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Research paper

Combined EXAFS and *ab initio* study of copper complex geometries adsorbed on natural illite

David M.S. Martins^{a,b}, José P. Mirão^c, Jörg Göttlicher^d, Marco Molinari^{b,e}, Ralph Steininger^d, Stephen C. Parker^b, Mário A. Gonçalves^{a,*}

^a Departamento de Geologia and Instituto Dom Luiz, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

^b Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom

^c Geoscience Department and HERCULES, University of Évora, Apt. 94, 7002-554 Évora, Portugal

^d Karlsruhe Inst. of Technol., ANKA Synchrotron Radiat. Facil., D-76344 Eggenstein Leopoldshafen, Germany

^e Department of Chemistry, University of Huddersfield, Huddersfield, HD1 3DH, United Kingdom

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ABSTRACT

The adsorption of copper on the 2:1 clay mineral illite (0.4 to 20 μm in size) was studied using a combination of extended X-ray adsorption fine structure (EXAFS) and hybrid-Density Functional Theory (DFT) modelling. The study evaluates the effect of varying pH and copper concentration on the mechanisms of copper adsorption in solutions at background electrolyte concentration typical of natural surface continental freshwaters in granitic environments. The EXAFS spectra revealed both the elongated square pyramidal and Jahn-Teller octahedral coordinated copper clusters as feasible with the former providing better fits using spertiniite (crystalline copper hydroxide) as model compound. Additionally, *ab initio* calculations also predicted the square pyramidal geometry to be more stable. Copper ions have four O_{eq} at an average distance of 1.95(1) Å and two independent O_{ax} at average distances of 2.32(16) Å and 3.06(9) Å, with the latter decreasing to 2.97(2) Å as copper concentration and pH are increased. This may reveal different mechanism by which copper adsorbs on illite, as a weakly bound complex at low pH likely at exchange and edge sites and changing towards more strongly bound complexes at high affinity edge sites at higher pH and copper loads. Above 1% Cu model fits suggest formation of copper oligomers with average Cu-Cu distance of 3.10(2) Å. These occur at pH > 6, where the correlation between Cu-Cu and Al-Al distances in the illite edge surfaces supports the formation of surface precipitates.

1. Introduction

An understanding of the interaction of metal ions with mineral surfaces is a key requirement for assessing the fate of metals in the environment (Bradl, 2004; Egirani et al., 2005; Mellouk et al., 2011). Clay minerals are amongst the most important inorganic phases in natural systems due to their high exchange and adsorption capacities of metal ions, and they have been considered in many applications including remediation of mining areas and radioactive waste disposal facilities, as well as engineered retention and reactive barriers (Sanchez et al., 1999; Vengris et al., 2001; Alvarez-Puebla et al., 2005; Udiin, 2017). Thus developing models for the mechanisms of retention of metal ions on clays is fundamental to predicting their fate and obtaining an accurate evaluation of the environmental risks.

Surface complexation modelling (SCM) is a well-established approach to evaluate the condition of metal retention and stability at the mineral-water interface (Sherman, 2009). While SCM has proven

successful in providing insight for the molecular scale mechanisms, additional structural information (coordination geometries) of the adsorbed metals onto surfaces is needed to validate the models. Structural insights are generally achieved using X-ray Absorption Spectroscopy (XAS) performed at synchrotron radiation sources (Cheah et al., 1998; Scheidegger et al., 1998; Thompson et al., 2000; Brigatti et al., 2004; Peacock and Sherman, 2004, 2005a; Peacock and Sherman, 2005b; Schlegel and Manceau, 2013) or more recently using atomistic modelling (Kerisit and Parker, 2004; Martins et al., 2009; Martins et al., 2014; Zhang et al., 2016; Zhang et al., 2017).

