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Solution speciation controls mercury isotope fractionation of Hg(II) sorption to goethite

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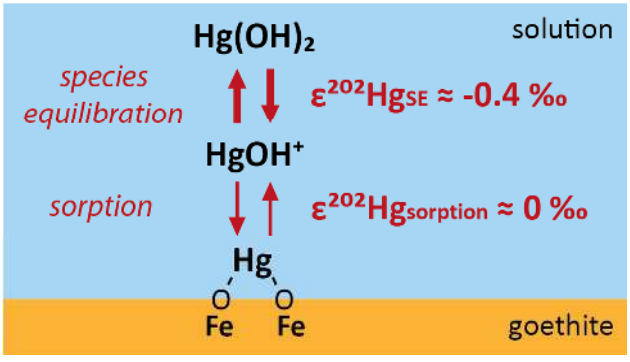
ABSTRACT

The application of Hg isotope signatures as tracers for environmental Hg cycling requires the determination of isotope fractionation factors and mechanisms for individual processes. Here, we investigated Hg isotope fractionation of Hg(II) sorption to goethite in batch systems under different experimental conditions. We observed a mass-dependent enrichment of light Hg isotopes on the goethite surface relative to dissolved Hg (ε^{202}Hg of -0.30 ‰ to -0.44 ‰) which was independent of pH, chloride and sulfate concentration, type of surface complex, and equilibration time. Based on previous theoretical equilibrium fractionation factors, we propose that Hg isotope fractionation of Hg(II) sorption to goethite is controlled by an equilibrium isotope effect between Hg(II) solution species, expressed on the mineral surface by the adsorption of the cationic solution species. In contrast, the formation of outer-sphere complexes and subsequent conformation changes to different inner-sphere complexes appeared to have insignificant effects on the observed isotope fractionation. Our findings emphasize the importance of solution speciation in metal isotope sorption studies and suggest that the dissolved Hg(II) pool in soils and sediments, which is most mobile and bioavailable, should be isotopically heavy, as light Hg isotopes are preferentially sequestered during binding to both mineral phases and natural organic matter.

TOC Art



Introduction

Soils worldwide contain a total pool of 1.15×10^6 tons of mercury (Hg) and represent the most important terrestrial sink for atmospherically deposited Hg from natural and anthropogenic sources.[1] Mercury in soils can be exported to aquatic environments, re-emitted as Hg^0 to the atmosphere, or methylated under anoxic conditions to form neurotoxic and bioaccumulating methyl-Hg.[2] However, the largest Hg pool in soils is bound to organic and mineral soil phases, where it is immobilized.[1] In organic topsoils, Hg is mainly bound to reduced organic sulfur groups,[3] whereas in soils and sediments with low organic matter contents, mineral phases like Fe and other metal (oxyhydr)oxides and clay minerals play an important role as sorbents.[4,5] In addition, Fe (oxyhydr)oxides form colloidal particles in natural aquatic and terrestrial environments and can thus act as carriers of sorbed metals such as Hg by colloidal transport.[6]

The fractionation of stable Hg isotopes in nature has gained much attention in recent years,[7,8,9] as it provides a promising tracer for environmental Hg cycling. Mercury isotopes have been shown to exhibit mass-dependent fractionation (MDF) as well as mass-independent fractionation (MIF), caused by nuclear volume fractionation (NVF)[10] or magnetic isotope effects (MIE)[11], together generating a multidimensional isotope signature. In order to apply stable Hg isotopes as a tool to understand the fate of Hg in the environment, one needs to understand Hg isotope fractionation factors and mechanisms of individual biogeochemical pathways. With this mechanistic information, it will be possible to deconvolute different sources and processes using measured stable Hg isotope ratios in natural samples. So far, Hg isotope fractionation has been studied experimentally for photoreduction of Hg^{2+} and methyl-Hg,[12,13] abiotic and biotic methylation of Hg,[14,15] abiotic and biotic reduction of Hg^{2+},[16,17] photolytic and microbial methyl-Hg degradation,[18,19] volatilization of elemental liquid Hg,[20,21] and aqueous to gas phase transfer of elemental Hg.[22] In a previous study, we investigated equilibrium isotope fractionation between dissolved Hg(II) species and thiol-bound Hg as a model system for sorption of Hg(II) to natural organic matter.[23] No data are available yet for stable isotope fractionation of Hg sorption to mineral phases. However, stable isotope fractionation during sorption to minerals has been described for other metals. Sorption studies for Cu(II),[24,25] Zn(II),[25,26] and Fe(II),[27,28] to mineral phases (Fe- and Mn-

(oxyhydr)oxides) revealed that sorption was in most cases associated with an enrichment of heavy isotopes on mineral surfaces relative to the dissolved phase. The observed isotope fractionation was explained by the lower vibrational frequencies of the sorption complexes with heavy isotopes and thus a lower zero-point energy compared with complexes with light isotopes.[29] In contrast, an isotope fractionation towards light isotopes on the mineral surface for metals sorbing as cations has been observed for some Zn experiments[30] and preliminary Cd data,[31] a mechanistic interpretation is however lacking. Mo(VI) and U(VI), both predominantly present in anionic form, showed a preferential sorption of light isotopes to Mn-(oxyhydr)oxides.[32,33] The interpretation of these isotope effects is still under debate: in the case of U(VI), the isotope fractionation was attributed to a change in coordination environment between the dissolved and sorbed phase.[33] For Mo(VI) it has been proposed that the isotope fractionation is caused by an equilibrium isotope effect between different solution species, where only the minor species is actively sorbing.[34,35] However, a newer study postulates a fractionation between the dissolved Mo and a polynuclear surface precipitate.[36]

In this study we present the first data for Hg isotope fractionation during sorption processes to mineral surfaces. Goethite (α-FeOOH) was chosen as sorbent because it is the most abundant iron (oxyhydr)oxide in soils[37] and Hg(II) sorption to goethite has been studied both with macroscopic[38,39] and spectroscopic techniques.[40,41] The objectives of this study were (i) to investigate stable Hg isotope fractionation associated with sorption of Hg(II) to goethite under different environmentally relevant pH conditions, chloride and sulfate concentrations, and after different equilibration times, and (ii) to elucidate the mechanisms driving Hg isotope fractionation of sorption based on our experimental results, previously presented surface complexation studies, and theoretical calculations for equilibrium fractionation factors of Hg species.

Experimental Section

Materials and reagents. The goethite was synthesized following a standard method (preparation from an alkaline system after Böhm, 1925) described in Schwertmann and Cornell[42] and was already used and characterized in previous studies.[43,44] The structure of the synthesized goethite was confirmed by

X-ray diffraction (XRD) and a surface area of 38 m^2 g^{-1} was measured using the N_2-BET method.[43] All chemicals used in this study were analytical grade and used without further treatment, if not indicated otherwise. A detailed list of reagents, chemical impurities, and preparation procedures is provided in the Supporting Information (SI).

