Environmental Pollution 216 (2016) 9-17

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Cd isotope fractionation during simulated and natural weathering \star

Yuxu Zhang ^a, Hanjie Wen ^{a, *}, Chuanwei Zhu ^a, Haifeng Fan ^a, Chongguang Luo ^a, Jie Liu ^{a, b}, Christophe Cloquet ^c

^a State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c Centre de Recherches Petrographique et Geochimiques, CNRS/UMR 7358, 15, Rue Notre-Dame-Pauvres, B. P. 20, 54501 Vandoeuvre-les-Nancy Cedex, France

ARTICLE INFO

Article history: Received 27 October 2015 Received in revised form 17 March 2016 Accepted 16 April 2016 Available online 24 May 2016

Keywords: Cd isotope fractionation Leaching experiment Weathering processes Pollution sources

ABSTRACT

In practice, stable Cd isotope ratios are being applied to trace pollution sources in the natural environment. However, Cd isotope fractionation during weathering processes is not yet fully understood. We investigated Cd isotope fractionation of Pb–Zn ore in leaching experiments and in the environment under natural weathering processes. Our leaching experiments demonstrated that the leachate was enriched with heavy Cd isotopes, relative to initial and residual samples ($\Delta^{114/110}$ Cd_{leachate – initial state} = 0.40–0.50‰, $\Delta^{114/110}$ Cd_{leachate – residual state} = 0.36–0.53‰). For natural samples, $\delta^{114/110}$ Cd values of stream sediments were higher than those of the corresponding soil samples collected from the riverbank, $\Delta^{114/110}$ Cd_{stream sediment – soil} can be up to 0.50‰. This observation is consistent with our leaching experiments, which indicate significant Cd isotope fractionation during natural weathering processes. Therefore, natural contributions should be considered when using Cd isotopes to trace anthropogenic pollution in water and sediment systems.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Cd has eight isotopes (¹⁰⁶Cd, ¹⁰⁸Cd, ¹¹⁰Cd, ¹¹¹Cd, ¹¹²Cd, ¹¹³Cd, ¹¹⁴Cd, and ¹¹⁶Cd), and their abundances range from 0.89% (¹⁰⁸Cd) to 28.17% (¹¹⁴Cd). Studies have revealed that terrestrial samples, e.g. mid-ocean ridge basalt (MORB), oceanic-island basalt (OIB), loess, sediments and sulfides, show clear isotopic fractionation, the magnitude of which may be as great as 1.5‰ in $\delta^{114/110}$ Cd value, however the Cd isotopic compositions of the bulk silicate Earth (BSE) are relatively identical at $\delta^{114/110}$ Cd \approx 0 (Wombacher et al., 2003; Schmitt et al., 2009; Zhu et al., 2013). Evaporation and condensation processes can yield larger Cd isotopic fractionation in meteorite samples, with the value of $\delta^{114/110}$ Cd ranging from -8% to +16% (Wombacher et al., 2008). Industrial production processes can also produce substantial Cd isotope fractionation (Wombacher et al., 2004; Cloquet et al., 2005, 2006; Shiel et al., 2010; Gao et al., 2013). For example, Cloquet et al. (2005, 2006) found that dust and

E-mail address: wenhanjie@vip.gyig.ac.cn (H. Wen).

slag produced by smelters have distinctly different Cd isotopic compositions, with $\delta^{114/110}$ Cd of -0.64% in dust (vapor phase), and +0.36‰ in slag (residue phase). Significant Cd isotope fractionation has also been observed during the metallurgical processing of Zn and Pb ores, giving a mean fractionation of 1.04‰ for $\delta^{114/110}$ Cd (+0.39‰ to +0.64‰ for $\delta^{114/110}$ Cd in the refined Cd metal and -0.52‰ in the fume) (Shiel et al., 2010). These findings demonstrate that, in evaporation processes, the vapor phase is usually enriched with relatively light Cd isotopes, while the residue has a greater proportion of heavy Cd isotopes. In addition, these findings also suggest that different final components of man-made pollutants may have different $\delta^{114/110}$ Cd values. This implies that Cd releasing into the environment from anthropogenic sources would affect the Cd isotopic compositions in the contaminated area. Cd isotopes can therefore be used to trace the source of Cd in the environment and a number of researchers have utilized this technique. Cloquet et al. (2006) examined Cd isotope ratios in soil surrounding an abandoned Pb-Zn smelter in northern France and found three major types of Cd pollution sources: industrial dust, slag, and agriculture. Shiel et al. (2012) found that Cd contaminants from anthropogenic sources in marine bivalves were mainly enriched with light isotopes ($\delta^{114/110}$ Cd of -1.2% to -0.54%), whereas bivalves contaminated by natural sources were mainly





CrossMark

POLLUTION

^{*} This paper has been recommended for acceptance by W. Wen-Xiong.

^{*} Corresponding author. State Key Laboratory of Ore Deposit Geochemistry (SKLODG), Institute of Geochemistry, Chinese Academy of Sciences, Guanshui Road 46, Guiyang, Guizhou Province, 550002, China.

enriched with heavy Cd isotopes ($\delta^{114/110}$ Cd of -0.69% to -0.09%). Gao et al. (2013) found that the Cd isotope ratios in a stream sediment were potential indicators for tracing the source of the Cd pollution. Wen et al. (2015) examined Cd isotopes in soil near a Pb–Zn mine, and showed that the sources of Cd pollution were primarily mining production activities. Chrastný et al. (2015) determined Cd isotope ratios in soil near the Olkusz Pb–Zn smelter in southern Poland, and found that the soil humus layer was more enriched with light Cd isotopes than the topsoil near the soil profile further from the smelter. It remains unclear whether isotope fractionation occurs during the process of Cd migration and transformation in the environment, and this limits the application of Cd isotope tracing in identifying Cd pollution sources.

In this study we simulated supergene weathering of a Pb–Zn ore in the laboratory to measure the Cd isotopic compositions in leachates and within Pb–Zn ores before and after leaching. In addition, we determined the Cd concentration and isotopic composition of stream sediments from a severely polluted river and soil samples collected from riverbanks in the Jinding Pb–Zn mine area. By comparing the results of the laboratory simulation and the field observations, we aimed to provide a methodology for the use of Cd isotope ratios in tracing the sources of Cd pollution and improve understanding of the underlying processes of isotope fractionation in the environment.

2. Materials and methods

2.1. Samples and materials

A 5 kg Pb–Zn ore sample was collected from the Jinding Pb–Zn mine in Lanping County, Yunnan Province, China, for use in the leaching experiments. The sample mineralogy was mainly sphalerite (ZnS), with a small amount of galena (PbS) and a large amount of wall rock (carbonate). After air drying the sample was crushed and passed through a 10 mesh (sieve size: 1.9 mm) nylon sieve, then the screen underflow was mixed evenly for use in the leaching experiment.

