Chromium au naturel: Chromium(VI) generation within structured soils and sediments

D. M. HAUSLADEN[1*], M. G. ARREDONDO[2] AND S. FENDORF[1]

[1]Department of Earth System Science, Stanford University, Stanford, CA 94305, USA (*correspondence: hausladen@stanford.edu)

[2]Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, NY 14850, USA

Cr(VI) contamination of soils and waters has historically been attributed to anthropogenic sources; however, indigenous Cr residing within geologic strata represents a far more distributed threat to human health. Chromium(III) within minerals common to ultramafic rocks, their metamorphic derivatives, and weathering products can be oxidized to Cr(VI) via reaction with Mn-oxides. Limiting the reaction, however, is the physical separation of solids having limited solubilities, resulting in transport limited rates. Here we examine, within soil aggregates, the coupled processes leading to the oxidation of Cr(III)- and mixed Cr(III),Fe(III)-hydroxides by biogenic and abiogenic Mn-oxides.

In order to investigate the mechanism of Cr oxidation within structured media, artificial soil aggregates were constructed from $Cr(OH)_3$- and $Cr_{0.25}Fe_{0.75}(OH)_3$-coated quartz grains; aerated solute flow was then induced around the soil aggregate. For abiogenic Mn-oxides, synthetic birnessite was mixed into the aggregates; for biogenic Mn-oxides, aggregates were inoculated with the Mn(II)-oxidizing bacteria *Leptothrix cholodnii* and Mn(II) was provided within solutes. In aggregates simulating low carbon environments such as fractured serpentinite or subsurface sediments, we observe Cr(VI) concentrations within advecting solutes more than twenty-times the California drinking water standard. Chromium(VI) production is highly dependent on Cr-mineral solubility; increasing Fe-substitution decreases aqueous Cr(VI) generation. Further reduction occurs in carbon-rich environments, such as surface horizons of soils, aggregate interiors become anaerobic and experience metal reducing conditions. Aggregates inoculated with dissimilatory metal-reducing bacteria result in limited Cr(VI) production with abiogenic or biogenic Mn-oxides. In all aggregates Cr(III)-oxidation is dependent on proximity to higher-valent Mn-oxides. Using μ-XRF imaging, we observe Cr(VI) enrichment within Mn-oxide hotspots. Our results illustrate Cr(VI) generation from reaction with Mn-oxides within (unmixed) structured media and highlights the control of microbial communities on both Cr oxidation and reduction.