Vol. 29 — N°1 03 05 p.95-106

GEOSTANDARDS and GEOANALYTICAL RESEARCH

Natural Cadmium Isotopic Variations in Eight Geological Reference Materials (NIST SRM 2711, BCR 176, GSS-1, GXR-1, GXR-2, GSD-12, Nod-P-1, Nod-A-1) and Anthropogenic Samples, Measured by MC-ICP-MS

Christophe **Cloquet** (1)*, Olivier **Rouxel** (1, 2), Jean **Carignan** (1) and Guy **Libourel** (1, 3)

(1) Centre de Recherche Pétrographiques et Géochimiques-CNRS, 15 rue Notre Dame des Pauvres, 54501 Vandoeuvre-lès-Nancy, France
(2) Present address: Woods Hole Oceanographic Institution, MS 25360 Woods Hole Road, Woods Hole, MA 02543, USA
(3) Ecole Nationale Supérieure de Géologie-INPL, BP40, 54501 Vandoeuvre-lès-Nancy, France
* Corresponding author. e-mail: cloquet@crpg.cnrs-nancy.fr

In this study, the Cd isotopic composition of various geological reference materials and anthropogenic samples was investigated. The measurements were made by multicollector ICP-MS and instrumental mass fractionation was controlled using a "sample-standard bracketing" technique. Cadmium isotopic data are reported relative to an internal Cd solution (Cd Spex) and expressed as the ^{114}Cd/^{110}Cd delta value. Two other Cd solutions (Prolabo and JMC) were analysed and yielded the same 0‰ delta value. A fractionated Cd metal sample (Münster Cd) was used as a secondary reference material for Cd isotopic measurements and we obtained a ^{114}Cd/^{110}Cd delta value of 4.48‰ relative to Cd Spex solution. As opposed to multi-stage Cd purification previously published in the literature, a new one step anionic exchange purification using dilute HCl for the analysis of Cd isotopes in geological samples was developed. This method enabled a high recovery (› 95%) and effective separation of the sample matrix to be achieved. The long-term external reproducibility was evaluated at 0.12‰ (2 standard deviations) for the ^{114}Cd/^{110}Cd ratio, based on reference solutions and replicated measurements of samples over one year. The variation of Cd isotopic composition of natural terrestrial samples is restricted to a small range of 0.4‰, which is similar to previously reported results. In contrast, large variations of Cd isotopic composition were found for anthropogenic samples with values as low as -0.64‰ for a dust sample issued from a lead smelter and values as high as +0.50‰ for NIST SRM 2711 (metal-rich soil). These variations are 10 times larger than the

Dans cette étude, les compositions isotopiques du Cd de certains matériaux géologiques de références ont été étudiées. Les mesures ont été effectuées par Multicollecteur-ICP-MS et le fractionnement de masse instrumental est corrigé en utilisant la technique du "sample-standard bracketing". Les données isotopiques de Cd sont reportées relativement a une solution interne de Cd (Cd Spex) et exprimées en valeur delta pour le rapport ^{114}Cd/^{110}Cd. Deux autres solutions de référence de Cd (Prolabo et JMC) ont été mesurées et donnent la même valeur delta de 0‰. Un échantillon de Cd métal fractionné (Münster Cd) a été utilisé comme deuxième matériau de référence pour les mesures isotopiques de Cd et nous avons obtenu une valeur delta de 4.48‰ sur le rapport ^{114}Cd/^{110}Cd relativement à la solution de Cd Spex. Contrairement aux traitements multiples pour la purification du Cd précédemment publiés, une nouvelle technique de purification en une étape sur résine anionique utilisant de l'HCl dilué a été développée pour l'analyse des échantillons géologiques. Cette méthode permet un bon rendement de récupération du Cd (› 95%) ainsi qu'une bonne séparation de la matrice. La reproductibilité externe à long terme est de 0.12‰ (2 écarts types) sur le rapport ^{114}Cd/^{110}Cd et estimée sur les solutions de référence et sur réplicats totaux d'échantillons sur un an. La variation de la composition isotopique de Cd observée pour les échantillons terrestres naturels est restreinte à une faible plage de 0.4‰, ce qui est similaire à celle précédemment observée. En revanche, une plus grande variation est trouvée pour les échantillons

Received 23 Apr 04 — Accepted 14 Jan 05

reproducibility and suggest that Cd isotopes can be useful as tracers of anthropogenic sources of Cd in the environment.

Keywords: reference materials, cadmium isotopes, environmental tracing.

anthropiques avec des valeurs variant de -0.64‰, pour un échantillon de poussières issu d'une fonderie de plomb, à +0.50‰ pour le NIST SRM 2711 (sol riche en métaux). Cette variation est 10 fois supérieure à l'incertitude des mesures et suggère que les isotopes du Cd puissent être intéressants comme traceur de sources anthropiques dans l'environnement.

Mots-clés : matériaux de référence, isotopes de cadmium, traçage environnemental.

Cadmium has eight stable isotopes covering 10 mass units from mass number 106 to 116 (Figure 1). Cadmium elemental and isotopic abundances were first measured on meteorites and terrestrial samples (Schmitt *et al.* 1963, Rosman and de Laeter 1974, 1975, 1976a, 1978, 1980, Rosman *et al.* 1980a) using thermal ionisation mass spectrometry (TIMS) and Cd concentration data were used to survey the Cd level in the environment (Rosman and de Laeter 1976b, Rosman *et al.* 1980b) using the isotope dilution mass spectrometric technique. Further investigations devoted to Cd isotopes systematics in meteorites (Loss *et al.* 1990, Rosman and de Laeter 1988) have shown that Cd isotopes can be useful tracers of cosmochemical processes. However, mainly because of the analytical uncertainties related to most of these measurements (typically 0.5 to 1‰ per atomic mass unit (amu)), terrestrial variations of Cd isotope abundance remained poorly known. Within the last five years, the Cd isotopic composition has been measured in lunar soils by TIMS (Sands *et al.* 2001) and in rocks and meteorites by MC-ICP-MS with a high precision (Wombacher *et al.* 2003). The large variations in the Cd isotope composition reported for some meteorites and lunar soils are mainly related to the high volatility of Cd and isotopic fractionation during evaporation-condensation processes.

