

Behavior of As(III) and As(V) during Ferrihydrite Sulfidation

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The mobility and release of As in the environment is influenced by Fe and S redox cycling. Reducing environments promote As release through reductive dissolution of Fe(III)-(oxyhydr)oxides. However, in the presence of dissolved sulfide, As can form thiol species and/or be re-sequestered by sorption to Fe-S minerals, such as mackinawite and pyrite. The sorption behavior is different for thiolated vs. oxoanions of As and As sorption to Fe(III)-(oxyhydr)oxides also differs mechanistically from that to Fe-sulfide minerals. The reductive dissolution of Fe(III)-(oxyhydr)oxides and subsequent Fe-S precipitation is controlled by S/Fe ratios, but the effect of sulfidation on the fate and speciation of As is poorly understood.

The primary aim of this study was to investigate the fate of surface sorbed As in sulfidic environments. We added various amounts of dissolved sulfide (0.1-2 S:Fe mass ratios) to abiotic batch reactors containing As(III)- or As(V)-bearing ferrihydrite nanoparticles at pH 5. Using x-ray absorption spectroscopy at the As-, Fe-, and S-K-edges, we examined the oxidation state and solid phase transformations. Ion chromatography coupled with mass spectroscopy was used to quantify soluble As species. We found that sulfide addition produced solid and aqueous phase thio-As species in both the As(III)- and As(V)-bearing ferrihydrite systems. Furthermore, As impacted solid phase Fe-S speciation and decreased the reductive dissolution of Fe(III) from ferrihydrite. These results underline the importance of thio-As and S:Fe ratios in defining the fate of As under reducing conditions. Such information is needed for improved predictions of the fate of As in acid mine drainages and other redox-sensitive environments.

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