

# $\delta^{114/110}\text{Cd}$ Values of a Suite of Different Reference Materials

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The  $\delta^{114/110}\text{Cd}$  values of thirty-four environmental and geological reference materials, including rocks, sediments, soils and biological samples, were determined on a Neptune Plus MC-ICP-MS instrument using a  $^{111}\text{Cd}$ - $^{113}\text{Cd}$  double spike technique. An intermediate measurement precision of better than  $\pm 0.074\%$  (2s) was achieved with different reference materials (RMs) of highly variable matrices and Cd contents. The uncertainty of  $\delta^{114/110}\text{Cd}$  values was assessed by calculating the 95% confidence interval of the results from this study and the literature using Student's *t*-test. Our measurements of nine previously analysed RMs yielded  $\delta^{114/110}\text{Cd}$  values that were indistinguishable from previous results. New reference values for the thirty-four geological and biological RMs are reported here. The comprehensive data set for these RMs provides guidelines for quality assurance and inter-laboratory comparison for Cd isotope determination. The large range of  $\delta^{114/110}\text{Cd}$  values in rock (-0.001 to +0.287‰) and biological RMs (-0.806 to +0.142‰) suggests that Cd isotope ratio measurement results are a useful tool to study biogeochemical processes.

Keywords: Cd isotopes, reference materials,  $\delta^{114/110}\text{Cd}$ , double spike, MC-ICP-MS.

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Cadmium (Cd) is a trace element with low natural abundances. The Cd content of the upper continental crust is only  $0.09 \mu\text{g g}^{-1}$  (Rudnick and Gao 2003). It has similar chemical properties to zinc (Zn), and  $\text{Cd}^{2+}$  is the dominant species. Cadmium is not only a lithophile element, but also has a stronger chalcophile affinity than zinc. Generally, Cd is hosted in crystal lattices isomorphically rather than forming independent minerals. For instance, Cd replaces Zn in sulfide minerals, and substitutes for Ca and Mn in oxide minerals (Liu *et al.* 1984). In cosmochemistry, Cd is a highly volatile element with a low condensation temperature ( $T_c$ ) of 652 K, which means that Cd is an essential tool in its ability to provide unique constraints on evaporation and condensation processes of the early solar system (Lodders 2003). In marine chemistry, Cd is a nutrient-like element, depleted in the surface seawater because of uptake of dissolved Cd by phytoplankton (Nolting and de Baar 1994). Cadmium is also a toxic element and can be enriched in soils as a consequence of the application of phosphorus fertiliser, discharge of sewage and industrial waste (Imseng *et al.*

2018). Cadmium in soils and aquatic environments can be extracted by crops and enter the human body via the food chain (Nagajyoti *et al.* 2010).

Cadmium has eight stable isotopes:  $^{106}\text{Cd}$  (1.25%),  $^{108}\text{Cd}$  (8.9%),  $^{110}\text{Cd}$  (12.49%),  $^{111}\text{Cd}$  (12.80%),  $^{112}\text{Cd}$  (24.12%),  $^{113}\text{Cd}$  (12.23%),  $^{114}\text{Cd}$  (28.73%) and  $^{116}\text{Cd}$  (7.50%) (Meija *et al.* 2016). Cadmium isotope ratio fractionation is typically expressed as  $\delta^{114/110}\text{Cd}$  in parts per thousand deviation of sample  $^{114}\text{Cd}/^{110}\text{Cd}$  from the same ratio of the isotope reference material (RM) NIST SRM 3108. Evaporation, condensation and biological uptake are the main processes that cause large Cd isotope fractionation in nature (Wombacher *et al.* 2008, Homer *et al.* 2013, Xue *et al.* 2013, Wiggerhauser *et al.* 2016, de Baar *et al.* 2017). Adsorption and precipitation also produce measurable Cd isotope fractionation (Horner *et al.* 2011, Wasylenki *et al.* 2014, Guinoiseau *et al.* 2018). Due to the unique mechanisms of Cd isotope fractionation, Cd isotopes show great potential for tracing the source and path of Cd

pollution in soils (Cloquet *et al.* 2006, Chrastný *et al.* 2015), assessing the migration of Cd in plants (Wiggenhauser *et al.* 2016, 2019, Imseng *et al.* 2018), evaluating Cd containment level in coastal environments (Shiel *et al.* 2012, 2013) and estimating the primary productivity of ancient oceans (Georgiev *et al.* 2015, John *et al.* 2017, Zhang *et al.* 2018).

Because Cd is an important toxic heavy metal, there has been extensive attention paid to its migration and transformation mechanisms in soils, sediments and organisms (Gao *et al.* 2013, Chrastný *et al.* 2015, Wiggenhauser *et al.* 2016, Imseng *et al.* 2018). However, current studies mostly focus on samples with high Cd mass fractions (Gao *et al.* 2013, Chrastný *et al.* 2015, Yang *et al.* 2019), while the background Cd isotopic compositions of the terrestrial environment are still poorly constrained.

On the one hand, Cd biomagnifies along the food chain, while on the other, Cd mass fractions vary among different organs and tissues (Guo and Marschner 1995, Kim *et al.* 2015). It is particularly important to understand the source, migration and transformation of Cd in organisms in order to manage the health risk of Cd. Cadmium isotopes have direct advantages in this regard (Shiel *et al.* 2012, 2013, Wiggenhauser *et al.* 2016, Imseng *et al.* 2018, Wei *et al.* 2018, 2019). However, prior studies focused only on a limited number of biological species, which hinders the comparative study of Cd distributions among different organisms. Moreover, several popular foods such as kelp, laver and pork liver have high Cd contents, but their Cd isotopic compositions are still to be constrained in order to assess their Cd contributions to the human body.

Oceanic Cd cycles are another focus in current Cd research. Specifically, the GEOTRACES programme has investigated Cd concentrations and  $\delta^{114/110}\text{Cd}$  values in the global oceans (Abouchami *et al.* 2011, 2014, Xue *et al.* 2013, Conway and John 2015a,b, Xie *et al.* 2017, George *et al.* 2019, Sieber *et al.* 2019). Nevertheless, the  $\delta^{114/110}\text{Cd}$  of deep-sea ferromanganese crusts, nodules and marine sediments, which are important Cd sinks from seawater, are poorly studied. Here we report  $\delta^{114/110}\text{Cd}$  values of three marine sediments from neighbouring seas of China and three Co-rich ferromanganese crusts from the central and western Pacific, in order to provide a first order view of Cd isotope systematics in these marine sediments.

The successful application of Cd isotope ratios depends on small measurement uncertainties on isotope ratio measurement results in actual samples. One of the key issues is small measurement uncertainties of the measurement results of  $\delta^{114/110}\text{Cd}$  in geological RMs, which not only guarantees

the reliability of measurement results, but also provides basic data comparison between laboratories (He *et al.* 2015, Wu *et al.* 2020). As well as this, geological RMs provide benchmarks for similar samples and preliminary constraints on the  $\delta^{114/110}\text{Cd}$  values of corresponding reservoirs. Previous studies report the  $\delta^{114/110}\text{Cd}$  values of several igneous rock RMs such as basalt BHVO-2, andesite AGV-2, granodiorite GSP-2 and carbonatite COQ-1, (Wombacher *et al.* 2003, Schediwiy *et al.* 2006, Wiggenhauser *et al.* 2016, Baker *et al.* 2017, Palk *et al.* 2017, Liu *et al.* 2019), but few  $\delta^{114/110}\text{Cd}$  data have been reported for sedimentary and metamorphic rock RMs such as shale SGR-1b (Tan *et al.* 2020), dolomite JDo-1 and amphibolite GSR-15. This study reports the  $\delta^{114/110}\text{Cd}$  values of thirty-four RMs (details given in Table S1) based on a  $^{111}\text{Cd}$ - $^{113}\text{Cd}$  double spike MC-ICP-MS method. It aims to enlarge the  $\delta^{114/110}\text{Cd}$  database of RMs for inter-laboratory cross-calibration and to improve our understanding of the variance of  $\delta^{114/110}\text{Cd}$  of natural reservoirs.

## Experimental procedure

### Reagents and materials

Hydrochloric, nitric and hydrofluoric acids used in the study were distilled by individual sub-boiling stills (Savillex™ DST-4500), twice for  $\text{HNO}_3$  and  $\text{HCl}$ , and once for  $\text{HF}$ . High purity water (HPW, resistivity =  $18.2 \text{ M}\Omega \text{ cm}$ ) was purified by a Milli-Q Element system (Burlington, MA, USA). All PFA beakers (Savillex™, Eden Prairie, MN, USA) were cleaned with 50% v/v  $\text{HNO}_3$ , 50% v/v  $\text{HCl}$  and HPW. Pipette tips were cleaned using 10% v/v  $\text{HNO}_3$  and HPW. The pre-treatment of all samples was performed in a class 1000 ultra-clean laboratory, and chemistry separation of Cd was accomplished in a class 100 hood at the Isotope Geochemistry Laboratory, China University of Geosciences (Beijing, China).

