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Cadmium Isotope Fractionation during Adsorption onto Edge Sites and Vacancies in Phyllosulfate

Hui Yin^{1,*,#}, Xinran Yan¹, Chuanwei Zhu^{2,*}, Kideok D. Kwon^{3,#}, Xueyuan Gu⁴, Wei Zhao⁵, Bruno Lanson⁶, Wei Li⁷, Jingyuan Ma⁸, Yan Li⁹, Jiangshan Li¹⁰, Guohong Qiu¹, Xionghan Feng¹, Wenfeng Tan¹, Hanjie Wen², Qiaoyun Huang¹, Fan Liu¹

¹Hubei Key Laboratory of Soil Environment and Pollution Remediation, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China

²School of Earth Sciences and Resources, Chang'an University, Xi'an 710054, China

³Department of Geology, Kangwon National University, Chuncheon 24347, Republic of Korea

⁴State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, 163, Xianlin Ave., Nanjing 210023, China

⁵State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, Northwest A&F University, Yangling, Shaanxi Province 712100, China

⁶Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, Univ. Gustave Eiffel, ISTerre, F-38000 Grenoble, France

⁷Key Laboratory of Surficial Geochemistry, Ministry of Education, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China

⁸Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China

⁹Beijing Key Laboratory of Mineral Environmental Function, School of Earth and Space Sciences, Peking University, Beijing 100871, China

¹⁰State Key Laboratory of Geomechanics and Geotechnical Engineering, Institute of Rock and Soil Mechanics, Chinese Academy of Sciences, Wuhan 430071, China

[#]These two authors contribute equally.

*Corresponding Authors:

Tel.: +86 27 87280271. Fax: +86 27 87288618.

Email: yinhui666@mail.hzau.edu.cn; zhuchuanwei@chd.edu.cn.

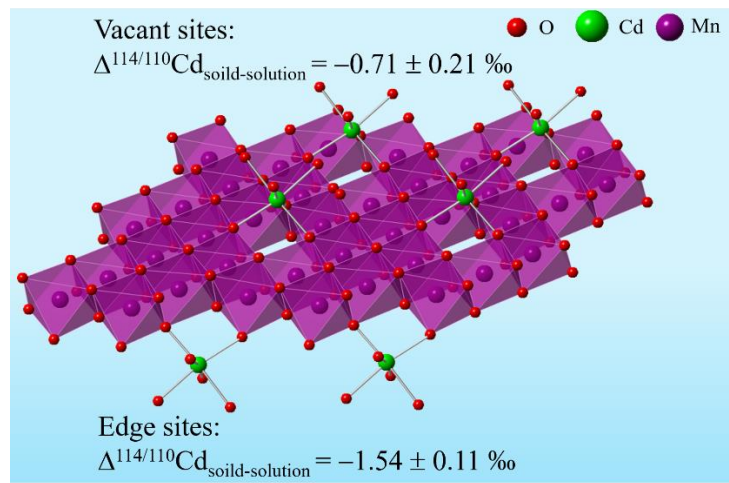
ABSTRACT: Cadmium (Cd) geochemical behavior is strongly influenced by its adsorption onto natural phyllosulfates, which contain both layer edge sites and vacancies; Cd isotope fractionation mechanisms at these sites have not yet been addressed, however. In the present work, Cd isotope fractionation during adsorption onto hexagonal (containing both types of sites) and triclinic birnessite (almost only edge sites) was investigated using a combination of batch adsorption experiments, extended X-ray absorption fine structure (EXAFS) spectroscopy, surface complexation modeling and density functional theory (DFT) calculations. Light Cd isotopes are preferentially enriched on solid surfaces, and the negative isotope fractionation induced by Cd²⁺ adsorption on edge sites ($\Delta^{114/110}\text{Cd}_{\text{edge-solution}}=-1.54\pm 0.11\%$) is larger than that on vacancies ($\Delta^{114/110}\text{Cd}_{\text{vacancy-solution}}=-0.71\pm 0.21\%$), independent of surface coverage or pH. Both Cd K-edge EXAFS and DFT results indicate the formation of double corner-sharing complexes on layer edge sites and mainly triple corner-sharing complexes on vacancies. The distortion of both complexes results in the negative isotope fractionation onto the solids, and the slightly longer first Cd–O distances and smaller number of nearest Mn atoms around Cd at edge sites probably account for the larger fractionation magnitude compared to vacancies. These results provide deep insights into Cd isotope fractionation mechanisms during interactions with phyllosulfates.

KEYWORDS: Phyllosulfate, cadmium adsorption, isotope fractionation, vacancies, edge sites

SYNOPSIS

Cd isotope fractionation during adsorption onto hexagonal birnessite layer vacancies is larger than that on edge sites.

TOC



1. Introduction

The increase in cadmium (Cd) contamination has greatly enhanced the study of its sources and behavior in the environment owing to its toxicity and carcinogenicity for living organisms including humans¹. Anthropogenic activities, such as mining, smelting, chemical industries, and fertilizer use result in the release of Cd into soils and aquatic and atmospheric environments, which is significantly larger than that from natural weathering². Source identification is of prime importance for the prediction and remediation of Cd pollution, and Cd isotopic signature may bring key information to deciphering Cd biogeochemical cycling and fingerprinting Cd sources and fates³⁻⁶. Notably, biogeochemical reactions, such as adsorption and desorption⁷, precipitation and dissolution⁸, evaporation and condensation⁹, weathering¹⁰, and biological uptake¹¹ may induce isotope fractionation and modify Cd isotopic signature. Therefore, the identification of isotope fractionation during these geochemical processes at environmentally relevant interfaces is key to constraining Cd isotopic signatures in nature.

One of the important interface reactions affecting Cd isotope fractionation is adsorption to manganese (Mn) dioxides. Mn dioxides occur naturally and widely as lamellar compounds (phyllosulfates) in aquatic systems, soils, and marine sediments and play significant roles in controlling the geochemical cycling and fate of heavy metals due to their small particle sizes, structural defects, and negatively charged surfaces¹²⁻¹⁷. Layers of the phyllosulfate birnessite are composed of edge-sharing Mn(IV)O₆ and Mn(III)O₆ octahedra and vacancies. Since Mn(III)O₆ octahedra are distorted by the Jahn-Teller effect, different concentrations and spatial distributions of Mn(III) in the birnessite layers result in the layer symmetry being either hexagonal or orthogonal. Birnessite with orthogonal layer symmetry (triclinic birnessite, TBir) contains almost no or only a small amount of layer vacancy but high amounts (~33%) of layer Mn(III) aligned in rows¹⁸⁻²² (Figure 1a). In contrast, birnessite with hexagonal layer symmetry (hexagonal birnessite, HBir) contains a relatively high concentration of vacancies (10-20%) but few or no layer Mn(III) (Figure 1b). The presence of vacancies

