Mycogenic manganese oxide structural changes and nickel incorporation with aging

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Manganese (Mn) oxide minerals commonly control the uptake and release of heavy metals (e.g., nickel (Ni), zinc, cobalt) in natural and metal-polluted sites. In coal mine drainage passive remediation sites, Mn oxidizing microbes, particularly fungi, remediate aqueous Mn(II) by forming highly reactive phyllomanganates: Mn(III/IV) (hydr)oxide minerals with variable Mn(III) and Mn(IV) vacancy contents. Ni binds to phyllomanganates via adsorption above or below Mn(IV) vacancies or to sheet edges or incorporation into vacancies. In abiotic systems, the timing of Ni addition (i.e., coprecipiated with Mn or added to a preformed phyllomanganate) alters Mn oxide structures and Ni binding.

Here we explore the partitioning and stability of solid-associated Ni in mycogenic phyllomanganates produced by the Mn-oxidizing fungi *Stagonospora sp.*SRC1lsM3a when coprecipitated with Mn and when added after Mn oxidation. Ni and Mn uptake by biomass and Mn oxides were tracked with wet chemistry techniques and paired Ni and Mn K-edge extended X-ray absorption fine structure (EXAFS) sepctroscopy to determine Ni binding behaviors and Mn oxide structures. Unlike abiotic Mn oxides, we find there is little to no difference in the binding behavior of solid-associated Ni, with both timing-of-addition scenarios yielding approximately the same amount of incorporated and adsorbed Ni. We also observe that aging increases Ni incorporation (a maximum of 2 mol% Ni, in line with abiotic Mn oxides) despite the fact that overall Ni uptake is unaffected by aging. This increase in Ni incorporation with time occurs in both live and dead cultures, suggesting that any role fungi have in promoting Ni incorporation is limited to extracelluar metabolite production. Incorporated Ni is likely more stable than adsorbed Ni, thus mycogenic manganese oxides may provide a more stable long term solution for Ni contamination sequestration than abiotic phyllomanganates.