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Article

Cadmium isotope compositions of Fe-Mn nodules and surrounding soils: Implications for tracing Cd sources



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ABSTRACT

Cadmium (Cd) pollution in agricultural soils has become a severe threat to food security and human health in recent years. Stable Cd isotopes are a potentially powerful tool for identifying the sources of Cd in soils. However, many Earth surface processes, including adsorption, leaching, and biogeochemical cycles in plants, may generate Cd isotope fractionation, which can complicate the potential application of Cd isotopes in tracing the sources of Cd pollution in soils. In this work, the Cd isotope compositions of typical Fe-Mn nodules (FMNs) and surrounding soils in two different soil profiles are investigated. Our results show that the FMNs in lower layers (i.e., C and W horizons) are isotopically lighter than the surrounding soils by -0.114‰ to -0.156‰ ($\Delta^{114/110}\text{Cd}_{\text{FMN-soil}}$). We interpret this fractionation as the result of preferential adsorption of isotopically light Cd onto the surface of goethite. In the upper layers (i.e., P and A horizons), the $\Delta^{114/110}\text{Cd}_{\text{FMN-soil}}$ values are more negative in the P horizon (-0.213‰ to -0.388‰) but more positive in the A horizon (0.061‰ to 0.204‰). We interpret these fractionations as the result of natural biogeochemical processes (i.e., leaching and biological cycling) during soil development. Soil leaching preferentially releases isotopically heavy Cd into the underlying soil (i.e., P horizon), shifting the topsoil towards lower $\delta^{114/110}\text{Cd}$ values but the underlying soils towards higher $\delta^{114/110}\text{Cd}$ values. Moreover, biological cycling contributes isotopically heavy Cd to the topsoil, probably shifting the topsoil towards higher $\delta^{114/110}\text{Cd}$ values. Our study demonstrates that the formation of Fe oxyhydroxides, leaching, and biological cycling can considerably modify the soil Cd isotope signature, highlighting the need to consider natural biogeochemical processes when using Cd isotopes to trace heavy metal pollution in soils.

1. Introduction

Cadmium (Cd) is a toxic heavy metal that has been considered one of the most severe contaminants in agricultural soils [1]. Cadmium is emitted into soils mainly through anthropogenic activities such as mining and smelting [2], waste disposal [3], and phosphate fertilizer applications [4]. Cadmium can be transferred from contaminated soil to plants and humans via the food chain [5]; thus, soil Cd pollution has become a significant threat to food security and human health [1].

Better identification of Cd sources is urgently required for the control of soil heavy metal pollution. Stable Cd isotopes are potentially powerful tools for such identification in soils [6–13]. The prerequisites

for using Cd isotopes as source identification tracers are that the end-members must have distinct Cd isotope signatures and isotope fractionation must be very limited and/or well constrained. Previous studies indicated that high-temperature industrial processes such as smelting and coal combustion can produce large Cd isotope fractionation, with volatile matter (e.g., flue gas, ash, and dust) often enriched in light Cd isotopes [6,7,10,14]. On this basis, researchers have successfully identified sources of heavy metals in soils [6–10]. For example, Cloquet et al. [6] found that polluted topsoils surrounding Pb-Zn refineries have dust-like Cd isotope signatures. The authors pointed out that the soil Cd isotope signals mainly reflect refining processes. Similarly, Wen et al. [9] observed that the Cd isotope compositions of contaminated soil near a Pb-Zn mine fell in a binary mixture between the ores and background

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signals, which suggested that soil Cd pollution was mainly attributed to the deposition of dust emitted by mining and refining activities.

Nevertheless, many biogeochemical processes (e.g., leaching, coprecipitation, adsorption, and biological processes) can produce pronounced Cd isotope fractionation in soil systems [15], which may weaken or even completely obscure the Cd isotope signals from industrial processes and thus hinder the application of Cd isotopes as environmental tracers [8]. Simulation experiments on the leaching of Pb-Zn ores showed that, compared to the ores, the leachates were enriched in isotopically heavy Cd, with $\Delta^{114/110}\text{Cd}_{\text{ore-leachate}}$ ranging from -0.4‰ to -0.5‰ [16]. This result is further supported by the observation that river water samples draining from mining areas have higher $\delta^{114/110}\text{Cd}$ values than tailings and ore minerals [17]. These findings are consistent with the results from laboratory studies, which indicate that light Cd isotopes are preferentially involved in Cd adsorption onto Mn oxyhydroxides and coprecipitation into sulfide/calcite [18–21]. In these processes, the aqueous phases are always enriched in heavier Cd isotopes than the solid phases. Additionally, biological uptake may greatly modify the Cd isotope composition of soils, with phytoplankton and plants being more enriched in light Cd isotopes than the growth solution [22–25].

Fe oxyhydroxides are common natural mineral constituents that are widely distributed in soils, especially in highly mature soils that have formed over very long periods [26]. Fe oxyhydroxides have been shown to exert strong control on the mobility and bioavailability of Cd in soil systems because the Cd in Fe oxyhydroxide-bound forms can be readily transformed to an easily bioavailable form (e.g., the exchangeable form) as the soil pH decreases [27]. Natural soil Fe-Mn nodules (FMNs) are so-called aggregates of Fe-Mn oxides cemented together with other minerals, such as quartz, K-feldspar, plagioclase, and clay minerals [28,29]. FMNs are common components in soils characterized by imperfect drainage or limited permeability and are formed under alternating changes in soil Eh and pH [30,31]. Due to their high adsorption and enrichment abilities, FMNs can concentrate and control the distribution and mobility of metals in soils and are thus considered to play a key role in the soil environmental behavior of Cd [30,31]. However, to our knowledge, Cd isotope fractionation during the formation of Fe oxyhydroxides and its controls on soil Cd isotope compositions remain unclear.

