

Fe(II) oxidation in the presence of Sb(V): Mutual effects on Fe(III) precipitates and Sb sequestration

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In redox-variable environments, the mobility of antimony (Sb), a toxic metalloid of increasing concern, is closely linked to the biogeochemical cycling of Fe. Antimony has a high affinity for Fe(III) oxides, and microbial production of soluble Fe(II) has been shown in various studies to release co-associated Sb under anaerobic conditions. In contrast, the Sb-Fe interactions during aerobic Fe(II) oxidation and subsequent Fe(III) precipitation have received little attention.

Here, we investigated the effect of Fe(II) oxidation in the presence of a range of environmentally relevant Sb(V) concentrations on the nature of the resulting Fe(III) precipitates and on coupled sequestration of Sb. All oxidation experiments were carried out in oxygen-saturated buffer solutions (pH 7) containing an initial Fe(II) concentration of 1 mM and Sb(V) at Sb:Fe molar ratios of 0, 1:100, 1:25, 1:10, and 1:4. After Fe(II) oxidation was complete, solid phase samples were characterized using a combination of spectroscopic, microscopic, and wet chemical extraction techniques.

In the absence of Sb(V) and at low levels of Sb(V), X-ray diffractometry and transmission electron microscopy revealed lepidocrocite as the only solid-phase Fe(II) oxidation product. In contrast, higher Sb:Fe molar ratios (1:10 and 1:4) inhibited lepidocrocite precipitation, and instead resulted in increasing formation of feroxyhyte – a rarely reported FeOOH polymorph. Phosphate-extractions suggested that >99% of the sorbed Sb was incorporated into the structure of the precipitated Fe(III) oxides. Our findings were confirmed by ⁵⁷Mössbauer spectroscopy, which showed a paramagnetic doublet with hyperfine parameters characteristic of lepidocrocite and a sextet indicating the presence of feroxyhyte. However, the hyperfine magnetic field of feroxyhyte (33 T) was substantially less than the magnetic field of pure feroxyhyte (46 T), and showed a strong asymmetric line broadening, which is consistent with incorporation of diamagnetic Sb(V).

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