XAFS Determination of Pb and Cd Speciation with Siderophores and the Metal/Siderophore/Kaolinite System

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Abstract. We provide evidence for hexadentate complexes of Pb2+ and Cd2+ with the trihydroxamate siderophore desferrioxamine B (DFO-B) at pH 7.5, and 9.0, respectively. Analysis of the species of Pb2+ and Cd2+ adsorbed at the surface of kaolinite clay under the same pH conditions and in the presence of DFO-B indicate that Pb2+ is sorbed as a metal-siderophore complex while Cd2+ is not.

Keywords: XAFS, siderophores, kaolinite, Pb, Cd, Ternary Complex
PACS: 61.10.Ht X-ray absorption spectroscopy: EXAFS, NEXAFS, XANES, etc.

INTRODUCTION

Siderophores are small organic molecules exuded by many microorganisms and plants to acquire Fe. In addition to having a high affinity for Fe(III), they can also bind a host of other metals [1]. Bulk studies have shown that siderophores affect the partitioning of toxic metals between solution and minerals surfaces [2,3]; however, spectroscopic studies are needed to better characterize the metal-siderophore adsorption complexes. This manuscript describes the metal (Cd; pH 9.0 and Pb; pH 7.5)-siderophore complexes present in solution and at the surface of the aluminosilicate clay mineral, kaolinite, providing a more molecular-scale understanding of the adsorption process.

METHODS

We used pre-washed [3] well-ordered kaolinite KGa-1b (Clay Minerals Society) and the commercially available trihydroxamate siderophore desferrioxamine-B (DFO-B; Sigma-Aldrich). Stock solutions of DFO-B were prepared in ultra-pure water; siderophore concentration quantified by total organic nitrogen analysis (Shimadzu TOC-V) and metals analyzed by ICP-OES (Perkin Elmer).

Metal-siderophore solutions were 20 mM in DFO-B and 10 mM in Cd or Pb (nitrate salts; Fisher Scientific). Solution pH values were adjusted to highlight various metal-siderophore complexes as predicted using PhreeqC [4] and published stability constants [5]. Adsorption of Pb and Cd to kaolinite in the presence of DFO-B was examined using 2.06 g/L clay, 240 μM DFO-B, 120 μM metal cation and 0.1 M NaClO4. Metal-siderophore solutions were adjusted to pH 4 prior to addition of clay, with subsequent pH adjustment to pH 7.5 (Pb) and 9.0 (Cd). Samples were shaken for 3 hour [3] then centrifuged to separate pastes. 12-17% of the nominal metal concentrations were sorbed for both metals.

XAFS measurements were performed at the MRCAT sector 10-ID beamline[6] at the Advanced Photon Source. The beamline optics and setup parameters for the Pb L(III) and Cd K edge XAFS measurements were as follows: The energy of the incident X-rays was scanned by using the (111) reflection of a cryogenically-cooled Si double-crystal monochromator. The beamline was optimized for 2nd and 3rd harmonic of the undulator for Pb and Cd measurements respectively. The undulator was optimized for 2nd and 3rd harmonic of the undulator for Pb and Cd measurements respectively. The undulator was tapered by approximately 2.5 and 3.5 KeV, respectively, to reduce the variation in the incident intensity to less than 15% over the scanned energy range. Higher harmonics were rejected using a Rh-coated mirror at the Pb edge and a Pt-coated mirror at the Cd edge. Gas(es) used in the I0 ion chamber were 40/60% He/N for Pb and 100% N for Cd measurements and Ar was used in both the transmitted and reference ion chambers in all analyses. The fluorescence detector in
the Stern-Heald geometry[7] was filled with Ar gas and an As filter of six absorption lengths was used to reduce the background signal at the Pb L edge. For the Cd K edge, Kr gas was used in the fluorescence detector and no filter was required. The incident X-ray beam profile was 1 mm square. Linearity tests[8] indicated < 0.1% nonlinearity for a 50% decrease in incident X-ray intensity. Scans were aligned by simultaneous collection of Pb or Cd foil data. The first inflection points were set to 13,035 (Pb) and 26,711 eV (Cd).