In this study, we investigated the Cd isotope compositions of FMNs and surrounding soils developed in a tangerine orchard soil profile in a dry land area and a paddy soil profile in an irrigated land area. We explored the mechanisms controlling the Cd isotope compositions in FMNs and potential sources of the Cd in the soils. Then, we revealed the implications of FMNs in controlling the Cd isotope compositions of soils. Our findings are expected to help improve our knowledge of the behavior of Cd isotopes during the formation of Fe oxyhydroxides and provide implications for the tracing of Cd sources in soil systems.

2. Materials and methods

2.1. Sample collection and preparation

The studied samples were collected in Binyang County, Guangxi Province, in southwestern China. The climate in this area is categorized as a subtropical climate, with a mean annual temperature of 21.3 °C and a mean annual rainfall of 1491 mm (averaged between 1981 and 2010; all data were collected from the China Meteorological Administration, <http://data.cma.cn/>). Carbonate rocks are the dominant lithology across the study area. Two soil profiles (SO for the tangerine orchard planted in the dry land area and SR for the rice in the irrigated land area) were collected and were < 100 m apart. Samples were taken from the soil profile with a vertical 90-cm horizon depth. Four horizons (A: plow horizon, 0–17.5 cm; P: plow horizon, 17.5–41.0 cm; W: waterloggogenic horizon, 41.0–72.0 cm; C: parent material horizon, 72.0–90.0 cm) along profile SO and three horizons (A: plow horizon, 0–18.0 cm; P: plow horizon, 18.0–70.5 cm; C: parent material horizon, 70.5–90.0 cm) along profile

SR were classified based on soil color, organic matter, and particle diameter. Bulk samples (containing FMNs) from each horizon were collected and immediately sealed in airtight plastic bags. Afterwards, samples were stored frozen and transported to the laboratory within 24 h. In the lab, these samples were air-dried for 72 h to remove water. FMNs were manually picked from the bulk samples with tweezers, and the remaining soil was labeled "surrounding soil". The hand-picked FMNs were washed three times with Milli-Q water ($18.2\text{ M}\Omega\cdot\text{cm}$) to remove loose surface particles and then air-dried again. Finally, the FMNs and surrounding soils were crushed by using an agate mortar and passed through a nylon sieve ($<0.075\text{ mm}$, $>200\text{ mesh}$).

2.2. Sample digestion

All reagents used during sample treatments were of ultrapure grade and prepared with ultrapure water from a Milli-Q system (Merck Millipore, USA). HNO_3 , HCl, and HF were further distilled by sub-boiling distillation (Savillex, USA). All procedures were conducted in a class 1000 clean lab. Approximately 100 mg of sample was digested using a microwave digestion system (Milestone, Italy) in a mixture of concentrated HNO_3 and HF and then evaporated on a hotplate in Teflon beakers (Savillex, USA). Afterwards, samples were treated with 30% H_2O_2 and concentrated HNO_3 and subsequently heated on a hot plate with a cap at 70 °C for 1 h to oxidize organic compounds. Finally, each sample solution was stored in a Teflon beaker in preparation for analysis of element concentration and column purification.

2.3. Analysis of element concentrations

The analysis of element concentrations was conducted at the Institute of Geochemistry, Chinese Academy of Sciences. Major elements (K, Ca, Al, Fe, and Mg) were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Wasst-mpx, Agilent, USA). Trace elements (V, Cr, Mn, Ni, Cu, Zn, Mo, Cd, Sn, Ba, Tl, Zr, and Pb) were determined by inductively coupled plasma mass spectrometry (ICP-MS, NexION 300X, PerkinElmer, USA). The geological reference material of BHVO-2 was used as an external standard for quality control. The relative standard deviations (RSDs) of our measurements were better than 2% for major element analyses and 10% for trace concentration measurements.

2.4. Determination of mineral phases

The mineral modes were characterized by X-ray powder diffraction (XRD, Bruker D2, Germany) at the Institute of Eco-environmental and Soil Sciences, Guangdong Academy of Sciences, China. $\text{Co}/\text{K}\alpha$ radiation was used, and scanning was performed over $5\text{--}85^\circ$ at a speed of $\sim 1.2^\circ/\text{min}$ with a step size of $\sim 0.02^\circ$. TOPAS V5 software (Bruker AXS, Germany) was used to quantify the mineral mode using the Rietveld method [32].

2.5. Cadmium purification and isotope analysis

Purification of Cd was conducted at the Isotope Geochemistry Laboratory of China University of Geosciences, Beijing. The detailed procedures for the column chemistry and analytical protocol used have been reported in Tan et al. [33]. Briefly, digested samples were well mixed with a ^{111}Cd - ^{113}Cd double spike and then evaporated to dryness. The dried samples were subsequently dissolved in 2 mL of 2 M HCl and separated from matrix elements by anion column chromatography according to the procedures by Tan et al. [33]. To eliminate the isobaric interference of residual Sn on Cd during measurements, the same column procedure was repeated to further purify Cd. Finally, purified samples were dissolved in 1 mL of 2% HNO_3 in preparation for isotope determination.

Cadmium isotope ratios were determined on a Neptune Plus multicollector ICP-MS (MC-ICP-MS) instrument (Thermo Scientific, USA)

at the Isotope Geochemistry Laboratory of China University of Geosciences, Beijing [33]. Samples were introduced into the plasma through an Aridus II desolvator (Teledyne CETAC Technologies Omaha, USA). Samples were measured at 10 ng/g with an average beam intensity of 640 V/ppm for ^{112}Cd and bracketed by a spiked NIST-3108 solution to correct for instrumental drift. Cd isotope values are reported as $\delta^{114/110}\text{Cd}$ relative to NIST-3108, which is defined as:

$$\delta^{114/110}\text{Cd}(\%) = \left[\left(\frac{{}^{114/110}\text{Cd}_{\text{sample}}}{{}^{114/110}\text{Cd}_{\text{NIST-3108}}} \right) - 1 \right] \times 1000. \quad (1)$$

The geological standard materials NIST 2711a and GSS-1 processed together with the studied samples yielded average $\delta^{114/110}\text{Cd}$ values of $0.567 \pm 0.051\%$ and $0.024 \pm 0.077\%$, respectively, which are consistent with previously published results [33–35].

