Cadmium Isotope Ratios of Standard Solutions and Geological Reference Materials Measured by MC–ICP-MS

Dandan **Li**, Meng-Lun **Li**, Wen-Ran **Liu**, Zhen-Zhen **Qin** and Sheng-Ao **Liu*** (ID)

State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing, China
* Corresponding author. e-mail: lsa@cugb.edu.cn

We report high-precision cadmium isotope ratios for a series of standard solutions and geological reference materials for interlaboratory comparison. Complete separation of Cd from a matrix in geological samples was achieved using AG MP-1M anion exchange resin with > 97.8% recovery. Cadmium isotope ratios were measured by both *Neptune plus* multi-collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) and *Nu Plasma* II MC-ICP-MS at low-resolution mode. Both sample calibrator bracketing (SSB) and double-spike techniques (DS) were utilised for mass bias correction. Cadmium isotope ratio data of standard solutions (BAM I012 Cd, SPEX Cd, Alfa Aesar Cd, GSB Cd) and geological reference materials (GSS-1, GXR-1, GXR-2, GSD-12, NIST SRM 2711a) are reported relative to Cd solution (NIST SRM 3108). The intermediate precision over a three-year period was better than ± 0.09‰ (2*s*) for $\delta^{114}Cd/^{110}Cd$ and ± 0.06‰ (2*s*) for $\delta^{112}Cd/^{110}Cd$ ratios. SPEX Cd was used as a secondary reference material for Cd isotopic measurement with a $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ value of -2.13 ± 0.09‰ (2*s*). The soil reference material NIST SRM 2711a has a significantly heavier isotopic composition than other soil materials, GXR-1, GXR-2 and GSS-1. New recommended values are presented for future interlaboratory calibration.

Keywords: cadmium isotope ratios, reference materials, MC-ICP-MS, NIST SRM 3108, recommended values.

Cadmium possesses eight stable isotopes, ^{106}Cd, ^{108}Cd, ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd and ^{116}Cd, with the relative abundances of 1.25%, 0.89%, 12.47%, 12.80%, 24.11%, 12.23%, 28.75% and 7.51%, respectively (Meija *et al.* 2016). The maximum relative mass difference for Cd isotopes (106–116) is approximately 10%, which makes Cd isotope ratios a potential tool to resolve mechanisms of mass-dependent fractionation processes (Wombacher *et al.* 2004, Horner *et al.* 2011, Wasylenki *et al.* 2014, Zhang *et al.* 2016) and to trace Cd oceanic cycle (Lacan *et al.* 2006, Ripperger *et al.* 2007, Abouchami *et al.* 2011, Yang *et al.* 2012, Xue *et al.* 2013, Abouchami *et al.* 2014, Bridgestock *et al.* 2017, Xie *et al.* 2017) and anthropogenic pollution sources (Cloquet *et al.* 2006, Sivry *et al.* 2006, Shiel *et al.* 2007, Wen *et al.* 2015, Gao 2016, Martinková *et al.* 2016, Zhang *et al.* 2016, Zhu *et al.* 2018) in the environment. Variations in stable Cd isotopes have been observed since 1976 (Rosman and DeLaeter 1976). The largest variations ($\delta^{114/110}Cd_{JMC\ Cd}$ of -7.8‰ to + 14.8‰) are of extraterrestrial and anthropogenic origins (Wombacher *et al.* 2003, Cloquet *et al.* 2005, 2006, Lacan

et al. 2006, Sivry *et al.* 2006, Ripperger *et al.* 2007, Shiel *et al.* 2007, 2008) relative to the 'JMC Cd' solution (Johnson Matthey Company) (Wombacher and Rehkämper 2004). The researchers have also identified a relatively narrow range of ~ 1.5‰ in $\delta^{114/110}Cd_{Spex-1\ Cd}$ ratios of terrestrial samples, for example ocean island basalts, mid-ocean ridge basalts, loess, sediments and sulfides. The Cd isotopic value of the bulk silicate Earth (BSE) is at $\delta^{114/110}Cd_{Spex-1\ Cd}$ of 0 ± 0.4‰ relative to Spex-1 Cd (Wombacher *et al.* 2003, Schmitt *et al.* 2009a, Zhu *et al.* 2013). Given the modest Cd isotopic variation in most of terrestrial materials, precise and accurate measurement results is crucial to expanding the application of Cd isotope ratios to geological processes.

Accurate measurement of isotope ratios requires the removal of spectral interferences and calibration of the mass discrimination effects induced by the instrument (Douglas and Tanner 1998, Wombacher *et al.* 2003, Rehkämper *et al.* 2004, Wombacher and Rehkämper 2004). Recently, new chemical separation methods of Cd from matrix elements have been presented. Based on earlier studies (Rosman and

DeLaeter 1974, 1975, Loss *et al.* 1984, 1990, Sands and Rosman 1997), Wombacher *et al.* (2003) proposed a two-stage column chemical procedure, involving a strongly basic anion exchange resin and an Eichrom TRU Spec resin, to isolate Cd from geological matrices. A three-stage column chemical procedure was also used to separate Cd from seawater samples with very low Cd mass fraction, which allows Cd to be isolated sufficiently from the matrices (Ripperger and Rehkämper 2007). These procedures can effectively separate Cd from matrices, but are relatively complex using different acids and different resins. The more stages the samples were processed, the less likely they were to achieve 100% recovery of all fractions. Cloquet *et al.* (2005) proposed a one-stage purification procedure to separate Cd from digested soil and sediment samples using HCl and AG MP-1 strong anion exchange resin. This method is relatively simple and has been widely used (Cloquet *et al.* 2005, Lacan *et al.* 2006, Gao *et al.* 2008, Zhang *et al.* 2010, Wen *et al.* 2015). In this study, one-stage column chemical procedure modified from previous studies was used to separate Cd from matrix elements. This procedure serves to effectively isolate Cd from Sn, Zn and other ions in the solution.

To date, few geological reference materials have been reported for Cd isotope ratio results, which hinders the comparisons of Cd isotope results obtained in different laboratories but also makes method validation more difficult. Also, multiple in-house Cd solutions have been used for ratio normalisation in different laboratories, which requires data obtained from different groups to be converted and thus brings extra deviation. A fixed reference standard for Cd isotope ratio measurement results needs to be developed. Recently, although NIST SRM 3108 has popularly become the recommended zero value for Cd isotopes and standard solutions have been used to test the purification processes in most previous studies when the soil or sediment samples were measured, geological reference materials were rarely used and measured directly relative to NIST SRM 3108. In this study, we report all of the obtained $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ values of standard solutions and geological reference materials directly relative to NIST SRM 3108, and the new recommended values are presented for interlaboratory calibration in the future. This would facilitate the comparison of almost all published data and strongly encourage other laboratories to do so as well in future Cd isotope studies.

Reagents and standard solutions

Reagents

Nitric, hydrochloric and hydrofluoric acids used in this study were purified in-house by double distillation in Teflon®

still. High-purity ($\geq 18.2\ M\Omega\ cm$), prepared by deionisation of reverse osmosis water using a Milli-Q® system (Merck Millipore, Burlington, MA, USA), was used to prepare all solutions. Savillex® PFA vials were cleaned with 1:1 *v/v* nitric acid, 1:1 *v/v* HCl and high-purity water. Other materials, including columns, pipette tips and tubes, were washed in a heated bath of 3% HNO_3 and rinsed with high-purity water prior to use.

