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## Combined EXAFS and FTIR investigation of sulfate and carbonate effects on Pb(II) sorption to goethite ( $\alpha$ -FeOOH)

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Understanding the effects of carbonate and sulfate on Pb(II) sorption to iron (hydr)oxides is critically important in developing accurate models of Pb fate and transport in natural environments. Macroscopic measurements show that Pb(II) uptake on iron (hydr)oxides can be altered significantly by dissolved sulfate and carbonate. Our investigation elucidates the molecular-scale processes giving rise to these macroscopic effects by characterizing the structures of Pb(II) sorption complexes forming on goethite ( $\alpha$ -FeOOH) in the presence of carbonate and, in separate experiments, sulfate using *in-situ* Pb L<sub>III</sub>-EXAFS and ATR-FTIR spectroscopies. Under all conditions studied, Pb(II) forms predominantly bidentate inner-sphere complexes to Fe(O,OH)<sub>6</sub> octahedra. Both corner- and edge-sharing complexes are observed by EXAFS spectroscopy. The relative fraction of corner-sharing complexes increases at low pH (5-6) for carbonate concentrations up to 1atm (i.e., we see the same behavior in samples free of added ligands and in those with carbonate present up to 1atm), and is enhanced in the presence of sulfate. The formation of ternary surface complexes is evaluated as a possible explanation for enhanced Pb uptake in the presence of high CO<sub>2</sub> (1atm) and in the presence of sulfate.

**Keywords:** Pb, sulfate, carbonate, sorption, goethite

### 1. Introduction

Lead contamination is a byproduct of a variety of human activities, most notably mining, battery production and recycling, and, historically, from vehicle emissions and the use of lead-based paint. This study of lead speciation at the goethite ( $\alpha$ -FeOOH)/water interface is motivated by the fact that lead bioavailability and environmental mobility vary dramatically with speciation, and that sorption complexes (esp. on iron (hydr)oxides) are recognized as being among the most bioavailable and mobile forms of Pb in natural environments. The presence and importance of adsorbed Pb(II) in environmental media (e.g., contaminated soils and mine wastes) have recently been confirmed through XAFS-based investigations by our group [Ostergren et al., 1998a, Morin et al., 1998].

Previous EXAFS investigations of Pb(II) sorption to (hydr)oxide surfaces in model systems have shown that, in the absence of complexing ligands, Pb bonds directly to oxide surfaces forming dominantly inner-sphere surface complexes [Bargar et al., 1997, Manceau et al., 1992, Farquhar et al., 1997]. This investigation builds directly on these previous studies by evaluating the effects of carbonate and sulfate oxoanions on Pb sorption, and also builds on recent investigations of the sorption behavior of these ligands on iron (hydr)oxides [Eggleston et al., 1998; Hug, 1997, Persson and Lovgren, 1996, van Geen et al.,

1994]. Carbonate typically exceeds ambient air concentrations (approx. 10<sup>-3.5</sup> atm) by 1-2 orders of magnitude in soil pore gas, and ranges up to nearly pure CO<sub>2</sub> in some environments of interest, such as mine tailings (for example, see [Blowes et al., 1991]). Sulfate concentrations in natural waters are commonly on the order of 10<sup>-4</sup> M, and rapid oxidation of sulfide minerals can lead to concentrations of 1 M in metal-rich acidic mine drainage environments (for discussion, see [Alpers et al., 1994]). The ubiquity of these ligands motivates our interest in understanding their impacts on processes that control metal bioavailability and transport in natural environments.