2.6. Evaluation of element mobility

The enrichment or depletion of Cd is defined as the percentage change in the concentration ratio of the element over a conservative element in a sample relative to that in the parent material (i.e., the C horizon) [36]:

$$\tau_{\text{Cd}} = 100 \times \left[\left(\frac{C_{\text{Cd,w}}/C_{\text{j,w}}}{C_{\text{Cd,p}}/C_{\text{j,p}}} \right) - 1 \right], \quad (2)$$

where $C_{\text{Cd,w}}$ and $C_{\text{Cd,p}}$ are the Cd concentrations in soils and their parent materials, respectively, and $C_{\text{j,w}}$ and $C_{\text{j,p}}$ are concentrations of the relatively conservative element (j) in soils and their parent materials, respectively. Zirconium (Zr) was chosen as the conservative element in this study since it has been demonstrated to be resistant to chemical weathering [36].

3. Results

3.1. Mineral mode

The mineral contents in FMNs and surrounding soils are reported in Table 1 and plotted in Fig. 1. The XRD patterns of samples WL1–1F and WL1–1S, as examples of FMNs and surrounding soils, respectively, are displayed in Fig. 2. In both profiles, the FMNs predominantly contain goethite (59.4–74.2 wt%), kaolinite (9.4–12.1 wt%), and gibbsite (12.5–18.0 wt%), with lower amounts of quartz (0.7–6.5 wt%) and anatase (0.9–1.7 wt%). In particular, boehmite and hematite are locally observed in FMNs from profile SR. In contrast, the surrounding soils in the two profiles mainly consist of quartz (17.9–36.7 wt%), goethite (15.1–25.3 wt%), kaolinite (24.7–31.6 wt%), and gibbsite (15.8–28.1 wt%), with less anatase (3.0–4.2 wt%).

3.2. Distribution of Cd

The element concentrations of the FMNs and surrounding soils are reported in Table 2, and the average values calculated from soil profile samples at different horizons are plotted in Fig. 3a and 3b. The average element values display a similar distribution in the FMNs and surrounding soils in the two profiles. To quantitatively evaluate the enrichment

ability of FMNs relative to surrounding soils for an element, the enrichment factor was calculated based on Ahrens et al. [37] ($EF = C_{\text{FMN}}/C_{\text{soil}}$, where C refers to the element concentration). The average EF values show that the degree of enrichment varies from element to element, whereas the enrichment pattern is generally similar for both nodule varieties (Fig. 3c). The results demonstrate that compared with the surrounding soil matrix, the FMNs in both profiles are enriched in trace

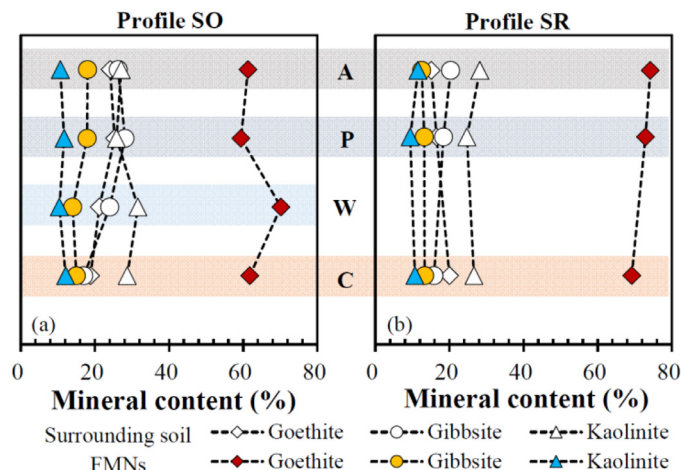


Fig. 1. Mineral content variations in FMNs and surrounding soils in profiles SO and SR.

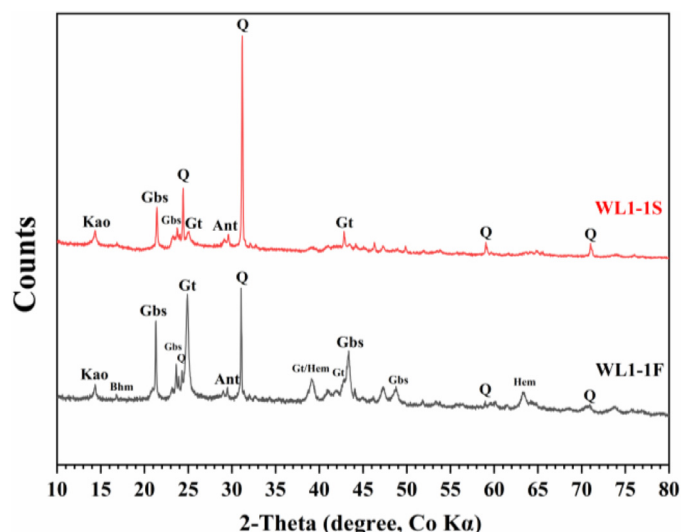


Fig. 2. Powder XRD patterns of sample WL1–1F and WL1–1S (Q: quartz; Gt: goethite; Kao: kaolinite; Gbs: gibbsite; Bhm: boehmite; Ant: anatase; Hem: hematite).

Table 1

Mineral compositions (in wt%) of FMNs and surrounding soils in profiles SO and SR.

