

Structural Characterization of Pb(II) Sorption Complexes at the Calcite-Water Interface

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X-ray absorption fine structure spectroscopy (XAFS) was used to determine operative mechanisms and characterize surface adsorption complexes formed by Pb(II) species at the calcite surface. Adsorption experiments were performed using pre-equilibrated calcite solutions at pH 8.3, ambient temperature, and atmospheric PCO_2 . XAFS collected at the Pb L_{III} edge at 13035 eV indicate that Pb(II) binds to the calcite surface as an inner-sphere complex. Pb is coordinated by 3 to 4 oxygens with first shell Pb-O distances of 2.34 Å, and a Pb-Ca distance of 4.08 Å (Figure 1). There is no indication of a co-precipitation mechanism as Pb in natural and synthetic samples is in octahedral co-ordination with first shell Pb-O distances of 2.51 and 2.52 Å respectively (Figure 1). The surface adsorption complex is interpreted as having either square pyramidal geometry similar to that of orthorhombic and tetragonal Pb(II)oxides (1), or a trigonal pyramidal geometry as interpreted for Pb(II) adsorption complexes on Al(III) [1], Fe(II) [2] and Mn(III, IV) [3] oxide surfaces. Formation of non-octahedral surface adsorption complexes can provide inferences for differential incorporation of lead on calcite (104) faces during coprecipitation mechanisms. A general understanding of Pb sorption behavior can have significant implications for sequestration of Pb(II) in aqueous environmental systems by calcite containing materials.

References: [1] Bargar J.R., Brown Jr G.E., Parks G.A. (1997), "Surface complexation of Pb (II) at oxide-water interfaces. I. XAFS and bond valence determination of mononuclear and polynuclear Pb (II) sorption products on aluminum oxides," *Geochimica et Cosmochimica Acta*, **61**, 2617-2637. [2] Elzinga E.J., Peak D., and Sparks D.L. (2001), "Spectroscopic studies of Pb (II)-sulfate interactions at the goethite-water interface," *Geochimica et Cosmochimica Acta*, **65**, 2219-2230. [3] Matocha C.J., Elzinga E.J., and Sparks D.L. (2001), "Reactivity of Pb (II) at the Mn (III, IV) (oxyhydr)oxide-water interface," *Environmental Science & Technology*, **35**, 2967-2972.

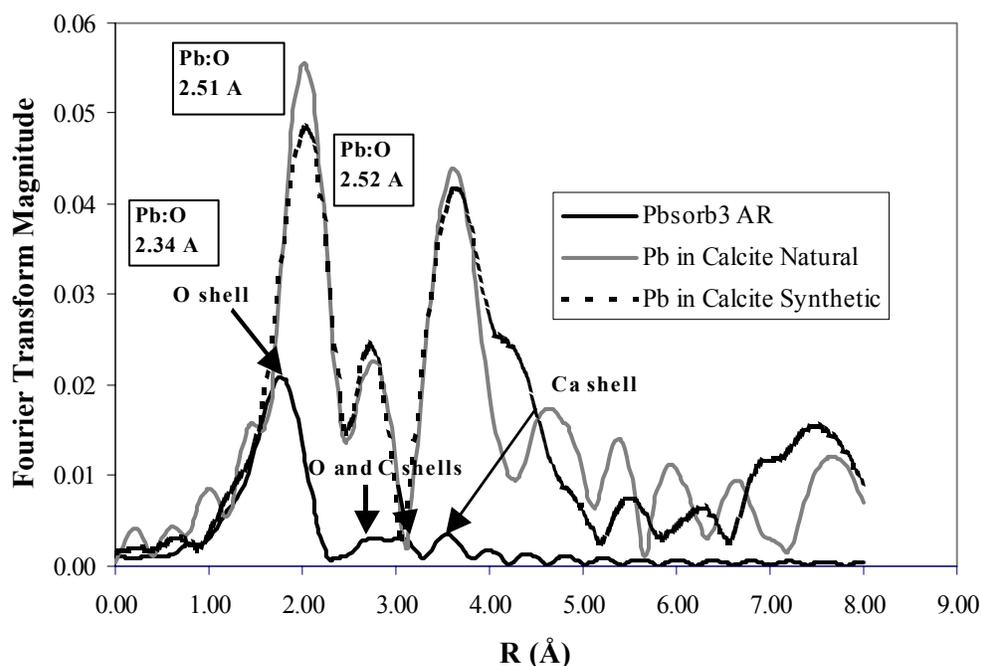


Figure 1. Fourier transform for Pb adsorption as well as natural and synthetic calcite EXAFS data. Inset are ball and stick models depicting possible geometry of Pb incorporated in calcite, as well as adsorbed at the mineral surface.