Reference materials

Five different mono-elemental Cd solutions were used: (a) NIST SRM 3108, diluted from a 10.00 mg ml^{-1} solution and used as a reference solution; (b) BAM I012 Cd, an isotopic reference material (Lot: C152382M, 1000 μg ml^{-1}); (c) SPEX Cd (Lot: CL8-71CDY, 1000 μg ml^{-1}); (d) Alfa Aesar Cd (Lot: 855869B, 1000 μg ml^{-1}); and (e) GSB Cd (1000 μg ml^{-1}). BAM I012 Cd was already reported in previous studies (Wombacher and Rehkämper 2004, Pritzkow *et al.* 2007, Ripperger and Rehkämper 2007, Gao *et al.* 2008, Schmitt *et al.* 2009a, Shiel *et al.* 2009, Xue *et al.* 2012, Yang *et al.* 2012, Xue *et al.* 2013, Brand *et al.* 2014, Murphy *et al.* 2016, Wiggenhauser *et al.* 2016, Bridgestock *et al.* 2017, Imseng *et al.* 2018) and was also used in this study to estimate the accuracy of Cd isotope ratio measurement results. However, SPEX Cd was not reported before, which is not the same as Spex-1 Cd reported in previous studies (Cloquet *et al.* 2005, Gao *et al.* 2008, Wei *et al.* 2015).

Geological reference materials analysed in this study include the following: (a) soils: GSS-1 (China), GXR-1 & GXR-2 (USGS quality control materials) and NIST SRM 2711a (USA); (b) sediment reference material: GSD-12 (China); and (c) ferromanganese nodules: Nod-A-1 and Nod-P-1. GSS-1 and GSD-12 are distributed by the Institute of Geophysical and Geochemical Prospecting, People's Republic of China (IGGE), GXR-1, GXR-2, Nod-A-1 and Nod-P-1 by US Geological Survey, (USGS), and NIST SRM 2711a by National Institute of Standards and Technology, USA (NIST). NIST SRM 2711a (Montana II soil) was collected from the top 10 cm to 12 cm of an agricultural field located near a site formerly used by smelting plant, in east Helena, Montana. The description of other geological reference materials is given in detail by Cloquet *et al.* (2005).

Measurement procedures

The detailed procedures for sample digestion, chemical purification procedure and instrumental measurements are presented in the following sections.

© 2018 The Authors. Geostandards and Geoanalytical Research © 2018 International Association of Geoanalysts

Sample digestion

Cadmium mass fraction in the analysed geological reference materials varies from 3 to 55 µg g^{-1}, and thus, 10 to 100 mg of the materials were weighed such that the resulting subsamples contained at least ~ 0.1 µg Cd for isotope analysis. First, samples were digested in double-distilled nitric acids (15.8 mol l^{-1}) in high-pressure bombs, followed by ultrasonic treatment and then heated at 185 °C in an air circulation drying oven for about 24 h. H$_2$O$_2$ (1 ml, 40% m/m) was added to remove any organic materials. The solutions were evaporated at 150 °C, refluxed with 3:1 v/v mixture of HF (23.1 mol l^{-1}) and HNO$_3$ (15.8 mol l^{-1}) at 160 °C, and then evaporated to dryness at 160 °C. Then, the samples were refluxed with a 1:3 v/v mixed HNO$_3$ and HCl, followed by heating and then evaporating to dryness at 80 °C. Finally, the samples were redissolved with concentrated HCl (10.8 mol l^{-1}) until complete dissolution was achieved and subsequently dried down at 80 °C. A 1 ml of 2 mol l^{-1} HCl was added to the beaker and then heated to dryness. This process was repeated to ensure that all cations were converted to chloride species. The final material was dissolved in 2 ml of 2 mol l^{-1} HCl in preparation for ion exchange separation.

Ion exchange chromatography

Chemical separation procedures for Cd rely on its affinity to ion exchange resins in acid media (Wombacher *et al.* 2003, Cloquet *et al.* 2005, Lacan *et al.* 2006, Ripperger and Rehkämper 2007, Gao *et al.* 2008, Zhang *et al.* 2010, Zhu *et al.* 2013, Wen *et al.* 2015). Here, the chemical analyte-matrix separation method is modified from a one-stage purification procedure (Cloquet *et al.* 2005, Lacan *et al.* 2006, Gao *et al.* 2008, Zhang *et al.* 2010, Wen *et al.* 2015). The major differences between this study and previous studies are the size of polypropylene column and the volume of the resin. The procedure that was used to separate the Cd from the matrix is shown in Table 1 and described below. The Bio-Rad AG MP-1M strong anion exchange resin (100–200 mesh, chloride form) was precleaned with 2 mol l^{-1} HCl, 0.012 mol l^{-1} HCl and 0.0012 mol l^{-1} HCl alternating with high-purity water twelve times. The precleaned polypropylene column (7.4 mm in diameter) was filled with 2.5 ml of precleaned resin and washed with 5 ml 2 mol l^{-1} HCl, 4 ml 0.012 mol l^{-1} HCl and 4 ml 0.0012 mol l^{-1} HCl alternating with high-purity water six times. A 10 ml of 2 mol l^{-1} HCl was added to the column for conditioning, and then, samples dissolved in 2 ml 2 mol l^{-1} HCl were loaded onto the column. Matrix elements (e.g., Al, Cr, Zr, Zn and Sn) were eluted with HCl in stepwise decreases in concentrations of 2, 0.3, 0.06 and 0.012 mol l^{-1}. Cadmium fraction was eluted from the resin with 15 ml of

0.0012 mol l^{-1} HCl. The elution sequence was checked by artificial mixed solution (Cd : Zn : Sn = 1 µg: 1 µg: 1 µg) and reference sample (GXR-1) (Figure 1). The ratios of all other ions (such as Pd, Zn and Ge) to Cd were found to be less than 0.01. These interferences generated undetectable influence on Cd isotope ratio measurement. The two compositionally different artificial solutions/samples yielded analogous elution curves (Figure 1), suggesting that this method is widely suitable to samples with various matrix compositions. However, little Sn (Sn/Cd < 0.1) was observed in the Cd fraction of soil sample, so that Sn-doped SPEX Cd solutions are required to verify the accuracy of the spectral interference corrections (see Matrix effect). Cadmium fraction was evaporated to dryness and then refluxed with 100 µl concentrated nitric acid (15.8 mol l^{-1}) to remove all resin-derived organics. The residues were dissolved in 3% m/m HNO$_3$, re-evaporated to dryness and redissolved in 3% HNO$_3$ to remove all chlorides prior to isotopic ratio determination.

Mass spectrometry

Elemental mass fractions were quantified using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent Technologies Inc., Agilent 7900) with PerkinElmer Model AS93F autosamples, skimmer cones and a Scott-type spray chamber in the Mineral Laser Microprobe Analysis Laboratory of the China University of Geosciences, Beijing. The calibration of elemental mass fractions was performed with Rh in 3% HNO$_3$ m/m as an internal standard element.

For isotope ratio, aliquots of samples were diluted with 3% HNO$_3$ m/m to a final mass fraction of 100 ng g^{-1} for analysis. The samples were measured on a Thermo Scientific Neptune plus MC-ICP-MS at the Isotope Geochemistry Lab of the China University of Geosciences, Beijing (Lab 1, CUGB), with a Cetac ASX-110 automatic sampler and a PFA Teflon self-aspirating micronebuliser system at 100 ng g^{-1}. The same rock powers digested and purified independently were also measured on a Nu Plasma II MC-ICP-MS

Table 1.
Elution scheme for separation of Cd for isotopic determination

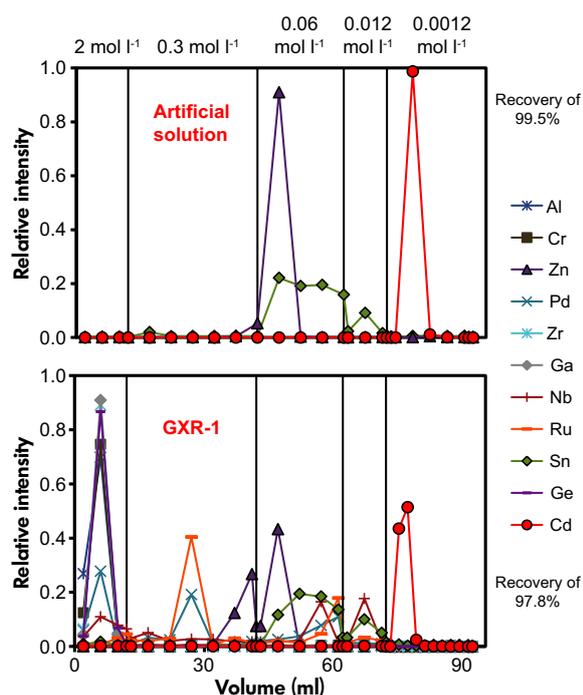| Reagent	Volume (ml)	Procedure
AG-MP-1M	2.5	Resin
2 mol l^{-1} HCl	10	Condition
2 mol l^{-1} HCl	2	Load sample
2 mol l^{-1} HCl	10	Collect matrix
0.3 mol l^{-1} HCl	30	Collect matrix
0.06 mol l^{-1} HCl	20	Collect matrix
0.012 mol l^{-1} HCl	10	Collect matrix
0.0012 mol l^{-1} HCl	15	Collect Cd