Sample Name	Profile SO								Profile SR						
	WL1–1F	WL1–2F	WL1–3F	WL1–4F	WL1–1S	WL1–2S	WL1–3S	WL1–4S	WL4–1F	WL4–2F	WL4–3F	WL4–1S	WL4–2S	WL4–3S	
Type	FMN	FMN	FMN	FMN	Soil	Soil	Soil	Soil	FMN	FMN	FMN	Soil	Soil	Soil	
Horizon	C	W	P	A	C	W	P	A	C	P	A	C	P	A	
Quartz	6.5	0.7	1.0	1.6	31.5	19.7	17.9	19.5	5.1	3.6	0.9	34.5	36.7	32.2	
Goethite	61.8	70.2	59.4	61.3	18.8	21.2	25.3	24.1	69.2	72.9	74.2	20.0	16.5	15.1	
Kaolinite	12.1	10.4	11.7	10.7	28.7	31.6	25.8	27.1	10.7	9.4	11.5	26.6	24.7	28.2	
Gibbsite	15.0	14.0	17.9	18.0	17.0	24.0	28.1	26.3	13.3	13.2	12.5	15.8	18.4	20.3	
Boehmite	0.4		4.1	0.6											
Anatase	1.1	1.1	1.3	0.9	4.1	3.4	3.0	3.0	1.7	0.9	0.9	3.1	3.7	4.2	
Hematite	3.0	3.6	4.6	7.0											

elements and depleted in major alkali and alkaline earth elements (K, Ca, Mg, and Ba).

For Cd, the EF values range from 1.7 to 2.8 along profile SO and from 1.8 to 2.0 along profile SR, with average values of 2.3 ± 0.9 and 1.9 ± 0.2 , respectively. In profile SO, the FMNs have Cd contents ranging from 1.7 $\mu\text{g/g}$ to 2.3 $\mu\text{g/g}$. The surrounding soils have Cd contents

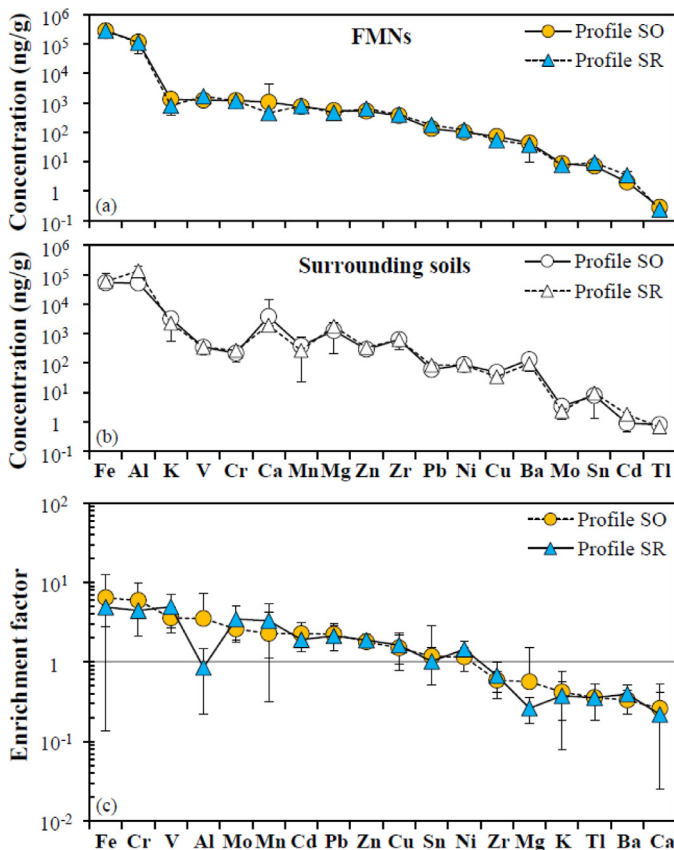


Fig. 3. Average elemental concentrations (in a decreasing order) in FMNs (a) and surrounding soils (b), and average EFs of elements in FMNs (c) relative to surrounding soils in profiles SO and SR. Error bars represent 2SD uncertainties calculated from soil profile samples at different horizons.

ranging from 0.67 $\mu\text{g/g}$ to 1.2 $\mu\text{g/g}$ and display a decreasing trend from the bottom towards the top of the profile. In contrast, in profile SR, the FMNs and surrounding soils show an increase in Cd content from the bottom towards the top of the profile, with Cd contents ranging from 2.9 $\mu\text{g/g}$ to 4.0 $\mu\text{g/g}$ and from 1.6 $\mu\text{g/g}$ to 2.0 $\mu\text{g/g}$, respectively.

3.3. Cadmium isotope compositions

The Cd isotope compositions of FMNs and surrounding soils are presented in Table 3 and plotted in Fig. 4. In profile SO, the $\delta^{114/110}\text{Cd}$ values of bulk FMNs vary from -0.319% to -0.487% , with an average value of $-0.392 \pm 0.144\%$. The surrounding soils have higher $\delta^{114/110}\text{Cd}$ values (-0.099% to -0.248%) than do the FMNs in the lower section (C, P, and W horizons) but lower $\delta^{114/110}\text{Cd}$ values in the A horizon (-0.562%). In profile SR, the FMNs have $\delta^{114/110}\text{Cd}$ values ranging from -0.208% to -0.381% , with an average value of $-0.320 \pm 0.193\%$. Similar to profile SO, the surrounding soils have higher $\delta^{114/110}\text{Cd}$ values (-0.255% to -0.168%) in the lower section (C and P horizons) but lower $\delta^{114/110}\text{Cd}$ values in the A horizon (-0.269%). In both profiles, the $\delta^{114/110}\text{Cd}$ values of the FMNs decrease from the C horizon to the P horizon and then increase towards the A horizon. In contrast, the $\delta^{114/110}\text{Cd}$ values of the surrounding soils show the opposite trend ex-

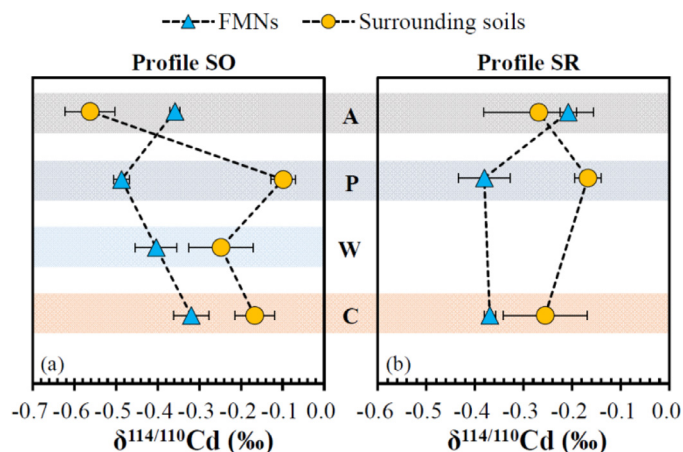


Fig. 4. Cadmium isotope compositions of FMNs and surrounding soils in profiles SO (a) and SR (b). Error bars represent 2SD uncertainties calculated from repeat measurements.

