Copper isotope fractionation during adsorption onto kaolinite: Experimental approach and applications

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A R T I C L E   I N F O

A B S T R A C T

The adsorption of copper and other heavy metals onto clay minerals is an important process that controls the distribution of trace metals in natural environments. Copper isotopes are a potentially useful tool to track the source of contaminated metals in soils formed in natural systems, but Cu isotope fractionation during adsorption onto clay minerals, the major component in soils, has not been thoroughly studied. In this study, we carried out for the first time a series of experiments to investigate the isotope fractionation of Cu during adsorption onto kaolinite for a wide range of conditions, including the contact time (t = 10–360 min), temperature (T = 1–50 °C), initial Cu concentration of the starting solution (C_0 = 2–100 µg/g), pH value (4.0–6.0) and ionic strength ($NaNO_3$; I = 0–0.1 mol/L). Our results indicate that Cu isotopes are significantly fractionated with preferential adsorption of the light isotope (^{63}Cu) onto the mineral surface. The fractionation factors ($\Delta^{65}Cu_{adsorbed-solution} = \delta_{65}Cu_{adsorbed} - \delta^{65}Cu_{solution}$) weakly depend on the pH and temperature with a constant value of approximately −0.27‰ at C_0 = 20 µg/g and in the absence of $NaNO_3$. Addition of $NaNO_3$ into the starting solution has a dramatic negative influence on the $\Delta^{65}Cu_{adsorbed-solution}$ values that range from −1.46‰ to −0.29‰. Such results are useful for interpreting Cu isotopic variations observed in sediments, soils and water from estuarine settings or industrial sewage pollution areas. The $\Delta^{65}Cu_{adsorbed-solution}$ values significantly increase with increasing initial Cu concentration of the starting solutions at C_0 < 30 µg/g, but approach a stable value of −0.17 ± 0.10‰ (2SD) when the kaolinite has reached its maximum adsorption capacity at C_0 > 30 µg/g. The results imply that the isotopic compositions of the Cu adsorbed onto natural soils may vary greatly at relatively low Cu concentrations of the soil solutions. Furthermore, the pore waters after draining kaolinite-bearing rocks would become isotopically heavier due to the preferential adsorption of ^{63}Cu onto kaolinite. Given that no redox change occurred in all experiments, we propose that the most likely mechanism responsible for such Cu isotope fractionation is the different adsorption capacities of isotopically different species in aqueous solutions and the formation of outer-sphere surface Cu(II) complexes. Our study represents one important step for future studies to use Cu isotopes to trace the source of metal contaminants in natural soils.

1. Introduction

Copper (Cu) is a common trace metal in sediments, soils and aquatic environments at relatively low concentration levels, and it acts as an important nutrient for vegetation and biota. However, at elevated concentrations Cu can become toxic. Due to the enhancement of its toxicity through accumulation in living organisms and consequent biomagnification in the food chain (An et al., 2001), excess Cu and other heavy metals can cause various diseases and disorders and have become important environmental and human health issues (Balistrieri and Mebane, 2014).

Weathering is the primary way for the formation of clays and clay minerals at the Earth's surface. It releases dissolved metals to natural systems and controls their distribution in pore waters and soils (Rubio et al., 2000; Liaghati et al., 2004). Soil, composed mainly of microorganisms, metal oxy(hydr)oxides and silicate clays, is a dominant carrier of Cu and other heavy metals. During weathering, the released Cu is incorporated into pedogenic minerals such as clay minerals and metal oxy(hydr)oxides (Contin et al., 2007) and partly bonded to organic matter during pedogenesis (Alcacio et al., 2001). Copper isotopes may act as a potentially useful tool to trace the source of Cu in soils. For example, significant Cu isotopic variations have been observed in soils (Bigalke et al., 2010a, 2011; Liu et al., 2014a). Several mechanisms have been proposed to explain Cu isotopic variations in soils, including redox weathering of Cu-bearing sulfides (Mathur et al., 2012), adsorption by soil microorganisms (Pokrovsky et al., 2008; Navarrete et al., 2011; Liu et al., 2014a), and adsorption onto metal oxy(hydr)oxides (Balistrieri et al., 2008; Pokrovsky et al., 2008).

Adsorption is an important physicochemical process retaining inorganic and organic substances in soils and concentrating trace metals in

solutions (Essington, 2004). Natural clay minerals can be used as adsorbents for removal of heavy metals from contaminated waters and soils (Ikhsan et al., 1999; Gupta and Bhattacharyya, 2005; Gu and Evans, 2008). Several studies have experimentally documented the Cu isotope fractionation during adsorption onto organic matter or metal oxy(hydr) oxides. Pokrovsky et al. (2008) observed a significant enrichment of the light Cu isotope on the cell surface of the soil bacterium *P. aureofaciens* at pH 1.8–3.5, and an enrichment of the heavy Cu isotope on the surface of metal oxy(hydr)oxides at pH 4–6. Balistrieri et al. (2008) also reported that the heavy Cu isotope is preferentially adsorbed onto the surface of amorphous ferric oxy(hydr)oxides. Navarrete et al. (2011) reported that lab strains and natural consortia preferentially incorporate the light Cu isotope with $\Delta^{65}Cu_{solution-solid}$ varying from 1.0‰ to 4.4‰.

In soil, Cu can also be adsorbed onto clay minerals (Yavuz et al., 2003; Veli and Alyüz, 2007; Šljivić et al., 2009; Jiang et al., 2010), in addition to metal oxy(hydr)oxides. Most clay minerals form where rocks are in contact with water, air, or steam (Foley, 1999). Kaolinite is one of the most abundant components in clay minerals. It occurs widely in tropical and sub-tropical soils and is the second most abundant clay mineral in ocean sediments (Grim, 1968). Kaolinite has high surface areas with cation-exchange capacities. It is a representative layered aluminosilicate mineral with a simple structure. It contains negatively charged functional groups, including the silanol ($\equiv$SiOH) and aluminol ($\equiv$AlOH) hydroxyl groups on the mineral edges, and permanently charged sites ($\equiv$X$^-$) on the basal surfaces (Yavuz et al., 2003; Gräfe et al., 2007; Gu and Evans, 2008). These functional groups readily form complexes with aqueous metal cations including Cu (Sen et al., 2002; Yavuz et al., 2003; Bhattacharyya and Gupta, 2008b). Previous studies suggested that the permanent structural charge of kaolinite is minor (Ferris and Jepson, 1975), and thus adsorption takes place mainly at the proton-bearing surface functional groups such as silanols and aluminols exposed at the edge of the sheets (Zachara et al., 1988) (Fig. 1). Despite recent advances on the understanding of such adsorption processes, little is known about the relationship between adsorption and isotope fractionation.

In this study, for the first time we carried out batch adsorption experiments under various experimental conditions to investigate the magnitude and direction of Cu isotope fractionation during adsorption onto clay mineral surfaces. Our results show that significant Cu isotope fractionation occurs in this process, and such fractionation should play a fundamental role in determining the isotopic composition of metals in natural soils and solutions. The results may provide insights into the mechanisms of metal adsorption that occurs in natural environments.

