Influence of Microbial Nitrate Reduction on Subsurface Iron Biogeochemistry and Contaminant Metal Mobilization

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Our objectives are to determine (1) the extent to which nitrate will inhibit microbial reduction of iron minerals; (2) the effect of mineral reduction on the mobility of representative toxic metals; and (3) the kinetics of nitrate-dependent, microbial oxidation of Fe(II). In the past year, we have examined (i) the effects of NO_3^- on microbial reduction of synthetic iron oxides, and the effect of iron reduction on the mobility of zinc which had previously been sorbed to the oxides; (ii) the effects of goethite on NO_3^- and NO_2^- reduction; (iii) competitive interactions between nitrate and Fe(III) oxide reduction in enrichment cultures of natural sediment bacteria; (iv) microbially-catalyzed nitrate-dependent oxidation of solid-phase Fe(II) compounds at circumneutral pH; and (v) Zn^{2+} sorption properties of Fe(III) oxides generated via biological nitrate-dependent oxidation of aqueous Fe(II).

In batch experiments in an artificial groundwater medium containing 10 mM lactate, we previously showed that production of Fe(II) via microbial reduction of synthetic goethite and lepidocrocite is inhibited by the presence of NO_3^- and NO_2^-. When Zn was adsorbed onto the surface of the goethite or lepidocrocite prior to inoculation with *S. putrefaciens*, the weakly bound Zn (soluble in cold, 0.5 N HCl) was sequestered within a strongly bound phase (soluble in 6 N HCl, but insoluble in 0.5 N HCl). Zn immobilization was not observed in cultures containing NO_3^- or NO_2^- in which Fe^{2+} production was inhibited. Current work is in progress to identify the biogenic minerals responsible for Zn incorporation, to determine if metals other than Zn behave similarly, and to ascertain if similar processes take place during reduction of natural sediments.

Recent work with slurries containing both NO_3^- and goethite have demonstrated that the presence of goethite also inhibited NO_3^- and NO_2^- reduction. Based upon these results and the enhanced production of N_2O in the presence of goethite, we hypothesize that microbially generated NO_2^- and Fe(II) abiotically react to form Fe(III) and N_2O. The Fe(III) oxides precipitating on the cell surface can then potentially inhibit transport of NO_2^- within the cell. Experiments utilizing differences in _$^{15}N_2O$ to discriminate between biogenic N_2O and chemically generated N_2O are underway.

Studies with an autotrophic, circumneutral Fe(II)-oxidizing enrichment culture have demonstrated the potential for rapid, biologically-catalyzed, nitrate-dependent oxidation of solid-phase Fe(II) compounds generated via microbial reduction of amorphous Fe(III) oxide, goethite and two Fe(III) oxide-rich subsoils. Only very low concentrations (~ 15 uM) of nitrite were detected in most cultures, suggesting that Fe(II) oxidation was the result of direct enzymatic catalysis rather than abiotic oxidation of Fe(II) coupled to reduction of nitrite generated from the partial reduction of nitrate. Biological nitrate-dependent Fe(II) oxidation has the potential to generate large quantities of reactive Fe(III) oxide surfaces under anaerobic conditions, a phenomenon which has broad-ranging implications for the mobility of metals in saturated subsurface sediments.

We have also examined sorption of Zn^{2+} onto Fe(III) oxides generated via microbially-catalyzed nitrate-dependent oxidation of soluble Fe(II) in culture medium containing three different levels of inorganic phosphate (0.05, 0.5 or 1.5 mM). The presence of increasing levels of P led to formation of Fe(III) oxides which were more susceptible to dissolution in dilute (0.5M) HCl during short-term (1 hr) extractions. XRD studies and specific surface area measurements showed that the oxides formed under the different P conditions were all essentially amorphous and had similar specific surfaces areas (ca. 250 m^2/g). In addition, the different oxides had comparable Zn^{2+} sorption properties which were also similar to those determined for high-surface-area goethite preparations.