

## The role of Mn(II) mobility on Cr(VI) generation in groundwater

CYNTHIA MCCLAIN<sup>1\*</sup>, SHANE JOHNSON<sup>1</sup>,  
SCOTT FENDORF<sup>2</sup> AND KATE MAHER<sup>1</sup>

<sup>1</sup>Department of Geological and Environmental Sciences,  
Stanford University, Stanford, CA 94305 USA  
(\*correspondence: cynthia.mcclain@stanford.edu)

<sup>2</sup>Department of Environmental Earth Systems Science,  
Stanford University, Stanford, CA 94305 USA

Mn(II) mobility and pH changes are two key factors that may govern both the distribution of naturally occurring Cr(VI), a toxic carcinogen found in California drinking water aquifers, and Cr re-oxidation following reductive remediation at anthropogenically contaminated sites. At circum-neutral pH values characteristic of California's aquifers, Cr(III) is oxidized by Mn(III,IV)-oxides. Both natural and anthropogenically generated Cr(III) occur as fine grained oxy-hydroxides [1, 2, 3]. In aquifer materials, Mn-oxide concentrations are often orders of magnitude higher than Cr, and Mn-oxides commonly coat mineral surfaces [1]. Further, Mn(II), formed typically under reducing conditions, is far more soluble than Cr(III). We hypothesize that, because of the higher concentration and mobility of Mn in the environment, the distribution and oxidation state of Mn in relation to Cr(III) minerals is a primary control on Cr oxidation.

To investigate the influence of pH and Mn(II) concentrations on Cr(III) oxidation, we conducted well-mixed, aerated, batch experiments with synthetic Cr(OH)<sub>3</sub>-coated quartz sand. Aqueous Mn(II) was added (as MnCl<sub>2</sub>) to batch reactors buffered at pH 7, 8 and 9. The evolution of fluids and solids were tracked for two weeks. Within one day, Mn-oxides formed and Cr(VI) concentrations exceeded the proposed CA drinking water limit of 10 µg/L. Cr(VI) concentrations generated at pH 8 and 9 exceeded those generated at pH 7. TEM imaging and selected area diffraction indicate that Cr and Mn mineral phases varied in morphology, crystallinity and juxtapositioning. Higher valence, less crystalline Mn-oxides precipitated under lower Mn(II) concentrations where more Cr(VI) was generated. These results indicate that Mn(II) mobilization, either natural or anthropogenically stimulated, followed by oxic conditions may lead to the precipitation of Mn oxides in close proximity to Cr(III) minerals generating Cr(VI) concentrations above 10 µg/L on a timescale of days.

- [1] Izbicki *et al* (2008) *Applied Geochemistry* **23**, 1325-1352  
[2] Mills *et al* (2011) *Applied Geochemistry* **26**, 1488-1501 [3]  
Varadharajan *et al* (2010) *AGU Meeting*, B51C-0377