The precision improvement by at least a factor of 2, obtained with MC-ICP-MS (Wombacher *et al.* 2003) (~ 0.1‰ per amu, 0.05‰ per amu for Cd-rich minerals) compared to the best TIMS double spike study (0.2 to 0.4‰ per amu), allows the investigation of small variations in the Cd isotopic composition of terrestrial samples. In this study, a new and simple procedure for Cd purification by the macroporous anion exchange resin AG-MP-1 is reported. Such a development was found to be necessary because the previously published purification methods were found inconvenient for this study (e.g., Sands and Rosman 1997, Wombacher *et al.* 2003). Combining this Cd purification procedure with MC-ICP-MS analysis, high precision measurements of the Cd isotopic composition (~ 0.12‰ on the δ^{114}Cd/^{110}Cd, which correspond to ~ 0.03‰ per amu) were obtained.

Using this new method, the isotopic composition of geological and anthropogenic samples was investigated. Several reference materials were selected (Table 1), one of which being a residue of municipal waste combustor. Other anthropogenic samples (from a lead smelter) were also analysed. These materials, covering a large range of composition, were selected according to their high Cd concentration, and their possible environmental applications. Indeed, Cd together

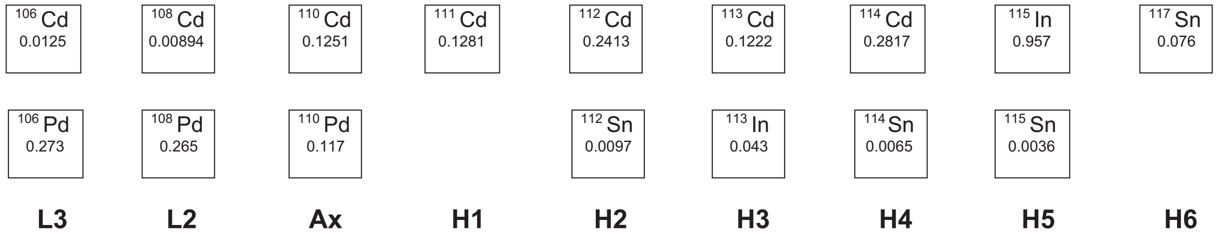

Figure 1. Cadmium data acquisition scheme. Configuration of the nine Faraday collectors made it possible to measure seven Cd isotopes at masses 106, 108, 110-114 and to monitor In and Sn isobaric interference at masses 115 and 117.

Table 1.
Nature, selected concentration, total recovery and isotopic composition of the studied samples

Name	Type	Cd (μg g^{-1})	Cu (μg g^{-1})	In (μg g^{-1})	Pb (μg g^{-1})	Sn (μg g^{-1})	Zn (μg g^{-1})	Cd introduced (μg)	Cd found (μg) after total chemistry	Cd total recovery (%)	δ$^{114/110}$Cd (‰)	2 sd	δ$^{114/111}$Cd (‰)	2 sd	δ$^{114/112}$Cd (‰)	2 sd	δ$^{114/113}$Cd (‰)	2 sd
NIST SRM 2711	Montana Soil	41.7	114	1.1	1162	nd	350.4	4.21	4.10	97.35	0.52		0.37		0.24		0.12	
								4.21	4.11	97.59	0.50		0.42		0.28		0.14	
								12.51	11.89	95.04	0.51		0.37		0.26		0.11	
								1.82	1.81	99.45	0.51		0.39		0.27		0.13	
	Mean										**0.51**	**0.02**	**0.39**	**0.04**	**0.26**	**0.03**	**0.13**	**0.03**
BCR 176	City Waste	470^{+}	1302^{+}	2.4^{+}	10870^{+}	6^{+}	25770^{+}	16.92	16.70	98.70	-0.25		-0.18		-0.11		-0.08	
	incineration							20.21	19.52	96.59	-0.31		-0.22		-0.16		-0.08	
	Ash							41.36	35.15	84.99	-0.35		-0.25		-0.17		-0.09	
	Mean										**-0.30**	**0.10**	**-0.22**	**0.07**	**-0.14**	**0.06**	**-0.08**	**0.02**
Nod-A-1	Mn-Nodule	7.5	1110	nd	846	3*	587	2.03	2.00	98.77	-0.07		-0.04		-0.08		-0.04	
GSS-1	Soil	4.3	21	0.081	98	6.1	680	1.11	1.10	99.00	0.16		0.15		0.07		0.08	
								1.25	1.25	99.84	0.00		0.03		-0.07		0.07	
	Mean										**0.08**	**0.23**	**0.09**	**0.16**	**0.00**	**0.19**	**0.07**	**0.02**
GXR-1	Jasperoid	3.3	1110	0.77	730	54	760	1.37	1.30	94.96	**0.18**		**0.16**		**0.15**		**0.04**	
GXR-2	Soil	4.1	76	0.252	690	1.7	530	1.45	1.40	96.88	**-0.06**		**-0.02**		**0.02**		**-0.01**	
GSD -12	Sediment	4	1230	0.96	285	54	498	1.36	1.30	95.94	**-0.38**		**-0.28**		**-0.27**		**-0.02**	
Nod-P-1	Mn-Nodule	22.6	11500	nd	555	1.9*	1595	2.94	2.80	95.30	**0.13**		**0.10**		**0.07**		**0.02**	
Slag	Residue phase	13	1572	99	17968	793	107638	1.92	1.92	99.74	**0.36**		**0.28**		**0.15**		**0.08**	
Dust 1	Volatile phase	12195	405	153	141219	884	68197	47.19	46.49	98.50	**-0.64**		**-0.44**		**-0.22**		**-0.19**	
Dust 2	Volatile phase	1431	3208	33	173916	277	43705	5.15	5.16	100.16	**-0.64**		**-0.48**		**-0.32**		**-0.18**	

nd not determined.

Values are from Govindaraju (1994) except * which are from Axelsson *et al.* (2002) and + are from BCR. Every single analysis represents the mean of two to ten reference bracketed measurements.

with Hg and Pb is one of the most toxic elements for the living environment. It is responsible for serious disease, such as the Itaï Itaï disease. Also Cd has been continuously monitored by all the French air quality national networks. Therefore, this study is motivated by the potential use of Cd isotopes as new tracers of anthropogenic sources of Cd pollution in the environment.