Stream sediment samples were collected from the Bijiang River in Lanping County, Yunnan Province, China. The Bijiang River flows through the Jinding Pb-Zn mining area, and it is considered heavily polluted (Li et al., 2008). A total of 29 stream sediment samples were collected. The sampling area had a total length of 18.5 km, and included the region polluted by the Pb-Zn mine and both its upstream and downstream areas. In the region contaminated by the Pb-Zn mine, the sampling interval was 0.5 km; in less polluted areas the sampling interval was 1 km. Soil samples were collected, at 0–10 cm soil depth, from the left and right banks of the river, corresponding to the stream sediment sampling positions (the left and right banks are defined as the sides to the left or right when facing downstream). A total of 29 soil samples were collected from the left bank, and 28 from the right bank (one sample on the right bank could not be collected because the river flows through a small town). The spatial distribution of the samples is shown in Fig. 1. The stream sediments and soil samples were air dried for 10 days, then crushed with a wooden stick by hand, and passed through an 80 mesh (sieve size: 0.18 mm) nylon sieve. Each sieved sample was ground further in an agate mortar and passed through a 200 mesh (sieve size: 0.074 mm) nylon sieve so that the most homogeneous powder possible was obtained for elemental and isotopic analysis.

Nitric (HNO₃), hydrochloric (HCl), and hydrofluoric (HF) acids used in this study were purified in-house from concentrated reagent grade acids by sub-boiling distillation. Ultra-pure water (\geq 18.2 M Ω), prepared by the de-ionization of reverse osmosis water using a Milli-Q[®] system (Millipore, USA), was used to prepare

all solutions.

2.2. Experimental setup

The leaching experiments were replicated two times (denoted here as Leaching Experiment 1 and 2). The leaching experiments simulated supergene weathering and leaching caused by acid rain, using a leaching device as shown in Fig. 2. The leaching device is a circulatory system consisting of three parts: rainwater evaporation, rainwater synthesis, and supergene weathering and leaching of ore. An electric stove with adjustable power was used to heat the leachate. Different concentration of hydrochloric acid is used as leachate, which was heated to form a weakly acidic vapor, and subsequently formed weakly acidic water (acid rain) after condensation. The weakly acidic water was used to leach Pb-Zn ore samples, simulating the supergene weathering and leaching caused by natural acid rain. The adjustment of the stove power controlled the amount of water vapor produced. In the experiment, the rate of water vapor condensation into water was 5-6 ml/min, and the amount of synthetic rainwater used to leach the samples ranged from 2400 to 2880 ml/day. Leaching was conducted for a total of 40 days, and each day for 8 h.

In the leaching experiments, the column used to hold the samples (leaching column) was made of glass, with an inner diameter of 45 mm (outer diameter 50 mm), and a height of 500 mm. A filter was installed at the bottom of the leaching column. In the experiment, a layer of quartz sand (20 mm thick, 20 mesh) was placed on the filter of each column, and then the samples were added. The filter and the quartz sands prevented micro-fine particles from entering the leachate. Prior to experimentation, water soluble state of heavy metals of all samples were removed by the deionized water in continuous oscillation under 20 °C for 30 min as described by Leleyter and Probst (1999). The leaching device was soaked in 40% v/v HNO₃ for 48 h and then thoroughly rinsed with Ultra-pure water to remove any potential contamination. In both experiments, 1 kg leached samples were collected from the 5 kg Pb–Zn ore sample. After the samples were poured into the leaching column, they were soaked in ultra-pure water for 6 h, and then the valve at the bottom of the filter was opened to drain excess water. The samples were washed 5 times with ultra-pure water. Then the corresponding leaching experiment was conducted.

In Leaching Experiment 1, each day before leaching, the pH of the leachate in the flask (labelled a in Fig. 2) was adjusted to 4.0 with HCl. In Leaching Experiment 2, each day before leaching, the pH of the leachate in the flask (labelled a in Fig. 2) was adjusted to 3.0 with HCl. For Experiment 2, after the experiment reached 20 days, the leachate in the flask was removed and stored. New leachate (1000 ml) was used for the remaining 20 days of the experiment. In both leaching experiments, changes in the pH of the synthetic rain obtained (labelled b in Fig. 2) over time during the leaching process is shown in Fig. 3. Table 1 details the experimental conditions for the two experiments.

2.3. Element analyses

For solid samples (including soil, stream sediments, and the Pb–Zn ore used in the leaching experiments and its residual fraction), a 100 mg sample was weighted and placed into a high-pressure digestion vessel. Next, 1 ml of 21 mol/L HF and 0.5 ml of 15 mol/L HNO₃ were added, and the vessel was placed on a hot plate to first dissolve the sample and then evaporate the solution, in order to remove the majority of silicate minerals. Next, 1 ml 21 mol/L HF and 0.5 ml 15 mol/L HNO₃ was added, and the high-pressure digestion vessel was sealed, put into an oven, and heated at 200 °C for 12 h. After cooling, the digestion vessel was opened and



Fig. 1. A: Sampling sites in the Jinding Mine district, China. B: Cd concentrations (μg/g) and δ^{114/110}Cd (‰) in soil and stream sediment samples along the Bijiang River from upstream to downstream. (): right bank, []: stream sediment, {}: left bank. The left and right banks are defined as the sides to the left or right when facing downstream.

placed on a hot plate (about 150 °C), 1 ml of Rh solution (1 μ g/ml) was added as an internal standard, and the solutions were evaporated to dryness. Then 1 ml of 15 mol/L HNO₃ was added and the solution was evaporated to dryness. Next, 6 ml of 6 mol/L HNO₃ was added, and the high-pressure digestion vessel was again sealed and placed in an oven for heating at 140 °C for 3 h. After cooling, the solution was diluted to 100 ml.

For leachate, it was left until the supernatant layer was completely clear. Then 1 ml of supernatant was transferred to a Teflon beaker, then 0.5 ml of 15 mol/L HNO₃ and 1 ml of Rh solution $(1 \ \mu g/ml)$ were added. The beaker was placed on a hot plate to evaporate the solution. Then 1 ml 15 mol/L HNO₃ was added and the solution was evaporated again. Next 1 ml of 15 mol/L HNO₃ was added to dissolve the residue, which was then diluted to 100 ml.

The Cd, Zn and Pb concentrations for all samples were determined by inductively coupled plasma optical emission spectrometer (ICP-OES; Varian Vista MPX) and inductively coupled plasma—mass spectrometry (ICP-MS; PE EIAN DRC-e) at the State Key Laboratory of Ore Deposit Geochemistry, at the Institute of Geochemistry, Chinese Academy of Sciences. Samples were firstly measured by ICP-OES with the correction using multi-element (Cd, Zn, and Pb) calibration curves. In order to obtain more accurate data, those samples with low concentration (Cd < 1 μ g/ml, Zn < 2 μ g/ml, Pb < 4 μ g/ml) were then analyzed using ICP-MS. The concentrations were determined with satisfactory precision for most of the elements, and the relative standard deviations were typically lower than 5%. The sample preparation and calibration procedures and the operating conditions used for the instrument were established previously and have been published by Qi and Grégoire (2000). The international reference materials AGV-2, AMH-1, and GBPG-1 and the Chinese National reference material GSR-1 were analyzed so that the quality of the data could be controlled.

