Thick as thieves: Antimony sequestration during ferrous iron oxidation

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The geochemical behavior of antimony (Sb), a priority pollutant of increasing concern, is closely linked to the redox cycling of iron (Fe). Microbial reduction of Fe(III) oxides and production of soluble Fe(II) under anoxic conditions has been shown to release co-associated Sb (occurring as Sb(V) and/or Sb(III)). In redox-dynamic environments, Fe(II) can be re-oxidized and precipitate as Fe(III) oxides. The extent to which these processes affect Sb mobility, however, is still poorly understood and likely depends on an array of factors such as pH, Sb species and the nature of the newly formed Fe(III) oxides.

Here, we investigated the effect of Fe(II) oxidation on Sb sequestration and on the mineralogy of the resulting Fe(III) precipitates in a pH range typical of Sb-contaminated systems (i.e., pH 6, 6.5, and 7). To initiate the oxidation reaction, 0.5 mmol L⁻¹ Fe(II) was added to an oxygen-saturated electrolyte solution containing 0 – 50 µmol L⁻¹ Sb(V) or Sb(III). Changes in aqueous Sb and Fe(II) were tracked during the experiments, and solid phase samples were collected at the end of the oxidation reaction for characterization by diffractometric, spectroscopic, and microscopic techniques.

Iron(II) oxidation kinetics and Sb sequestration varied with pH and Sb species, with Sb(III) retarding the oxidation reaction. In the absence of Sb, Fe K-edge X-ray absorption spectroscopy (XAS) analysis revealed lepidocrocite as the only solid-phase product. In the presence of Sb, ferroxyhyte and goethite formed instead of lepidocrocite. The shift in Fe(III) oxide assemblage was more pronounced when Sb was present as Sb(V) and at a lower pH. Antimony K-edge XAS spectra showed an almost complete oxidation of Sb(III) to Sb(V) followed by the incorporation of Sb(V) into the structure of the Fe(III) oxide precipitates.

Our results allow for a better understanding of Sb geochemistry in redox-dynamic environments as they demonstrate that Sb itself can influence the pathways of secondary Fe(III) oxide formation. Our study also provides important information for the development of appropriate remediation practices for Sb-contaminated soils and sediments that are subject to changes in redox conditions as induced by flooding or waterlogging.