Zn isotopes variation in field hyperaccumulator plant species

TANG YT.[1,2,3], CLOQUET C.[3*], STERCKEMAN T.[2], MOREL JL[2], CARIGNAN J.[4], QIU RL[1], ECHEVARRIA G[2]

[1]School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou, P.R.China, eestyt@googlemail.com

[2]LSE-INRA, Nancy, France, Thibault.Sterckeman@ensaia.inpl-nancy.fr

[3]CRPG-CNRS, Nancy, France, cloquet@crpg.cnrs-nancy.fr (* presenting author)

[4]Takuvik, CNRS-ULaval, Québec, Canada, Jean.Carignan@takuvik.ulaval.ca

Abstract

Stable Zn isotope signatures offer a potential tool to trace the mechanisms of Zn uptake and transfer within plant-soil system. In this study, we determined Zn isotopic compositions in three ecotypes of the Zn hyperaccumulator *Noccaea caerulescens* collected at a Zn-contaminated site (Viviez), a non-contaminated site (Ste Eulalie) and a serpentine site (Vosges) in France. The Zn-tolerant species *Silene vulgaris* collected from Viviez was also studied for comparison. While the δ^{66}Zn differentiated substantially among ecotypes, *N. caerulescens* exhibited a similar pattern with an enrichment in heavy Zn isotopes of 0.40–0.72‰ from soil to root, followed by a depletion in heavy Zn from root to stem (–0.05 to –0.31‰) and from stem to leaf (–0.05 to –0.22‰). The positive or negative shift of isotopes is probably attributed to the high ability of Zn accumulation and translocation in the hyperaccumulator, as δ^{66}Zn in *N. caerulescens* showed a significant and negative correlation with Zn concentration and bioconcentration factor. In *S. vulgaris*, however, the root was slightly depleted in heavy Zn with respect to soil, indicative of an ion-channel controlled diffusion into root cell under Zn excess conditions. The mass balance yields bulk Zn isotopic composition between plant and soil Zn $\Delta\delta^{66}Zn_{plant\text{-}soil}$ of –0.01‰ to 0.63‰ in *N. caerulescens* and –0.05‰ in *S. vulgaris*. We confirm that quantifying Zn stable isotopes is useful to study Zn accumulation pathways in plant and to document Zn status in media.

Cr(III) oxidation by biogenic maganese oxides

YUANZHI TANG*, COLLEEN M. HANSEL

School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02143, USA. ytang@seas.harvard.edu (*presenting author), hansel@seas.harvard.edu

Chromium (Cr) is a significant anthropogenic metal contaminant in soils and aquatic systems due to its widespread industrial applications. The toxicity and transport behavior of Cr depends strongly on its valence state. Cr(VI) compounds are typically soluble, mobile, bioaccessible, and are considered carcinogenic upon inhalation exposure. Cr(III) generally forms sparingly soluble (oxyhydr)oxides and is a essential micronutrient.

The redox transformation between Cr(III) and Cr(VI) in the environment is strongly mediated by (bio)geochemical reactions involving iron (Fe) and manganese (Mn) (oxyhydr)oxides, with Mn oxides (MnOx) being the only known natural oxidant of Cr(III). Understanding the impact of reaction conditions and MnOx structure are key for assessing the transport and fate of Cr. Given the much faster rate of microbially mediated Mn(II) oxidation as compared to solution or mineral-surface-catalyzed oxidation, MnOx are generally considered biogenic. However, most previous studies on the structural impacts of MnOx on Cr(III) oxidation were either limited because of the use of sythetic MnOx or complicated by the microbe species used, which required the presence of cells for MnOx production. Recent studies of *Roseobacter* sp. AzwK-3b, a bacterium that oxidizes Mn(II) through the production of extracellular superoxide and maintains oxidative activity in the cell-free filtrate[1,2], provides a good opportunity for studing the structure-reactivity relationship of biogenic MnOx toward Cr(III) oxidation.

In this study, we examined the roles of light, organics, pH, and structure of biogenic MnOx on Cr(III) oxidation. MnOx produced by the cell-free filtrate of *R.* AzwK-3b were aged in an organic-rich (K) medium for varied amounts of time under light or dark conditions, which induced structural change from a hexagonal birnessite phase to triclinic birnessite phase. MnOx with different structures were then reacted with Cr(III) at varied pH, concentration and time in K medium or artificial sea water (ASW) under light or dark conditions. Batch uptake results show that Cr(III) oxidation efficiency is highest at near neutral pH (7.2). With the same MnOx, under light conditions, the oxidation effiency is higher in the organic-rich medium than ASW. For fixed solution composition and varied MnOx age, a negative correlation is observed between the age of MnOx and oxidative reacitivity in the presence of organics and light, whereas no changes in reactivity is shown under ASW and dark conditions. These results strongly point to the role of photo-induced organic radicals. We propose that the Mn(II) produced from the oxidation of Cr(III) and reduction of MnOx is recycled in the system under organics and light conditions, and is responsible for the continuous oxidation of Cr(III). Ongoing structural analysis of the initial and reacted MnOx by synchrotron X-ray absorption spectrosocpy (XAS) will provide more insights on the reaction kinetics and mechanisms.

[1] Hansel (2006) *Appl. Environ. Microbiol.* **72**, 3543-3549.

[2] Learman (2011) *Nature Geoscience* **4**, 95-98.