2.4. Cd isotope analysis

After the Cd concentrations in the powder samples were determined, an aliquot that would have contained more than 1 μ g Cd was taken from each sample and oxidized using 1:2 mixture of HF (21 mol/L) and HNO₃ (15 mol/L) at 120 °C for at least 16 h, until



Fig. 2. Diagram illustrating the device used for the leaching experiments.



Fig. 3. The pH of synthetic rainwater in leaching experiments.

the sample was completely dissolved. The sample solution was evaporated to dryness and then dissolved in 2 mol/L HCl. The leachate was acidified by adding 2 ml of 15 mol/L HCl, and evaporated to dryness on a hot plate at 100 °C. It also was then dissolved in 2 mol/L HCl. A procedure using an anion exchange resin (AG-MP-1M) column, which has been described by Zhang et al. (2010) and Wen et al. (2015), was used to separate the Cd from the matrix. And the same amount of Cd (2 ml, about 0.5 μ g/ml) was loaded onto each chromatography column. For all samples, both before and after the chemical separation, a small amount of solution was collected for trace elements measurement, in order to assess the Cd recovery and the removal of the matrix. We only measured the Cd isotopic compositions of the sample in which the recovery of Cd was up to 97% and the potential interferences were present at negligible levels (Pd/Cd < 0.08, Sn/Cd < 0.08, In/Cd < 0.08, Zn/

Cd < 0.08). The study by Cloquet et al. (2005) demonstrated that when the recovery of Cd can attain to 95%, the potential Cd isotopic fractionation were negligible during the chemical purification process.

The Cd isotope measurements were performed at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, using a Neptune plus multi collector ICP-MS instrument. Delta values were calculated using the standard sample bracketing method. Instrumental drift was corrected by averaging the ratios measured in the bracketing reference solutions. Only sections with linear or smooth drifts for the reference solution were used to calculate the delta values for the samples. The ¹⁰⁵Pd, ¹¹⁵In and ¹¹⁷Sn were monitored to correct for the possible isobaric interferences on ¹¹⁰Cd, ¹¹²Cd, ¹¹³Cd, and ¹¹⁴Cd. The samples and bracketing reference solutions were run in 3 blocks of 15 measurement cycles for each m/z ratio. Spex Cd solution (supplied by Dr Cloquet, CRPG, France) was used as the Cd isotope reference standard, and Münster Cd (supplied by Dr Cloquet, CRPG, France), NIST SRM 3108 Cd and JMC Cd (lot#74-075219k) were used as secondary reference standards. During measurement of isotope ratios, one secondary reference standard was measured after measuring three samples. The accuracy of the instrument was monitored according to the delta values obtained from the secondary reference standard. The concentrations in the samples and reference Cd samples were 200 ppb, and the difference in Cd concentration between the samples and the reference solution was less than 10%. In this study, the measured $\delta^{114/110}$ Cd of Münster Cd ranged from 4.46% to 4.53%, with a mean of $4.50 \pm 0.04\%$ (2SD, N = 31) (recommended value in Cloquet et al. (2005) 4.48 \pm 0.04‰); the measured $\delta^{114/110}$ Cd of NIST SRM 3108 ranged from 0.08‰ to 0.14‰, with a mean of 0.11 \pm 0.03‰ (2SD, N = 30) (long-term average of the laboratory measurement: 0.11 ± 0.04 %, from 10 measurement sessions over one year, and the $\delta^{114/110}\text{Cd}$ ranged from 0.07‰ to 0.14‰. The recommended value in Abouchami et al. (2012) 0.089 \pm 0.04‰); the measured $\delta^{114/110}$ Cd of JMC Cd (lot#74-075219k) ranged from -1.56‰ to -1.63‰, with a mean of $-1.58 \pm 0.05\%$ (2SD, N = 30) (long-term average of the laboratory measurement: $-1.59 \pm 0.04\%$, from 8 measurement sessions over one year, and the $\delta^{114/110}$ Cd ranged from -1.55%to -1.63%). The relationship between two delta values reported indicates the mass dependent fractionation, suggesting that all measurements were free of, or corrected for, any possible isobaric interference. The relationship between $\delta^{114/110}$ Cd and $\delta^{112/110}$ Cd for all samples and reference standards used in this study are illustrated in Fig. 4.

A Spex Cd solution was used as an internal reference standard. Considering NIST 3108 (Cd) has popularly become the recommended zero value for Cd isotopes, therefore we re-calculated all $\delta^{\times/110}$ Cd values relative to NIST 3108, which would facilitate the comparison of almost all published data. The δ notation was used to present the results, as defined by the following relationship:

$$\begin{split} \delta^{x/110}Cd(\textbf{‰}) &= \left[({}^{x}Cd/{}^{110}Cd)_{sample} \Big/ ({}^{x}Cd/{}^{110}Cd)_{std} - 1 \right] \\ &\times 1000. \end{split}$$

where ^xCd represents the ¹¹¹Cd, ¹¹²Cd, ¹¹³Cd, or ¹¹⁴Cd isotope.

Table '	1

Detailed parameters of the two leaching experiments.

	Sample weight (g)	Leaching volume (ml)	Initial pH	Leaching time (day)	Total leaching volume (ml/day)
Leaching Experiment 1	1000	1000	4	40	2400–2880
Leaching Experiment 2	1000	1000	3	20 + 20	2400-2880

The initial pH is represented by the pH of the leachate before leaching



Fig. 4. Relationship between $\delta^{114/110}Cd$ and $\delta^{112/110}Cd$ in samples and reference solutions.



Fig. 5. The leachability of Cd, Zn, and Pb in leaching experiments.

3. Results and discussion

3.1. Cd, Zn, and Pb concentrations of samples from the leaching experiments

Cd, Zn, and Pb concentrations in samples from the leaching experiments are shown in Table 2. We defined the leachability of metal M as follows: (total amount of metal M in the leachate)/(total amount of metal M in the initial sample) \times 100%. In Leaching Experiment 1, after 40 days, the leachability of Cd, Zn, and Pb were 0.090%, 0.124%, and 0.03%, respectively. In Leaching Experiment 2, after the first 20 days of leaching, the leachability of Cd. Zn. and Pb were 0.043%, 0.054%, and 0.016%, respectively, and in the next 20 days, the leachability of Cd, Zn, and Pb were 0.049%, 0.067%, and 0.020%, respectively. The total leachability of Cd, Zn, and Pb throughout 40 days were 0.092%, 0.121%, and 0.036% for Experiment 2, respectively. In our leaching experiments, we found that the leachability of Cd and Zn were relatively high and positively correlated, whereas Pb was relatively low (Fig. 5), which is consistent with observations of Domènech et al. (2002) and Kossoff et al. (2011).