and/or Mn(III) in the birnessite layers and the unsaturated O atoms at the layer edges result in a large negative layer charge^{23, 24}. This leads to a high reactivity of birnessite towards heavy metal adsorption. Previous studies using powder X-ray diffraction, extended X-ray absorption fine structure (EXAFS), differential pair distribution function (d-PDF) and density functional theory (DFT) analyses reported that heavy metals (such as Pb, Co, Cu, Ni, and Zn) are adsorbed onto hexagonal birnessite mainly as triple-corner-sharing (TCS) surface complexes on vacancies, triple-edge-sharing (TES) complexes above tridentate cavities on birnessite basal planes, and/or double-corner sharing (DCS) and double-edge sharing (DES) complexes on lateral edge surfaces²⁴⁻³⁴. By contrast, only a few studies investigated molecular mechanisms of Cd adsorption on birnessites. The d-PDF analysis of Cd adsorption onto poorly crystalline hexagonal birnessite demonstrated the major role of layer vacancies³⁵. More precisely, Cd K-edge EXAFS analysis showed that during adsorption onto hexagonal birnessite with uncapped vacancies, Cd was mainly adsorbed as TCS complexes on vacancies with a minor amount of DCS complexes on edge sites, whereas Cd was predominantly bound onto edge sites as DCS and DES complexes on Mn(III)-rich hexagonal birnessite³⁶.

Adsorption of heavy metals onto solid surfaces can induce isotope fractionation³⁷⁻⁴¹. Previous studies have demonstrated that light Cd isotopes are preferentially adsorbed onto soil active minerals (e.g., Fe/Mn/Al (hydr)oxides, clay minerals, calcite and quartz).^{7, 42-44} However, fractionation mechanisms during such interface reactions are not clearly constrained. Our previous study on Cd isotope fractionation during adsorption onto Fe (hydr)oxides revealed that the isotope offsets were independent of reaction conditions, such as ionic strength, initial Cd concentration and pH, as well as mineral type, but were attributed only to the strong distortion of CdO₆ octahedra formed at mineral surfaces.⁷ Similarly, Cd adsorbed onto calcite surfaces was also reported to form distorted octahedra and to induce isotope fractionation independent of reaction conditions, the presence of inorganic ligands (e.g., phosphate) reducing the fractionation magnitude, however⁴⁴. The sole study on Cd isotope fractionation during

adsorption onto Mn dioxides demonstrated that Cd isotope fractionation during adsorption onto hexagonal birnessite was dependent on ionic strength and reaction time⁴⁰. The fractionation magnitude was larger in synthetic seawater than that at low ionic strength, probably because of the abundance of isotopically light chloro-complexes (e.g., CdCl⁺) under the former conditions.⁴⁰ Although fractionation reached a reversible equilibrium at low ionic strength, fractionation magnitude decreased gradually with time in synthetic seawater; after 1 h, 24 h and 912 h reaction times, the fractionations ($\Delta^{114/110}\text{Cd}_{\text{solid-solution}}$) were -0.8‰, -0.4‰ and -0.2‰. Alterations in the mineral structure and crystallinity and in the molecular mechanisms of Cd binding with time were hypothesized as possible explanations.⁴⁰ This may also suggest a change in the relative proportions of Cd²⁺ binding to vacancies and edge sites. However, no data coupling the Cd isotope fractionation behaviors with these distinct active sites in the birnessite structure were available to support the hypothesis.

The present study thus aimed at determining Cd isotope fractionation during adsorption onto birnessite vacancy sites and layer edge sites. Cd isotope fractionation during adsorption onto triclinic birnessite and hexagonal birnessite over pH 4–8 was investigated first. Then, Cd K-edge EXAFS and DFT calculations were combined to investigate Cd binding mechanisms to birnessite surface active sites, and surface complexation modeling was used to determine the relative proportions of Cd²⁺ binding to birnessite vacancies and edge sites. Finally, the Cd isotope fractionation onto birnessite vacancies was determined by using triclinic birnessite as an end member for layer edge sites, and the Cd isotope fractionation on these two types of active sites on birnessite was coupled to the Cd²⁺ binding mechanisms at the molecular level. These results greatly enhance the understanding of Cd isotope fractionation and underlying mechanisms induced by its sorption to phyllosulfates and the application of Cd isotopes as tracers in natural environments.

2. Materials and Methods

2.1 Synthesis and properties of hexagonal and triclinic birnessite samples

All reagents were used as received, and detailed information is provided in [Text S1](#). For

triclinic birnessite (TBir) synthesis, 250 mL of 5.5 M NaOH solution was refrigerated at 4 °C for 5 h and then quickly added to 200 mL of 0.5 M MnCl₂ solution in a 500 mL Erlenmeyer flask. Immediately, high-purity oxygen gas (99.999%) was flowed in the obtained suspension at 2 L·min⁻¹ for 5 h under vigorous stirring⁴⁵. For hexagonal birnessite (HBir) synthesis, 300 mL of 0.667 M KMnO₄ solution in a 500 mL Erlenmeyer flask was heated to 100 °C in an oil bath with a glass condenser. Then, 45 mL of 6 M HCl solution was added at a constant rate of 0.7 mL·min⁻¹, and allowed to react for 30 min. The resulting suspension was cooled naturally at room temperature and then aged at 60 °C for 12 h⁴⁶. After synthesis, the solids were obtained through centrifugation, washed until the conductivity was below 20 μS·cm⁻¹, freeze-dried, ground, sieved and stored at 4 °C.

Mineral phases and morphologies were identified by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) (Figure S1). For chemical analysis, 0.01 g of solid and 0.1 g of hydroxylamine hydrochloride were accurately weighed and diluted in 250 mL of deionized water. The contents of K, Na and Mn in solution were determined by a flame atomic absorption spectrometer (FAAS, Agilent Technologies 200 Series AA). The Mn and K contents are 53.50±0.06% and 8.72±0.07% for HBir, and the Mn and Na contents are 57.22±0.40% and 5.64±0.00% for TBir. HBir and TBir points of zero charge (PZCs) were determined to be ~0.9 and ~3.4, respectively, by a Zeta potential method⁴⁷ (Figure S2), and their N₂-BET specific surface areas are 26.33±0.25 and 25.92±0.21 m²·g⁻¹. Mn average oxidation states of HBir and TBir were determined to be 4.02±0.01 and 3.67±0.02, respectively, by potentiometric titration³⁴.

The microstructural characteristics of HBir, including vacancy content and crystallite size, were determined by a specific trial-and-error method^{34, 48} (Text S2, Figures S3,4 and Table S1). The structural formula was determined to be K_{0.22}(Mn_{0.94}□_{0.06})O₂·0.33H₂O (□ denotes vacancy). Typically, an orthogonal setting was used for the unit cell with a = 4.922 Å, b = 2.842 Å and c* = 7.20 Å. The diameter of disk-like coherent scattering domains (CSD) in the ab plane was calculated to be 180 Å or 160 Å from (20,11) and (02,31) diffraction band modeling, respectively, while that

along the c^* axis was determined to be 79 ± 2 Å by the Scherrer formula⁴⁹.

