysis is 10 ng mL⁻¹. ^g The injected concentration of sample per analysis is 20 ng mL⁻¹. ^h The injected concentration of sample per analysis is 2.5 ng mL⁻¹. ⁱ The number of repeated purification and measurement steps. ^j The analytical uncertainty of samples with only one determination was replaced by the long-term reproducibility of sample measurements (0.070‰).

interferents on the different sensitivities of the three MC-ICP-MS instruments in the IGCAS and CUGB.

As shown in Fig. 3, when measured on the Nu II (IGCAS) and Nu III (CUGB) in a 2% HNO₃ medium, $\delta^{114/110}\text{Cd}$ is not significantly affected by isobaric and matrix interference when the purified samples have Sn/Cd \leq 0.5, Mo/Cd < 10, Zr/Cd < 0.01 and Zn/Cd < 1 for the Nu II and Sn/Cd \leq 0.02, Mo/Cd < 1, Zr/Cd < 0.01 and Zn/Cd < 1 for the Nu III. When measured on the NP (CUGB), the threshold ratios become Sn/Cd < 0.2, Mo/Cd < 0.1, Zr/Cd < 0.005 and Zn/Cd < 0.1 (Fig. 4) for 25 ng mL⁻¹ in 2% HNO₃ and Sn/Cd < 0.2, Mo/Cd < 1, Zr/Cd < 0.001 and Zn/Cd < 0.01 for 10 ng mL⁻¹ in 2% HNO₃-0.1% HF. These observations are significantly different than those reported in previous studies (*e.g.* Liu *et al.* 2019 (ref. 46), Cloquet *et al.* 2005 (ref. 36), Gao *et al.* 2008 (ref. 37) and Kruijer *et al.* 2013 (ref. 43)). Our results showed that except Sn, the higher the sensitivity, the smaller the interference tolerance and mass bias (the average fractionation factor of the instrument is 1.96 ± 0.06 for the Nu II, 1.73 ± 0.14 for the Nu III and 1.00 ± 0.18 for the NP in our analytical sessions). For example, the NP has the highest sensitivity (average 640 V ppm⁻¹ for ¹¹²Cd) and a relatively lower tolerance to the matrix effect from Mo, Zr, and Zn (except Sn) in 2% HNO₃ media, whereas the Nu II (IGCAS) has the lowest sensitivity (average 60 V ppm⁻¹ for ¹¹²Cd) and higher tolerance to the aforementioned interferents. The threshold value of Zn/Cd (<1) for the Nu II/III in our work is identical to that reported by Cloquet *et al.* (2005)³⁶ but Sn/Cd and Mo/Cd varied significantly among different instruments and different acid media. Accordingly, the tolerance of interference is likely related to the type of instrument, sensitivity, measuring concentration and acid media. Under the high-sensitivity setup, it is better to determine Cd isotopes in a 2% HNO₃-0.1% HF medium with Sn/Cd \leq 0.02, Mo/Cd < 0.1, Zr/Cd < 0.001 and Zn/Cd < 0.01. Since these ratios in our twice purified sample solution are very

low (Fig. S1† and Table 4), the isobaric and polyatomic interference of Sn, Mo, Zr, and Zn on Cd isotope analysis is negligible, as confirmed by data measured at 5 and 10 ng mL⁻¹ levels (Table 4).

Although we rarely found Fe and Ge in the purified Cd (Fig. S1†), consistent with previous studies,⁴⁶ we still evaluated matrix effects caused by these two elements, and did not observe any resolvable shifts of $\delta^{114/110}\text{Cd}$ with Fe/Cd up to 1–10 on the Nu II/III and NP (Fig. S3†). This result is similar to those presented in Liu *et al.*⁴⁶ However, when the ratio of Ge/Cd is >0.1 on the NP, the $\delta^{114/110}\text{Cd}$ value shows an obvious drift.

Gallium can easily form ⁷¹Ga⁴⁰Ar⁺ and interfere with ¹¹¹Cd measurements. However, our improved method using 10 mL of 2 M HCl followed by 10 mL of 1 M HCl can reduce Ga/Cd to 0.006, even if this ratio was up to 97.1 in unpurified BHVO-2 (Table S3 and Fig. S2†). The concentration of Pd in geological samples is very low, and both Pd/Cd and In/Cd can be reduced to 0.001 after purification (Fig. S1†). Therefore, the influences of Ga, Pd and In on Cd isotope determination are minimal. Moreover, results of a previous study showed that when In/Cd < 1, the interference of In on Cd isotopes was negligible.⁶¹ In summary, the procedure presented here can reduce almost all matrix elements to acceptable levels for the Cd isotope analysis at 5–10 ng mL⁻¹ levels.