3.2. Cd isotopic fractionation during leaching experiments

The Cd isotopic compositions of samples collected from the leaching experiments are shown in Table 2. In Leaching Experiment 1, after 40 days of leaching, the $\delta^{114/110}$ Cd of the leachate differed

from those of the residual and initial states by 0.53‰ and 0.50‰, respectively. In Leaching Experiment 2, after the first 20 days, the $\delta^{114/110}$ Cd of the leachate differed from those of the residual and initial states by 0.42‰ and 0.46‰, respectively. Over the final 20 days of leaching, the $\delta^{114/110}$ Cd of the leachate differed from those of the residual and initial states by 0.36‰ and 0.40‰, respectively. For the total leachate in Leaching Experiment 2, the calculated value of $\delta^{114/110}$ Cd of the leachate differed from those of the total leachate in Leaching Experiment 2, the calculated value of $\delta^{114/110}$ Cd = (0.043 \times 0.28 + 0.049 \times 0.22)/(0.043 + 0.049) = 0.25‰, and the $\delta^{114/110}$ Cd of the leachate differed from those of the residual and initial states by 0.39‰ and 0.43‰, respectively. In both leaching experiments, there was little difference in $\delta^{114/110}$ Cd between the residual and initial states.

Fernandez and Borrok (2009) measured the Fe, Cu, and Zn isotopic compositions of the fluids generated during leaching experiments with sulfide, and found that the oxidative weathering of sulfide-rich rocks can produce substantial variations in Fe (-1.75 to +1.0‰ Δ^{56} Fe_{solution – pyrite}) and Cu isotope ratios (0.0 to +2.0‰ Δ^{56} Cu_{solution – chalcopyrite}), and small variations in Zn isotope ratios (0.0 to +0.2‰ Δ^{56} Zn_{solution – sphalerite}) between the fluid phase and the rock. However, Cd isotope fractionation during supergene weathering is not well established. Our simulation experiments demonstrated that leaching of Pb–Zn ore can produce substantial variations in Cd isotopes ($\Delta^{114/110}$ Cd_{leachate – initial state} = 0.50‰) between the fluid phase and the Pb–Zn ore. The leachate was enriched with heavy Cd isotopes relative to the Pb–Zn ore.

In Leaching Experiment 1, the pH of the synthetic rain ranged from 4.2 to 6.5 during the leaching process (Fig. 3), the isotopic fractionation between the leachate and the initial state ($\Delta^{114/}$

Table 2

Cd, Zn, and Pb concentrations and Cd isotopic compositions in different stage samples from two leaching experiments.

	Initial state Leaching experiments 1			Leaching experiments 2					
	Leached samples	Residual state	Leaching solutions	Leachability (%)	Residual state	Leaching solutions (A)	Leaching solutions (B)	Leachability A (%)	Leachability B (%)
Cd	457 μg/g	n. m.	0.41 μg/ml	0.090	n. m.	0.195 μg/ml	0.224 µg/ml	0.043	0.049
Zn	28,900 μg/g	n. m.	45.8 µg/ml	0.124	n. m.	15.7 µg/ml	19.4 µg/ml	0.054	0.067
Pb	770 μg/g	n. m.	0.25 µg/ml	0.03	n. m.	0.12 µg/ml	0.15 µg/ml	0.016	0.02
$\delta^{111/110}$ Cd (‰) (2SD, N = 3)	-0.05 ± 0.01	-0.06 ± 0.01	0.07 ± 0.02	n. d.	-0.03 ± 0.01	0.08 ± 0.02	0.06 ± 0.01	n. d.	n. d.
$\delta^{112/110}$ Cd (‰) (2SD, N = 3)	-0.09 ± 0.02	-0.10 ± 0.03	0.18 ± 0.02	n. d.	-0.06 ± 0.02	0.16 ± 0.03	0.12 ± 0.02	n. d.	n. d.
$\delta^{113/110}$ Cd (‰) (2SD, N = 3)	-0.13 ± 0.03	-0.15 ± 0.03	0.24 ± 0.03	n. d.	-0.10 ± 0.04	0.21 ± 0.03	0.17 ± 0.04	n. d.	n. d.
$\delta^{114/110} Cd \ (\text{\ensuremath{\infty}}) \ (2SD, N=3)$	-0.18 ± 0.05	-0.21 ± 0.04	0.32 ± 0.05	n. d.	-0.14 ± 0.05	0.28 ± 0.04	0.22 ± 0.05	n. d.	n. d.
	Leaching expe	eaching experiments 1 (1–40 days) Leaching ex		Leaching exp	periments 2 (1–20 days)		Leaching experiments 2 (21-40 days)		–40 days)
$\Delta^{114/110}$ Cdleachate-initial state (%)	0.50			0.46			0.40		
$\Delta^{114/110}$ Cd _{leachate-residual state}	0.53			0.42			0.36		
(%)									

(700

Note: The δ values relative to NIST SRM 3108 Cd. During the leaching experiments 2, (A) is 1–20 days leaching solution and (B) is 21–40 days leaching solution. n. m.: not measured. n. d.: not defined. The volume of leachate is 1000 ml.

¹¹⁰Cd_{leachate – initial state}) was 0.50‰. In Leaching Experiment 2, the pH of the synthetic rain ranged from 3.5 to 6.5 during the leaching process (Fig. 3), and the isotopic fractionation between the total leachate and the initial state ($\Delta^{114/110}$ Cd_{leachate – initial state}) was 0.43‰. The difference in $\Delta^{114/110}$ Cd_{leachate – initial state}) was 0.43‰. The difference in $\Delta^{114/110}$ Cd_{leachate – initial state}) was 0.43‰. The difference in $\Delta^{114/110}$ Cd_{leachate – initial state} between the Leaching Experiment 1 and Leaching Experiment 2 was 0.07‰, but it is unclear whether the little difference of $\Delta^{114/110}$ Cd_{leachate – initial state} is dependent on pH or caused by analytical error. In Leaching Experiment 2, the leaching conditions over the first 20 days were the same as those over the last 20 days, and the Cd isotope fractionation between the leachate and the initial sample ($\Delta^{114/110}$ Cd_{leachate – initial state}) for these two time periods were identical within analytical error. A possible conclusion from these results is that for the same samples, the fractionation of Cd isotopes caused by supergene weathering and leaching is only related to the leaching conditions are the same, the Cd isotopic fractionation is likely to be the same.

3.3. Cd, Zn, and Pb concentrations of stream sediment and soil samples

Cd, Zn, and Pb concentrations in stream sediment samples and soil samples collected on both banks of the Bijiang River are shown in Table 3 and Fig. 6. Before entering the Pb–Zn mine contamination area, Cd, Zn, and Pb concentrations in stream sediment samples exhibited a gradual increasing trend. After entering the Pb–Zn mine contamination area, the Cd, Zn, and Pb concentrations rapidly increased. In the stream sediment samples, Cd concentrations range from 6.3 μ g/g (mean values) in the upstream section (SSD-12) to 77.0 μ g/g (mean values) in the downstream section (SSD-13 to SSD-29). Zn concentrations also yield a wide range from 572 μ g/g (mean values) in the upstream section to 6010 μ g/g (mean values) in the downstream section to 1620 μ g/g (mean values) in the upstream section to 1620 μ g/g (mean values) in the downstream section.