### Sample preparation and digestion

Four Cd reference solutions were analysed in this study: NIST SRM 3108 (Lot No. 130116), BAM-I012, Münster Cd and Spex Cd-CUGB ( $1000 \mu\text{g ml}^{-1}$  in 2% v/v  $\text{HNO}_3$ ; Cat: CLCD2-2Y; Lot: CL8-71CDY). NIST SRM 3108 is widely used as the 'delta-zero' Cd RM (Abouchami *et al.* 2013); BAM-I012 is a recognised Cd concentration and isotope RM provided by the Federal Institute for Materials Research and Testing, Germany (BAM) (Pritzkow *et al.* 2007) and recommended by the International Union of Pure and Applied Chemistry (IUPAC) (Brand *et al.* 2014, Meija *et al.* 2016). The Münster Cd solution (Wombacher and Rehkämper 2004) is a mixture of JMC Cd metal and evaporation

residues of Cd metal from Wombacher *et al.* (2004). Spex Cd-CUGB is our in-house Cd solution purchased from Merck (China) and was measured by Li *et al.* (2018) and Tan *et al.* (2020); this solution is derived from a different stock from the SPEX Cd and SPEX-1 Cd solutions used in previous studies (Cloquet *et al.* 2005, Gao *et al.* 2008, Wei *et al.* 2015, Yang *et al.* 2019). These reference solutions are widely used by different laboratories as quality control isotope RMs for cross-calibration (Gault-Ringold *et al.* 2012, Murphy *et al.* 2016, Wiggenhauser *et al.* 2016, Baker *et al.* 2017, Fouskas *et al.* 2018, Imseng *et al.* 2018, Li *et al.* 2018, Liu *et al.* 2019).

The digestion methods for all samples in this study were similar to those in Zhu *et al.* (2018) and Wu *et al.* (2019). In brief, in order to achieve sufficient Cd for high-precision isotope measurement results and to ensure fast and complete dissolution, four to six aliquots comprising ~ 50 mg powder of igneous rocks, such as BCR-2 and BHVO-2 with low Cd contents, were individually weighed into 15-ml PFA beakers. Samples were digested by a mixture of 2 ml HF (23 mol l<sup>-1</sup>) and 1 ml HNO<sub>3</sub> (15.8 mol l<sup>-1</sup>) and 4 ml *aqua regia* (HCl: HNO<sub>3</sub> = 3:1) successively. Completely digested aliquots of samples were remixed together for subsequent Cd purification. For soils, stream sediments and biological samples, high-pressure bombs were employed. Generally, ~ 100 mg of sample powder was accurately weighed into 30 ml PTFE-lined vials, and a 3.2 ml mixture of HF (23 mol l<sup>-1</sup>) and HNO<sub>3</sub> (15.8 mol l<sup>-1</sup>) was added. The PTFE-lined vials were loaded into high-pressure bombs and placed in an oven at 185 °C for 48 h. One millilitre of 30% *m/m* H<sub>2</sub>O<sub>2</sub> and 0.1–0.4 ml HF (23 mol l<sup>-1</sup>) were added after cooling. Sample solutions were then sealed on a hot plate for 1 h at 130 °C. After evaporation to dryness, samples were dissolved in 3 ml HNO<sub>3</sub> (15.8 mol l<sup>-1</sup>) and again placed in an oven at 185 °C for 24 h before being transferred to PFA beakers prior to the addition of 1 ml 30% *m/m* H<sub>2</sub>O<sub>2</sub> and 0.3 ml HF (23 mol l<sup>-1</sup>). Subsequently, solutions were heated at 130 °C for 2 h. After evaporation to dryness, samples were dissolved in 1 ml 10% *v/v* HNO<sub>3</sub>.

### Chromatographic analyte-matrix separation

The chemical purification procedures followed Tan *et al.* (2020). Before separation, sample aliquots containing 20–200 ng Cd were mixed with a <sup>111</sup>Cd-<sup>113</sup>Cd double spike solution with an optimised <sup>111</sup>Cd<sub>spike</sub>:<sup>112</sup>Cd<sub>sample</sub> ratio of 2.0. The mixed samples were reconstituted in a 2 ml, 2 mol l<sup>-1</sup> HCl medium and loaded into Muromac polypropylene columns preloaded with 2.8 ml acid-cleaned AGMP-1 M resin (100–200 mesh, Bio-Rad) and conditioned with 10 ml 2 mol l<sup>-1</sup> HCl. Cadmium was collected

using 20 ml 0.0012 mol l<sup>-1</sup> HCl after eluting the matrix elements. In order to avoid isobaric interference of residual Sn on Cd, the same separation procedures were repeated to purify Cd further. Finally, the purified samples were evaporated to dryness and dissolved in 1 ml 2% *v/v* HNO<sub>3</sub> for Cd isotope ratio measurements with a MC-ICP-MS. The recovery of the double-column procedures used in this study was consistently higher than 90%. The total procedural blank of Cd was below 90 pg.

### Double spike method

The double spike <sup>111</sup>Cd-<sup>113</sup>Cd method (Homer *et al.* 2010, Xue *et al.* 2012) was employed to correct for isotope fractionation during chemical purification and mass spectrometry (e.g., Rudge *et al.* 2009, Klaver and Coath 2018, Zhu *et al.* 2018, Wu *et al.* 2019, 2020). The <sup>111</sup>Cd (97.23%) and <sup>113</sup>Cd (93.35%) spikes were purchased from ISOFLEX (USA). As mentioned in Tan *et al.* (2020), the ratios of <sup>111</sup>Cd<sub>spike</sub>/<sup>113</sup>Cd<sub>spike</sub> in the double spike and <sup>111</sup>Cd<sub>spike</sub>/<sup>112</sup>Cd<sub>sample</sub> in the DS-sample mixture were optimised by the Monte Carlo and nest iteration method (e.g., Russell *et al.* 1978, Johnson *et al.* 1999, Rudge *et al.* 2009, Tan *et al.* 2020). With an optimal <sup>111</sup>Cd<sub>spike</sub>/<sup>113</sup>Cd<sub>spike</sub> ratio of 1.5, the ideal range of <sup>111</sup>Cd<sub>spike</sub>/<sup>112</sup>Cd<sub>sample</sub> was 0.8–6.0, in which the measured δ<sup>114/110</sup>Cd value did not show obvious shifts (Tan *et al.* 2020). The <sup>111</sup>Cd<sub>spike</sub>/<sup>113</sup>Cd<sub>spike</sub> in the double spike was calibrated to be 1.549727 using <sup>107</sup>Ag/<sup>109</sup>Ag of 1.076378, and the isotope ratio of NIST SRM 3108 was also calibrated by this Ag method (Tan *et al.* 2020). In this study, the optimum mixing ratio <sup>111</sup>Cd<sub>spike</sub>/<sup>112</sup>Cd<sub>sample</sub> of 2.0 was employed for all samples.

### Mass spectrometry

Cadmium isotope ratios were determined on a Neptune Plus MC-ICP-MS at the Isotope Geochemistry Laboratory, China University of Geosciences (Beijing). The instrument was equipped with nine Faraday cups connected to 10<sup>11</sup> Ω resistors in the standard amplifiers. Static and low-resolution modes were adopted, and typical operating conditions and instrument parameters were similar to Tan *et al.* (2020). Sample solutions containing 10 ng g<sup>-1</sup> Cd in 2% *v/v* HNO<sub>3</sub> + 0.1% *v/v* HF were introduced into the plasma by an improved Aridus II desolvator (100 μl min<sup>-1</sup>) with an ice chamber (Wu *et al.* 2020). The signal of <sup>112</sup>Cd was approximately 640 V per μg g<sup>-1</sup>. Indium was scanned before the sequence measurements, and the typical ion beam intensity of <sup>115</sup>In<sup>+</sup> was below 0.2 mV, which was negligible compared with Cd signals. Tin (Sn) interferences on Cd were monitored by <sup>117</sup>Sn<sup>+</sup> (117 *m/z*). Other details

of the isobaric interferences and matrices are discussed in Tan *et al.* (2020).