2. Experimental methods

All experiments were performed in a clean laboratory fitted with HEPA-filtered Class 100 air supply and laminar-flow clean benches. All working acids were purified in-house by sub-boiling distillation in a Teflon® still, and >18.2 MΩ H$_2$O was made from a Milli-Q (MQ) water system. All reaction labwares, including Teflon® and glassware, were cleaned with 1:1 (v) nitric acid, 1:1 (v) hydrochloric acid and MQ H$_2$O. Other materials, including columns, pipette tips, test tubes and caps, were washed in a heated bath of 3% HNO$_3$ and rinsed with MQ H$_2$O prior to use.

2.1. Starting materials

Kaolinite used in this study is the Chinese mineral standard of GBW 03121(200 mesh). It was dried at 105 °C for 2 h using a partially enclosed hot plate (designed to limit airborne contamination) and finally stored in a Teflon bottle. The starting sample contains mainly kaolinite (~55 wt.%) and quartz (~35 wt.%) with other minerals in trace levels (<10 wt.%). The general formula of kaolinite is Al$_2$O$_3$–2SiO$_2$–2H$_2$O. The major elemental compositions of the used sample are: SiO$_2$ 54.6 wt.%, Al$_2$O$_3$ 31.4 wt.%, TiO$_2$ 0.69 wt.%, TFe$_2$O$_3$ 0.50 wt.%, K$_2$O 0.34 wt.%, MgO 0.12 wt.%, P$_2$O$_5$ 0.10 wt.%, CaO 0.05 wt.%, Na$_2$O 0.02 wt.%. Note that natural kaolinite contains a certain amount of Cu, which must be taken into account in the adsorption experiments. The Cu concentration of the used kaolinite is 47.3 μg/g, and its $\delta^{65}Cu$ value determined in this study is 2.10 ± 0.05‰ (n = 6) relative to NIST 976. This amount of Cu will be deducted when calculating the actual amounts adsorbed onto kaolinite (see details below). The adsorbate is a stock solution of Cu(NO$_3$)$_2$ with a Cu concentration of 1000 μg/g prepared from an in-house mono-elemental Cu standard solution (GSB Cu; >99.99%).

2.2. Experimental conditions and XRD analysis

All experiments were designed to provide a quantitative characterization of Cu isotope fractionation during adsorption onto the surface of kaolinite under different conditions. These conditions include: (a) contact time ranging from 10 to 360 min; (b) Cu concentration of the starting solutions ranging from 2 to 100 μg/g at constant pH; and (c) pH consisting of five parallel experiments at pH 4.0, 4.5, 5.0, 5.6 and 6.0. In addition, reaction temperature and ionic strength (background electrolyte) were also investigated. All experiments were conducted at an initial pH value equal to or less than 6.0, so that aqueous Cu(II) did not appreciably hydrolyze or reach saturation with formation of Cu oxide or Cu-oxy(hydr)oxide phases (Šljivić et al., 2009).
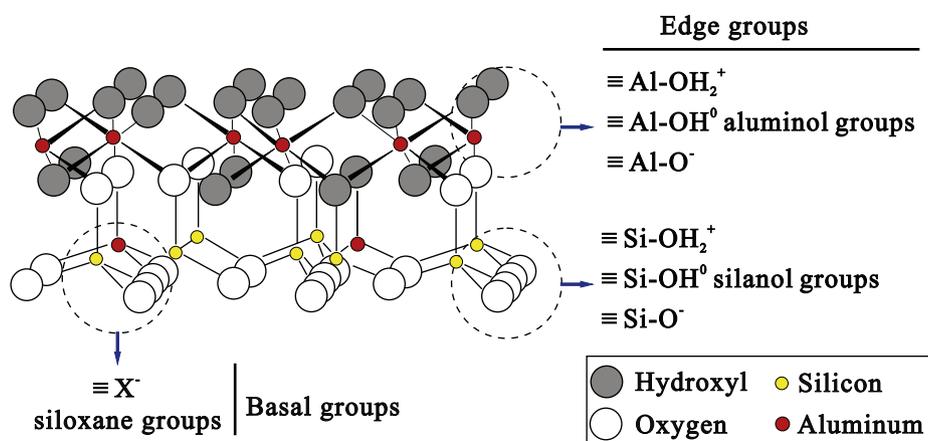

Fig. 1. Proposed charged sites on kaolinite used in the two site adsorption model (Gu and Evans, 2008).

Batch adsorption experiments were carried out in 100 ml Erlenmeyer flasks by mixing a constant amount of kaolinite (500.0 ± 0.1 mg) with 20 ml of the aqueous solution of Cu(II)(NO$_3$)$_2$. The mixture in the flasks was shaken using a rotary shaker at 150 rpm in a water bath under different experimental conditions. No buffer was used; instead, HNO$_3$ acid was used to adjust the pH of the initial solution. The pH was measured via a pH meter with an uncertainty of ± 0.1. Na and K or other elements can be used as the dominant ions to change the ionic strength of the solution. We used Na because it is a very important element in soils and does not affect the clay mineral structure (Jung et al., 1998; Bhattacharyya and Gupta, 2008a; Gu and Evans, 2008; Jiang et al., 2010). The samples were vacuum filtered using 0.22 μm membrane filters, and then the solids were rinsed three times using MQ H$_2$O. The final solutions (Cu$_{measured}$) were kept in Teflon beakers for measuring Cu concentration and isotopic composition.

The amount of Cu adsorbed onto kaolinite (Cu$_{adsorbed}$) in each reaction is calculated by subtracting the amount of Cu in the final solution from the total amount of Cu in the initial solution, plus the amount of Cu released from the starting kaolinite. Blank experiments in Cu-free solutions were run as the terminal endpoint for each experimental condition. The amount of Cu released from kaolinite in the adsorption experiments is assumed to be equal to the amount of Cu released in the blank experiments under the same conditions. Cu concentrations were measured using inductively coupled plasma mass-spectrometry (ICP-MS), with an uncertainty of $\pm 3\%$ (2SD). The level of Cu contamination (<2 ng) from the filtration and transformation procedure is negligible.

X-ray diffraction analysis (XRD) was used to determine whether or not phase changes occurred during the adsorption processes. The starting kaolinite and residual solids after adsorption were powdered to ~200 mesh and analyzed by an X-ray power diffraction (SmartLab) with Cu Kα1 radiations at the China University of Geosciences, Beijing. The analyses were scanned from 3° to 70° 2θ using a step of 0.02° at a rate of 8°/min.

2.3. Cu isotope analysis

Copper isotopic ratios were measured using a sample-standard bracketing method on a *Neptune plus* MC-ICP-MS at the Isotope Geochemistry Laboratory of the China University of Geosciences, Beijing. Sample dissolution, column chemistry and instrumental analysis followed the method of Liu et al. (2014b). Only a brief description is given below.

The residual solids were dissolved in a 1:1 (v/v) mixture of double-distilled HF and HNO$_3$ in Savillex screw-top beakers and heated at 160 °C on a hotplate in an exhaust hood (Class 100). The solutions were evaporated to dryness at 150 °C. The residue was then added with 1:3 (v/v) mixed HNO$_3$ and HCl and heated on a hot plate for a few hours before evaporation to dryness at 80 °C. The samples were refluxed with concentrated HNO$_3$ and subsequently dried down at 80 °C. 1 ml of 8 N HCl + 0.001% H$_2$O$_2$ was added to the beakers and the samples were heated to dryness. This process was repeated three times to ensure that all cations were converted to chloride species prior to ion-exchange separation.