For soil samples of upstream section (LS-1 to LS-12, RS-1 to RS-12), prior to the contaminated area, Cd, Zn, and Pb concentrations are relatively low and show no strong variations with the Cd, Zn, and Pb concentrations ranging from 0.51 to 9.74 μ g/g, 82.0–949 μ g/ g, 41.8–350 µg/g, respectively. In the Pb–Zn mine contamination area, Cd, Zn, and Pb concentrations exhibited a rapid increase and were variable with several peaks (high values, Cd, Zn, and Pb concentrations up to 180 µg/g, 10000 µg/g, and 3650 µg/g, respectively). In all soil samples, Cd concentrations ranged from 0.51 μ g/g to 180 μ g/g, Zn concentrations ranged from 82 μ g/g to 10,000 μ g/g, and Pb concentrations ranged from 35 µg/g to 3650 µg/g. In particular, samples with higher metal concentrations in the downstream section, for example LS-13 to LS-29 and RS-14 to RS-29. always have good corresponding with the location of potential contamination source as shown in Fig. 1. Moreover, high Cd concentrations in these samples were always correlated with high Zn and Pb concentrations, indicating that these samples were strongly affected by adjacent pollution sources from the Jinding Pb-Zn mine. This also is evidenced from our previous studies (Wen et al., 2015), which have shown that higher concentrations of metals always were found near most adjacent pollution sources.

3.4. Cd isotopic fractionation during natural conditions

The Cd isotopic compositions in stream sediment samples and soil samples collected from both banks of Bijiang River are shown in Table 3 and Fig. 6. Except for one sample (SSD-15), all sediment samples show heavy Cd isotope enrichment, compared with the corresponding soil samples from the riverbanks. The lighter Cd isotopic value in sample SSD-15 may be related to the strong influence from the adjacent smelters where refined oxide ores have a very light $\delta^{114/110}$ Cd value as reported by Wen et al. (2015). The difference in Cd isotopic composition between sediment and soil samples from upstream was similar to that between the leachate and the residual state in the leaching experiments ($\Delta^{114/110}$ Cd_{leachate} – residual state = 0.36–0.53‰). Especially, the largest difference of Cd isotopic composition ($\Delta^{114/110}$ Cd_{sediment} – soil = 0.50‰) was found between the first stream sediment samples (SSD-1) and soil samples (LS-1 and RS-1), which is closely consistent with the measured Cd isotopic fractionation in the leaching experiment.

Through supergene weathering process, bedrocks (or ores) are eventually converted into soil. The bedrock and ores correspond to the initial phase in the leaching experiments, whereas the soil corresponds to the residual phase. In this very slow geological process, Cd is gradually leached out from the bedrock and ores into the river water. When conditions of the river water (such as pH) change, Cd will form precipitates or become adsorbed, thereby incorporated into the stream sediment. This is an important source of Cd in stream sediment. Data from Public Health Service Agency for Toxic Substances and Disease Registry (1999) show that the total annual global emissions of Cd reach 25,000 to 30,000 tons, and about half of the Cd enters the supergene environment via natural weathering of rocks and minerals. Cd concentration and isotopic composition in the river water may be affected by random floods and droughts, whereas stream sediments represent a longterm effect of supergene weathering process.

It is interesting to note that the variation in $\delta^{114/110}$ Cd of stream sediment samples could be clearly divided into two sections (Fig. 6D). Before entering the Pb–Zn mine contamination area, $\Delta^{114/2}$ ¹¹⁰Cd_{sediment} – soil values were relatively larger with a mean of 0.25‰, but in the contamination area, $\Delta^{114/110}$ Cd_{sediment} – soil values decreased to 0.14‰ in the mean $\delta^{114/110}$ Cd value. The $\delta^{114/110}$ Cd values of sediment samples before entering the contamination area (SSD-1 to SSD-12) varied considerably, decreasing gradually from +0.29‰ to -0.11‰. After entering the Pb–Zn mine contamination area, $\delta^{114/110}$ Cd values of stream sediment samples (SSD-13 to SSD-29) were stabilized, ranging from -0.11% to -0.19%. Conversely, for riverbank soil samples, no clear sections in $\delta^{114/}$ ¹¹⁰Cd variation were observed. Before entering the contamination area, the $\delta^{114/110}$ Cd values of riverbank soil samples averaged -0.23% which was 0.25% lower than the mean $\delta^{114/110}$ Cd value of the corresponding stream sediment samples. After entering the contamination area, the mean $\delta^{114/110}$ Cd of the riverbank soil samples was -0.30%, which was 0.14% lower than the mean $\delta^{114/110}$ Cd value of the corresponding stream sediment samples. The relationship between Cd concentration and $\delta^{114/110}$ Cd (Fig. 7) shows that stream sediment samples with lower Cd concentrations show a greater difference in $\delta^{114/110}$ Cd than the corresponding riverbank soil samples. Conversely, stream sediment samples with higher Cd concentrations show a smaller difference in $\delta^{114/110}$ Cd than the corresponding riverbank soil samples. These observations could indicate that additional Cd sources could shift the Cd concentrations and isotopic composition.

Fertilizers and pesticides used in agricultural production may be a source of Cd in river sediments. However, previous studies have shown that Cd concentration ranged from 6 μ g/g to 7500 μ g/g with a mean of 2090 μ g/g in the ores of the Jinding Pb–Zn mine (Ye et al., 2010). Given such high Cd concentrations in Pb–Zn ores, the contribution of fertilizers and pesticides to the Cd concentration in the stream sediment in the study area is probably negligible. Our previous study had suggested that the transportation of dust generated through anthropogenic activities (the mining and refining of ore) is responsible for the serious pollution that we found in the area within about 5 km of the Jinding mine (Wen et al., 2015). Therefore, atmospheric dust and micro-fine soil particles