In order to monitor instrumental stability and normalise the sample data, spiked NIST SRM 3108 was measured every three to four samples. Cadmium isotope data are reported in the delta notation ( $\delta$ ) as parts per thousand deviation relative to NIST SRM 3108:

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

The measured Cd isotope ratios were reduced via offline calculation in an EXCEL worksheet. The double spike method was applied to samples as well as the bracketing standard (calibrator). Within some measurement sessions, the drift in the  $\delta^{114/110}\text{Cd}$  of spiked NIST SRM 3108 was typically  $< 0.1\%$  on the Neptune Plus instrument after double spike reduction, and the  $\delta^{114/110}\text{Cd}$  values of samples were normalised to the mean of bracketing NIST SRM 3108 measurement results:

$$\delta^{114/110}\text{Cd}_{\text{corrected - sample}} = \delta^{114/110}\text{Cd}_{\text{sample}} - \delta^{114/110}\text{Cd}_{\text{NIST SRM 3108}} \quad (2)$$

As different notation and 'delta-zero' reference isotope standards have been used in previous studies (e.g., Cloquet *et al.* 2005, Schmitt *et al.* 2009a, Horner *et al.* 2010), we converted literature data discussed in this study to  $\delta^{114/110}\text{Cd}$  relative to NIST SRM 3108 according to Wombacher and Rehkämper (2004) and Abouchami *et al.* (2013).

The double spike method also yields the Cd mass fractions (Tables 1 and 2) according to the following simple formula (details in Appendix A):

$$\omega(\text{Cd}) = \omega(\text{Cd})_R \times \frac{R_0}{R_T} \quad (3)$$

where  $\omega(\text{Cd})$  is Cd mass fraction recalibrated by double spike method;  $\omega(\text{Cd})_R$  is the Cd mass fraction recommended by GeoReM or information in the literature, and this value was adopted for mixing the sample solution and double spike;  $R_T$  is the true ratio of  $^{111}\text{Cd}_{\text{spike}}:^{112}\text{Cd}_{\text{sample}}$  reduced by the double spike program code;  $R_0$  is the given ratio ( $^{111}\text{Cd}_{\text{spike}}:^{112}\text{Cd}_{\text{sample}} = 2.0$ ) of spiked samples.

## Results and discussion

In this study, reference solutions (NIST SRM 3108, Münster Cd, BAM-I012, Spex Cd-CUGB) and well-studied

geological RMs were repeatedly measured to assess the intermediate measurement precision over a period of one year. The long-term determined  $\delta^{114/110}\text{Cd}$  values of NIST SRM 3108, BAM I012 and Spex Cd -CUGB on the Neptune Plus instrument at the  $10 \text{ ng g}^{-1}$  level were  $0.000 \pm 0.049\%$  ( $2s$ ,  $n = 36$ ),  $-1.337 \pm 0.043\%$  ( $2s$ ,  $n = 16$ ) and  $-2.113 \pm 0.041\%$  ( $2s$ ,  $n = 13$ ). These results agree well with those determined by other laboratories within stated precisions (Cloquet *et al.* 2005, Gault-Ringold *et al.* 2012, Yang *et al.* 2012, Abouchami *et al.* 2013, Murphy *et al.* 2016, Li *et al.* 2018).

### Recommended $\delta^{114/110}\text{Cd}$ values of nine reported RMs

The  $\delta^{114/110}\text{Cd}$  of geological RMs, BCR-2, BHVO-2, NOD-A-1, NOD-P-1, GSD-7a and NIST SRM 2711a (Table 1 and Figure 1) determined in our laboratory were  $0.008\%$  ( $n = 6$ ),  $0.021\%$  ( $n = 6$ ),  $0.127 \pm 0.035\%$  ( $2s$ ,  $n = 7$ ),  $0.135\%$  ( $n = 4$ ),  $-0.034\%$  ( $2s$ ,  $n = 6$ ) and  $0.561 \pm 0.055\%$  ( $2s$ ,  $n = 28$ ), respectively, which matched published values (Cloquet *et al.* 2005, Schmitt *et al.* 2009b, Pallavicini *et al.* 2014, Du 2015, Li *et al.* 2018, Liu *et al.* 2019, Borovička *et al.* 2021). The  $\delta^{114/110}\text{Cd}$  of SGR-1b and GSD-21 measured in this study were consistent with our published values (Tan *et al.* 2020). The intermediate precision of  $\delta^{114/110}\text{Cd}$  values was better than  $\pm 0.074\%$  ( $2s$ ,  $n = 9$  for GBW08401) based on the long-term independent measurement of different geological RMs with highly variable matrices and Cd mass fractions ( $0.064 \mu\text{g g}^{-1}$  to  $45.04 \mu\text{g g}^{-1}$ , Tables 1 and 2). Hence, the intermediate precision,  $\pm 0.074\%$  ( $2s$ ), was applied to all samples analysed fewer than three times (Table 2). Data for individual measurement results of all RMs (Table S1) are listed in Table S2 and S3.

Previous work reported the  $\delta^{114/110}\text{Cd}$  of the geological RMs mentioned but their measures of variance were reported differently. Here we calculate the 95% confidence intervals for previously reported data that take Student's  $t$ -distribution into account:

$$U = \frac{s}{\sqrt{p}} t_{\alpha/2}(p-1) \quad (4)$$

where  $U$  is uncertainty;  $s$  is the standard deviation of independent means of the individual laboratory results;  $\alpha$  is confidence level, in this study  $\alpha = 0.05$ ;  $p$  is the number of independent measurement results;  $t_{\alpha/2}(p-1)$  is the critical value which is based on  $(p-1)$  degrees of freedom.

The calculated uncertainty is better than  $0.090\%$  when independent results are more than three (Table 1) according

**Table 1.**  
The recommended  $\delta^{114/110}\text{Cd}$  values for commonly used reference materials

Sample name <sup>a</sup>	Sample type	Cd <sup>b</sup> ( $\mu\text{g g}^{-1}$ )	Reference	Measurement	Method <sup>c</sup>	$\delta^{114/110}\text{Cd}$ (%)	2s <sup>d</sup>	P <sup>e</sup>	U <sup>f</sup>	N <sup>g</sup>	
BCR-2	Basalt	0.18 (0.69)	This study	Replicate	DS	0.009	0.027	3	0.063	3	
				Replicate	DS	0.007	0.050			3	
				Overall mean			0.008			0.074	6
							0.018			0.067	14
Recommended BHVO-2	Basalt	0.09 (0.152)	This study	Replicate	DS	-0.030	0.063	3	0.090	4	
				Replicate	DS	-0.001	0.051			3	
				Overall mean			0.042			0.066	3
							0.000			0.034	3
Recommended SGR-1b	Shale	0.91	This study	Replicate	DS	0.021	0.074	2	0.093	6	
				Replicate	DS	0.039	0.047			8	
				Overall mean			0.021			0.074	6
							0.039			0.047	8
Recommended NOD-A-1	Mn-Nodule	6.13	This study	Replicate	DS	-0.031	0.077	3	0.090	4	
				Replicate	DS	0.010	0.073			3	
				Overall mean			0.061			0.031	3
							0.047			0.023	3
Recommended NOD-P-1	Mn-Nodule	17.49	This study	Replicate	DS	0.054	0.074	9	0.038	6	
				Replicate	DS	0.069	0.049			6	
				Overall mean			0.062			0.021	2
							0.139			0.057	3
							0.107				2
							0.134				2
							0.127			0.035	7
							-0.070			0.120	
							0.122			0.032	2
							0.210			0.120	2
							0.086			0.031	4
							0.170			0.050	2
							0.160			0.100	4
							0.040			0.060	6
Recommended GSD-7a	Sediment	7.48	This study	Replicate	DS	0.124	0.067	10	0.018	14	
				Replicate	DS	0.12	0.01			4	
				Overall mean			0.129			0.098	9
							0.145			0.018	3
							0.126				1
							0.135			0.074	4
							0.130			0.120	
							0.160			0.032	2
							0.180			0.120	3
							0.120			0.038	4
							0.160			0.080	4
							0.090			0.050	6
							0.163			0.040	8
							0.133			0.038	23
			0.14	0.07	5						
Recommended	Sediment	7.48	This study	Replicate	DS	0.141	0.052	3	0.086	3	
				Replicate	DS	0.033	0.033			3	
				Overall mean			0.036			0.010	6
							0.034			0.074	6
Recommended	Sediment	7.48	Du (2015)	Replicate	SSB	-0.020	0.120	3	0.086	8	
				Replicate	DS	-0.030	0.033			8	
Recommended	Sediment	7.48	Tan et al. (2020)	Replicate	DS	-0.005	0.069	3	0.086	8	