3.4 The precision and accuracy for Cd isotope measurement

3.4.1 Blank contribution. The blank is thought to be mostly derived from the AGMP-1M resin.^{18,36,37,41} Therefore, we developed a new cleaning procedure to eliminate Cd from the resin (Table 1). The total blank of Cd from sample digestion to Cd isotope measurement is generally lower than 0.09 ng, occasionally 0.14 ng, which is approximately 0.70% of the lowest sample size (Cd \approx 20 ng) for chemical purification. In order to assess the influence of blank on $\delta^{114/110}\text{Cd}$ measurement,

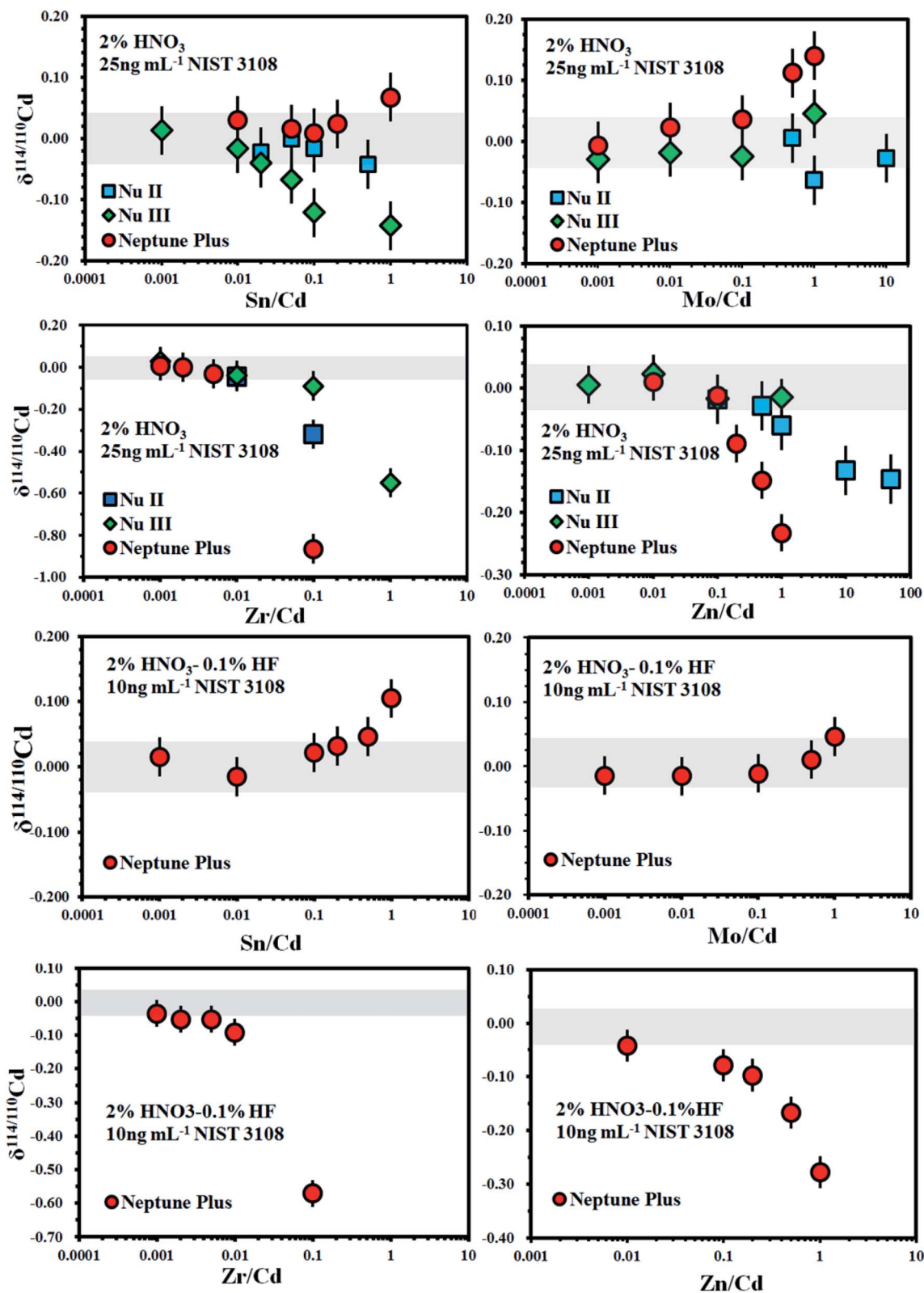


Fig. 3 The effects of different elements with varying [element]/[Cd] on the $\delta^{114/110}\text{Cd}$ values measured at 25 and 10 ng mL⁻¹ for NIST 3108. The gray band denotes the long-term external precision ($\pm 0.040\text{‰}$, 2SD) of $\delta^{114/110}\text{Cd}$ on the Nu II, Nu III and Neptune Plus.