Batch experiments. Two types of sorption experiments were performed in batch reactors to assess the Hg isotope fractionation at different fractions of the total Hg sorbed to goethite. In the pH series, the sorbed fraction of Hg was varied by adjusting the suspension pH to values between 3.1 and 6, and in the mercury-to-goethite-ratio (MGR) series, the ratio between total Hg and goethite was varied at constant pH 7. Goethite (between 0.5 to 20 g L^{-1}, see Table 1) was added to acid-washed 30-mL Teflon centrifuge tubes and was dispersed by ultrasonication in 20 mL matrix solution. The experiments at pH 7 were performed in a buffer solution containing 2.5 mM 3-morpholino-propanesulfonic acid (MOPS), whereas pH-series were unbuffered. Experiments were conducted in the absence and presence of chloride and sulfate, respectively, which influences the speciation of Hg(II) in solution and on the surface.[41,45] For chloride-bearing experiments, the solution matrix contained 0.5 mM NaCl, for sulfate-bearing experiments, 0.95 M Na_2SO_4 was added, as listed in Table 1. The pH was adjusted by titration with diluted HNO_3 or NaOH. Aliquots of a Hg(II)-nitrate stock solution were then added to the goethite suspension to yield an initial Hg concentration of 5 to 25 µM and equilibrated during 18 h, 72 h, or 720 h on an end-over-end shaker at room temperature in the dark. To separate the sorbed and dissolved pools, the equilibrated samples were centrifuged at 3000 rpm for 15 min. The supernatants were decanted and filtered through 0.2-µm Nylon filters to obtain the dissolved pool. The goethite, containing the sorbed Hg, was dissolved in 6 M HCl at 80°C. All samples were stabilized with 1 % BrCl (v/v) (0.2 M BrCl in $HCl_{conc.}$) and stored at 4°C prior to analysis.

Analytical methods. Hg concentrations were measured by cold vapor atomic fluorescence spectrometry (CV-AFS, Millennium Merlin, PS Analytical, U.K.). Samples were diluted to 2.5 to 25 nM for concentration measurements. Standards prepared in triplicate reproduced with ±3.6 % (2σ), which is reported as the uncertainty of the concentration measurements. Hg isotope ratios were measured by cold

vapor generation (HGX-200, Cetac, Omaha, U.S.) coupled to a multicollector inductively-coupled plasma mass spectrometer (MC-ICPMS, Nu instruments; Wrexham, U.K.). In addition to standard bracketing, mass bias was corrected by Tl addition using a desolvating nebulizer. This method was previously described in detail[23] and further information is provided in the SI. All isotope ratios of samples and secondary standards were measured relative to NIST-3133, which was used as bracketing standard. We report Hg isotope data following the nomenclature suggested by Blum and Bergquist,[46] adapted to recent recommendations of IUPAC:[47]

$$\delta^{202}\mathrm{Hg}_{\mathrm{NIST-3133}} = \frac{(^{202}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{Sample}}}{(^{202}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{NIST-3133}}} - 1 \quad (1)$$

$$\Delta^{199}\mathrm{Hg} = \delta^{199}\mathrm{Hg} - (\delta^{202}\mathrm{Hg} \times 0.2520) \quad (2)$$

The mass-independent fractionation, expressed here as Δ^{199}Hg, represents the deviation of the isotope ratio from the mass dependent fractionation line, where 0.2520 was used as the kinetic mass dependent scaling factor for δ^{199}Hg, calculated in analogous manner to δ^{202}Hg based on ^{199}Hg/^{198}Hg. Please note that the use of the equilibrium mass dependent scaling factor (0.2539) would not alter our results in a significant manner and we decided to use the kinetic factor for reasons of consistency with the nomenclature used in field studies.[46] Our in-house standard (ETH Fluka) was regularly measured between samples and reproduced at $\delta^{202}Hg_{NIST-3133}$= -1.38 ±0.09 ‰, Δ^{199}Hg = +0.08 ±0.03 ‰ (2σ, n=16). For the UM-Almadèn standard (provided by Joel Blum, University of Michigan), we obtained isotope ratios of $\delta^{202}Hg_{NIST-3133}$= -0.55 ±0.02 ‰, Δ^{199}Hg = -0.02 ±0.05 ‰ (2σ, n=4), which is in excellent agreement with published values ($\delta^{202}Hg_{NIST-3133}$ = -0.54 ±0.08 ‰, Δ^{199}Hg = -0.01 ±0.05 ‰ (2σ, n=4)).[12] Multiple measurements of the Hg(II)-nitrate salt used in the sorption experiments resulted in values of $\delta^{202}Hg_{NIST-3133}$ = -0.69 ± 0.09 ‰ and Δ^{199}Hg = +0.01 ± 0.03 ‰ (2σ, n=4). The ETH Fluka in-house standard and Hg(II)-nitrate salt both reproduced with ±0.09 ‰ (2σ) for δ^{202}Hg and ±0.03 ‰ (2σ) for Δ^{199}Hg, which is considered to be the analytical precision for all reported measurements. To simplify further data analysis and presentation, Hg isotope ratios of all experimental data are in the

following reported relative to the composition of the Hg(II)-nitrate salt used in all experiments, representing the starting condition:

$$\delta^{202}\mathrm{Hg} = \delta^{202}\mathrm{Hg}^{\mathrm{sample}}_{\mathrm{NIST-3133}} - \delta^{202}\mathrm{Hg}^{\mathrm{Hg(II)-nitrate\ salt}}_{\mathrm{NIST-3133}} \quad (3)$$

The fractionation of Hg isotopes on the goethite surface relative to the solution is expressed as enrichment factor **ε** for mass-dependent fractionation (MDF):

$$\varepsilon^{202}\mathrm{Hg}_{\mathrm{sorbed-dissolved}} = \delta^{202}\mathrm{Hg}_{\mathrm{sorbed}} - \delta^{202}\mathrm{Hg}_{\mathrm{dissolved}} \quad (4)$$

and as enrichment factor **E** for mass-independent fractionation (MIF):

$$\mathrm{E}^{199}\mathrm{Hg} = \varepsilon^{199}\mathrm{Hg} - (\varepsilon^{202}\mathrm{Hg} \times 0.2520) \quad (5)$$

Calculating the enrichment factors (ε^{202}Hg and E^{199}Hg) as difference of the isotope signature between the sorbed and the dissolved pool averaged over the number of batches in an experimental series (n = 3 to 5) allowed us to ensure mass balance criteria. The uncertainties of the enrichment factors, reported as one standard deviation σ, were calculated from the error propagation of the difference calculation based on the above reported analytical precision (±0.09 ‰ (2σ) for δ^{202}Hg and ±0.03 ‰ (2σ) for Δ^{199}Hg). All statistical tests were performed based on a 95 % confidence level. Further details on data analysis, mass balance criteria, error propagation, and statistical tests are provided in the SI.

Results and Discussion

Sorption of Hg to goethite. In accordance with previous studies,[38,39,48] the sorption of Hg(II) to goethite exhibited a strong pH-dependence characterized by a distinct increase of the sorbed fraction with increasing pH; for instance, from 15 % at pH 3.6 to 64 % at pH 5.3 (Figure S2, Table S4a). Addition of chloride resulted in a pronounced decrease in Hg sorption compared to the chloride-free series (Figures S2 and S3), which is due to the formation of stable Hg(II)-chloro complexes in solution.[45] The variation of the mercury-to-goethite ratio (MGR) at constant pH 7 resulted in Hg surface coverages between 0.025 and 0.30 μmol m^{-2}. In the MGR-sulfate series, Hg showed a slightly lower sorption affinity compared to the series in the absence of chloride and sulfate (Figure S3). Comparing the experiments with different equilibration times (18 h, 72 h, and 720 h), we observed an increase in the sorbed fraction

of about 10 to 17 % between 18 h and 720 h equilibration (Figure S4). Similar observations were previously reported for a time series from 2 h up to 8 weeks with an increase in the Hg fraction sorbed to goethite without any clear endpoint.[49] EXAFS spectroscopy on Hg(II) sorbed to goethite at a surface coverage (Γ) of 0.4 μmol m^{-2} provided no evidence for surface precipitation of Hg.[40,41] As the surface coverage in our experiments never exceeded 0.3 μmol m^{-2}, we conclude that surface precipitation is unlikely and Hg was sorbed as outer-sphere and/or inner-sphere complexes.