Figure 1. Elution curves for 'mixed' standard solution (a) Sn : Zn : Cd = 1 μg : 1 μg : 1 μg and geological reference material and (b) GXR-1 on a 2.5 ml resin bed of AG MP-1M. See text for details

Table 2.
Neptune plus operating conditions for Cd isotopic ratio measurements

Instrument parameters	Lab 1 (CUGB)
Rf power	1250 W
Cooling Ar	~ 16 l min^{-1}
Auxiliary Ar	~ 1.0 l min^{-1}
Nebuliser Ar	~ 1.0 l min^{-1}
Extraction voltage (hard)	-2000 V
Vacuum	4–8 × 10^{-9} Pa
^{114}Cd sensitivity	~ 12.5 V μg g^{-1} (LR)
Cones, sample + skimmer	Ni (X) + Ni (Jet)
Sample uptake rate	~ 100 μl min^{-1}

LR, low resolution.

and skimmer cones are made of Ni, and high-sensitivity (X) cones are used to increase transmission by a factor of 2–3 relative to the routine H-cones (Liu *et al.* 2014). The samples containing 0.15 μg Cd can be measured for at least four blocks of thirty cycles each (100 ng g^{-1} in 1.5 ml solution), and thus, each value reported is an average of 120 ratios. This is particularly important for measurement of samples with a low mass fraction of Cd. Cd isotopic ratios were measured in low-resolution mode with ^{111}Cd$^+$ in the central cup. ^{109}Ag$^+$ and ^{117}Sn$^+$ in the L2 and H4 Faraday cup were monitored to correct possible Ag and Sn interferences. Furthermore, instrumental mass bias method was also performed using ^{111}Cd-^{113}Cd double spike with an aim to evaluate whether there is a significant difference in measurement results between the two methods. The results will be discussed in the section 'Matrix effect'. For each rock power digested independently, the isotope spike and sample solution was mixed in terms of c(^{111}Cd$_{spike}$)/ c(^{112}Cd$_{sample}$) ~ 2.0. The spiked samples were evaporated to dryness and dissolved in 2 ml 2 mol l^{-1} HCl and then left to equilibrate for overnight prior to further processing. Tin was monitored to correct possible isobaric interference. Correction of Sn interference on ^{112}Cd$^+$, ^{114}Cd$^+$ and ^{116}Cd$^+$ was enabled by the measurement of ^{118}Sn$^+$.

instrument at the Institute of Geochemistry, Chinese Academy of Sciences (Lab 2, CAS), with an Apex desolvation system, at 100 ng g^{-1}. No significant differences in Cd isotopic compositions measured on the two instruments are observed (see Matrix effect). Measurement results with the Neptune plus MC-ICP-MS are reported mainly in this paper, and the specific instrument parameters are listed in Table 2.

Different measurement and data reduction procedures can be used to obtain precise measurements for Cd isotopic compositions: external normalisation (Wombacher *et al.* 2003), sample calibrator bracketing (SSB) (Cloquet *et al.* 2005, Gao *et al.* 2008, Xue *et al.* 2013, Zhu *et al.* 2013) and double-spike techniques (DS) (Schmitt *et al.* 2009b, Horner *et al.* 2011, Xue *et al.* 2012, Yang *et al.* 2012, Xue *et al.* 2013, Murphy *et al.* 2016, Palk *et al.* 2018). Prior to sample introduction, samples and reference materials were diluted to produce ~ 100 ng g^{-1} Cd solution in 3% *m/m* HNO$_3$ and the difference in Cd mass fraction between the samples and the reference materials were less than 10%. The uptake rate was 100 μl min^{-1}, and the take-up time was 140 s. Prior to each analysis, sequential rinses of two separate 3% *m/m* HNO$_3$ of 130 s were used to reduce baselines to < 1 mV on the m/z 114 channel. The sampler

To date, there is no fixed international measurement standard for normalising measured Cd isotopic data. In this study, NIST SRM 3108 was used as 'zero-delta' Cd reference material, which is increasingly used by recent studies (Xue *et al.* 2012, Abouchami *et al.* 2013, Conway *et al.* 2013, Wasylenki *et al.* 2014, Martinková *et al.* 2016, Murphy *et al.* 2016, Zhang *et al.* 2016, De Baar *et al.* 2017, Wei *et al.* 2017, Imseng *et al.* 2018, Palk *et al.* 2018, Zhu *et al.* 2018). All Cd isotope ratio data were reported as the deviation relative to Cd reference material NIST SRM 3108, which are given in per mil (delta) notation following the equations (Coplen 2011):

$$\delta^{114/110}Cd_{NIST\,SRM\,3108}$$
$$= R(^{114}Cd/^{110}Cd)_{sample}/R(^{114}Cd/^{110}Cd)_{NIST\,SRM\,3108} - 1$$
$$(1)$$

$$\delta^{112/110}Cd_{NIST\,SRM\,3108}$$
$$= R(^{112}Cd/^{110}Cd)_{sample}/R(^{112}Cd/^{110}Cd)_{NIST\,SRM\,3108} - 1$$
$$(2)$$

As the delta values of Cd isotope ratios of the sample relative to different Cd standards are different, $\delta^{114/110}Cd$ values for each sample reported in previous studies need to be recalculated. The conversion of $\delta^{114/110}Cd$ relative to two different Cd standards is as follows:

$$\delta^{114/110}Cd_{X-A} = \delta^{114/110}Cd_{X-B} + \delta^{114/110}Cd_{B-A}$$
$$+ (\delta^{114/110}Cd_{X-B} \times \delta^{114/110}Cd_{B-A})/1000$$
$$(3)$$

where X represents the sample, and A and B stand for NIST SRM 3108 and other Cd RMs, respectively.

Results and discussion

Analyte yield

Significant cadmium isotope fractionation can occur during ion exchange chromatography due to incomplete recovery of Cd (Wombacher *et al.* 2003, Cloquet *et al.* 2005). Similar ion exchange fractionation has also been found for other metal isotopes, for example Cu (Maréchal and Albarède 2002, Zhu *et al.* 2002, Liu *et al.* 2014) and Mg (Teng *et al.* 2007). Cadmium that was eluted earlier was always isotopically heavier than those eluted later, and the isotope fractionation can be as large as 2.4‰ (Cloquet *et al.* 2005). Therefore, to reduce the impact from chemical purification and to achieve accurate Cd isotope ratio data, complete recovery must be achieved. A Cd solution (SPEX Cd, 1 μg) and a natural sample (GXR-1, 50 mg) with well-known Cd mass fraction were purified to check the yield. The Cd cut (total 15 ml) eluted from these samples was compared with the amount of Cd in the samples. These yielded a recovery of 97.8 ± 0.5% (2s, n = 3) and 99.5 ± 0.6% (2s, n = 3), respectively (Figure 1). Clearly, this purification method yielded closely complete recovery for Cd. Previous studies show that Cd isotopes are not fractionated during chemical purification when the total yield is more than 95% (Cloquet *et al.* 2005, Gao *et al.* 2008). This is verified by the same Cd isotopic ratios between unpurified and purified fractions of the same standard solutions (e.g., SPEX Cd vs. NIST SRM 3108; Table 3 and Figure 4). The total procedural blanks (from sample dissolution to mass spectrometry) were lower than 100 pg, which was always negligible compared to the total amount of Cd loaded in this study (more than 0.12 μg).

