Antimony mobility and influence on iron(II)-catalyzed ferrihydrite transformation pathways

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The mobility of antimony (Sb), a toxic metalloid of increasing environmental concern, is largely controlled by sorption to iron (Fe) oxides. In wetland soils and sediments, Fe(II) may accelerate the transformation and crystallization of poorly ordered Fe oxides such as ferrihydrite to more stable phases. These changes in Fe oxide mineralogy can cause major shifts in the number of sites available for surface complexation and may thus affect the partitioning and bioavailability of associated Sb.

Here, we investigated Sb partitioning during the Fe(II)-induced transformation of Sb-bearing ferrihydrite across a range of Sb(V) loadings (molar ratios of Sb:Fe = 0.003, 0.016 and 0.08) at pH 7. Changes in Fe mineral assemblages and Sb sorption mechanisms were evaluated using extended X-ray absorption fine structure (EXAFS) spectroscopy, powder X-ray diffraction (XRD) and wet chemical extraction techniques.

Addition of Fe(II) induced the rapid conversion of ferrihydrite via metastable lepidocrocite to goethite at low and medium Sb loadings. The highest Sb:Fe ratio favored the formation of feroxyhyte from precursor ferrihydrite. The transformation of ferrihydrite was faster in the presence of Sb compared to no-Sb control treatments and was paralleled by a decrease in aqueous and phosphate-extractable Sb concentrations. EXAFS shell-fit analyses revealed that this Sb immobilization was attributable to the incorporation of Sb into the structure of the neo-formed Fe oxides.

Our results are important for a robust understanding of Sb geochemistry in redox-dynamic environments as they demonstrate that Sb itself influences the pathways and kinetics of Fe oxide transformations. This study also suggests that Fe oxide transformation pathways in Sb-contaminated systems may differ strongly from the well-known pathways that occur under Sb-free conditions.