

A Common Reference Material for Cadmium Isotope Studies – NIST SRM 3108

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Research into natural mass-dependent stable isotope fractionation of cadmium has rapidly expanded in the past few years. Methodologies are diverse with MC-ICP-MS favoured by all but one laboratory, which uses thermal ionisation mass spectrometry (TIMS). To quantify the isotope fractionation and correct for instrumental mass bias, double-spike techniques, sample-calibrator bracketing or element doping has been used. However, easy comparison between data sets has been hampered by the multitude of in-house Cd solutions used as zero-delta reference in different laboratories. The lack of a suitable isotopic reference material for Cd is detrimental for progress in the long term. We have conducted a comprehensive round-robin assay of NIST SRM 3108 and the Cd isotope offsets to commonly used in-house reference materials. Here, we advocate NIST SRM 3108 both as an isotope standard and the isotopic reference point for Cd and encourage its use as 'zero-delta' in future studies. The purity of NIST SRM 3108 was evaluated regarding isobaric and polyatomic molecular interferences, and the levels of Zn, Pd and Sn found were not significant. The isotope ratio $^{114}\text{Cd}/^{110}\text{Cd}$ for NIST SRM 3108 lies within $\sim 10 \text{ ppm Da}^{-1}$ of best estimates for the Bulk Silicate Earth and is validated for all measurement technologies currently in use.

La recherche sur le fractionnement naturel dépendant de la masse des isotopes stables du cadmium a connu une expansion rapide ces dernières années. Les méthodologies sont diverses mais la technique MC-ICP-MS est favorisée par tous les laboratoires sauf un, qui utilise le TIMS. Pour quantifier le fractionnement isotopique et corriger les biais instrumentaux sur la masse, les techniques dites du « double spike », du « bracketing » par un échantillon étalon et du dopage élémentaire ont été utilisés. Toutefois, la comparaison entre les différentes bases de données a été rendue difficile par la multitude des solutions internes de Cd utilisées en tant que référence 'delta-zéro' dans les différents laboratoires. L'absence d'un matériau de référence isotopique approprié pour le Cd est préjudiciable pour les progrès dans le long terme. Nous avons mené un vaste test «round-robin» du NIST SRM 3108 et des décalages isotopiques du Cd par rapport aux matériaux de référence communément utilisés en interne dans les laboratoires. Ici, nous préconisons le NIST SRM 3108 à la fois comme étalon de mesure des isotopes du Cd et comme point de référence isotopique pour le Cd, et nous encourageons son utilisation comme 'delta-zéro' dans les études futures. La pureté du NIST SRM 3108 a été évaluée en ce qui concerne les interférences isobares et moléculaires polyatomiques, et les niveaux de concentration de Zn, Pd et Sn trouvé ne sont pas significatifs. Le

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rapport isotopique $^{114}\text{Cd}/^{110}\text{Cd}$ du NIST SRM 3108 se situe dans les limites $\sim 10 \text{ ppm Da}^{-1}$ des meilleures estimations pour la Terre silicatée, et est validée pour toutes les technologies de mesure couramment utilisées.

Mots-clés : Isotopes du cadmium, Matériaux de référence isotopique, TIMS, MC-ICP-MS, NIST SRM 3108.

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The first study to search for cadmium isotope variations in nature was that of Rosman and de Laeter (1975). In this, and in subsequent papers by this group, the principal interests were to look for evidence of mass-dependent fractionation in meteoritic and lunar materials, as well as isotopic changes arising from the reaction $^{113}\text{Cd} (n, \gamma) ^{114}\text{Cd}$, which can potentially quantify neutron fluence. This pioneering work can be viewed as a prelude to the modern era of Cd isotope studies, ushered in by Wombacher *et al.* (2003) in a far-ranging survey of mass-dependent variations in nature. The change from single-collector TIMS (thermal ionisation mass spectrometry), in the earlier studies, to MC-ICP-MS (multiple-collector inductively-coupled plasma mass spectrometry) instruments also led to an order-of-magnitude improvement in external reproducibility, enabling resolution of mass-dependent Cd isotope variations in terrestrial materials for the first time.

Over the past decade, around a dozen groups worldwide have either developed stable Cd isotope methodologies or are intending to do so. The reasons for this renewed interest are manifold but mainly centre on the potential of Cd stable isotopes as a monitor for pollutant cadmium in the environment and as a tracer of biogeochemical cycling of cadmium in the oceans. While cadmium is known to be toxic for humans and a serious environmental pollutant, in the oceans, paradoxically, cadmium acts as a micronutrient (Boyle *et al.* 1976). In some marine diatoms, cadmium has a true biochemical function and can substitute for zinc in carbonic anhydrase, a vital enzyme directly involved in the photosynthetic fixation of carbon (Price and Morel 1990, Xu *et al.* 2008).

The scientific potential of Cd isotopes is highlighted by the wide-ranging spectrum of recent studies. These studies have included investigations of environmental and anthropogenic samples (Cloquet *et al.* 2006, Gao *et al.* 2008, Shiel *et al.* 2010), marine Cd isotope fractionation (Lacan *et al.* 2006, Ripperger *et al.* 2007, Schmitt *et al.* 2009a, Abouchami *et al.* 2011a), terrestrial versus

meteoritic cadmium (Wombacher *et al.* 2008, Baker *et al.* 2010) and biological activity in the Precambrian oceans (Abouchami *et al.* 2011b). The international GEOTRACES programme, dedicated to understanding the biogeochemical cycles of trace metals in the oceans, has included Cd isotopes as one of the key parameters to measure, and mapping the oceanic distribution of Cd isotopes is a major goal of the programme. An important, interrelated issue is understanding the mechanisms of stable Cd isotope fractionation during biological and inorganic cycling, which has been the focus of several recent studies (Homer *et al.* 2011, Lee *et al.* 2011, Powell *et al.* 2011, Xue *et al.* 2012, Gault-Ringold and Stirling, 2012).

Technical overview and standardisation problems

Measurement methodologies for stable Cd isotopes are quite diverse, and general summaries can be found in Schmitt *et al.* (2009b) and Rehkämper *et al.* (2011). In terms of mass spectrometry, MC-ICP-MS is favoured by most, but one group uses TIMS (MPI-Mainz), as in the original studies by Rosman and co-workers. Quantifying the natural, stable isotope fractionation of cadmium in a sample also requires correction for instrumental mass bias. Here, five of the seven laboratories are using double-spike techniques, while a few MC-ICP-MS users utilise either sample calibrator bracketing or element doping to quantify the fractionation. Chemical techniques for separating cadmium from rock, mineral and seawater samples also vary extensively between the laboratories.

With the publication of many sizable Cd isotope data sets over the past few years, two important issues have arisen. The first of these is which isotope ratio to use as a reference – in other words, which ratio to report deviations relative to. At the moment, most Cd isotope data are reported relative to $^{114}\text{Cd}/^{110}\text{Cd}$, following the original suggestion of Wombacher and Rehkämper (2004). This

choice was made originally to avoid the minor isotopes ^{106}Cd , ^{108}Cd and isobaric interference from Sn (on ^{112}Cd , ^{114}Cd and particularly ^{116}Cd) and Pd (on ^{106}Cd , ^{108}Cd and ^{110}Cd), which are serious considerations for MC-ICP-MS analyses. For TIMS measurements, such issues are largely irrelevant and, for reasons outlined in Schmitt *et al.* (2009b), the MPI-Mainz group uses the ratio $^{112}\text{Cd}/^{110}\text{Cd}$ as a reference. Converting between data sets based on $^{112}\text{Cd}/^{110}\text{Cd}$ or $^{114}\text{Cd}/^{110}\text{Cd}$ is easily performed, however.