Quick scans (continuous scanning of the monochromator with signal sampled every 0.5 eV in the entire scanning range) were used with an integration time of 0.1 second per point. About 50 consecutive scans of each sample were averaged, and resulting data from all the samples were normalized and background subtracted using ATHENA[9].

The data were analyzed using codes from the UWXAFS package[10]. Data range used for Fourier transforming the $k$ space data was $2.3 - 9.8$ Å$^{-1}$. Hanning window function was used with a $\delta k$ of 1.0 Å$^{-1}$. Simultaneous fitting of the two data sets with multiple $k$-weighting ($k'_1$, $k'_2$, $k'_3$) of each spectrum was performed in $r$-space. The fitting range for the solution and solid data sets were set to 1.2 – 3.0 and 1.2 – 3.4 Å respectively.

RESULTS AND DISCUSSION

DFO-B has three hydroxamate groups (R-CONOH-R) and the proton associated with each of these groups can be exchanged to bind the central metal atom. Thus, the metal cation binds through the carbonyl and oxime oxygen atoms of one hydroxamate group (bidentate complex), through two groups (tetradeutate) or through all three groups (hexadentate). We determined which of these complexes occurred in solutions of Pb and Cd with DFO-B, at pH 7.5 and 9.0 respectively. Then, the species of each metal sorbed at the surface of kaolinite in the presence of DFO-B were examined at the same pH values.

Figures 1 and 2 show the comparison of $k^3\chi$ data for the Pb/DFO-B solution and the Pb/DFO-B/kaolinite ternary system at pH 7.5, and Cd/DFO-B solution and the Cd/DFO-B/kaolinite ternary system at pH 9.0, respectively. Magnitudes of the Fourier transform of Pb and Cd data sets and their fits are shown in Figures 3 and 4 respectively. In solution, EXAFS fits are consistent with “caged” hexadentate complexation of both metals by DFO-B. Fits for Pb$^{2+}$ were optimized with three paths: O$_1$ (shorter Pb-O interatomic distance), O$_2$ (longer Pb-O) and C/N. The best fit value for the number of closer oxygens O$_1$ of Pb/DFO-B solution was approximately 6. Because of the geometry of the siderophore, the coordination number for the C/N path was constrained to that of the O$_1$ path. The inclusion of O$_2$ significantly improved the fit (Table 1). Correspondingly, the best fit value for the coordination number of Cd-O and Cd-C/N (constrained) paths in the Cd/DFO-B system at pH 9.0 were 5.8 ± 0.3 (Table 1).

When sorbed, best fit values for Pb$^{2+}$ were obtained with 4.51 ± 0.8 Pb-O$_1$, at interatomic distance of 2.30 ± 0.01 Å, and second shells at 3.38 ± 0.03 Å for Al/Si and 3.15 ± 0.03 for C/N (Table 1). These results are consistent with Pb acting as a bridge between the mineral surface and the siderophore, and specifically with a bidentate edge-sharing inner-sphere complex between silanol/aluminol functional group and Pb$^{2+}$ and binding of the metal through one hydroxamate group.
Although not directly comparable due to differences in pH between the two systems, our results suggest that a different surface complex is formed in the Cd/kaolinite/DFO-B system than the one observed for Pb$^{2+}$. The data set was fitted with an O path of coordination number $5.4 \pm 0.3$ and an Al/Si path with fixed coordination number of 1 (Figure 4, Table 1). The absence of a C/N path suggests that Cd/DFO-B aqueous complexes do not adsorb to the surfaces of kaolinite. Rather, Cd$^{2+}$ appears to adsorb as a hydrated cation to active sites at the kaolinite surface.

In conclusion, we have provided direct evidence for hexadentate complexes of the siderophore DFO-B with both Pb$^{2+}$ and Cd$^{2+}$. However, under the conditions examined, a ternary complex was observed at the kaolinite surface whereby Pb$^{2+}$ bridges the clay surface and the siderophore molecule, while the same adsorption complex is not observed for Cd$^{2+}$.

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**REFERENCES**