Table 2

Major (in mg/g) and trace (in $\mu\text{g/g}$) element concentrations of FMNs and surrounding soils in profiles SO and SR.

Sample Name	Profile SO							Profile SR						
	WL1-1F	WL1-2F	WL1-3F	WL1-4F	WL1-1S	WL1-2S	WL1-3S	WL1-4S	WL4-1F	WL4-2F	WL4-3F	WL4-1S	WL4-2S	WL4-3S
Type	FMN	FMN	FMN	FMN	Soil	Soil	Soil	Soil	FMN	FMN	FMN	Soil	Soil	Soil
Horizon	C	W	P	A	C	W	P	A	C	P	A	C	P	A
K	1.98	1.08	0.91	1.31	3.01	2.65	3.42	3.80	0.97	0.72	0.71	3.18	1.49	2.11
Ca	3.60	0.16	0.27	0.19	11.90	1.55	1.25	0.46	0.79	0.12	0.44	3.10	1.13	1.50
Al	129	150	100	93	36	29	22	123	148	96	91	128	109	174
Fe	247	297	287	296	56	30	35	93	261	292	288	69	49	58
Mg	0.75	0.54	0.47	0.43	0.59	1.82	1.50	1.14	0.49	0.52	0.37	1.95	1.67	1.65
V	1162	1405	1240	1047	289	335	369	373	1482	1739	1793	376	282	373
Cr	1284	1451	1164	939	211	191	168	291	1041	1211	1205	308	214	282
Mn	691	720	821	763	638	312	363	219	873	718	752	423	187	186
Ni	98	98	108	94	71	92	88	99	112	122	128	77	74	103
Cu	65	62	88	72	57	46	44	47	52	53	56	38	27	37
Zn	506	525	572	490	266	310	296	298	570	648	680	305	310	401
Mo	8.5	8.9	9.4	7.8	3.7	3.1	3.2	3.5	7.5	7.7	7.8	2.9	1.8	2.2
Cd	2.1	1.9	2.3	1.7	1.2	0.88	0.84	0.67	2.9	3.4	4.0	1.6	1.7	2.0
Sn	7.3	6.8	7.8	6.4	3.0	9.3	8.9	10	9.0	9.5	9.4	10	7.3	11
Ba	69	39	32	34	173	108	110	124	44	33	34	117	73	97
Tl	0.36	0.27	0.24	0.27	0.76	0.76	0.74	0.97	0.27	0.22	0.22	0.76	0.57	0.68
Zr	369	363	400	328	636	716	714	461	407	384	404	489	562	798
Pb	117	127	153	134	56	57	54	73	147	185	202	86	77	90

Table 3
Cadmium isotope compositions of FMNs and surrounding soils in profiles SO and SR.

Profile	Sample name	Horizon	Type	$\delta^{114/110}\text{Cd}$ (‰)	2SD (‰)	$\Delta^{114/110}\text{Cd}_{\text{FMN-soil}}$ (‰)	τ_{Cd} (%)
Profile SO	WL1-1S	C	Soil	-0.167	0.048	-	/
	WL1-1F		FMN	-0.319	0.042	0.152	/
	WL1-2S	W	Soil	-0.248	0.077	-	-36.4
	WL1-2F		FMN	-0.404	0.050	0.156	/
	WL1-3S	P	Soil	-0.099	0.029	-	2.8
	WL1-3F		FMN	-0.487	0.018	0.388	/
	WL1-4S	A	Soil	-0.562	0.060	0.204	-24.4
Profile SR	WL1-4F		FMN	-0.358	0.012	/	/
	WL4-1S	C	Soil	-0.255	0.087	-	/
	WL4-1F		FMN	-0.370	0.012	0.114	/
	WL4-2S	P	Soil	-0.168	0.027	-	-7.8
	WL4-2F		FMN	-0.381	0.053	0.213	/
Geological standard	WL4-3S	A	Soil	-0.269	0.113	0.061	-24.8
	WL4-3F		FMN	-0.208	0.017	/	/
	NIST 2711a	/	Soil	0.567	0.051	/	/
	GSS-1	/	Soil	0.024	0.077	/	/

cept for the W horizon in profile SO, in which the $\delta^{114/110}\text{Cd}$ value of the surrounding soil is lower than that in the C horizon.

4. Discussion

4.1. Cadmium isotope fractionation during the formation of soil FMNs

FMNs are important constituents in soils formed as a result of alternating oxidizing and reducing conditions [30,31]. Because of their strong adsorption and enrichment abilities, FMNs are highly enriched in many toxic metals [28]. Consequently, FMNs are regarded to play an important role in the soil environmental behavior of metals. As observed in our study, many potentially hazardous metals, such as Cd, Cu, Ni, Zn, Cr, and Pb, are highly enriched in soil FMNs (Fig. 3c). In particular, the soil FMNs in both profiles have a high affinity for Cd, with the average Cd concentration in the FMNs being 1.7–2.8 times higher than that in the surrounding soils (Fig. 3). This result is consistent with previously published data, which suggest that the Cd concentration in soil FMNs is higher than that in surrounding soils [28,30].

The enrichment of hazardous metals in FMNs is mainly caused by the fact that the sorption ability of Fe oxyhydroxides (e.g., goethite) is often orders of magnitude higher than that of other phases [38]. Goethite comprises 59–74 wt% of FMNs (Table 1). This suggests that goethite is the dominant control on metals in FMNs. The sorption of aqueous metals, e.g., Cu and Zn, onto Fe oxides has been suggested to significantly fractionate metal stable isotopes [39–41]. Isotope fractionation mainly reflects a difference in bond strength between aqueous and adsorbed metals, with heavier isotopes being preferentially partitioned into a stronger bonding environment [42].

