Sorption of antimony(III) and antimony(V) to mackinawite (FeS)

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The mobility of toxic antimony (Sb) in soils and sediments is largely controlled by sorption to mineral surfaces [1]. While iron oxides are important in oxic environments, iron sulfides dominate in sulfur-rich anoxic environments. The initial iron sulfide produced by reaction between iron (Fe) and sulfide (S^{2-}) under most environmental conditions is nanocrystalline mackinawite (FeS) [2]. Over time, FeS transforms to more stable Fe sulfides, such as greigite (Fe_3S_4) and pyrite (FeS_2). This reaction may be enhanced in the presence of pentavalent Sb, since Sb(V) may oxidize structural Fe(II), thereby forming greigite [3]. Except for one preliminary study [3], Sb geochemistry in sulfidic solutions in the presence of Fe has not yet been examined. This lack of knowledge hampers reliable risk assessments for Sb-contaminated soil, sediment and groundwater systems and constrains the development of optimal remediation strategies.

Here, we investigate Sb sorption to FeS as a function of Sb species, pH, reaction time and Sb loading. Various concentrations of either Sb(III) or Sb(V) (2 mM, 10 mM and 50 mM) were added to FeS and allowed to react for 24 hours. The pH was varied between pH 5 and 10 and selected treatments were equilibrated for periods of up to three months.

First results show that 80% of the added Sb(III) sorbed to FeS in the studied pH range after 24 hours. In contrast, Sb(V) substantially (>20%) bound to FeS only at pH <6. The initial Sb concentration did not affect this pattern. Sorption of Sb(III) to FeS reached equilibrium after 24 hours. When Sb(V) was spiked, equilibrium concentrations did not establish within three days, which may point at structural transformations of the FeS phase after reduction of Sb(V). X-ray absorption spectroscopy (XAS) experiments are yet to be completed to determine the valence and coordination environment of the sorbed Sb and to characterize structural changes in the solid phase.

[1] Wilson *et al*. (2010) *Env. Pol*. **158**, 1169–1181. [2] Rickard & Morse (2005) *Mar. Chem*. **97**, 141-197. [3] Kirsch *et al*. (2008) *Mineral. Mag*. **72**, 185-189.