Sample description

Three different Cd solutions were used: (1) Cd solution from Spex (certiprep, lot # 7-29Cd), Metuchen, USA, diluted from a 1000 µg ml^{-1} solution and used as a reference solution, (2) Cd solution from Prolabo, VWRI, Fontenay sous bois , France (1000 µg ml^{-1} solution) and (3) a Cd Johnson Matthey Company (JMC, LOT502552A), Alfa Aesar, Germany, as used by Wombacher *et al.* (2003) and Wombacher and Rehkämper (2004). The secondary reference solution used in this study is a fractionated Cd solution called "Münster Cd". This solution is a mixture between pure Alfa JMC metal and a strongly industrially fractionated Cd metal as described in Wombacher and Rehkämper (2004).

The samples used in this study include various geological reference materials. GSS-1, GSD-12 distributed by the Institute of Geophysical and Geochemical Prospecting, People's Republic of China (IGGE), Nod-A-1 and Nod-P-1 distributed by United States Geological Survey, Reston (USGS), GXR-1 and GXR-2 distributed by USGS-AEG, NIST SRM 2711 distributed by National Institute of Standards and Technology, USA (NIST) and CRM-BCR 176 distributed by Community Bureau of Reference, Brussels (BCR). Sample descriptions and selected trace metal concentrations are presented in Table 1. Additional details on sample composition and descriptions are available in Axelsson *et al.* (2002) and Govindaraju (1994). Synthetic cadmium sulfide (CdS) purchased from Prolabo and dust and slag from a lead smelter were also analysed. A short description is given below.

GSS-1 is a dark brown podzolitic soil, typical of the mountainous terrain of Northeast China. The underlying granitic bedrock is a part of a lead-zinc mineralisation district. GXR-1 from Drum Mountains (Utah) is a jasperoid and GXR-2 is a soil from Park City (Utah). The last soil studied is NIST SRM 2711 (Montana soil), which is an agricultural soil collected in the till layer (upper 15.2 cm) of a wheat field. GSD-12 stream sediment is from a tributary draining river in the Yangchun ore field (Cu, W, Sn), Guangdong, China. The rock of the basin includes sandstone, shale, carbonate rocks, granite and granodiorite. Two different ferromanganese nodules were also studied. Nod-P-1 was obtained from Deep Sea Ventures, taken at a depth of 4340 metres in the Pacific Ocean and Nod-A-1 comes from the Blake Plateau at a depth of 788 metres in the Atlantic Ocean. Finally, the last geological reference material studied was BCR 176, which is a city waste incineration fly ash. The anthropogenic materials were sampled in a lead smelter, two of which were dusts trapped by filters (volatile phase) and the other one being a slag from the ore purification process (residue phase).

Sample decomposition

Water was purified using a Millipore deionising system at 18.2 MΩ. Quartz-distilled nitric and hydrochloric acid were used for all analytical procedures. For sample dissolution, suprapur hydrofluoric acid (48% v/v), purchased from Aldrich and suprapur H_2O_2 (30% v/v) purchased from Merck were used.

The samples were digested with a mixture of different concentrated acids. Depending on the Cd concentration, between 4 and 400 mg of sample was dissolved with 4 ml concentrated HNO_3 + 0.4 ml H_2O_2. The mixture was left at room temperature for one day. The samples were then taken to dryness at 70 °C on a hot plate. The residue was dissolved in 8 ml of concentrated HNO_3 + 1 ml concentrated HF + 3 ml concentrated HCl and covered beakers were put on a hot plate at 120 °C until complete dissolution. After evaporation at 70 °C, samples were dissolved in 1 ml of 1.2 mol l^{-1} HCl, centrifuged at 10 000 rpm for 10 minutes and were then ready for the purification step.

Purification step

In order to obtain precise and accurate analysis by MC-ICP-MS, an anionic exchange chromatographic procedure to separate the element of interest from its spectral and non-spectral interferences was used. This chemical procedure used Biorad® columns filled with 2 ml of wet AG-MP-1 resin (macroporous anionic resin). The reservoir of the column contained 10 ml.

The one-step purification procedure developed in this study was as follows. The sample in 1 ml of 1.2 mol l^{-1} HCl was loaded onto the resin previously washed and conditioned with 1.2 mol l^{-1} HCl. The elution of the matrix started with 4 ml of 1.2 mol l^{-1} HCl followed by 15 ml of 0.3 mol l^{-1} HCl. The elution continued with 16 ml of 0.012 mol l^{-1} HCl to recover Zn. Cadmium was finally eluted in 17 ml of 0.0012 mol l^{-1} HCl. The use of 0.0012 mol l^{-1} HCl was found to be effective in fixing the platinum-group elements on the resin. However, Sn was marginally observed in the sample Cd fraction, so that Sn-doped Cd solutions were analysed to verify the accuracy of the spectral interference corrections (see Results section). The purification procedure developed in this study allowed the complete separation of Zn from Cd with a total procedural blank level of less that 200 pg, which was always negligible compared to the total amount of Cd used in this study (more than 1 µg).

The total Cd recovery, including the digestion and purification steps, was generally higher than 95% for all the samples (Table 1). The Cd recovered from the purification step was dissolved in dilute nitric acid (0.1 mol l^{-1}). The same acid was used to dilute pure Cd solution and samples in order to ensure an exact match in matrix and acid concentration.

Instrumental settings

The isotopic measurements were performed at the Centre de Recherhes Pétrographiques et Géochimiques (CRPG) using a MC-ICP-MS Micromass® (now GV instruments) Isoprobe™ equipped with nine Faraday cups. A Teflon nebuliser with an uptake rate of 100 µl min^{-1} coupled with a cooled (4 °C) cyclonic chamber was used for sample introduction. All the operating parameters are listed in Table 2.