Soil samples on the left bank	Stream sediment samples	Soil samples on the right bank	Distance*
Sample Cd Zn Pb $\delta^{112/110}$ Cd (‰) $\delta^{114/110}$ Cd (‰)	Sample Cd Zn Pb $\delta^{112/110}$ Cd (‰) $\delta^{114/110}$ Cd (%)	Sample Cd Zn Pb $\delta^{112/110}$ Cd (%) $\delta^{114/110}$ Cd (%)	(km)
$(\mu g/g) (\mu g/g) (\mu g/g) 2SD, N = 3$ 2SD, N = 3	$(\mu g/g) (\mu g/g) (\mu g/g) 2SD, N = 3$ 2SD, N = 3	$(\mu g/g) (\mu g/g) (\mu g/g) 2SD, N = 3$ 2SD, N = 3	
LS-1 1.72 159 72.6 -0.11 ± 0.02 -0.23 ± 0.02	SSD-1 1.59 142 22.0 0.15 ± 0.02 0.29 ± 0.04	RS-1 1.68 149 53.6 -0.09 ± 0.03 -0.19 ± 0.06	0
LS-2 0.92 82.0 50.3 -0.11 ± 0.03 -0.23 ± 0.04	SSD-2 0.99 114 26.1 0.06 ± 0.01 0.10 ± 0.02	RS-2 1.88 175 110 -0.11 ± 0.01 -0.22 ± 0.01	1
LS-3 1.73 302 245 -0.10 ± 0.02 -0.23 ± 0.02	SSD-3 3.42 242 60.7 0.07 ± 0.02 0.13 ± 0.05	RS-3 8.02 766 318 -0.07 ± 0.03 -0.14 ± 0.05	2
LS-4 1.85 158 $80.7 - 0.12 \pm 0.01$ -0.24 ± 0.01	SSD-4 3.57 325 136 0.04 ± 0.01 0.08 ± 0.02	RS-4 7.41 746 251 -0.06 ± 0.02 -0.13 ± 0.02	3
LS-5 2.54 331 98.7 -0.11 ± 0.03 -0.25 ± 0.04	SSD-5 4.81 347 232 0.03 ± 0.02 0.05 ± 0.04	RS-5 4.54 949 232 -0.05 ± 0.01 -0.10 ± 0.02	4
LS-6 0.92 98.0 54.2 -0.13 ± 0.03 -0.29 ± 0.05	SSD-6 8.58 390 165 0.02 ± 0.02 ± 0.04	RS-6 1.95 262 95.3 -0.07 ± 0.02 -0.15 ± 0.04	5
LS-7 0.51 91.0 41.8 -0.11 ± 0.02 -0.24 ± 0.02	SSD-7 8.70 535 158 0.02 ± 0.03 0.03 ± 0.05	RS-7 2.85 247 112 -0.08 ± 0.02 -0.17 ± 0.03	6
LS-8 2.50 271 186 -0.09 ± 0.03 -0.20 ± 0.04	SSD-8 7.50 680 264 -0.05 ± 0.02 -0.08 ± 0.04	RS-8 2.11 151 141 -0.14 ± 0.02 -0.31 ± 0.03	7
LS-9 7.65 586 320 -0.15 ± 0.02 -0.32 ± 0.04	SSD-9 7.24 854 361 -0.05 ± 0.01 -0.09 ± 0.03	RS-9 3.60 285 250 -0.15 ± 0.01 -0.31 ± 0.01	8
LS-10 1.60 208 $69.4 - 0.10 \pm 0.01$ -0.21 ± 0.01	SSD-10 10.2 1130 364 -0.04 ± 0.02 -0.09 ± 0.04	RS-10 2.23 151 80.2 -0.13 ± 0.01 -0.27 ± 0.01	8.5
LS-11 9.74 807 350 -0.11 ± 0.01 -0.24 ± 0.01	SSD-11 9.58 1040 467 -0.04 ± 0.03 -0.10 ± 0.05	RS-11 3.60 344 347 -0.16 ± 0.02 -0.31 ± 0.04	9
LS-12 6.81 438 220 -0.11 ± 0.03 -0.24 ± 0.06	SSD-12 9.96 1070 417 -0.06 ± 0.02 -0.11 ± 0.02	RS-12 5.77 368 179 -0.13 ± 0.01 -0.26 ± 0.02	9.5
LS-13 37.9 3770 1930 -0.09 ± 0.03 -0.20 ± 0.04	SSD-13 21.2 1830 646 -0.09 ± 0.02 -0.17 ± 0.03		10
LS-14 10.4 807 137 -0.13 ± 0.02 -0.27 ± 0.04	SSD-14 20.2 1840 503 -0.05 ± 0.01 -0.11 ± 0.03	RS-14 16.8 1060 450 -0.15 ± 0.02 -0.29 ± 0.02	10.5
LS-15 68.4 4980 1170 -0.09 ± 0.02 -0.20 ± 0.04	SSD-15 61.2 4740 1050 -0.09 ± 0.01 -0.18 ± 0.02	RS-15 26.9 1830 316 -0.07 ± 0.01 -0.13 ± 0.02	11
LS-16 21.5 1660 $301 - 0.13 \pm 0.02 - 0.27 \pm 0.04$	SSD-16 99.7 7550 2290 -0.07 ± 0.01 -0.14 ± 0.02	RS-16 180 10,000 2650 -0.11 ± 0.03 -0.20 ± 0.06	11.5
LS-17 18.1 1110 379 -0.18 ± 0.01 -0.36 ± 0.01	SSD-17 119 7680 2340 -0.08 ± 0.01 -0.17 ± 0.02	RS-17 22.0 1320 289 -0.18 ± 0.01 -0.35 ± 0.02	12
LS-18 5.01 348 87.7 -0.18 ± 0.02 -0.36 ± 0.04	SSD-18 89.3 7360 2090 -0.08 ± 0.03 -0.18 ± 0.05	RS-18 8.72 535 159 -0.15 ± 0.02 -0.30 ± 0.02	12.5
LS-19 4.41 328 49.3 -0.17 ± 0.03 -0.35 ± 0.06	SSD-19 88.3 7530 1470 -0.08 ± 0.02 -0.17 ± 0.03	RS-19 8.57 635 248 -0.20 ± 0.01 -0.39 ± 0.02	13
LS-20 26.9 1880 501 -0.09 ± 0.01 -0.20 ± 0.02	SSD-20 79.1 6540 1550 -0.09 ± 0.02 -0.19 ± 0.04	RS-20 119 10,000 1950 -0.12 ± 0.04 -0.24 ± 0.06	13.5
LS-21 7.63 535 362 -0.16 ± 0.01 -0.36 ± 0.02	SSD-21 88.8 7050 1920 -0.07 ± 0.01 -0.13 ± 0.02	RS-21 7.83 546 184 -0.16 ± 0.03 -0.32 ± 0.05	14
LS-22 5.37 348 190 -0.17 ± 0.02 -0.36 ± 0.06	SSD-22 61.7 5320 885 -0.10 ± 0.02 -0.19 ± 0.03	RS-22 4.87 350 92.7 -0.13 ± 0.02 -0.27 ± 0.04	14.5
LS-23 1.61 158 $45.5 - 0.13 + 0.01 - 0.27 + 0.01$	SSD-23 105 7990 2190 $-0.07 + 0.02$ $-0.14 + 0.03$	RS-23 3.72 261 112 $-0.16 + 0.01$ $-0.32 + 0.01$	15
LS-24 1.25 127 35.0 -0.13 + 0.01 -0.30 + 0.02	SSD-24 74.1 5990 2010 -0.08 + 0.01 -0.16 + 0.02	RS-24 3.29 233 86.1 -0.16 + 0.02 -0.33 + 0.04	15.5
LS-25 2.36 165 $68.4 - 0.18 \pm 0.03 - 0.40 \pm 0.05$	SSD-25 76.1 6120 1730 -0.07 ± 0.01 -0.14 ± 0.03	RS-25 2.34 162 78.9 -0.19 ± 0.02 -0.39 ± 0.02	16
LS-26 11.8 735 $304 - 0.12 + 0.02 - 0.26 + 0.04$	SSD-26 110 8220 2380 $-0.09 + 0.02$ $-0.17 + 0.03$	RS-26 3.50 223 $104 - 0.24 + 0.02 - 0.50 + 0.04$	16.5
LS-27 80.4 7580 $3650 -0.14 + 0.02 -0.28 + 0.04$	SSD-27 49.1 3610 1010 $-0.07 + 0.02$ $-0.14 + 0.03$	RS-27 17.1 1640 520 -0.15 ± 0.01 -0.27 ± 0.02	17
LS-28 2.71 216 118 -0.19 ± 0.03 -0.37 ± 0.05	SSD-28 79.1 6180 1710 -0.08 ± 0.03 -0.16 ± 0.06	RS-28 20.7 2040 701 -0.09 ± 0.01 -0.17 ± 0.02	17.5
LS-29 47.6 4010 1270 -0.12 ± 0.03 -0.25 ± 0.06	SSD-29 88.8 6560 1710 -0.08 ± 0.02 -0.15 ± 0.03	RS-29 18.7 1440 482 $-0.13 + 0.03$ $-0.25 + 0.05$	18.5