The results show that the FMNs have lower $\delta^{114/110}\text{Cd}$ values than the surrounding soils in the C and W horizons (Fig. 4). In addition, these two horizons in the two profiles have nearly the same $\Delta^{114/110}\text{Cd}_{\text{FMN-soil}}$ values (–0.114‰ to –0.156‰) (Table 3). This is quite understandable since the influence of exogenous inputs of Cd on the lower layers is relatively limited. It is likely that such isotope fractionation is caused by the preferential uptake of light Cd isotopes by goethite. Although few studies regarding Cd isotope fractionation during sorption of Cd onto Fe oxyhydroxides (e.g., goethite) have been conducted, Wasylenki et al. [19] pointed out that light Cd isotopes are preferentially adsorbed onto Mn oxyhydroxide. This is mainly caused by the shorter Cd–O bond length and stronger bond strength in aqueous Cd species than in the sorbed complex with a longer Cd–O bond length and weaker bond strength [19]. The Cd–O bond length for aqueous Cd species in octahedral coordination has been investigated by both extended X-ray absorption fine structure (EXAFS) and XRD. Pioneers analyzed Cd perchlorate solution ($\text{Cd}(\text{ClO}_4)_2$) and found the Cd–O length to be 2.27 Å

[43,44]. The Cd–O bond lengths for Cd sorbed to various mineral substrates may be slightly longer than those for aqueous Cd species. Spadini et al. [45] reported an average Cd–O bond length of 2.30 Å when Cd was sorbed as inner-sphere complexes to goethite and 2.27–2.30 Å when sorbed to hydrous ferric oxide.

Due to the lack of $\delta^{114/110}\text{Cd}$ values in soil solutions, we could not qualitatively constrain the Cd isotope fractionation during the formation of goethite. However, this isotope fractionation could be directly assessed through stable isotope mass balance calculations based on the averaged data from the C and W horizons in the two profiles. For these calculations, we simplified the FMN-soil system and assumed that the isotope fractionation between Cd sorbed onto minerals and aqueous Cd was in equilibrium. The Cd in FMNs and surrounding soil was simplified by assuming it was hosted only in kaolinite and goethite; thus, the Cd isotope compositions of the FMNs and surrounding soils can be expressed by:

$$\delta^{114/110}\text{Cd}_{\text{FMN}} = \delta^{114/110}\text{Cd}_{\text{goethite}} \times f_{\text{FMN}} + \delta^{114/110}\text{Cd}_{\text{kaolinite}} \times (1 - f_{\text{FMN}}), \quad (3)$$

$$\delta^{114/110}\text{Cd}_{\text{soil}} = \delta^{114/110}\text{Cd}_{\text{goethite}} \times f_{\text{soil}} + \delta^{114/110}\text{Cd}_{\text{kaolinite}} \times (1 - f_{\text{soil}}), \quad (4)$$

where f_{FMN} and f_{soil} refer to the percentage of the Cd fraction in goethite for FMNs and surrounding soils, respectively. Therefore, the Cd isotope fractionation between FMNs and surrounding soils can be expressed by:

$$\Delta^{114/110}\text{Cd}_{\text{FMN-soil}} = (\delta^{114/110}\text{Cd}_{\text{goethite}} - \delta^{114/110}\text{Cd}_{\text{kaolinite}}) \times (f_{\text{FMN}} - f_{\text{soil}}). \quad (5)$$

Vasconcelos et al. [44] found that kaolinite has Cd–O bond lengths identical to those of aqueous Cd. Therefore, we can assume that Cd isotope fractionation between kaolinite and aqueous solution could be very limited during Cd sorption onto kaolinite. As such, sorbed Cd in kaolinite reflects a fluid phase, so its $\delta^{114/110}\text{Cd}$ value should be consistent with that of the soil solution. Eq. (5) can be alternately expressed by:

$$\Delta^{114/110}\text{Cd}_{\text{FMN-soil}} = (\Delta^{114/110}\text{Cd}_{\text{goethite-solution}}) \times (f_{\text{FMN}} - f_{\text{soil}}). \quad (6)$$

Assuming that the Cd concentration of goethite or kaolinite in FMNs and surrounding soils is the same, then the Cd fraction in goethite in FMNs (f_{FMN}) and surrounding soils (f_{soil}) can be expressed by:

$$f_{\text{FMN}} = \frac{w_{\text{goethite}}^{\text{FMN}} \times C_{\text{goethite}}}{w_{\text{goethite}}^{\text{FMN}} \times C_{\text{goethite}} + w_{\text{kaolinite}}^{\text{FMN}} \times C_{\text{kaolinite}}}, \quad (7)$$

$$f_{\text{soil}} = \frac{w_{\text{goethite}}^{\text{soil}} \times C_{\text{goethite}}}{w_{\text{goethite}}^{\text{soil}} \times C_{\text{goethite}} + w_{\text{kaolinite}}^{\text{soil}} \times C_{\text{kaolinite}}}, \quad (8)$$

where w refers to the percentage of goethite or kaolinite in FMNs and surrounding soils, and C refers to the Cd concentration of goethite or kaolinite. The enrichment factor (EF_{Cd}) of Cd in FMNs relative to surrounding soils can be expressed by:

$$EF_{Cd} = \frac{w_{\text{goethite}}^{\text{FMN}} \times C_{\text{goethite}}^{\text{FMN}} + w_{\text{kaolinite}}^{\text{FMN}} \times C_{\text{kaolinite}}^{\text{FMN}}}{w_{\text{goethite}}^{\text{soil}} \times C_{\text{goethite}}^{\text{soil}} + w_{\text{kaolinite}}^{\text{soil}} \times C_{\text{kaolinite}}^{\text{soil}}} \quad (9)$$

Based on Eq. (6)–(9), we calculated the $\Delta^{114/110}\text{Cd}_{\text{goethite-solution}}$ value to be -0.36% . This value is identical to the Cd isotope fractionation (-0.54% at a high ionic strength and -0.24% at a low ionic strength) between Mn oxyhydroxides and aqueous solution within uncertainty [19]. Here, we indirectly inferred Cd isotope fractionation during the formation of soil Fe-Mn nodules through theoretical geometry. However, the isotope fractionation mechanism should be further examined in the future through theoretical calculations and laboratory experiments.