### 2. Experimental

EXAFS data were collected at the Stanford Synchrotron Radiation Lab (SSRL) on wiggler beamline 4-3 using Si(111) or Si(220) monochromator crystals (2mm slits before the monochromator) and either a 13-element Ge detector or a Stern-Heald detector [Lytle et al., 1984] filled with Ar or Xe. Data were processed using EXAFSPAK [George and Pickering, 1995]. Phase and amplitude functions for quantitative fitting were generated from model structures using FEFF 6 [Zabinsky et al., 1995]. Three separate batches of phase-pure and well-crystalline synthetic goethite were used (BET surface areas of 45, 70, and 90 m<sup>2</sup>/g, respectively). Samples for EXAFS and for sulfate FTIR analyses were prepared in 0.1M NaNO<sub>3</sub>. Carbonate FTIR samples were prepared in 0.1 M NaHClO<sub>4</sub> to avoid nitrate interferences. All samples were actively purged with appropriate gas during preparation and equilibration periods prior to analysis (12-24 hrs @ pH<sub>i</sub>) (Ar for CO<sub>2</sub>-free samples, and CO<sub>2</sub> mixed with N<sub>2</sub> for carbonate samples). All samples were analyzed as moist pastes. Preparation conditions for EXAFS samples are summarized in Table 1.

Figure	pH	P <sub>CO2</sub> (atm)	S <sub>T</sub> (mM)	Pb <sub>T</sub> (mM)	[goeth] (g/L)	SA <sub>goeth</sub> (m <sup>2</sup> /g)	Γ <sub>Pb</sub> (μmol/m <sup>2</sup> )
1-a	7	-	-	2.25	5	90	3.6
1-b	5	-	-	0.45	5	90	0.5
3-a	7	1	-	0.1	5	45	0.4
3-b	5	1	-	0.045	1	90	0.4
3-c	7	10 <sup>-3.5</sup>	-	0.05	0.5	45	2.1
3-d	5	10 <sup>-3.5</sup>	-	1.0	10	45	1.3
4-a	7	-	10	0.126	2	90	0.7
4-b	7	-	0.32	0.18	2	90	1.0
4-c	6	-	3.16	0.1	1.5	45	1.3
4-d	6	-	0.63	0.1	1.5	45	1.3
4-e	5	-	0.63	0.3	5	90	0.5
4-f	5	-	0.1	0.3	5	90	0.5

**Table 1**

Sample preparation conditions {partial pressure of CO<sub>2</sub> (P<sub>CO2</sub>), total sulfate (S<sub>T</sub>), total lead (Pb<sub>T</sub>), goethite solids concentration ([goeth]), and goethite surface area (SA<sub>goeth</sub>)}. Corresponding figure numbers as noted.

### 3. Results and Discussion

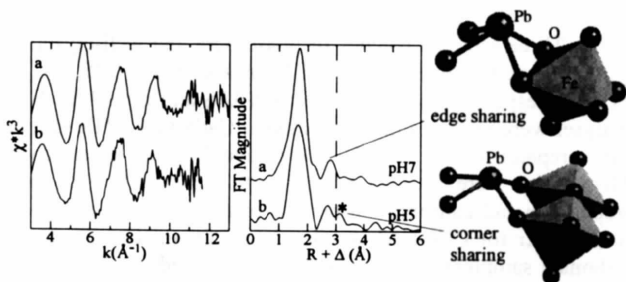
#### 3.1 Carbonate- and sulfate-free systems

EXAFS data show that lead occurs in at least two different coordination environments on the goethite surface and that the relative proportion of Pb in these sites varies as a function of pH. At pH7 (Fig. 1a), the dominant Pb species are edge-sharing with Fe(O,OH)<sub>6</sub> octahedra (R<sub>Pb-Fe</sub>=3.3-3.4Å) {see also, [Bargar et al., 1997, and Manceau et al., 1992]}, whereas at pH5 (Fig. 1b) approximately one half the total adsorbed Pb is bound to the surface as corner-sharing complexes, as evidenced by a second Fe shell at 3.88Å (Table 2). Data collected at lower coverages (1 μmol/m<sup>2</sup>) at pH7 confirm that the apparent trend with pH (i.e., the (dis)appearance of the ~3.9Å Fe shell) is not an artifact of variations in surface coverage.