Stable Hg isotope fractionation. In all experiments, Hg sorbed to goethite was found to be enriched in light Hg isotopes. Figure 1a displays the δ^{202}Hg isotope signature as a function of the fraction of total Hg which was sorbed to goethite in the experimental series with no chloride and variable pH (pH series; Table 1) and for an experimental series with varying mercury-to-goethite-ratio (MGR-72h series). Both data sets exhibited an increase of δ^{202}Hg in the dissolved phase with increasing fraction of sorbed Hg. The sorbed pool was correspondingly enriched in light Hg isotopes, as indicated by negative δ^{202}Hg values. The δ^{202}Hg signatures of the sorbed and dissolved Hg pools in the presence of 0.5 mM chloride followed the same trends (Figure 1b). The enrichment factors ε^{202}Hg, calculated from the difference between the sorbed and dissolved δ^{202}Hg averaged over the number of batches in one experimental series (n = 3 to 5), fell in a narrow range between -0.30 ±0.04 ‰ and -0.44 ±0.04 ‰ (Table 1). A statistical test comparing the determined enrichment factors (ε^{202}Hg, see SI) of the MGR-72h series in the absence of chloride and the MGR-Cl series with 0.5 mM Cl^- revealed no significant differences. Furthermore, the isotopic results of the two approaches used to vary the fraction of sorbed Hg (pH and MGR series) were not significantly different from each other, both in the absence of chloride and with 0.5 mM Cl^-. Figure 2 shows the comparison between the experimental series with 0.95 M sulfate (MGR-sulfate) and with no sulfate (MGR-72h). The enrichment factors for the MGR-sulfate and for the MGR-72h series (see Table 1) were not significantly different from each other. Figure 3 shows a time series of Hg(II) sorption to goethite with equilibration times of 18 h, 72 h, and 720 h. Even though there was a significant increase in the fraction of sorbed Hg with time (Figure S4), the comparison of the time series revealed no statistically significant difference between their enrichment factors (ε^{202}Hg).

Therefore, although the adsorption of Hg was continuing, we observed no dependence of the Hg isotope fractionation on equilibration time. The comparison of two alternative model approaches did not yield conclusive results concerning the reversibility of the sorption process (see SI). None of the experimental series showed mass independent fractionation expressed by $E^{199}Hg$ being significantly different from zero (Figure 4b, Table 1, Table S2).

Table 1. Parameters of the experimental series: Number of batches in experimental series (n), amount of goethite (g L^{-1}), initial Hg concentration (Hg) in µM, pH, solution matrix with MOPS (2.5 mM), SO_4^{2-} (0.95 M) and Cl^- (0.5 mM), equilibration time (t_{eq}) in h, expected dominating Hg(II) surface complex with *b* for bidentate and *m* for monodentate, and isotopic enrichment factors of stable Hg isotopes on the goethite surface relative to the solution for mass-dependent fractionation ($\varepsilon^{202}Hg$) and mass-independent fractionation ($E^{199}Hg$) with 1σ uncertainties (see SI for details). Each experimental series was performed with different fractions of total Hg sorbed, which was varied by different mercury-to-goethite-ratio (MGR series) or by different pH (pH series).

series	n	goethite (g L^{-1})	Hg (µM)	pH	solution matrix	t_{eq} (h)	Hg(II) surface complex	$\varepsilon^{202}Hg$ (‰)	σ (‰)	$E^{199}Hg$ (‰)	σ (‰)
pH	5	5	5	3.1 - 6	-	72	$b^{50,40}$	-0.37	0.03	0.03	0.011
MGR-18h	4	0.5 - 20	25	7	MOPS	18	$b^{50,40}$	-0.36	0.03	-0.02	0.013
MGR-72h	4	0.5 - 20	25	7	MOPS	72	$b^{50,40}$	-0.32	0.03	-0.02	0.013
MGR-720h	3	0.5 - 9	25	7	MOPS	720	$b^{50,40}$	-0.42	0.04	-0.03	0.015
MGR-sulfate	3	0.5 - 9	25	7	MOPS, SO_4^{2-}	72	m^{41}	-0.30	0.04	0.01	0.015
pH-Cl	3	5	5	5 - 6	Cl^-	72	m^{41}	-0.32	0.04	0.00	0.015
MGR-Cl	3	0.5 - 9	10	7	MOPS, Cl^-	72	m^{41}	-0.44	0.04	-0.03	0.015

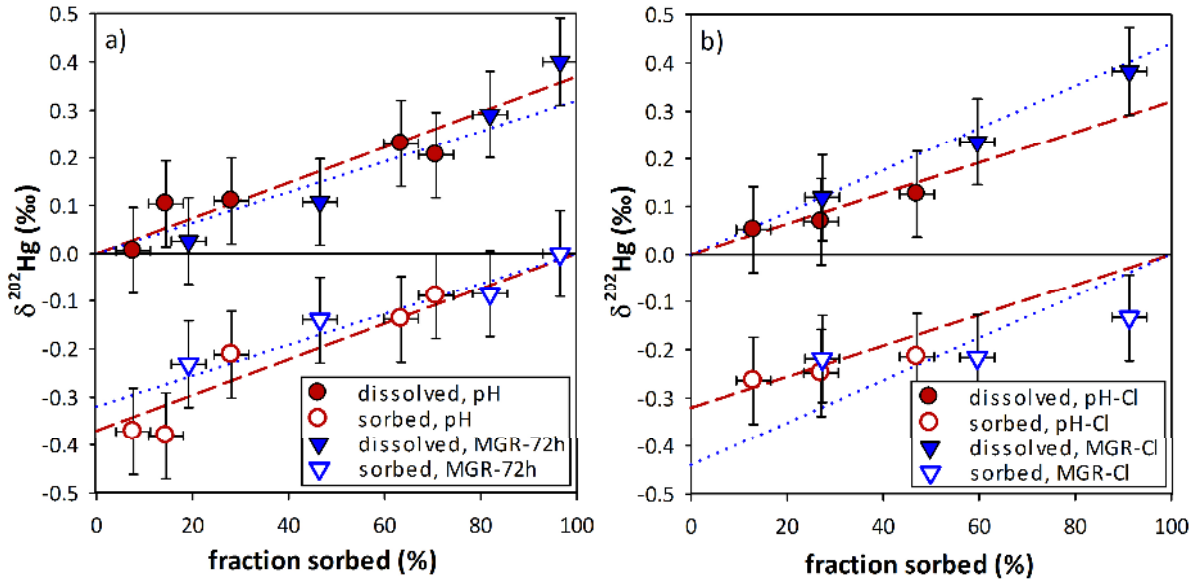


Figure 1. δ^{202}Hg of sorbed (open symbols) and dissolved (closed symbols) pool as a function of the Hg-fraction sorbed (in %). Experiments in the absence of chloride (a) and with 0.5 mM chloride (b) performed with 72 h equilibration time. The sorbed fraction was varied by changing the pH (pH and pH-Cl series) and by changing the mercury-to-goethite ratio (MGR-72h and MGR-Cl series). The equilibrium fractionation lines, derived from the calculated enrichment factors (see Table 1), are shown as dotted lines for the MGR series and dashed lines for the pH series.

