

ER 11098074

2004 Fall Meeting  
Search ResultsCite abstracts as **Author(s) (2004), Title, *Eos Trans. AGU*, 85(47), Fall Meet. Suppl., Abstract xxxxx-xx**

Your query was:

chromium and sc=hydrology

HR: 10:50h

AN: H42C-03

TExperimental Determination of Isotopic Fractionation of Chromium(III) During Oxidation by Manganese Oxides

\*Bain, D J

EMdjebain@usgs.gov

AFU. S. Geological Survey, 345 Middlefield Rd., Menlo Park, CA 94025  
United States

Bullen, T D

EMtdbullen@usgs.gov

AFU. S. Geological Survey, 345 Middlefield Rd., Menlo Park, CA 94025  
United States

In environmental conditions, chromium (Cr) exists in either the immobile, micronutrient trivalent form (Cr(III)) or the mobile, toxic hexavalent (Cr(VI)) form. Cr(VI) quickly reduces upon encountering Fe(II) or soil organic material (SOM). Therefore, it is often assumed that human Cr additions to terrestrial systems will impact localized areas and natural sources pose minimal threat to human or ecosystem health. However, oxidation and mobilization of Cr(III) by common manganese (Mn) oxides is less understood, especially in field settings. Moreover, Cr(VI)'s anionic form should enhance mobility through Fe- and SOM-poor soil and saprolite matrices. The variety of redox environments along a flowpath makes Cr source identification difficult with only concentration and speciation data. However, Cr has four stable isotopes (50, 52, 53, and 54), and characteristic fractionations during redox transformations might allow clarification of sources and flowpaths. For example, Cr(VI) reduction by a variety of reductants discriminates against heavy Cr, resulting in an increasingly heavy Cr(VI) fraction as reduction proceeds ( $\alpha_{\text{Cr(III)-Cr(VI)}} \sim 0.996$ ). Measurement of isotopic fractionation in other environmental Cr transformations, including oxidation, is necessary to understand Cr fate and transport. Recent estimates of isotopic fractionation between Cr aqueous species based on theoretical considerations indicate that at equilibrium  $\alpha_{\text{Cr(III)-Cr(VI)}} \sim 0.994$ . To test this theoretical prediction, we are assessing the isotopic variability of aqueous Cr during oxidation of Cr(III) on  $\text{MnO}_2$  materials such as birnessite in laboratory experiments. Initial results indicate that the isotopic composition of the product Cr(VI) ranges from -2.50 to +0.71  $\text{‰} \delta^{53}\text{Cr}$ , suggesting an important role for kinetic isotope effects during the initial oxidation process. Large fluctuations in isotopic composition continue after dissolved Cr(VI) and Cr(III) ratios

30783



stabilize and net Cr(VI) production rates are very slow. Moreover, the Cr(VI) isotopic composition fluctuates between heavy and light compositions several times over the course of reaction. Overall, however, the long term trend appears to be toward the equilibrium fractionation predicted by theory. This adds further credence to hypothesized multiple oxidation pathways existing in the system and suggests that multiple processes with off-setting fractionations are driving the system. If these results are representative of natural systems, environmental Cr samples that have been oxidized or been oxidized/reduced multiple times along a flowpath, will have isotopic compositions that vary widely, depending predominantly on sample collection time. In turn, this suggests that Cr isotopic compositions alone will not clarify Cr fate and transport, especially at larger scales (e.g., catchments), and other geochemical and hydrologic constraints will be required.

DE: 1803 Anthropogenic effects

DE: 1806 Chemistry of fresh water

DE: 1030 Geochemical cycles (0330)

DE: 1040 Isotopic composition/chemistry

DE: 1065 Trace elements (3670)

SC: Hydrology [H]

MN: 2004 AGU Fall Meeting

---

## New Search