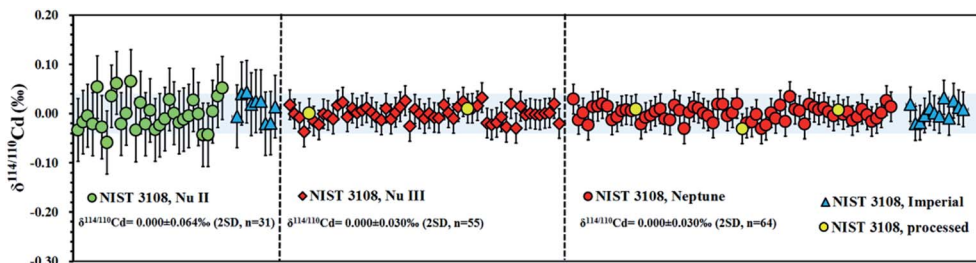


Fig. 4 The long-term reproducibility of $\delta^{114/110}\text{Cd}$ measured at 25 ng mL^{-1} on the Nu III/NP (2SD: $\pm 0.040\text{‰}$) and 100 ng mL^{-1} on the Nu II (2SD: $\pm 0.072\text{‰}$) for NIST 3108 over one year. Error bars represent 2 standard deviations of each measurement. The yellow circles represent processed NIST 3108 ($-0.008 \pm 0.0348\text{‰}$; 2SD, $n = 5$). The blue triangles denote $\delta^{114/110}\text{Cd}$ values of NIST 3108 ($0.009 \pm 0.040\text{‰}$; 2SD, $n = 21$) provided by the Prof. Rehkämper group at ICL.

a spiked NIST 3108 solution containing 25 ng Cd was passed through the column, yielding a mean of $\delta^{114/110}\text{Cd}_{\text{NIST 3018-Processed}}$ of $-0.001 \pm 0.035\text{‰}$ (2SD, $n = 5$). We also used the processed blank solution to dilute the unprocessed NIST 3018 and found no effect on the measured $\delta^{114/110}\text{Cd}_{\text{NIST 3018-BLK}}$ ($-0.002 \pm 0.010\text{‰}$, 2SD, $n = 3$). These values are within uncertainty the same as the unprocessed standard ($\pm 0.040\text{‰}$, 2SD) (Table S5[†]). However, it is noted that although we did not observe Cd memory in the reused AGMP-1M resin, we still used new resin when preparing low-Cd samples containing $\leq 30 \text{ ng Cd}$.

3.4.2 Precision and accuracy. The long-term precision of NIST 3108 was $\pm 0.064\text{‰}$ (2SD, $n = 31$) for the Nu II, $\pm 0.030\text{‰}$ for the Nu III (2SD, $n = 65$) and $\pm 0.036\text{‰}$ for the NP (2SD, $n = 116$) (Fig. 4 and Table S5[†]). International reference standard solutions Münster Cd, BAM-I012 and an in-house Spex Cd-CUGB were determined for more than one year. The long-term external precisions of these standard solutions were $\pm 0.072\text{‰}$ (2SD, $n = 7$), $\pm 0.064\text{‰}$ (2SD, $n = 9$) and $\pm 0.065\text{‰}$ (2SD, $n = 5$) on the Nu II, and $\pm 0.028\text{‰}$ (2SD, $n = 12$), $\pm 0.028\text{‰}$ (2SD, $n = 12$) and $\pm 0.040\text{‰}$ (2SD, $n = 13$) on the Nu III/NP (Table S5[†]). Based on the above data, the long-term external precision for the standard solution is $\leq 0.072\text{‰}$ (2SD) for the Nu II and $\leq 0.040\text{‰}$ (2SD) for the Nu III and NP.

In order to evaluate the long-term external precision of real samples, several GRMs such as NIST 2711a, GSD-12, BCR-2 and NOD-P-1 were measured. The precision of NIST 2711a measured using the Nu II was $\pm 0.082\text{‰}$ (2SD, $n = 7$). On the Nu III and NP, the long-term external precision values of NIST 2711a, GSD-12, BCR-2 and NOD-P-1 were $\pm 0.020\text{‰}$ (2SD, $n = 19$), $\pm 0.060\text{‰}$ (2SD, $n = 8$), $\pm 0.063\text{‰}$ (2SD, $n = 4$) and $\pm 0.040\text{‰}$ (2SD, $n = 20$), respectively (Table 4). The analytical precision of all the above-mentioned GRMs was estimated at $5\text{--}25 \text{ ng mL}^{-1}$ on the NP and Nu III and 100 ng mL^{-1} on the Nu II. At present, the external precision of Cd isotope measurements in many laboratories is generally $0.05\text{--}0.10\text{‰}$ for pure standard solutions,^{12–14,19,38,39,42,46} and the best precision of 0.028‰ was obtained with TIMS by Schmitt *et al.* (2009)⁵⁶ and Hohl *et al.* (2017).²¹ However, the analytical precision for real samples ranges from 0.067 to 0.15‰ on a MC-ICP-MS.^{12–14,19,36–42,46} Based on our tests for various real samples, the long-term precision of Cd isotopes in natural samples determined on the Nu II was $\sim 0.080\text{‰}$ (2SD) and on

the Nu III/NP it was typically $\leq 0.070\text{‰}$ (2SD), consistent with previous studies.^{38–42,46} This analytical precision can distinguish the fractionation of Cd isotopes in various geochemical processes in nature.