2.3 Cd²⁺ adsorption experiments

Two series of adsorption experiments were conducted, including kinetic adsorption experiments with different reaction times (0-360 h for TBir and 0-720 h for HBir) at pH 6 and adsorption edge experiments varying from pH 4 to 8 for 72 h. Prior to the addition of the Cd²⁺ solution, solids were equilibrated at pH 6 ± 0.05 in 0.1 M NaNO₃ solution for 24 h with mineral concentrations of 0.5 g·L⁻¹ for TBir and 0.1 g·L⁻¹ for HBir. To initiate the adsorption reaction, volumes of Cd²⁺ stock solution were added to mineral suspensions to obtain the concentrations of 133.4 µM for TBir and 266.9 µM and 177.9 µM for HBir in kinetic and pH edge experiments, respectively. These Cd²⁺ concentrations were selected to prevent Cd²⁺ precipitation and investigate the relationships between adsorption and isotope fractionation over a wide range of adsorption proportions. The suspension pH was adjusted and maintained by adding 1 M HNO₃ or 1 M NaOH.

At the end of the reactions, mineral suspensions were filtered through 0.2 µm cellulose membranes to separate the solid and solution phases. The obtained solid was then sealed with Kapton tape, and stored at 4 °C within 24 h prior to Cd K-edge-extended X-ray absorption fine structure (EXAFS) analysis. The Cd²⁺ concentrations in the filtrates were determined using FAAS with a detection limit of 6.77 µg·L⁻¹ and an uncertainty of 0.3%. Control experiments were carried out with no Cd²⁺ added to the mineral suspensions to exclude potential Cd²⁺ contamination. Duplicate experiments were carried out to ensure reproducibility.

To investigate the possible mineral transformation of TBir under acidic conditions used for Cd²⁺ adsorption, 0.5 g·L⁻¹ TBir suspension was processed as described above for adsorption experiments without Cd²⁺, however. At the end of reaction, the suspension was centrifugated; the solid obtained (TBir_pH4_72h) was characterized using powder XRD analysis and the supernatant analyzed by FAAS for dissolved Mn concentration.

2.4 Cd isotope measurements

Prior to isotope analysis, solids with adsorbed Cd were transferred to 25 mL acid-cleaned Teflon vials and dissolved by adding 10 mL of warm 3 M HCl solution⁴⁰. Another aliquot of each sample containing ~600 ng Cd was then mixed with a ¹¹¹Cd-¹¹⁰Cd double-spike solution containing an equal mass of Cd, and subjected to chemical separation and purification as described previously^{7, 50, 51}. The total Cd recovery was > 95% for all samples. Cadmium isotopic ratio measurements were performed using a Thermo Scientific Neptune plus multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, CAS. The double spike method allowed correcting the mass bias. Measurement details were described previously⁷.

Double spike data reduction was performed offline to calculate Cd isotopic compositions of the samples and standards using a MATLAB-based script^{7, 52, 53}. These compositions were reported relative to the NIST SRM 3108 Cd standard according to eq. (1):

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

In this study, $\delta^{114/110}\text{Cd}$ values of the secondary reference standards were $-1.76 \pm 0.06 \text{ ‰}$ (2SD; n=4) for JMC Cd and $-1.27 \pm 0.05 \text{ ‰}$ (2SD; n=4) for Spex Cd, consistent with previous results^{7, 52, 54}. The long-term reproducibility of this method was better than $\pm 0.08 \text{ ‰}$ (2SD; N = 20) for $\delta^{114/110}\text{Cd}$. Cd isotopic fractionation ($\Delta^{114/110}\text{Cd}_{\text{solid-solution}}$) between the adsorbed and aqueous phases is defined as eq. (2):

$$\Delta^{114/110}\text{Cd}_{\text{solid-solution}} = \delta^{114/110}\text{Cd}_{\text{solid}} - \delta^{114/110}\text{Cd}_{\text{solution}} \quad (2)$$

2.5 EXAFS data collection and analysis

The Cd K-edge EXAFS spectra of Cd-adsorbed Mn dioxides, Cd hydroxide and aqueous Cd(NO₃)₂ standards were collected in fluorescence or transmission mode at the Shanghai Synchrotron Radiation Facility on a BL14W1 beamline with a pair of Si(111) monochromators. Energy calibration ($E_0 = 25,529 \text{ eV}$) was conducted using a silver foil. IFEFFIT software was used for data processing⁵⁵. The parameters used for background removal were as follows: $E_0 = 26,715 \text{ eV}$, k-weight = 2, and Rbkg = 1.0.

Structural parameters, including the interatomic distance (R), coordination number (CN) and Debye-Waller factor (σ^2), were obtained by fitting the experimental k^2 -weighted spectra to the standard equation⁵⁶ over a k range of 2.5-9.8 \AA^{-1} and an R range of 1-4 \AA . An amplitude reduction factor (S_0^2) of 0.95 was adopted from previous studies^{7, 36}. During the first Cd-O shell fitting, a Gaussian or a non-Gaussian distribution model was assumed, with a third cumulant in the latter to interpret the asymmetry of the [CdO₆] octahedron⁵⁷.

2.6 Modeling of Cd²⁺ adsorption on hexagonal birnessite edge sites and vacancies

To determine the relative proportions of Cd²⁺ adsorbed to vacancy and edge sites of hexagonal birnessite, surface complexation modeling (SCM) of the Cd²⁺ adsorption envelope at pH 4-8 was conducted as described previously⁵⁸. Hexagonal birnessite surfaces are divided into internal surfaces (three $\equiv\text{Mn}_2\text{O}^{-2/3}$ sites around each vacancy) and external edge surfaces ($\equiv\text{Mn}_2\text{O}^{-2/3}$ and $\equiv\text{MnOH}^{-1/3}$ sites), and a two-site model was used to describe mineral surface heterogeneity. The constant capacity model (CCM) was used to describe surface electrostatic effects on internal surfaces, while charge-distribution multisite ion complexation (CD-MUSIC) combined to the triple-layer model (TLM) was used to describe electrostatic effects on edge sites. The software ECOSAT 4.9⁵⁹ and the fitting program FIT⁶⁰ were used to fit the data.

2.7 DFT geometry optimization

An edge-sharing Mn octahedral nanodisk with a diameter of approximately 1.5 nm (i.e., Mn₁₉O₅₄H₃₀) was used as a model for birnessite (Figures S5). A Mn(IV) vacancy was created in the nanodisk model by removing one Mn octahedron, and two Cd cations were placed above and below the vacancy site to model TCS surface complexes. Each Cd was additionally coordinated to three H₂O molecules to ensure its octahedral coordination. TES surface complexes were created by placing a Cd cation on top of a tridentate cavity defined by three Mn octahedra, representing surface complexes formed on a vacancy-free birnessite basal surface. For DCS surface complex, Cd was initially coordinated to two singly coordinated O atoms of the lateral edge and four H₂O molecules. For the DES surface complexes, Cd·3H₂O was initially coordinated to one

doubly coordinated O (DESI) or one triply coordinated O (DESII), and two singly coordinated O atoms on the lateral edge.