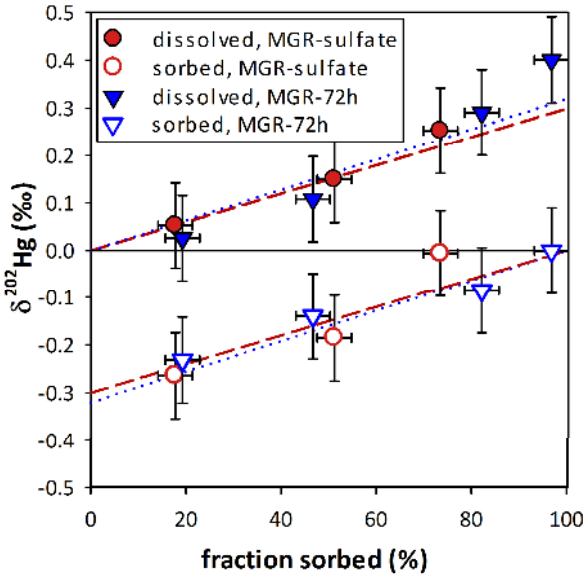


Figure 2. δ^{202}Hg of sorbed (open symbols) and dissolved (closed symbols) pool as function of fraction sorbed (in %). Experiments were performed with 0.95 M sulfate (circles, MGR-sulfate series) and in the absence of sulfate (triangles, MGR-72h series). The equilibrium fractionation lines, derived from the calculated enrichment factors, are shown as dashed lines for the MGR-sulfate series and dotted lines for the MGR-72h series without sulfate (see Table 1).

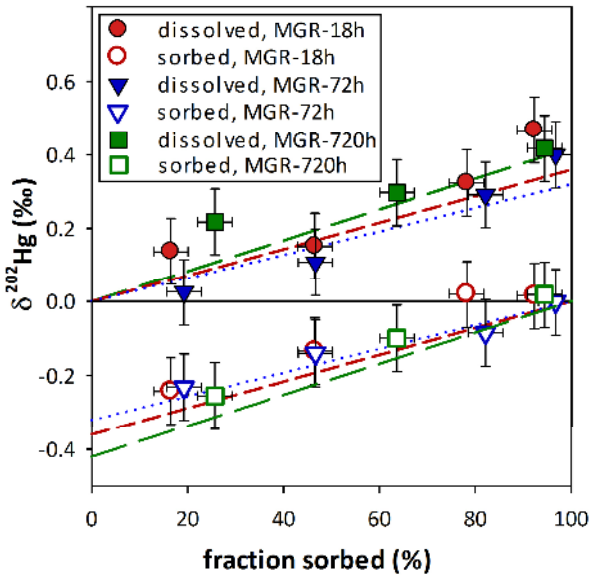


Figure 3. Hg isotope fractionation during sorption of Hg(II) to goethite as a function of equilibration time (18 h, 72 h, and 720 h, see Table 1). δ^{202}Hg of sorbed (open symbols) and dissolved (closed symbols) pool as function of fraction sorbed (in %). The equilibrium fractionation lines, derived from the calculated enrichment factors, are shown as short-dashed line for the MGR-18h series, as dotted lines for the MGR-72h series, and as long-dashed lined for the MGR-720h series (see Table 1).

Possible Hg isotope fractionation mechanisms. Previous studies identified the cationic Hg(II) species ($HgOH^+$ and $HgCl^+$) as the sorption active solution species as discussed further below.[39,51] Following this, the sorption of Hg(II) to a mineral surface, in this case goethite (α-FeOOH), can be described by the following reaction steps, which all might be potentially associated with an isotopic enrichment (IE):

$$HgL_n \overset{IE_{SE}}{\longleftrightarrow} HgL^+_{n-1} + L^- \quad (6)$$

$$HgL^+_{n-1} + \equiv FeOH \overset{IE_{OS}}{\longleftrightarrow} \equiv FeOH{-}HgL^+_{OS} \overset{IE_{IS}}{\longleftrightarrow} \equiv FeO{-}Hg_{IS} + H^+ \quad (7)$$

Neutral dissolved Hg(II) species (HgL_n) dissociate to the cationic Hg(II) species (HgL^+_{n-1}) and the ligand (L^-, in our experiments OH^- or Cl^-). This species equilibration (SE) in solution might be associated with an equilibrium isotope effect (IE_{SE}). The sorption active Hg(II) cationic species (HgL^+_{n-1}) adsorbs to the goethite surface to form an outer-sphere complex ($\equiv FeOH{-}HgL^+_{OS}$) followed by the dehydration of the outer-sphere complex and a deprotonation of the goethite surface hydroxyl

group to form an inner-sphere complex ($\equiv FeO-Hg_{IS}$). The conformation change between the bonding environment of the Hg(II) cation in solution and the outer-sphere complex could potentially cause an isotopic enrichment (IE_{OS}), as well as the conformation change between the outer-sphere complex and the inner-sphere complex during dehydration (IE_{IS}).

Isotope fractionation during species equilibration in solution (IE_{SE}). Species equilibration under the experimental conditions presented here usually involves hydroxide as ligand and can be therefore denoted for the most part as hydrolysis, with the exception of the dissociation of $HgCl_2$, where chloride is the leaving ligand. Based on the observed strong correlation between metal's first hydrolysis constant and the surface complexation constant for metal sorption to mineral surfaces, the concept of hydrolysis as first reaction step in the adsorption of Hg(II) to goethite was established.[52] Following this, the adsorption of Hg(II) to mineral phases was successfully modeled by the solution concentration of $HgOH^+$ and $HgCl^+$ in the absence and presence of chloride, respectively, which were considered as the sorption active species.[39,51] Based on calculations performed using Visual MINTEQ[53] (database NIST 46.7), in the absence of Cl^- and at pH 7, $HgOH^+$ occurs with an abundance of 0.06 % and all the remaining Hg is present as $Hg(OH)_2$. With 0.5 mM Cl^- at pH 7, $HgCl^+$ is present with 0.006 % and the main solution species are $HgClOH^0$ (49.6 %), $Hg(OH)_2^0$ (37.0 %), and $HgCl_2^0$ (13.4 %). It is important to consider that after the removal of cationic species from solution by adsorption to surfaces, a re-equilibration takes place which replenishes the small stock of cationic species by dissociation of the dominant neutral Hg(II) species, which is very fast with a dehydration rate constant (k_w) for Hg(II) of 9.3×10^{10} s^{-1}.[54] Thus, the small pool size of the cationic Hg(II) species in solution does not preclude that adsorption of larger amounts of Hg(II) to surfaces can proceed via the positively charged species which exhibit a higher affinity for surface binding. Based on this fast equilibration between cationic and neutral Hg species, an equilibrium isotope effect between those species can be transferred to the goethite surface as the low abundance cations interact dominantly with the mineral surface.

Calculated predictions of MDF and NVF. We calculated the isotopic enrichment factor of cationic species relevant in our experiments based on theoretical equilibrium isotope fractionation factors for

individual Hg species relative to elemental Hg vapor (calculated in gas phase) published by Wiederhold et al.[23] The equilibrium enrichment factors consist of a mass-dependent fractionation (MDF) component based on density functional theory and a nuclear volume fractionation (NVF) component based on relativistic Dirac-Coulomb calculations following the work of Schauble.[10] The sum of the MDF and NVF component resulted in the predicted isotopic enrichment factor for each Hg species (MDF + NVF). Based on the assumption that $1000\ln\beta^{202\text{-}198} \approx \varepsilon^{202}\mathrm{Hg}$, the enrichment factor of the cationic species $\varepsilon^{202}\mathrm{Hg_{cat}}$ ($HgOH^+$ or $HgCl^+$) was calculated from the difference between the $1000\ln\beta_{\mathrm{cat}}^{202-198}$ of the cationic species and the average of the $1000\ln\beta_{\mathrm{n_i}}^{202-198}$ of the neutral species n_i, where $f_{\mathrm{n_i}}$ is their relative abundance.

$$\varepsilon^{202}\mathrm{Hg_{cat}} = 1000\ln\beta_{\mathrm{cat}}^{202-198} - \sum_i (f_{\mathrm{n_i}} \times 1000\ln\beta_{\mathrm{n_i}}^{202-198}) \quad (8)$$

