

## Interactions of vanadium(V) with iron(II)/(III)-bearing minerals

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Fe(II)-bearing minerals (green rust, magnetite, siderite, etc.) provide a reservoir of reducing capacity in many subsurface environments that may contribute to the reduction of redox active contaminants such as vanadium, which can exist as V(V), V(IV), and V(III) under conditions typical of near-surface environments. We examined the interactions of V(V) (1 mM) in aqueous suspensions containing 50 mM Fe(II) as magnetite, sulfate green rust (GR), or biogenic carbonate green rust (BioGR, formed during the bioreduction of lepidocrocite by *Shewanella putrefaciens* CN32) using X-ray absorption fine-structure spectroscopy (XAFS) to determine the valence state and chemical speciation of V.

Within 48 h, total solution-phase V concentrations decreased to <15  $\mu$ M, corresponding to >98% uptake by the solids. Analysis of these solids by V K-edge X-ray absorption near edge structure (XANES) spectroscopy indicated 60% reduction of V(V) to V(III) within 2 days by GR, and 100% reduction within 3 months. Reduction of V(V) by BioGR was slower and less extensive, with 28%, 60%, and 83% reduction to V(III) at 2 days, 3 months, and 7 months, respectively. Given the different synthesis routes, it is not clear if the difference in reactivity between the GR and BioGR is due to the different interlayer anions (sulfate vs carbonate) or some other factor. Magnetite was even less reactive than either green rust, showing 16%, 35%, 55%, and 77% reduction at 2 days, 3 months, 4 months, and 7 months, respectively.

Preliminary analysis of V K-edge extended X-ray absorption fine structure (EXAFS) spectra of the solids suggests that the V(III) in the GR and BioGR systems is present as either a well defined V mineral phase or is incorporated into the structure of an Fe mineral. In contrast, the V(III) in the magnetite systems appears to be present as a complex (i.e., not as a discrete precipitated bulk phase). Further refinement of the analysis of the EXAFS spectra is ongoing.