Amongst the transition metals, copper is a common cation, and its environmental concentration has increased due to a diversity of anthropogenic activities, such as mining, manufacturing, agriculture, and waste disposal (Berti and Jacobs, 1996; Madrid and Díaz-Barrientos, 1998). Adsorption studies of copper onto clay minerals have been generally focused on swelling clays, especially montmorillonite (Papelis and Hayes, 1996; Scheidegger et al., 1998; Chen and Hayes, 1999;

* Corresponding author at: Departamento de Geologia, Faculdade de Ciências, Universidade de Lisboa, Edifício C6, Piso 4, Campo Grande, 1749-016 Lisboa, Portugal.
E-mail address: mgoncalves@ciencias.ulisboa.pt (M.A. Gonçalves).

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Hyun et al., 2000; Morton et al., 2001; Dähn et al., 2003; Brigatti et al., 2004; Schlegel and Manceau, 2006; Yang et al., 2015), whereas less attention has been paid to the role of non-swelling clays (Hesterberg et al., 1997; Chen and Hayes, 1999; Gier and Johns, 2000; Flogeac et al., 2004; Alvarez-Puebla et al., 2005; Saijdu et al., 2008; Strawn and Baker, 2009; Bradbury and Baeyens, 2009; Turan et al., 2011). However, non-swelling clays, such as illite, are amongst the most common phyllosilicates at the Earth surface (Srodon and Eberl, 1984; Du et al., 1997a, 1997b) and can be the dominant clay mineral in some surface environments, such as in poorly developed soils in granitic areas (Gonçalves et al., 2004). Therefore, their interaction with metals such as copper and many others may significantly control their distribution and partitioning between the terrestrial and aqueous environment. Many factors control the adsorption of transition metals onto clay minerals, such as, the structure of the adsorbate metal species, surface composition, and charge which in turn largely depend on the aqueous environment conditions in contact with the mineral phase. However, some of these factors have not been fully addressed yet, and lack of a general theoretical basis that can predict unequivocally how and where does a transition metal ion adsorb on a mineral surface still requires the exploration of particular systems under pre-determined aqueous solution conditions. For example, the structure (coordination and geometry) of the adsorbed copper cluster onto clay minerals has been subject of debate, with 6-, 5- and 4-fold coordination clusters and possibly even dynamic coexistence having all been proposed (e.g., Bryantsev et al., 2008; Frank et al., 2015; Hyun and Hayes, 2015; La Penna et al., 2015; Liu et al., 2015). In contrast, controlled laboratory experiments normally focus on the influence that variables such as the pH or the background electrolyte concentration have on the adsorption of metals. The choice of adequate conditions defines the type of sites it is possible to probe, either high or low energy sites and cation exchange (Tournassat et al., 2013). However, depending on the substrate geology, many natural surface waters have fairly low electrolyte concentrations ($< 10^{-3}$ M), while heavily polluted circumscribed areas are likely to develop highly concentrated solutions (Gonçalves et al., 2004; Figueiras et al., 2009). In contrast, although several experiments in the literature span a wide range of ionic strength conditions (Tournassat et al., 2013) the majority favor the use of high background electrolyte concentration (≈ 0.1 M) which only in very particular circumstances occur in natural environments. There are also several models for illite surface properties and divalent cation adsorption published in the literature (e.g. Du et al., 1997a,b; Alvarez-Puebla et al., 2005; Bradbury and Baeyens, 2009), that do not fully agree. Besides, only a few of the available studies have considered adsorption of copper onto the basal (001) surfaces of montmorillonite, a mechanism that was found to increase as ionic strength decreases (Morton et al., 2001). This situation still raises many uncertainties on the detailed mechanisms and geometrical configurations of divalent metal ions adsorbed onto clay mineral surfaces under typical natural freshwater ionic strength conditions.

In this study, we have used a combined approach of experimental (EXAFS) and modelling techniques (*ab initio* calculations) to study the effect of pH and Cu concentration on the adsorption geometries of copper on pure illite samples to unravel the mechanisms and influence of the non-swelling components of the clay mineral phase on copper adsorption at low ionic strength conditions.