All supernatant samples were dried down at 80 °C, and then 1 ml 8 N HCl + 0.001% H$_2$O$_2$ was added to each beaker. Because matrix elements (e.g., Na) might be released from the starting kaolinite when it reacts with the Cu(NO$_3$)$_2$ solution, all supernatant solutions were subject to column chemistry. Cu was isolated from matrix elements using the strong anion exchange resin AG-MP-1M (Bio-Rad). 2 ml pre-cleaned resin was loaded into the column and then washed using 0.5 N HNO$_3$ and 8 N HCl + 0.001% H$_2$O$_2$ alternating with MQ water three times. Matrix elements were eluted in the first 10 ml of 8 N HCl + 0.001% H$_2$O$_2$, and Cu was collected in the following 24 ml of 8 N HCl + 0.001% H$_2$O$_2$. The total procedural blanks are <2 ng. The Cu fractions were evaporated to dryness and dissolved in 3% HNO$_3$ (m/m). This process was

repeated three times to ensure that all cations were converted to nitrate species prior to isotopic ratio analysis. Cu isotopic ratios of the supernatant solutions are reported relative to the starting Cu solution (GSB Cu). The filtration of the supernatant solutions in the adsorption experiments caused no Cu isotopic offset (± 0.05‰) by measuring the filtered known Cu solution. The Cu isotopic analysis in our working conditions is sensitive to the presence of matrix Na (Liu et al., 2014b). To overcome the matrix Na interference, chemical purification is necessary for Cu isotopic analysis. The ratios of Na to Cu are less than 0.01 in all supernatant solutions after column chemistry. The low signal of matrix Na yielded a negligible influence on Cu isotopic ratio analysis. The long-term external reproducibility of δ^{65}Cu is ± 0.05‰ (2SD) based on repeated analyses of natural rocks and in-house solutions (Liu et al., 2014b).

The final solutions in all adsorption experiments were analyzed for Cu isotopic ratios (δ^{65}Cu$_{measured}$). The isotopic compositions of Cu adsorbed onto kaolinite (δ^{65}Cu$_{adsorbed}$) were calculated based on mass balance using Eqs. (1) and (2), where $f_{adsorbed}$ and $f_{released}$ are the percentage of Cu absorbed onto kaolinite and the percentage of Cu released from kaolinite measured in the blank experiment, respectively. The δ^{65}Cu$_{initial}$, δ^{65}Cu$_{measured}$, δ^{65}Cu$_{released}$ and δ^{65}Cu$_{solution}$ are the Cu isotopic compositions of the starting solution, solution fraction including the released fraction, Cu released from kaolinite and solution fraction excluding the released fraction (residual solution), respectively.

$$\delta^{65}Cu_{solution} = \left[\delta^{65}Cu_{measured} - \delta^{65}Cu_{released} \times f_{released}\right]/(1 - f_{released}) \quad (1)$$

$$\delta^{65}Cu_{adsorbed} = \left[\delta^{65}Cu_{initial} - \delta^{65}Cu_{solution} \times (1 - f_{adsorbed})\right]/f_{adsorbed}. \quad (2)$$

Similarly, the isotopic compositions of Cu adsorbed onto kaolinite (δ^{65}Cu$_{adsorbed}$) were also calculated based on the solid fraction, expressed as follows:

$$\delta^{65}Cu_{solid} = \left[\delta^{65}Cu_{kaolinite} - \delta^{65}Cu_{released} \times f_{released}\right]/(1 - f_{released}) \quad (3)$$

$$\delta^{65}Cu_{adsorbed} = \left[\delta^{65}Cu_{measured} - \delta^{65}Cu_{solid} \times (1 - f_{adsorbed})\right]/f_{adsorbed}. \quad (4)$$

The δ^{65}Cu$_{kaolinite}$ and δ^{65}Cu$_{solid}$ represent Cu isotopic compositions of the starting kaolinite and the solid fraction including the adsorbed fraction, respectively.

The isotope fractionation factor ($\Delta^{65}Cu_{adsorbed-solution} = 1000 \cdot ln\alpha$) between the adsorbed Cu (calculated based on the solution fraction) and residual Cu in the solutions is calculated as follows:

$$\Delta^{65}Cu_{adsorbed-solution} = \delta^{65}Cu_{adsorbed} - \delta^{65}Cu_{solution}. \quad (5)$$

3. Results

3.1. Effects of experimental conditions on adsorption amount

The original data of Cu concentrations and isotopic ratios are reported in the Supplementary Tables S1–S7 and are plotted in Figs. 2–6. The percentage of adsorbed Cu is not constant, which quickly increases in the first 60 min and then slowly approaches equilibrium with a constant percentage of adsorbed Cu (~20%) (Fig. 2a). This is consistent with previous studies (Bhattacharyya and Gupta, 2006, 2008b; Jiang et al., 2010). Although apparent equilibrium was achieved at 60 min, we selected 240 min as the contact time for other experiments in order to ensure sufficient equilibrium.

The effect of the initial Cu concentration of the starting solution was examined and the results are shown in Fig. 3a. As the initial concentration increases from 2 to 100 μg/g, the percentage of adsorbed Cu rapidly decreases at concentrations up to 30 μg/g and then decreases slowly at higher concentrations. For example, at an initial Cu concentration of 2 μg/g, approximately 46.8% of Cu was adsorbed onto the kaolinite. At

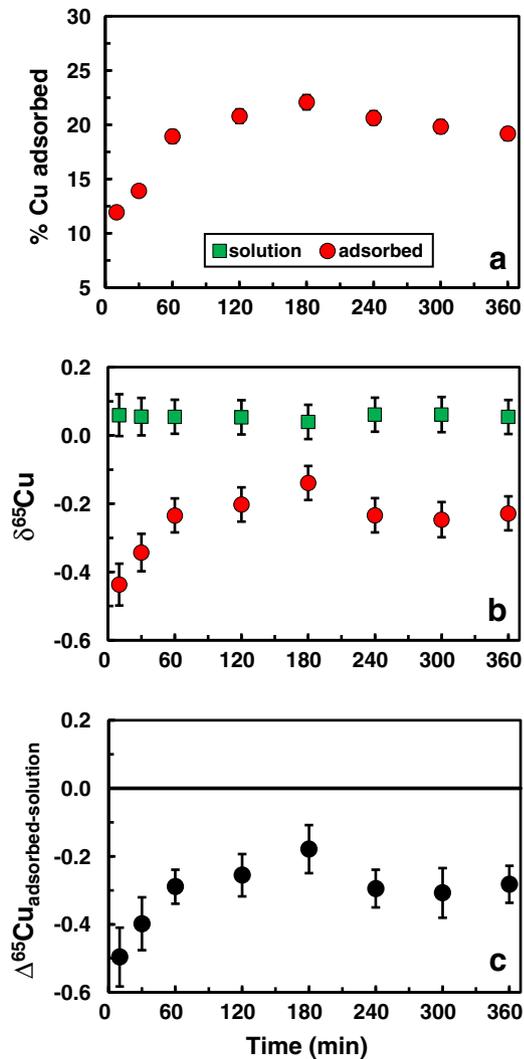Fig. 2. The variation of fraction of Cu adsorbed onto kaolinite as a function of time (min) at $C_0 = 20$ µg/g, pH = 5.6, T = 25 °C, without NaNO$_3$. a. The percentage of adsorbed Cu vs. time. b. $\delta^{65}Cu$ of measured residual Cu in the solutions (green squares) and of calculated adsorbed Cu (red circles). c. The fractionation values ($\Delta^{65}Cu_{adsorbed-solution}$) between adsorbed Cu and residual Cu in the solutions. All the following figures have the same plots of a, b and c except for changing the x-axis to the corresponding variable (Fig. 3, initial Cu concentration; Fig. 4, pH; Fig. 5, temperature; and Fig. 6, ionic strength).