NVF is related to the nuclear charge radii of the Hg isotopes which do not scale linearly with mass, therefore, NVF is associated with mass independent fractionation (MIF). The expected mass independent enrichment in $E^{199}Hg$ is calculated from the cationic enrichment factor of the nuclear volume component ($\varepsilon^{202}\mathrm{Hg_{NVF}}$) using the scaling factors of $^{199/198}Hg$ relative to $^{202/198}Hg$,[23] where SF_{MDF} is the kinetic mass dependent scaling factor of 0.252 and SF_{NVF} is the nuclear volume scaling factor of 0.0525 using nuclear charge radii from Landolt-Boernstein:[55]

$$\mathrm{E^{199}Hg} = (\varepsilon^{202}\mathrm{Hg_{NVF}} \times \mathrm{SF_{NVF}}) - (\varepsilon^{202}\mathrm{Hg_{NVF}} \times \mathrm{SF_{MDF}}) \quad (9)$$

Figure 4a shows the calculated Hg isotope enrichment factor of the cationic species $HgOH^+$ and $HgCl^+$ relative to the main solution species for the experimental series at pH 7. The 95 % confidence interval for all experimental series at pH 7 in the absence of chloride overlapped with the calculated enrichment factor (MDF+NVF) for $HgOH^+$ ($\varepsilon^{202}Hg$ = -0.37 ‰). The calculated enrichment factor for $HgCl^+$ ($\varepsilon^{202}Hg$ = -0.28 ‰), although not within the 95 % confidence interval of the chloride experiment (-0.36 ‰ to -0.52 ‰), was still in reasonable agreement with the experimental series. The NVF component of the calculations predicts a MIF of -0.08 ‰ in $E^{199}Hg$ both for the $HgOH^+$ and the $HgCl^+$ experiments, as illustrated by the NVF values in Figure 4b. However, none of the experimental series

showed any mass independent fractionation expressed by $E^{199}Hg$ being statistically different from zero (Figure 4b, Table 1, Table S2). This discrepancy between the experimental findings and the theoretical calculations for the Hg species is not yet fully understood. We can only speculate that there might be a certain overestimation of the NVF component or the resulting extent of MIF in the calculations. Errors on the species calculations might result from uncertainties of input parameters (nuclear charge radii), the neglected influence of solvation effects, or the adequacy of the model; a quantification of these errors however was not feasible (see SI of Wiederhold et al.[23] for detailed discussion on errors). The species calculations for lower pH are not shown here, but they were in qualitative agreement with the results at pH 7, although there are large uncertainties due to a lack of calculated $1000\ln\beta^{202-198}$ values for some species present at lower pH (e.g., Hg^{2+}).

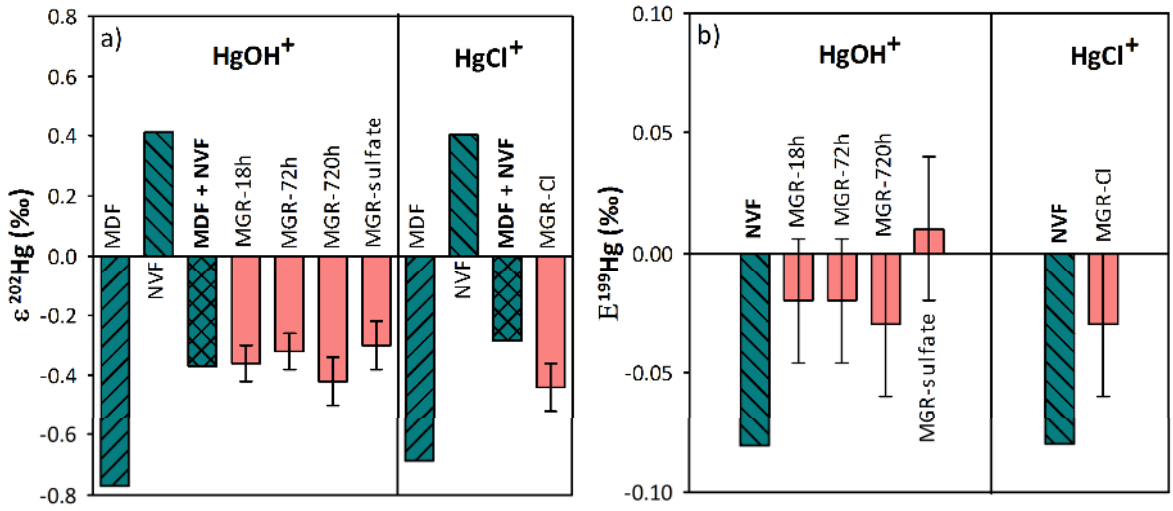


Figure 4. Calculated isotopic enrichment factors ($\varepsilon^{202}Hg$ and $E^{199}Hg$) of cationic Hg species relative to the dominant solution species at pH 7 are plotted as hatched bars.[23] In the absence of chloride the isotopic fractionation was calculated for $HgOH^+$, in the presence of chloride for $HgCl^+$. The calculations include two components from mass-dependent fractionation (MDF) and nuclear volume fractionation (NVF). The sum of these results is the expected net effect (MDF+NVF). Plain bars represent experimental enrichment factors (a: $\varepsilon^{202}Hg$ for MDF, b: $E^{199}Hg$ for MIF, Table 1) of the Hg pool sorbed to goethite relative to dissolved Hg.

Isotope fractionation during surface complex formation (IE_{OS}, IE_{IS}). As mentioned above, the change in conformation between the dissolved Hg species and the sorption complexes (outer-sphere and inner-sphere complex) could cause isotope fractionation as proposed in the example of Mo and U.[32,33] There are no calculations of enrichment factors for surface bound Hg species available and an assessment of potentially different Hg isotope signatures of outer-sphere and inner-sphere complexes was not possible, as only total sorbed Hg was measured. However, previous studies have identified different types of inner-sphere surface complexes for different experimental conditions presented here. Hg(II) sorbed to goethite forms bidentate inner-sphere complexes over the entire pH range investigated, as shown by extended X-ray absorption fine structure (EXAFS) spectroscopy.[40,50] High sulfate concentrations (~1 M) were found to trigger the formation of ternary monodentate complexes (≡Fe-O-Hg-SO_4),[41] whereas the solution speciation of Hg is not significantly altered by sulfate addition. Calculations with stability constants using Visual MINTEQ and literature data[45] predicted a >10^6 times lower abundance of $HgSO_4$ and $Hg(SO_4)_2^{2-}$ compared to the predominant $Hg(OH)_2$ species (over 99.99 % at pH 7), which was in agreement with previous calculations.[41] There was no statistical difference between Hg isotope fractionation of Hg(II) sorption to goethite in systems expected to form bidentate surface complexes (MGR-72h series, Figure 2) and monodentate complexes (MGR-sulfate series, Figure 2), which indicates that the conformation of inner-sphere complexes (IE_{IS}) does not significantly influence the Hg isotope fractionation. This finding is supported by the experiments in the presence of chloride, as the Hg isotope enrichment did not significantly vary compared with the absence of Cl^-, although a change in surface complexation towards ternary monodentate inner-sphere complexes (≡Fe-O-Hg-Cl) was expected based on previous studies.[41,56]

Control of Hg isotope fractionation. The measured isotopic enrichment between the sorbed and dissolved pool can be expressed as a function of the isotopic enrichment of the cationic species during equilibration in solution ($\varepsilon^{202}Hg_{SE}$) and the isotopic enrichment during sorption of the cationic species ($\varepsilon^{202}Hg_{sorption}$) (derivation shown in SI):

$$\varepsilon^{202}\mathrm{Hg}_{\mathrm{sorbed-dissolved}} = \varepsilon^{202}\mathrm{Hg}_{\mathrm{sorption}} + (1 - \mathrm{f}_{\mathrm{cat}}) \times \varepsilon^{202}\mathrm{Hg}_{\mathrm{SE}} \quad (10)$$

