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Biogeochemical Impacts of the Microbially-Mediated Cycling of Iron and Sulfur

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Microorganisms in the subsurface respire using a variety of terminal electronacceptors, and the resultant geochemical transformations are critical steps in the biogeochemical regulation of these environments. Of these organisms, two of the most important groups are dissimilatory metal-reducing bacteria (DMRB) and sulfate-reducing bacteria (SRB). Through their metabolism, these organisms directly affect the geochemistry of the subsurface through the dissolution of ferric minerals, the consumption of sulfate by SRB, and the subsequent production of reactive ferrous iron and sulfide species. The extent to which either group is active, however, depends upon the geochemical conditions of the particular subsurface environment, such as the pH, temperature, or salinity of the groundwater. In bioreactor experiments of wetland sediment amended with ferric iron minerals, sulfate, and acetate conducted at pH 6 and pH 7.5, we found that pH had a larger influence than acetate concentration on controlling the flux of electrons through iron reduction and sulfate reduction. Under acidic conditions, the amount of iron reduced was a factor of three greater than the amount of sulfate reduced in reactors receiving little (0.25 mM) or no acetate compared to a factor of two in reactors receiving 1 mM acetate. Under alkaline conditions, iron and sulfate were reduced in nearly equal proportions regardless of influent acetate concentration. Results from sulfate-deficient control reactors show that the presence of sulfate reduction increased the extent of iron reduction in all experiments, but particularly in alkaline reactors. Under acidic conditions, the extent of iron reduction was greater by a factor of 1.2 if sulfate reduction occurred simultaneously than if it did not. Under alkaline conditions, that factor increased to 8.2. Hence, pH influenced the extent to which sulfate reduction promoted iron reduction. We also conducted similar experiments employing a newly isolated DMRB from the deep subsurface, *Orenia metallireducens* strain Z6, which can reduce crystalline ferric minerals like goethite and hematite. In similar bioreactors, we examined the effects of a number of environmental factors (pH, temperature, salinity, anion concentration, and availability of electron shuttles) on the bioreduction of a suite of ferric iron minerals (ferrihydrite, lepidocrocite, goethite, hematite, and magnetite). We found that the chemistry of the environment controls not only the rate of microbial iron reduction, but the formation of secondary iron minerals. These controlled laboratory experiments inform ongoing efforts to examine iron and sulfur cycling in redox dynamic environments like wetlands.