4.2. Anthropogenic Cd in the soil system

Compared with the values of the C and W horizons, the $\Delta^{114/110}\text{Cd}_{\text{FMN-soil}}$ values in the P and A horizons are quite different. In the P horizon, although the FMNs have lower $\delta^{114/110}\text{Cd}$ values than the surrounding soils, the $\Delta^{114/110}\text{Cd}_{\text{FMN-soil}}$ values are more negative (-0.388% in profile SO and -0.213% in profile SR) (Table 3). In the A horizon, the $\delta^{114/110}\text{Cd}$ value of the surrounding soil decreases, and that of FMNs increases, potentially resulting in the $\delta^{114/110}\text{Cd}$ value of FMNs being higher than that of the surrounding soil (Fig. 4). One potential mechanism responsible for such a change in soil Cd isotope composition is the input of anthropogenic Cd (via, for example, atmospheric deposition and phosphate fertilizer application).

One possible Cd source to soils is atmospheric deposition from anthropogenic activities [46,47]. Cloquet et al. [6] measured the dust surrounding a Pb-Zn refinery and found that the dust had lower $\delta^{114/110}\text{Cd}$ values than the slag due to the preferential volatilization of isotopically light Cd during evaporation processes. Similarly, Shiel et al. [7] and Martinková et al. [10] found that flue gas and ash were enriched in light Cd isotopes relative to the raw material. Profiles SO and SR are <100 m apart, but these two topsoil samples had considerably different Cd isotope compositions (Table 2). If inputs from atmospheric deposition (regardless of whether these inputs are from natural or anthropogenic sources) contribute a large amount of Cd to the soils, the topsoil samples in the two profiles should not have such a difference in Cd isotope composition. Thus, the input of atmospheric Cd is unlikely to be responsible for modifying the soil Cd isotope signals.

Another possible source of Cd in soils is the application of phosphate fertilizers [48–49]. Salmanzadeh et al. [11] and Imseng et al. [12] examined the Cd isotope ratios of phosphate fertilizers and found that their $\delta^{114/110}\text{Cd}$ values fell in the range from -0.17% to 0.25% . The $\delta^{114/110}\text{Cd}$ values of phosphate fertilizers are substantially higher than those of soils and FMNs. As a result, inputs from such fertilizers are unlikely to lower the soil Cd isotope composition.

4.3. Cadmium isotope fractionation during soil development

Since anthropogenic activities contribute limited Cd to the studied soils, there must have been another process fractionating Cd isotopes in the soil system. Previous studies indicated that natural processes, such as leaching, coprecipitation, adsorption, and biological uptake, can produce pronounced variations in Cd isotope compositions during soil development [15], which may result in changes in the soil Cd isotope composition. In profile SO, the τ_{Cd} value of topsoil indicates that 24% of the initial Cd in the parent material (C horizon) was lost, most likely through the soil solution. It has been suggested that compared to the liquid phase, soil minerals are often enriched in isotopically light Cd [16,18–21]. Consequently, the topsoil has a lower $\delta^{114/110}\text{Cd}$ value than

the parent material, and the $\delta^{114/110}\text{Cd}$ value of the surrounding soil may therefore be lower than that of the FMNs. The Cd released from the topsoil may then be retained in the underlying soil (e.g., P horizon), which agrees with the positive τ_{Cd} value in the P horizon. As such, the soil in the P horizon has a higher $\delta^{114/110}\text{Cd}$ value than the parent material.

If only the leaching process influences the distribution of Cd in topsoils, the topsoil in profile SR should also be highly enriched in isotopically light Cd compared to the parent material, as observed in profile SO. However, the topsoil in profile SR shows an identical soil $\delta^{114/110}\text{Cd}$ value to the parent material (Fig. 4). Thus, there must have been another process affecting the distribution of Cd in the topsoil. Previous studies have already revealed the importance of biological cycling for the distribution of Cd in soil systems [50]. This influence may have also been at play in our study. It has been suggested that plants have higher $\delta^{114/110}\text{Cd}$ values than bulk soils [12,23,51,52], even though biological uptake prefers light Cd isotopes [23–25], because the available Cd pool in soils (e.g., the soil solution) is more enriched than the bulk soil in heavy isotopes [12,23]. Thus, the soil Cd distribution in profile SR can be explained by two processes: (i) weathering of parent material resulting in leaching of heavy Cd isotopes into the underlying soil (e.g., P horizon) and shifting the isotope composition of the topsoil towards lower values, and (ii) biological cycling contributing isotopically heavy Cd to the topsoil and in turn shifting the isotope composition of topsoil towards higher values.

4.4. Implications for the use of Cd isotopes as environmental tracers

Stable Cd isotopes can potentially be used as a proxy of soil heavy metal pollution if the Cd isotope signal is faithfully preserved in soils. To date, many studies have been conducted and have successfully identified the sources of heavy metals in soil systems [6–13]. Significant Cd isotope fractionation is produced by high-temperature industrial processes, such as smelting and coal combustion, with volatile matter (flue gas, ash, and dust) becoming enriched in light Cd isotopes and tailings and slags becoming enriched in heavy Cd isotopes [6,7,10,14]. This indicates that the topsoil potentially preserves different Cd isotope signatures than the parent material if the topsoil is seriously influenced by industrial input and the isotope fractionation caused by other processes is very limited.