Fig. 3. The variation of fraction of Cu adsorbed onto kaolinite as a function of initial concentration (µg/g) at t = 240 min, pH = 5.6, T = 25 °C, without NaNO$_3$.

For example, ~20% of Cu was adsorbed in the absence of NaNO$_3$, but the percentage decreased to ~6% when 0.1 mol/L NaNO$_3$ was added.

3.2. Cu isotope results

Copper isotopic compositions of the residual Cu in the solutions and calculated values for adsorbed Cu are presented in Figs. 2–6, respectively. The errors of the calculated $\Delta^{65}Cu_{adsorbed-solution}$ values are based on the methods of Liu et al. (2011), by considering the errors of $\delta^{65}Cu$ values of both residual solutions and adsorbed Cu. Additionally, the errors of $\Delta^{65}Cu_{adsorbed-solution}$ are also related to the uncertainty of the measured Cu concentrations as illustrated in Eqs. (1) and (2). Although the uncertainty of the Cu concentration measurements ($\pm 3\%$) is significantly larger than the uncertainty of Cu isotopic measurements, the offset of $\Delta^{65}Cu_{adsorbed-solution}$ values is less than ± 0.10‰ even though the uncertainty of the concentration measurements is considered.

In the contact time experiments, the residual solutions are enriched in the heavy Cu isotope (^{65}Cu) relative to the starting solution, with a mean $\delta^{65}Cu = 0.05 \pm 0.01$‰ (2SD) (Fig. 2b). The residual solution is significantly heavier than the starting solution, indicating that the light Cu isotope (^{63}Cu) was preferentially adsorbed onto kaolinite (Fig. 2b). The $\Delta^{65}Cu_{adsorbed-solution}$ values vary from -0.50‰ to -0.18‰ in the range of the contact time (10–360 min) and tend to be constant (-0.27 ± 0.09‰; 2SD) after 60 min (Fig. 2c).

In the initial concentration experiments, the residual solutions are also enriched in the heavy Cu isotope relative to the Cu adsorbed onto

initial Cu concentrations larger than 60 µg/g, the percentage is less than 10%. An initial Cu concentration of 20 µg/g in the starting solutions was used in the following experiments.

Copper ions undergo hydrolysis, and the solubility of Cu is low at pH > 6. For example, at pH > 7, the consumption of OH$^-$ ions results in the precipitation of Cu(OH)$_2$ (Bosso and Enzweiler, 2002; Šljivić et al., 2009). This process could cause large Cu isotope fractionation (Ehrlich et al., 2004). Therefore, all experiments were carried out at pH ≤ 6 to prevent the production of insoluble Cu species. The percentage of adsorbed Cu increases as the initial pH increases from 4.0 to 5.0 and then becomes relatively constant (~20%) at pH = 5.0–6.0 (Fig. 4a). An initial pH of 5.6 was chosen for other experiments because apparent adsorption equilibrium is achieved at this pH value.

To study thermodynamics of the adsorption process, experiments at different temperatures were carried out. The results are shown in Fig. 5a. As the temperature increases from 1 to 50 °C, the percentage of adsorbed Cu slightly increases. The influences of ionic strength on Cu adsorption are shown in Fig. 6a. The adsorption capacities of kaolinite decrease with increasing concentrations of background electrolytes.
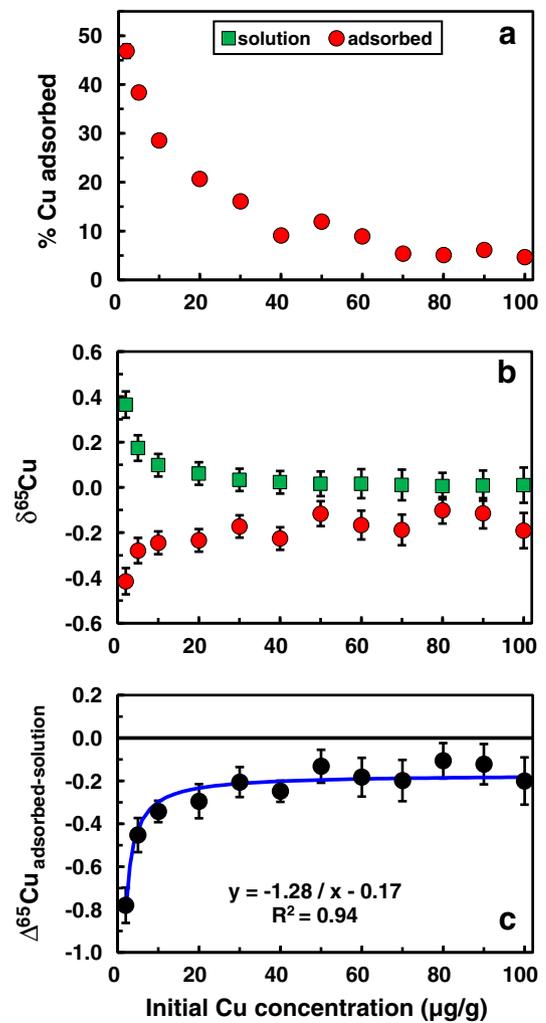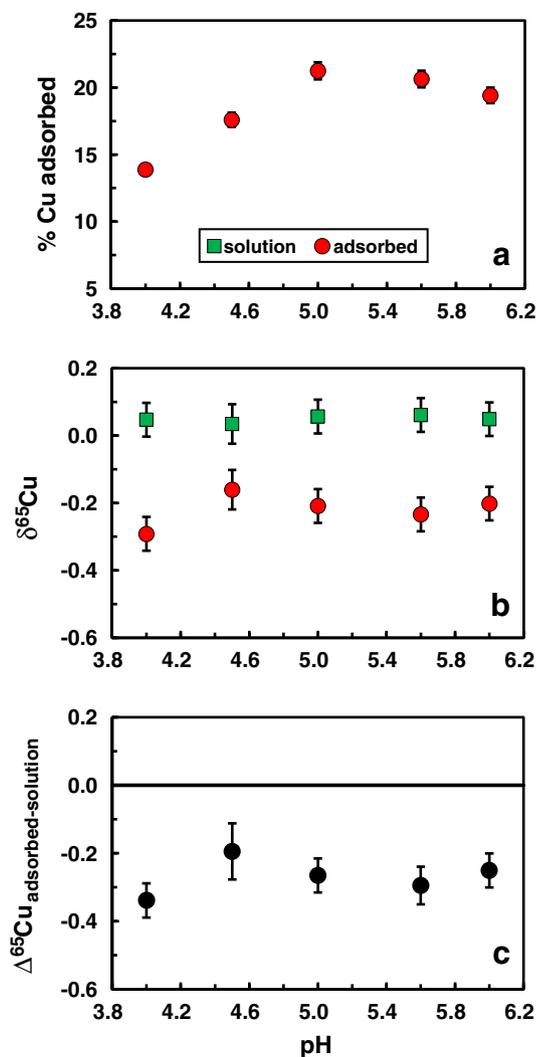
Fig. 4. The variation of fraction of Cu adsorbed onto kaolinite as a function of pH at t = 240 min, C_0 = 20 µg/g, T = 25 °C, without $NaNO_3$.
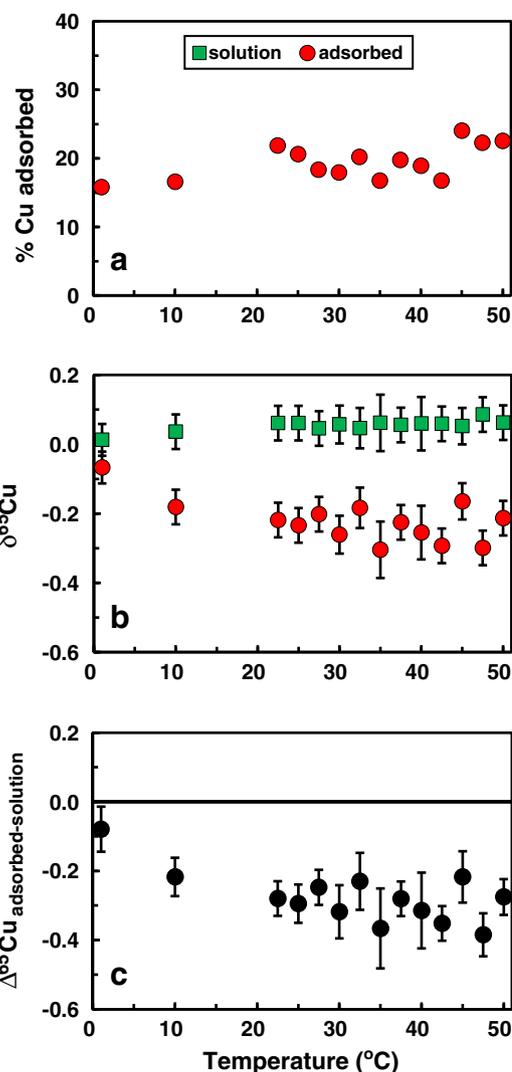

