

Microbial mineral transformations in the Fe(II)-Fe(III)-H₂O system

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The Fe(II)-Fe(III)-H₂O system is of particular geomicrobiological interest owing to the behavior of iron in energy metabolism, depending on oxidation state, as either an electron donor or an electron acceptor. This means that iron is not only subject to intense biogeochemical cycling in nature, but also plays a critical role in the cycling of other elements such as carbon and oxygen. Apart from redox stability in Eh-pH space, another important feature of iron biogeochemistry is the limited solubility of Fe(II) and Fe(III). Of the two redox species, Fe(III) is particularly sensitive to hydrolysis and precipitation, which contributes to its behavior as a strong oxidant (i.e., electron acceptor) under reducing conditions. On the other hand, in anaerobic sulfide-rich environments Fe(II) tends to form insoluble sulfide phases (e.g., pyrite, mackinawite), or mixed oxide phases (e.g., hematite, green rust) under non-sulfidogenic conditions. These solubility constraints promote a wide range of mineral transformations owing to metabolic exploitation of the Fe(II)-Fe(III) redox couple by bacteria. Interesting examples include the oxidative dissolution of Fe(II)-sulfides in mine wastes by bacteria, which gives rise to Fe(III)-hydroxy sulfates such as jarosite, and formation of green rust in response to reductive dissolution of hydrous Fe(III)-oxide. More recent studies have focused on oxidation of dissolved Fe(II) at circumneutral pH where bacteria must compete efficiently with chemical oxidation to generate energy for growth. In most situations the Fe(II)-Fe(III) mineral transformation reactions proceed in association with bacterial cell surfaces. This frequently results in the preservation of fully mineralized, structurally intact cells that resemble microfossils in ancient sedimentary rocks. The implication is that microbial mineral transformations in the Fe(II)-Fe(III)-H₂O system have contributed to biogeochemical cycling over a considerable period of Earth history.

Microbial transformation of AQDS, Fe(III), Cr(VI), and U(VI) by a novel *Clostridiales*, Strain UFO1

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The activities of metal-reducing microorganisms offer potential bioremediation strategies for the immobilization of toxic metals in the environment. Strain UFO1 was isolated under strictly anaerobic conditions from an enrichment established with pristine sediment from the NABIR Field Research Center in Oak Ridge, TN on acetate and 2-line ferrihydrite. Strain UFO1 appears to be a novel genus within the bacterial order *Clostridiales*. Direct reduction of Fe(III)-nitrilotriacetic acid occurred in the presence of lactate. Additionally, strain UFO1 reduced the humic acid analog anthraquinone-2,6-disulfonate (AQDS) to its reduced form, AH₂DS, using a variety of electron donors including lactate and H₂. Ferrihydrite was not directly reduced in the absence of an electron-shuttling moiety. Synchrotron-XPS spectra revealed the mineral transformation of ferrihydrite from Fe(III) to Fe(II) by a culture of UFO1 containing lactate and AQDS, suggesting that the reduction of insoluble Fe(III) was shuttle-mediated. Reduction of 1, 3, and 5 ppm Cr(VI) occurred within 24 hours using lactate; in the presence of 1 mM AQDS, 3 and 5 ppm Cr(VI) were reduced to 0.1 ppm within 2 hours. Whereas Cr(VI) was directly reduced by UFO1, results suggest that UFO1 cannot directly reduce U(VI) in the absence of AQDS. U(VI) and phosphate profiles suggested however that UFO1 could immobilize U(VI) as uranyl phosphate. Fluorescence microscopy using exopolysaccharide (EPS)-specific probes showed colonization of ferrihydrite by UFO1, with copious EPS, suggesting an EPS-mediated cell-mineral association. The reduction of AQDS, Fe(III), and Cr(VI) and precipitation of U(VI) suggest a potentially important role for strain UFO1 in the biogeochemistry of pristine and contaminated geologic media at the Field Research Center.