

## Does Iron dissociation from siderophores lead to Iron isotope fractionation?

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Over the last decade iron isotope geochemistry has increased our potential to trace the geochemical cycling of iron, but the mechanisms responsible for iron cycling in subsurface environments are poorly understood and correlation of iron isotope signals to distinct subsurface processes is difficult to show. As the mechanisms which govern iron isotope fractionation in natural ecosystems are under debate, we will focus our research on the poorly constrained process of iron dissociation from siderophores and other iron chelators.

Siderophores are low molecular weight organic ligands released by bacteria or fungi to increase the bioavailability of iron. Even though the high stability of iron siderophore complexes suggests the chelated Fe(III) is largely unavailable for inorganic processes, we observed that Fe(III) can be dissociated by a reductive mechanism using ascorbic acid.

Initial abiotic kinetic experiments show distinct variations in the kinetics of iron dissociation from ferric acetohydroxamic acid (Fe-AHA<sub>3</sub>), ferric EDTA (Fe-EDTA<sup>-</sup>), and ferrioxamine B (Fe-DFOB<sup>+</sup>). The pseudo first order rate constants (*k'*) vary four orders of magnitude with *k'*(Fe-AHA<sub>3</sub>) > *k'*(Fe-EDTA<sup>-</sup>) > *k'*(Fe-DFOB<sup>+</sup>) resulting in half-lives from seconds for Fe-AHA<sub>3</sub>, to minutes for Fe-EDTA<sup>-</sup>, and to days for Fe-DFOB<sup>+</sup>. The displacement of iron from Fe-DFOB<sup>+</sup> can be accelerated in the presence of Ga, which reduces the half-life to hours. Furthermore, the presence of a catalyst like oxalic acid and a competing ligand like EDTA can accelerate this dissociation process as well.

In order to understand iron cycling in natural environments we will extend our studies on possible iron fractionation during the abiotic reductive displacement of Fe(III). Such iron isotope signals could improve our understanding of iron cycling in terrestrial subsurface environments. Initial measurements indicate that preferentially light iron is removed from the ligands.

## Augustine Volcano: Mg, Cr, & Ni-rich; LILE, REE and HFSE-poor

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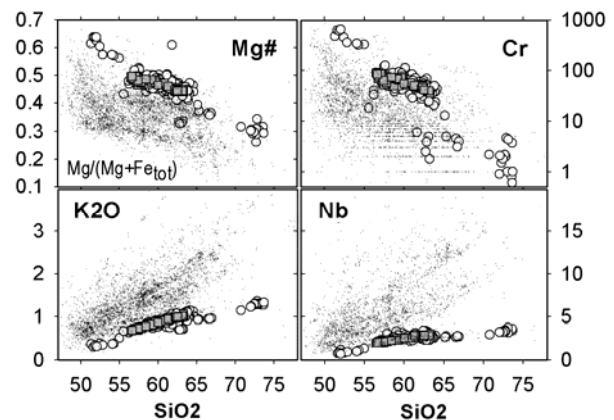
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Augustine is a ~1300m tall, active volcano near the eastern end of the Aleutian Arc. Each of five major eruptions in the past century has erupted banded and hybridized crystal-rich andesite spanning ~56 to ~64% SiO<sub>2</sub>. Basalt and rhyolite are restricted to late Pleistocene time. A continuum of lavas spanning the entire basalt-rhyolite compositional range of the volcano is notably absent, and distinguishes Augustine from many other Aleutian arc volcanoes.

Augustine is among several Aleutian arc volcanoes sharing the characteristics, relative to the rest of the arc, of high Mg, Cr, Ni, Mg# and low LILE, REE, HFSE, U, Th, Pb.



**Figure 1:** Compositions of Augustine lavas compared to other Aleutian Arc lavas (dots). Filled squares are from the 2006 eruption, open circles are from all pre-2006 samples.

The low concentrations of incompatible elements reflect a span of concentrations that is half or less of that of typical Aleutian suites (relative to base-level) as well as low initial concentrations. This, and the lack of Eu anomalies in evolved rocks severely limits petrogenetic relationships involving plagioclase-dominated fractionation. The chemical, petrographic, and mineralogic data suggest petrogenesis is a complex process involving deep crustal or near-Moho crystallization, entrainment of crystalline residues from previous magma batches, and mixing.