Pb speciation in the presence of siderophores and clay surfaces – XAFS study

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Although siderophores are low molecular weight organic ligands produced by microorganisms to acquire Fe, the ligands also have high binding affinities for other metals, such as Pb. This work is part of a larger project by our group that has examined the impact of the trihydroxamate siderophore DFO-B on Pb sorption to kaolinite. Results indicate that the presence of DFO-B affects the partioning of Pb from the aqueous to the solid phase; Pb adsorption is enhanced in the presence of DFO-B around pH 5-6 and is inhibited at pH values > 6.5.

To better understand these results, we measured Pb speciation at the molecular level, using x-ray absorption spectroscopy (XAFS), in the mixed Pb-DFO-B (aqueous phase), Pb-kaolinite (solid phase), and Pb-kaolinite-DFO-B (solid phase) systems at pH 4, 6 and 7.5. XAFS results confirm that pH affects the coordination environment of Pb complexed by DFO-B in solution, and XANES suggests a change in chemical state between complexes. At the kaolinite surface, Pb is sorbed dominantly as a Pb-DFO-B complex at pH $\geq$ 5. Further, the extent of Pb sorption at pH 6 exceeded that at pH 7.3 in the mixed Pb-kaolinite-DFO-B solid phase as measured by X-ray fuoresence, in agreement with the results of the bulk adsorption study. Comparison of the three different phases suggests that the mixed Pb-kaolinite-DFO-B solid phase is not a simple linear combination of the solid Pb-kaolinite and Pb-DFO-B aqueous phase at any of the pH values examined. Taken together, bulk adsorption measurements and XAFS experiments represent a powerful approach for determining metal speciation and refining existing models of metal distribution at water-rock interfaces.

Effect of synthetic and biogenic surfactants on iron oxide dissolution

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Bio-surfactants are released by microorganisms and plants into soils and sediments. They modify the properties of solid/water interfaces and facilitate microbial attachment (biofilm formation) or nutrient acquisition. We have investigated the effect of synthetic and biogenic surfactants on the physico-chemical properties of iron oxide (goethite) surfaces, on the adsorption of organic ligands, and on ligand controlled weathering. The ligands chosen for this investigation included microbial siderophores and other common biogenic low molecular weight organic ligands. They were selected for their significance in biogeochemical processes in natural systems and for their contrasting properties regarding charge and hydrophobicity.

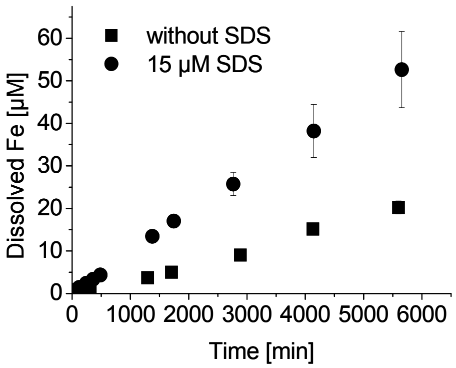

Figure 1: Dissolution of goethite in presence of 80 µM DFOB with and without SDS.

We observed slow adsorption kinetics of surfactants on goethite surfaces. Adsorption rates increased with increasing surface charge and with increasing surfactant concentrations. Adsorption of surfactants had a strong effect on the mineral surface charge as indicated by electrophoretic mobility measurements. Surface charge reversal at pH 6 was observed in adsorption equilibrium with very low surfactant concentrations in the micromolar range. In this low concentration range, we observed a significant effect of surfactants on the adsorption of the microbial siderophore DFO-B and on the rates of ligand (i.e. DFO-B) controlled dissolution (figure 1). These observations indicate that even low concentrations of surfactants can have a significant effect on important biogeochemical processes including nutrient acquisition and mineral weathering.