Figure	Pb-O		Pb-Fe		Pb-Fe	
	N	R (Å)	N	R (Å)	N	R (Å)
1-a	2.7(1)	2.26(1)	0.5(1)	3.33(2)		
1-b	2.3(1)	2.28(1)	0.4(1)	3.34(3)	0.4(2)	3.88(3)
3-a	2.4(2)	2.30(1)	0.3(1)	3.30(3)		
3-b	2.1(1)	2.26(1)	0.3(1)	3.31(4)	0.3(2)	3.95(4)
3-c	2.7(2)	2.27(1)	0.5(2)	3.34(2)		
3-d	2.5(2)	2.28(1)	0.4(2)	3.34(3)	0.5(2)	3.91(4)
4-a	2.3(1)	2.28(1)	0.3(1)	3.40(2)	0.5(1)	3.88(2)
4-b	2.5(1)	2.28(1)	0.3(1)	3.34(2)	0.4(2)	3.89(3)
4-c	2.5(1)	2.27(1)	0.2(2)	3.36(5)	0.6(2)	3.89(3)
4-d	2.3(2)	2.27(1)	0.3(2)	3.36(4)	0.4(2)	3.88(4)
4-e	2.1(2)	2.28(1)	0.5(2)	3.36(3)	0.6(2)	3.90(3)
4-f	2.2(1)	2.29(1)	0.4(1)	3.34(2)	0.5(2)	3.89(3)

**Table 2**

Pb  $L_{III}$ -EXAFS fitting results, including coordination numbers (N) and radial distances (R). Corresponding figure numbers as noted. Standard deviations of 95% confidence intervals for N and R are listed in parentheses. Debye-Waller factors ( $\sigma^2$ ) were fixed to 0.01 Å<sup>2</sup> for all shells.

**Figure 1**

Pb  $L_{III}$ -EXAFS and Fourier Transforms (FTs) from Pb sorbed to goethite at pH 7 (a,  $\Gamma_{Pb} = 3.6 \mu\text{mol}/\text{m}^2$ ), and at pH 5 (b,  $\Gamma_{Pb} = 0.5 \mu\text{mol}/\text{m}^2$ ), and structural models corresponding to best fits (see Table 2). The fit at pH 7 consists of edge-sharing complexes alone, while the pH5 fit includes contributions from both edge and corner-sharing complexes. The presence of corner-sharing complexes at pH5 is indicated by an additional feature in the FT at  $R+\Delta = 3-3.3\text{Å}$ .

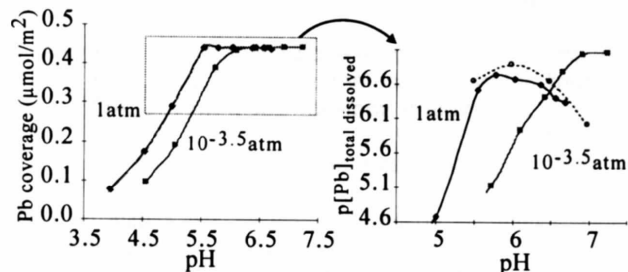
### 3.2 Carbonate effects

Macroscopically, Pb(II) uptake from solution onto goethite is enhanced below pH 6 and inhibited at higher pH by equilibration with CO<sub>2</sub> (Fig. 2). Decreased uptake at near-neutral pH is consistent with competition for Pb from dissolved Pb-carbonate complexes (see also [Smith and Langmuir, 1987]). Increased Pb uptake below pH 6 could result from either formation of a ternary surface complex with increased affinity for the goethite surface and/or by an indirect mechanism, such as alteration of the goethite surface charge by carbonate sorption.

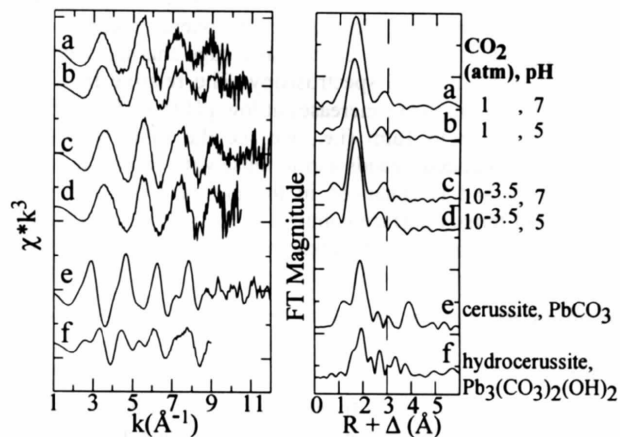
EXAFS data (Fig. 3) show no detectable effects of carbonate on the structure of Pb sorption complexes under all conditions studied. The relative abundance of edge- and corner-sharing Pb complexes in samples equilibrated with carbonate varies as a function of pH; pH5 samples have a larger contribution from corner-sharing complexes ( $R_{Pb-Fe} \sim 3.9\text{Å}$ ) than those prepared at pH7, which are dominated by edge-sharing complexes ( $R_{Pb-Fe} \sim 3.3\text{Å}$ ). These pH-dependent changes in Pb sorption complexes are the same as those observed in carbonate-free samples (cf. Fig. 1).