Table 2.
Instrumental and operating conditions and signal measurement parameters used for Cd isotope measurements on the Micromass® Isoprobe™ (now GV Instruments®)

RF Power	1350 W
Plasma gas flow	13.32 l min^{-1}
Interfaces cones	Nickel/Aluminium
Acceleration voltage	*ca.* -6.00 kV
Ion lens setting	Optimised for maximum intensity
Instrumental resolution	~ 300
Mass analyser pressure	$5.17*10^{-8}$ mbar
Detectors	9 Faraday collectors
Collision cell gas	Ar flow ~ 1.8 ml min^{-1}
Nebuliser	Teflon
Sample uptake rate	100 µl min^{-1}
Typical sensitivity	20 V (1µg ml^{-1})
Cd concentration measured	0.5 µg ml^{-1} in solution
Sampling time	25 measurements of 10 s

The signal acquisition was done according to the collector configuration as reported in Figure 1. Indium and Sn were monitored at the masses 115 and 117 in order to correct for possible isobaric interferences. Each isotopic value corresponds to a measurement of twenty-five cycles of 10 seconds and bracketed by the Cd reference solution (0.5 µg ml^{-1}). Different procedures can be used to obtain accurate and precise measurements by MC-ICP-MS: the "sample-standard bracketing" (Belshaw *et al.* 1998, Rouxel *et al.* 2003), external normalisation (Rehkämper and Halliday 1999, Maréchal *et al.* 1999) and double spike techniques (Thirlwall 2002). All these procedures have advantages and inconveniences described elsewhere (Wombacher *et al.* 2003, Mason *et al.* 2004, Albarède and Beard 2004). Here, the reference-sample bracketing technique was used to measure all the samples because it was the easiest technique to operate and provided, depending on the stability of the mass spectrometer, a good control on instrumental mass bias. Between two and ten bracketed measurements of each sample were made during several analytical sessions. The uncertainty reported is expressed as two times the standard deviation from the mean of all the bracketed measurements. The acid blank signal was subtracted for both unknown and reference samples. All the results were expressed as the deviation relative to the Cd Spex reference solution and are given in per mil (delta) notation following the equation:

$$\delta^{114}Cd/^{x}Cd = [(^{114}Cd/^{x}Cd)_{sample}/((^{114}Cd/^{x}Cd)_{reference1} + (^{114}Cd/^{x}Cd)_{reference2})/2) -1]*1000 \qquad (1)$$

where x represents Cd isotopes 110, 111, 112 or 113 and reference 1 and reference 2 represent the reference solution measured just before and after the sample. The isotopes 106 and 108 were monitored but were omitted in this study because the relative abundances of these masses were too low.

Results

The "sample-standard bracketing" technique often requires a matrix match (including Cd concentration) between samples and reference solutions. Different experiments were done to quantify how the accuracy and precision of the Cd isotopic measurements could be affected during this study.

Effect of dilution

Samples having different concentrations (sample/reference ratios varying between 0.25 and 1)

Table 3.
Cadmium isotopic composition relative to Spex obtained from Cd reference solutions and from different experiments

Sample name	Type	$\delta^{114/110}$Cd (‰)	2 sd	$\delta^{114/111}$Cd (‰)	2 sd	$\delta^{114/112}$Cd (‰)	2 sd	$\delta^{114/113}$Cd (‰)	2 sd	N
Spex [1]	**Cd reference solution**	**0.00**	0.09	**0.00**	0.07	**0.00**	0.05	**0.00**	0.09	**5**
Prolabo [3]	Cd reference solution	-0.01	0.09	0.00	0.08	-0.01	0.04	-0.01	0.02	1
JMC Mean [2]	**Cd reference solution**	**0.05**	0.12	**0.03**	0.10	**0.02**	0.07	**0.01**	0.03	**4**
Spex ech/Spex ref =0.25 [3]	Cd reference solution	0.18	0.05	0.15	0.02	0.09	0.04	0.08	0.05	1
Spex ech/Spex ref =0.50 [3]	**Cd reference solution**	**0.10**	0.15	**0.08**	0.10	**0.05**	0.09	**0.03**	0.03	**2**
Spex ech/Spex ref =0.75 [3]	Cd reference solution	0.16	0.19	0.11	0.13	0.07	0.09	0.04	0.06	1
Spex ech/Spex ref =0.90 [3]	Cd reference solution	0.03	0.21	0.04	0.16	0.02	0.10	0.01	0.05	1
Spex / Sn = 10 [3]	Cd ref. sol. + Sn ref. sol.	-0.13	0.30	-0.09	0.24	-0.07	0.16	-0.03	0.09	1
Spex / Sn = 5 [3]	Cd ref. sol. + Sn ref. sol.	0.03	0.06	0.04	0.03	0.05	0.01	0.05	0.04	1
Spex / Sn = 3.33 [3]	Cd ref. sol. + Sn ref. sol.	0.20	0.05	0.11	0.02	0.03	0.08	0.03	0.11	1
Spex / Sn = 2.5 [3]	Cd ref. sol. + Sn ref. sol.	-0.05	0.04	-0.03	0.04	-0.02	0.01	-0.04	0.04	1
Spex / Sn = 0.1 [3]	Cd ref. sol. + Sn ref. sol.	0.24	0.02	0.18	0.02	0.13	0.01	0.05	0.02	1
Spex / Zn = 10 [3]	Cd ref. sol. + Zn ref. sol.	-0.06	0.17	-0.02	0.12	-0.01	0.09	0.00	0.05	1
Spex / Zn = 1 [3]	Cd ref. sol. + Zn ref. sol.	0.24	0.01	0.19	0.00	0.13	0.00	0.07	0.02	1
Spex / Zn = 0.5 [3]	Cd ref. sol. + Zn ref. sol.	-0.37	0.20	-0.26	0.13	-0.17	0.10	-0.11	0.06	1
Spex / Zn = 0.1 [3]	Cd ref. sol. + Zn ref. sol.	-0.36	0.11	-0.25	0.08	-0.15	0.05	-0.14	0.01	1
Cadmium sulfide [3]	CdS metal	0.16	0.07	0.12	0.06	0.07	0.05	0.04	0.03	1
Spex through chemistry [3]	**Cd ref. sol. + various matrix**	**-0.13**	0.33	**-0.09**	0.24	**-0.06**	0.16	**-0.03**	0.10	**3**
Münster Cd Mean [2]	**Cd metal**	**4.48**	0.04	**3.35**	0.03	**2.24**	0.04	**1.120**	0.005	**5**
Münster Cd through chemistry [3]	**Cd metal**	**4.46**	0.21	**3.32**	0.16	**2.20**	0.12	**1.12**	0.04	**2**

[1] The number of reference bracketed measurements was between 10 and 20 for each session.

[2] The calculations are based on the mean of the mean obtained for each session. The number of reference bracketed measurements for each session was between 7 and 22.

[3] The number of reference bracketed measurements was between 2 and 10.

