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Fractionation of Fe Isotopes by Soil Microbes and Organic Acids

Susan Brantley (brantley@geosc.psu.edu)[1], **Laura Liermann** (ljl8@psu.edu), **Robin Guynn** (rguynn@essc.psu.edu) & **Tom Bullen** (tdbullen@usgs.gov)[2]

[1] Dept of Geosciences, Penn State, Univ Pk, PA, 16802, USA
[2] US Geological Survey, Menlo Park, CA, USA

Virtually all bacteria assimilate Fe from the environment. If fractionation of Fe occurs during extraction from minerals, then bacteria should selectively assimilate isotopically light Fe. Bacteria often manufacture low molecular weight organic molecules with large association constants for Fe(III) (siderophores) to chelate Fe under aerobic, neutral pH conditions. In previous experiments we have shown that siderophores secreted from soil bacteria can promote dissolution of Fe-containing minerals under aerobic conditions. Here we present the isotopic composition of Fe released from a silicate mineral in the presence of two soil bacteria, and compare these signatures to Fe released abiotically with or without organic chelate molecules. Sterile medium (pH = 6.5) was used in batch experiments in flasks with or without hornblende powder. Two bacterial isolates (a putative streptomycete and arthrobacter) obtained from hornblende-containing soil were used because of their ability to extract Fe from hornblende using catecholate siderophores. Two flasks each were inoculated with 1-week old culture of either the streptomycete or arthrobacter, with no other additions (bacteria controls). Three flasks were not inoculated, but contained hornblende (hornblende controls). Three flasks each were inoculated but also contained hornblende. Three hornblende-containing flasks each with either desferrioxamine mesylate (DFAM) or oxalic acid were also prepared (without bacteria). Aliquots were sampled at days 1 and 4. Samples were filtered, measured for pH, and then aliquots were frozen for analysis. After 6 days, bacteria-containing cultures were poured out of flasks, leaving hornblende powder. These supernatants were then centrifuged to pellet cells. Bacteria entrained with powder were further separated from hornblende, washed, dried and weighed. Samples from the hornblende-containing soil developed on tailings at the Gore Mountain garnet mine were extracted for exchangeable Fe and Fe oxides and oxyhydroxides using standard methods. For both extractions, decanted liquid was filtered, acidified, and analyzed for Fe isotopes, along with a process blank. $^{56}Fe/^{54}Fe$ ratios were measured using a ^{57}Fe-^{58}Fe double spike amendment to correct for analytical fractionation on a Finnigan MAT 261 multicollector thermal ionization mass spectrometer (TIMS). All analyses are quoted in per mil notation with BIR-1 Icelandic basalt as the standard. Using this notation, positive values are heavier than negative values. Cell counts increased faster in the presence of hornblende for both bacterial species, although absolute cell counts were orders of magnitude higher for the arthrobacter. Release rates (δ[Fe]/δt) increased for experiments in the following order: experiments with hornblende only "w/oxalic acid<w/DFAM<w/streptomycete<w/" arthrobacter. Fe released into solution in arthrobacter experiments varied from 0.08% to 0.06% of the total Fe in the reacting hornblende. Isotopic composition of hornblende (-0.25 +_ 0.1, Table 1) was similar to values published for terrestrial igneous rocks, and was the same within error before and after dissolution. Fe in powder was also identical within error to Fe released into solution in abiotic experiments. In contrast, dissolution in the presence of the arthrobacter or streptomycete released Fe lighter by up to 1.1 per mil than found in the hornblende substrate. Fe released during dissolution with DFAM was lighter by up to 0.9 per mil, and with oxalic acid by up to 0.5 per mil. Fe released from the soil exchangeable fraction was 0.9 per mil lighter than hornblende Fe while Fe in the oxyhydroxide fraction was indistinguishable from the hornblende. In summary, both soil microbes extract isotopically light Fe from hornblende during growth. However, relatively light Fe was also extracted using organic chelates. These observations are consistent with a model whereby Fe chelation by strong ligands at the mineral surface preferentially extracts lighter Fe, regardless of whether bacteria are present. The preliminary observation of isotopically light Fe on the exchangeable fraction of the soil suggests that this exchangeable fraction is closely related to Fe in solution in the soil pores, and that this Fe is organically chelated. In contrast, the Fe oxyhydroxide fraction is isotopically indistinguishable from the Fe contained in the primary silicate. These results may indicate that certain fractions of Fe in rocks or soils may document the previous presence of organic ligands.