All DFT calculations were performed using CASTEP code⁶¹ under the spin-polarized generalized gradient approximation, with the Perdew–Burke–Ernzerhof (PBE) functional⁶². The valence electron states of the Mn, Cd, O, and H ultrasoft pseudopotentials⁶³ were $3s^23p^63d^54s^2$, $4d^{10}5s^2$, $2s^22p^4$, and $1s^1$, respectively. The kinetic energy cutoff was 500 eV. The k -point grid for the first Brillouin zone⁶⁴ was $1 \times 1 \times 1$ for vernadite models. The k -point grids for CdO, Cd(OH)₂, and Cd(NO₃)₂ were $6 \times 6 \times 6$, $8 \times 8 \times 6$, and $4 \times 2 \times 4$, respectively. The calculated atomic forces converged to less than 0.01 eV/Å. The magnetic ordering among edge-sharing Mn octahedra was ferromagnetic in birnessite models. Geometry optimization was performed until the following conditions were met: total energy ≤ 0.000005 eV, atomic forces ≤ 0.05 eV/Å, stress ≤ 0.03 GPa and atomic displacement ≤ 0.0005 Å. The crystal structures were rendered using VESTA software⁶⁵.

3 Results and Discussion

3.1 Cd isotope fractionation behaviors during adsorption onto birnessites

At pH 6, surface coverages of Cd²⁺ adsorbed to Mn dioxides rapidly increase to reach a plateau (Figure S6a, b). After 72 h of the reaction, the percentages of Cd²⁺ adsorbed are $57.0 \pm 1.1\%$ for TBir and $64.2 \pm 0.3\%$ for HBir, resulting in surface coverages of $5.87 \pm 0.11 \mu\text{mol}\cdot\text{m}^{-2}$ and $65.02 \pm 0.32 \mu\text{mol}\cdot\text{m}^{-2}$, respectively (Table S2). These results suggest that adsorption equilibrium between solids and solutions was reached after 72 h, and pH edge experiments were thus performed for 72 h. The density of Cd²⁺ sorbed to Mn dioxides increases as pH increases from 4 to 8 (Figure S6c,d). As pH increases, the surface coverage of Cd²⁺ increases from $3.00 \pm 0.10 \mu\text{mol m}^{-2}$ to $9.83 \pm 0.01 \mu\text{mol m}^{-2}$ for TBir and from $46.39 \pm 0.12 \mu\text{mol}\cdot\text{m}^{-2}$ to $62.36 \pm 0.03 \mu\text{mol}\cdot\text{m}^{-2}$ for HBir (Table S3). Correspondingly, the percentages of Cd²⁺ adsorbed vary from 29.1 ± 1.0 to $95.5 \pm 0.1 \%$ and 68.7 ± 1.2 to $92.3 \pm 0.3 \%$, respectively. These results indicate that Cd²⁺ adsorption to HBir is enhanced compared to TBir owing to the lower point of zero charge (PZC) (Figure S2) and the presence of highly undersaturated layer O atoms in

HBir owing to layer vacancies^{66, 67}.

For TBir the isotopic composition ($\delta^{114/110}\text{Cd}$) of aqueous Cd^{2+} rapidly increases at the initial stage of the reaction and then reaches isotopic equilibrium (Figure S7 and Table S4). In detail, the $\delta^{114/110}\text{Cd}$ value of the aqueous phases increases from $-1.49 \pm 0.08 \text{ ‰}$ to $-1.10 \pm 0.08 \text{ ‰}$ for TBir as the reaction time increases from 1 h to 72 h, and then the remains essentially constant. Compared to the $\delta^{114/110}\text{Cd}$ value of the Cd^{2+} bulk solution ($-1.74 \pm 0.08\text{‰}$), heavy Cd isotopes are preferentially enriched in the aqueous phase.

The $\delta^{114/110}\text{Cd}$ values of both solutions and solids increase when increasing the fraction of Cd^{2+} adsorbed to Mn dioxides, and those of the solutions are greater than those of the solids (Figure 1c,d). This indicates that lighter Cd isotopes are preferentially enriched on mineral surfaces, heavier isotopes remaining in the solution. As proportions of Cd adsorbed increase from 28.2 to 95.6% for TBir and from 59.4 to 90.0% for HBir over the 4-8 pH range, Cd isotope fractionations ($\Delta^{114/110}\text{Cd}_{\text{solid-solution}}$) are almost the same for the two systems: $-1.47 \pm 0.09\text{‰}$ (1SD; n=5) for TBir and $-0.88 \pm 0.03\text{‰}$ (1SD; n=5) for HBir (Tables S5, S6).

Both equilibrium and Rayleigh models were considered to fit the Cd isotope fractionation processes induced by adsorption. These models are described by eqs. (3) and (4):

$$\delta^{114/110}\text{Cd}_{\text{solution}} = \frac{\delta^{114/110}\text{Cd}_{\text{stock}} - 1000 \cdot f \cdot (\alpha_{\text{solid-solution}} - 1)}{1 - f + (f \cdot \alpha_{\text{solid-solution}})} \quad (\text{equilibrium model}) \quad (3)$$

$$\delta^{114/110}\text{Cd}_{\text{solution}} = (1000 + \delta^{114/110}\text{Cd}_{\text{stock}}) \cdot (1 - f)^{(\alpha_{\text{solid-solution}} - 1)} - 1000 \quad (\text{Rayleigh model}) \quad (4)$$

where $\alpha_{\text{solid-solution}}$ refers to the estimated isotope fractionation factor between adsorbed and aqueous Cd, f is the proportion of Cd adsorbed, $\delta^{114/110}\text{Cd}_{\text{stock}}$ being the isotopic composition of the stock solution.

Consistent with previous studies, Cd isotopic fractionation on Mn dioxides are best described by the equilibrium model^{7, 40}, fractionation factors ($\alpha_{\text{adsorbed-aqueous}}$) being 0.99846 ± 0.00011 for TBir and 0.99904 ± 0.00006 for HBir. The theoretical isotopic fractionation between adsorbed and aqueous Cd can be calculated according to eq. (5).

$$\Delta^{114/110}\text{Cd}_{\text{solid-solution}} \cong 1000 \times \ln\alpha_{\text{solid-solution}} \quad (5)$$

As-derived $\Delta^{114/110}\text{Cd}_{\text{solid-solution}}$ values are $-1.54 \pm 0.11\%$ and $-0.96 \pm 0.06\%$ for TBir and HBir, respectively, consistent with measured values. These results suggest that the magnitude and direction of Cd isotope fractionation during the adsorption of Mn dioxides are controlled by differences in the bonding environments between aqueous and adsorbed Cd, independent of the reaction conditions (e.g., reaction time and pH).