Samples analysed during more than one session are shown in bold type. N represents the number of sessions in which the sample was analysed.

were run to document any effect on the measured Cd isotopic composition. Results are reported in Table 3. For samples having a ratio of 0.25, we obtained a $\delta^{114}Cd/^{110}Cd$ slightly higher (0.18‰ ± 0.05) than the expected value (0‰). For other sample/reference ratios, the Cd isotopic compositions are statistically indistinguishable from the reference value but best results were obtained for sample/reference ratios between 0.90 and 1. For this study, the sample and the reference were analysed at the same concentration to within a 10% difference.

Sn and Zn monitoring

As mentioned above, residual amounts of Sn were sometimes observed in the Cd fraction. A Sn spectral interference occurs on two of the Cd isotopes measured (Figure 1) and needed to be monitored and corrected if necessary. To ensure an accurate correction, we analysed Cd reference solutions doped with different Sn concentrations. Samples with Cd/Sn ratios of 10, 5, 3.33, 2.5 and 0.1 were analysed and yielded $\delta^{114}Cd/^{110}Cd$ values of -0.13, 0.03, 0.20, -0.05 and 0.24‰ respectively (Table 3). A Cd/Sn ratio of 0.1 and 3.33 resulted in a slight Cd isotopic deviation relative to the Cd reference solution without Sn.

Because Zn is very abundant relative to Cd and because Zn and Cd have similar chemical behaviour during purification procedures, it is important to study the effect induced by the addition of Zn to the Cd fraction. Measurements were made with Cd reference solution Zn-doped with Cd/Zn ratios of 10, 1, 0.5 and 0.1. These Zn-doped solutions yielded isotopic compositions deviating from the Cd reference by -0.06, 0.24, -0.37 and -0.36‰ respectively (Table 3).

Column chemistry fractionation

In order to verify that no isotopic deviation was created by the purification procedures, a Cd reference solution was passed directly through the anion exchange column. The Cd solution had previously been doped with different elements (Al, Ca, Na, Mg, Fe, Pb, Zn, Sn, Cd, Cu) that would correspond to matrices similar to those of the samples (six different matrices). The mean $^{114}Cd/^{110}Cd$ delta values obtained on these solutions was -0.13‰ ± 0.33. The chemical procedure did not introduce a systematic Cd isotopic bias within the uncertainty whatever the matrix added. For our samples, Cd recoveries, through the full preparation scheme (digestion + purification), were greater than 95% except for one of the three preparations of the BCR 176 sample, which yielded a recovery of only 85% (Table 1). However, no relationship between recovery yields and Cd isotopic composition was observed (Table 1). This suggests that the loss of 15% Cd occurred through a process that did not fractionate Cd isotopes.

Because the elution volume of Cd in diluted HCl medium is large, isotopic fractionation may occur during the Cd elution. In order to document such an effect, several fractions of reference solution taken at different steps of the elution were measured for their Cd isotopic composition. A significant Cd isotopic fractionation was observed and is in the same range as already reported for Cd (Wombacher *et al.* 2003), although the column chemistry was different. The same effect is also reported for Cu (Maréchal *et al.* 1999). The fractionation is progressive and can be as large as 2.4‰ for $\delta^{114}Cd/^{110}Cd$. The Cd isotope fractionation ranged from 0.72‰ for the first eluted fraction to -1.65‰ for the last eluted fraction (Figure 2). The cumulative Cd concentrations in the fractions correspond to more than 99% yield and the weighted average Cd

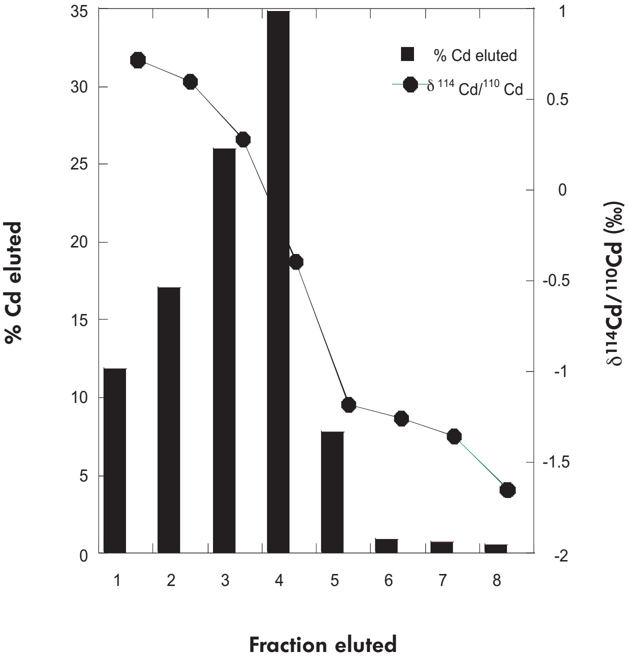

Figure 2. Cadmium isotopic variation in different fractions eluted during the column chemistry along with the Cd concentration in the fractions. A Cd isotopic fractionation is induced during the purification step but the integration of the delta Cd values yielded the expected results of 0‰ within the experimental uncertainties.

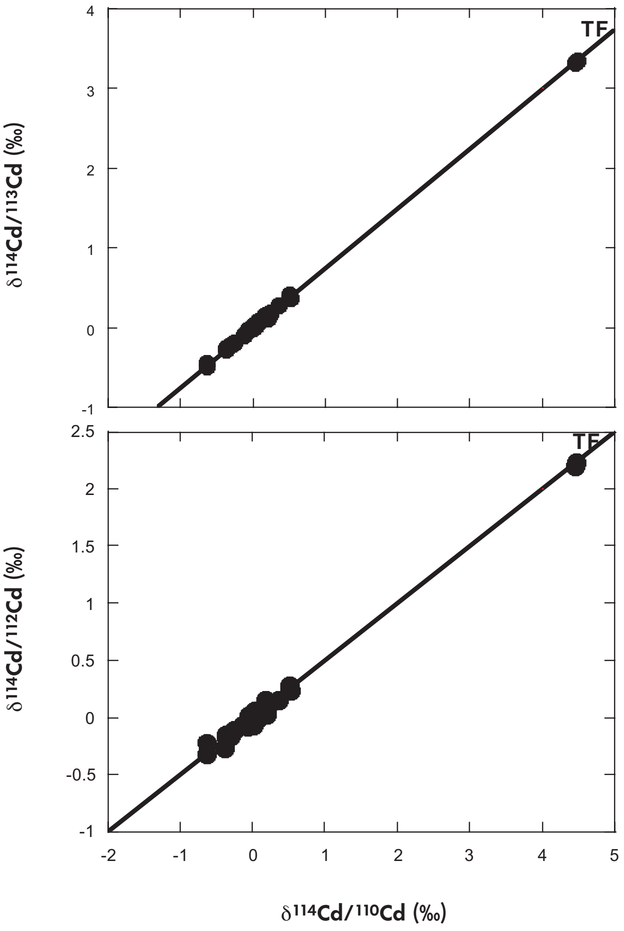

Figure 3. Cadmium three isotope plots for samples and experiments presented in this study. All the samples plot on the theoretical mass fractionation line (TF) within the uncertainty. The measured samples are not affected by spectral interferences.

