Sb release and Fe transformations during sulfidization of Sb(V)-bearing ferrihydrite

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Iron (Fe) (hydr)oxides are important host phases for antimony (Sb), a toxic metalloid of environmental concern. In wetland soils and sediments, poorly ordered Fe (hydr)oxides such as ferrihydrite may undergo reductive dissolution upon reaction with dissolved sulfide (S(-II)) [1]. This reaction involves the production of aqueous Fe(II), which can interact with excess S(-II) to precipitate as nano-crystalline mackinawite (FeS) or with the existing Fe(III)-(hydr)oxides to facilitate their transformation and recrystallization. Dissolved S(-II) may also react with Sb to form soluble thioantimony species. The net effect of these reactions on the mobility and speciation of Sb remains unknown.

Here, we subjected Sb-rich ferrihydrite (2,800 μg Sb g^{-1}) to abiotic reactions with three levels of S(-II) (Fe:S(-II) = 0.2, 0.5, and 1) at pH 6 and 8 and studied the speciation and concentration changes of Fe, S, and Sb over 32 days through a combination aqueous phase, wet chemical extraction and synchrotron X-ray techniques. Due to the nanocrystalline nature of FeS, the colloidal fraction (i.e. 3 kDa to <0.45μm) was separated and included in the analyses.

Addition of sulfide caused an immediate reduction of Fe(III) and the precipitation of FeS under S(-II) excess, followed by a slow transformation of the Fe phases to mostly goethite and pyrite. The rapid reduction was paralleled by a fast release of Sb into the aqueous phase. This mobilization was followed by an Sb immobilization caused by the structural incorporation and re-adsorption of Sb to the neo-formed Fe (hydr)oxides. Antimonate was the primary Sb aqueous phase species throughout the experiment with negligible contribution of thiolated Sb. In contrast, up to 40% and 20% of solid-phase Sb was present as Sb(III) at pH 6 and 8, respectively. At pH 8 and medium to high S(-II) additions, ~15% of the aqueous phase Sb was associated with colloidal FeS, while no colloidal Sb was found in all other treatments.

Our results provide first insights into the co-evolution of Fe mineralogy and Sb mobility in sulfidic environments.

[1] Poulton *et al*. (2004) *GCA* **68**, 3703−3715.