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In situ structural study of the surface complexation of lead(II) on the chemically mechanically polished hematite $(1\bar{1}02)$ surface

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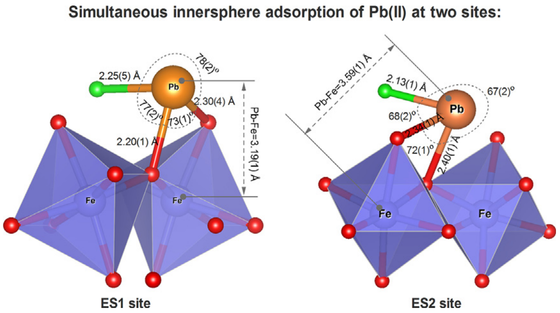
GRAPHICAL ABSTRACT



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ABSTRACT

A structural study of the surface complexation of Pb(II) on the $(1\bar{1}02)$ surface of hematite was undertaken using crystal truncation rod (CTR) X-ray diffraction measurements under *in situ* conditions. The sorbed Pb was found to form inner sphere (IS) complexes at two types of edge-sharing sites on the half layer termination of the hematite $(1\bar{1}02)$ surface. The best fit model contains Pb in distorted trigonal pyramids with an average Pb—O bond length of 2.27(4) Å and two characteristic Pb-Fe distances of 3.19(1) Å and 3.59(1) Å. In addition, a site coverage model was developed to simulate coverage as a function of sorbate-sorbate distance. The simulation results suggest a plausible Pb-Pb distance of 5.42 Å, which is slightly larger than the diameter of Pb's first hydration shell. This relates the best fit surface coverage of 0.59(4) Pb per unit cell at monolayer saturation to steric constraints as well as electrostatic repulsion imposed by the hydrated Pb complex. Based on the structural results we propose a stoichiometry of the surface complexation reaction of Pb(II) on the hematite $(1\bar{1}02)$ surface and use bond valence analysis to assign the protonation schemes of surface oxygens. Surface reaction stoichiometry suggests that the proton release in the course of surface complexation occurs from the Pb-bound surface O atoms at pH 5.5.

1. Introduction

Surface complexation at the mineral water interface is a key process controlling the fate and dispersion of trace metals in the environment [1–6]. Iron-(oxyhydr)oxides are ubiquitous in soils

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worldwide and they are usually of high specific surface area with abundant reactive sites capable of binding aqueous metal species [7,8]. As a consequence, they are among the most important environmental substrates for the mediation of a variety of geochemical and biochemical reactions on Earth's surface. The reactivity of a particular mineral surface is largely dependent on both the composition and structure of the surface. Therefore, understanding the reactivity of a mineral surface relies on a detailed knowledge of molecular-scale surface structure. The availability of this information is generally limited due to the difficulty in probing surface structure directly. This limits our ability to identify fundamental reactions that govern the sources, sinks, and transport of trace metals in the natural environment.

Lead (Pb) contamination of the environment is of serious concern due to its notorious toxic effects on a diversity of organisms including humans [9,10]. Sources of Pb to the environment, in addition to mining and metallurgical recovery, include its historic usage as an anti-knocking fuel additive [11] and as a pigment in paints [12]. Lead is currently used widely in the battery industry [13] and as a material for ammunition [14–16]. The environmental concern for Pb is mainly focused on its potential mobility under a variety of geochemical conditions [17–19]. To better model the environmental fate and transport of Pb we need to fully characterize the surface complexation of Pb at the mineral-water interface [20,21].

To date, there have been extensive studies of Pb(II) adsorption on a variety of iron-(oxyhydr)oxides under a range of experimental conditions. The majority of the published results have focused on Pb(II) adsorption behavior based on macroscale uptake experiments coupled with surface complexation models (SCMs) [22–29]. In those published results, there is a general consensus that Pb(II) binding on many substrates occurs via inner sphere (IS) complexation. However, details of the binding configuration and stoichiometry diverge widely among different studies. This discrepancy between surface binding configurations results from a lack of structural constraints needed to uniquely interpret the measurements [23,29,30].

