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ABSTRACT TITLE: Coupled Processes in the Biogeochemical Dynamics of Fe, S, and C under Sulfate- and Iron-Reducing Conditions

ABSTRACT: The mobility of contaminants, the availability of C and nutrients, and the geochemical character of groundwater in subsurface environments is closely tied to the biogeochemical cycling of the major elements, particularly the redox cycling of C, Fe, and S. Because these cycles occur concurrently and interdependently, predicting each element's transformations requires a fundamental understanding of the highly coupled biotic and abiotic processes that drive the biogeochemical cycling of C, Fe, and S in subsurface environments.

To better understand the effects of specific electron donors on the biogeochemical dynamics of Fe, S, and C under sulfate- and iron-reducing conditions, we created batch systems containing either acetate, lactate, or glucose as electron donors and ferrihydrite and sulfate as electron acceptors. The batch systems were inoculated with the native microbial community present in sediment from the Rifle, CO, IFRC site. Mineral transformations were monitored by XRD and XAFS spectroscopy, and changes in the microbial communities were determined from 16S rRNA-based tag sequence inventories. All electron donors tested promoted ferrihydrite reduction to varying extents: glucose >> lactate > acetate. The rates and extents of sulfate reduction were faster with lactate than with acetate, while glucose did not stimulate sulfate reduction. Surprisingly, the two replicates of the glucose-amended incubations exhibited different rates and extents of FeII production and glucose fermentation product profiles. The communities in both of the glucose-amended incubations shifted rapidly and remained stable for the rest of the experiment, consistent with the rapid initial reduction of iron with glucose; however, the microbial populations in each replicate were very different. The incubations with acetate and lactate also showed major community shifts over time, but they were different from each other and from the community profiles in glucose amended incubations.

A parallel set of incubations containing lactate as the electron donor and ferrihydrite, goethite, or lepidocrocite in the presence of high (10 mM) or low (0.2 mM) sulfate was also examined. In the presence of low sulfate, FeIII reduction was slow and limited for all of the FeIII oxides. However, the extent of FeIII reduction increased more than 10 times in the presence of high sulfate. In addition, the extent of FeIII reduction was higher in ferrihydrite and lepidocrocite incubations than in goethite incubations. The concurrence of FeIII and sulfate reduction in the high-sulfate incubations, along with the low levels of FeII production in the low-sulfate incubations, suggests that FeIII oxide reduction in these systems was primarily the result of abiotic reduction of FeIII by sulfide produced by dissimilatory sulfate-reducing bacteria (DSRB) and not via direct reduction by dissimilatory iron-reducing bacteria (DIRB). Distinctly different community profiles were observed for each of the FeIII oxides. These results suggest that when dissimilatory iron reduction is slow and both sulfate and FeIII oxide are available, sulfide produced by DSRB can drive FeIII oxide reduction. However, the rate and extent of the FeII reduction by sulfide are strongly affected by the specific FeIII oxide.

We also examined the potential coupling of Fe and S redox processes under alkaline conditions, where the reduction of FeIII by DIRB ceases to be energetically favorable; under these conditions, metal
reducers must utilize alternate electron acceptors. One possible alternative is elemental sulfur (S\textsuperscript{0}), which is produced when dissolved sulfide (a product of microbial sulfate reduction) reacts with Fe\textsuperscript{III} phases. Using geochemical modeling, we show that unlike the reduction of ferric minerals, the reduction of S\textsuperscript{0} becomes more energetically favorable as pH increases. We observed experimentally that, under alkaline conditions, \textit{Shewanella oneidensis} MR-1 is capable of reducing S\textsuperscript{0} to sulfide, which then reacts with ferric minerals to form Fe\textsuperscript{II}. These results suggest that in slightly alkaline environments where both sulfate and Fe\textsuperscript{III} are available, metal-reducing bacteria may survive primarily by respiring the S\textsuperscript{0} created by DSRB.