The second and far more serious issue is the choice of reference material to use as 'zero-delta' (*cf.* Wombacher and Rehkämper 2004). This major problem remains unresolved and is currently hindering comparison of data sets collected in different laboratories. This is because most laboratories use their own, unique, in-house Cd reference solutions for 'zero-delta', but it is becoming clear that these exhibit significant differences in Cd isotope composition. As a consequence, there is now an urgent need for cross-calibrating the relative offsets between the various reference materials in use in a systematic way, as well as the adoption of a common Cd reference value by the Cd isotope community. This issue is also becoming more acute as the precision of Cd isotope measurements continues to improve. While some attempts at cross-calibration have been made (e.g., Wombacher and Rehkämper 2004, Cloquet *et al.* 2005, Schmitt *et al.* 2009b), the situation remains unsatisfactory in the long run.

Additional issues to consider in choosing suitable isotope reference materials concern characterisation, traceability and possible certification, as well as availability. In this regard, the in-house reference solutions in current use are all highly inappropriate as reference materials. This situation is particularly unfortunate, but has arisen because a certified isotope reference material for Cd is presently not available from official bodies such as NIST (Virginia, USA), IRMM (JRC, Brussels, Belgium) or IAEA (Vienna, Austria). Vogl and Pritzkow (2010) have written a useful review of all presently available isotopic RMs (IRM) and the steps involved in IRM preparation.

A candidate IRM for Cd, called BAM-I012, was prepared at BAM (Berlin, Germany) from high-purity metal and had been evaluated and calibrated by Pritzkow *et al.* (2007). Unfortunately, this material has an isotopic composition that is extremely fractionated with respect to normal terrestrial Cd (Wombacher and Rehkämper 2004, Pritzkow *et al.* 2007, Schmitt *et al.* 2009b). This effectively disqualifies BAM-I012 as a primary reference for 'zero-delta' for cadmium, but it may be useful as a secondary IRM for

calibration purposes, and it has been used to this effect in the present study by some groups.

The main purpose of the present contribution is the characterisation of a new 'zero-delta' reference for Cd isotopes, namely NIST SRM 3108. This is a RM certified by NIST as a primary calibrator for the quantitative determination of cadmium concentrations, and is not an isotopic RM *per se*. Thus, the choice of NIST SRM 3108 must remain an interim solution pending the preparation and certification of a true IRM for cadmium isotopes. Nonetheless, we intend to use NIST SRM 3108 as a common isotopic reference material in future Cd isotope studies and strongly encourage other laboratories to do so as well. To address this goal, we undertook a comprehensive round-robin assay of the Cd isotope offsets between NIST SRM 3108 and current Cd isotope reference solutions that are used as in-house 'zero-delta' reference by various laboratories. These results will thus allow conversion of literature data to and from any reference material used in previous publications.

Experimental details

Seven laboratories (Bonn, Mainz, London, Oxford, Manchester, Otago and Vancouver) took part in the determination of the Cd isotopic composition of NIST SRM 3108. A single bottle of 50 ml (Lot: 060531) was purchased by MPI and distributed in 1 ml aliquots to the other laboratories for assay. The certified concentration of NIST SRM 3108 is $10.005 \pm 0.019 \text{ mg g}^{-1}$. Additional bottles were purchased subsequently by Imperial College (London) and Oxford University to address possible issues of inhomogeneity. The methodologies used in the individual laboratories that participated in this study are briefly described below and summarised in Table 1.

Max Planck Institute for Chemistry (Mainz, Germany)

Cadmium isotope ratios were measured by TIMS using a Triton instrument (ThermoFisher, Bremen, Germany) operating in static multi-collection mode. The isotope fractionation and instrumental bias were quantified by the addition of a ^{106}Cd – ^{108}Cd double spike, whose composition was optimised using numerical methods (Galer 2007, Schmitt *et al.* 2009b). The odd-mass isotopes of cadmium, ^{111}Cd and ^{113}Cd , display mass-independent fractionation during thermal ionisation (Abouchami *et al.* 2008) and were consequently explicitly avoided. The double spike was prepared and calibrated in 2006 against our in-house JMC Cd Plasma solution (Lot: 15922032), which was taken to have $^{110}\text{Cd}/^{112}\text{Cd} = 0.520089$ (Rosman

Table 1.
Laboratories and experimental methodologies

Laboratory	Instrument	Mass bias correction method
Mainz (Germany)	TIMS (Triton)	Double spike (^{106}Cd – ^{108}Cd)
Bonn (Germany)	MC-ICP-MS (Neptune)	Ag normalisation with 'Maréchal-method'
London Imperial (UK)	MC-ICP-MS (Nu Plasma)	Double spike (^{111}Cd – ^{113}Cd)
Manchester (UK)	MC-ICP-MS (Nu Plasma)	Double spike (^{111}Cd – ^{113}Cd)
Oxford (UK)	MC-ICP-MS (Nu Plasma)	Double spike (^{111}Cd – ^{112}Cd and ^{111}Cd – ^{113}Cd)
Otago (NZ)	MC-ICP-MS (Nu Plasma)	Double spike (^{110}Cd – ^{111}Cd)
UBC (Canada)	MC-ICP-MS (Nu Plasma)	Ag normalisation + bracketing

TIMS, thermal ionisation mass spectrometry; UBC, University of British Columbia.

et al. 1980) for internal normalisation purposes. Further details regarding methods and choice of double spike can be found in Schmitt *et al.* (2009b).

Double-spike data reduction used home-brew code, written in Python, in which it is assumed that the natural and in-run mass fractionation (i.e., the instrumental mass bias) follow the so-called exponential law. Because this is a multi-dimensional non-linear problem, it was solved numerically by iteration to convergence using a Newton-Raphson algorithm, making explicit use of the Jacobian matrix of partial derivatives. Masses of the isotopes were taken from conventional sources (Audi and Wapstra 1995). Each measurement cycle (8 s integration) during the run was reduced to yield a single fractionation-corrected datum, with the statistical uncertainties calculated from the whole data set for each run.