**Table 1 (continued).**  
The recommended  $\delta^{114/110}\text{Cd}$  values for commonly used reference materials

Sample name <sup>a</sup>	Sample type	Cd <sup>b</sup> ( $\mu\text{g g}^{-1}$ )	Reference	Measurement	Method <sup>c</sup>	$\delta^{114/110}\text{Cd}$ (‰)	2s <sup>d</sup>	p <sup>e</sup>	U <sup>f</sup>	N <sup>g</sup>			
GSD-12	Sediment	3.78 (4)	This study	Replicate	DS	-0.081	0.049	4	0.083	3			
			This study	Replicate	DS	-0.115				2			
			This study	Replicate	DS	-0.092	0.021			3			
Overall mean						-0.096	0.035			8			
						Cloquet <i>et al.</i> (2005)				SSB	-0.380	0.120	
						Du (2015)				SSB	0.010	0.170	4
						Li <i>et al.</i> (2018)				SSB	0.000	0.130	3
						Yang <i>et al.</i> (2019)				SSB	0.290	0.050	
						Tan <i>et al.</i> (2020)				DS	-0.071	0.060	8
											-0.039	0.104	
Recommended GSD-21	Sediment	0.71	This study	Replicate	DS	0.020	0.025	2	0.211	3			
			This study	Replicate	DS	0.029	0.021			3			
Overall mean						0.024	0.074			6			
						Tan <i>et al.</i> (2020)				DS	-0.009	0.009	4
Recommended NIST SRM 2711a	Soil	45.04				0.008	0.047						
						This study	Replicate			DS	0.568	0.009	3
						This study	Replicate			DS	0.587	0.027	4
						This study	Replicate			DS	0.513	0.019	4
						This study	Replicate			DS	0.555	0.048	5
						This study	Replicate			DS	0.558	0.044	9
						This study	Replicate			DS	0.586	0.010	3
						Overall mean					0.561	0.055	28
											0.570	0.070	5
											0.551	0.051	8
Recommended						0.532	0.038			26			
						Borovička <i>et al.</i> (2021)				DS	0.57	0.05	9
											0.557	0.032	5
													0.020

<sup>a</sup> Individual mean is the arithmetic mean of the same purified sample measured on different instruments. Overall mean is the arithmetic mean of replicate analyses (independent digestions of different aliquots of bulk raw sample powder, column chemistry and measurement) in this study. The recommended value is calculated from the arithmetic mean of independent data in this study and literature.

<sup>b</sup> The data in brackets are the recommended values in GeoReM database (Jochum *et al.* 2005).

<sup>c</sup> DS, double spike; SSB, sample-standard bracketing.

<sup>d</sup> Intermediate measurement precision ( $\pm 0.074\%$ ) is used for samples analysed less than three times.

<sup>e</sup> Number of independent results.

<sup>f</sup> The uncertainty  $U$  is calculated from 95% confidence interval of independent replicate analyses that take the Student  $t$ -distribution into account.

<sup>g</sup> Number of analyses.

to the compiled data published in all literature and this study. The recommended  $\delta^{114/110}\text{Cd}$  values are calculated as the arithmetic mean of literature data and our result (Table 1).

Data with significant differences (outside of 2s of all literature data) from those of other laboratories were excluded before the calculation of recommended values and uncertainties. Excluded data include a stream sediment GSD-12 from Cloquet *et al.* (2005) and Yang *et al.* (2019) and the manganese nodule NOD-A-1 from Cloquet *et al.* (2005). What these two papers had in common was centrifugation before chromatographic separation, which could lead to the lower Cd recovery if sample digestions were not complete. The different digestion procedures, assessed by the sample–standard bracketing (SSB) method in Park *et al.* (2020), can lead to large variation ( $-0.20 \pm 0.13\%$  to  $0.51 \pm 0.22\%$ ) of the measured

$\delta^{114/110}\text{Cd}$  of soil RM NIST SRM 2711a at an ~ 90% recovery. For GSD-12, Cloquet *et al.* (2005) reported  $-0.38 \pm 0.12\%$  while Yang *et al.* (2019) reported  $0.29 \pm 0.05\%$ . The stated recoveries of both studies were higher than 95% and both studies used the SSB method. Centrifugation before Cd purification and SSB were also used for biological samples by Pallavicini *et al.* (2014), but the difference in the  $\delta^{114/110}\text{Cd}$  value between centrifuged and uncentrifuged sample was  $< 0.1\%$  when Cd recovery was above 95%. These observations suggest that the complete digestion of samples with complex matrices such as soils and sediments is necessary for the precise and accurate determination of  $\delta^{114/110}\text{Cd}$ , especially using the SSB method.

The Cd mass fractions of nine RMs were recalibrated using the double spike method (Table 1), which produced lower values than those values recommended in the

**Table 2.**  
The  $\delta^{114/110}\text{Cd}$  values of new reference materials reported in this study

Sample name <sup>a</sup>	Sample type	Cd <sup>b</sup> ( $\mu\text{g g}^{-1}$ )	Measurement	$\delta^{114/110}\text{Cd}$ (‰)	2s	N
GSR-15	Amphibolite	0.11 (0.14)	Replicate	0.040	0.040	3
			Replicate	0.009	0.009	3
			Replicate	-0.029	0.035	3
Overall mean			0.007	0.069	9	
JDo-1	Dolomite	0.58 (0.644)	Replicate	0.008	0.057	3
			Replicate	-0.010	0.017	3
			Replicate	0.009	0.038	3
Overall mean			0.002	0.022	9	
GSMC-1	Cobalt-rich crust	2.71 (4)	Replicate	0.264	0.024	3
			Replicate	0.264	0.027	3
			Replicate	0.234	0.047	3
Overall mean			0.254	0.035	9	
GSMC-2	Cobalt-rich crust	2.05 (3.6)	Replicate	0.295	0.008	3
			Replicate	0.293	0.071	3
			Replicate	0.277	0.030	3
			Replicate	0.285	0.008	3
Overall mean			0.287	0.017	12	
GSMC-3	Cobalt-rich crust	2.46 (3.3)	Replicate	0.267	0.012	3
			Replicate	0.249	0.046	3
			Replicate	0.233	0.053	3
Overall mean			0.250	0.034	9	
GSS-27	Stream sediment	0.55	Replicate	-0.004	0.041	3
			Replicate	0.007	0.031	3
			Replicate	0.017	0.047	3
Overall mean			0.007	0.021	9	
GSD-15	Stream sediment	0.31	Replicate	-0.205	0.016	3
			Replicate	-0.208	0.010	3
			Replicate	-0.236	0.073	3
Overall mean			-0.217	0.035	9	
JSd-2	Stream sediment	3.12	Replicate	-0.354	0.019	3
			Replicate	-0.412	0.022	4
			Replicate	-0.350	0.016	3
			Replicate	-0.376	0.013	3
Overall mean			-0.373	0.057	13	
JSd-3	Stream sediment	0.91	Replicate	-0.221	0.014	3
			Replicate	-0.252	0.069	4
			Replicate	-0.258	0.044	3
			Replicate	-0.245	0.016	3
Overall mean			-0.244	0.032	13	
GBW07319	Stream sediment	3.59 (3.76)	Replicate	-0.130	0.053	3
			Replicate	-0.141	0.040	3
			Replicate	-0.148	0.014	3
			Replicate	-0.095	0.037	3
Overall mean			-0.129	0.047	12	
GBW07323	Stream sediment	0.29 (0.33)	Replicate	-0.049	0.012	3
			Replicate	-0.085	0.016	3
			Replicate	-0.040	0.074 <sup>c</sup>	2
Overall mean			-0.058	0.048	8	
GBW07325	Stream sediment	0.49 (0.57)	Replicate	-0.042	0.057	3
			Replicate	-0.039	0.071	3
			Replicate	-0.069	0.036	3
Overall mean			-0.050	0.033	9	
MNS-1	Marine sediment	0.26 (0.25)	Replicate	-0.087	0.047	3
			Replicate	-0.107	0.022	3
			Replicate	-0.099	0.038	3
Overall mean			-0.098	0.021	9	
MS-E1	Marine sediment	0.064 (0.2)	Replicate	-0.145	0.037	3
			Replicate	-0.200	0.028	3
			Replicate	-0.160	0.027	3
Overall mean			-0.168	0.057	9	