Fig. 5. The variation of fraction of Cu adsorbed onto kaolinite as a function of temperature (°C) at t = 240 min, C_0 = 20 µg/g, pH = 5.6, without $NaNO_3$.

kaolinite. At a relatively low Cu concentration of 2 µg/g, the residual Cu in the solution has a $\delta^{65}Cu$ value of 0.37 ± 0.06‰ (2SD). However, at higher Cu concentrations (>30 µg/g), $\delta^{65}Cu$ of the residual Cu in the solution is close to that of the starting solution, due to the small amounts of adsorbed Cu (<~10%) (Fig. 3b). The $\Delta^{65}Cu_{adsorbed-solution}$ values vary from −0.78‰ to −0.21‰ as the initial Cu concentrations increase from 2 to 30 µg/g, and the values tend to be constant (−0.17‰) at higher initial Cu concentrations of 40–100 µg/g (Fig. 3b, c). The curve-fitting results yield a best fitting with $\Delta^{65}Cu_{adsorbed-solution}$ = −1.28/C_o − 0.17 and R^2 = 0.94 (Fig. 3c).

In the pH experiments, $\delta^{65}Cu$ values of the residual solutions remain constant at pH varying from 4.0 to 6.0. The average $\delta^{65}Cu$ value (0.05 ± 0.02‰; 2SD) is significantly greater than zero (Fig. 4b), indicating that light Cu isotope is preferentially adsorbed onto kaolinite. The average of $\delta^{65}Cu_{adsorbed}$ is −0.22 ± 0.10‰ (2SD) (Fig. 4b). The $\Delta^{65}Cu_{adsorbed-solution}$ values are also almost constant with an average of −0.27 ± 0.11‰ (2SD) (Fig. 4c).

In the temperature experiments, the residual solutions are enriched in heavy Cu isotope and have an average $\delta^{65}Cu_{solution}$ = 0.05 ± 0.03‰ (2SD). $\delta^{65}Cu_{adsorbed}$ is negatively correlated with the temperature at T < 10 °C, but the correlation becomes weaker at higher temperatures (Fig. 5b). The $\Delta^{65}Cu_{adsorbed-solution}$ values vary from −0.38‰ to −0.08‰ when temperatures increase from 1 to 50 °C (Fig. 5c).

In the ionic strength experiments, $\delta^{65}Cu$ values of the residual solutions show insignificant variations at background electrolyte concentrations varying from 0 to 0.1 mol/L. The average value (0.09 ± 0.03‰; 2SD) is significantly larger than zero (Fig. 6b). The Cu isotopic compositions of the adsorbed Cu (−1.38‰ to −0.23‰) decrease significantly with increasing background electrolyte concentration (Fig. 6b). The $\Delta^{65}Cu_{adsorbed-solution}$ values vary from −1.46‰ to −0.29‰. The curve-fitting yielded a best fitting with $\Delta^{65}Cu_{adsorbed-solution}$ = −11.25 I_{NaNO3} − 0.30 and R^2 = 0.94 (Fig. 6c).

The copper isotopic compositions of the adsorbed Cu are also calculated based on the solid fraction. The data are listed in the Supplementary Table S7. The mean $\delta^{65}Cu$ value at different conditions is −0.27 ± 0.03‰, consistent within error with the calculated value (−0.22 ± 0.09‰) based on the solution fraction.

4. Discussion

In this section, we first discuss the effects of various experimental conditions on Cu isotope fractionation between adsorbed Cu and residual Cu in the solutions. Then, we discuss the possible mechanism responsible for the Cu isotope fractionation during adsorption onto the kaolinite mineral. Finally, we discuss the potential applications of our experimental findings to natural systems.
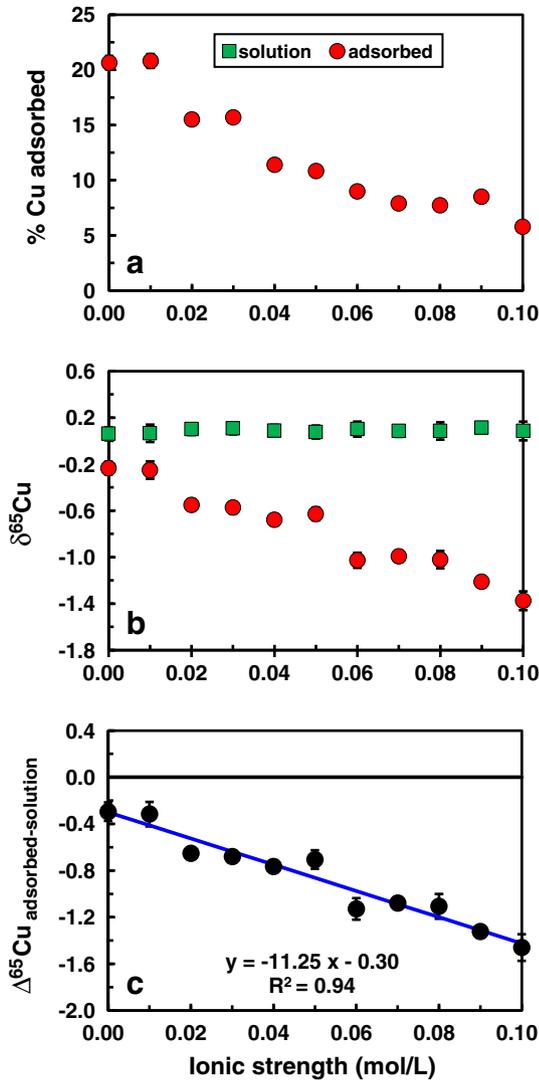
Fig. 6. The variation of fraction of Cu adsorbed onto kaolinite as a function of ionic strength (mol/L) at pH = 5.6, $C_0 = 20$ µg/g, t = 240 min, 25 °C.
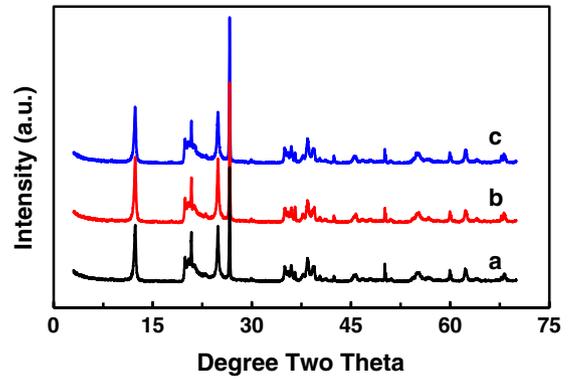