The scaling term representing the relative fraction of cationic species (1-f_{cat}) was close to one in both experimental series (MGR-72h and MGR-Cl) as the cationic species occurred at very low abundances at pH 7 ($f_{cat(HgOH^+)}$ = 0.06 %, $f_{cat(HgCl^+)}$ = 0.006 %). As shown in Figure 4, the observed isotope fractionation between the sorbed and dissolved Hg-pool ($\varepsilon^{202}\mathrm{Hg}_{\mathrm{sorbed-dissolved}}$) is in good agreement with the predicted isotope enrichment of the cationic species during species equilibration ($\varepsilon^{202}\mathrm{Hg}_{\mathrm{SE}}$). Therefore, we conclude that the isotope fractionation of Hg(II) sorption ($\varepsilon^{202}\mathrm{Hg}_{\mathrm{sorbed-dissolved}}$) is controlled by an equilibrium isotope effect between Hg(II) solution species, expressed on the goethite surface by the adsorption of the cationic solution species. The isotopic fractionation during sorption of the cationic species ($\varepsilon^{202}\mathrm{Hg}_{\mathrm{sorption}}$), consisting of possible effects during conformation change between the cationic solution species and the outer-sphere complex (IE_{OS}) as well as during the dehydration of the outer-sphere complex to form an inner-sphere complex (IE_{IS}), appear to have an insignificant contribution. This is supported by the fact that the isotopic enrichment factors for experimental conditions forming monodentate inner-sphere complexes (MGR-sulfate and MGR-Cl series) were statistically indistinguishable from experiments forming bidentate complexes (e.g., MGR-72 h series). In addition, the finding that the observed isotope effect was insensitive to equilibration time provided further evidence that the different reaction steps at the mineral surface, some of which are expected to exhibit much slower kinetics compared with species equilibration in solution and thus explaining why the sorption had not yet reached a maximum, did not exert an important influence of the Hg isotope distribution in our system. Figure 5 shows the proposed schematic overview of the reaction steps involved in the sorption of Hg(II) to goethite and their associated Hg isotope enrichment factors for the example of $HgOH^+$ sorption.

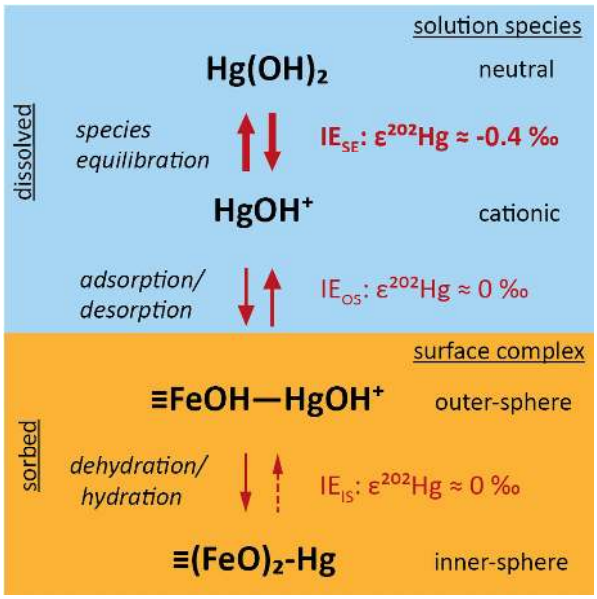


Figure 5. Proposed reaction scheme controlling Hg isotope fractionation of Hg(II) sorption to goethite. The equilibrium isotope effect between Hg(II) solution species is transferred to the goethite surface through the sorption active cationic species which are isotopically lighter than the neutral solution species. Subsequent conformation changes between dissolved species and outer-sphere complexes as well as during dehydration to form inner-sphere complexes appear to have an insignificant effect on the overall isotopic fractionation.

Implications for other metal isotope and surface complexation studies.

We think that the detailed mechanistic insights provided by this study will have implications for other metal isotope systems as well as for the general understanding of metal sorption processes to mineral surfaces. On the one hand, the postulated importance of equilibrium isotope fractionation during hydrolysis, or in more general terms equilibration of solution species which are involved to a different extent in sorption processes, may influence the isotope fractionation during sorption for other metals as well. Apart from Hg(II), the correlation between the metal's hydrolysis constant and the metal's surface complexation constant was shown for other metal cations (Ag^{+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}),[52,57] most of which possess several stable isotopes. Theoretical investigations of stable isotope fractionation between solution species were recently published for some metal isotope systems (e.g., Ni, Zn).[58,59,60] A comparison with experimental data for metal isotope fractionation during sorption to a mineral phase

could potentially help in further identifying the mechanisms causing metal isotope fractionation for these elements too and may provide further validation for the concept presented here. On the other hand, stable isotope fractionation during sorption of other metals could also be influenced to a larger extent by surface reactions depending on the relative importance of the factors and processes described in equation 10, which could be different compared with the specific example of Hg(II) presented here. In the context of surface complexation, this study demonstrates that stable isotope fractionation studies can offer new insights into reaction mechanisms at mineral surfaces and provide further evidence for existing surface complexation models.

Implications for stable Hg isotopes as environmental tracer. The observed MDF and the absence of MIF during sorption of Hg(II) to goethite have been shown to be constant over a range of pH, as well as chloride and sulfate concentrations which trigger the formation of different surface complexes. Although the experiments were performed at higher concentrations than generally found in the environment, the constant Hg isotope fractionation over a large range of surface coverages (between 0.002 and 0.3 μmol m^{-2}) allows the transfer of our results to environmental systems, as there is no indication of a concentration dependence of the determined enrichment factors. This lack of dependence upon concentration, chemical conditions, and equilibration time will facilitate the interpretation of natural Hg isotope fractionation in soils and sediments driven by sorption processes.

Previous field studies have reported systematic differences between Hg isotope compositions of different environmental compartments or Hg pools. For instance, a consistent offset of 0.60 ±0.16 ‰ between fish and sediment samples (δ^{202}Hg, corrected for photochemical effects deduced from MIF) was reported from the San Francisco Bay, USA[61] and water leachates were found to be enriched by 0.70 ± 0.13 ‰ in δ^{202}Hg compared with soil samples from a mining site in China.[62] We suggest, based on the results of this study as well as the previously published work on Hg(II)-thiol binding,[23] that sorption processes may be at least partially responsible for these observed systematic offsets and influence the isotope signature of natural Hg pools to a significant extent. Sorption of Hg(II) to goethite as well as sorption of Hg(II) to thiol groups,[23] studied as a model system for binding to natural organic matter,

revealed a very similar isotopic enrichment of light Hg isotopes onto the surfaces. Based on these laboratory studies we expect that light Hg isotopes are preferentially sequestered in soils and sediments with enrichment factors in a relatively narrow range of about -0.3 ‰ to -0.6 ‰ in δ^{202}Hg for both thiol-bound and mineral-bound Hg(II). As a consequence, the mobile phase, eventually leaching from soils and sediments, is expected to be correspondingly enriched in heavy Hg isotopes. Furthermore, the proposed enrichment of heavy Hg isotopes in the mobile Hg(II) pool should also be considered when dealing with Hg isotope fractionation during bioaccumulation, as the mobile fraction is bioavailable.

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Supporting Information

Experimental details, statistical tests, additional figures, and data tables. This material is available free of charge via the internet at http://pubs.acs.org.

References

(1) Selin, N. E., Global biogeochemical cycling of mercury: A review. *Annu. Rev. Environ. Resour.* **2009,** *34*, 43-63.

(2) Skyllberg, U.; Westin, M. B.; Meili, M.; Bjorn, E., Elevated concentrations of methyl mercury in streams after forest clear-cut: A consequence of mobilization from soil or new methylation? *Environ. Sci. Technol.* **2009,** *43*, (22), 8535-8541.