FTIR data show that an additional carbonate surface species arises in the presence of Pb and that the relative abundance of this surface species grows with increasing Pb coverage [Ostergren et al., 1998b]. The new carbonate species has a spectrum ( $\nu_3$  splitting) similar to that observed in Pb-free samples, which has been interpreted as carbonate bound in a monodentate fashion to

the goethite surface [Su and Suarez, 1997]. This suggests that the additional carbonate species observed in the presence of Pb in the present study is bound in a monodentate fashion to Pb. The fact that Pb uptake is enhanced (at pH  $\leq 6$ ) by carbonate further suggests that the additional species corresponds to a ternary surface complex with enhanced affinity for the goethite surface. EXAFS data suggest that this species is bound to the goethite surface through Pb forming a Type A ternary complex as defined by Benjamin and Leckie (1981) [i.e., surface-Pb-carbonate].

**Figure 2**

Pb uptake on goethite as a function of pH at 1 atm and  $10^{-3.5}$  atm P<sub>CO<sub>2</sub></sub>, with Pb uptake plotted as Pb coverage (left) and the final dissolved Pb concentration (right). All samples were prepared as goethite (45 m<sup>2</sup>/g) suspensions in 0.1 M NaNO<sub>3</sub>. Samples connected by solid line have a solids concentration of 3 g/l and  $10^{-2}$  M total Pb. Samples connected by dashed line (right) have a solids concentration of 5 g/l and  $10^{-4}$  M total Pb.

**Figure 3**

Pb  $L_{III}$ -EXAFS and Fourier transforms (FTs) of Pb sorbed to goethite at various pHs and carbonate conditions (partial pressures of CO<sub>2</sub> as listed). See Table 1 for detailed sample conditions, and Table 2 for EXAFS fit parameters. Spectra collected from pH7 samples (a,c,d) each show single second shells corresponding to edge-sharing complexes (Fe @ 3.30-3.34Å), whereas those collected at pH5 (b,e) show evidence for a combination of edge- and corner-sharing complexes (Fe @ ~3.9Å). Spectra of Pb-carbonate minerals (cerussite and hydrocerussite) are shown for comparison.