Comparing the $\delta^{114/110}\text{Cd}$ of two different batches of NIST 3108 measured in this study can shed some light on whether there is difference in Cd isotope composition between different batches of NIST 3108. The results analyzed over one year showed that the $\delta^{114/110}\text{Cd}$ of the NIST 3108 (lot no. 060531) used in Imperial College London (ICL) was $0.007 \pm 0.041\text{‰}$ (2SD, $n = 22$) relative to that of the NIST 3108 (lot no. 130116, $\delta^{114/110}\text{Cd} = 0.000 \pm 0.040\text{‰}$, 2SD, $n = 212$ calculation including the data measured on the Nu II) used in our laboratory (Fig. 4 and Table S5[†]). Therefore, there is no resolvable

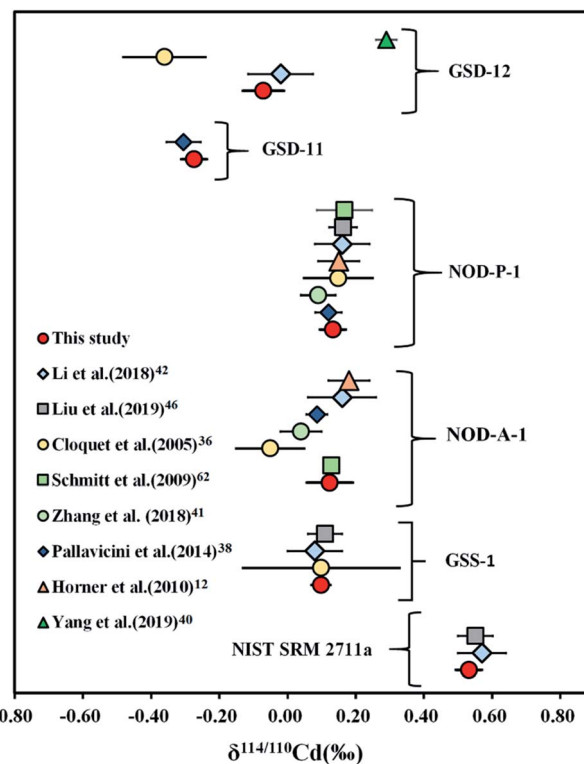


Fig. 5 An inter-laboratory comparison of the $\delta^{114/110}\text{Cd}$ values of GRMs.

difference in Cd isotope composition between these two batches of NIST 3108. In addition, the $\delta^{114/110}\text{Cd}$ of processed NIST 3108 was $-0.001 \pm 0.035\text{‰}$ (2SD, $n = 5$), the same as that of unprocessed NIST 3018 ($0.000 \pm 0.040\text{‰}$). The long-term measurement of the international standard solutions yielded $\delta^{114/110}\text{Cd}$ of $4.461 \pm 0.047\text{‰}$ (2SD, $n = 19$) for Münster Cd and $-1.329 \pm 0.045\text{‰}$ (2SD, $n = 21$) for BAM-I012 (Table S5[†]), well identical with the reported values.^{13,14,35,42,45,46,50,56}

GRMs including NOD-P-1, NOD-A-1, NIST 2711a, GSS-1, GSD-11, and GSD-12 have been reported in previous studies.^{12,36,38,40-42,46} The $\delta^{114/110}\text{Cd}$ value of NOD-P-1 measured in this ($0.133 \pm 0.038\text{‰}$; 2SD, $n = 23$) is analytically indistinguishable from the published data (Table 4 and Fig. 5).

The $\delta^{114/110}\text{Cd}$ value of NOD-A-1 ($0.124 \pm 0.067\text{‰}$; 2SD, $n = 14$) is also in agreement with those values presented in the literature,^{12,38,42,46,62} although slightly different from $-0.051 \pm 0.100\text{‰}$ by Cloquet *et al.* (2005),³⁶ which is possibly related to powder heterogeneity.⁶³ Our measured Cd isotope compositions were $0.532 \pm 0.038\text{‰}$ for NIST 2711a and $0.098 \pm 0.027\text{‰}$ for GSS-1, the same as those reported by Liu *et al.* (2019),⁴⁶ Li *et al.* (2018)⁴² and Cloquet *et al.* (2005).³⁶ The $\delta^{114/110}\text{Cd}$ values of GSD-11 and GSD-12 analyzed in this study were $-0.274 \pm 0.037\text{‰}$ (2SD, $n = 3$) and $-0.071 \pm 0.060\text{‰}$ (2SD, $n = 8$), respectively, which are consistent with those determined by Pallavicini *et al.* (2014)³⁸ for GSD-11 at $-0.305 \pm 0.054\text{‰}$ (2SD, $n = 4$) and Li *et al.* (2018)⁴² for GSD-12 at $-0.02 \pm 0.095\text{‰}$ (2SD, $n = 4$). However, the $\delta^{114/110}\text{Cd}$ of GSD-12 was also determined to be -0.361‰ and $0.29 \pm 0.030\text{‰}$ by Cloquet *et al.* (2005)³⁶ and Yang *et al.* (2019),⁴⁰ respectively. These discrepancies may be related to sample powder heterogeneity, and/or digestion procedures (the centrifugation step was utilized in both studies), which needs further investigation. In summary, due to obviously

fractionated and relatively homogeneous Cd isotope composition in NOD-P-1, NIST 2711a and GSD-11, they can be used as reference materials for interlaboratory comparison. Our comparisons show that our methods can produce reliable $\delta^{114/110}\text{Cd}$ data for a wide range of samples.