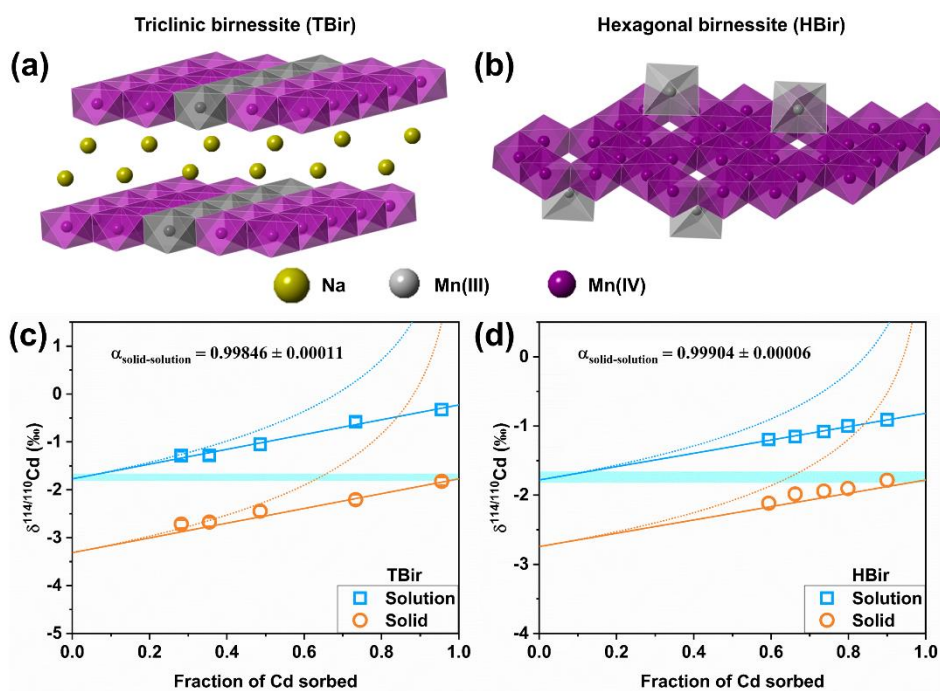


Figure 1 Idealized structures of triclinic birnessite (a) and hexagonal birnessite (b) and Cd isotopic compositions of the solution and solid phases as a function of the adsorbed Cd fraction (f) during adsorption onto triclinic birnessite TBir (c) and hexagonal birnessite HBir (d). The $\delta^{114/110}\text{Cd}$ of the bulk solution is $-1.74 \pm 0.08\%$. In panels c and d, the solid and dotted lines are the best fittings based on the equilibrium and Rayleigh models respectively.

3.2 Cd binding environments revealed by Cd K-edge EXAFS analysis

The Cd K-edge EXAFS spectra of typical Cd-adsorbed Mn dioxides were collected to reveal the Cd coordination mechanisms at mineral surfaces. The k^2 -weighted EXAFS spectra and corresponding Fourier transforms (FTs) of the Cd^{2+} -adsorbed samples are distinct from those of the $\text{Cd}(\text{NO}_3)_2$ solution and $\text{Cd}(\text{OH})_2$ (Figure 2), indicating the formation of inner-sphere complexes at mineral surfaces and the absence of $\text{Cd}(\text{OH})_2$

precipitates. In the FTs of Cd^{2+} -adsorbed samples, the peak at $R+\Delta R \sim 1.8 \text{ \AA}$ corresponded to the first shell of Cd-O pairs, while the peak at $R+\Delta R \sim 3.2 \text{ \AA}$ may be assigned to Mn backscattering^{33, 36}.

Cd K-edge EXAFS spectra were then analyzed by shell-by-shell fitting, taking into consideration or not a third contribution to the first Cd-O shell. Addition of such a third contribution to the first Cd-O shell greatly improves fit quality, reducing R-factor, χ^2 and reduced χ^2 by 16-19%, 16-19% and 1-3% respectively, compared to that without this additional contribution (Table 1 and Table S6). In addition, average Cd-O distances within this first Cd-O shell are slightly longer ($2.28 \pm 0.03 \text{ \AA}$ and $2.28 \pm 0.04 \text{ \AA}$ for HBir and TBir, respectively) when using this third contribution than those derived without it ($2.24 \pm 0.01 \text{ \AA}$ and $2.23 \pm 0.01 \text{ \AA}$), while they are similar for $\text{Cd}(\text{NO}_3)_2$ ($2.27 \pm 0.02 \text{ \AA}$ vs $2.27 \pm 0.01 \text{ \AA}$). All these results indicate the formation of highly distorted Cd octahedra when adsorbed onto the birnessite surfaces^{7, 57}.

The Cd-Mn shell was fitted with a single Cd-Mn path, resulting in similar Cd-Mn distances of 3.66-3.67 \AA but different coordination numbers (CNs), 10.9 ± 3.3 and 2.8 ± 0.9 for HBir and TBir, respectively. The much higher CN derived for Cd sorbed on HBir suggests that it is predominantly forming TCS complexes at HBir vacant sites^{33, 36}. Furthermore, the large Debye-Waller factor ($\sigma^2=0.0150$) of this Cd-Mn shell (Table 1) may indicate the formation of a minor amount of DCS complexes at HBir layer edge sites^{33, 36}. For TBir, CN and R of the Cd-Mn pairs are consistent with the formation of DCS complexes at layer edge sites³⁶.

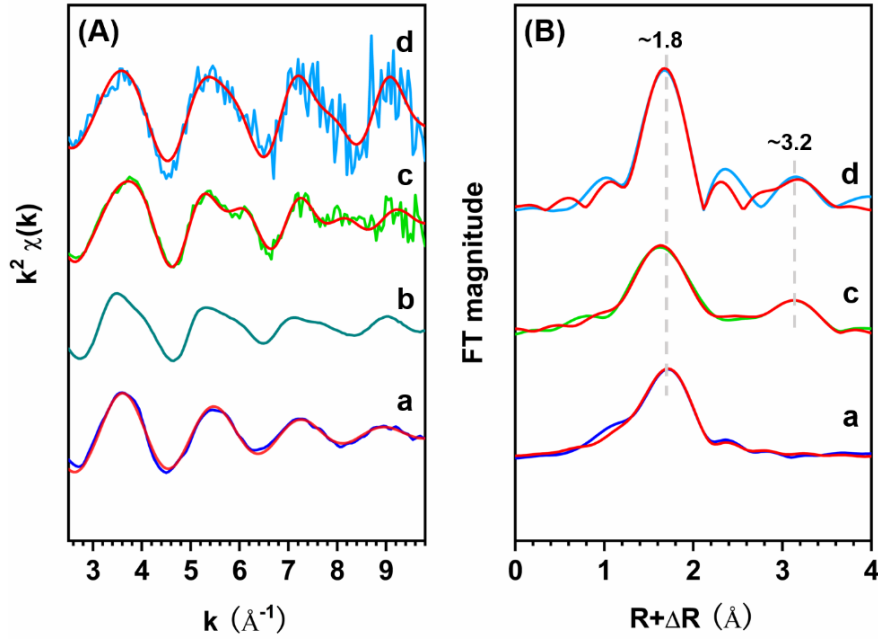


Figure 2 k^2 -weighted Cd K-edge EXAFS spectra (A) of aqueous $\text{Cd}(\text{NO}_3)_2$ (a) and $\text{Cd}(\text{OH})_2$ (b) standards, Cd-adsorbed HBir (c) and TBir (d) samples and the corresponding Fourier transforms (FTs, B), overlaid with the best fits with the addition of a third cumulant in the first Cd-O shell fitting for HBir and TBir. The experimental data and the best fits are shown as colored and red lines, respectively. The initial Cd concentrations were $133.4 \mu\text{M}$ for TBir and $177.9 \mu\text{M}$ for HBir in the pH-edge experiments, and the initial concentrations of the mineral suspensions were $0.5 \text{ g}\cdot\text{L}^{-1}$ for TBir and $0.1 \text{ g}\cdot\text{L}^{-1}$ for HBir, with a background electrolyte of 0.1 M NaNO_3 solution, pH 7.