A variety of approaches have been used to add structural constraints, such as X-ray absorption fine structure (XAFS) spectroscopy [31,32], Fourier transform infrared spectroscopy [33] and computational methods, like density functional theory (DFT) [34,35]. Numerous XAFS studies [36–41] have concluded that the adsorption of Pb(II) on various substrates (including aluminum oxide, goethite, and ferrihydrite) under a range of environmental conditions occurs in an inner-sphere (IS) mode, a result consistent with macroscale batch experiments. In addition, the binding configurations of Pb surface complexes have been found to be pH dependent. For example, Ostergren et al. [40] investigated Pb(II) adsorption on goethite, and found a bidentate edge-sharing binding mode over a pH range from 5.0 to 7.0 and a bidentate corner-sharing structure at pH 5.0. The bidentate edge-sharing binding structure was also identified in an earlier XAFS study by Bargar et al. [37], on both goethite and hematite powder over a solution pH range from 6.0 to 8.0. The underlying mechanism for the pH dependence of binding structure was unclear, although Ostergren et al. [40] suggested it could be due to the distinct proton affinity for different types of surface functional groups. Besides the solution pH, the presence of anionic ligands, including phosphate [41], sulfate [39], carbonate [40] and chloride [38], were also found to affect surface binding configurations through the formation of ternary surface complexes which exert synergistic effects on Pb(II) uptake on mineral surfaces.

Although XAFS spectroscopy has allowed great strides in understanding surface binding configurations of Pb(II) on different substrates, the potential of multiple reactive sites at mineral surfaces has posed a challenge for determining unique reaction stoichiometry for surface complexation reactions. In addition, the local structures derived from XAFS spectra are limited in representing the surface chemistry on a larger scale, since the technique is largely insensitive to the structural modifications caused by substrate termination and relaxation [42–52].

In order to develop a unique set of surface complexation reaction stoichiometries, and to examine structure-reactivity relationships, the interfacial structure, including the binding configuration of the sorbate and surface structure, must be known. Crystal truncation rod (CTR) X-ray diffraction provides this capability when it is used to probe the surfaces of single crystal samples [53]. To date, CTR has been used to investigate the surface structures of numerous (oxyhydr)oxides in the presence of water (liquid or vapor), including hematite $(1\bar{1}02)$ [47–49,54,55], hematite (0001) [46], hematite $(11\bar{2}0)$ [56], corundum (0001) [42], corundum $(11\bar{2}0)$ [57], goethite (100) [51], and muscovite mica (0 0 1) [58]. Characterization of the surface structures of clean hydrated oxide samples provides the basis to extend structural studies to a surface reacted with aqueous ions, like heavy metals. This allows for a broader analysis of the surface chemical composition that is more representative of the natural environment.

In this study CTR diffraction was utilized to investigate the adsorption of Pb(II) on the hematite $(1\bar{1}02)$ surface. Hematite was chosen because it serves as a model substrate with similar types of surface functional groups to those exposed on other common forms of iron-(oxyhydr)oxides, such as goethite, lepidocrocite, and ferrihydrite, all playing key roles in the diversity of biogeochemical processes at the Earth's surface [8]. The structure of the hydrated hematite $(1\bar{1}02)$ has also been well characterized using both theoretical [59] and experimental approaches [47–49,54,55]. The choice of Pb(II) is due to its environmental toxicity. The objective of this study is to provide a deeper insight into the metal adsorption mechanism on the hematite surface with a particular focus on the relationship between surface reactivity and surface structure.

2. Methods and experiments

2.1. Sample preparation

A natural single crystal hematite was first core drilled round with a diameter of ~1 cm and a thickness of ~2 mm, and was oriented parallel to the $(1\bar{1}02)$ plane within 0.1° using a custom orientation and polishing jig. The sample surface was ground and polished using successively smaller sizes of diamond paste down to 0.25 μm. The final step was chemical mechanical polishing (CMP) as in Tanwar et al. [49]. (See Supplemental Information for details.)

Metal solutions were prepared in a 4% H_2/96% N_2 purged glove box to avoid CO_2 contamination. Reagent grade $Pb(NO_3)_2$ was dissolved in de-ionized water which was previously de-gassed by boiling then sparging with pure N_2 (>99.999%) for 2 h. All metal solutions were diluted to 200 μM and adjusted to pH 5.5(±0.1) using NaOH and HNO_3. A pH of 5.5 was chosen to ensure maximum Pb adsorption in a system free of $Pb(OH)_2$ precipitates [60] as well as to prevent the oligomerization of $Pb_n(OH)_m^{m-2n}$ that may occur at higher pH [61]. The metal solution was added to the hematite surface using a liquid cell designed for surface diffraction measurements [62]. See Supplemental Information for more details.

2.2. CTR data collection

CTR measurements were performed at the GSECARS bending magnet beamline 13BMC of the Advanced Photon Source (APS) at Argonne National Laboratory, Argonne, Illinois. The energy of the incoming X-ray beam was fixed at 15 keV and the beam was focused to 0.25 × 0.4 mm. The sample in its liquid cell was