isotopic composition from these fractions was about -0.18‰ for the ^{114}Cd/^{110}Cd delta value. This result is close to the expected value of 0‰ when taking into account the uncertainty of the mass balance and the measurements.

The measured isotopic composition of all Cd reference solutions and samples plot, within the uncertainty, on a single theoretical mass fractionation line in a three-isotope diagram (Figure 3). This indicates that there was no spectral interference for these isotopes.

Cadmium reference solutions

The isotopic composition of the reference solutions Spex, Prolabo and JMC were analysed. The δ^{114}Cd/^{110}Cd obtained for the reference solution Spex against itself was 0.00‰ ± 0.09‰. The δ^{114}Cd/^{110}Cd measured for the Prolabo solution relative to the Cd Spex solution was -0.01‰ ± 0.09 and the δ^{114}Cd/^{110}Cd of Cd JMC was 0.05‰ ± 0.12 (Table 3). These average values include measurements obtained during different analytical sessions over a one-year period. These Cd solutions gave the same isotopic composition within the uncertainty (Table 3). As no official primary reference material for Cd is yet adopted, this implies that inter-laboratory comparison is still possible if one of these commercial Cd solutions is used. The Münster Cd solution was used as a secondary isotopic reference. In this study, the measurements of this solution yielded a δ^{114}Cd/^{110}Cd of 4.48‰ ± 0.04. This value is identical to the theoretical value calculated (δ^{114}Cd/^{110}Cd of 4.5‰, Wombacher and Rehkämper 2004). A purification procedure was applied to the Münster Cd solution and measurements yielded an isotopic composition of 4.46‰ ± 0.21, which is identical within error to the value measured by analysing directly the sample without chemical purification. Because of its large deviation relative to other Cd reference solutions, this result further confirms that our purification procedure does not introduce significant Cd isotopic fractionation. Finally, a synthetic Cd sulfide was also analysed. This sample showed a relative deviation of 0.16‰ ± 0.07 in δ^{114}Cd/^{110}Cd. This material provides a slightly different Cd isotopic variation compared to the other commercial Cd solutions.

Geological reference materials and anthropogenic materials

The isotopic compositions measured in the geological reference materials and anthropogenic materials are reported Table 1 and illustrated in Figure 4. The overall isotopic variation was 1.14‰ in δ^{114}Cd/^{110}Cd, which is ten times larger than our long-term external reproducibility. Soil samples GXR-1, GXR-2 and GSS-1 yielded Cd isotopic compositions of 0.18‰ ± 0.19, -0.06‰ ± 0.19 and 0.08‰ ± 0.23 respectively, and did not show a significant Cd isotopic variation relative to the Cd Spex solution. On the other hand, the other soil NIST SRM 2711 yielded a δ^{114}Cd/^{110}Cd value of 0.50‰ ± 0.02, an isotopic composition significantly heavier than the Spex solution and the other soil reference materials, GXR-1, GXR-2 and GSS-1. The value obtained for GSS-1 corresponds to a mean of two different digestions and that for NIST SRM 2711 is the mean of four different digestions analysed in different sessions. The replicates suggest that these materials are not significantly heterogeneous. The only sediment

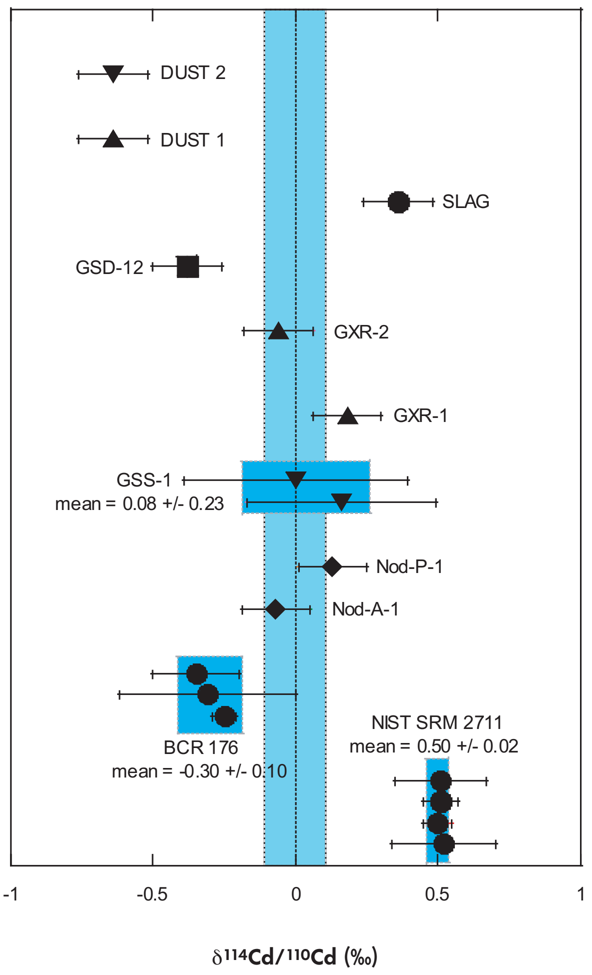

Figure 4. Cadmium isotopic variation in δ^{114}Cd/^{110}Cd (‰) relative to Cd Spex reference solution obtained for geological reference materials and anthropogenic samples (see text for samples description). The Cd isotopic variations in geological reference materials exist but are of limited magnitude. Some industrial processes may introduce a Cd isotopic fractionation as reflected by the dusts (volatile phase) and the slag (residue phase) from a lead smelter.

material studied here (GSD-12) showed a slight depletion in heavier isotopes relative to the Cd Spex solution.

