



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



Dandan Li, Sheng-Ao Liu*, Shuguang Li

State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, China

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ABSTRACT

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 ($t = 10\text{--}360$ min), temperature ($T = 1\text{--}50$ °C), initial Cu concentration of the starting solution ($C_0 = 2\text{--}100$ µg/g), pH value (4.0–6.0) and ionic strength (NaNO_3 ; $I = 0\text{--}0.1$ 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 ($\Delta^{65}\text{Cu}_{\text{adsorbed-solution}} = \delta_{\text{es}}\text{Cu}_{\text{adsorbed}} - \delta^{65}\text{Cu}_{\text{solution}}$) 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 $\Delta^{65}\text{Cu}_{\text{adsorbed-solution}}$ 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 $\Delta^{65}\text{Cu}_{\text{adsorbed-solution}}$ values significantly increase with increasing initial Cu concentration of the starting solutions at $C_0 < 30$ µg/g, but approach a stable value of $-0.17 \pm 0.10\text{‰}$ (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.

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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

* Corresponding author at: China University of Geosciences, No. 29, Xueyuan Road, Haidian District, Beijing 100083, China.
E-mail address: lsa@cugb.edu.cn (S.-A. Liu).

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 $\Delta^{65}\text{Cu}_{\text{solution-solid}}$ 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 ($\equiv\text{SiOH}$) and aluminol ($\equiv\text{AlOH}$) hydroxyl groups on the mineral edges, and permanently charged sites ($\equiv\text{X}^-$) 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 H₂O 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 H₂O. Other materials, including columns, pipette tips, test tubes and caps, were washed in a heated bath of 3% HNO₃ and rinsed with MQ H₂O 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 Al₂O₃–2SiO₂–2H₂O. The major elemental compositions of the used sample are: SiO₂ 54.6 wt.%, Al₂O₃ 31.4 wt.%, TiO₂ 0.69 wt.%, TFe₂O₃ 0.50 wt.%, K₂O 0.34 wt.%, MgO 0.12 wt.%, P₂O₅ 0.10 wt.%, CaO 0.05 wt.%, Na₂O 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 $\delta^{65}\text{Cu}$ value determined in this study is $2.10 \pm 0.05\%$ (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(NO₃)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).

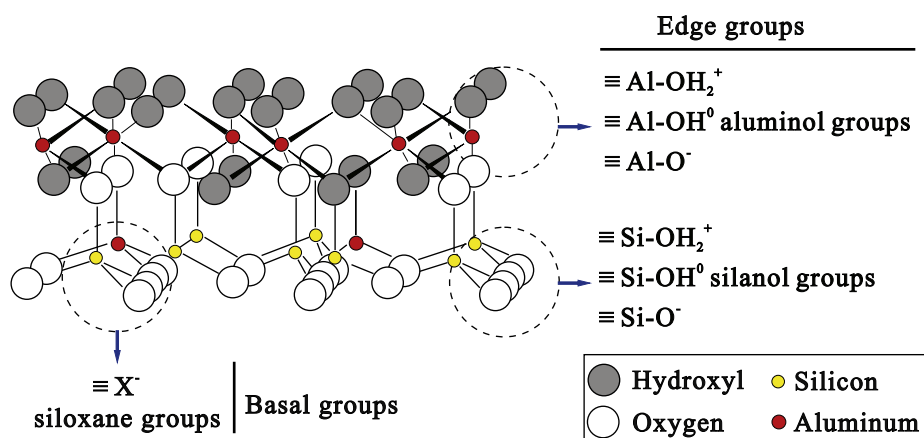


Fig. 1. Proposed charged sites on kaolinite used in the two site adsorption model (Gu and Evans, 2008).

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