Matrix effect

The impact of matrices requires interference monitoring and possible correction for Cd isotope ratio measurement results. Sn, especially because of its ubiquity in metal alloys and anticorrosion coatings, can be a problematic contaminant leading to a bias as noted in previous studies (Wombacher

Table 3.
Cadmium isotopic composition relative to NIST SRM 3108 obtained from different experiments

Name	Type	Cd (μg g^{-1})	$\delta^{114/110}$ Cd$_{NIST\,SRM\,3108}$ (‰)	2s	$\delta^{112/110}$ Cd$_{NIST\,SRM\,3108}$ (‰)	2s	$\delta^{114/110}$Cd$_{NIST\,SRM\,3108}$ (‰)/ $\delta^{112/110}$ Cd$_{NIST\,SRM\,3108}$ (‰)
Sn:Cd = 0.01	SPEX Cd + GSB Sn	0.1	0.06	0.12	0.04	0.06	
Sn:Cd = 0.05	SPEX Cd + GSB Sn	0.1	0.00	0.04	0.03	0.04	
Sn:Cd = 0.1	SPEX Cd + GSB Sn	0.1	0.07	0.07	0.09	0.07	
Sn:Cd = 0.3	SPEX Cd + GSB Sn	0.1	0.15	0.06	0.19	0.03	
Sn:Cd = 0.5	SPEX Cd + GSB Sn	0.1	0.17	0.09	0.29	0.08	
Sn:Cd = 0.8	SPEX Cd + GSB Sn	0.1	0.25	0.09	0.46	0.11	
Sn:Cd = 1.0	SPEX Cd + GSB Sn	0.1	0.32	0.12	0.58	0.07	
Through chemistry							
SPEX Cd	Reference solution	0.2	-2.12	0.10	-1.06	0.09	2.00
SPEX Cd	Reference solution	1	-2.14	0.04	-1.08	0.03	1.98
SPEX Cd	Reference solution	5	-2.16	0.08	-1.09	0.03	1.98
GXR-1	Jasperoid	0.12	-0.29	-0.16	0.04	0.00	1.87
GXR-1	Jasperoid	0.33	-0.32	-0.16	0.11	0.08	1.97
Cd:Zn = 1:1	SPEX Cd + GSB Zn	1	-2.16	0.19	-1.09	0.10	1.97
Cd:Zn = 1:400	SPEX Cd + GSB Zn	1	-2.12	0.09	-1.05	0.05	2.01
Cd:Zn = 1:1000	SPEX Cd + GSB Zn	1	-2.15	0.09	-1.08	0.04	1.96

et al. 2003, Cloquet et al. 2005, Gao et al. 2008). The potential isobaric interference for Cd isotopic analysis includes $^{114}Sn^+$ on $^{114}Cd^+$ and $^{112}Sn^+$ on $^{112}Cd^+$. Significant influence of Sn on Cd isotope measurement results has been found using both SSB and DS methods (Wombacher et al. 2003, Cloquet et al. 2005, Ripperger and Rehkämper 2007, Gao et al. 2008). To ensure an accurate Cd measurement results, the interference of Sn is investigated here by measuring standard solutions doped with interfering elements at widely varying concentration levels (Figure 2). The plot shows that Cd isotope ratio data in our working conditions (SSB) is sensitive to the presence of Sn. The influence of Sn on Cd isotope measurement result towards a heavy isotopic composition is likely a result of $^{114}Sn^+$ interference on the heavier isotope of Cd ($^{114}Cd^+$). Nevertheless, the influence can be neglected when Sn/Cd molar ratio is less than 0.1 in both SSB and DS working conditions. After chemical purification, the molar ratio of Sn/Cd for all samples analysed was much below 0.1 and often below 0.01, which causes an undetectable deviation on the measured isotope ratios and can be negligible. This allows measurement results with small uncertainties using sample calibrator bracketing or double-spike techniques.

Cadmium has a similar geochemical behaviour as Zn and can replace Zn in many minerals, such as sphalerite, smithsonite, hydrozincite, etc. These minerals commonly have extremely high Zn/Cd ratios (e.g., up to 500) (Wen et al. 2016). A significant influence of Zn on Cd isotope ratio measurement result was previously found by Cloquet et al. (2005). Here, a set of synthetic solutions with a fixed amount of Cd in a solution of variable Zn mass fractions were investigated to test the capability of complete Zn purification. The synthetic solutions

were made with mono-elemental Zn standard and SPEX Cd, and the molar ratios of Zn/Cd vary from 1 to 1000. All mixed solutions were processed through column chemistry as the same as done for natural samples and yield a mean $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ = -2.14 ± 0.12‰ (2s, n = 3). The obtained $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ values are in good agreement within current precision with those ($\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ = -2.13 ± 0.09‰, 2s, n = 74) obtained without through column chemistry (Figure 5), indicating that Cd can be well separated from Zn for considerably high Zn/Cd (up to 1000) samples with complete recovery.

The measured isotope ratios of all reference solutions and reference materials fall on the theoretical mass fractionation line in a three-isotope diagram with the theoretical slope of
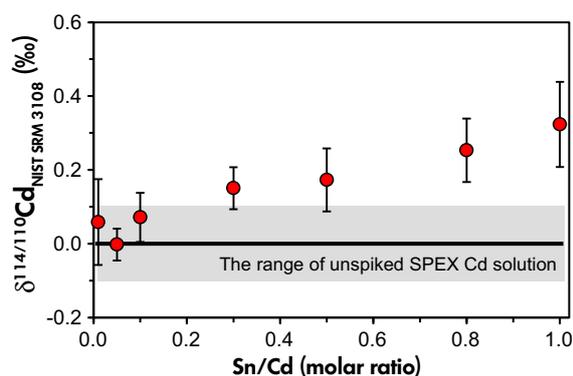

Figure 2. Cadmium isotopic variations of SPEX Cd spiked with different amounts of Sn relative to the unspiked Cd solution. The Cd mass fraction for samples and bracketing calibrators is the same (100 ng g^{-1}). See text for details
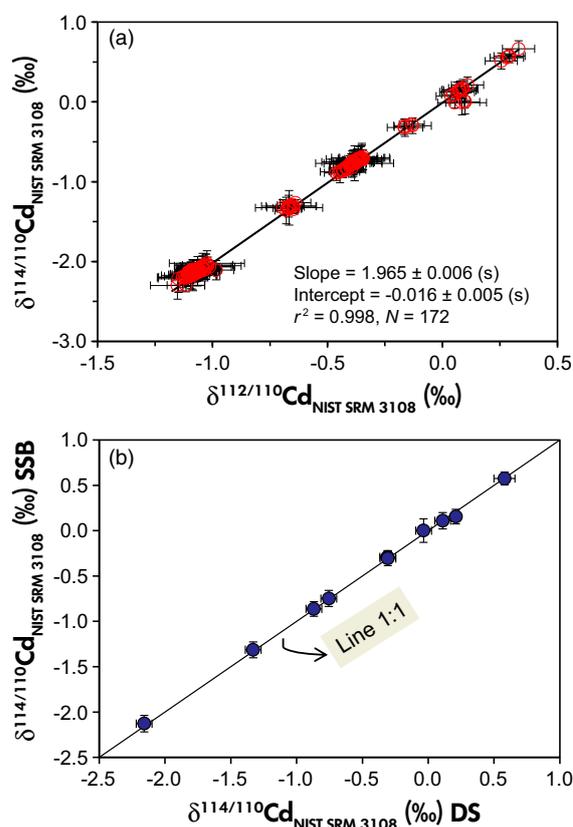

Figure 3. Cadmium three-isotope plot for reference and digested geological reference material solutions measured by sample calibrator bracketing method in this study (a). All samples fall on the theoretical mass fractionation line, indicating limited spectral interferences. Comparison of values obtained with the SSB and double-spike mass bias correction methods (b). The data are reported in Tables 3 and 4

1.9649 (Young *et al.* 2002) (Figure 3a). This indicates that spectral interferences and nucleosynthetic or other non-mass-dependent isotope anomalies are insignificant. The $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ values of all samples obtained with SSB and DS methods follow the 1:1 linear trend, indicating the consistency of the two methods and validating the use of the efficient SSB method for correction of instrumental mass bias in Cd isotope ratio measurement results (Figure 3b).

