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XAFS Studies of Pb(II)-Chloro and Hg(II)-Chloro Ternary Complexes on Goethite

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Abstract: EXAFS spectroscopy was used to study Pb(II) and Hg(II) adsorption complexes on goethite (α-FeOOH) in the presence of Cl^-. At pH 7, the dominant Pb(II) species are bonded to edges of FeO_6 octahedra and are similar to complexes that occur in the absence of Cl^-. At pH $\leq$ 6, Pb(II)-chloro ternary complexes predominate and are bonded to corners of FeO_6 octahedra. At pH 6.5, linear Hg(OH)Cl ternary complexes predominate that are bonded to goethite through surface oxygens in a bent Hg-O-Fe geometry. In the absence of Cl^-, the Hg(II) surface complexes retain this basic geometry, but an OH group replaces the chloride ion in the first coordination shell.

1. INTRODUCTION

The formation of Pb(II)-chloro and Hg(II)-chloro ternary adsorption complexes on Fe-oxide surfaces is believed to be an important control on the fate and transport of these toxic heavy metals in natural waters and sediments. XAFS spectroscopy is ideally suited for studing these adsorption products because it can be performed on wet samples at low sorption densities and provides quantitative structural and compositional information. Such information is of critical importance to accurately describing Pb(II) and Hg(II) speciation in natural environments.

2. EXPERIMENTAL

CO_2-free goethite (surface area 45 m^2/g), was equilibrated in CO_2-free 0.1 M NaCl solutions containing 0.24 - 4.42 mM $Pb(NO_3)_2$ at pH 6 - 8 for 24 - 36 hrs. Samples were subsaturated with respect to Pb(OH)Cl. Hg samples were prepared in 0.1 M $NaNO_3$ containing 0.75 mM $Hg(NO_3)_2$ at pH 3, 6.5 and 8; the pH 6.5 sample also contained 1.5 mM NaCl. Samples were centrifuged and supernatants were analyzed for dissolved metals. EXAFS data were collected from the remaining wet pastes at SSRL (3.0 GeV and 60 - 100 mA) on beamlines 6-2 and 4-3, which were equipped with Si (111) and Si (220) monochromator crystals, respectively. Harmonics were rejected using x-ray mirrors or detuning. Fluoresence-yield data were collected using a Lytle-type detector (Pb samples) and a Ge array detector at count rates of ≈ 40,000 cps (Hg samples).

Spectra were background-subtracted, spline-fit, k^3-weighted, and fit using EXAFSPAK (G. George, SSRL), and phase and amplitude parameters calculated by FEFF 5.0 [1] and calibrated against model compound spectra. The inflection points of simultaneously monitored Pb- and Hg-L_{III} foil edges were set at 13,055 eV and 12,285 eV, respectively.

3. RESULTS and DISCUSSION

3.1 Pb(II)/goethite samples

Results from EXAFS analysis of Pb/goethite samples are shown in Table 1. The 1st-shell results (2 - 3 oxygens at ≈ 2.3 Å) are typical of distorted trigonal-pyramidal Pb(II) coordination by three hydroxide ions or surface oxygens [2]. Fe atoms are present as 2nd-neighbors (Fig 1), and two Pb-Fe distances are observed; at pH 7 the higher-sorption-density samples show Pb-Fe ≈ 3.3 Å, which indicates sorption of Pb(II) to edges of FeO_6 octahedra [2]. In contrast, at pH 5, Pb-Fe ≈ 3.86 Å, which indicates adsorption to corners of FeO_6 octahedra. The samples in between show either one of these Pb-Fe distances or both. These observations suggest the existence of two Pb(II) surface species, each having a characteristic Pb-Fe distance, which coexist at intermediate pH and sorption density.

In a previous study of Pb(II) adsorbed on goethite and hematite in the *absence* of Cl^- (but at similar pHs and sorption densities) [2], only the 3.3 Å edge-sharing Pb-Fe distance was observed. Therefore, we ascribe the Pb-Fe ≈ 3.9 Å distance to Pb-chloro ternary complexes. Cl backscattering was not observed due to static and thermal disorder of Cl ligands and to destructive interference of backscattering with solvating water molecules. Comparison to Pb(OH)Cl(s) (trigonal pyramidal coordination of Pb(II) by OH), in which Cl backscattering was not detected for similar reasons, suggests that Pb-Cl ≥ 3.11 Å in the adion complexes. The observation that Pb(II)-chloro complexes adsorb in corner-sharing configurations instead of the preferred edge-sharing geometry implies that Cl^- ligands are interposed between Pb(II) and the surfaces, *i.e.*, Pb-Cl-Fe_{sfc} bonding occurs in addition to Pb-O-Fe_{sfc} bonding.