**Table 2 (continued).**  
The  $\delta^{114/110}\text{Cd}$  values of new reference materials reported in this study

Sample name <sup>a</sup>	Sample type	Cd <sup>b</sup> ( $\mu\text{g g}^{-1}$ )	Measurement	$\delta^{114/110}\text{Cd}$ (‰)	2s	N
MS-S1	Marine sediment	0.22 (0.31)	Replicate	-0.145	0.050	3
			Replicate	-0.121	0.032	3
			Replicate	-0.161	0.078	3
Overall mean				-0.142	0.041	9
GSS-25	Loess	0.14	Replicate	-0.083	0.028	3
			Replicate	-0.090	0.047	3
			Replicate	-0.087	0.046	3
			Replicate	-0.110	0.019	3
Overall mean				-0.093	0.024	12
GBW08401	Coal fly ash	0.13 (0.16)	Replicate	-0.728	0.030	3
			Replicate	-0.672	0.034	3
			Replicate	-0.658	0.053	3
Overall mean				-0.686	0.074	9
GBW08503c	Wheat flour	0.18 (0.211)	Replicate	0.112	0.032	3
			Replicate	0.121	0.065	3
			Replicate	0.088	0.022	3
Overall mean				0.107	0.035	9
GBW08517	<i>Laminaria japonica</i> Aresch	1.1 (1.14)	Replicate	-0.425	0.002	3
			Replicate	-0.481	0.039	3
			Replicate	-0.442	0.033	3
Overall mean				-0.449	0.057	9
GSB-14	<i>Porphyra</i>	0.62	Replicate	-0.410	0.036	3
			Replicate	-0.439	0.014	3
			Replicate	-0.436	0.024	3
Overall mean				-0.429	0.032	9
GSB-15	Scallop	1.06	Replicate	-0.780	0.043	3
			Replicate	-0.800	0.022	3
			Replicate	-0.817	0.058	3
			Replicate	-0.828	0.026	3
Overall mean				-0.806	0.041	12
GSB-16	<i>Spirulina platensis</i>	0.39	Replicate	-0.038	0.041	3
			Replicate	-0.073	0.053	3
			Replicate	-0.097	0.006	3
Overall mean				-0.069	0.059	9
GSB-27	Scallion	0.17	Replicate	0.129	0.062	3
			Replicate	0.155	0.034	3
			Replicate	0.141	0.045	3
Overall mean				0.142	0.025	9
GSB-29	Pork liver	0.99	Replicate	-0.574	0.007	3
			Replicate	-0.643	0.021	3
			Replicate	-0.616	0.014	3
Overall mean				-0.611	0.069	9
GSV-3	Poplar leaves	0.35 (0.33)	Replicate	-0.120	0.022	3
			Replicate	-0.163	0.019	3
			Replicate	-0.107	0.010	3
Overall mean				-0.130	0.058	9

<sup>a</sup> Individual mean is the arithmetic mean of the same purified sample measured on different instruments. Overall mean is the arithmetic mean of replicate (independent digestions of different aliquots of bulk raw sample powder, column chemistry and measurement) analyses in this study.

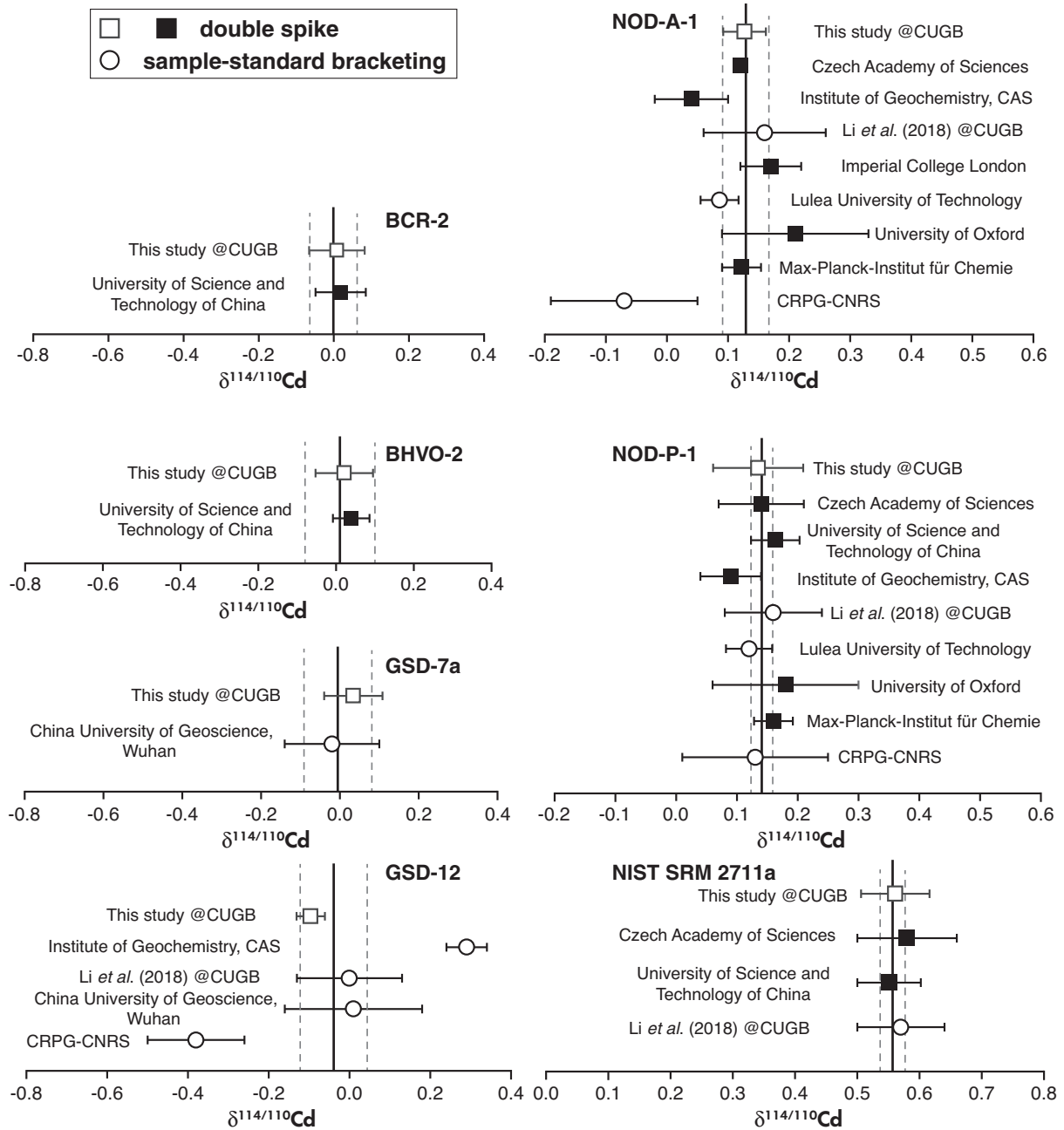
<sup>b</sup> The data in brackets are the recommended values from the GeoReM database (Jochum *et al.* 2005).

<sup>c</sup> Intermediate measurement precision ( $\pm 0.074\%$ ) is used for samples analysed fewer than three times.

GeoReM database. We propose that the difference can be attributed to polyatomic interferences. Elements such as Zr, Mo and Zn can produce polyatomic interference ( $\text{ZrO}^+$ ,  $\text{MoO}^+$ ,  $\text{ZnAr}^+$ , etc.) on Cd isotopes when determining Cd mass fractions of unpurified samples by ICP-MS (Tan *et al.* 2020). Moreover, the mass fractions of Zr, Mo and Zn in many RMs, such as basalt, sediment and uncontaminated soil, are much

higher than that of Cd (Table S2). Thus, a false high Cd mass fraction would be obtained from unpurified samples measured on an ICP-MS. Although the recommended values of RMs in GeoReM and the literature are from various analytical techniques such as ICP-MS, ICP-AES, AAS and XRF, ICP-MS is still the dominant method. When chemical separation of Cd from these elements is done, the