(3) Skyllberg, U., Chemical Speciation of Mercury in Soil and Sediment. In *Environmental Chemistry and Toxicology of Mercury*, Liu, G.; Cai, Y.; O'Driscoll, N. J., Eds. John Wiley & Sons, Inc.: 2011; pp 219-258.

(4) Gabriel, M. C.; Williamson, D. G., Principal biogeochemical factors affecting the speciation and transport of mercury through the terrestrial environment. *Environ. Geochem. Health* **2004,** *26*, (4), 421-434.

(5) Skyllberg, U., Mercury Biogeochemistry in Soils and Sediments. In *Synchrotron-based Techniques in Soils and Sediments*, Singh, B.; Gräfe, M., Eds. Elsevier B.V.: Netherlands, 2010; Developments in Soil Science; Vol. 34, pp 379-410.

(6) Kretzschmar, R.; Schäfer, T., Metal retention and transport on colloidal particles in the environment. *Elements* **2005,** *1*, (4), 205-210.

(7) Bergquist, B. A.; Blum, J. D., The odds and evens of mercury isotopes: applications of mass-dependent and mass-independent isotope fractionation. *Elements* **2009,** *5*, (6), 353-357.

(8) Blum, J. D., Applications of Stable Mercury Isotopes to Biogeochemistry. In *Handbook of Environmental Isotope Geochemistry*, Baskaran, M., Ed. Springer Berlin Heidelberg: 2011; Advances in Isotope Geochemistry; pp 229-245.

(9) Hintelmann, H.; Zheng, W., Tracking Geochemical Transformations and Transport of Mercury through Isotope Fractionation. In *Environmental Chemistry and Toxicology of Mercury*, Liu, G.; Cai, Y.; O'Driscoll, N. J., Eds. John Wiley & Sons, Inc.: 2011; pp 293-327.

(10) Schauble, E. A., Role of nuclear volume in driving equilibrium stable isotope fractionation of mercury, thallium, and other very heavy elements. *Geochim. Cosmochim. Acta* **2007,** *71*, (9), 2170-2189.

(11) Buchachenko, A. L., Mercury isotope effects in the environmental chemistry and biochemistry of mercury-containing compounds. *Russ. Chem. Rev.* **2009,** *78*, (4), 319-328.

(12) Bergquist, B. A.; Blum, J. D., Mass-dependent and -independent fractionation of Hg isotopes by photoreduction in aquatic systems. *Science* **2007,** *318*, (5849), 417-420.

(13) Zheng, W.; Hintelmann, H., Isotope fractionation of mercury during its photochemical reduction by low-molecular-weight organic compounds. *J. Phys. Chem. A* **2010,** *114*, (12), 4246-4253.

(14) Rodriguez-Gonzalez, P.; Epov, V. N.; Bridou, R.; Tessier, E.; Guyoneaud, R.; Monperrus, M.; Amouroux, D., Species-specific stable isotope fractionation of mercury during Hg(II) methylation by an anaerobic bacteria (Desulfobulbus propionicus) under dark conditions. *Environ. Sci. Technol.* **2009,** *43*, (24), 9183-9188.

(15) Malinovsky, D.; Vanhaecke, F., Mercury isotope fractionation during abiotic transmethylation reactions. *International Journal of Mass Spectrometry* **2011,** *307*, (1-3), 214-224.

(16) Zheng, W.; Hintelmann, H., Nuclear field shift effect in isotope fractionation of mercury during abiotic reduction in the absence of light. *J. Phys. Chem. A* **2010,** *114*, (12), 4238-4245.

(17) Kritee, K.; Blum, J. D.; Johnson, M. W.; Bergquist, B. A.; Barkay, T., Mercury stable isotope fractionation during reduction of Hg(II) to Hg(0) by mercury resistant microorganisms. *Environ. Sci. Technol.* **2007,** *41*, (6), 1889-1895.

(18) Malinovsky, D.; Latruwe, K.; Moens, L.; Vanhaecke, F., Experimental study of mass-independence of Hg isotope fractionation during photodecomposition of dissolved methylmercury. *J. Anal. At. Spectrom.* **2010,** *25*, (7), 950-956.

(19) Kritee, K.; Barkay, T.; Blum, J. D., Mass dependent stable isotope fractionation of mercury during mer mediated microbial degradation of monomethylmercury. *Geochim. Cosmochim. Acta* **2009,** *73*, (5), 1285-1296.

(20) Estrade, N.; Carignan, J.; Sonke, J. E.; Donard, O. F. X., Mercury isotope fractionation during liquid-vapor evaporation experiments. *Geochim. Cosmochim. Acta* **2009,** *73*, (10), 2693-2711.

(21) Ghosh, S.; Schauble, E. A.; Lacrampe Couloume, G.; Blum, J. D.; Bergquist, B. A., Estimation of nuclear volume dependent fractionation of mercury isotopes in equilibrium liquid–vapor evaporation experiments. *Chem. Geol.* **in press**, (doi:10.1016/j.chemgeo.2012.01.008).

(22) Zheng, W.; Foucher, D.; Hintelmann, H., Mercury isotope fractionation during volatilization of Hg(0) from solution into the gas phase. *J. Anal. At. Spectrom.* **2007,** *22*, (9), 1097-1104.

(23) Wiederhold, J. G.; Cramer, C. J.; Daniel, K.; Infante, I.; Bourdon, B.; Kretzschmar, R., Equilibrium mercury isotope fractionation between dissolved Hg(II) species and thiol-bound Hg. *Environ. Sci. Technol.* **2010,** *44*, (11), 4191-4197.

(24) Pokrovsky, O. S.; Viers, J.; Emnova, E. E.; Kompantseva, E. I.; Freydier, R., Copper isotope fractionation during its interaction with soil and aquatic microorganisms and metal oxy(hydr)oxides: Possible structural control. *Geochim. Cosmochim. Acta* **2008,** *72*, (7), 1742-1757.

(25) Balistrieri, L. S.; Borrok, D. M.; Wanty, R. B.; Ridley, W. I., Fractionation of Cu and Zn isotopes during adsorption onto amorphous Fe(III) oxyhydroxide: Experimental mixing of acid rock drainage and ambient river water. *Geochim. Cosmochim. Acta* **2008,** *72*, (2), 311-328.

(26) Juillot, F.; Marechal, C.; Ponthieu, M.; Cacaly, S.; Morin, G.; Benedetti, M.; Hazemann, J. L.; Proux, O.; Guyot, F., Zn isotopic fractionation caused by sorption on goethite and 2-lines ferrihydrite. *Geochim. Cosmochim. Acta* **2008,** *72*, (19), 4886-4900.

(27) Mikutta, C.; Wiederhold, J. G.; Cirpka, O. A.; Hofstetter, T. B.; Bourdon, B.; Von Gunten, U., Iron isotope fractionation and atom exchange during sorption of ferrous iron to mineral surfaces. *Geochim. Cosmochim. Acta* **2009,** *73*, (7), 1795-1812.

(28) Beard, B. L.; Handler, R. M.; Scherer, M. M.; Wu, L. L.; Czaja, A. D.; Heimann, A.; Johnson, C. M., Iron isotope fractionation between aqueous ferrous iron and goethite. *Earth Planet. Sci. Lett.* **2010,** *295*, (1-2), 241-250.

(29) Schauble, E. A.; Meheut, M.; Hill, P. S., Combining metal stable isotope fractionation theory with experiments. *Elements* **2009,** *5*, (6), 369-374.

(30) Pokrovsky, O. S.; Viers, J.; Freydier, R., Zinc stable isotope fractionation during its adsorption on oxides and hydroxides. *J. Colloid Interface Sci.* **2005,** *291*, (1), 192-200.