The amount of loaded Cd

Because most of natural rocks have very low Cd mass fraction, it is necessary to evaluate any possible influence of the amount of loaded Cd on the precision of Cd isotope ratios by considering the contribution from blank. Therefore, different masses of in-house mono-elemental Cd standard solutions (SPEX Cd) ranging from 0.2 to 5 μg and GXR-1 from 0.12 to 0.33 μg were routinely purified. The results yielded consistent $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ values within analytical errors for samples containing Cd from 0.2 to 5 μg, with the mean $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ of -2.14‰ (SPEX Cd) and -0.31‰ (GXR-1) relative to NIST SRM 3108 (Figure 4). This suggests that the contribution from blank (< 100 pg) is still insignificant when the amount of Cd loaded to the column is as low as 0.12 μg.

Uncertainty contributions

Repeated measurements of an in-house Cd standard solution (SPEX Cd) have been performed. The results are plotted in Figure 5. The intermediate precision over a 3-year period gave a mean $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ of -2.13 ± 0.09‰ (2*s*, *n* = 74) and $\delta^{112/110}Cd_{NIST\ SRM\ 3108}$ of

-1.07 ± 0.06‰ (2*s*, *n* = 74) relative to NIST SRM 3108. SPEX Cd has a lighter Cd isotope ratio than other batches of Spex-1 Cd solution reported by the previous studies (Cloquet *et al.* 2005, Gao *et al.* 2008, Wei *et al.* 2015, Zhang *et al.* 2016, Zhu *et al.* 2018). The SPEX Cd solutions produced in different batches show a large isotopic distinction, and this may form a subject of further study. The results for SPEX Cd purified through column chemistry yield consistent $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ values indistinguishable from different loaded amounts of Cd (from 0.2 to 5 μg).

$\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ and $\delta^{112/110}Cd_{NIST\ SRM\ 3108}$ ratios of reference materials

The Cd isotope ratios of standard solutions and geological reference materials obtained in this study and a comparison with published data are illustrated in Figure 6 and Table 4. At least two repeat measurements were taken over a 1-year period for all samples in this study. These measurement results include independent digestion and duplicate measurements of unprocessed standard solutions and geological reference materials.

In-house SPEX Cd solution was most frequently analysed, and we recommend a mean $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ of -2.13 ± 0.09‰ (2*s*, *n* = 74) and $\delta^{112/110}Cd_{NIST\ SRM\ 3108}$ of -1.07 ± 0.06‰ (2*s*, *n* = 74) for SPEX Cd relative to NIST SRM 3108. However, batch number must be indicated when SPEX Cd is reported in different laboratories, because of the large difference in $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ values obtained in different batches, for example $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ of Spex-1 are -0.09 ± 0.01 ‰ for Lot: 74-075219K and -1.25 ± 0.06‰ for Lot: CL6-30CDY relative
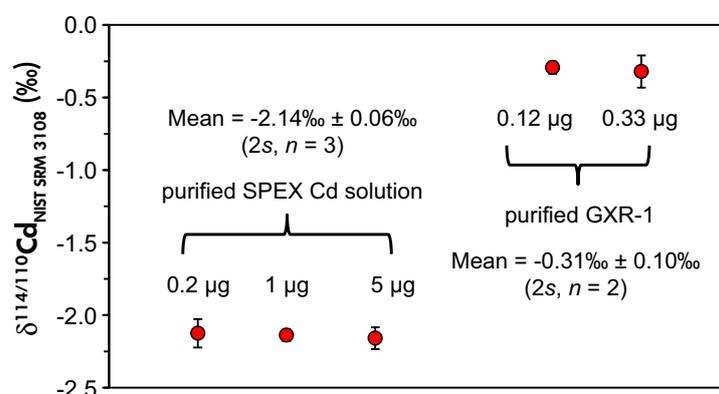

Figure 4. Test of the influence of the amount of loaded Cd on the bias and precision of Cd isotopic analysis. In-house mono-element standard solutions and geological RMs were prepared to contain different amounts of Cd (0.2–5 μg for SPEX Cd and 0.12–0.33 μg for GXR-1) and were purified through column chemistry. See text for details
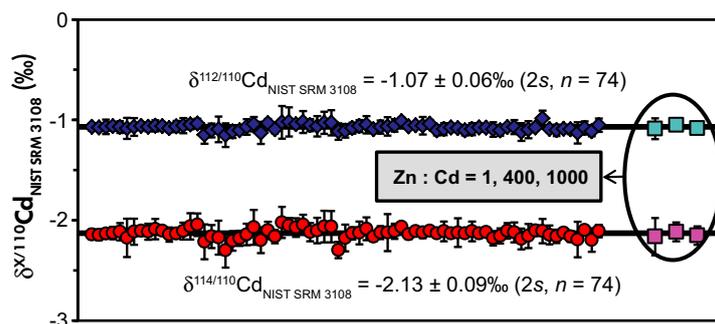
Figure 5. Long-term measurement results of in-house mono-element standard solutions (SPEX Cd) relative to NIST SRM 3108 on the Neptune plus. The synthetic solutions (SPEX Cd : Zn = 1, 400, 1000; molar ratio) were processed through column chemistry, whose $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ values are indistinguishable from the results without column chemistry treatment. The data are reported in Table 3
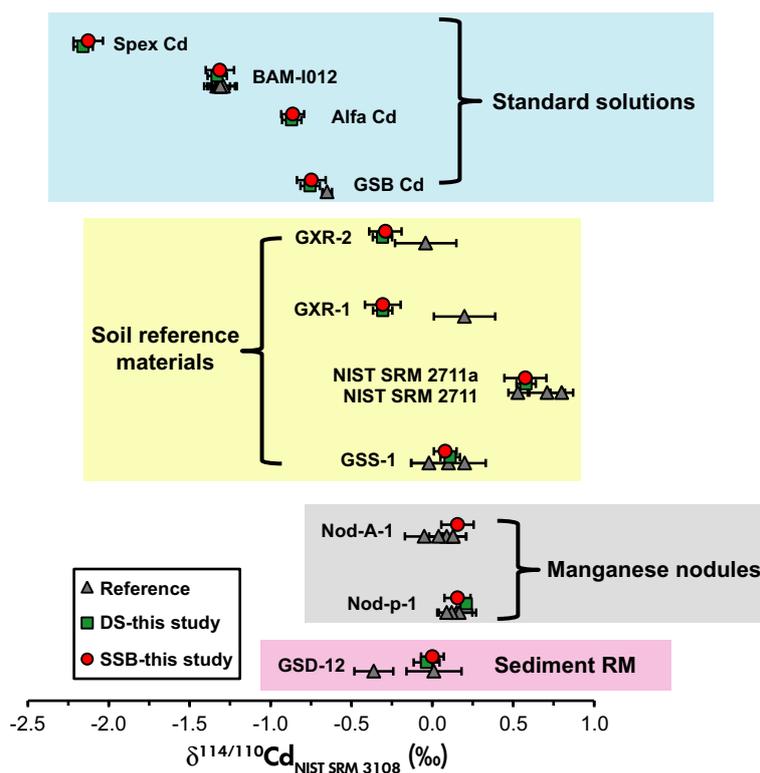

Figure 6. Cadmium isotopic ratios of reference solution and geological RMs (relative to NIST SRM 3108). The red circles and green squares represent the samples calibrated by SSB on Neptune Plus and double-spike correction on Nu Plasma II. Previously published data are listed for comparison. Source: Brand *et al.* (2014), Cloquet *et al.* (2005), Gao *et al.* (2008), Schmitt *et al.* (2009a), Abouchami *et al.* (2013), Brand *et al.* (2014), Pallavicini *et al.* (2014), Du (2015), Wei *et al.* (2015) Murphy *et al.* (2016), Wiggenhauser *et al.* (2016), Bridgestock *et al.* (2017), Imseng *et al.* (2018) and Zhang *et al.* (2018). The data of this study are reported in Table 4