The incinerator fly ash BCR 176 yielded a Cd isotopic composition of -0.28‰ ± 0.10. This value corresponds to the mean of three different digestions out of which eight samples were purified and analysed over one year. The BCR 176 material has an isotopic composition just outside the uncertainty of the Cd Spex solution. It is slightly depleted in heavier Cd isotopes relative to the Cd Spex solution and relative to the soil reference material studied GXR-1, GXR-2, GSS-1 and NIST SRM 2711. Finally, the two Mn-nodule reference materials, Nod-P-1 and Nod-A-1, yielded Cd isotopic compositions of 0.13‰ ± 0.12 and -0.07‰ ± 0.12 respectively. These values are the same, taking into account the respective uncertainty on the measurements.

Two dust samples from a lead smelter were also analysed. These samples provided the same δ^{114}Cd/^{110}Cd of -0.64‰. These are anthropogenic materials resulting from industrial processes. A residue from the same smelter (slag) yielded an isotopic composition of 0.36‰ ± 0.12. The difference between the evaporated phase and its residue is about 1‰. Such a difference strongly suggests that Cd isotopes were fractionated during the purification of Cd in the smelter.

Discussion

The purification procedure for Cd developed in this study represents an improvement when compared to other purification methods already published. Indeed, the purification described above is very efficient in recovering Cd compared to those described in Sands and Rosman (1997), which provided only a 85% recovery. Such low yields are less important when the double spike technique is used, but the external normalisation and the reference-sample bracketing techniques require close to 100% yields to ensure no isotope fractionation during treatments. Moreover, the simple one-step purification described here, using only diluted HCl, permits an efficient separation of the Cd contained in the sample from its matrix and spectral elemental interferences are avoided. This is an improvement compared to the purification of Wombacher *et al.* (2003), where residual Ru, Zn or Sn can be found in the Cd fraction. Such elements could produce spectral or non-spectral interferences. Non-spectral interferences, due to the matrix component in solution with the analyte fraction, could affect the accuracy and/or the precision of the measurements (Galy *et al.* 2001, Ingle *et al.* 2003, Wombacher *et al.* 2003, Archer and Vance 2004, this work). The principal explanations considered for non-spectral interferences are space charge and plasma vaporisation effects (Albarède and Beard 2004). In the experiments done in this work, the Sn spectral interferences were found to be accurately corrected when the Cd/Sn ratio was as low as 5. The higher δ^{114}Cd/^{110}Cd deviation observed with lower ratios reflects the inaccurate correction of the Sn spectral interference onto the Cd mass 114. Fortunately, a Cd/Sn ratio of more than 50 was always observed in the samples. From these results, the correction applied on samples containing traces of tin could be considered accurate.

The reference-sample bracketing technique or external normalisation are more sensitive to the non-spectral interferences than the double spike technique. This observation was confirmed when analysing Zn-doped Cd solutions. Indeed, solutions having Cd/Zn ratios lower than 10 yielded a significant shift in δ^{114}Cd/^{110}Cd (0.24‰) relative to the Zn-free Cd solution. This has already been observed when using Ag external normalisation (Wombacher *et al.* 2003). In the latter, the deviation observed is larger (0.12‰/amu, ~ 0.48‰ for δ^{114}Cd/^{110}Cd) mainly due to Zn-argide interferences occurring on the Ag mass 107. During the course of this study, no significant traces of Zn were found in the purified Cd samples.

In order to obtain accurate and precise Cd isotopic measurements with MC-ICP-MS without using the double spike technique, it is necessary to verify that the Cd concentration of the sample and reference solution are equal within 10%, to remove the possible spectral and non-spectral interferences and to ensure a near 100% Cd recovery.

Our results show that variations in the Cd isotopic composition exist in terrestrial material but that these are of limited magnitude. However, they certainly reflect different sources and/or processes leading to isotopic mass fractionation. For example, evaporation-condensation processes have been inferred to explain large isotopic heterogeneity measured in meteorites and lunar soils (Sands *et al.* 2001, Wombacher *et al.* 2003, 2004, Wombacher and Rehkämper 2004). Such processes certainly took place in waste incinerators and fly ash materials. Materials like BCR 176 probably contain Cd that has passed through different chemical forms. Considering that the volatile phase of Cd metal is depleted in the heavy isotopes (because the Cd residue is highly enriched in heavy Cd; see Münster Cd metal, Table 3), the presence of a few percentage of Cd gas condensates on fly ashes might readily explain the negative δ^{114}Cd/^{110}Cd value of -0.28‰. This could also explain the negative δ^{114}Cd/^{110}Cd value of -0.64‰ for industrial dusts and the positive δ^{114}Cd/^{110}Cd value of 0.36‰ for the residual phases (slag). This suggests that industrial processes may introduce isotopically-fractionated Cd into the environment.

The similar Cd isotopic composition measured for Mn-nodules may reflect the isotopic homogeneity of ocean water masses. Lacan and Francois (2004) report a variation of less than 0.2‰ of δ^{114}Cd/^{110}Cd in a seawater depth profile of the North Pacific. Wombacher *et al.* (2003) report the possibility of Cd isotopic fractionation during chemical precipitation of aragonite, the Cd in the mineral phase being depleted in heavy isotopes. This has not yet been observed in natural environments. The different soil samples analysed yielded slightly different Cd isotopic compositions that might reflect different sources of contamination, such as industrial or agricultural, particularly for NIST SRM 2711. Moreover, other mechanisms such as adsorption, complexion and bio-accumulation may be responsible for Cd isotopic fractionation. Vegetation does not need Cd for life, but does need Zn. Because of the similar geochemical behaviour of both Cd and Zn, plants uptake Cd from soils and Cd may be fractionated as observed for Zn and Cu (Mason 2003), leaving a fractionated Cd in the soil.

