



Indirect microbial ferric iron reduction via sulfur cycling

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Observations in freshwater enrichment cultures under ferric iron-reducing conditions indicated that ferrihydrite was reduced to ferrous iron via sulfur cycling with sulfide as the reductant: Even after repeated transfers, whitish ferrous iron minerals (siderite and vivianite) that formed during complete reduction of 5 to 10 mM of ferrihydrite were accompanied by traces of black ferrous monosulfides. To explore a possible reduction of ferrihydrite to siderite and vivianite via sulfur cycling in greater detail, experiments were conducted with a pure culture of *Sulfurospirillum deleyianum*. This organism was isolated as sulfur-reducing bacterium and was unable to reduce ferric citrate or ferrihydrite directly. However, with low thiosulfate concentrations, growth with ferrihydrite was possible via sulfur cycling. Due to the low concentration of thiosulfate only little sulfide was produced by *S. deleyianum*. In addition, spatially distant ferrihydrite that was embedded in 1% agar was available as electron acceptor. The low concentration of sulfide allowed the delivery of electrons to ferrihydrite with no or only little formation of ferrous sulfides. Ferrous iron and oxidized sulfur species were produced instead, and the latter served again as electron acceptor for *S. deleyianum*. Due to the enzymatic specificity of the bacterium, elemental sulfur and possibly traces of thiosulfate are the oxidized sulfur species. We suggest that diffusible sulfur species can act as electron shuttles between bacterial cells and ferric iron oxides in natural environments. Particularly in freshwater habitats with small pools of available sulfur, bacteria may funnel electrons to abundant reservoirs of ferric iron oxides by means of sulfur cycling. Preliminary results of microcosm experiments inoculated with freshwater sediments indicated that the addition of low concentrations of sulfur compounds can indeed stimulate reduction of ferrihydrite.