

Examining Coupled Mineralogical-Redox Controls on Chromium Cycling in Soils and Sediments

MICHAEL A. CHEN,¹ HAYLEY GADOL¹, AND BENJAMIN D. KOCAR^{1*}

¹MIT CEE, 15 Vassar St., Cambridge, MA 02139

*Correspondance: kocar@mit.edu

Iron (hydr)oxides are important sorbents of many trace elements, and play a key role in the soil-sedimentary cycling of contaminants such as Cr or U [1]. Following the onset of reducing conditions, sorbed constituents may be liberated to solution through complete reductive dissolution of host iron (hydr)oxides. Alternatively, thermodynamic limitations on structural Fe(III) reduction may constrain the extent of reduction and Fe(II) accumulation, even under persistent reducing conditions [2]. Under similar conditions, previous studies using iron isotopes have illustrated that sorbed/surficial Fe²⁺ may donate an electron to the “bulk” mineral, which migrates to a different crystal face where Fe³⁺ is reduced liberated as Fe²⁺(aq). This conduction mechanism has been posed to explain the extensive turnover (dissolution-precipitation) of structural Fe(III) [3]. We hypothesize that this mechanism of electron conduction through iron (hydr)oxides also links Fe(II) production by dissimilatory metal reducing bacteria (DMRB) with reduction of sorbed, redox-sensitive metals such as Cr(VI); i.e. DMRB will reduce surficial Fe(III), with subsequent electron transfer through the bulk mineral to sorbed Cr(VI), which is then reduced to Cr(III).

Here, we use an electrochemical cell to examine electron transfer from the DMRB *S. putrefaciens* to Cr(VI)-sorbed to an iron (hydr)oxide (hematite). A chamber containing lactate (electron donor), *S. putrefaciens*, and a graphite electrode (anode) is physically separated from a second chamber containing Cr(VI) and hematite (cathode) by a cation exchange membrane. Electron transfer is quantified through continuous voltage measurements over the two electrodes, and changes in solution chemistry quantified by ICP-MS. Initial experimental results confirm that electrons are passed from the *S. putrefaciens*-graphite anode to the hematite-cathode. Ongoing experiments will illustrate the extent of Cr(VI) reduction associated with the hematite-cathode surface.

[1] Stumm and Sulzberger (1992), *Geochimica et Cosmochimica Acta* 56, 3233-3257.

[2] Pedersen et al. (2005), *Geochemica et Cosmochimica Acta*, 69, 3967-3977.

[3] Handler et al. (2014), *Environ. Sci. Tech.* 48, 11302-11311