Fig. 7. X-ray power diffraction (XRD) patterns of the initial kaolinite and residual solids after the adsorption experiments: a. starting material, kaolinite; b. residual solid, without Cu(II) added into the solution; c. residual solid, with 20 µg/g Cu(II) in the solution. Other experimental conditions are pH = 5.6, t = 240 min, 25 °C, without NaNO$_3$.

(~20%) (Fig. 2a). This is due to the inhabitation of adsorption sites on the kaolinite surface through time until equilibrium is reached.

Isotopically, the $\Delta^{65}Cu_{adsorbed-solution}$ values initially increase with contact time and then become constant after 60 min (Fig. 2b, c). This is difficult to explain by thermodynamic equilibrium fractionation which is controlled by temperature and is not related to time. A possible explanation is that the transport of Cu species from the solutions to the actual adsorption sites needs some time and isotopic equilibrium had not been reached before apparent adsorption equilibrium. Other possible explanations may include (i) the desolvation kinetics of the Cu species or the surface adsorption sites and (ii) the diffusion kinetics through the interface between the solid surface and the bulk solution, etc.

4.2.2. The effect of initial concentration on Cu adsorption and isotope fractionation

At a certain weight of kaolinite, the percentage of metal adsorption onto kaolinite is determined by the adsorption capacity of the clay mineral (Fig. 3a). The percentage of adsorbed Cu decreases with increasing Cu concentration of the starting solutions, indicating that adsorption sites are widely available for the Cu ions at lower concentrations ($C_0 < 30$ µg/g). However, the competition between Cu and other elements becomes stronger at higher Cu concentrations ($C_0 > 30$ µg/g). Thus, a unit mass of kaolinite can adsorb a higher proportion of ions at a lower ion concentration. Given that the amounts of the adsorbate remain constant, the percentage of adsorption decreases with increasing initial Cu concentration of the solutions (Bhattacharyya and Gupta, 2008c).

The high percentage of adsorbed Cu at low initial Cu concentrations (<30 µg/g) dramatically changes the amount and isotopic composition of the Cu in the initial solution. Consequently, adsorption causes significant Cu isotope fractionation between adsorbed Cu and residual Cu in the solutions. However, when the initial Cu concentration increases, the maximum adsorption capacity of kaolinite will be reached and the percentage of adsorbed Cu is very low (<10%). Cu isotopic composition of the final solution mainly depends on $\delta^{65}Cu$ value of the initial solution. Thus, the $\delta^{65}Cu_{solution}$ values are close to the $\delta^{65}Cu_{initial}$ value (zero) and do not change substantially in the adsorption experiments; the $\Delta^{65}Cu_{adsorbed-solution}$ values also remain relatively constant.

4.2.3. The effect of pH value on Cu adsorption and isotope fractionation

The pH value of solutions is one key factor that affects the adsorption capacity of Cu and other metal ions (Bar-Yosef, 1979; Bolland et al., 1980; Zachara et al., 1988; Schulthess and Huang, 1990; Jung et al., 1998; Hizal and Apak, 2006; Gu and Evans, 2008; Jiang et al., 2010). The permanent structural charges of kaolinite are very minor, so metal adsorption takes place mainly at the proton-bearing surface functional

4.1. Characterization of the initial kaolinite and residual solids

Whether or not phase changes occurred during the adsorption experiments should be evaluated before discussing the influence of adsorption on Cu isotope fractionation. XRD patterns of the initial kaolinite and residual solids after adsorption experiments are given in Fig. 7. No significant differences of mineral assemblages between the initial kaolinite and residual solids were found. Importantly, no precipitation of copper phases and other minerals occurred during the adsorption process. Thus, we speculated that Cu adsorption onto kaolinite did not induce chemical reactions, and is only a physical absorption process with the formation of outer-sphere surface Cu(II) complexes.

4.2. Cu isotope fractionation during adsorption onto kaolinite

4.2.1. The effect of contact time on Cu adsorption and isotope fractionation

The adsorption rate depends on the metal ions that are transported from the bulk solutions to the actual adsorption sites, and adsorption equilibrium is established rapidly (Dalang et al., 1984; Veglio and Beolchini, 1997; Yu et al., 2000; Yavuz et al., 2003; Jiang et al., 2010). The results of the contact time experiments show that maximum uptake was achieved within 60 min with constant percentage of adsorbed Cu

groups (e.g., silanols and aluminols) exposed at the edge of sheets (Zachara et al., 1988). The pH-dependent surface charges of kaolinite can be explained by proton donor–acceptor reactions that occur simultaneously on these groups (Bolland et al., 1980; Zhou and Gunter, 1992). As illustrated in Fig. 4a, the percentage of adsorbed Cu is generally low (<15%) at low pH value (4.0), but increases at higher pH from 5.0 to 6.0. This occurs because the active sites on the kaolinite surface are weakly acidic and gradually deprotonated at higher pH, resulting in more negative surface charges and ultimately more bivalent metal cations (Cu(II)) adsorbed onto the surface.

Interestingly, the Cu isotope fractionation between adsorbed Cu and residual solutions ($\Delta^{65}Cu_{adsorbed-solution}$) is insensitive to the change of pH. This may be attributed to the fact that the concentration of H^+ in the solutions is significantly lower than the concentration of Cu(II) (20 μg/g) within the pH range (4.0–6.0), so the amounts of original Cu(II) species in the solutions do not change significantly. This could result in a stable Cu isotope fractionation between the adsorbed Cu and residual solutions (Fig. 4b, c).

4.2.4. The effect of temperature on Cu adsorption and isotope fractionation

The percentage of adsorbed Cu is the highest (22.6%) at high temperature (50 °C) and the lowest (15.8%) at low temperature (1 °C), indicating that adsorption is promoted by higher temperatures. The results indicate that the interactions between aqueous Cu and kaolinite are endothermic (Fig. 5a). There are three possible interpretations for this observation.

