Fate of arsenic during sulfidation of Fe^{III}-(oxyhydr)oxides

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The fate of arsenic (As) in the environment is controlled in part by the biogeochemistry of iron (Fe) and sulfur (S) via sorption onto iron-(oxyhydr)oxides, incorporation of As into metal sulfides and/or sorption on Fe-sulfide minerals surfaces. In subsurface environments, redox conditions can change from oxic to anoxic and may trigger microbial sulfate reduction, which can cause transformation of Fe^{III}-(oxyhydr)oxides to Fe^{II}-sulfides, result in sorption of As, and/or trigger reactions of As with dissolved sulfide. Dissolved sulfide is able to reduce As^{V} to As^{III} and also forms more mobile complexes, including thio-As species, triggering partial mobilization of As. In addition, aqueous sulfide may promote As sequestration into As-sulfide minerals such as realgar (AsS), orpiment (As_2S_3), arsenopyrite, and Fe-sulfide minerals in the presence of Fe. The rate and kinetics of As reduction and transformation in these systems thus depends on the availability of dissolved sulfide. Understanding this reaction is critical in determining whether or not the released As will remain mobile in the subsurface. The fate and speciation of As in sulfidic systems with high Fe, remain unresolved.

We conducted batch experiments focusing on the reaction between As^{V}-bearing (125 μmol/g) ferrihydrite or goethite nanoparticles with dissolved sulfide at various S/Fe ratios (0.1 upto 2) at pH 7. The Fe^{III}-(oxyhydr)oxides were selected because both are dominant sinks of As in the environment and, owing to their crystalinity differences, have markedly different reactivity toward dissolved sulfide. We used x-ray absorption spectroscopy at the Fe-, S-, and As-K-edges to examine the transformation and reductive dissolution of As-bearing ferrihydrite/goethite nanoparticles and subsequent As repartitioning amongst secondary phases during this reaction. The aqueous speciation of Fe, As and S were also determined. Experimental results will be reported and discussed during the presentation.