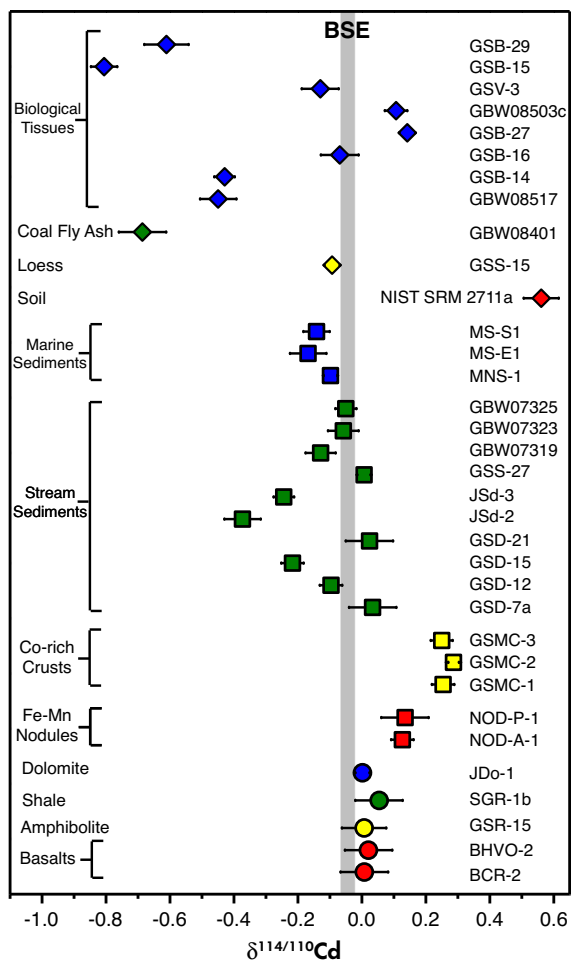


**Figure 1. Comparison of mean  $\delta^{114/110}\text{Cd}$  values for geological reference materials obtained in our laboratory and others. Range bars represent two standard deviations. The vertical solid and dotted lines represent the recommended arithmetic mean (Table 1) and corresponding uncertainty (95% confidence intervals).**

corresponding interference signals are eliminated. Consequently, the recalibrated Cd mass fractions by the double spike method in this study are lower than the recommended values in the GeoReM database (Jochum *et al.* 2005) or certificates provided by commercial suppliers (Table S2).

### $\delta^{114/110}\text{Cd}$ values of rock, sediment and soil RMs

Amphibolite GSR-15 is reported for the first time with a  $\delta^{114/110}\text{Cd}$  value of  $0.007 \pm 0.069\text{‰}$  ( $2s$ ;  $n = 9$ ), which is within precision the same as the mean value



**Figure 2.** The  $\delta^{114/110}\text{Cd}$  values of geological reference materials measured in this study. Range bars represent two standard deviations. The grey vertical bar represents the  $\delta^{114/110}\text{Cd}$  range of the Bulk Silicate Earth ( $-0.042 \pm 0.024\text{‰}$ ; Schmitt *et al.* 2009b).

( $-0.030 \pm 0.097\text{‰}$ ,  $2s$ ,  $n = 7$ ) of published basalt samples (Schmitt *et al.* 2009b, Liu *et al.* 2019) and the bulk silicate earth (BSE) value of  $-0.042 \pm 0.024\text{‰}$  (Schmitt *et al.* 2009b). This limited set of igneous and metamorphic rock RMs suggests lack of Cd isotope fractionation in high-temperature rocks.

The  $\delta^{114/110}\text{Cd}$  values of shale and carbonate rocks have been used to evaluate ancient marine productivity (Georgiev *et al.* 2015, John *et al.* 2017, Zhang *et al.* 2018), yet the  $\delta^{114/110}\text{Cd}$  of shale and carbonate RMs are still lacking. As shales SDO-1 and SCO-1 have been discontinued, we measured shale SGR-1b with a  $\delta^{114/110}\text{Cd}$  value of  $0.054 \pm 0.074\text{‰}$ , in agreement with  $0.069 \pm 0.049\text{‰}$

( $2s$ ,  $n = 6$ ) reported by Tan *et al.* (2020). However, the measured Cd mass fraction ( $0.91 \mu\text{g g}^{-1}$ ) in this study was different from the  $0.65 \mu\text{g g}^{-1}$  value reported by Tan *et al.* (2020). Since all purification and analytical protocols were identical between the two studies, the disparity is probably due to heterogeneity of the powder. However, further experiments are needed to identify the cause of this difference, whether due to sample heterogeneity or sample preparation and measurement (Meisel *et al.* 2001). The  $\delta^{114/110}\text{Cd}$  value of SGR-1b is within the range of  $-0.50\text{‰}$  to  $0.24\text{‰}$  of published shales (Wombacher *et al.* 2003, Georgiev *et al.* 2015), suggesting that SGR-1b could be an alternative shale RM to replace the discontinued SDO-1. Furthermore, we report the  $\delta^{114/110}\text{Cd}$  value of dolomite JDo-1 ( $0.002 \pm 0.022\text{‰}$ ; Table 2 and Figure 2) for the first time, falling into the range of carbonates ( $-0.27\text{‰}$  to  $0.60\text{‰}$ ) presented by John *et al.* (2017) and Zhang *et al.* (2018), but lower than that of the modern deep seawater value of  $0.2\text{--}0.5\text{‰}$  (Ripperger *et al.* 2007, Yang *et al.* 2012, Xue *et al.* 2013, Conway and John 2015a,b, Janssen *et al.* 2017). The large difference of  $\delta^{114/110}\text{Cd}$  within shale or carbonate rocks is usually attributed to fluctuations in primary productivity (Georgiev *et al.* 2015, Zhang *et al.* 2018).

Three hydrogenetic cobalt-rich ferromanganese crusts GSMC-1, GSMC-2 and GSMC-3 (Table 2 and Figure 2) from the eastern and central Pacific Ocean were analysed for the first time with  $\delta^{114/110}\text{Cd}$  values of  $0.254 \pm 0.035\text{‰}$  ( $2s$ ,  $n = 9$ ),  $0.287 \pm 0.017\text{‰}$  ( $2s$ ,  $n = 12$ ) and  $0.250 \pm 0.034\text{‰}$  ( $2s$ ,  $n = 9$ ), respectively, which are indistinguishable from six other Pacific crusts ( $0.20\text{--}0.41\text{‰}$ ) reported by Horner *et al.* (2010) and fall within the range of Pacific deep water ( $0.2\text{--}0.3\text{‰}$ ; Ripperger *et al.* 2007, Conway and John 2015b, Janssen *et al.* 2017, John *et al.* 2018, Sieber *et al.* 2019). Adsorption of Cd onto iron and manganese (oxyhydr)oxides is probably the dominant factor affecting the enrichment of Cd in cobalt-rich crusts. Moreover, the adsorption experiments using birnessite in synthetic seawater showed that  $\Delta^{114/110}\text{Cd}_{\text{fluid-solid}}$  ( $\Delta^{114/110}\text{Cd}_{\text{fluid-solid}} = \delta^{114/110}\text{Cd}_{\text{fluid}} - \delta^{114/110}\text{Cd}_{\text{solid}}$ ) was  $0.2\text{‰}$  after 912 h (Wasylenki *et al.* 2014), although adsorption equilibrium was still not reached. The minimal fractionation between crusts and deep seawater suggested that Co-rich crusts could faithfully record the Cd isotope signature of the ambient seawater (Horner *et al.* 2010), and it may serve as a long-term archive of seawater  $\delta^{114/110}\text{Cd}$ . The formation of ferromanganese nodules is more complicated than cobalt-rich ferromanganese crusts, probably involving hydrogenetic, hydrothermal and diagenetic processes (Bau *et al.* 2014). Our measured  $\delta^{114/110}\text{Cd}$  values for nodules NOD-A-1 ( $0.127 \pm 0.035\text{‰}$ ) and NOD-P-1 ( $0.135 \pm 0.074\text{‰}$ ), both ferromanganese nodules, are approximately  $0.1\text{‰}$

lower than those of Co-rich crusts and deep seawater, probably due to the influence of hydrothermal activities. This implies that Cd isotopes have the potential to trace the formation processes of ferromanganese nodule and/or crust.