The first possible interpretation is that the Cu ions are well hydrated, and for Cu to be adsorbed onto kaolinite, the complex compounds have to lose the hydration shell, which consumes energy (Chen and Wang, 2006; Sheng et al., 2009). The second likely interpretation is that the adsorption process has to overcome a small activation barrier, and increasing the temperature facilitates Cu adsorption onto the kaolinite surface (Shukla et al., 2002; Ho, 2003). The third possibility is that the number of adsorption sites on the surface of clay minerals increase due to the dissociation of some surface components of the clay at higher temperatures which promotes Cu(II) uptake (Al-Asheh and Duvnjak, 1999).

We investigated Cu isotope fractionation in the range of temperatures (1–50 °C), which can be expected for oxic depositional settings in the global ocean (except in the early Archean) (Knauth, 2005). The results show that $\delta^{65}Cu_{solution}$ is not significantly correlated with temperature; whereas $\delta^{65}Cu_{adsorbed}$ values have a weak negative correlation with temperature (Fig. 5b). This suggests that higher temperatures would promote the adsorption of light Cu isotope onto kaolinite. The $\Delta^{65}Cu_{adsorbed-solution}$ values also weakly depend on temperature, although there is a slightly negative correlation at T < 10 °C (Fig. 5c).

4.2.5. The effect of ionic strength on Cu adsorption and isotope fractionation

As shown in Fig. 6a, increasing ionic strength has a negative influence on the percentage of adsorbed Cu. This may be due to competition between the background electrolyte ions and Cu(II), which decreases the number of active sites on the kaolinite as more electrolyte ions are adsorbed (Spark et al., 1995). The experimental results demonstrate that $\Delta^{65}Cu_{adsorbed-solution}$ is highly sensitive to ionic strength (Fig. 6c). The adsorbed Cu becomes isotopically much lighter with the increase of ionic strength of the solution. Similarly, the $\Delta^{65}Cu_{adsorbed-solution}$ values become lower as the ionic strength increases (Fig. 6b, c). The reason for this relationship is unclear. Generally, ionic strength significantly affects the amount of Cu adsorbed onto kaolinite at pH < 6; at these pH values, outer-sphere complexation reactions occur (Hayes and Leckie, 1987; Gu and Evans, 2008). As shown in Fig. 6a, the adsorption process is greatly influenced by changes in the background electrolytes. Therefore, Cu(II) forms outer-sphere complexes with negatively charged sites on kaolinite at pH = 5.6. The background electrolytes compete with Cu(II), which probably results in very low amounts and light Cu isotopic composition of the adsorbed Cu.

In summary, our results show that light Cu isotope (^{63}Cu) is always preferentially adsorbed onto the surface of kaolinite under various

experimental conditions. Cu isotope fractionation between the adsorbed Cu and residual Cu in the solutions is weakly correlated with the pH values and temperature, moderately correlated with the reaction time, and strongly depends on the initial Cu concentration and ionic strength. The general Cu isotope fractionation factor ($\Delta^{65}Cu_{adsorbed-solution}$) under these conditions (t = 240 min, C_0 = 20 μg/g, pH = 4.0–6.0, T = 1–50 °C and without $NaNO_3$) is -0.29 ± 0.06‰ (2SD).

4.3. Mechanism of Cu isotope fractionation during adsorption onto kaolinite

Redox transformation is a key mechanism for Cu isotope fractionation in nature. For example, Zhu et al. (2002) reported that the reduction of $Cu(II)_{aq}$ and $Cu(I)_{iodide}$ at 20 °C generates a large Cu isotope fractionation ($\Delta_{Cu(II)-Cu(I)} = 4.03 \pm 0.04$‰). Ehrlich et al. (2004) also found that Cu(I)S precipitation from $Cu(II)_{aq}$ yields a fractionation of $\Delta_{Cu(II)-CuS} = 3.06 \pm 0.14$‰ at 20 °C. By contrast, the precipitation of insoluble Cu(II) species from Cu(II) solution generates a much smaller Cu isotope fractionation ($\Delta_{Cu(II)-Cu(OH)2} = 0.28 \pm 0.02$‰; $\Delta_{Cu(II)-malachite} = 0.20 \pm 0.04$‰) at 30 °C (Maréchal and Sheppard, 2002; Ehrlich et al., 2004). In addition, Cu adsorption onto amorphous ferric oxyhydroxide also yields a small Cu isotope fractionation with $\Delta_{solution-solid} = -0.73 \pm 0.08$‰ (Balistrieri et al., 2008). The Cu isotope fractionation during adsorption of Cu onto kaolinite obtained in this study is also much smaller than that generated under redox reactions. This is consistent with the fact that our adsorption experiments were made in aerobic conditions; thus, no redox changes have occurred.

However, the mechanisms responsible for Cu isotope fractionation between solids and aqueous solutions remain unknown. The Cu isotope fractionation during adsorption onto kaolinite in our experiments is inconsistent with a kinetic isotope effect (Fig. 8), reflecting equilibrium fractionation between adsorbed Cu and residual Cu in the solutions. Previous studies on metal adsorption onto metal oxy(hydr)oxides suggest two potential mechanisms for equilibrium isotope fractionation during adsorption. The first one suggests that there is an equilibrium isotope fractionation between co-existing aqueous species of metal in the solution, and one of these species is preferentially adsorbed (Siebert et al., 2003; Barling and Anbar, 2004; Balistrieri et al., 2008; Pokrovsky et al., 2008). In this case, isotope fractionation is generated among different aqueous phases in the initial solution. The second mechanism suggests an equilibrium isotope fractionation between an aqueous species of metal and metal adsorbed onto the mineral surface (Siebert et al., 2003; Barling and Anbar, 2004; Balistrieri et al., 2008; Pokrovsky et al., 2008). In this case, isotope fractionation is generated during the adsorption process.

Pokrovsky et al. (2008) assumed that Al–OH sites in the kaolinite surface are an analogue of gibbsite surface centers. If this is correct, a
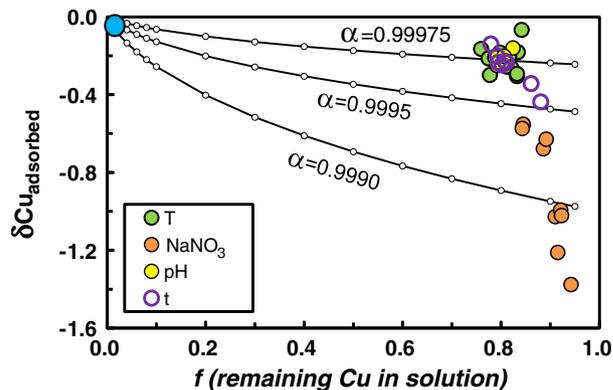
Fig. 8. Rayleigh modeling of the isotopic composition of adsorbed Cu as a function of remaining Cu (f) in the solution at various values of the fractionation factor (α). The α values represent the fractionation factor between adsorbed Cu and remaining Cu in the solution [α = ($^{65}Cu/^{63}Cu$)$_{adsorbed}$/($^{65}Cu/^{63}Cu$)$_{solution}$]. The Rayleigh equation: $\delta^{65}Cu_{adsorbed} = (\delta^{65}Cu_{initial} + 1000) \times (1 - f^{\alpha})/(1 - f) - 1000$.

