

EXPERIMENTAL STUDIES OF ALUMINOUS GOETHITE NANO/MICRO  
MINERAL STRUCTURE AND INTERACTIONS BETWEEN AQUEOUS METAL,  
SIDEROPHORES, BACTERIA AND MINERAL SURFACES

ABSTRACT

By

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The studies presented in this dissertation have been focusing on utilizing advanced microscopy (TEM), diffraction and spectroscopy techniques (XRD, PDF, ICP-OES, and XAFS), in tandem with quantitative analysis and modeling to study the interactions between aqueous metals and geological and biological surfaces and interfaces as well as the structure of aluminous goethite micro/nano minerals.

We measured the valence state and speciation of the Au that was removed from Au(III)-chloride solutions by non-metabolizing Gram-positive *Bacillus subtilis* and Gram-negative *Pseudomonas putida* cells. XANES and EXAFS measurements were conducted on Au-bacteria samples as a function of pH at two different Au loadings. Additionally, Au- *B. subtilis* exudates samples were also examined by using XANES. XANES spectra of Au-bearing solutions that contained *B. subtilis* exudates suggest that

bacterial exudates are capable of reducing Au (III) to Au (I) at circumneutral pH (pH 5.8) but not under low pH (pH 3.3) conditions. In addition, the EXAFS data suggest that Au on the *B. subtilis* and *P. putida* cell walls is present almost exclusively as Au(I) bound to a mixture of amine/carboxyl sites as well as to sulfhydryl functional groups. The relative importance of the sulfhydryl groups increases with increasing pH and with decreasing Au loading on the cell walls. The coordination numbers for all of the biomass samples studied here are consistent with bidentate binding of Au on the bacterial cell walls, and the bond distances indicate inner-sphere binding of the Au.

In addition, we investigated the effects of pH, ionic strength, and the siderophore desferrioxamine on Cd sorption to montmorillonite using batch experiments, EXAFS analysis, and XRD measurements. The extent of Cd sorption to montmorillonite increased with increasing pH and decreasing ionic strength. The presence of DFOB inhibited Cd sorption at  $\text{pH} < \sim 7$  and enhanced Cd sorption at  $\text{pH} > \sim 7$ . Sorption densities ranged from 1.1 (11% sorption) to 10.0 (100% sorption)  $\mu\text{mol sorbed/gram of clay}$ . EXAFS analysis showed that the detailed sorption mechanism varied as a function of pH, ionic strength and DFOB concentration (0 or 1.0 mM). In the absence of DFOB, at low pH ( $\sim 5.0$  for samples in 0.1M  $\text{NaNO}_3$  and  $\sim 5.0$  and  $\sim 7.5$  for samples in 0.01M  $\text{NaNO}_3$ ), EXAFS showed that Cd sorbed outer-spherically; at higher pH ( $\sim 7.5$  and  $\sim 8.5$  for samples in 0.1M  $\text{NaNO}_3$  and 8.5 for samples in 0.01M  $\text{NaNO}_3$ ), Cd sorbed as a mixture of inner-sphere and outer-sphere complexes. In the presence of DFOB, at pH  $\sim 5.0$ , Cd sorbed outer-spherically; at pH  $\sim 7.5$  and 8.5, Cd sorbed as a mixture of inner-sphere and outer-sphere Cd-DFOB complexes. Furthermore, the ratio between inner-sphere and outer-sphere sorption increased with both pH and ionic strength. XRD measurements

indicate that layer spacing did not vary substantially as a function of Cd concentration, ionic strength, or pH. However, in the presence of DFOB, the d-spacing expanded by  $\sim 2\text{\AA}$ , which is consistent DFOB absorption.

Furthermore, aluminous goethite nano/micro particle samples with several mol% Al were investigated by Fe K edge EXAFS and x-ray diffuse scattering with PDF analysis. The results indicate that Al uniformly incorporated into the goethite crystal structure in all samples, with no separate Al (hydr)oxide phase observed. Additionally, the lattice parameter decreases with increasing Al incorporation, which is consistent with smaller Al atoms replacing Fe. EXAFS data demonstrate Al incorporation does not change the coordination environment of the three nearest O shells around Fe. The more distant Fe shells are significantly affected, however, consistent with the change in bond lengths around individual incorporated Al atoms.