The  $\delta^{114/110}\text{Cd}$  values of marine sediments MNS-1, MS-E1 and MS-S1 (Table 2 and Figure 2) from adjacent seas of China are  $-0.098 \pm 0.021\text{‰}$  (2s),  $-0.168 \pm 0.057\text{‰}$  (2s) and  $-0.142 \pm 0.041\text{‰}$  (2s), respectively. Another marine sediment, PACS-2, from the National Research Council of Canada, yields a  $\delta^{114/110}\text{Cd}$  value of  $-0.204 \pm 0.040\text{‰}$  (Pallavicini *et al.* 2014), slightly lower than MNS-1 but consistent with MS-E1 and MS-S1. Marine sediments are isotopically lighter than seawater, with  $\Delta^{114/110}\text{Cd}_{\text{seawater-marine sediment}} (\delta^{114/110}\text{Cd}_{\text{seawater}} - \delta^{114/110}\text{Cd}_{\text{marine sediment}} \geq 0.3\text{‰})$  much larger than that of ferromanganese crusts. This can be explained by preferential adsorption of low atomic number (light) Cd isotopes onto clay minerals (Wasylenki *et al.* 2014). MNS-1, MS-E1 and MS-S1 are mainly composed of silty sands with varying proportions of clays (Wang *et al.* 2009). The  $\delta^{114/110}\text{Cd}$  values of loess that consists of silts and clays range from  $-0.056\text{‰}$  to  $0.031\text{‰}$  (Schmitt *et al.* 2009b), which are higher than marine sediments by  $0.037\text{--}0.216\text{‰}$ . However, if the Cd isotopic difference between seawater and marine sediments is induced by clay mineral adsorption, the fractionation would be more than  $0.3\text{‰}$ , which is larger than the non-equilibrium fractionation value obtained in Wasylenki *et al.* (2014). Future adsorption experiments that reach adsorption equilibrium are needed to confirm this conjecture. Furthermore, the Cd mass fraction ( $0.06\text{--}0.3 \mu\text{g g}^{-1}$ ) in marine sediments is 1 to 5 times higher than that in the upper continental crust and BSE (McDonough and Sun 1995, Rudnick and Gao 2003), indicating that marine sediments are potentially important sinks of light Cd isotopes from seawater.

The  $\delta^{114/110}\text{Cd}$  values of stream sediments range widely from  $-0.373\text{‰}$  to  $0.034\text{‰}$ , with a mean of  $-0.110 \pm 0.251\text{‰}$  (2s,  $n = 10$ ). Many of the stream sediment values are lower than the BSE range (Figure 2). In addition, the stream sediment  $\delta^{114/110}\text{Cd}$  is also evidently lighter than that of deep seawater ( $0.2\text{--}0.5\text{‰}$ ; Ripperger *et al.* 2007, Yang *et al.* 2012, Conway and John 2015a,b, John *et al.* 2018). These stream sediments of the GSD series were collected from different mines and major rivers in China. Previous studies mainly focused on high Cd samples (GSD-5a, GSD-6, GSD-7a, GSD-10, GSD-11, GSD-12, GSD-17, GSD-21, GSD-23). Among these samples, GSD-10 was collected from the Carboniferous and Permian carbonate terrain in the middle reach of Xijiang River in south China and yielded a  $\delta^{114/110}\text{Cd}$  value of  $-0.046 \pm 0.028\text{‰}$  (2s,

$n = 3$ ; Tan *et al.* 2020). Other high Cd stream sediments of the GSD series were taken from ore fields, with  $\delta^{114/110}\text{Cd}$  varying from  $-0.305\text{‰}$  to  $0.071\text{‰}$  (Pallavicini *et al.* 2014, Du 2015, Li *et al.* 2018, Tan *et al.* 2020), which probably represent the  $\delta^{114/110}\text{Cd}$  values of the weathering residues of Cd-rich ore bodies. These data suggest minor spatial  $\delta^{114/110}\text{Cd}$  variations in stream sediments from different mining areas in China, and the Cd mass fractions of these sediments are relatively high. Published Cd-rich deposits have a wide range of  $\delta^{114/110}\text{Cd}$  values from  $-0.38\text{‰}$  to  $0.70\text{‰}$  (Wen *et al.* 2016), and low-temperature deposits with the highest Cd mass fractions (mean  $0.9 \text{ mg g}^{-1}$ ) have the highest  $\delta^{114/110}\text{Cd}$  values ( $0.09\text{‰}$  to  $0.70\text{‰}$ ). However, this heavy Cd isotope signal is not inherited by stream sediments, indicating that heavy Cd isotopes preferentially run off to water during weathering. This is consistent with river water and seawater holding positive  $\delta^{114/110}\text{Cd}$  values (mainly between  $0.2\text{‰}$  and  $1.0\text{‰}$ ; Ripperger *et al.* 2007, Yang *et al.* 2012, Xue *et al.* 2013, Conway and John 2015a,b, Janssen *et al.* 2017).

In order to evaluate the background  $\delta^{114/110}\text{Cd}$  value of stream sediments in China, we analysed the sediment sample GSS-27 taken from the Yangtze River estuary, the largest river in China. The  $\delta^{114/110}\text{Cd}$  value of GSS-27 was  $0.007 \pm 0.021\text{‰}$  (2s), approaching the BSE value of  $-0.042 \pm 0.024\text{‰}$  (Schmitt *et al.* 2009b). Three stream sediments GBW07319, GBW07323 and GBW07325 from the Tibetan Plateau, the source of major rivers in east and south Asia (including the Yangtze River), yielded  $\delta^{114/110}\text{Cd}$  values of  $-0.129 \pm 0.047\text{‰}$  (2s),  $-0.058 \pm 0.048\text{‰}$  (2s) and  $-0.050 \pm 0.033\text{‰}$  (2s), respectively. They are consistent with the BSE. In summary, the  $\delta^{114/110}\text{Cd}$  values of background stream sediments (not ore-related) are similar to BSE but significantly lower than river water, suggesting that heavy Cd isotopes tend to be released into rivers, although the amount of Cd release is very limited.

The  $\delta^{114/110}\text{Cd}$  of contaminated stream sediments JSd-2 and JSd-3 (Table 2 and Figure 2) from Japan were reported to be  $-0.373 \pm 0.057\text{‰}$  (2s,  $n = 13$ ) and  $-0.244 \pm 0.032\text{‰}$  (2s,  $n = 13$ ), respectively, close to ore field stream sediments GSD-11 ( $-0.305 \pm 0.054\text{‰}$ ; Pallavicini *et al.* 2014) and GSD-15 ( $-0.217 \pm 0.035\text{‰}$ ), but significantly lower than most stream sediments mentioned above. This may be related to the mineralisation of the source rocks in the catchment area of the stream from which the sample was taken (Shigeru *et al.* 1990).

Loess is commonly used to estimate the geochemical composition of the upper continental crust (Rudnick and Gao 2003). Due to its low Cd mass fraction, limited Cd isotopic

data have been reported for loess. We determined the  $\delta^{114/110}\text{Cd}$  value of one loess RM, GSS-25 ( $-0.093 \pm 0.024\%$ , 2s; Table 2 and Figure 2), close to the other three loess samples ( $-0.056$ – $-0.031\%$ ) analysed by Schmitt *et al.* (2009b). The mean  $\delta^{114/110}\text{Cd}$  value of these four loess samples is  $-0.035 \pm 0.087\%$  (95% CL), which, if taken as representative of the upper continental crust, is indistinguishable from the BSE value of  $-0.042 \pm 0.024\%$  (Schmitt *et al.* 2009b). However, whether the  $\delta^{114/110}\text{Cd}$  value of the upper continental crust can be accurately represented by loess still needs to be confirmed by further studies.

The coal fly ash GBW08401 had a  $\delta^{114/110}\text{Cd}$  value of  $-0.686 \pm 0.074\%$  (2s; Table 2 and Figure 2), which is significantly higher than the coal ash ( $-0.86 \pm 0.02\%$ ) determined by Martinková *et al.* (2016), but lower than the coal fly ash ( $-0.51$ – $-0.47\%$ ) presented by Fouskas *et al.* (2018). Evaporation and condensation of Cd during coal combustion (Martinková *et al.* 2016, Fouskas *et al.* 2018) is usually accompanied by large Cd isotope ratio fractionation (Wombacher *et al.* 2004), with light Cd isotopes enriched in the evaporation phase (fly ash). This makes the Cd isotope system a potential proxy for tracing the origin of industrial wastes (Cloquet *et al.* 2006, Chrastný *et al.* 2015, Martinková *et al.* 2016, Fouskas *et al.* 2018).