similar direction of Cu isotope fractionation during adsorption onto gibbsite and kaolinite will be expected. Cu forms inner-sphere complexes with Cu–O during adsorption onto gibbsite or Fe(III) oxy(hydr)oxide, and the heavy Cu isotope is enriched in the solid phase (Balistrieri et al., 2008; Pokrovsky et al., 2008). This differs from our experimental studies, which show that light Cu isotope is preferentially absorbed onto kaolinite. Jung et al. (1998) found that Cu(II) forms inner-sphere complexes by strong bonds, but Cu adsorbed onto kaolinite may form inner-sphere complexes on Al sites and outer-sphere complex on Si sites. Previous work shows that Cd was not adsorbed by Si tetrahedral sheets of kaolinite, and Si tetrahedral sheets simultaneously impede Cd from binding to Al octahedral sheets (Gräfe et al., 2007). Thus, it is held as inner-sphere complexes on gibbsite and outer-sphere complexes on kaolinite. A study of Cu isotope fractionation during Cu interactions with microorganisms shows that outer-sphere complexes might change with pH, ionic strength and growth time (Pokrovsky et al., 2008). In our adsorption experiments, Cu isotopes are significantly fractionated at different ionic strengths, suggesting that Cu(II) forms outer-sphere surface complexes.

The hydrated Cu(II) ions exist as $Cu(H_2O)_6^{2+}$ complex with six-fold coordination (Sherman, 2001) and $Cu(H_2O)_5^{2+}$ complex with five-fold coordination (Pasquarello et al., 2001). Calculations by Fujii et al. (2013) show that the Cu isotope fractionation between aqueous $Cu(H_2O)_6^{2+}$ and $Cu(H_2O)_5^{2+}$ species with optimized geometries is −0.26‰ at 25 °C. This value is very similar to the general Cu isotope fractionation (−0.29‰ at 25 °C) between adsorbed Cu and residual Cu measured in this study. Thus, the more likely mechanism for the Cu isotope fractionation is the preferential adsorption of the $Cu(H_2O)_6^{2+}$ species onto the surface of kaolinite. However, more studies are needed to constrain the processes by which outer-sphere complexes control isotopic shift and relevant structural information.

4.4. Implications for application to natural systems

The study of Cu isotopic compositions in soils has important implications in tracing the biological cycling of trace metals in nature. Kaolinite is one of the major phases in soils produced during continental weathering and pedogenesis. In highly weathered soils, kaolinite has high surface areas and cation-exchange capacities, which can greatly absorb Cu and other heavy metals. In most cases, variations of Cu isotopic ratios result from more than one process in natural soils. Previous studies have suggested that several processes could result in significant Cu isotope fractionation, including redox transformation (Zhu et al., 2002; Ehrlich et al., 2004), precipitation (Maréchal and Sheppard, 2002; Ehrlich et al., 2004), adsorption onto Fe(III) oxy(hydr)oxide (Balistrieri et al., 2008) and biological processes (Mathur et al., 2005; Bigalke et al., 2010b; Liu et al., 2014a). Our experimental results show that adsorption of Cu onto the surface of clay minerals (e.g., kaolinite) can also significantly fractionate Cu isotopes. The results may be applied to explain variation of Cu isotopic ratios observed in natural soils.

Bigalke et al. (2010a) studied three types of soils and showed that ^{65}Cu is preferentially adsorbed onto oxy(hydr)oxides, organic matter and possibly other adsorption sites in soils, leaving the solution enriched in light Cu isotope. They also speculated that these adsorption processes might generally enrich the solid phases in heavy isotopes. However, our experimental results indicate that light Cu isotope is preferentially adsorbed onto the surface of kaolinite at various conditions, in contrast to Cu isotope fractionation during adsorption onto iron oxy(hydr)oxides. Liu et al. (2014a) recently studied a basalt weathering profile from Hainan Island, China. They found negative correlations of δ^{65}Cu values with both the contents of total organic carbon (TOC) and the proportions of kaolinite minerals in bulk soils. Although the negative correlation between δ^{65}Cu and TOC indicates biological uptake, adsorption of Cu onto kaolinite may also play an important role. Thus, a better understanding of the behavior of Cu isotopes during adsorption

onto soil components is important to interpret the variations of Cu isotopic ratios in soils.

Pore waters, waters from acid mine drainage, river waters and seawaters have heavier Cu isotopic compositions than igneous rocks (Vance et al., 2008; Kimball et al., 2009; Mathur et al., 2012). This difference has been attributed to (1) oxidative leaching of sulfides with preferential release of isotopically heavy Cu under abiotic conditions or (2) isotope fractionation between a ligand-bound dissolved phase and a labile, adsorbed particulate phase. Kaolinite, which is one of the main clay minerals in soils and ocean sediments, may be an isotopically light source. For example, pore waters will become isotopically heavier after draining kaolinite.

Our results demonstrate that the $\Delta^{65}Cu_{adsorbed-solution}$ value is insensitive to pH and temperature. This is important for interpreting Cu isotopic compositions of the oceans in oxic depositional settings, regardless of variable temperatures in geological time. However, the $\Delta^{65}Cu_{adsorbed-solution}$ value is strongly affected by the ionic strength, which is critical for interpreting Cu isotopic variations in sediments from estuarine settings, where salinity varies substantially.

Our experimental data show that the $\Delta^{65}Cu_{adsorbed-solution}$ increases with the initial Cu concentration and then reaches a constant value. These results can be used to evaluate Cu isotopic compositions of soil solutions from which Cu was adsorbed and to trace the source of metals in natural soils, regardless of variations in pH and temperature. However, soils contain other phases, e.g., organisms and oxides. These phases preferentially absorb the heavy Cu isotope (^{65}Cu), which shifts the Cu isotopic compositions in the opposite direction. Further work is needed to evaluate the relative adsorption capacities of these phases in order to better apply Cu isotopes as a tracer of metal cycling in soils.

5. Conclusions

We report for the first time an experimental study of Cu isotope fractionation during adsorption onto kaolinite. The results show that light Cu isotopes are preferentially adsorbed onto the kaolinite surface, leaving the residual solutions enriched in heavy isotopes. Such isotope fractionation may have been caused by the preferential adsorption of isotopically different Cu species in aqueous solutions.

The results demonstrate that the effects of temperature and pH on Cu isotope fractionation during adsorption onto kaolinite are relatively weak. A consistent isotope fractionation of approximately −0.29‰ between adsorbed Cu and residual Cu in the solutions is obtained. The results can be applied to interpret Cu isotopic variations in the rock record in terms of global oxic conditions. By contrast, the isotope fractionation between adsorbed Cu and residual Cu in the solutions is largely related to ionic strength and Cu concentration of the starting solution. The significant effects of ionic strength (from 0 to 0.1 mol/L) on Cu isotope fractionation can be used to interpret the behavior of Cu isotopic signatures in sediments and soils from estuarine settings or industrial sewage pollution areas. The results have implications to trace the source of contaminated metals in natural soils using Cu isotopes. In addition, the isotope fractionation of Cu during adsorption onto kaolinite is important to explain Cu isotopic variations in natural soils and pore waters.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2014.12.020.

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