Aliquots of NIST SRM 3108 were evaporated to dryness with an 'optimal' amount of Cd double spike (*cf.* Schmitt *et al.* 2009b) to ensure homogenisation. A fraction corresponding to 100 ng Cd was then loaded stepwise onto outgassed single Re filaments, together with a colloidal silica gel-phosphoric acid activator solution. The most stable surface ionisation of Cd occurs at temperatures of $\sim 1150^\circ\text{C}$ and mostly resulted in a slowly decreasing signal during the run. In addition to NIST SRM 3108, several other Cd isotope in-house reference solutions were analysed alongside. These included our in-house JMC Cd Mainz (Plasma solution, Lot: 15922032), JMC Cd Münster (Lot: 502552A), Alfa Cd Zürich standard solution (Imperial College aliquot), BAM-1012 Cd (Pritzkow *et al.* 2007) and Münster Cd (Wombacher and Rehkämper 2004). We also measured our own in-house Cd reference solution, prepared by dissolution of high-purity JMC cadmium metal shot (purity 99.9999%, Lot: M14638), which is primarily a gravimetric reference material. Multiple runs were obtained on different reference solution spike mixtures and different measurement sessions over the period 2009–2010. Each measurement

session included analyses of double-spiked NIST SRM 3108 and JMC Mainz reference solutions. These data complement those for various Cd reference solutions previously reported in Schmitt *et al.* (2009b) using the same methods. Note that the MPI Cd isotope data set was obtained by the determination of the absolute $^{110}\text{Cd}/^{112}\text{Cd}$ ratio and thus $\epsilon^{112/110}\text{Cd}$ directly. This was then converted into $\epsilon^{114/110}\text{Cd}$ by multiplication by a factor of 2.000425. This factor is the power-law exponent for correcting $^{112}\text{Cd}/^{110}\text{Cd}$ to $^{114}\text{Cd}/^{110}\text{Cd}$ ratio given the relevant atomic masses (Audi and Wapstra 1995) and is accurate enough as a first-order approximation for $\epsilon^{114/110}\text{Cd}$.

The data set for JMC Cd Mainz and NIST SRM 3108 was large, so the statistics were evaluated as usual. However, for the other reference solutions, we report the weighted means and weighted standard deviations, because the number of repeat runs was more limited (see Table 2) and standard deviations therefore meaningless. The long-term external reproducibility on $\epsilon^{114/110}\text{Cd}$ is $\pm 0.16\ \epsilon$ for reference solutions at the 2s level (2 standard deviations).

Imperial College London (UK)

The Cd isotope analyses were performed by MC-ICP-MS using a ^{111}Cd – ^{113}Cd double spike, following methods described in Xue *et al.* (2012) and Ripperger and Rehkämper (2007). In brief, appropriate stock solution aliquots of the various Cd reference solutions and the Cd double spike were mixed in a Teflon beaker to obtain molar spike-to-sample ratios (with respect to Cd) of $\text{Sp}/\text{Nat} \approx 1$. These mixtures were evaporated to dryness, dried down again with a drop of concentrated HNO_3 and diluted to an appropriate volume with $0.1\ \text{mol l}^{-1}\ \text{HNO}_3$. These solutions were then analysed with a Nu Plasma MC-ICP-MS (Nu Instruments, Wrexham, UK), using a Nu Instruments DSN-100 desolvator and Micromist glass nebulisers (with flow rates of $\sim 120\ \mu\text{l min}^{-1}$) for sample introduction.

Table 2.
Intercalibration of Cd isotope results for NIST SRM 3108 and various in-house reference materials, expressed as $\varepsilon^{114/110}\text{Cd}$

Laboratory	BAM 1012	JMC Cd Münster	Alfa Cd Zürich	JMC Cd Mainz	NIST SRM 3108	Münster Cd	JMC metal MPI	JMC Cd Bonn	Ox-Cd (JMC)	PCIG-1	NZ JMC Cd
Oxford (UK)	0			14.5 ± 1.0 (5) ^a	13.0 ± 0.4 (10) ^b				4.9 ± 0.9 (10) ^a		
Manchester (UK)	0			14.9 ± 0.9 (5)	13.6 ± 0.9 (7)						
Otago (NZ)	0	12.4 ± 0.8 (16/5)			13.6 ± 0.9 (21)	58.7 ± 1.3 (12/2)					
UBC (Canada)	0					57.6 ± 0.9 (3)					
Imperial College London (UK)	-12.4 ± 0.7 (24/13)	0	0.5 ± 0.5 (34/6)	2.6 ± 0.4 (5/1)	1.0 ± 0.2 (25/4)	46.2 ± 0.5 (2/1)					-2.6 ± 1.1 (71)
UBC (Canada)	-13.7 ± 2.5 (5)	0				45.0 ± 0.3 (4)					
Oxford (UK)			0		0.0 ± 0.8 (11) ^b						
Manchester (UK)	-13.6 ± 0.4 (7)	-0.4 ± 1 (2)	0	1.3 ± 0.5 (5)	-0.1 ± 0.7 (5)						
Mainz (Germany) ^e	-14.53 ± 0.44 (2)	-2.21 ± 0.16 (2)	-1.69 ± 0.08 (6)	0	-1.44 ± 0.15 (12)	43.60 ± 0.24 (2)	-14.56 ± 0.38 (1)	1.3 ± 0.3 (11)			
Bonn (Germany) ^d	-13.2 ± 0.5 (11)	-0.8 ± 0.5 (11)		1.4 ± 0.4 (11)	0	44.6 ± 0.4 (8)					
Imperial College London (UK)	-13.4 ± 0.7 (30/18) ^a	-1.0 ± 0.2 (25/4) ^f	-0.5 ± 0.4 (39/7) ^a	1.6 ± 0.4 (5/1) ^f	0	45.2 ± 0.5 (2/1) ^a					
Imperial College London (UK)	-13.4 ± 0.6 (8/7)		-0.4 ± 0.2 (9/2)		0						
Manchester (UK)	-13.5 ± 0.8 (7) ⁱ	-0.7 ± 1.2 (2) ⁱ	0.1 ± 0.7 (5)	1.4 ± 0.9 (5) ⁱ	0				-8.1 ± 1.0 ^a		-16.2 ± 1.1 (71/7) ^a
Oxford (UK)	-13.0 ± 0.4 ^a		0.0 ± 0.8 ^a	1.5 ± 1.1 ^a	0						-16.3 ± 0.6 (25/3) ⁱ
Otago (NZ)	-13.6 ± 1.4 (24/3) ^a	-1.2 ± 0.8 (16/5) ^a			0	45.1 ± 1.3 (12/2) ^a					
Otago (NZ)	-13.4 ± 1.0 (12/2) ^b				0						
UBC (Canada)	-11.0 ± 1.5 (5)	-0.37 ± 1.0 (4)			0	45.5 ± 1.8 (6)					
Mainz (Germany)	-13.05 ± 0.44 (2)	-0.73 ± 0.16 (2)	-0.21 ± 0.08 (6)	1.46 ± 0.17 (23)	0	45.06 ± 0.20 (2)	-13.10 ± 0.38 (1)				
Mean	-13.32	-0.89	-0.20	1.47	0	44.99					
2s	0.43	0.42	0.51	0.17	0	0.53					

Uncertainties are 2s. Values in italic type denote number of measurements/number of sessions.

UBC: University of British Columbia.

^a Double spike ^{111}Cd - ^{112}Cd .

^b Double spike ^{111}Cd - ^{113}Cd .

^c $^{110}\text{Cd}/^{112}\text{Cd}$ relative to JMC Cd Mainz ($^{110}\text{Cd}/^{112}\text{Cd} = 0.520083 \pm 5, n = 23$) converted to $\varepsilon^{114/110}\text{Cd}$.

^d Measured relative to NIST SRM 3108.

^e Overall average determined from analyses relative to both NIST SRM 3108 and JMC Cd Münster; the latter data were corrected for an offset of -0.96 ‰. The number of measurements and measurement sessions given can differ from the total number listed for analyses relative to JMC Cd Münster and NIST SRM 3108 to avoid duplicate counting.

^f Overall average determined from analyses relative to JMC Cd Münster only; the data were corrected for an offset of -0.96 ‰.

^g Double spike ^{110}Cd - ^{111}Cd = 0.5, relative to NIST SRM 3108 based on analyses relative to NZ JMC Cd; corrected for an offset of -1.62 ‰.

