# Active bacterial Mn(II)-oxidation accelerates Cr(III) oxidation compared to abiotic oxidation by Mn oxide minerals

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Bioremediation through reduction has been suggested as a cost-effective and non-invasive way to immobilize and detoxify Cr(VI) contamination. However, the long term immobilization of environmental Cr(VI) contamination by reduction to Cr(III) may be hindered by the presence Mn oxides, the only known environmental oxidants of Cr(III). Previous work has used rates of Cr(III) oxidation by well-characterized Mn oxide minerals to predict the potential for Cr(III) re-oxidation. Because bacteria are known to catalyze the rapid oxidation of Mn(II), forming reactive amorphic oxides, we hypothesized that Mn(II)-oxidizing bacteria would accelerate Cr(III) oxidation.

*Bacillus sp*. strain SG-1 is a marine bacterium whose spores oxidize Mn(II) to Mn(IV) via a multicopper oxidase-like enzyme located on its spore coat. Previously this bacterium has been shown to oxidize Mn(II) through two sequential one-electron transfers, resulting in an Mn(III) intermediate before formation of Mn(IV). Additionally, the Mn(II)-oxidizing enzyme is thought to be somewhat non-specific, leading to the possibility that Cr(III) could be directly oxidized by Mn(II)-oxidizing bacteria.

Incubation experiments with SG-1 showed that rates of Cr(III) oxidation during active Mn(II) oxidation by this bacterium are much faster than those by either biologically formed or abiotic Mn oxides. These results indicate that the process of bacterial Mn(II) oxidation may be more important in Cr(III) oxidation than the Mn oxide minerals that are produced. Although it acts competitively at higher amounts, our experiments show that some Mn is required for Cr(III) oxidation, ruling out direct oxidation by the Mn(II)-oxidizing enzyme. Abiotic experiments with Mn(III) compounds did not result in Cr(III) oxidation, while incubations with a colloidal Mn oxide resulted in rapid Cr(III) oxidation, suggesting that it is likely the Mn(IV) immediately produced by bacteria that is reacting with Cr(III). Possible explanations for the reactivity of the Mn(IV) product may be that the smaller particles are more reactive, or that the Mn oxide minerals are quickly passivated by sorption of other chemicals to their surfaces.

# Dependence of microbial dissimilatory U(VI) reduction on U(VI) chemical speciation

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Predicting how bacteria in natural systems can influence uranium (U) biogeochemistry depends on an accurate understanding of how the enzymatic reactivity of U(VI) varies according to its chemical form. In this study we present the results of laboratory experiments demonstrating the dependence of microbial dissimilatory reduction rates on the speciation of U(VI) both in aqueous solution and as U(VI) surface complexes on selected metal oxides. The facultatively aerobic bacterium *Shewanella putrefaciens* was used as a model metal-reducing organism, and U(VI) was supplied as sole terminal electron acceptor in a defined minimal medium under strictly anaerobic conditions. Uranium was provided either in the form of dissolved organic complexes with a series of low-molecular weight organic ligands (oxalic, malonic, succinic, glutaric, adipic, pimelic, citric, NTA, EDTA, tiron, and humic acid), or as adsorbed surface complexes on amorphous silica ($SiO_2$), corundum, ($Al_2O_3$) and anatase ($TiO_2$). Experimental results illustrate that the reductive bioavailability of U(VI) to *S. putrefaciens* depends strongly on the structure and stability of available U(VI) species. Rates of microbial U(VI) reduction under the experimental conditions varied systematically as a function of the stability of aqueous U(VI) complexation, with more stable aqueous U(VI)-organic complexes resulting in slower rates of U(VI) bioreduction. Strong aqueous chelation of U(VI) effectively suppresses bioreduction. If U(VI) is supplied in the form of adsorbed surface complexes, the properties of the adsorbing surface and the resulting adsorbed complexes has a governing effect on microbial reductive availability. For example, adsorption of U(VI) onto silica severely limits bioreduction rates (relative to aqueous U(VI)), while adsorption onto corundum does not. The experimental data suggest that under natural conditions, microbial U(VI) reduction will tend to be limited by coordination with available ligands, mineral surfaces, and organic matter.