(31) Wasylenki, L. E.; Montanez, G.; Anbar, A. D. *Cd isotope fractionation during adsorption varies with salinity* AGU, 90(52), Fall Meet. Suppl., San Francisco, 2009; Eos Trans.: San Francisco, 2009.

(32) Barling, J.; Anbar, A. D., Molybdenum isotope fractionation during adsorption by manganese oxides. *Earth Planet. Sci. Lett.* **2004,** *217*, (3-4), 315-329.

(33) Brennecka, G. A.; Wasylenki, L. E.; Bargar, J. R.; Weyer, S.; Anbar, A. D., Uranium isotope fractionation during adsorption to Mn-oxyhydroxides. *Environ. Sci. Technol.* **2011,** *45*, (4), 1370-1375.

(34) Siebert, C.; Nagler, T. F.; von Blanckenburg, F.; Kramers, J. D., Molybdenum isotope records as a potential new proxy for paleoceanography. *Earth Planet. Sci. Lett.* **2003,** *211*, (1-2), 159-171.

(35) Weeks, C. L.; Anbar, A. D.; Wasylenki, L. E.; Spiro, T. G., Density functional theory analysis of molybdenum isotope fractionation. *J. Phys. Chem. A* **2007,** *111*, (49), 12434-8.

(36) Wasylenki, L. E.; Weeks, C. L.; Bargar, J. R.; Spiro, T. G.; Hein, J. R.; Anbar, A. D., The molecular mechanism of Mo isotope fractionation during adsorption to birnessite. *Geochim. Cosmochim. Acta* **2011,** *75*, (17), 5019-5031.

(37) Cornell, R. M.; Schwertmann, U., Soils. In *The Iron Oxides*, Wiley-VCH Verlag GmbH & Co. KGaA: 2004; pp 433-474.

(38) Forbes, E. A.; Posner, A. M.; Quirk, J. P., Specific adsorption of inorganic Hg(II) apecies and Co(II) complex ions on goethite. *J. Colloid Interface Sci.* **1974,** *49*, (3), 403-409.

(39) Barrow, N. J.; Cox, V. C., The effects of pH and chloride concentration on mercury sorption. I. By goethite. *J. Soil Sci.* **1992,** *43*, (2), 295-304.

(40) Kim, C. S.; Rytuba, J. J.; Brown, G. E., Jr., EXAFS study of mercury(II) sorption to Fe- and Al-(hydr)oxides I. Effects of pH. *J. Colloid Interface Sci.* **2004,** *271*, (1), 1-15.

(41) Kim, C. S.; Rytuba, J.; Brown, G. E., Jr., EXAFS study of mercury(II) sorption to Fe- and Al-(hydr)oxides - II. Effects of chloride and sulfate. *J. Colloid Interface Sci.* **2004,** *270*, (1), 9-20.

(42) Schwertmann, U.; Cornell, R. M., *Iron Oxides in the Laboratory - Preparation and Characterisation*. Wiley-VCH: Weinheim, 2000; Vol. second edition.

(43) Reichard, P. U.; Kraemer, S. M.; Frazier, S. W.; Kretzschmar, R., Goethite dissolution in the presence of phytosiderophores: Rates, mechanisms, and the synergistic effect of oxalate. *Plant Soil* **2005,** *276*, (1-2), 115-132.

(44) Wiederhold, J. G.; Kraemer, S. M.; Teutsch, N.; Borer, P. M.; Halliday, A. N.; Kretzschmar, R., Iron isotope fractionation during proton-promoted, ligand-controlled, and reductive dissolution of goethite. *Environ. Sci. Technol.* **2006,** *40*, (12), 3787-3793.

(45) Powell, K. J.; Brown, P. L.; Byrne, R. H.; Gajda, T.; Hefter, G.; Sjoberg, S.; Wanner, H., Chemical speciation of Hg(II) with environmental inorganic ligands. *Aust. J. Chem.* **2004,** *57*, (10), 993-1000.

(46) Blum, J.; Bergquist, B., Reporting of variations in the natural isotopic composition of mercury. *Anal. Bioanal. Chem.* **2007,** *388*, (2), 353-359.

(47) Coplen, T. B., Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. *Rapid Commun. Mass Spectrom.* **2011,** *25*, (17), 2538-2560.

(48) Mathur, S. S.; Dzombak, D. A., Chapter 16 Surface complexation modeling: goethite. In *Interface Science and Technology*, Lützenkirchen, J., Ed. Elsevier: 2006; Vol. Volume 11, pp 443-468.

(49) Fischer, L.; Brümmer, G. W.; Barrow, N. J., Observations and modelling of the reactions of 10 metals with goethite: adsorption and diffusion processes. *Eur. J. Soil Sci.* **2007,** *58*, (6), 1304-1315.

(50) Collins, C. R.; Sherman, D. M.; Ragnarsdottir, K. V., Surface complexation of Hg^{2+} on goethite: Mechanism from EXAFS spectroscopy and density functional calculations. *J. Colloid Interface Sci.* **1999,** *219*, (2), 345-350.

(51) Sarkar, D.; Essington, M. E.; Misra, K. C., Adsorption of mercury(II) by variable charge surfaces of quartz and gibbsite. *Soil Sci. Soc. Am. J.* **1999,** *63*, (6), 1626-1636.

(52) Dzombak, D. A.; Morel, F. M., *Surface complexation modeling: hydrous ferric oxide*. Wiley: New York, 1990.

(53) Gustafsson, J. P. *Visual MINTEQ 3.0*, KTH (Royal Institute of Technology): Sweden, 2011.

(54) Wilkins, R. G., *Kinetics and Mechanism of Reactions of Transition Metal Complexes*. 2nd ed.; Wiley-VCH Verlag 2003.

(55) Fricke, G.; Heilig, K., 80-Hg Mercury. In *Landolt-Boernstein. Numerical Data and Functional Relationships in Science and Technology. Group 1. Elementary Particles, Nuclei and Atoms*, Springer: Heidelberg, 2004; Vol. 20.

(56) Gunneriusson, L.; Sjöberg, S., Surface complexation in the H^+-goethite ([alpha]-FeOOH)-Hg (II)-chloride system. *J. Colloid Interface Sci.* **1993,** *156*, (1), 121-128.

(57) Barrow, N. J.; Gerth, J.; Brümmer, G. W., Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. II Modelling the extent and rate of reaction. *J. Soil Sci.* **1989,** *40*, (2), 437-450.

(58) Fujii, T.; Moynier, F.; Dauphas, N.; Abe, M., Theoretical and experimental investigation of nickel isotopic fractionation in species relevant to modern and ancient oceans. *Geochim. Cosmochim. Acta* **2011,** *75*, (2), 469-482.

(59) Black, J. R.; Kavner, A.; Schauble, E. A., Calculation of equilibrium stable isotope partition function ratios for aqueous zinc complexes and metallic zinc. *Geochim. Cosmochim. Acta* **2011,** *75*, (3), 769-783.

(60) Fujii, T.; Moynier, F.; Telouk, P.; Abe, M., Experimental and theoretical investigation of isotope fractionation of zinc between aqua, chloro, and macrocyclic complexes. *J. Phys. Chem. A* **2010,** *114*, (7), 2543-2552.

(61) Gehrke, G. E.; Blum, J. D.; Slotton, D. G.; Greenfield, B. K., Mercury isotopes link mercury in San Francisco bay forage fish to surface sediments. *Environ. Sci. Technol.* **2011,** *45*, (4), 1264-1270.

(62) Yin, R.; Feng, X.; Wang, J.; Bao, Z.; Yu, B.; Chen, J., Mercury isotope variations between bioavailable mercury fractions and total mercury in mercury contaminated soil in Wanshan Mercury Mine, SW China. *Chem. Geol.* **in press** (doi: 10.1016/j.chemgeo.2012.04.017).