

## Reduction of Hg(II) to Hg(0) by biogenic magnetite

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Elevated levels of mercury in groundwater have been observed sporadically in aquifers world-wide. In some cases, groundwater is supersaturated with respect to elemental mercury [Hg (0)]. The mechanisms of Hg (0) formation in saturated sediments are currently poorly understood. The aim of this study is to evaluate the occurrence of biotic/abiotic reduction of Hg (II) to Hg (0) under anoxic conditions by dissimilatory iron reducing bacteria.

Laboratory experiments were conducted to examine Hg (II) reduction by a novel obligate anaerobic bacterium, FRC-RU4, isolated from Oak Ridge Field Research Center subsurface sediments. Experiments were performed with cells grown on either ferrihydrite, ferric-citrate, or fumarate (30 mM) was used as terminal electron acceptors, and acetate (20 mM) as electron donor. The loss of mercury was analyzed by cold vapor atomic absorbance spectroscopy. The production of volatile Hg [0] was measured by purging the reaction vessel with N<sub>2</sub> into a trapping solution of acidified potassium permanganate. The formation of secondary iron minerals in the bacterial cultures was examined using electron microscopy, X-ray diffraction, and Mössbauer Spectroscopy.

The experimental data indicated that reduction of Hg (II) to Hg (0) by FRC-RU4 is significantly enhanced under iron-reducing conditions as compared to fumarate-reducing conditions. When grown on ferrihydrite, FRC-RU4 induced the formation of goethite and magnetite. Abiotic experiments demonstrated that magnetite can rapidly reduce Hg (II), whereas ferrous iron sorbed to goethite cannot. Reduction of Hg (II) to Hg (0) by magnetite occurs within minutes, with reaction rates varying as a function of magnetite surface area, pH, and chloride concentration. Spectroscopic analysis of mercury-reacted magnetite samples revealed a decrease in Fe (II) content, corresponding to the oxidation of Fe (II) to Fe (III) in the magnetite structure. These results suggest that Hg (II) reaction with biogenic magnetite is a kinetically favorable pathway for the formation of Hg (0) by dissimilatory iron reducing bacteria.

## Iron cycling in the Shale Hills watershed of Central Pennsylvania: Possible links between microbiology and iron chemistry

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The goal of this study is to gain a better understanding of the ways in which iron (Fe) is cycled within the Shale Hills watershed of Central Pennsylvania. A related question involves whether bacteria play an important role in these transformations. Normalized plots of iron concentration with depth in the regolith indicate that both total Fe and Fe (II) concentrations tend to be depleted relative to bedrock concentrations. Total microbial cell counts peak in the surface horizons and then decrease with depth in the soil at all positions along the catena. In contrast, the abundance of iron-related bacteria, iron-oxidizing bacteria and heterotrophic microorganisms increases at the bedrock/soil interface at certain locations. Elevated total cell counts in the surface horizons can be attributed to higher concentrations of carbon and nitrogen at the surface of the soil profile. On the other hand, we suspect that elevated levels of culturable microorganisms at greater depths are related to the preferential flow of water and nutrients along the soil/bedrock interface. Stable isotope signatures of Fe indicate that the mean  $\delta^{56}\text{Fe}$  value in bedrock material from the basin is  $\sim +0.1\%$ . Meanwhile, the average  $\delta^{56}\text{Fe}$  value in total soil samples collected from different depths along the catena was  $+0.1\%$ , with a standard deviation of only  $0.1\%$ . Despite the overall lack of variation,  $\delta^{56}\text{Fe}$  values roughly appear to mirror microbiological trends in many of the regolith profiles.