3.2 Hg(II)/goethite samples

The results from the quantitative analysis of the Hg L_{III} edge EXAFS data are summarized in Table 1, and the raw k^3-weighted EXAFS together with the Fourier transforms are presented in Fig. 2. The low first shell coordination numbers and Hg-O and

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Hg-Cl distances of 2.07 and 2.33 Å, respectively, are indicative of linear $Hg(OH)_2$ or Hg(OH)Cl surface complexes. In all samples a 2nd shell of Fe atoms is observed (Fig. 2) at 2.83 to 2.95 Å. In the *absence* of Cl^-, these short Hg-O and Hg-Fe distances suggest that Hg(II) coordinates to the surface in a predominantly monodentate, bent Fe-O-Hg geometry (Fe-O-Hg ≈ 113°). Structural considerations also suggest that a 2nd oxygen atom is present at 2.8 - 2.9 Å. However, these long Hg-O distances are approximately equivalent to the sum of the Van der Waals radii for Hg and O, and therefore should not be considered as directly bonded. In the *presence* of Cl^-, the non-surface OH^- ligand is replaced by Cl^-, and the Hg-Cl distance is in good agreement with the distance in $HgCl_2$(s). In contrast to Pb(II), the Hg-Fe distance is not significantly changed (neither is $R_{Hg\text{-}O}$), which indicates that Hg-chloro complexes are coordinated to goethite through surface oxygens (*i.e.*, Fe-O-Hg-Cl). It is clear that the adsorption products of the heavy metals Pb(II) and Hg(II) on goethite are structurally very different, both in the absence and presence of Cl^-. This is consistent with the very different coordination chemistries of Pb(II) and Hg(II).

Table 1. Results of numerical analysis of XAFS.

Sample*	Med.	N_O	R_O (Å)	σ^2	N_{Fe}	R(Å)	σ^2	N		R(Å)	σ^2
Pb(II)/ Goethite											
pH 5.03 Γ = 3.0	NaCl	2.1	2.28	0.010	††	††	††	0.4	Fe	3.86	0.01
pH 6.00 Γ = 2.2	NaCl	2.6	2.31	0.010	††	††	††	1.1	Fe	3.88	0.01
pH 6.01 Γ = 4.1	NaCl	2.1	2.33	0.010	0.3	3.36	0.01	0.3	Fe	3.92	0.01
pH 7.02 Γ = 2.0	NaCl	2.5	2.29	0.010	0.5	3.34	0.01	0.6	Fe	3.93	0.01
pH 7.01 Γ = 4.2	NaCl	2.9	2.26	0.010	0.7	3.32	0.01	††	††	††	††
pH 7.02 Γ = 5.0	NaCl	2.4	2.27	0.010	0.3	3.30	0.01	††	††	††	††
Hg(II)/ Goethite											
pH 3.0 Γ = 1.3	$NaNO_3$	1.3	2.07	0.002	0.5	2.95	0.006	††	††	††	††
pH 6.5 Γ = 1.3#	$NaNO_3$	1.6	2.07	0.002	0.7	2.88	0.007	0.4	Cl	2.33	0.006
pH 8.0 Γ = 1.3	$NaNO_3$	1.5	2.07	0.002	0.8	2.83	0.004	††	††	††	††

**Γ* is sorption density in units of μmoles/m^2. †† Not Fitted. #Prepared in presence of 1.5 mM NaCl.

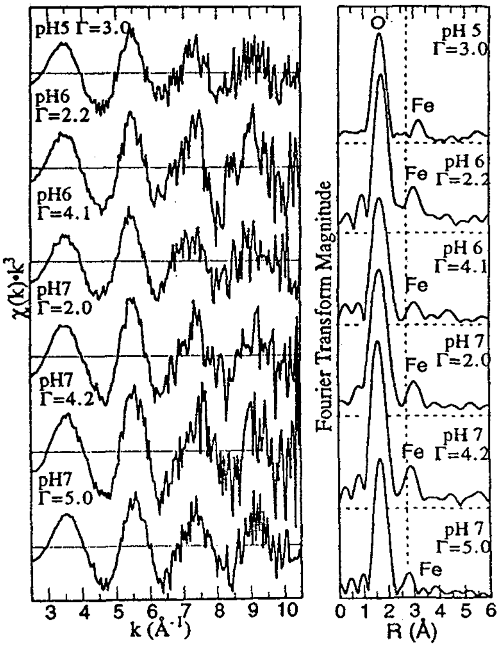

Figure 1: EXAFS and Fourier Transforms for Pb(II) samples.

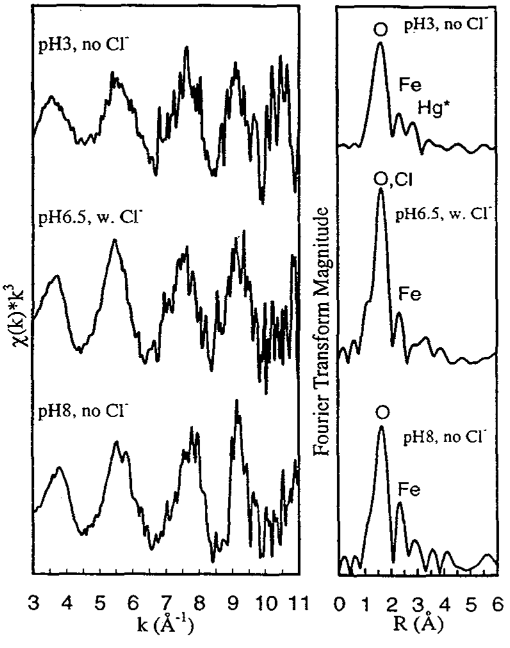

Figure 2: EXAFS and Fourier Transforms for Hg(II) samples.
*Due to presence of HgO(s).

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