 Table 3

 Cd, Zn, and Pb concentrations and Cd isotopic compositions of stream sediment and soil samples.

Note: The δ values relative to NIST SRM 3108 Cd. distance* is the distance from the first sampling point.



Fig. 6. Cd, Zn, Pb concentrations, and Cd isotopic compositions in soil and stream sediment samples from the Bijiang River, China. Error bars are 2 sd on 3 replicate analyses of the same sample.



Fig. 7. Relationship between the $\delta^{114/110}$ Cd and Cd concentrations in soil and stream sediment samples from the Bijiang River, China.

washed into the river during floods should be important sources of Cd in stream sediments of the pollution area, which would have the same effects on stream sediments and soils at riverbanks, and thus will not result in isotope fractionation between the soil on both banks and the stream. More importantly, dust generated through anthropogenic activities (the mining and refining of ore) have extraordinarily high metal concentrations (several tens to thousands of micrograms of Cd and Pb per gram of soil in comparison

with the Cd and Pb concentrations in natural background (Ye et al., 2010). This would result in the complete elimination for signals from natural sources.

The Cd isotopic fractionation during the precipitation or adsorption processes of Cd in stream sediments is not well known. In a simulation study, Horner et al. (2011) investigated the fractionation of Cd isotopes during precipitation of CaCO₃ in seawater. They also conducted a simulation experiment to examine Cd isotopic fractionation during precipitation of CaCO₃ in freshwater. Cd isotopes did not show fractionation between CaCO₃ (calcite) and freshwater. Wasylenki et al. (2014) studied Cd isotopic fractionation during Cd adsorption by manganese oxide. At a low ionic strength, there was relatively little fractionation of Cd isotopes and $\Delta^{114/}$ 110 Cd_{fluid - solid} was +0.24‰. However, at a high ionic strength, $\Delta^{114/}$ $^{110}\text{Cd}_{fluid}$ $_{-$ solid was +0.54‰. Organisms (or organic matter) also preferentially uptake lighter Cd isotopes (Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011; Horner et al., 2013; Xue et al., 2013; John and Conway, 2014; Conway and John, 2015). We would expect the $\delta^{114/110}$ Cd values of river water to be higher than those of sediments. Where stream sediments are more enriched with heavy Cd isotopes than riverbank soils, the implication is that the leachate that enters the river is more enriched with heavy Cd isotopes than riverbank soils. Based on the previous discussion, we believe in that in supergene weathering and leaching under natural conditions, leachate is more enriched with heavy Cd isotopes than the solid phase (initial state or residual state), and the isotopic fractionation $\Delta^{114/110}$ Cd_{fluid – solid} can exceed 0.50%. We suggest that the river and lake water are likely to be more enriched with heavy Cd isotopes than the solid phase (crust)

in natural conditions, which probably play an important role in enriching heavy Cd isotopes in seawater than the inputs and crustal (Xue et al., 2013; Janssen et al., 2014; Conway and John, 2015).

4. Conclusion

The results of our leaching experiments demonstrate that supergene weathering process can produce considerable Cd isotopic fractionation. The leachate is more enriched with heavy Cd isotopes than the initial state (sulfide ore), and Cd isotopic fractionation ($\Delta^{114/110}$ Cd_{leachate – initial state}) ranged from 0.40 to 0.50‰. The similar Cd isotopic fractionation (about 0.50‰ in $\delta^{114/110}$ Cd value) has been also observed in natural conditions. The stream sediments are always enriched in heavier Cd isotopes relative to riverbank soil samples, and the $\Delta^{114/110}$ Cd_{stream sediment – soil} was up to 0.50‰. On the other hand, the major Zn–Pb ore pollution source can change Cd isotopic compositions of stream sediments and soils, and might completely eliminate signals from natural sources by weathering processes.

Thus supergene weathering process can result in significant Cd isotopic fractionation under natural and experimental conditions, which could explain the enrichment of heavier Cd isotopes in almost all fluid systems. When using Cd isotope ratios to trace the pollution source of Cd, the Cd isotopic fractionation caused by supergene weathering, leaching and migration should be taken into account, especially in studies that aim to trace the pollution source of Cd in water bodies and stream sediments.

Acknowledgments

This project was financially supported by National Natural Science Foundation of China (Grant Nos 40930425, 41173029, 41173026, 41573007 and 41503011), the CAS/SAFEA International Partnership Program for Creative Research Teams (KZZD-EW-TZ-20), the 12th Five-Year Plan project of State Key Laboratory of Oredeposit Geochemistry, Chinese Academy of Sciences (SKLODG-ZY125-07), the Science and Technology Foundation of Guizhou Province ([2014]2162), and the ANR-10-LABX-21-01 project in France. We are grateful for the anonymous comments that helped us to improve this manuscript.

References

- Abouchami, W., Galer, S.J.G., Horner, T.J., Rehkämper, M., Wombacher, F., Xue, Z.C., Lambelet, M., Gault-Ringold, M., Stirling, C.H., Schönbächler, M., Shiel, A.E., Weis, D., Holdship, P.F., 2012. A common reference material for cadmium isotope studies - NIST SRM 3108. Geostand. Geoanal. Res. 37, 5–17.
- Abouchami, W., Galer, S.J.G., De Baar, H.J.W., Alderkamp, A.C., Middag, R., Laan, P., Feldmann, H., Andreae, M.O., 2011. Modulation of the southern ocean cadmium isotope signature by ocean circulation and primary productivity. Earth Planet. Sci. Lett. 305 (1–2), 83–91.
- Chrastný, V., Čadková, E., Vaněk, A., Teper, L., Cabala, J., Komárek, M., 2015. Cadmium isotope fractionation within the soil profile complicates source identification in relation to Pb-Zn mining and smelting processes. Chem. Geol. 405, 1–9.
- Cloquet, C., Rouxel, O., Carignan, J., Libourel, G., 2005. Natural cadmium isotopic variations in eight geological reference materials (NIST SRM 2711, BCR 176, GSS-1, GXR-1, GXR-2, GSD-12, Nod-p-1, Nod-A-1) and anthropogenic samples, measured by MC-ICP-MS. Geostand. Geoanal. Res. 29, 95–106.
- Cloquet, C., Carignan, J., Libourel, G., Sterckeman, T., Perdrix, E., 2006. Tracing source pollution in soils using cadmium and lead isotopes. Environ. Sci. Technol. 40, 2525–2530.