3.4.3 Effect of concentration on the accuracy and precision of Cd isotope measurement. Different injecting concentrations at 50, 25 and 10 ng mL⁻¹ NIST 3018 on the Nu III and 25, 20, 10 and 5 ng mL⁻¹ NIST 3018 on the NP were tried to test whether the precision and accuracy of Cd isotope data can be affected (Fig. 6). We observed that the uncertainty did slightly increase with decreasing Cd concentration, consistent with Liu *et al.* (2019).⁴⁶ However, our lowest required sample amount of 5 ng mL⁻¹ per analysis is lower than 20 ng mL⁻¹ suggested by Liu *et al.* (2019);⁴² the accuracy and precision of Cd isotope determination in our work remained good down to 5 ng mL⁻¹ (or ~5 ng Cd, based on 5 ng mL⁻¹ × 110 μL min⁻¹ uptake rate × ~9 min measuring time), identical with 10, 20 and 25 ng mL⁻¹. It should be noted that there is a very small positive drift in the $\delta^{114/110}\text{Cd}$ value from 25 to 5 ng mL⁻¹ (e.g. NOD-P-1: $0.121 \pm 0.029\text{‰}$; $0.116 \pm 0.025\text{‰}$; $0.156 \pm 0.025\text{‰}$ and $0.150 \pm 0.042\text{‰}$) on the NP (Fig. 5). A possible explanation for this is either the memory effect of a small amount of residual Sn and/or Mo in the Aridus II, or some uniquely unknown effect for Cd isotope analysis on a MC-ICP-MS proposed by Schmitt *et al.* (2009).⁵⁶ To test if they affect the accuracy and precision for real samples, NIST 2711a, NOD-P-1 and GSS-1 at 25, 20, 10 and 5 ng mL⁻¹ were also determined (Fig. 5), and the $\delta^{114/110}\text{Cd}$ values were in excellent agreement with previously reported results. In a word, the analytical precision of $\leq 0.07\text{‰}$ (2SD) can be achieved for sample sizes as low as 5 ng, provided that the total procedural blank is low enough.

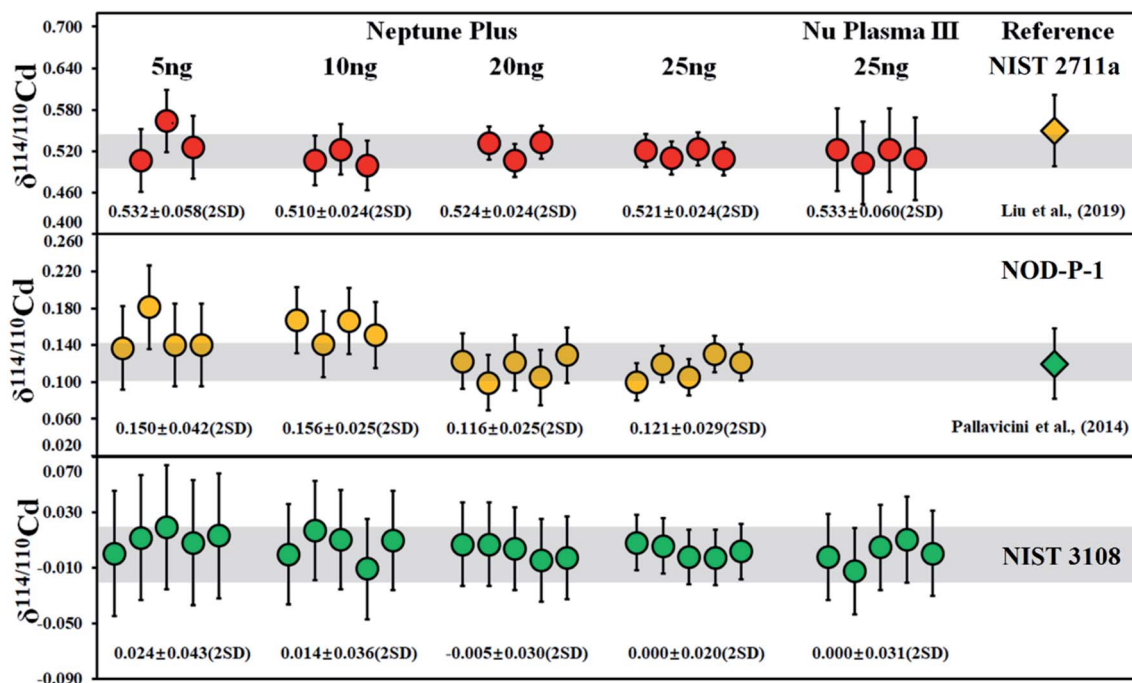


Fig. 6 Comparisons of measured results for NIST 3108, NOD-P-1 and NIST 2711a at varying concentrations.

