

Spatial coupling of chromium and manganese cycling: Visualizing microbial communities within complex chemical environments

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Toxic levels of hexavalent chromium (Cr(VI)), a known carcinogen, have primarily been attributed to anthropogenic sources. Recently, however, naturally occurring chromium residing within geologic strata poses a far more widespread threat to human health. Weathering processes enrich Cr(III) within sediments where subsequent oxidation can release the more toxic and mobile Cr(VI) into groundwater. Many studies have investigated Mn(III/IV) oxidation of aqueous Cr(III), but the spatial proximity necessary for the oxidation of Cr(III) solids by Mn-oxides is not yet known.

Here we examine first how the varying solubility of Cr(III) minerals impacts oxidation by birnessite using Cr(III) hydroxides with varying amounts of Fe(III). Donnan reactors, in which Cr and Mn solids were separated by an ion-permeable membrane, were used to simulate diffusion-limited transport of solubilized Cr(III). As predicted with solubility, Cr(VI) production decreased with increasing Fe-substitution.

In order to examine the spatial relation of Mn(III/IV) precipitation, formed via microbial oxidation of Mn(II), with respect to Cr(III) phases within complex mineralogical assemblages, we examined the spatial relationship between *Leptothrix cholodnii*, a Mn-oxidizing bacteria, and *Shewanella putrefaciens*, an Fe-reducing bacteria, within synthetic aggregates. Catalyzed reporter deposition fluorescence *in situ* hybridization (CARD-FISH) allowed us to visualize the co-location of *L. cholodnii* and *S. putrefaciens* within the context of advective and diffusive flow networks. *S. putrefaciens* was found to correspond with depleted zones of Cr and Fe within the anaerobic aggregate interior, while *L. cholodnii* formed a thick biofilm on the aggregate surface. Further, Mn and Cr were enriched in the outer-rim of the aggregate proximal to the advective flow channel. Collectively, our results illustrate how coupled microbial and geochemical process operate to potentially form Cr(VI) within the physical structure of soils and sediments.