Table 1 Fitting results of the EXAFS spectra for aqueous Cd(NO₃)₂ standards and typical Cd-adsorbed samples, including a third cumulant (Cum.) in the first Cd–O coordination shell fitting.

Sample	Path	CN	R (Å)	σ^2 (Å ²)	Third Cum.	ΔE (eV)	Reduced χ^2	χ^2	R-factor
Cd(NO ₃) ₂ , _{aq}	Cd-O	7.8 ± 0.5	2.27 ± 0.02 (2.27 ± 0.01)	0.0101 ± 0.0010	0.0001 ± 0.0004	2.9 ± 1.2	545.91	4768.76	0.0063
HBir	Cd-O	8.2 ± 0.8	2.28 ± 0.03 (2.24 ± 0.01)	0.0113 ± 0.0016	0.0009 ± 0.0008	3.4 ± 2.0	3.72	15.71	0.0054
	Cd-Mn	10.9 ± 3.3	3.66 ± 0.05	0.0150 ± 0.0035					
TBir	Cd-O	5.9 ± 1.0	2.28 ± 0.04 (2.23 ± 0.01)	0.0001 ± 0.0018	0.0008 ± 0.0008	2.2 ± 3.2	1.60	10.79	0.0372
	Cd-Mn	2.8 ± 0.9	3.67 ± 0.03	0.0030 ^a					

^aFixed during fitting.

3.3 Geometry optimization of Cd surface species on birnessites

From the simulations of reference CdO, Cd(OH)₂, and Cd(NO₃)₂ structures, DFT calculations appear to overestimate dimensions of experimental structures by less than 3% (Table 2). CdO and Cd(OH)₂ have symmetric octahedral Cd coordination. Their optimized lattice parameters are $a = 4.796 \text{ \AA}$ and $c = 2.398 \text{ \AA}$ for CdO and $a = 3.593 \text{ \AA}$ and $c = 4.829 \text{ \AA}$ for Cd(OH)₂, whereas experimentally determined parameters are $a = 4.770 \text{ \AA}$ and $c = 2.353 \text{ \AA}$ for CdO⁶⁸ and $a = 3.194 \text{ \AA}$ and $c = 4.702 \text{ \AA}$ for Cd(OH)₂⁶⁹. In Cd(NO₃)₂, the sixfold coordination of Cd is asymmetric. The DFT-calculated lattice parameters of Cd(NO₃)₂ are $a = 7.877$, $c = 7.853$, and $b = 15.992 \text{ \AA}$, which are 4.0 – 4.9% greater than experimental values ($a = c = 7.507 \text{ \AA}$, $b = 15.369 \text{ \AA}$)⁷⁰. The average $d(\text{Cd-O})$ in Cd(NO₃)₂, CdO and Cd(OH)₂ are larger than the experimental values (2.33 Å, (Louër, 1976 #18137) 2.35 Å⁶⁸ and 2.31 Å⁶⁹) by less than 3%.

Table 2 DFT-calculated interatomic distances (in Å) of Cd in solid phases

	CdO	Cd(OH) ₂	Cd(NO ₃) ₂	Surface complexes on birnessite				
				TES	TCS	DCS	DESI	DESII
$d(\text{Cd-O})$	2.40	2.35	2.37	2.40	2.30	2.22	2.23	2.31
	2.40	2.35	2.37	2.38	2.31	2.24	2.30	2.49
	2.40	2.35	2.37	2.46	2.29	2.36	2.42	2.32
	2.40	2.35	2.39	2.30	2.36	2.42	2.44	2.30
	2.40	2.35	2.39	2.33	2.36	2.49	2.33	2.42
	2.40	2.35	2.44	2.30	2.36	2.50	2.42	2.32
	<2.40>	<2.35>	<2.39>	<2.36>	<2.33>	<2.37>	<2.36>	<2.36>
$d(\text{Cd-Mn})$	–	–	–	3.18	3.70	3.54	3.17	3.18
	–	–	–	3.35	3.72	3.57	3.22	3.36
	–	–	–	3.36	3.70			4.19
	–	–	–		3.70			
	–	–	–		3.70			
	–	–	–		3.70			
	–	–	–	<3.29>	<3.70>	<3.56>	<3.19>	<3.57>

Table 2 lists the results of DFT geometry optimization for Cd surface complexes formed at birnessite surfaces. The wide variation of $d(\text{Cd-O})$ for Cd complexes indicates highly distorted octahedral coordination, and $d\langle\text{Cd-O}\rangle$ of TCS complex is smaller than that of edge species such as DCS, DESI, and DESII complexes (Figure S5), $d\langle\text{Cd-O}\rangle$ of the TES complex being similar to those of the edge species. On the other hand, TCS shows larger $d\langle\text{Cd-Mn}\rangle$ than edge species. In contrast with $d\langle\text{Cd-O}\rangle$,

$d\langle\text{Cd-Mn}\rangle$ significantly differs among edge species, thus making this parameter more suitable than $d\langle\text{Cd-O}\rangle$ for species identification based on structural parameters. However, it should be noted that the present calculations of $d\langle\text{Cd-Mn}\rangle$ for edge species were based on Cd^{2+} binding to Mn(IV) sites, and are expected to be shorter than that for Cd^{2+} binding to Mn(III) sites³⁶. This limitation of DFT calculations may also account for the similar $d\langle\text{Cd-Mn}\rangle$ computed for TCS Cd^{2+} on HBir and DCS Cd^{2+} on TBir (Table 1).

3.4 Cadmium isotope fractionations onto birnessite edge sites and vacancies

Since Cd^{2+} may be adsorbed onto hexagonal birnessite edge and vacant layer sites, relative proportions of Cd binding at these sites were first quantified from SCM modelling. The modeling of Cd^{2+} adsorption data over the 4-8 pH range fits satisfactorily the data (Figure 3 and Table S7) and shows that vacancy sites are the dominant active sites for Cd^{2+} adsorption onto HBir. With increasing pH conditions, the contribution of vacancies slightly decreases, however, to the benefit of edge sites. In detail, at pH 4, 59% of the total Cd adsorbed onto the solids is adsorbed onto vacancies, while at pH 8, 39% of the total Cd retained on the solid is located on the edge sites, with the rest being adsorbed at vacancies. Over the whole pH range, no $\text{Cd}(\text{OH})_2$ is formed.

