

## X-ray Absorption Study of the Uptake of Pb(II) at the Solid-Water Interface of Amorphous Silica

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*The bonding mechanism of Pb(II) at the amorphous silica surface was characterized with Extended X-Ray Absorption Fine Structure (EXAFS). The mode of Pb uptake was found to strongly depend on solution pH: At pH < 4.4, monomeric complexes are formed by mostly electrostatic interactions with the silica surface, whereas dimeric covalent Pb surface complexes form at pH > 6. These findings imply that the effectiveness of SiO<sub>2</sub> in retaining Pb<sup>2+</sup> strongly depends on the conditions in the solution in contact with the SiO<sub>2</sub> surface.*



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Characterizing the bonding mechanisms of trace metals on mineral surfaces is important in understanding and predicting their solubility and mobility in the environment. Dissolved metal concentrations in the pore water of soils and sediments are controlled by the extent of metal partitioning to the mineral matrix contacting the solution phase. Metal uptake at the mineral-water interface may occur via a number of different mechanisms. These include electrostatic interactions between oppositely charged metal ions and surface groups; direct chemical bonding of metal ions at the surface by the coordination to surface ligands; and the formation of metal precipitates at the surface. Distinguishing between these different modes of metal uptake is important, because they determine the stability of the partitioned metal ions. Electrostatically held complexes are weakly bound compared to chemically bonded complexes, and may therefore be more readily transferred back into solution, whereas precipitates are generally quite resistant to metal remobilization.

We investigated the interaction between Pb<sup>2+</sup> and the surface of hydrous amorphous silica (SiO<sub>2</sub>). Amorphous silica is abundant in marine environments, and serves as a high surface area analogue for quartz, a mineral found in essentially all soils and sediments. Experiments were run at low, intermediate, and high pH values, and at different concentration levels of co-adsorbing Na<sup>+</sup> cations to simulate a range of environmentally relevant solution conditions.

**Figure 1** shows the uptake of Pb<sup>2+</sup> by silica as a function of pH and Na concentration. Both system parameters affect the amount of Pb held at the silica surface: Pb uptake increases with increasing pH, and decreasing Na<sup>+</sup> concentration. The arrows in **Figure 1** indicate the samples for which we collected EXAFS data to characterize the bonding environment of Pb at the silica surface.

The EXAFS data shown in **Figure 2** indicate that the mechanism of Pb uptake by silica drastically changes as a function of pH. At low pH (<4.4), sorbed Pb has a first-shell O coordination similar to that of aqueous Pb<sup>2+</sup> cations, which indicates that the interaction with the SiO<sub>2</sub> surface is mostly electrostatic. At high pH (>6.3), however, the surface-held Pb cations are in a covalent bonding state, as indicated by the similarity of their first-shell O coordination with that of aqueous

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ous  $\text{Pb}_4(\text{OH})_4^{4+}$  polymers; moreover, the presence of Pb atoms in the local coordination sphere of the sorbed Pb cations indicates that the Pb surface complexes formed at high pH are polymers, most likely dimers. The Pb surface complexes formed between pH 4.8 and 6.3 are intermediate between those observed at low and high pH, indicating that a mixed population of ionic (i.e. electrostatically held) and covalent Pb complexes is present at the silica surface in this pH range.

The presence of electrostatically held Pb surface complexes at low and intermediate pH implies that Pb may be effectively remobilized by competing with other cations for uptake at surface sites, as demonstrated by the decreased Pb uptake at high Na concentrations (**Figure 1**). With increasing pH, however, Pb becomes less susceptible to desorption due to the more covalent nature of the interaction with silica surface sites. The effectiveness of  $\text{SiO}_2$  in retaining  $\text{Pb}^{2+}$  therefore strongly depends on the conditions in the solution in contact with the  $\text{SiO}_2$  surface.

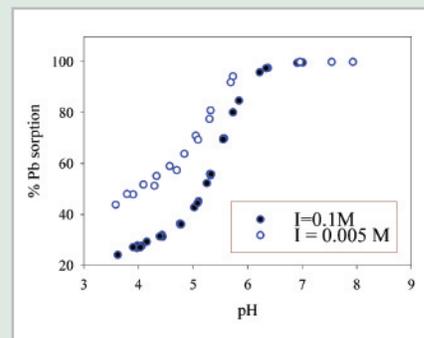


Figure 1. Comparison of the pH edges of Pb sorption at  $I = 0.1$  and  $0.005$  M.

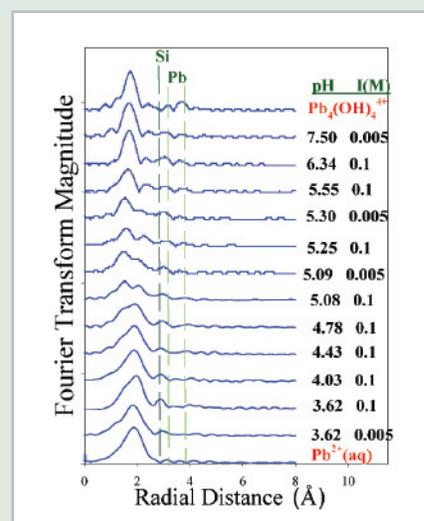


Figure 2. Radial structure functions (not corrected for phase shift) obtained by Fourier transforming the raw  $k^3$ -weighted spectra.