

Pb, Cu, and Zn distributions at humic acid-coated metal-oxide surfaces

Yingge Wang^a, F. Marc Michel^{a,b,1}, Yongseong Choi^c, Peter J. Eng^d,
Clement Levard^{a,2}, Hagar Siebner^{a,3}, Baohua Gu^e, John R. Bargar^b,
Gordon E. Brown Jr.^{a,b,f,*}

^a Surface & Aqueous Geochemistry Group, Department of Geological Sciences, School of Earth, Energy, and Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA

^b Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, MS 69, 2575 Sand Hill Road, Menlo Park, CA 94025, USA

^c Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439, USA

^d Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637, USA

^e Environmental Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

^f Department of Photon Science, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA

Received 31 August 2015; accepted in revised form 4 May 2016; available online 9 May 2016

Abstract

Mineral surfaces are often coated by natural organic matter (NOM), which has a major influence on metal-ion sorption and sequestration because of the abundance of binding sites in such coatings and the changes they cause in local nanoscale environments. The effects of NOM coatings on mineral surfaces are, however, still poorly understood at the molecular level due to the complexity of these systems. In this study, we have applied long-period X-ray standing wave-fluorescence yield (LP-XSW-FY) spectroscopy to measure the partitioning of naturally present Cu(II) (0.0226%), Zn(II) (0.009%), and Pb(II) (~0.0004%) between Elliott Soil Humic Acid (ESHA) coatings and three model single-crystal metal-oxide substrates: α -Al₂O₃ (0001), α -Al₂O₃ (1–102), and α -Fe₂O₃ (0001). The competitive sorption effects among these metal ions for binding sites in the ESHA coatings and on the metal-oxide surfaces were investigated as a function of reaction time, calcium content, and solution pH. Pb(II) ions present in the ESHA coatings were found to redistribute to reactive α -Al₂O₃ (1–102) and α -Fe₂O₃ (0001) surfaces after 3 h of reaction (pH = 6.0, [Ca(II)] = 2 mM). Pb(II) partitioning onto these reactive metal-oxide surfaces increased with increasing reaction time (up to 7 d). In addition, the partitioning of Cu(II) and Zn(II) from the ESHA coating to the α -Fe₂O₃ (0001) substrate increased slightly with reaction time (2.4% and 3.7% for Cu(II) and Zn(II), respectively, after 3 h and 6.4% and 7.7% for Cu(II) and Zn(II), respectively, after 72 h of reaction time). However, no changes in the partitioning of Cu(II) and Zn(II) onto the α -Al₂O₃ (1–102) surface were observed with increasing reaction time, suggesting that these ions strongly complex with functional groups in the ESHA coatings. Similar results were obtained for Cu(II) and Zn(II) on the ESHA-coated α -Al₂O₃ (1–102) surfaces in samples without the addition of calcium. However, the amounts of Pb(II) mobilized from the ESHA coatings onto the α -Al₂O₃ (1–102) surfaces increased from 40% (no added Ca) to 58% (with 2 mM Ca) after 72 h of reaction time, possibly due to displacement of Pb(II) by Ca(II) from binding sites in

* Corresponding author at: Department of Geological Sciences, Stanford University, Stanford, CA 94305-2115, USA. Tel.: +1 650 723 9168; fax: +1 650 729 2199.

E-mail address: gordon.brown@stanford.edu (G.E. Brown).

¹ Present address: Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA.

² Present address: CEREGE, Europôle Méditerranéen de l'Arbois, BP 80, 13545 Aix en Provence, Cedex 04, France.

³ Present address: The Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Midreshet Ben-Gurion, 84990, Israel.

the ESHA coatings. In contrast, Pb(II), Cu(II), and Zn(II) present in the ESHA coatings were found to be unreactive with the α -Al₂O₃ (0001) surface. The observed reactivities of the three ESHA-coated metal-oxide surfaces with respect to metal-ion sorption are consistent with the trend observed for the uncoated metal-oxide surfaces: α -Fe₂O₃ (0001) > α -Al₂O₃ (1–102) > α -Al₂O₃ (0001). In addition, Pb(II) partitioning onto α -Al₂O₃ (1–102) surfaces increased with increasing pH from 4.0 to 9.0 as a result of the increasingly negative surface charge. These results show that intrinsic properties (nature of binding sites, binding affinities, and surface charge) of the ESHA coatings and metal-oxide surfaces, as well as external parameters such as pH and competing ions, are key factors governing the distribution and speciation of metal ions at complex NOM/mineral interfaces.

© 2016 Elsevier Ltd. All rights reserved.