Table 4.
Cadmium isotopic composition of reference materials relative to NIST SRM 3108

Name	Type	Cd (µg g^{-1})	$\delta^{114/110}$Cd$_{NIST\ SRM\ 3108}$ (‰)	2s	$\delta^{112/110}$Cd$_{NIST\ SRM\ 3108}$ (‰)	2s	$\delta^{114/110}$Cd$_{NIST\ SRM\ 3108}$/ $\delta^{112/110}$Cd$_{NIST\ SRM\ 3108}$	n [a]	Comments
SPEX Cd	Reference solution		-2.13	0.09	-1.07	0.06	1.98	74	SSB-this study
			-2.16	0.06					DS-this study
BAMI012	Reference solution		-1.31	0.09	-0.66	0.08	1.99	13	SSB-this study
			-1.33	0.06					DS-this study
			-1.33 [b]	0.04					Abouchami et al. (2013)
			-1.305						Brand et al. (2014)
			-1.32	0.07					Murphy et al. (2016)
			-1.30	0.09					Wiggenhauser et al. (2016)
			-1.29	0.07					Bridgestock et al. (2017)
			-1.31	0.10					Imseng et al. (2018)
Alfa Cd	Reference solution		-0.86	0.08	-0.43	0.03	1.99	9	SSB-this study
			-0.87	0.06					DS-this study
GSB Cd	Reference solution		-0.75	0.09	-0.38	0.08	1.98	46	SSB-this study
			-0.76	0.06					DS-this study
			-0.65	0.03					Wei et al. (2015)
GSS-1	Soil	4.3	0.08	0.08	0.06	0.04	1.92	4	SSB-this study
			0.11	0.06					DS-this study
			0.10 [c]	0.23					Cloquet et al. (2005)
			0.20						Du (2015)
			-0.02 [c]	0.11					Gao et al. (2008)
GXR-1	Jasperoid	3.3	-0.31	0.08	-0.16	0.04	1.91	3	SSB-this study
			-0.31	0.06					DS-this study
			0.20 [c]	0.19					Cloquet et al. (2005)
GXR-2	Soil	4.1	-0.29	0.07	-0.13	0.07	1.96	2	SSB-this study
			-0.31	0.06					DS-this study
			-0.04 [c]	0.19					Cloquet et al. (2005)
NIST SRM 2711a	Montana II Soil	54.1	0.57	0.07	0.29	0.06	1.99	5	SSB-this study
			0.58	0.08					DS-this study
NIST SRM 2711	Montana Soil	41.7	0.53 [c]	0.06					Cloquet et al. (2005)
			0.80	0.07					Pallavicini et al. (2014)
			0.71	0.11					Pallavicini et al. (2014)
Nod-A-1	Mn-Nodule	7.5	0.16	0.10	0.08	0.06	1.95	4	SSB-this study
			-0.05 [c]	0.12					Cloquet et al. (2005)
			0.13 [c]	0.08					Schmitt et al. (2009a)
			0.09	0.03					Pallavicini et al. (2014)
			0.13	0.08					Murphy et al. (2016)
			0.04	0.06					Zhang et al. (2018)
Nod-P-1	Mn-Nodule	22.5	0.16	0.08	0.08	0.06	1.99	4	SSB-this study
			0.21	0.03					DS-this study
			0.15 [c]	0.12					Cloquet et al. (2005)
			0.17 [c]	0.08					Schmitt et al. (2009a)
			0.12	0.04					Pallavicini et al. (2014)
			0.09	0.05					Zhang et al. (2018)
GSD-12	Sediment	4	0.00	0.13	0.09	0.06		3	SSB-this study
			-0.04	0.06					DS-this study
			0.01	0.17					Du (2015)
			-0.36 [c]	0.12					Cloquet et al. (2005)

[a] n represents the number of sessions in which different primary samples were analysed.
[b] A single bottle of NIST SRM 3108 (50 ml) was distributed to the different laboratories for assay (Abouchami et al. 2013).
[c] The $^{114/110}$Cd of samples in previous studies was recalculated relative to NIST SRM 3108, according to Abouchami et al. (2013) and Wei et al. (2015).

to NIST SRM 3108 (Wei *et al.* 2015, 2017). BAM I012 yielded a $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ value of -1.31 ± 0.09‰ (2*s*, *n* = 13) and a $\delta^{112/110}Cd_{NIST\ SRM\ 3108}$ value of -0.66 ± 0.08‰ (2*s*, *n* = 13), which is indistinguishable from value reported by previous studies (Abouchami *et al.* 2013, Murphy *et al.* 2016, Wiggenhauser *et al.* 2016, Bridgestock *et al.* 2017, Imseng *et al.* 2018) and recommended value ($\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ = -1.305‰) by Brand *et al.* (2014). Two other standard solutions (Alfa Cd and GSB Cd) yielded Cd isotopic ratios of $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ = -0.86 ± 0.07‰ (2*s*, *n* = 9) and $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ = -0.75 ± 0.09‰ (2*s*, *n* = 46), respectively. These values are indistinguishable from the results measured by the DS method ($\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ = -0.87 ± 0.06‰ and $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ = -0.76 ± 0.06‰, respectively) in this study. Wei *et al.* (2015, 2017) reported that the $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ value of Spex-1 Cd solution (lot no.: 74-075219K) relative to NIST SRM 3108 was -0.09 ± 0.01‰, and the value of GSB Cd relative to Spex-1 Cd was -0.56 ± 0.03‰. The $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ value of GSB Cd solution relative to NIST SRM 3108 was -0.65 ± 0.03‰ calculated according to the formula (3), which is indistinguishable from our results.

Similarly, we calculated the $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ values of geological reference materials reported by previous studies according to Equation (3), and the values relative to NIST SRM 3108 were discussed below. The sediment sample GSD-12 has a mean Cd isotope ratio equivalent to NIST SRM 3108, with $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ = 0.00 ± 0.13‰ (SSB) and $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ = -0.04 ± 0.06‰ (DS). The $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ of GSD-12 obtained here is significantly heavier than the value (-0.36 ± 0.12‰) reported by Cloquet *et al.* (2005), but is identical to the value (0.01 ± 0.17‰) reported by Du (2015). The soil sample GXR-2 has a slightly lighter Cd isotope ratio than soil sample GSS-1, and $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ values of the two RMs obtained here are indistinguishable from those reported in the literature (Cloquet *et al.* 2005, Gao *et al.* 2008, Du 2015). NIST SRM 2711a (Montana II soil) has $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ values of 0.57 ± 0.07‰ (SSB) and 0.58 ± 0.08‰ (DS), significantly heavier than other soil reference materials. NIST SRM 2711a has a similar Cd isotope ratio to NIST SRM 2711 (Montana soil) (Cloquet *et al.* 2005, Pallavicini *et al.* 2014). The two manganese nodule reference materials, Nod-P-1 and Nod-A-1, have $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ of 0.16 ± 0.08‰ (2*s*, *n* = 4) and 0.16 ± 0.10‰ (2*s*, *n* = 4), respectively. These results are in excellent agreement with the $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ values (0.09‰ to 0.17‰ for Nod-P-1 and -0.05‰ to 0.13‰ for Nod-A-1) measured by Cloquet *et al.* (2005), Schmitt *et al.* (2009a), Pallavicini *et al.* (2014), Murphy *et al.* (2016) and Zhang *et al.* (2018),. The jasperoid sample GXR-1 has $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ = -0.31 ± 0.08‰ (2*s*, *n* = 3), which is lighter than the value (0.20‰) reported by Cloquet *et al.* (2005). The significant differences in Cd isotope ratio of GSD-12 and GXR-1 between this study and Cloquet *et al.* (2005) may reflect the following: (a) the utilisation of different measurement reference solutions, which vary from different laboratories and thus result in bias in the calculated values; (b) the $\delta^{114/110}Cd/\delta^{114/112}Cd$ ratios (0.18‰/0.15‰ for GXR-1 and -0.38/-0.27‰ for GSD-12, respectively) reported by Cloquet *et al.* (2005) deviate from the theoretical mass fractionation line (Young *et al.* 2002). We suggest that the two reference materials require future studies and list the values measured in this study in Table 4 as new references for future interlaboratory comparison.

