Molecular characterization of Selenium in the environment

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Selenium in the environment is an important element for ecosytem nutrition, but also can be toxic when present at slightly elevated concentrations. Selenium has similar chemistry as sulfur, and thus has multiple oxidation states and molecular forms in the environment. Availability of selenium for uptake by organisms or leaching to ground and surface waters is a function of its speciation. Thus understanding Se speciation and biogeochemistry in the environment is critical for evaluating risks and developing best management practices.

In this presentation results on speciation of Se in rocks, soils, plants, and stream waters located in an active mining region in southeastern Idaho will be presented. Phosphorus-ore in the region comprises the Western Phosphate Resource Area. The affected samples have elevated concentrations of Se relative to background levels, resulting from distribution of an ore interbed-shale (middle-waste shale) throughout the surficial environment during mine-site reclaimation.

Speciation of Se in the samples was investigated using microscopically focused X-ray absorption spectroscopy. This technique utilizes focused synchrotron-generated radiation to excite core electrons in Se atoms within a sample, and fluorescence or transmission can be monitored either spatially or as a function of impinging energy. It is ideally suited for speciation in natural samples because it is element specific, and has a resolution of a few microns, thus allowing for speciation in heterogeneous samples to be investigated.

In the middle-waste shale, Se existed as reduced Se(0) or Se(II-) species. Three end-members were identified in the shale: Se-substituted pyrite, an iron selenide mineral, and an organic Se phase. Within the soil, both reduced and oxidized Se phases were detected, with the oxidized phases primarily Se(IV) (selenite); very little Se(VI) (selenate) was detected. In the plant materials both reduced organic Se and Se(VI) were identified. Finally, in the stream sediments, reduced Se, and selenite and selenate were identified.

Using the speciation information together with known ecological and biogeochemical processes, we are developing a better understanding of reaction processes, sources, and sinks for Se in the Western Phosphate Resource Area. This detailed information will facilitate a better understanding of the biogeochemical cycling in the system.

Origin of sulfur rich apatite in silicic, calc-alkaline magmas

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We have investigated volcanic apatite from a well-known center of calc-alkaline magmatism – the Oligocene Central San Juan Caldera Complex (CSJCC), Colorado, USA – to constrain the origin of sulfur rich (> ~0.6 wt.% SO_3) apatite found in dacitic to rhyolitic, calc-alkaline magmas. All apatites are small (typically 20-100 µm) and apatite from most units investigated (Fish Canyon Tuff, tuffs and lavas of the San Luis caldera complex) yield SO_3 contents ranging from ≤0.2 wt.% to values of 0.8–2.0 wt.%; the bulk of apatite, however, indicate SO_3 contents of 0.3–0.5 wt.%.

We performed laser-ablation ICP-MS analyses on apatite with a range in sulfur concentrations from selected units to correlate variations observed in sulfur with variations in trace elements (e.g REE) to find evidence for melt compositional changes during crystallization of S-rich vs. S-poor apatites. Apatite among units indicates characteristic compositional changes but within single units, apatite tends to form tight compositional clusters in parameters like Eu/Eu*, La/Yb and Sr contents, while REE concentrations may vary by a factor of two. Exceptions are a few distinct apatites. REE concentrations are typically ≥50-60x of bulk rock and/or of interstitial glass in keeping with other natural systems (e.g. Dempster *et al.*, 2003) and suggest partition coefficients several times the ones of experimental studies.

To constrain actual melt composition from which apatites grew, we find the combination of REE, Sr concentrations and Eu/Eu* most useful. Based on the trend of decreasing Sr towards more silicic compositions of bulk rock & glass for the CSJCC (this study and Lipman, 2004) and a $D_{Sr} \geq 3$, all apatite grew from melts more silicic than ~68 wt.% SiO_2 at the exclusion of the most evolved melt composition (~6 ppm Sr, 77 wt.% SiO_2) that is too depleted in Eu to yield a D_{Eu} consistent with those of neighboring REE.

Our study suggests that apatite with low to high S concentrations grew in rhyodacitic/rhyolitic melt requiring either 100's of ppm of sulfur in the melt or alternative mechanisms to explain upper end of S range in apatite. One such alternative explanation may involve some sort of interraction of S-rich fluids (which could be largely derived from an underplated, degassing mafic magma) with crystallizing apatite.

References

Dempster, T.J., Jolivet, M., Tubrett, M.N., Braithwaite, C.J.R., (2003), *CMP* **145**: 568-577.

Lipman, P.W. (2004) *USGS Open File Rep*. 2004-1194.