BACTERIAL INFLUENCES ON THE CONCENTRATION OF TRACE METALS AND THE ISOTOPIC COMPOSITION OF FE RELEASED FROM MINERALS INTO SOLUTION. R. L. Guynn1, S. L. Brantley1, L. Liermann1, T. D. Bullen2, A. Anbar3 and, J. Barling1 1Penn State University (Dept. of Geosciences, University Park, PA 16801), 2U.S. Geological Survey (Water Resources Division, MS 420, 345 Middlefield Rd., Menlo Park, CA 94025), 3University of Rochester (Dept. of Earth and Environmental Science, Rochester, NY 14627).

Microorganisms can significantly impact the concentration of trace metals in natural solutions, especially when those metals are either nutrients or toxins. Bacteria can increase the concentration of metals in solution by changing the solution pH or releasing organic ligands, or they can decrease the concentration of metals in solution by assimilating them into cell material. We have conducted a series of experiments with a soil bacterium (genus Arthrobacter), which is known to produce siderophores. Siderophores are organic ligands with high affinities for Fe produced by bacteria and fungi under low Fe conditions. We have grown Arthrobacter cultures with hornblende or hornblende glass powders as the primary source of metal nutrients alongside abiotic experiments containing powders and sterile medium. Samples of the culture solutions and cell material have been analyzed for several trace metals including Fe, Cu, Mo, and Ni, which are micronutrients required by a variety of organisms for enzymes.

Concentrations of Fe in solution are higher in cultures with bacteria than in abiotic controls after 10 days of incubation. The isotopic composition of Fe in solution and in the powder has also been analyzed. Iron released from hornblende when bacteria are present is isotopically lighter than Fe released from hornblende in abiotic controls ($\delta^{56}$Fe =-0.7‰ and 0‰ respectively, relative to the hornblende). Abiotic experiments containing hornblende and sterile medium along with a siderophore or one of several low molecular weight organic acids show that organic ligands can produce Fe isotope fractionations ranging from -0.2‰ to -0.6‰ in the absence of bacteria. We find that the ligands with higher affinity for Fe are associated with the largest negative shifts (Figure 1). This is consistent with a kinetic isotope effect accompanying Fe complexation at the mineral surface. It is probable that bacterially-produced organic ligands are responsible for the fractionation observed when bacteria are present.

The Cu concentration in culture solutions containing hornblende glass rises to 70ppb within the first 24 hours of incubation in both abiotic and bacteria-containing cultures. The concentration remains steady during the remainder of the 10-day incubation period in the abiotic controls. In bacteria-containing cultures, the Cu concentration in solution drops to less than 20ppb by the fourth day of incubation. Analysis of cell material collected on day 10 shows that cells grown with glass contain 50 times more copper per gram of cell material than cells grown with no solid.

We believe that the increase in Fe concentration in culture solutions containing bacteria and powder is primarily due to the release of siderophores. Iron is assimilated into the cell material, but at a slower rate than it is released into solution. Siderophores can also form strong, soluble complexes with Cu. These complexes may be present in our experiments, but the Cu concentration decreases in bacteria-containing cultures because the rate of Cu uptake into the cell material exceeds the rate of its release into solution.

Concentrations of Mo and Ni in solution with hornblende glass powder appear unaffected by the presence of Arthrobacter. Solution samples from abiotic and bacteria-containing media incubated with hornblende glass contain similar concentrations of Mo and Ni and samples of cell material collected from cultures grown with and without glass show similar concentrations of these metals. It appears that this species of bacteria does not produce ligands that enhance the release of Mo and Ni into solution during our experiments. It is also possible that the bacteria can secrete such ligands, but that metal concentrations in our experiments are high enough that such ligands are not produced.

Trace metal concentrations in natural soil solutions are the result of a balance between the rates of release into solution, precipitation, and assimilation into microorganisms and organic matter. The dominance of any one of these factors over the others can vary from one element to another. Further experiments are being conducted with this bacteria and different solid substrates including goethite and basalt.

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**Figure 1:** $\delta^{56}$Fe relative to hornblende powder vs. log-$K_{assoc.}$ for ligand complexes with Fe$^{3+}$. 