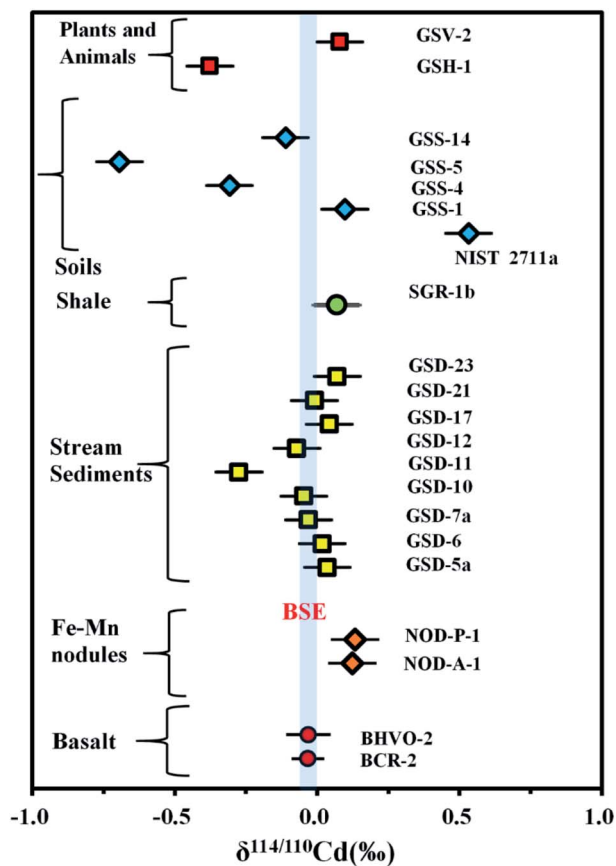


Fig. 7 Cd isotope compositions of geological and environmental reference materials measured in this study.

3.5 Cd isotope compositions of geological reference materials

Besides the aforementioned manganese nodules (NOD-P-1 and NOD-A-1) and soil (NIST 2711a), we have also reported the $\delta^{114/110}\text{Cd}$ values of 17 more GRMs (Table 4 and Fig. 7), including basalt (BCR-2, BHVO-2), shale (SGR-1b), sediment (GSD series), soils (GSS series), human hair (GSH-1) and deciduous shrubs (GSV-2).

The $\delta^{114/110}\text{Cd}$ values of BCR-2 and BHVO-2 were measured to be $-0.030 \pm 0.063\text{‰}$ (2SD, $n = 4$) and $-0.031 \pm 0.077\text{‰}$ (2SD, $n = 4$), respectively, consistent with the results of BCR-2 ($0.018 \pm 0.067\text{‰}$) and BHVO-2 ($0.034 \pm 0.049\text{‰}$) reported by Liu *et al.* (2019).⁴⁶ The variation of measured $\delta^{114/110}\text{Cd}$ for these two basalt samples in this study ranges from -0.058 to 0.025‰ , with an average of $-0.018 \pm 0.066\text{‰}$ (2SD, $n = 9$). This range is similar to that of the ocean island basalt samples ($-0.082 \pm 0.071\text{‰}$, OIB) reported in Schmitt *et al.* (2009),⁶² and to the mid ocean ridge basalt samples ($-0.002 \pm 0.070\text{‰}$, MORB) as well as BIR-1 ($0.14 \pm 0.52\text{‰}$) measured by Wombacher *et al.* (2003).¹¹ Hence, the Cd isotope composition in basalt samples appears to be homogeneous and is close to that of the bulk earth silicate (BSE) reported by Schmitt *et al.* (2009)⁶² at $-0.044 \pm 0.024\text{‰}$ and Wombacher *et al.* (2008)²³ at $-0.100 \pm 0.400\text{‰}$. The Cd concentration in BCR-2 and BHVO-2, based on isotope dilution, is $0.22 \mu\text{g g}^{-1}$ and $0.20 \mu\text{g g}^{-1}$, respectively. The former is less than $0.69 \mu\text{g g}^{-1}$

reported by Jochum *et al.* (2016).⁶⁴ The reason for this difference may be: (1) the Cd signal can be easily affected by polyatomic ions (ZrO^+ , MoO^+ , *etc.*) if unpurified BCR-2 ($\text{Mo}/\text{Cd} = 783$) is determined on an ICP-MS;⁶² (2) like Mo in BHVO-2, the Cd content in different batches of BCR-2 is heterogeneous.

The $\delta^{114/110}\text{Cd}$ in SGR-1b (shale) was measured to be $0.069 \pm 0.049\text{‰}$ (2SD, $n = 6$), close to $0.15 \pm 0.01\text{‰}$ ($n = 12$, 2SD) of two upper Permian laminated shale samples measured by Georgiev *et al.* (2015),⁶⁵ but very different from that of the Cambrian shale samples (NZ 404c, $-0.500 \pm 0.138\text{‰}$) reported by Wombacher *et al.* (2003).¹¹ Georgiev *et al.* (2015)⁶⁵ suggested that the Cd isotopic composition in shale is largely controlled by its sedimentary environment and the Cd isotopes of organic materials.

