Oxidation state and temperature influences Cr sorption with struvite

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Struvite ($MgNH_4PO_4{\cdot}6H_2O$; MAP) occurs naturally in animal and human kidney stones, poultry litter, bat guano and phosphate deposits [1]. It is produced anthropogenically in soils as a fertilizer by-product, and is a common precipitate in wastewater treatment processes, with optimal precipitation occurring within a 180-240 °C temperature range [2]. Substitution of the toxic metalloid chromium (Cr) into MAP structures has been reported [3], however Cr-MAP sorption processes are not completely elucidated. Oxidation state and resultant speciation dictates Cr mobility. While Cr (III) tends to interact strongly with solid particles, Cr (VI) is more mobile and easily transported in solution [4]. Sorption experiments were conducted with Cr (III, VI) in the presence of MAP at temperatures ranging from 25-300 °C. At 25 °C, ~70 and 2 % Cr (III) and Cr (VI), respectively is removed from solution. Insignificant sorption of Cr (VI) may be due to competition with P species for similar sorption sites. With increasing temperature, removal of both Cr (III) and Cr (VI) is enhanced, maximizing at 90 and 85 %, respectively at 300 °C. Increased removal of Cr (VI) with temperature is suggestive of an enhanced or altered sorption mechanism, which may be accompanied by a change in oxidation state. Preliminary results from x-ray absorption near-edge spectroscopy (XANES) studies suggest similarities in Cr-MAP sorption complexes regardless of initial oxidation state. Results of this research provide insight into Cr-MAP associations in low and high temperature biological, geochemical and anthropogenic systems.

[1] Abdelrazig & Sharp (1988), *Thermochim. Acta 129,* 197-215. [2] Arakane *et al.* (2006) *Water Sci. Technol. 54,* 81-86. [3] Ravikumar *et al.* (1999) *Cryst. Res. Technol. 34,* 911-914. [4] Fendorf (1995) *Geoderma* **67**, 55-71.

Chlorite formation during hydrotermal alteration of Troctolite: An experimental study at 420°C and 500bars

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The >360°C high temperature Rainbow system vents fluid enriched in H_2, CH_4, and Fe fluids that can be accounted for by hydration of ultramafic rock assemblages, although the distinctly low pH, high Ca and Si concentrations are greater than would be expected for such a process. The coexistence of these rocks with plagioclase-bearing gabbro, however, could provide Al and Si for chlorite formation needed for pH lowering, while at the same time dissolved H_2 could be buffered by chlorite-magnetite fluid equilibria. Gabbro intrusions into ultramafic lithologies are often associated with detachment faults at slow spreading mid-ocean ridges. Accordingly, chlorite and amphibole bearing assemblages may be more pervasive than serpentine in rocks altered at greenschist to amphibolite-facies conditions [1].

To test the role of gabbro (troctolite) alteration on mass transfer reactions during hydrothermal alteration, we conducted a series of hydrothermal experiments 420°C, 500 bars and monitored changes in fluid chemistry. Dissolved H_2 increased rapidly to >20mmol/kg before slowly decreasing to concentrations of approximately 7 mmol/kg. Preliminary examination of alteration minerals indicates chloritization of the olivine and plagioclase bearing reactants.

[1] Blackman, Ildefonse, John, Ohara, Miller, MacLeod (2006) *Proceedings of the IODP*, 304/305