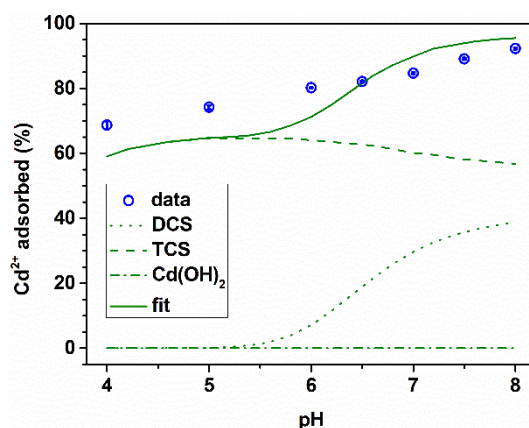


Figure 3 Modeling of Cd^{2+} adsorption edges on HBir over a pH range of 4-8. The experimental conditions were as follows: initial Cd^{2+} concentration=177.9 μM , reaction time=72 h, ionic strength=0.1 M NaNO_3 solution, solid/solution ratio=0.1 $\text{g}\cdot\text{L}^{-1}$, and temperature= 25 ± 2 °C.

Triclinic birnessite is commonly recognized as vacancy free^{18, 71, 72} and only adsorbs heavy metals onto edge sites. The theoretical $\Delta^{114/110}\text{Cd}_{\text{solid-solution}}$ of $-1.54 \pm 0.11\%$ induced by Cd adsorption to TBir should thus be that of edge sites. This value was also used for the fractionation induced during Cd adsorption to HBir edge sites. If the proportions of Cd adsorbed to HBir edge sites and vacancies are f_1 and f_2 , respectively, and $\Delta^{114/110}\text{Cd}_{\text{edge-solution}}$ and $\Delta^{114/110}\text{Cd}_{\text{vacancy-solution}}$ the isotopic fractionation induced by Cd sorption at these sites, the overall $\Delta^{114/110}\text{Cd}_{\text{solid-solution}}$ induced by Cd sorption can be expressed according to eq. 6:

$$\Delta^{114/110}\text{Cd}_{\text{solid-solution}} = \frac{f_1}{f_1 + f_2} \times \Delta^{114/110}\text{Cd}_{\text{edge-solution}} + \frac{f_2}{f_1 + f_2} \times \Delta^{114/110}\text{Cd}_{\text{vacancy-solution}} \quad (6)$$

As a result, calculated values of $\Delta^{114/110}\text{Cd}_{\text{vacancy-solution}}$ at pH 4, 5, 6, 7 and 8 were $-0.92 \pm 0.11\%$, $-0.83 \pm 0.11\%$, $-0.80 \pm 0.12\%$, $-0.55 \pm 0.18\%$, and $-0.43 \pm 0.22\%$, respectively, leading to an average $\Delta^{114/110}\text{Cd}_{\text{vacancy-solution}}$ of $-0.71 \pm 0.21\%$.

XXXX New and additional modifications starting from here.

Alternatively, it is possible to hypothesize that, at a given pH, Cd^{2+} adsorption density on edge sites is similar for HBir and TBir. In this case, proportions of Cd^{2+} on hexagonal birnessite edge sites are calculated to be 6%, 7%, 9%, 13%, and 16% of the total Cd^{2+} adsorbed at pH 4, 5, 6, 7, and 8, respectively. The $\Delta^{114/110}\text{Cd}_{\text{vacancy-solution}}$ values may then be calculated and range from $-0.75 \pm 0.14\%$ to $-0.89 \pm 0.12\%$, with an average of $-0.80 \pm 0.05\%$. Both sets of values match those derived from SCM modeling.

3.5 Cadmium isotope fractionation mechanism

Our results show that lighter Cd isotopes are preferentially adsorbed to birnessite surfaces, consistent with previous studies⁴⁰. In the present study, both Cd K-edge EXAFS results and DFT geometry optimization analyses indicate that Cd mainly exists as distorted octahedral complexes when adsorbed to birnessite surfaces. This probably accounts for the enrichment of light Cd isotopes onto solids, because, as a general rule, heavy isotopes are preferred in stronger binding environments (e.g., shorter bond lengths). Similarly, the enrichment of light Cd isotopes on iron (oxyhydr)oxides is attributed to the adsorption of highly distorted CdO_6 octahedra to mineral surfaces⁷. In addition, the exchange of various aqueous Cd species may also affect isotope

fractionation. Theoretical calculations of aqueous Cd species under current experimental conditions (pH range of 4–8) show that Cd mainly exists as Cd^{2+} (84–87%) and $\text{Cd}(\text{NO}_3)^+$ (~12%) with negligible amounts of $\text{Cd}(\text{NO}_3)_2$, $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{HCO}_3)^+$, and $\text{CdCO}_{3,\text{aq}}$ (Figure S9). Compared to $\text{Cd}(\text{NO}_3)^+$, Cd^{2+} preferentially sorbs to birnessite surfaces, owing to its larger positive charge, thus contributing to the enrichment of light Cd isotopes onto solids, as $\text{Cd}(\text{NO}_3)^+$ is isotopically slightly “heavier” than Cd^{2+} .⁷³

Values of $\Delta^{114/110}\text{Cd}_{\text{solid-solution}}$ derived from equilibrium model are $-1.54 \pm 0.11\%$ and $-0.96 \pm 0.06\%$ for TBir and HBir, respectively. Analysis of isotopic fractionation kinetic (Figure S7) and modeling of the solution and solid isotopic compositions all show that equilibrium fractionation, rather than kinetic effects, causes the isotope offsets observed in the present system. In addition, the magnitude of Cd isotope fractionation induced by adsorption to TBir is greater compared to HBir, most likely owing the different binding sites and complex structures of Cd adsorbed on the two species. For comparison, Cd isotope fractionation resulting from its adsorption to different Fe (hydr)oxides is similar, with consistent $\Delta^{114/110}\text{Cd}_{\text{solid-solution}}$ values of -0.5% for goethite, hematite and ferrihydrite.⁷ A similar effect was reported for the sorption of other heavy metals to birnessite-like minerals. For example, light Zn isotopes are enriched at vacant sites during Zn^{2+} adsorption to birnessite, while heavy isotopes are bound at edge sites.³³ Considering the local environments of Cd^{2+} sorbed to birnessite vacancies and edge sites (Figure 3, Tables 1, 2), it is reasonable to expect different isotope fractionation magnitudes onto the two types of site. Consistently, Cd isotope fractionations induced by adsorption to edge sites ($\Delta^{114/110}\text{Cd}_{\text{edge-solution}}$) and vacancies ($\Delta^{114/110}\text{Cd}_{\text{vacancy-solution}}$) were $-1.54 \pm 0.11\%$ and $-0.71 \pm 0.21\%$, respectively. Several factors may account for this difference. First, although Cd K-edge EXAFS analysis indicates similar Cd-O distances in both cases (Table 1), DFT geometry optimization supports a shorter average Cd-O distance (2.33 Å) for TCS complexes on birnessite vacancies than for DCS and DES complexes on edge sites (2.36–2.37 Å) (Table 2). Second, CNs for Cd–Mn shells may also influence isotope fractionation and EXAFS

analysis indicates TCS complexes with large Cd–Mn CNs for Cd sorbed at vacancy sites and DCS complexes with low Cd–Mn CNs at birnessite edge sites (Table 1). Previous studies suggested indeed that the greater magnitudes of Sb and Ni isotope fractionation on goethite compared to ferrihydrite were probably due to the formation of weaker surface complexes with lower CNs for Sb/Ni–Fe pairs on goethite.^{74, 75}