Conclusions

In this study, Cd was purified by anion exchange chemistry and successfully analysed by MC-ICP-MS, using the "sample-standard bracketing" technique, providing an average long term external reproducibility of ± 0.12‰ (2 sd) for δ^{114}Cd/^{110}Cd . This purification procedure for Cd gave a recovery of greater than 95% Cd and effectively reduced the possible Sn spectral interferences to a near negligible level, which were in all cases successfully corrected. Three different Cd solutions (Spex, Prolabo and JMC) have an indistinguishable Cd isotopic composition within uncertainty. Until a primary reference material is adopted, the use of one of these solutions as delta "zero" will allow the comparison of data between laboratories. The measured value for Münster Cd, proposed as a possible secondary isotopic reference material, yielded a δ^{114}Cd/^{110}Cd value of 4.48‰ ± 0.04.

The total range observed in geological reference materials and anthropogenic materials in δ^{114}Cd/^{110}Cd was 1.14‰. This is larger than that described so far in the literature for terrestrial material. Such small isotopic variations can now be resolved with the high precision obtained in this study. Some industrial processes may introduce Cd with a fractionated isotopic composition into the environment allowing possible isotope tracing. The next step is to study the biogenic fractionation of Cd and to establish its impact on the global Cd cycle.

Isotopic variations in natural terrestrial materials and anthropogenic materials exist, and suggest strongly that Cd isotopes have a potential for environmental studies.

Acknowledgements

We thank F. Wombacher for providing the Cd JMC solution and the Münster Cd solution. The authors are grateful to the two anonymous reviewers for their careful reading of the manuscript and for many helpful comments. Financial support was provided by the CNRS, the French agency for environment and energy management (ADEME) and by the society Haganis. CRPG contribution No. 1739.

References

Albarède F. and Beard B.L. (2004)
Analytical methods for non-traditional isotopes. Reviews in Mineralogy and Geochemistry: Geochemistry of non-traditional stable isotopes, 55, 113-152.

Archer C. and Vance D. (2004)
Mass discrimination correction in multiple-collector plasma source mass spectrometry: An example using Cu and Zn isotopes. Journal of Analytical Atomic Spectrometry, 19, 656-665.

Axelsson M.D., Rodushkin I., Ingri J. and Öhlander B. (2002)
Multielemental analysis of Mn-Fe nodules by ICP-MS: Optimisation of analytical method. The Analyst, 127, 76-82.

Belshaw N.S., Freedman P.A., O'Nions R.K., Frank M. and Guo Y. (1998)
A new variable dispersion double-focusing plasma-mass spectrometer with performance illustrated for Pb isotopes. International Journal of Mass Spectrometry, 181, 51-58.

Galy A. Belshaw N.S., Halicz L. and O'Nions R.K. (2001)
High-precision measurement of magnesium isotopes by multiple-collector inductively coupled plasma-mass spectrometry. International Journal of Mass Spectrometry, 208, 89-98.

Govindaraju K. (1994)
Compilation of working values and sample description for 383 geostandards. Geostandards Newsletter, 18 (Special Issue), 158pp.

Ingle C.P., Sharp B.L., Horstwood M.S.A., Parrish R.R. and Lewis D.J. (2003)
Instruments response functions, mass bias and matrix effects in isotope ratio measurements and semi-quantitative analysis by single and multi-collector ICP-MS. Journal of Analytical Atomic Spectrometry, 18, 219-229.

Lacan F. and Francois R. (2003)
Cadmium isotopic composition: A new tracer in oceanography. EOS Transactions, American Geophysical Union, 84, Ocean Science Meeting Supplement, 2003.

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

Maréchal C.N., Télouk P. and Albarède F. (1999)
Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. Chemical Geology, 156, 251-273.

Mason T.F.D. (2003)
High precision transition metal isotope analysis by plasma-source mass spectrometry and implications for low temperature geochemistry. Unpublished Ph.D. Thesis, University of London, 298pp.

Mason T.F.D., Weiss D.J., Horstwood M., Parrish R.R., Russell S.S., Mullane E. and Coles B.J. (2004)
High-precision Cu and Zn isotope analysis by plasma source mass spectrometry Part 2. Correcting for mass discrimination effects. Journal of Analytical Atomic Spectrometry, 19, 218-226.

Rehkämper M. and Halliday A.N. (1999)
The precise measurement of Tl isotopic compositions by MC-ICP-MS: Application to the analysis of geological materials and meteorites. Geochimica et Cosmochimica Acta, 63, 935-944.

Rosman K.J.R. and de Laeter J.R. (1974)
The abundances of cadmium and zinc in meteorites. Geochimica et Cosmochimica Acta, 38, 1665-1677.

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

Rosman K.J.R. and de Laeter J.R. (1976a)
Low level determinations of environmental cadmium. Nature, 261, 685-686.

Rosman K.J.R. and de Laeter J.R. (1976b)
Isotopic fractionation in meteoritic cadmium. Nature, 261, 216-218.

Rosman K.J.R. and de Laeter J.R. (1978)
A survey of cadmium isotopic abundances. Journal of Geophysical Research, 83, 1279-1287.

Rosman K.J.R. and de Laeter J.R. (1980)
Mass spectrometric isotope dilution determination of cadmium in geochemical reference samples. Geostandards Newsletter, 4, 1-3.

Rosman K.J.R. and de Laeter J.R. (1988)
Cadmium mass fractionation in unequilibrated ordinary chondrites. Earth and Planetary Science Letters, 89, 163-169.

Rosman K.J.R., de Laeter J.R. and Gorton M.P. (1980a)
Cadmium isotope fractionation of two H3 chondrites. Earth and Planetary Science Letters, 48, 166-170.

references

Rosman K.J.R., de Laeter J.R. and Chedwidden A. (1980b)
Distribution of cadmium in Cockburn Sound, Western Australia. The Science of the Total Environment, 16, 117-130.

Rouxel O., Ludden J. and Fouquet Y. (2003)
Antimony isotope variations in natural systems and implications for their use as geochemical tracers. Chemical Geology, 200, 25-40.

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

Sands D.G., Rosman K.J.R. and de Laeter J.R. (2001)
A preliminary study of cadmium mass fractionation in lunar soils. Earth and Planetary Science Letters, 186, 103-111.

Schmitt R.A., Smith R.H. and Olehy D.A. (1963)
Cadmium abundances in meteoritic and terrestrial matter. Geochimica et Cosmochimica Acta, 27, 1077-1088.

Thirlwall M.F. (2002)
Multicollector ICP-MS analysis of Pb isotopes using a ^{207}Pb-^{204}Pb double spike demonstrates up of 400 ppm/amu systematic errors in Tl-normalization. Chemical Geology, 184, 255-279.

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

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

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