^h Double spike ^{110}Cd - ^{111}Cd = 0.5, relative to NIST SRM 3108 directly.

ⁱ Double spike ^{110}Cd - ^{111}Cd = 2, relative to NIST SRM 3108 directly.

^j Averages determined from analyses relative to Alfa Cd Zürich and corrected for an offset of 0.1 ‰.

For the isotopic determinations, the ion currents at masses 111 (Cd), 112 (Cd + Sn), 113 (Cd + In), 114 (Cd + Sn), 115 (In) and 117 (Sn) were measured simultaneously with Faraday cups in three blocks of twenty cycles (5 s each) that were each preceded by a 15 s baseline measurement (Ripperger and Rehkämper 2007). Most reference materials were analysed as solutions with total Cd concentrations of 40–60 ng ml⁻¹ (at Sp/Nat ≈ 1), and each analysis of about 6 min of duration thus required about 20–30 ng of natural Cd. In general, these measurements were carried out at total Cd sensitivities of about 250–350 V/μg ml⁻¹, equivalent to a transmission efficiency of up to about 0.25%.

The Cd isotope results that were collected online during mass spectrometry were further processed offline, using an iterative data reduction scheme, to determine the ‘true’ isotope compositions of the unspiked samples, following correction for both instrumental mass bias and isobaric interferences (Ripperger and Rehkämper 2007, Xue *et al.* 2012). These data were used to determine the $\epsilon^{114/113}\text{Cd}$ values of the different reference solutions relative to a given zero-delta reference material. The $\epsilon^{114/113}\text{Cd}$ values were finally converted to $\epsilon^{114/110}\text{Cd}$ data using conventional conversion methods (Xue *et al.* 2012).

The Imperial College data were collected during numerous separate measurement sessions that were conducted between May 2008 and October 2010. In the majority of the analyses, the various standard solutions were measured directly relative to JMC Cd Münster whilst in a few, NIST SRM 3108 served as the zero-delta reference material. These two separate suites of results were combined into a single dataset (with $\epsilon^{114/110}\text{Cd}$ reported relative to NIST SRM 3108) by correcting for an offset of $\epsilon^{114/110}\text{Cd} = +0.96$ for NIST SRM 3108 relative to JMC Cd Münster, based on the results of twenty-five measurements that were carried out on 4 days. For three reference solutions that were analysed on between four and thirteen different measurement sessions (Table 2), the reported precision (2s) was calculated from the daily averages, which are typically based on 1–5 individual analyses. For two standard solutions that were only analysed during a single session (Table 2), the 2s values are based on the precision determined from the individual measurements.

University of Manchester (UK)

The isotopic determinations were obtained with a Nu Plasma MC-ICP-MS (Nu Instruments, Wrexham, UK) at the University of Manchester in conjunction with a DSN-100 desolvating nebuliser system from Nu Instruments. Mass

bias correction was performed using a ^{111}Cd – ^{113}Cd double spike. The analytical methods and data acquisition procedures were identical to those used at Imperial College, as summarised in the previous section and described in Xue *et al.* (2012). The standard solutions analysed included NIST SRM 3108, JMC Cd Mainz, JMC Cd Münster and BAM-I012 Cd, which were measured relative to Alfa Cd Zürich (Table 2). The uncertainties are given as two standard deviations (2) of all repeat measurements for each reference solution. These results were furthermore recalculated with reference to NIST SRM 3108 as the zero-delta reference material using an offset of $\epsilon^{114/110}\text{Cd} = 0.1 \pm 0.7$ (2s) between NIST SRM 3108 and Alfa Cd Zürich (Table 2). The uncertainties of the recalculated values were estimated by error propagation using the 2 values of the original measurements.

University of Oxford (UK)

Measurements were performed using a Nu Instruments MC-ICP-MS (Nu Instruments, Wrexham, UK) at the University of Oxford using a ^{111}Cd – ^{112}Cd or ^{111}Cd – ^{113}Cd double spike for mass bias correction (see Table 2). Analytical protocols were identical to those reported elsewhere (Homer *et al.* 2011). Data are shown for OxCad (Alfa Aesar Specpure Cd concentration, lot number 81-081192A), Alfa Cd Zürich, JMC Cd Mainz and NIST SRM 3108, relative to BAM-I012 Cd. Uncertainties are reported as two times the standard deviation of the *n* isotopic measurements.

Standard impurity measurements were made using a ThermoFisher ELEMENT 2 ICP-MS (ThermoFisher, Bremen, Germany) at the University of Oxford. Samples were introduced into the plasma using a Glass Expansion 20 ml Cinnabar quartz-glass cyclonic spray chamber in conjunction with a PFA MicroFlow Nebuliser at rates of ~ 100 μl min⁻¹. The torch, cones and injector used were supplied by the manufacturer.

Gravimetrically prepared aliquots of NIST SRM 3108 Cd were diluted 1000-fold (~ 10 μg g⁻¹ Cd) for elemental determination. The limits of detection were determined at the start of each session by running multiple (minimum of five) blanks of the same acid used for the dilution of NIST SRM 3108. Five aliquots of NIST SRM 3108 were then analysed, using Cd as the internal standard to correct for instrumental drift (typically ± 2.5% over the session). Intensities were evaluated for all elements where potential isobaric (e.g., Sn) or major molecular (e.g., $^{40}\text{Ar}^{16}\text{O}$) interferences could generate an overlapping signal with any of the eight isotopes of Cd. All elements were measured in low mass resolution mode (LR) with the exception of Zn in

medium resolution (MR) and Ge, As, Se (and Cd) in high resolution mode (HR). Element abundances were calculated based on an external calibration to a gravimetrically prepared in-house multi-element reference solution, measured subsequent to NIST SRM 3108. The data were further corroborated by running additional reference solutions, treated as unknowns, at the end of the analysis session to monitor instrument drift and within-session reproducibility.

Determination of In concentration in NIST SRM 3108 was complicated by the potential formation of CdH in the plasma, which interferes across the mass range of In ($^{112}\text{Cd}^1\text{H}$, ^{113}Cd on ^{113}In and $^{114}\text{Cd}^1\text{H}$ on ^{115}In), and the high concentrations of Cd relative to any potential In interference. The mass resolution required to separate CdH from In is in excess of 15000 and is therefore beyond the maximum resolving power of the ELEMENT 2 instrument (~ 10000). Further, there are no 'empty' mass windows adjacent to Cd; thus, it was not possible to determine CdH formation rates directly from Cd. To measure the In contamination in NIST SRM 3108, we estimated the expected $^{114}\text{Cd}^1\text{H}$ contribution to the measured ^{115}In intensity based on the average long-term E^1H (element hydride) formation rate for our instrumental set-up. This correction, to a first order, was able to determine whether any In was present, when applied in conjunction with a minor ^{115}Sn correction and a normal blank correction, as with the other elements reported here.

University of Otago (New Zealand)

Cadmium isotopic measurements were carried out at the Centre for Trace Element Analysis, University of Otago, on a Nu Plasma-HR MC-ICP-MS (Nu Instruments, Wrexham, UK) with a ^{110}Cd - ^{111}Cd double spike for reliable correction of instrumental mass fractionation. Following Ripperger and Rehkämper (2007), initial measurements used a double spike with a $^{110}\text{Cd}/^{111}\text{Cd}$ of ~ 0.5 , and standard solutions were spiked to obtain a spike-to-sample molar ratio of 4 (Gault-Ringold and Stirling, 2012). Recent measurements employ a double-spike with a $^{110}\text{Cd}/^{111}\text{Cd}$ of 2 and spike-to-sample molar ratio of 2 that has been optimised using procedures reported in Rudge *et al.* (2009), resulting in a twofold improvement in analytical precision.