However, it should be noted that under acidic conditions Mn(III) initially present in TBir layers can disproportionate and migrate out of the layer, creating layer vacancies and leading to the transformation of triclinic birnessite to hexagonal birnessite^{21, 22}. This transformation is confirmed by the powder XRD analysis of the reaction product of TBir acidification at pH4 for 72 h (TBir_pH4_72h; Text S3 and Figure S10). If Mn³⁺ was released to solution, a large portion of Cd²⁺ would adsorb at vacancy sites, thus increasing Cd²⁺ adsorption density and decreasing Cd isotope fractionation magnitude. This is not observed however as Cd²⁺ adsorption density on TBir remains much lower than that on HBir even under acidic conditions (e.g. pH 4-5, Table S3), and $\Delta^{114/110}\text{Cd}_{\text{solid-solution}}$ values induced by Cd²⁺ adsorption to TBir remain constant over the whole pH 4-8 range (Table S4). This may be due to the presence of Mn^{2+/3+} (coming from TBir layers) on at least one side of layer vacancies formed during TBir equilibration at low pH (e.g., TBir_pH4_72h, protons being present on the other side to compensate for the remaining layer charge deficit²¹). Analysis of the dissolved Mn concentration after equilibration of TBir at pH4 for 72h indicates a negligible Mn release (4.00±0.05% of total Mn), confirming the capping of newly formed layer vacancies by Mn^{2+/3+}. Exchanging Cd²⁺ for these cations may not be favored especially because of the ionic background electrolyte (0.1 M NaNO₃)⁷⁶. As a consequence, adsorption of Cd²⁺ occurs mainly onto layer edge sites over the whole pH range investigated leading to similar Cd isotope fractionations on TBir.

Finally, the $\Delta^{114/110}\text{Cd}_{\text{solid-solution}}$ during Cd²⁺ adsorption onto HBir at pH 8±0.05 (-0.87±0.12‰) is larger than that previously reported (-0.24--0.56‰) for an analogous mineral.⁴⁰ This difference can be related to the relative proportions of Cd²⁺ on vacancies vs. edge sites as our results show that formation of DCS complexes at edge sites causes

a larger isotope offset ($\Delta^{114/110}\text{Cd}_{\text{edge-solution}} = -1.54 \pm 0.11\%$) than that of TCS complexes on vacancies ($\Delta^{114/110}\text{Cd}_{\text{vacancy-solution}} = -0.71 \pm 0.21\%$); the more Cd adsorbed on edge sites, the greater the magnitude of isotope fractionation on the solid. Wasylenki et al. (2014) also revealed that isotope offsets decreased from -0.8% after 1 h reaction time to -0.2% after 912 h, as the result of Cd migration adsorbed to vacancy sites into the mineral structure,⁴⁰ which is unlikely owing to the ionic radius of Cd^{2+} . Alternatively, this kinetic effect may be caused by a modification in Cd binding mode from DCS and DES inner-sphere complexes on edges to TCS complexes on vacancies, owing to the decrease in the number of edge sites accompanying the aging and aggregation of birnessite nanoparticles under alkaline conditions ($\text{pH} \sim 8.3$)⁷⁷.

4 Environmental Implications

Cd isotopes have great potential for effectively tracking Cd sources and fate and for understanding Cd behavior. Due to their high scavenging ability, phyllosulfates are significant Cd reservoirs and thus mediate Cd geochemical cycling as well as its isotopic composition in natural environments. The present study shows that different Cd isotope fractionation stem from adsorption onto birnessite edge sites ($\Delta^{114/110}\text{Cd}_{\text{edge-solution}} = -1.54 \pm 0.11\%$) and vacancy sites ($\Delta^{114/110}\text{Cd}_{\text{vacancy-solution}} = -0.71 \pm 0.21\%$), thus providing a direct clue to the interpretation of isotopic signatures measured in natural settings. For example, the isotope fractionation ($\Delta^{114/110}\text{Cd}_{\text{sediment-river}}$) of -0.91 – -1.0% observed between water and sediments in acid mine drainage,⁴ can be accounted for by Cd adsorption to secondary oxides and hydroxides, and more especially to Mn (hydr)oxides. Similarly, magnitudes of Cd isotope fractionation on birnessite edge and vacancy sites can be used as end members to assess isotopic offsets during Cd adsorption onto birnessite-like minerals, from relative proportions of Cd^{2+} at these sites. From a practical point of view, reconstruction of isotope fractionation of solids by using the two end members may be used to assess the relative proportions of Cd^{2+} adsorbed onto birnessite edge sites and vacancies, which is currently challenging. The present results also suggest that Mn (hydr)oxides affect Cd isotope fractionation to a larger extent than other active components, such as Fe/Al (hydr)oxides, clay minerals, calcite,

quartz, or humic acids^{42-44, 78}. In addition to birnessite structural characteristics, such as the relative proportions of vacant and edge sites, different binding modes of Cd²⁺ adsorption onto Mn (hydr)oxides (e.g., tectomanganates with different tunnel sizes), and under contrasting environmental conditions (e.g., presence and nature of inorganic and organic ligands, temperature), may influence Cd isotope fractionation further^{7, 40, 44, 78}. Additional studies are thus needed to fully elucidate the intrinsic mechanisms and influencing factors of the directions and magnitudes of Cd isotopic fractionation during its interaction with environmentally relevant Mn (hydr)oxides.

ASSOCIATED CONTENT

Supporting Information

Reagent information; powder XRD and SEM of birnessite samples; structure determination of HBir using a specific trial-and-error method; Cd²⁺ adsorption kinetics and pH edge experiments on TBir and HBir; Cd isotope fractionation kinetics during adsorption onto TBir; initial Cd concentrations and Cd adsorption density and fraction on birnessite samples in adsorption kinetics, pH edge experiments, and corresponding isotopic compositions of the solution and solid; fitting results of Cd K-edge EXAFS spectra for aqueous Cd(NO₃)₂ standard and typical Cd adsorbed samples, without a third cumulant for the first Cd–O shell fitting; experimental and modeling proportions of Cd adsorbed onto HBir edge sites and vacancies over a pH range of 4-8; DFT-calculated Cd surface complexes formed at different adsorption sites of birnessite; changes in aqueous Cd species as a function of pH.

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