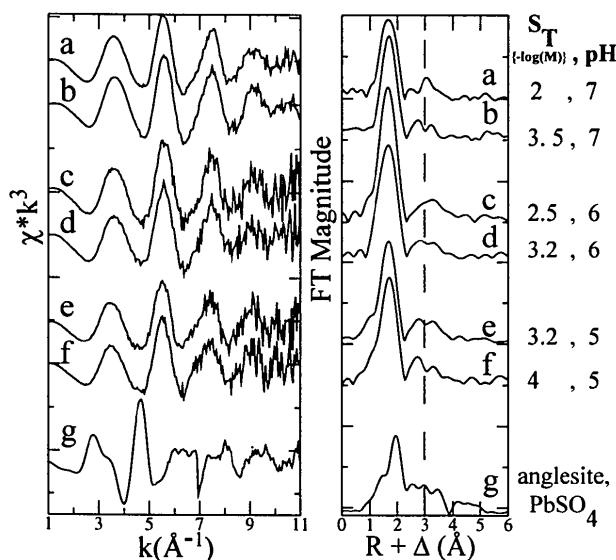
### 3.3 Sulfate effects

Pb uptake onto goethite is enhanced by sulfate at pH  $\leq 6$  for the solution conditions of our samples (see also [Balistreri and Murray 1982]). Changes in Pb  $L_{III}$ -EXAFS spectra with addition of sulfate are manifest as increased intensity of the Fourier transform feature at  $R+\Delta = 3-3.3\text{Å}$  with increasing sulfate concentrations (Fig. 4). In the pH6 and pH7 samples (Figs. 4a-b and 4c-d, respectively), these changes are observed quantitatively as an increase in the proportion of corner-sharing relative to edge-sharing complexes ( $N_{Pb-Fe, \text{corner-sharing}}/N_{Pb-Fe, \text{edge-sharing}}$ ) with increasing sulfate (Table 2). In contrast to the ligand-free and

carbonate-bearing systems, we observe no pH dependence in the relative contribution from this more distant corner-sharing Fe shell (cf. Fig. 4b, d, and e).

The growing preference for corner-sharing sites with increasing sulfate concentrations observed by EXAFS could plausibly result from either site blocking or ternary complex formation (a site blocking mechanism would, presumably, require that sulfate bind strongly in an inner-sphere mode as described by Hug [1997] and Eggleston et al. [1998]). FTIR data collected at pH 5 show growth of an additional sulfate surface species ( $\nu_3$  splitting) with Pb coverage. At pH 7, no changes in sulfate surface speciation were noted by FTIR with increasing Pb coverage [Ostergren et al., 1998b].

Given that sulfate enhances Pb uptake, it appears most consistent to interpret our EXAFS and FTIR data as evidence for a ternary surface-Pb-sulfate complex (a Type A species bound to goethite through corner-sharing Pb). While our EXAFS data could also be explained by sulfate acting to "block" Pb from preferred binding sites, this alternative mechanism is not expected to increase Pb uptake. Furthermore, a ternary complex directly explains the appearance of a new sulfate surface species in the presence of Pb (at pH5) as shown by FTIR spectra. Taken together, these data suggest that a sulfate ternary complex forms with Pb and that its relative abundance is greater in acidic than in neutral pH solutions.



**Figure 4**

Pb  $L_{III}$ -EXAFS and Fourier transforms (FTs) for Pb sorbed on goethite at pH and total sulfate concentrations ( $S_T$ ,  $-\log(M)$ ) indicated at right. See Table 1 for detailed sample conditions, and Table 2 for EXAFS fit parameters. Spectra collected at pH7 (a,b), pH6 (c,d), and pH5 (e,f) show increasing contributions from Fe at  $\sim 3.9\text{\AA}$  (corresponding to the FT intensity at  $R+\Delta \sim 3.3\text{\AA}$ ) with increasing concentrations of sulfate. No significant changes are seen in spectra as a function of pH at fixed  $S_T$  (cf. b, d, e). The spectrum and FT of the mineral anglesite ( $PbSO_4$ ) is shown for comparison.

#### 4. Summary

The findings of this work include:

1. Direct identification of changes in surface Pb(II) speciation as a function of pH. In particular, we find that corner-sharing complexes are more prevalent at low pH (5-6), whereas edge-sharing complexes dominate at neutral pH in the absence of sulfate and carbonate.

2. Confirmation of Pb(II) inner-sphere binding at sulfate and carbonate concentrations spanning conditions found in natural environments.
3. Increased affinity of Pb(II) for corner-sharing sites with increasing sulfate concentrations.
4. Appearance of additional carbonate and sulfate surface species upon addition of Pb(II).

These data provide useful constraints and guidance for understanding and modeling the molecular scale process of Pb(II) sorption. Our interpretations of Pb surface complexes forming in the presence of carbonate and sulfate draw upon a combination of complementary techniques including EXAFS, FTIR, and macroscopic uptake data. EXAFS spectra do not change in the presence of carbonate, whereas the relative fraction of Pb bound as corner-sharing complexes increases in the presence of sulfate. In both systems, enhanced Pb uptake and the appearance of additional ligand surface species detected by FTIR spectroscopy suggest formation of ternary surface complexes (i.e., surface-Pb-ligand).

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