Aliquots of the Cd reference solutions were mixed with the appropriate amount of spike, evaporated to dryness and redissolved in $0.1 \text{ mol l}^{-1} \text{ HNO}_3$ in preparation for analysis. Samples were introduced through a Nu Instruments DSN-100 desolvator fitted with a PFA $50 \mu\text{l min}^{-1}$ nebuliser. Cadmium isotopic data were collected as two consecutive static measurements on an array of Faraday collectors operating with $10^{11} \Omega$ resistors. Masses 110–

118 were measured simultaneously during the main run, and masses 105–113 were measured during the interference run. The two runs allowed both Sn and Pd isobaric interferences to be corrected for if necessary. The main run consisted of four blocks of twenty cycles and the interference run consisted of one block of ten cycles, both using 5 s integration times. In both runs, the ion beam was deflected off-axis and the electronic baseline was monitored before each block for 40 and 20 s during the main run and interference run, respectively. Each analysis took approximately 12 min, including time for background measurements and peak centring. Each measurement yielded total ion beams averaging $14 \times 10^{-11} \text{ A}$ and therefore consumed approximately 12 ng of natural Cd.

Following analysis, data were reduced offline at the cycle level based on the iterative methods reported in Siebert *et al.* (2001) to correct the measured $^{114}\text{Cd}/^{110}\text{Cd}$ ratios for both isobaric interferences and instrumental mass fractionation, assuming an exponential mass fractionation law. This approach was adapted using improved interference corrections as discussed in Ripperger and Rehkämper (2007).

Data were obtained during several measurement sessions over a 3-year period from 2008 to 2011. An in-house standard solution, NZ JMC Cd (Alfa Aesar Specpure Cd, Lot number: 250421H) and the NIST SRM 3108 Cd CRM each served as the zero-delta reference materials. All of the data are reported as $\epsilon^{114/110}\text{Cd}$ relative to NIST SRM 3108 by correcting, if required, for the offset between NZ JMC Cd and NIST SRM 3108 of $\epsilon^{114/110}\text{Cd} = -16.2 \pm 0.1 \epsilon$ (2 SE) (Table 2). Uncertainties are reported as two standard deviations (2s) of the total number of measurements taken for each reference material.

Bonn University (Germany)

Stable cadmium isotope determinations were performed relative to NIST SRM 3108 at the Steinmann-Institut in Bonn using a Neptune MC-ICP-MS (ThermoFisher, Bremen, Germany). The analytical procedure was set up specifically for the cross-calibration of different reference solutions, that is, no real samples accompanied these analyses and the amount of Cd consumed was of minor concern. The 'Maréchal' method (Maréchal *et al.* 1999) was employed for mass bias drift correction. The latter is based on empirical correlations observed for the measured $^{109}\text{Ag}/^{107}\text{Ag}$ and $^{114}\text{Cd}/^{110}\text{Cd}$ ratios [see Wombacher *et al.* (2003) for details].

The 'samples' (standard solutions) consisted of JMC Cd Mainz (Lot number: 15922032), Bonn-JMC Cd (Lot number: 100131010), the Münster/Zürich-JMC Cd (Lot

number: 502552A), BAM-I012 and Münster Cd. Solutions containing 300 ng ml^{-1} Cd and 200 ng ml^{-1} Ag were prepared in 0.14 mol l^{-1} HNO_3 . The same Ag solution was added during the day of analysis to all Cd solutions. Each analysis consisted of forty integrations of 4.2 s each, with a 30 s baseline read during sample solution uptake. Thus, about 120 ng Cd was consumed per analysis.

Sample introduction was facilitated using an Elemental Scientific SC-2 autosampler, a glass spray chamber (ThermoFisher stable inlet system) and a PFA nebuliser with an uptake rate of $110 \mu\text{l min}^{-1}$. The ^{109}Ag and ^{114}Cd ion beams were $5.7 \pm 0.3 \text{ V}$ and $4.1 \pm 0.3 \text{ V}$ (2s), respectively. Between analyses, the introduction system was rinsed with 0.14 mol l^{-1} HNO_3 for 30 s only. A 0.14 mol l^{-1} HNO_3 blank followed each set of twelve Cd–Ag solutions (7× NIST SRM 3108, 5× ‘sample’) and the ^{111}Cd blank intensity was $\leq 54 \mu\text{V}$, emphasising the efficient washout performance of the glass spray chamber.

Data on the following isotopes were collected: ^{107}Ag , $^{108}\text{Cd} + \text{Pd}$, ^{109}Ag , $^{110}\text{Cd} + \text{Pd}$, ^{111}Cd , $^{112}\text{Cd} + \text{Sn}$, $^{114}\text{Cd} + \text{Sn}$ and ^{120}Sn for the correction of ^{112}Sn and ^{114}Sn contributions to the respective Cd ion beams. Corrections for Sn were $< 5 \text{ ppm}$, except for the $^{112}\text{Cd}/^{110}\text{Cd}$ ratios where corrections up to 9 ppm were made. The 2s uncertainties (± 0.31 to ± 0.51 for $\epsilon^{114/110}\text{Cd}$) reported in Table 2 refer to eleven analyses per sample (Münster Cd 8×) in only one measurement session. To test the consistency of the data, $\epsilon^{114/110}\text{Cd}$ was recalculated from measured $\epsilon^{114/111}\text{Cd}$ and $\epsilon^{114/112}\text{Cd}$ using the equations given in Wombacher and Rehkämper (2004) and Rehkämper *et al.* (2011). Deviations recalculated from directly measured $\epsilon^{114/110}\text{Cd}$ were from -0.12 to $+0.24 \epsilon$, well within the stated 2s reproducibility.

University of British Columbia (Vancouver, Canada)

Experimental work was carried out in metal-free Class 1000 clean laboratories at the Pacific Centre for Isotopic and Geochemical Research (PCIGR), University of British Columbia (UBC). Sample preparation for isotopic determinations was performed in Class 100 laminar flow hoods in the instrument room. Isotopic determination was performed on a Nu Plasma MC-ICP-MS using a DSN-100 desolvating nebuliser system (Nu Instruments, Wrexham, UK) for sample introduction. The Cd isotopic determination technique was adapted from Wombacher *et al.* (2003) and is described by Shiel *et al.* (2009). In brief, Cd determinations comprised thirty measurements (two blocks of fifteen \times 5 s integrations with a 20 s ESA deflected baseline before

each block). A conventional sample-calibrator bracketing (SSB) measurement protocol was followed where secondary reference materials (JMC Cd Münster, BAM-I012, Münster Cd and PCIGR-1 Cd) were run alternately with the primary ‘zero-delta’ reference material (in most cases, NIST SRM 3108). The $^{114}\text{Cd}/^{110}\text{Cd}$ values are reported as external normalisation–SSB-corrected, where external normalisation of Cd was made using Ag. The ^{114}Sn ion signal intensity (calculated from the measured ^{118}Sn signal intensity) was 0.008 – 0.012 mV on a ^{114}Cd signal of 5.4 – 5.8 V . Therefore, Sn contributed only 1.4 – 2.1 ppm to the measured intensity at $m/z = 114$. Tin is present in the NIST SRM 3108 Cd CRM at a level comparable to that observed in the other Cd isotopic reference materials.