Summary

High-precision Cd isotope ratios for natural samples has been obtained on MC-ICP-MS in this study using both SSB and DS mass bias correction methods. The purification procedure for Cd gave a chemical yield of > 97.8% and effectively reduced the possible Sn spectral interference to a near-negligible level using one-stage column chemical procedure. The intermediate precision over three years of better than ± 0.09‰ (2*s*) for $\delta^{114/110}Cd_{NIST\ SRM\ 3108}$ measurement was routinely obtained. We strongly recommend the use of NIST SRM 3108 as a zero-delta reference in different laboratories, which will eliminate any extra deviation brought by frequent conversion in different reference materials. In this study, we reported all Cd isotopic data of standard solutions and geological reference materials directly against NIST SRM 3108, which were recommended for future interlaboratory comparison.

Acknowledgements

References

Abouchami W., Galer S., De Baar H., Alderkamp A., Middag R., Laan P., Feldmann H. and Andreae M. (2011)
Modulation of the southern Ocean cadmium isotope signature by ocean circulation and primary productivity. Earth and Planetary Science Letters, 305, 83–91.

Abouchami W., Galer S.J., Horner T.J., Rehkämper M., Wombacher F., Xue Z., Lambelet M., Gault-Ringold M., Stirling C.H. and Schönbächler M. (2013)
A common reference material for cadmium isotope studies – NIST SRM 3108. Geostandards and Geoanalytical Research, 37, 5–17.

Abouchami W., Galer S.J.G., de Baar H.J.W., Middag R., Vance D., Zhao Y., Klunder M., Mezger K., Feldmann H. and Andreae M.O. (2014)
Biogeochemical cycling of cadmium isotopes in the southern Ocean along the zero meridian. Geochimica et Cosmochimica Acta, 127, 348–367.

Brand W.A., Coplen T.B., Vogl J., Rosner M. and Prohaska T. (2014)
Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report). Pure and Applied Chemistry, 86, 425–467.

Bridgestock L., Rehkämper M., van de Flierdt T., Murphy K., Khondoker R., Baker A.R., Chance R., Strekopytov S., Humphreys-Williams E. and Achterberg E.P. (2017)
The Cd isotope composition of atmospheric aerosols from the tropical Atlantic Ocean. Geophysical Research Letters, 44, 2932–2940.

Cloquet C., Rouxel O., Carignan J. and Libourel G. (2005)
Natural cadmium isotopic variations in eight geological reference materials (NIST SRM 2711, BCR 176, GSS-1, GXR-1, GXR-2, GSD-12, Nod-P-1, Nod-A-1) and anthropogenic samples measured by MC-ICP-MS. Geostandards and Geoanalytical Research, 29, 95–106.

Cloquet C., Carignan J., Libourel G., Sterckeman T. and Perdrix E. (2006)
Tracing source pollution in soils using cadmium and lead isotopes. Environmental Science and Technology, 40, 2525–2530.

Conway T.M., Rosenberg A.D., Adkins J.F. and John S.G. (2013)
A new method for precise determination of iron, zinc and cadmium stable isotope ratios in seawater by double-spike mass spectrometry. Analytica Chimica Acta, 793, 44–52.

Coplen T.B. (2011)
Guidelines and recommended terms for expression of stable isotope-ratio and gas-ratio measurement results. Rapid Communications in Mass Spectrometry, 25, 2538–2560.

De Baar H.J.W., van Heuven S.M.A.C., Abouchami W., Xue Z., Galer S.J.G., Rehkämper M., Middag R. and van Ooijen J. (2017)
Interactions of dissolved CO_2 with cadmium isotopes in the southern Ocean. Marine Chemistry, 195, 105–121.

Douglas D. and Tanner S. (1998)
Fundamental considerations in ICP-MS. Inductively coupled plasma mass spectrometry. In: Montaser A. (ed.), Wiley-VCH, 615–679.

Du C. (2015)
Cadmium isotope analytical method and its paleo-ocean environmental significance. PhD thesis (China University of Geosciences, Wuhan, China), 1–94 pp.

Gao B. (2016)
Cd isotopic signatures: A potential source tracer of metal pollution in the environment. Environmental Science and Pollution Research, 23, 941–942.

Gao B., Liu Y., Sun K., Liang X., Peng P.A., Sheng G. and Fu J. (2008)
Precise determination of cadmium and lead isotopic compositions in river sediments. Analytica Chimica Acta, 612, 114–120.

Horner T.J., Rickaby R.E. and Henderson G.M. (2011)
Isotopic fractionation of cadmium into calcite. Earth and Planetary Science Letters, 312, 243–253.

Imseng M., Wiggenhauser M., Keller A., Müller M., Rehkämper M., Murphy K., Kreissig K., Frossard E., Wilcke W. and Bigalke M. (2018)
Fate of Cd in agricultural soils: A stable isotope approach to anthropogenic impact, soil formation and soil-plant cycling. Environmental Science and Technology, 52, 1919–1928.

Lacan F., Francois R., Ji Y. and Sherrell R.M. (2006)
Cadmium isotopic composition in the ocean. Geochimica et Cosmochimica Acta, 70, 5104–5118.

Liu S.-A., Li D., Li S., Teng F.-Z., Ke S., He Y. and Lu Y. (2014)
High-precision copper and iron isotope analysis of igneous rock standards by MC-ICP-MS. Journal of Analytical Atomic Spectrometry, 29, 122–133.

Loss R., Rosman K. and DeLaeter J. (1984)
Mass spectrometric isotope dilution analyses of palladium, silver, cadmium and tellurium in carbonaceous chondrites. Geochimica et Cosmochimica Acta, 48, 1677–1681.

Loss R., Rosman K. and DeLaeter J. (1990)
The isotopic composition of zinc, palladium, silver, cadmium, tin, and tellurium in acid-etched residues of the Allende meteorite. Geochimica et Cosmochimica Acta, 54, 3525–3536.

Maréchal C. and Albarède F. (2002)
Ion-exchange fractionation of copper and zinc isotopes. Geochimica et Cosmochimica Acta, 66, 1499–1509.

Martinková E., Chrastný V., Francová M., Šípková A., Čuřík J., Myška O. and Mižič L. (2016)
Cadmium isotope fractionation of materials derived from various industrial processes. Journal of Hazardous Materials, 302, 114–119.

references

Meija J., Coplen T.B., Berglund M., Brand W.A., De Bièvre P., Gröning M., Holden N.E., Irrgeher J., Loss R.D. and Walczyk T. (2016)
Isotopic compositions of the elements 2013 (IUPAC Technical Report). Pure and Applied Chemistry, 88, 293–306.

Murphy K., Rehkämper M., Kreissig K., Coles B. and van de Flierdt T. (2016)
Improvements in Cd stable isotope analysis achieved through use of liquid–liquid extraction to remove organic residues from Cd separates obtained by extraction chromatography. Journal of Analytical Atomic Spectrometry, 31, 319–327.

Palk C., Andreasen R., Rehkämper M., Stunt A., Kreissig K., Coles B., Schönbächler M. and Smith C. (2018)
Variable Tl, Pb, and Cd concentrations and isotope compositions of enstatite and ordinary chondrites-Evidence for volatile element mobilization and decay of extinct ^{205}Pb. Meteoritics and Planetary Science, 53, 167–186.

Pallavicini N., Engstrom E., Baxter D.C., Ohlander B., Ingri J. and Rodushkin I. (2014)
Cadmium isotope ratio measurements in environmental matrices by MC-ICP-MS. Journal of Analytical Atomic Spectrometry, 29, 1570–1584.

Pritzkow W., Wunderli S., Vogl J. and Fortunato G. (2007)
The isotope abundances and the atomic weight of cadmium by a metrological approach. International Journal of Mass Spectrometry, 261, 74–85.