Our study indicates that Cd is highly accumulated in soil FMNs, with light Cd isotopes being preferentially sorbed onto FMNs ($\Delta^{114/110}\text{Cd}_{\text{soil-FMN}}$ can be up to $\sim 0.4\%$). The preferential incorporation of light Cd isotopes into FMNs implies that the Cd isotope signal from contamination sources recorded in soils may be weakened and/or even be completely obscured if FMNs form in the soils. Assuming that the soil system is closed, a simple mass balance calculation was conducted to assess the influence of FMNs on soil Cd isotope composition:

$$\Delta^{114}\text{Cd}_{\text{soil}} = \frac{EF_{Cd} \times w}{1 - w} \times \Delta^{114}\text{Cd}_{\text{parent soil-FMN}}, \quad (10)$$

where $\Delta^{114/110}\text{Cd}_{\text{soil}}$ refers to the Cd isotope variation induced by the FMNs, $\Delta^{114/110}\text{Cd}_{\text{parent soil-FMN}}$ refers to the difference in Cd isotope composition between the parent soil and the FMNs, and w and EF_{Cd} refer to the weight percentage and the Cd enrichment factor of the FMNs, respectively. The $\Delta^{114/110}\text{Cd}_{\text{parent soil-FMN}}$ values of 0.1% and 0.2% were adopted as examples. The weight percentage was set to values between 0 and 0.5, a range twice as large as that in a previous report [29]. The modeled results are plotted in Fig. 5 and show that the FMNs can generate obvious variation in Cd isotope composition in soils. Our study represents a valuable first step towards understanding the influence of the formation of FMNs on soil Cd isotope signals. These findings indicate that careful consideration should be given when using FMN-containing soil to trace Cd sources.

Furthermore, our study demonstrates that leaching and biological processes could produce large Cd isotope fractionation during soil development. Preferential release of isotopically heavy Cd results in the

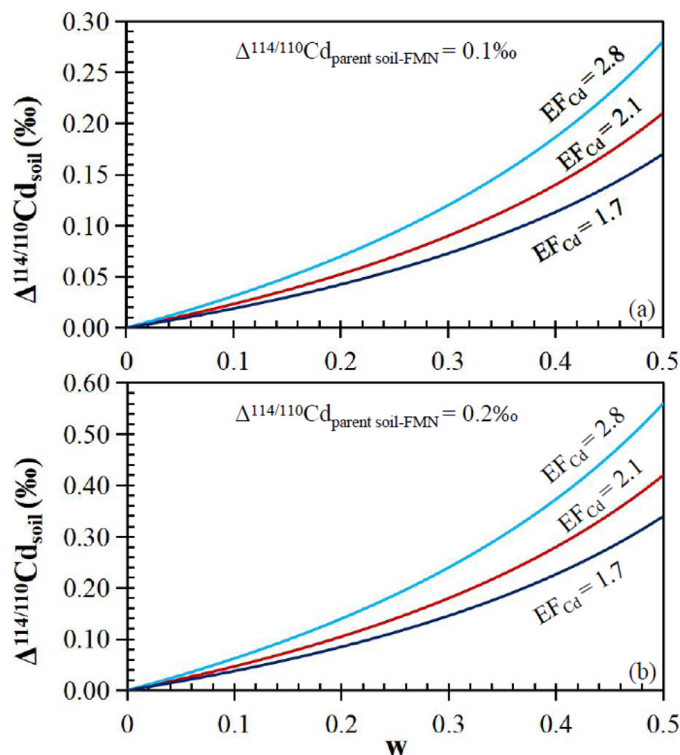


Fig. 5. Cadmium isotope variation ($\Delta^{114/110}\text{Cd}_{\text{soil}}$) induced by the formation of FMNs as a function of weight percentage of FMNs (w). (a) $\Delta^{114/110}\text{Cd}_{\text{parent soil-FMN}} = 0.1\text{‰}$; (b) $\Delta^{114/110}\text{Cd}_{\text{parent soil-FMN}} = 0.2\text{‰}$.

topsoil depleting heavy Cd isotopes compared to the parent material. Preferential uptake of light Cd isotopes can in turn shift the soil Cd isotope compositions towards higher values. These findings indicate that many biogeochemical processes need to be further considered and assessed when using Cd isotopes to trace soil Cd sources.

5. Conclusions

This study presents the Cd isotope compositions of FMNs and surrounding soils developing in a tangerine orchard soil profile in a dry land area and in a paddy soil profile in an irrigated area. Our results show that the FMNs in the lower layers (i.e., C and W horizons) are isotopically lighter than the surrounding soils. This is mainly caused by the preferential adsorption of isotopically light Cd onto the goethite surface. In the upper layers (i.e., P and A horizons), the $\Delta^{114/110}\text{Cd}_{\text{FMN-soil}}$ values become more negative in the P horizon but positive in the A horizon. These fractionations result from natural biogeochemical processes (i.e., leaching and biological cycling) during soil development. Soil leaching preferentially releases isotopically heavy Cd into the underlying soil (i.e., P horizon), shifting the topsoil towards lower $\delta^{114/110}\text{Cd}$ values but the underlying soils towards higher $\delta^{114/110}\text{Cd}$ values. In addition, biological cycling contributes isotopically heavy Cd to the topsoil. Our study highlights the importance of Fe oxyhydroxide formation, leaching, and biological cycling on the modification of soil Cd isotope compositions, which has important implications for the tracing of Cd sources using the Cd isotope technique in soil systems.

Author contributions

Ting Gao and Chengshuai Liu designed the research and wrote the manuscript. Ting Gao, Yuhui Liu, Yafei Xia, Qiqi Wu, Meng Qi, and Jianming Zhu collected and analyzed samples. Zhengrong Wang, Yizhang Liu, Zengping Ning, and Wenpo Xu discussed the data and revised the

manuscript. All authors discussed the results and implications and commented on the manuscript.

Declaration of Competing Interest

The authors declare that they have no competing interests.

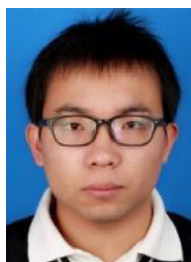
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