2. Methodology

2.1. EXAFS sample preparation

Samples for analysis with EXAFS, were prepared from a series of adsorption experiments performed in batch mode using the IMT-1 illite from Silver Hill, Montana (Cambrian Shale) (Hower and Mowatt, 1966) purchased from the Clay Minerals Society repository of “special clays”. To eliminate any surface interfering phase, illite was pre-treated using

standard procedures and its physical and chemical characterization was done by SEM-EDS, XRD, and ATR-FTIR at all stages of illite preparation (details in the Supporting Information file for these and other measured parameters of the illite used in this study). Solution pH was chosen according to 3 different groups of aqueous solutions studied and analysed in granitic areas (Figueiras et al., 2009): *i*) pH 4.5, infiltrating shallow groundwater after interaction with organic acids in soils; *ii*) pH 5.5, surface runoff waters in equilibrium with atmospheric CO₂; and *iii*) pH 6.5, solutions showing initial signs of pollution from landfill leachates. The concentration of copper used in the set of experiments ranged between 5×10^{-5} M and 10^{-3} M of Cu(NO₃)₂ such that a low, intermediate and high (saturation) concentration of adsorbed Cu on illite are obtained for each experimental set to analyze their differences by EXAFS, using a background electrolyte concentration of 10^{-3} M of KNO₃. The choice of the background electrolyte concentration was based in the average solution conductivities measured in granitic areas which corresponded to salt concentrations varying between slightly higher than 10^{-4} M up to 10^{-3} M. The reactors were filled with 0.20(0) g of illite for 50 ml of solution with the pH adjusted to the previously chosen values. Experiments ran in two stages:

1. *Illite pre-conditioning stage*: Illite is suspended in 50 ml of a KNO₃ solution only (10^{-3} M) and the pH is adjusted to 4.5, 5.5, or 6.5. Reactors are sealed and put into an orbital shaker for 24 h. After that time, the suspension is transferred into tubes and centrifuged at 4000 rpm for 45 min. The supernatant is transferred into a glass vial and the pH measured.
2. *Adsorption stage*: Another aliquot with 50 ml of a combined KNO₃/Cu(NO₃)₂ solution with the same background electrolyte concentration and initial pH but with different copper concentration is added into each centrifuge tube with the illite from the previous step. After vigorous shaking, the content is transferred into the reactors in the orbital shaker. The suspensions are agitated for 24 h and the pH corrected after 12 h with HNO₃, as deemed necessary to restore the initial pH of the solution. After the 24 h agitation, the suspensions are centrifuged at 4000 rpm for 45 min.

About 2/3 of the supernatant solution is retrieved for pH measurement and copper analysis by atomic absorption spectroscopy (Varian SPECTRAA FS 220). The concentration of copper adsorbed onto illite is determined by the difference between the initial and final solution copper concentration normalized to the mass of adsorbent used in each experiment. The remaining portion is transferred into a crucible for filtration under vacuum using 0.20 μ m membranes. A small volume of distilled water is added to wash the excess copper solution in the illite paste which is retrieved for the X-ray absorption fine structure (EXAFS) measurements.

2.2. EXAFS experiments

The EXAFS Cu-K edge measurements were conducted in the Laboratory for Environmental Studies (SUL-X) of the ANKA synchrotron facility (KIT, Germany). The light beam is produced in a Wiggler radiation source, monochromated with Si(111) crystals in a double-crystal monochromator and focused to approximately $50 \times 50 \mu$ m by an elliptical Kirkpatrick-Baez mirror system. The intensity of the incident beam (I_0) was measured using the first ionization chamber. The energy calibration was achieved measuring repeatedly a Cu-foil as reference (8.979 keV, first inflection point).

Spertiniite (Cu(OH)₂) and tenorite (CuO) were used as model materials, with the crystals structures obtained from Oswald et al. (1990) and Calos et al. (1996), respectively. The fine powdered copper models were measured as pressed pellets in transmission mode. When necessary they were finely ground and homogeneously dispersed in cellulose pellets.

The samples were mounted between two Kapton films and

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