Rehkämper M., Wombacher F. and Aggarwal J. (2004)
Stable isotope analysis by multiple collector ICP-MS. Handbook of Stable Isotope Analytical Techniques, 1, 692–725.

Ripperger S. and Rehkämper M. (2007)
Precise determination of cadmium isotope fractionation in seawater by double spike MC-ICP-MS. Geochimica et Cosmochimica Acta, 71, 631–642.

Ripperger S., Rehkämper M., Porcelli D. and Halliday A. (2007)
Cadmium isotope fractionation in seawater-A signature of biological activity. Earth and Planetary Science Letters, 261, 670–684.

Rosman K. and DeLaeter J. (1974)
The abundance of cadmium and zinc in meteorites. Geochimica et Cosmochimica Acta, 38, 1665–1677.

Rosman K. and DeLaeter J. (1975)
The isotopic composition of cadmium in terrestrial minerals. International Journal of Mass Spectrometry and Ion Physics, 16, 385–394.

Rosman K. and DeLaeter J. (1976)
Isotopic fractionation in meteoritic cadmium. Nature, 261, 216–218.

Sands D. and Rosman K. (1997)
Cd, Gd and Sm concentrations in BCR-1, BHVO-1, BIR-1, DNC-1, MAG-1, PCC-1 and W-2 by isotope dilution thermal ionisation mass spectrometry. Geostandards Newsletter: The Journal of Geostandards and Geoanalysis, 21, 77–83.

Schmitt A.-D., Galer S. and Abouchami W. (2009a)
Mass-dependent cadmium isotopic variations in nature with emphasis on the marine environment. Earth and Planetary Science Letters, 277, 262–272.

Schmitt A.-D., Galer S. and Abouchami W. (2009b)
High-precision cadmium stable isotope measurements by double spike thermal ionisation mass spectrometry. Journal of Analytical Atomic Spectrometry, 24, 1079–1088.

Shiel A., Orians K., Cossa D. and Weis D. (2007)
Anthropogenic contamination of bivalves revealed by Cd isotopes. Geochimica et Cosmochimica Acta, 71, A928.

Shiel A.E., Orians K., Cossa D. and Weis D. (2008)
Sourcing metals in bivalves using combined Pb, Zn and Cd isotopic compositions. Geochimica et Cosmochimica Acta Supplement, 72, A859.

Shiel A.E., Barling J., Orians K. and Weis D. (2009)
Matrix effects on the multi-collector inductively coupled plasma mass spectrometric analysis of high-precision cadmium and zinc isotope ratios. Analytica Chimica Acta, 633, 29–37.

Sivry Y., Dupre B., Sonke J., Viers J., Audry S., Schäfer J., Blanc G. and Riotte J. (2006)
Use of Cd and Zn isotopic variations in a sedimentary core to trace anthropogenic contamination. Geochimica et Cosmochimica Acta Supplement, 70, 595.

Teng F.-Z., Wadhwa M. and Helz R.T. (2007)
Investigation of magnesium isotope fractionation during basalt differentiation: Implications for a chondritic composition of the terrestrial mantle. Earth and Planetary Science Letters, 261, 84–92.

Wasylenki L.E., Swihart J.W. and Romaniello S.J. (2014)
Cadmium isotope fractionation during adsorption to Mn oxyhydroxide at low and high ionic strength. Geochimica et Cosmochimica Acta, 140, 212–226.

Wei R., Guo Q., Wen H., Yang J., Peters M., Zhu C., Ma J., Zhu G., Zhang H., Tian L., Wang C. and Wan Y. (2015)
An analytical method for precise determination of the cadmium isotopic composition in plant samples using multiple collector inductively coupled plasma-mass spectrometry. Analytical Methods, 7, 2479–2487.

Wei R., Guo Q., Wen H., Peters M., Yang J., Tian L. and Han X. (2017)
Chromatographic separation of Cd from plants via anion-exchange resin for an isotope determination by multiple collector ICP-MS. Analytical Sciences, 33, 335–341.

Wen H., Zhang Y., Cloquet C., Zhu C., Fan H. and Luo C. (2015)
Tracing sources of pollution in soils from the Jinding Pb-Zn mining district in China using cadmium and lead isotopes. Applied Geochemistry, 52, 147–154.

references

Wen H., Zhu C., Zhang Y., Cloquet C., Fan H. and Fu S. (2016)
Zn/Cd ratios and cadmium isotope evidence for the classification of lead-zinc deposits. Scientific Reports, 6, 25273.

Wiggenhauser M., Bigalke M., Imseng M., Müller M., Keller A., Murphy K., Kreissig K., Rehkämper M., Wilcke W. and Frossard E. (2016)
Cadmium isotope fractionation in soil–wheat systems. Environmental Science & Technology, 50, 9223–9231.

Wombacher F. and Rehkämper M. (2004)
Problems and suggestions concerning the notation of cadmium stable isotope compositions and the use of reference materials. Geostandards and Geoanalytical Research, 28, 173–178.

Wombacher F., Rehkämper M., Mezger K. and Münker C. (2003)
Stable isotope compositions of cadmium in geological materials and meteorites determined by multiple-collector ICP-MS. Geochimica et Cosmochimica Acta, 67, 4639–4654.

Wombacher F., Rehkämper M. and Mezger K. (2004)
Determination of the mass-dependence of cadmium isotope fractionation during evaporation. Geochimica et cosmochimica acta, 68, 2349–2357.

Xie R., Galer S., Abouchami W., Rijkenberg M., de Baar H., De Jong J. and Andreae M. (2017)
Non-Rayleigh control of upper-ocean Cd isotope fractionation in the western South Atlantic. Earth and Planetary Science Letters, 471, 94–103.

Xue Z., Rehkämper M., Schönbächler M., Statham P. and Coles B. (2012)
A new methodology for precise cadmium isotope analyses of seawater. Analytical and Bioanalytical Chemistry, 402, 883–893.

Xue Z., Rehkämper M., Horner T., Abouchami W., Middag R., van de Flierd T. and de Baar H. (2013)
Cadmium isotope variations in the Southern Ocean. Earth and Planetary Science Letters, 382, 161–172.

Yang S.-C., Lee D.-C. and Ho T.-Y. (2012)
The isotopic composition of cadmium in the water column of the South China Sea. Geochimica et Cosmochimica Acta, 98, 66–77.

Young E.D., Galy A. and Nagahara H. (2002)
Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. Geochimica et Cosmochimica Acta, 66, 1095–1104.

Zhang Y., Wen H., Fan H., Wang J. and Zhang J. (2010)
Chemical pre-treatment methods for measurement of Cd isotopic ratio on geological samples. Journal of Instrumental Analysis, 29, 633–637.

Zhang Y., Wen H., Zhu C., Fan H., Luo C., Liu J. and Cloquet C. (2016)
Cd isotope fractionation during simulated and natural weathering. Environmental Pollution, 216, 9–17.

Zhang Y., Wen H., Zhu C., Fan H. and Cloquet C. (2018)
Cadmium isotopic evidence for the evolution of marine primary productivity and the biological extinction event during the Permian-Triassic crisis from the Meishan section, South China. Chemical Geology, 481, 110–118.

Zhu X.K., Guo Y., Williams R., O'Nions R., Matthews A., Belshaw N., Canters G., de Waal E., Weser U., Burgess B. and Salvato B. (2002)
Mass fractionation processes of transition metal isotopes. Earth and Planetary Science Letters, 200, 47–62.

Zhu C., Wen H., Zhang Y., Fan H., Fu S., Xu J. and Qin T. (2013)
Characteristics of Cd isotopic compositions and their genetic significance in the lead-zinc deposits of SW China. Science China Earth Sciences, 56, 2056–2065.

Zhu C., Wen H., Zhang Y., Yin R. and Cloquet C. (2018)
Cd isotope fractionation during sulfide mineral weathering in the Fule Zn-Pb-Cd deposit, Yunnan Province, Southwest China. Science of The Total Environment, 616–617, 64–72.