Stream sediments in this study were collected from different areas in China, including polymetallic, lead-zinc and copper mining areas, and carbonate weathering zones. The average $\delta^{114/110}\text{Cd}$ value of these samples was $-0.009 \pm 0.116\text{‰}$ (2SD, $n = 9$), except for GSD-11 that was isotopically light ($-0.273 \pm 0.037\text{‰}$, 2SD, $n = 3$). The $\delta^{114/110}\text{Cd}$ of the majority of these samples was very similar to the Cd isotope composition of the BSE ($-0.044 \pm 0.024\text{‰}$),⁶² and the data reported by Zhang *et al.* (2016)⁶⁶ and Yang *et al.* (2019)⁴⁰ with $-0.085 \pm 0.236\text{‰}$ and $0.030 \pm 0.060\text{‰}$ respectively. In contrast to our stream sediment samples that lack Cd isotope variation, sediments contaminated by industrial Cd can have variable $\delta^{114/110}\text{Cd}$. For example, the $\delta^{114/110}\text{Cd}$ of sediments collected from the North River in China by Gao *et al.* (2008, 2013)^{31,37} averaged at $-0.717 \pm 0.301\text{‰}$ (2SD, $n = 14$). These sediments were clearly dominated by atmospheric dust influenced by anthropogenic activities.³¹ In addition, Martinková *et al.* (2016)¹⁹ also showed that heavier Cd isotopes are enriched in the waste residue during the industrial production of Cd metal, while lighter Cd isotopes are enriched in fly ash.

The $\delta^{114/110}\text{Cd}$ in the investigated soils was heterogeneous, ranging from -0.694‰ (GSS-5, yellow-red soil) to $0.532 \pm 0.038\text{‰}$ (2SD, $n = 23$) in Montana soil (NIST 2711a). Zhang *et al.* (2016)⁶⁶ reported that the aqueous phase is enriched in heavy Cd isotopes during weathering processes, with a $\delta^{114/110}\text{Cd}_{\text{aqueous-residual}}$ of $0.360\text{--}0.530\text{‰}$. Hence, the negative $\delta^{114/110}\text{Cd}$ in GSS-5 is reasonable because the heavy isotopes are lost during weathering. The reason for the extremely positive $\delta^{114/110}\text{Cd}$ in NIST 2711a may be related to industrial pollutants, fallen leaves with extremely positive isotopic compositions,³⁸ or simply because of accumulating Cd from isotopically heavy weathering fluids. The $\delta^{114/110}\text{Cd}$ in an agricultural soil GSS-14 ($-0.111 \pm 0.044\text{‰}$) was similar to the data reported by Zhang *et al.* (2016)⁶⁶ for 28 agricultural soils collected from the Bijiang river basin in China ($-0.281 \pm 0.161\text{‰}$).

Ferromanganese nodules are potential geological archives for reconstructing the Cd isotopic compositions of ancient seawater.^{12,36,61,62} The $\delta^{114/110}\text{Cd}$ values of NOD-A-1 and NOD-P-1 are $0.124 \pm 0.067\text{‰}$ (2SD, $n = 14$) and $0.133 \pm 0.038\text{‰}$ (2SD, $n = 23$), respectively, consistent with the results of previous studies with an average of $0.119 \pm 0.113\text{‰}$ (2SD, $n = 6$) and $0.142 \pm 0.056\text{‰}$ (2SD, $n = 7$), respectively (Table 4).^{12,36,38,41,42,46,62} These values are also in accordance with the $\delta^{114/110}\text{Cd}$ of ferromanganese nodules from other main ocean basins (>2000 m depth): $0.138 \pm 0.083\text{‰}$ (2SD, $n = 8$) from the Indian Ocean, $0.129 \pm$

0.124‰ (2SD, $n = 6$) from the Circum-Antarctic Ocean, and 0.177 ± 0.137‰ (2SD, $n = 7$) from the Pacific Ocean.⁶² This suggests that the distribution of Cd isotopes in ferromanganese nodules collected from >2000 m depth in different ocean basins is uniform, lower than that in seawater (0.273 ± 0.080‰).^{13,15,16,35}

The $\delta^{114/110}\text{Cd}$ values in human hair (GSH-1) and shrub leaves (GSV-2) were $-0.377 \pm 0.078\text{‰}$ and $0.080 \pm 0.077\text{‰}$, respectively (Table 4). The $\delta^{114/110}\text{Cd}$ of human hair agrees with fish liver data ($-0.789 \pm 0.048\text{‰}$) obtained by Pallavicini *et al.* (2014),³⁸ both isotopically lighter than the BSE ($-0.044 \pm 0.024\text{‰}$). This trend has also been observed for Zn isotopes: human hair being isotopically lighter than rocks, soils, and stream sediments.⁶⁷ In contrast, plant sample GSV-2 is enriched in heavy Cd isotopes, which is consistent with previous observations of 0.3–1.3‰ in deciduous shrubs.³⁸ More studies are needed to investigate these contrasting Cd isotope fractionations in animal and plant tissues.

