Cr(III) oxidation by soluble Mn(III) chelates: A potential biogeochemical pathway for the enhanced mobilization of Cr from spinels

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Soils derived from ultramafic (UM) rocks are enriched in Cr(III), mainly due to the presence of chromite ($FeCr_2O_4$) and other Cr(III)-bearing spinels. Weathering of UM rocks in the Coast Range and Sierra Nevada mountains of California has impacted the geochemistry of alluvial soils in the Sacramento Valley, which are enriched in Cr (30-1420 $\mu g\ g^{-1}$) relative to the U.S. geometric mean (37 $\mu g\ g^{-1}$). Although much of the Cr in these soils appears to be bound in refractory spinels, some mobilization of Cr is apparent in the coincidence of enriched soils with elevated Cr(VI) in ground water (up to 50 $\mu g\ L^{-1}$). It was recently reported that dissolution of chromite can be driven by the oxidation of the released aqueous Cr(III) on soil Mn oxides [1]. We are sudying the oxidative dissolution of chromite by soluble Mn(III) as a an additional Cr mobilization pathway. Free aqueous Mn(III) is a strong oxidant but rapidly disproportionates to Mn(II) and Mn(IV). Various chelates such as oxalate and pyrophosphate can stabilize Mn(III) in solution. Mn(III)-oxalate is produced by extracellular enzymes of white-rot fungi and acts as a diffusible oxidant in lignin degradation. Pyrophosphate (PP) is a hydrolysis product of ATP and is also a component of some fertilizers. Its reaction with soil Mn oxides can result in soluble Mn(III)-PP. We measured the reduction potential of a 1 mM solution of Mn(III)-PP as a funtion of pH. The E_r decreased from ~1.1 V (versus SHE) at a pH of 2 to ~0.6 V at a pH of 7. Consistent with these measurements, Mn(III)-PP oxidized a greater percentage of aqueous $CrCl_3$ at lower pHs. After 2 weeks reaction time, 94, 63, 28, 3, and <1% of Cr(III) was oxidized to Cr(VI) at pH of 3, 4, 5, 6 and 7, respectively. Forty-five times as much Cr(VI) was produced from chromite grains (63-150 µm diameter) incubated for 8 days in a Mn(III)-PP solution at a pH of 3 than incubated with solid manganese oxides at the same pH. As expected, the chromite and Mn(III)-PP incubation produced 10-fold less Cr(VI) at pH 5 than at pH 3. Our initial studies of Mn(III)-oxalate suggest its ability to oxidize aqueous $CrCl_3$, but only in a narrow, circumneutral pH range.

[1] Oze *et al.* (2007) *PNAS* **104**, 6544-6549.

Comparing the compositional patterns of volcanic and plutonic rocks using the NAVDAT database

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Igneous rock compositions generally fall along a line between basalt/gabbro and rhyolite/granite. Differences between volcanic and plutonic rocks across that range are poorly defined. A key question is whether plutons are largely cumulate residues of volcanic rocks, or are instead samples of magma that froze in the crust before eruption. Large geochemical datasets can be used to explore connections between volcanic and plutonic magma systems.

We used geochemical data for Cenozoic volcanic and plutonic rocks (~2000 ea., between 40 and 80 wt.% SiO_2) from the NAVDAT database (www.navdat.org) to identify major and minor chemical trends, chemical divergence between volcanic and plutonic rocks, and age-dependent variation in the systems. Equal numbers of analyses of volcanic and plutonic rocks were randomly selected from compositional bins (40-50, 50-60 wt.% SiO_2, etc.) to avoid bias between the rock types (e.g., volcanic rock data are dominated by basalts).

Preliminary observations include: 1) trends in compositional space are essentially identical for volcanic and plutonic rocks, 2) outliers for selected elements (e.g., CaO, Y, Ba, Nb) tend to lie on opposite sides of the main trends for volcanic and plutonic rocks, and 3) the average age of analyzed volcanic rocks is much younger (mean ~16 Ma) than the average age of analyzed plutonic rocks (mean ~37 Ma). Plutonic rock analyses are limited for young ages from 0-20 Ma, but are relatively consistent from 20-65 Ma. In contrast, the majority of volcanic rocks are less than 30 m.y old, with an asymptotic decline in the number of analyses from 30-65 Ma.

Overall, the analysis shows no evidence for a complementary relationship between typical volcanic and plutonic rocks, with plutons representing unerupted residue from differentiating magma systems. Rather, pluton compositions are dominantly equivalent to those of volcanic rocks. However, minor differences in trace-element trends may relate to important, yet to be understood processes that lead to eruption. The similarity of volcanic and plutonic rocks combined with the observation that volcanic rocks become scarce as one goes back in time, indicates that plutonic rocks are as useful as volcanic rocks for understanding the chemical evolution of continents.