Results and discussion

The steps necessary for preparation, certification and validation of an IRM have been summarised by Vogl and Pritzkow (2010). From a pragmatic perspective, a Cd isotope RM needs to fulfil four criteria: (a) a long-term supply of the IRM needs to be assured, (b) it must be isotopically homogeneous, which is most easily achieved if a solution is used, (c) elemental impurities should be minimal so as not to impede the isotope measurements, and especially so for isobaric elements, and (d) the Cd isotopic composition should be representative of the bulk silicate Earth (BSE), which has been characterised fairly precisely relative to in-house reference solutions (Wombacher *et al.* 2008, Schmitt *et al.* 2009a, Schönbächler *et al.* 2009). Criteria (a) and (b) are clearly met *de facto* by NIST SRM 3108, while (c) and (d) are discussed below.

Purity of NIST SRM 3108 solution

To assess the level of impurities in NIST SRM 3108, aliquots of the solution were analysed using an ELEMENT 2 single-collector ICP-MS (ThermoFisher, Bremen, Germany) in Oxford and the results are reported in Table 3. Contaminant levels are reported as mole ratios relative to Cd ($\text{mol}^{-1} \text{ Cd}$) and as mass fractions (ng g^{-1}) in the NIST SRM 3108 solution. Uncertainties are derived from multiple measurements of separate aliquots of NIST SRM 3108 from the same measurement session.

The analyses reveal minor contributions from Pd and Sn in NIST SRM 3108. These elements constitute the main isobaric interferences on Cd for MC-ICP-MS users, but are not a concern for TIMS (Schmitt *et al.* 2009a). For practical purposes, the measured concentrations are negligible at far below $1 \mu\text{mol mol}^{-1}$ Cd, however, and can be safely ignored.

Table 3.

Concentrations of contaminants and potential isobaric interfering elements in NIST SRM 3108 measured on a Thermo Finnigan ELEMENT 2 ICP-MS at the University of Oxford

Element	Interference(s) ^a in order of increasing mass	Mass resolution	x: Cd ± 1s (μmol mol ⁻¹) ^b	[x] in NIST SRM 3108 ± 1s (ng g ⁻¹)
³⁰ Zn	⁶⁶ Zn ⁴⁰ Ar on ¹⁰⁶ Cd, ⁶⁸ Zn ³⁸ Ar on ¹⁰⁶ Cd, ⁷⁰ Zn ³⁶ Ar on ¹⁰⁶ Cd, ⁶⁸ Zn ⁴⁰ Ar on ¹⁰⁸ Cd, ⁷⁰ Zn ⁴⁰ Ar on ¹¹⁰ Cd	MR on ⁶⁶ Zn	61.6 ± 18.2	358 ± 106
³¹ Ga	⁷¹ Ga ⁴⁰ Ar on ¹¹¹ Cd	LR on ⁶⁹ Ga	BLD	–
³² Ge	⁷⁰ Ge ³⁶ Ar on ¹⁰⁶ Cd, ⁷⁰ Ge ³⁸ Ar on ¹⁰⁸ Cd, ⁷² Ge ³⁶ Ar on ¹⁰⁸ Cd, ⁷² Ge ³⁸ Ar on ¹¹⁰ Cd, ⁷⁰ Ge ⁴⁰ Ar on ¹¹⁰ Cd, ⁷⁴ Ge ³⁶ Ar on ¹¹⁰ Cd, ⁷³ Ge ³⁸ Ar on ¹¹¹ Cd, ⁷⁴ Ge ³⁸ Ar on ¹¹² Cd, ⁷² Ge ⁴⁰ Ar on ¹¹² Cd, ⁷⁶ Ge ³⁶ Ar on ¹¹² Cd, ⁷³ Ge ⁴⁰ Ar on ¹¹³ Cd, ⁷⁴ Ge ⁴⁰ Ar on ¹¹⁴ Cd, ⁷⁶ Ge ³⁸ Ar on ¹¹⁴ Cd, ⁷⁶ Ge ⁴⁰ Ar on ¹¹⁶ Cd	HR on ⁷³ Ge	BLD	–
³³ As	⁷⁵ As ³⁶ Ar on ¹¹¹ Cd, ⁷⁵ As ³⁸ Ar on ¹¹³ Cd	HR on ⁷⁵ As	BLD ^c	–
³⁴ Se	⁷⁴ Se ³⁶ Ar on ¹¹⁰ Cd, ⁷⁶ Se ³⁶ Ar on ¹¹² Cd, ⁷⁷ Se ³⁶ Ar on ¹¹³ Cd, ⁷⁶ Se ³⁸ Ar on ¹¹⁴ Cd, ⁷⁸ Se ³⁶ Ar on ¹¹⁴ Cd, ⁷⁴ Se ⁴⁰ Ar on ¹¹⁴ Cd, ⁷⁸ Se ³⁸ Ar on ¹¹⁶ Cd, ⁷⁶ Se ⁴⁰ Ar on ¹¹⁶ Cd, ⁸⁰ Se ³⁶ Ar on ¹¹⁶ Cd	HR on ⁷⁷ Se	BLD ^c	–
³⁶ Kr	⁷⁸ Kr ³⁶ Ar on ¹¹⁴ Cd, ⁸⁰ Kr ³⁶ Ar on ¹¹⁶ Cd	–	–	–
³⁸ Sr	⁸⁸ Sr ¹⁸ O on ¹⁰⁶ Cd	LR on ⁸⁸ Sr	BLD	–
³⁹ Y	⁸⁹ Y ¹⁷ O on ¹⁰⁶ Cd	LR on ⁸⁹ Y	BLD	–
⁴⁰ Zr	⁹⁰ Zr ¹⁶ O on ¹⁰⁶ Cd, ⁹² Zr ¹⁶ O on ¹⁰⁸ Cd, ⁹⁰ Zr ¹⁸ O on ¹⁰⁸ Cd, ⁹⁴ Zr ¹⁶ O on ¹¹⁰ Cd, ⁹² Zr ¹⁸ O on ¹¹⁰ Cd, ⁹⁴ Zr ¹⁸ O on ¹¹² Cd	LR on ⁹⁰ Zr	BLD	–
⁴¹ Nb	⁹³ Nb ¹⁷ O on ¹¹⁰ Cd, ⁹³ Nb ¹⁸ O on ¹¹¹ Cd	LR on ⁹³ Nb	BLD	–
⁴² Mo	⁹² Mo ¹⁶ O on ¹⁰⁸ Cd, ⁹⁴ Mo ¹⁶ O on ¹¹⁰ Cd, ⁹² Mo ¹⁸ O on ¹¹⁰ Cd, ⁹⁵ Mo ¹⁶ O on ¹¹¹ Cd, ⁹⁶ Mo ¹⁶ O on ¹¹² Cd, ⁹⁴ Mo ¹⁸ O on ¹¹² Cd, ⁹⁷ Mo ¹⁶ O on ¹¹³ Cd, ⁹⁵ Mo ¹⁸ O on ¹¹³ Cd, ⁹⁸ Mo ¹⁶ O on ¹¹⁴ Cd, ⁹⁶ Mo ¹⁸ O on ¹¹⁴ Cd, ¹⁰⁰ Mo ¹⁸ O on ¹¹⁶ Cd	LR on ⁹⁵ Mo	BLD	–
⁴⁴ Ru	⁹⁶ Ru ¹⁶ O on ¹¹² Cd, ⁹⁸ Ru ¹⁶ O on ¹¹⁴ Cd, ⁹⁶ Ru ¹⁸ O on ¹¹⁴ Cd, ¹⁰⁰ Ru ¹⁶ O on ¹¹⁶ Cd	LR on ¹⁰¹ Ru	BLD	–
⁴⁶ Pd	¹⁰⁶ Pd on ¹⁰⁶ Cd, ¹⁰⁸ Pd on ¹⁰⁸ Cd, ¹¹⁰ Pd on ¹¹⁰ Cd	LR on ¹⁰⁵ Pd	BLD	–
⁴⁹ In	¹¹³ In on ¹¹³ Cd	LR on ¹¹⁵ In	BLD	–
⁵⁰ Sn	¹¹² Sn on ¹¹² Cd, ¹¹⁴ Sn on ¹¹⁴ Cd, ¹¹⁶ Sn on ¹¹⁶ Cd	LR on ¹¹⁸ Sn	BLD ^c	–
⁹⁰ Th	²³² Th ⁺⁺ on ¹¹⁶ Cd	LR on ²³² Th	BLD	–