### $\delta^{114/110}\text{Cd}$ values of biological RMs

The  $\delta^{114/110}\text{Cd}$  values of eight biological samples are reported here for the first time (Table 2 and Figure 2). The marine biological tissues *Laminaria japonica* Aresch GBW08517, *Porphyra* GSB-14 and *Spirulina platensis* GSB-16 are enriched in light Cd isotopes with  $\delta^{114/110}\text{Cd}$  values of  $-0.449 \pm 0.057\%$  (2s),  $-0.429 \pm 0.032\%$  (2s) and  $-0.069 \pm 0.059\%$  (2s), respectively, which are within the range of  $-0.93\%$  to  $0.70\%$  for plankton and other particulate matter presented by Yang *et al.* (2015) and Janssen *et al.* (2019), but remarkably lower than that of the surface seawater (mainly between  $0.2\%$  and  $1.0\%$ ; Ripperger *et al.* 2007, Yang *et al.* 2012, Xue *et al.* 2013, Conway and John 2015a,b, Janssen *et al.* 2017). Our results are consistent with the hypothesis that the depletion of Cd and positive Cd isotopic shift in surface seawater is due to biological uptake (e.g., Xie *et al.* 2017, Sieber *et al.* 2019). As for terrestrial plants, poplar leaves GSV-3 yielded a  $\delta^{114/110}\text{Cd}$  value ( $-0.130 \pm 0.058\%$ , 2s) lower than birch leaves ( $0.430 \pm 0.049\%$  to  $0.870 \pm 0.130\%$ , Pallavicini *et al.* 2014). Scallion GSB-27 ( $0.142 \pm 0.025\%$ , 2s) and wheat flour GBW08503c ( $0.107 \pm 0.035\%$ , 2s) yielded similar  $\delta^{114/110}\text{Cd}$  values. However, GBW08503c is significantly lighter than the wheat flour RM NIST SRM 1567b ( $0.93 \pm 0.08\%$ , 2s,  $n = 6$ ; Wiggenhauser *et al.* 2016),

possibly due to different  $\delta^{114/110}\text{Cd}$  values in soils from which the wheat was grown. Studies showed that variation of  $\delta^{114/110}\text{Cd}$  in wheat grains grown in different soil environments can be up to  $0.3\%$  (Imseng *et al.* 2018, 2019), and there is also large difference in the  $\delta^{114/110}\text{Cd}$  values of different wheat organs (e.g.,  $\Delta^{114/110}\text{Cd}_{\text{grain-root}} \geq 0.6\%$ ; Wiggenhauser *et al.* 2016, Imseng *et al.* 2019).

The large variation of  $\delta^{114/110}\text{Cd}$  ( $\geq 1.2\%$ ) in terrestrial plants can provide useful tools for studying Cd biological uptake mechanisms and tracing the sources of soil Cd. The  $\delta^{114/110}\text{Cd}$  of terrestrial plants are significantly higher than those of marine plants (Wiggenhauser *et al.* 2016, Imseng *et al.* 2018). Cadmium in terrestrial plants is mainly from soil fluids, whose  $\delta^{114/110}\text{Cd}$  varied from  $0.39\%$  to  $0.79\%$  and  $\Delta^{114/110}\text{Cd}_{\text{soil solution-soil}}$  ranged from  $0.46\%$  to  $0.71\%$  (Imseng *et al.* 2018, 2019), indicating that terrestrial plants prefer to uptake lower atomic number (lighter) Cd isotopes. Surface seawater is enriched in heavy Cd isotope, with  $\delta^{114/110}\text{Cd}$  generally ranging from  $0.2\%$  to  $1.0\%$  and can be as high as  $5.050\%$  (Ripperger *et al.* 2007, Yang *et al.* 2012, Xue *et al.* 2013, Conway and John 2015a,b, Janssen *et al.* 2017). In contrast, marine plants are isotopically lighter than seawater. This suggested that the mechanisms of Cd metabolism and uptake were probably the predominant factor controlling the Cd isotopic difference between marine plants and terrestrial plants (Lee and Morel 1995, Imseng *et al.* 2019).

The  $\delta^{114/110}\text{Cd}$  value of the scallop meat GSB-15 ( $-0.806 \pm 0.041\%$ , 2s; Table 2 and Figure 2) is within the range for bivalves ( $-1.20\%$  to  $-0.09\%$ , Shiel *et al.* 2012, 2013) and is close to herring liver ( $-0.789 \pm 0.048\%$ , 2s,  $n = 6$ ) presented by Pallavicini *et al.* (2014). Cadmium in bivalves is generally from dissolved Cd in seawater and diet (Strady *et al.* 2011). The  $\delta^{114/110}\text{Cd}$  of GSB-15 is much lower than that of seawater and marine algae, suggesting negative Cd isotope ratio fractionation across trophic levels.

A pork liver RM, GSB-29, yielded a  $\delta^{114/110}\text{Cd}$  value of  $-0.611 \pm 0.069\%$  (2s; Table 2 and Figure 2), remarkably lower than that of the pig kidney RM BB186 ( $0.465 \pm 0.062\%$ , 2s,  $n = 4$ ) and moose kidney sample ( $0.635 \pm 0.034\%$ , 2s,  $n = 8$ ) presented in Pallavicini *et al.* (2014). Cadmium is a toxic heavy metal, typically enriched in detoxifying organs such as liver and kidney (Kim *et al.* 2015). The large difference in the  $\delta^{114/110}\text{Cd}$  of liver and kidney can be attributed to different biochemical mechanisms of Cd enrichment and transformation in liver and kidney. The large  $\delta^{114/110}\text{Cd}$  variation among animal organs implies great prospects for applying Cd stable isotopes to tracing Cd metabolism in animals.

## Summary

The  $\delta^{114/110}\text{Cd}$  of various geological and environmental RMs were determined by double spike MC-ICP-MS (using a Neptune Plus instrument). For previously measured RMs, our  $\delta^{114/110}\text{Cd}$  values were in excellent agreement with published data. Our intermediate precision of  $\delta^{114/110}\text{Cd}$  values over two years was better than  $\pm 0.074\%$  (2s). In addition, this study provided  $\delta^{114/110}\text{Cd}$  data of a series of new RMs including Co-rich crusts, marine sediments and biological samples, which can be used for inter-laboratory comparison and assessment of data quality. The  $\delta^{114/110}\text{Cd}$  of RMs reported in this study varied from  $-0.806\%$  to  $0.561\%$  with a total range of  $1.37\%$ . Such large variations among natural samples, especially in soils and biological samples, may be employed to study weathering and biogeochemical processes.

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## Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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## Supporting information

The following supporting information may be found in the online version of this article:

Table S1. Description of geological reference materials.

Table S2. The mass fractions of Cd and its interfering elements in reference materials.

Table S3. Individual Cd isotope measurement results for reference materials.

This material is available from: <http://onlinelibrary.wiley.com/doi/10.1111/ggr.12380/abstract> (This link will take you to the article abstract).

## Appendix A

### Recalibration of Cd mass fractions in reference materials by the double spike method

The reference materials measured in this study had known Cd mass fractions ( $\omega(\text{Cd})_R$ ) either recommended by

GeoReM or published in previous literature. These values were used to estimate how much double spike to add in order to obtain a targeted  $^{111}\text{Cd}_{\text{spike}}:^{112}\text{Cd}_{\text{sample}}$  ratio ( $R_0$ ) of 2.0. The measured true  $^{111}\text{Cd}_{\text{spike}}:^{112}\text{Cd}_{\text{sample}}$  ratio ( $R_T$ ) was used to obtain the updated Cd mass fractions ( $\omega(\text{Cd})$ ). According to the known  $\omega(\text{Cd})_R$ , the Cd molarity ( $C_1$ ) in digested reference material solution can be expressed as:

$$C_1 = \omega(\text{Cd})_R \times m / (V \times M_{\text{Cd}}) \quad (\text{A1})$$

where  $m$ ,  $V$  and  $M_{\text{Cd}}$  refer to the mass of sample powder (g), volume of digested solution (l) and molar mass of cadmium ( $112.4 \text{ g mol}^{-1}$ ), respectively. Then, the mole of  $^{112}\text{Cd}$  in sample solution can be calculated as:

$$^{112}\text{N}_1 = C_1 \times V \times A_{112} \quad (\text{A2})$$

where  $A_{112}$  is the isotopic abundance of  $^{112}\text{Cd}$ , which is equal to 0.2412.

The amount of  $^{111}\text{Cd}_{\text{spike}}$  can be expressed as:

$$^{111}\text{S} = ^{112}\text{N}_1 \times R_0 \quad (\text{A3})$$

Substitute Equation (A2) into Equation (A3):

$$^{111}\text{S} = C_1 \times V \times A_{112} \times R_0 \quad (\text{A4})$$

After measurement on MC-ICP-MS, the true  $^{111}\text{Cd}_{\text{spike}}:^{112}\text{Cd}_{\text{sample}}$  ratio  $R_T$  was reduced by double spike program code (Tan *et al.* 2020). Thus, the actual Cd concentration of the digested sample solution can be calculated as:

$$C_A = ^{111}\text{S} / (R_T \times V \times A_{112}) = C_1 \times R_0 / R_T \quad (\text{A5})$$

Then the newly calibrated Cd mass fraction is:

$$\omega(\text{Cd}) = C_A \times V \times M_{\text{Cd}} / m \quad (\text{A6})$$

Substitute Equation (A1) and Equation (A5) into Equation (A6)

$$\omega(\text{Cd}) = \omega(\text{Cd})_R \times R_0 / R_T \quad (\text{A7})$$