- Conway, T.M., John, S.G., 2015. Biogeochemical cycling of cadmium isotopes along a high-resolution section through the North Atlantic Ocean. Geochimica Cosmochimica Acta 148, 269–283.
- Domènech, C., Ayora, C., de Pablo, J., 2002. Sludge weathering and mobility of contaminants in soil affected by the Aznalcollar tailing dam spill (SW Spain). Chem. Geol. 190, 355–370.
- Fernandez, A., Borrok, D.M., 2009. Fractionation of Cu, Fe, and Zn isotopes during the oxidative weathering of sulfide-rich rocks. Chem. Geol. 264, 1–12.
- Gao, B., Zhou, H.D., Liang, X.R., Tu, X.L., 2013. Cd isotopes as a potential source tracer of metal pollution in river sediments. Environ. Pollut. 181, 340–343.
- Horner, T.J., Rickaby, R.E.M., Henderson, G.M., 2011. Isotopic fractionation of cadmium into calcite. Earth Planet. Sci. Lett. 312, 243–253.
- Horner, T.J., Lee, R.B.Y., Henderson, G.M., Rickaby, R.E.M., 2013. Nonspecific uptake and homeostasis drive the oceanic cadmium cycle. Proc. Natl. Acad. Sci. U. S. A. 110 (7), 2500–2505. http://dx.doi.org/10.1073/pnas.1213857110.
- Janssen, D.J., Conway, T.M., John, S.G., Christian, J.R., Kramer, D., Pedersen, T.F., Cullen, J.T., 2014. An undocumented water column sink for cadmium in open ocean oxygen deficient zones. Proc. Natl. Acad. Sci. U. S. A. 111 (19), 6888–6893. http://dx.doi.org/10.1073/pnas.1402388111.
- John, S.G., Conway, T.M., 2014. A role for scavenging in the marine biogeochemical cycling of zinc and zinc isotopes. Earth Planet. Sci. Lett. 394, 159–167.
- Kossoff, D., Hudson-Edwards, K.A., Dubbin, W.E., Alfredsson, M.A., 2011. Incongruent weathering of Cd and Zn from mine tailings: a column leaching study. Chem. Geol. 281, 52–71.
- Lacan, F., Francois, R., Ji, Y.C., Sherrell, R.M., 2006. Cadmium isotopic composition in the ocean. Geochimica Cosmochimica Acta 70, 5104–5118.
- Leleyter, L., Probst, J.L., 1999. A new sequential extraction procedure for the speciation of particulate trace elements in river sediments. Int. J. Environ. Anal. Chem. 73 (2), 109–128.
- Li, H., Li, D.H., Xiao, T.F., He, L.B., Ning, Z.P., Sun, J.L., Zhu, C.S., Shuang, Y., 2008. Geochemistry and environmental effect of cadmium in the super-large Jinding Pb-Zn deposit, Yunnan Province, China. Chin. J. Geochem. 27, 21–27.
- Public Health Service Agency for Toxic Substances and Disease Registry, 1999. Toxicological Profile for Cadmium [R]. U S Department of Health and Human Services, pp. 3–65.
- Qi, L, Grégoire, D.C., 2000. Determination of trace elements in twenty-six Chinese geochemistry reference materials by inductively coupled plasma-mass spectrometry. Geostand. Geoanal. Res. 24 (1), 51–63.
- Ripperger, S., Rehkämper, M., Porcelli, D., Halliday, A.N., 2007. Cadmium isotope fractionation in seawater – a signature of biological activity. Earth Planet. Sci. Lett. 261, 670–684.
- Schmitt, A.D., Stephen, J.G., Wafa, A., 2009. Mass-dependent cadmium isotopic variations in nature with emphasis on the marine environment. Earth Planet. Sci. Lett. 277, 262–272.
- Shiel, A.E., Weis, D., Orians, K.J., 2010. Evaluation of zinc, cadmium and lead isotope fractionation during smelting and refining. Sci. Total Environ. 408, 2357–2368.
- Shiel, A.E., Weis, D., Orians, K.J., 2012. Tracing cadmium, zinc and lead sources in bivalves from the coasts of western Canada and the USA using isotopes. Geochimica Cosmochimica Acta 76, 175–190.
- Wasylenki, L.E., Swihart, J.W., Romaniello, S.J., 2014. Cadmium isotope fractionation during adsorption to Mn oxyhydroxide at low and high ionic strength. Geochimica Cosmochimica Acta 140, 212–226.
- Wen, H.J., Zhang, Y.X., Cloquet, C., Zhu, C.W., Fan, H.F., Luo, C.G., 2015. Tracing sources of pollution in soils from the Jinding Pb-Zn mining district in China using cadmium and lead isotopes. Appl. Geochem. 52, 147–154.
- Wombacher, F., Rehkämper, M., Mezger, K., Münker, C., 2003. Stable isotope compositions of cadmium in geological materials and meteorites determined by multiple-collector ICPMS. Geochimica Cosmochimica Acta 67 (23), 4639–4654.
- Wombacher, F., Rehkämper, M., Mezger, K., 2004. Determination of the massdependence of cadmium isotope fractionation during evaporation. Geochimica Cosmochimica Acta 68 (10), 2349–2357.
- Wombacher, F., Rehkämper, M., Mezger, K., Bischoff, A., Münker, C., 2008. Cadmium stable isotope cosmochemistry. Geochimica Cosmochimica Acta 72, 646–667.
- Xue, Z.C., Rehkämper, M., Horner, T.J., Abouchami, W., Middag, R., Van de Flierd, T., De Baar, H.J.W., 2013. Cadmium isotope variations in the Southern Ocean. Earth Planet. Sci. Lett. 382, 161–172.
- Ye, L., Cheng, Z.T., Pan, Z.P., Liu, T.G., Gao, W., 2010. A study on the distribution characteristics and existing states of cadmium in the Jinding Pb-Zn deposit, Yunnan Province, China. Chin. J. Geochem. 29, 319–325.
- Zhang, Y.X., Wen, H.J., Fan, H.F., Wang, J.S., Zhang, J.R., 2010. Chemical pre-treatment methods for measurement of Cd isotopic ratio on geological samples. J. Instrum. Anal. 29, 633–637 (In Chinese with English abstract).
- Zhu, C.W., Wen, H.J., Zhang, Y.X., Fan, H.F., Fu, S.H., Xu, J., Qin, T.R., 2013. Characteristics of Cd isotopic compositions and their genetic significance in the leadzinc deposits of SW China. Sci. China Earth Sci. 56, 2056–2065.