1s, 1 standard deviation.

^a Grey type indicates minor molecular interference; normal type indicates a molecular interference; bold type indicates an isobaric interference.

^b Minor peaks were observed; however, their abundance was irreproducible between analytical sessions.

^c BLD, below limit of detection.

Analyses by MC-ICP-MS can suffer from additional interferences in the form of polyatomic molecular ions. Of the elements that can be problematic in this respect, only Zn was found to be present in appreciable quantities in NIST SRM 3108, whilst very minor (and hence negligible) As and Se peaks were seen in some analyses. The Zn concentration of the Cd solution is sufficiently low however, at about 62 μmol mol⁻¹ Cd (~ 360 ng ml⁻¹), not to be of significant concern. This conclusion is underlined by the observation that (a) nAr⁺ ions typically feature formation rates (relative to Zn) of less than 5 × 10⁻⁴ (Ripperger and Rehkämper 2007), and (b) the major ZnAr species overlap with the minor isotopes of Cd, which are generally not measured by MC-ICP-MS.

Data assessment

The isotope data for various Cd standards are reported in Table 2 and expressed as ε^{114/110}Cd, following Wombacher and Rehkämper (2004), which is defined as follows:

$$\varepsilon^{114/110}\text{Cd} = \left(\frac{[^{114}\text{Cd}/^{110}\text{Cd}]_{\text{sample}}}{[^{114}\text{Cd}/^{110}\text{Cd}]_{\text{reference}}} - 1 \right) \times 10^4 \quad (1)$$

The ε^{114/110}Cd values are presented in the form of a tabular ‘matrix’, whereby the reference material used by individual laboratories is marked with a ‘O’, by definition.

A first observation is that several groups have been using the BAM-I012 Cd reference solution, primarily as a secondary reference material. As mentioned earlier, BAM-I012 and Münster Cd both have extremely fractionated cadmium isotope compositions, which are, unlike most natural, terrestrial materials, and are therefore unsuited as primary ‘zero-delta’ isotope reference materials (Wombacher and Rehkämper 2004, Schmitt *et al.* 2009b). A particularly interesting point is the isotopic fractionation seen amongst various commercially available Cd standard solutions. For example, the ε^{114/110}Cd of JMC (Johnson Matthey Company) plasma solutions vary by up to ~2.5 ε (60 ppm Da⁻¹) between batches; the total range amongst

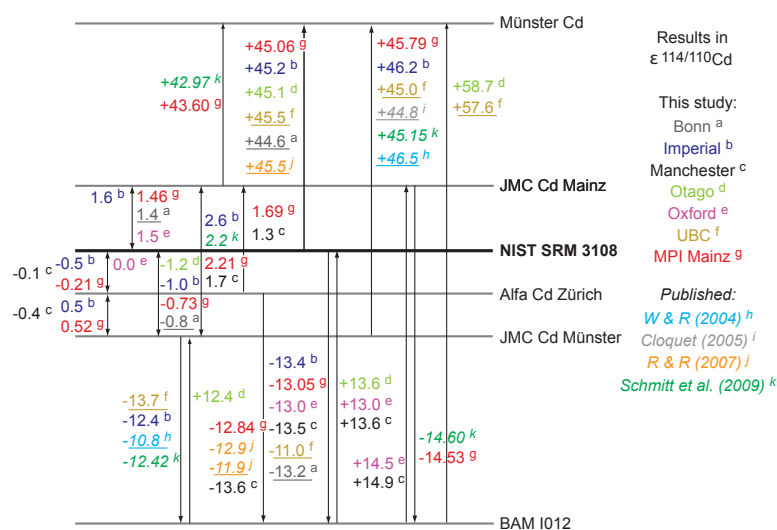


Figure 1. Inter-laboratory comparison of Cd isotopic compositions expressed as $\epsilon^{114/110}\text{Cd}$ of various Cd reference materials and the certified reference material NIST SRM 3108. Laboratories and methodology are colour-coded. Note that the direction of the arrow points from the material used as 'reference' towards the material measured as 'sample'. Underlined values were not obtained with double-spike methodology. Wombacher and Rehkämper (2004); W&R (2004); Ripperger and Rehkämper (2007); R&R (2007).

in-house reference solutions as a whole is more than $\sim 15 \epsilon$ (Table 2). These results highlight the implicit difficulties of comparing Cd isotope data sets between laboratories and the outstanding need for establishing a common zero-delta reference material for future Cd isotope studies.

'Validation and verification' means confirming that a product or service meets the needs of its end-users. With respect to the use of NIST SRM 3108 as a 'zero-delta' (or epsilon) reference point, this appears to be so. In the lower part of Table 2, the results obtained for the in-house Cd reference solutions by the different laboratories are presented and adjusted such that NIST SRM 3108 is defined as $\epsilon^{114/110}\text{Cd} = 0$. The consistency of the data obtained for individual reference solutions by all seven laboratories is remarkable and is also illustrated in Figure 1. For a given reference solution, the data agreement between laboratories is typically about 0.5 ϵ units, that is comparable to, or slightly better than, the 2s reported by individual laboratories. The homogeneity of NIST SRM 3108 is confirmed by preliminary analysis performed at Imperial College on a separate bottle of NIST SRM 3108, which yielded Cd isotopic compositions identical within $\pm 0.4 \epsilon$ to those of the MPI batch. The results also agree acceptably well with previously published data, reported for comparison in Figure 1 (Wombacher and Rehkämper 2004, Cloquet *et al.* 2005, Ripperger and Rehkämper 2007, Schmitt

et al. 2009b). Thus, we can safely conclude that NIST SRM 3108 meets the needs of its potential users in arriving at consistent data from different laboratories using entirely different methodologies.