Keywords: Humic acid; Pb; Cu; Zn; Ca; Metal-oxide surfaces; Single crystal; X-ray standing wave; LP-XSW-FY; Metal partitioning; Hematite; Alumina; pH effect

1. INTRODUCTION

NOM is ubiquitous in terrestrial and aquatic ecosystems, and humic substances are the predominant species of NOM in water, soils, and sediments (Leenheer et al., 1994; Aiken and Cotsaris, 1995; Benedetti et al., 1995; Gu et al., 1996a; Kinniburgh et al., 1999; Tipping, 2002; Koopal et al., 2005). The properties and concentrations of humic substances vary significantly with source because they are heterogeneous mixtures of biochemical degradation products from plant and animal residues (Aiken and Cotsaris, 1995; Tipping, 2002). For example, the concentration of humic substances in groundwater can vary from 1 to 70 mg/L (Thurman et al., 1982; Herbert and Bertsch, 1995) as dissolved organic carbon (DOC), whereas the DOC concentration in surface waters can range from 0.5 to 100 mg/L with an average concentration of 5 mg/L; the DOC concentration in ocean water is found to be 1 mg/L at the surface and 0.5 mg/L at depth (Tipping, 2002). The content of humic substances in soils can vary from less than 1% in some sandy soils to essentially 100% in peats (Tipping, 2002). The effective concentration of humic substances (mass of humic matter per unit volume of soil water) can be as high as 60 g/L in B horizons of forest soils to 5 g/L in the typical marine sediment (Lofts et al., 2001; Tipping, 2002). These results show that humic substances can be present in very high concentrations in soils and sediments, and thus can potentially influence metal-ion distributions in natural environments (Tipping, 2002).

Humic substances are complex mixtures of organic macromolecules containing various reactive functional groups such as carboxylic (–COOH), phenolic (–OH), amino (–NHR, –NH₂), and thiol (–RS) (Tipping, 1993, 2002; Leenheer et al., 1994; Gu et al., 1996a,b; Kinniburgh et al., 1999; Koopal et al., 2005; van Riemsdijk et al., 2006; Rey-Castro et al., 2009). Anionic functional groups (e.g., carboxylic) introduce negative charges and have a strong affinity for positively charged mineral surfaces, and thus often partially coat fine-grained minerals such as the common metal-(oxy)hydroxide minerals in soils (Neihof and Loeb, 1974; Davis, 1984; Ransom et al., 1997; Au et al., 1999; Mayer, 1999; Bonneville et al., 2009; Lalonde et al., 2012). Neihof and Loeb (1974) introduced the concept known as the “effective monolayer hypothesis”, which postulates that most particles in marine environments are

coated by thin films (effective monolayers) of organic matter. This hypothesis led to the notion that adsorption properties of marine particles are controlled by organic coatings (Balistrieri et al., 1981; Davis, 1984), which was followed by the notion that most particles in soils and aquatic systems are coated by a thin organic film (Mayer, 1994; Au et al., 1999). However, Ransom et al. (1997) found that most organic matter and microbial coatings in continental margin sediments are patchy in distribution and discontinuously associated with clay minerals, thus refuting the effective monolayer hypothesis. In a subsequent study, Mayer (1999) concluded that less than 15% of particle surfaces are covered by organic matter in marine aluminosilicate sediments with low to moderate loadings of organic matter (<3 mg organic carbon/m²). Mayer and Xing (2001) further suggested that the organic carbon content in B and C horizons of acidic soil samples is at the monolayer equivalent level (~1 mg organic carbon/m²), whereas the organic carbon content in surficial A and O horizons exceeds that level. Soil organic matter is often closely associated with mineral surfaces (Mikutta et al., 2009; Lalonde et al., 2012). For example, Lalonde et al. (2012) reported that 21.5 ± 8.6 percent of organic carbon is directly bound to reactive iron-oxide phases in sediment samples from a wide range of depositional environments, suggesting that reactive iron-oxide phases serve as an “extremely efficient rusty sink” for organic carbon.

The presence of such organic coatings on mineral surfaces, even discontinuous patchy ones, could potentially induce steric and electrostatic changes that modify the physicochemical properties of colloidal mineral particles such as surface charge and colloidal stability, and substantially alter the sorptive capacity of metal-(oxy)hydroxide minerals (e.g., Davis, 1984; Gu et al., 1996b; Tipping, 2002). In addition, various reactive functional groups present in humic substances are known to form strong complexes with metal contaminants such as Cu, Zn, Pb, and Hg, making them potentially important environmental sorbents and a major influence on the fate and transport of metal contaminants in environmental systems (Benedetti et al., 1995; Kinniburgh et al., 1999; Tipping, 2002). A recent study of the speciation of airborne Pb using X-ray adsorption spectroscopy demonstrated that the major species of Pb in air is primarily Pb-humate, suggesting that the Pb is from soils (Pingitore et al., 2009). Understanding

Download English Version:

<https://daneshyari.com/en/article/4701780>

Download Persian Version:

<https://daneshyari.com/article/4701780>

[Daneshyari.com](https://daneshyari.com)