3.6 Applications of high-sensitivity measurement of Cd isotopes

The high-sensitivity and high-precision (2SD ≤ 0.080‰) determination of Cd isotopes at the 2.5, 5 and 10 ng levels was successfully conducted on a MC-ICP-MS using the double spike technique. The cadmium isotope system can be employed to a broader range of samples with low-Cd content. The isotopic composition of Cd in seawater has been investigated in detail,^{13–15,18,35} but approximately 30–60 ng Cd needs to be pre-concentrated from 20L seawater for Cd isotope determination.¹³ With the establishment of the high-sensitivity measurement of Cd isotopes, the working efficiency will be improved significantly because of decreasing the sample size for purification. Cadmium contents in the atmospheric aerosol (~1–100 pg m⁻³),⁶⁹ igneous rocks (0.05–0.20 μg g⁻¹),⁷⁰ meteorites (1.75–770 μg g⁻¹)⁷¹ and river water (0.02–20 ng L⁻¹)⁷¹ are usually lower. Yet, they play a critical role in exploring our understanding of the global Cd cycle and paleo-environment evolution. The isotope compositions of Cd in these reservoirs on the earth and in extraterrestrial samples are still poorly reported. Now it is likely for us to determine their Cd isotopic composition to extend the application of Cd isotopes in tracing the source of Cd in air, the transport path in the food chain, the biogeochemical cycle of Cd in the surficial environment and mantle–crust evolution. In recent years, stable metal isotopes have also been widely used in studying the life processes,^{57,73,74} but due to the low-Cd concentration (*e.g.*, human urine, 0.053–0.3 μg L⁻¹; human hair, 0.095–0.11 μg g⁻¹)⁷² and the complex biological matrices in living organisms, a few studies on Cd isotopes in biological samples were carried out.⁵⁷ The high-sensitivity determination of Cd isotopes will allow us to obtain high-precision Cd isotope data in these low-Cd samples, expanding the application of Cd isotopes in studying the metabolism processes of Cd in human and animal bodies.

4. Conclusions

A modified purification scheme for high-sensitivity determination of Cd isotopes was presented that can be adapted to a wide

range of geological and environmental samples, especially samples with low Cd content and complex matrices. Interference elements Mo and Zr can be effectively removed even for samples with very high Mo/Cd (783) and Zr/Cd (778). The recovery of this improved scheme is ≥90% and suitable for a variety of sample types. The total blank of Cd from sample digestion to the end of Cd chemical separation is ≤0.09 ng. Thus, a sample containing ≥20 ng Cd can be used to extract Cd from isotope analysis. Because of good separation and high yields, interference from isobaric and polyatomic ions and matrix effects are tested to be insignificant under a high-sensitivity setup.

On the Nu III (¹¹²Cd sensitivity: ~280 V ppm⁻¹) or Neptune Plus (¹¹²Cd sensitivity: ~640 V ppm⁻¹) MC-ICP-MS, the long-term reproducibilities for Cd isotope determination are 0.000 ± 0.030‰ (2SD, $n = 119$) based on NIST 3108, 4.461 ± 0.047‰ (2SD, $n = 19$) based on Münster Cd, and $-1.329 \pm 0.045\text{‰}$ (2SD, $n = 21$, 2SD) based on BAM-I012, using a 25 ng mL⁻¹ injecting concentration. Furthermore, when the sensitivity of the ¹¹²Cd signal on the Neptune Plus increases up to 600–680 V ppm⁻¹, the injecting concentration can be reduced to 5–10 ng mL⁻¹, with the external precision still within the precision range obtained by laboratories around the world (<0.100‰). This will vigorously promote the application of Cd isotopes in multiple research areas such as the human body.

The $\delta^{114/110}\text{Cd}$ values for different batches of NIST 3108 are indistinguishable from each other: 0.000 ± 0.040‰ (2SD, $n = 212$) for lot no. 130116 and 0.007 ± 0.042‰ (2SD, $n = 22$) for lot no. 060531. Different types of geological reference materials such as NOD-A-1 (0.126 ± 0.067‰), NOD-P-1 (0.133 ± 0.038‰), NIST 2711a (0.532 ± 0.038‰), GSS-1 (0.098 ± 0.027), GSD-11 (-0.274 ± 0.037), BCR-2 ($-0.030 \pm 0.063\text{‰}$) and BHVO-2 ($-0.031 \pm 0.077\text{‰}$) are also consistent with the data published by previous studies. The $\delta^{114/110}\text{Cd}$ values of SGR-1b (0.069 ± 0.049‰) and GSH-1 ($-0.377 \pm 0.043\text{‰}$) are reported for the first time, together with a series of stream sediments and soils. The $\delta^{114/110}\text{Cd}$ values of stream sediments are mostly indistinguishable from the BSE. In summary, measurements of a wide range of GRMs at 5–10 ng levels under a high-sensitivity setup are applicable to various sample types with robust accuracy and precision. The high-sensitivity determination of Cd isotopes will allow us to extend the application of Cd isotopes in investigating the global Cd cycle, mantle–crust evolution and metabolism processes of Cd in human and animal bodies.

Conflicts of interest

There are no conflicts of interest to declare.

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