Overall, the results for NIST SRM 3108 showed excellent agreement even though the analyses were carried out using different procedures, instruments, methods of mass fractionation correction and double-spike compositions. This, in turn, provides tight constraints on the average values for the different Cd reference solutions that, to our knowledge, are in present usage. The mean $\epsilon^{114/110}\text{Cd}$ values relative to NIST SRM 3108 for the most commonly used reference solutions are BAM-I012: -13.32 ± 0.43 (-13.06 ± 1.6 , including UBC data); JMC Cd Münster: -0.81 ± 0.42 ; Alfa Cd Zürich: -0.20 ± 0.51 ; JMC Cd Mainz: 1.47 ± 0.17 ; and Münster Cd: 44.99 ± 0.53 (2s).

The Cd isotope composition of NIST SRM 3108 lies close to that estimated for the Bulk Silicate Earth (Wombacher *et al.* 2008, Schmitt *et al.* 2009a, Schönbächler *et al.* 2009). For example, the estimate of Schmitt *et al.* (2009a) corresponds to $\epsilon^{114/110}\text{Cd}$ of -0.44 ± 0.24 recalculated relative to NIST SRM 3108. Thus, NIST SRM 3108 is a suitable RM for addressing a wide range of Cd isotope problems in Earth System Sciences.

The inter-laboratory reference material calibration undertaken here demonstrates that normalisation of Cd isotope data to NIST SRM 3108 provides reproducible results between laboratories, independent of the instrument used, the instrumental mass bias correction (calibrator-sample bracketing or double spike). On the basis of this excellent agreement, NIST SRM 3108 fulfils the criteria for a common zero-delta reference material for future Cd isotope studies.

Absolute isotope composition of NIST SRM 3108

The absolute isotopic composition of an IRM does not need to be known accurately for it to be used as 'zero-delta', because it only serves as a relative reference point. In the present contribution, we have therefore assayed the isotopic offsets between different in-house Cd reference solutions and not any absolute compositions. However, Pritzkow *et al.* (2007) previously calibrated the isotopic composition of BAM-I012 in an absolute sense using a metrological approach. Since we have determined that BAM-I012 is characterised by $\epsilon^{114/110}\text{Cd} = -13.05$ relative to NIST SRM 3108, it is a simple matter to arrive at a first estimate of the true isotopic composition of NIST SRM 3108. The isotope abundances and isotopic composition are summarised in Table 4. The atomic weight is calculated to be 112.41330 using the respective masses of the isotopes (Audi and Wapstra 1995).

Unfortunately, there are difficulties with the calibration of BAM-I012 by Pritzkow *et al.* (2007), as have been highlighted by Schmitt *et al.* (2009b), and it would be worthwhile re-evaluating the calibration in this light. However,

the inferred composition of NIST SRM 3108 listed in Table 4 is far more accurate than other, previously published, results. For example, the Cd isotope data of Rosman *et al.* (1980) have generally been used to establish the 'known' reference values for isotope ratios that were subsequently used to correct 'raw' mass spectrometric results for the effects of instrumental mass fractionation (e.g., Wombacher *et al.* 2003, Schmitt *et al.* 2009b). Comparison of the ratios shown in Table 4 with those of Rosman *et al.* (1980) suggests that the latter data are isotopically light by around -2.6‰ Da^{-1} . This result is not surprising given that the data of Rosman *et al.* (1980) were obtained by TIMS with a silica gel activator, and this technique is known to produce a systematic offset (about -1.5‰ Da^{-1}) for 'raw' measured Pb isotope data relative to the true, absolute compositions. The composition of NIST SRM 3108 listed in Table 4 is hence useful, since it will likely lead to greater accuracy in internally normalising Cd isotope data, as well as in the calibration of double spikes against NIST SRM 3108.

Conclusions and outlook

We have undertaken a round-robin intercalibration of various in-house Cd isotope reference solutions that are currently used as isotopic reference points. This effort involved seven laboratories, to which material was distributed, which use varied measurement protocols and instrumentation.

The NIST SRM 3108 certified reference material was evaluated as a potential 'common' zero-delta isotope measurement standard for cadmium. We have demonstrated that NIST SRM 3108 yielded reproducible Cd

Table 4.
Preliminary absolute abundances and composition of NIST SRM 3108 Cadmium

Isotope i	Atomic mass ^a	Abundance ^b	Isotope ratios ^c		
			i/110	i/112	i/114
106	105.9064580	0.012458 ± 8	0.09987 ± 13	0.05167 ± 7	0.04334 ± 6
108	107.9041834	0.008888 ± 4	0.07125 ± 7	0.03686 ± 4	0.03092 ± 3
110	109.9030056	0.124744 ± 16	1	0.51733 ± 21	0.43400 ± 21
111	110.9041816	0.127980 ± 12	1.02594 ± 33	0.53075 ± 19	0.44526 ± 20
112	111.9027572	0.241130 ± 38	1.93300 ± 79	1	0.83892 ± 43
113	112.9044009	0.122274 ± 22	0.98020 ± 43	0.50709 ± 24	0.42540 ± 23
114	113.9033581	0.287430 ± 58	2.30416 ± 110	1.19201 ± 61	1
116	115.9047554	0.075097 ± 32	0.60201 ± 54	0.31144 ± 28	0.26127 ± 25

Atomic weight 112.41330 g mol⁻¹.

^a Atomic masses from Audi and Wapstra (1995).

^b Calculated from those of BAM I012 (Table 13 in Pritzkow *et al.* 2007) and the $\epsilon^{114/110}\text{Cd}$ offset of -13.05 between BAM I012 and SRM 3108.

Uncertainties are 95% confidence level.

^c Uncertainties propagated quadratically.

isotope results in all participating laboratories and is virtually free of elements that can generate isobaric or molecular interferences. Further, the measured $\varepsilon^{114/110}\text{Cd}$ offsets of the other in-house reference solutions relative to NIST SRM 3108 were reproducible and consistent. Thus, NIST SRM 3108 is validated and verified as a Cd isotope reference material, as it meets the demands of its potential end-users. In addition, NIST SRM 3108 has a $^{114}\text{Cd}/^{110}\text{Cd}$ ratio within 10 ppm Da^{-1} of the currently best estimates for the Bulk Silicate Earth. Thus, NIST SRM 3108 fulfils all reasonable criteria, and we therefore strongly encourage its adoption as 'zero-delta' reference material in future Cd isotope studies. The choice of NIST SRM 3108, which is only certified for cadmium concentration by NIST, must remain an interim solution, however, pending the certification of BAM-IO12 or some other material as a proper isotopic reference material for cadmium.

Acknowledgements

This contribution is dedicated to Kevin Rosman (1943–2009) and John de Laeter (1933–2010) in recognition of their pioneering and pivotal cadmium isotope studies. This intercalibration effort was initiated by a discussion at the 2009 Goldschmidt conference in Davos between M. Rehkämper, W. Abouchami and G. Henderson, who is thanked for his encouragement. We thank W. McDonough for editorial handling and two anonymous reviewers for their comments. Wafa Abouchami was supported by the DFG through the Leibniz award to Klaus Mezger. The Cd isotope research at Imperial College London was supported by a NERC grant to Mark Rehkämper. Frank Wombacher thanks Carsten Münker and the team that supported the Neptune laboratory in Bonn during the measurement sessions. Tristan Horner acknowledges support from NERC (NE/G524060/1) and thanks G.M. Henderson and A.N. Halliday for access to the Nu mass spectrometers. Claudine Stirling and Melanie Gault-Ringold were funded by the NZ Marsden Fund.

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