Mn(II)-oxidizing fungi in metal contaminated environments

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Manganese (Mn) oxides are environmentally abundant, highly reactive mineral phases that play important roles in the biogeochemical cycling of nutrients, contaminants, carbon, and numerous other elements. The oxidation of Mn(II) to these sparingly soluble, nanocrystalline Mn(III/IV) oxide phases is believed to be largely driven by microbiological activity. Indeed, a wealth of research has provided fundamental knowledge regarding the mechanisms and products of bacterially-mediated Mn(II) oxidation. However, oxidation processes employed by fungi remain largely unresolved, despite evidence suggesting that fungi-stimulated oxidation may be substantial in some environments (e.g., the remediation of Mn-rich waters). We are examining several, phylogenetically distinct Mn(II) oxidizing fungi isolated from metal-laden environments to define their biomineralization pathways, mechanisms, and byproducts.

To obtain a diverse group of fungal isolates for biogeochemical examination, we performed a culture-based survey of the Mn(II)-oxidizing microbial populations present in two distinctly different Mn(II)-rich surface environments – an industrially impacted freshwater pond and an acid mine drainage treatment system. Several representative species were subsequently selected for chemical assays (e.g. addition of specific protein inhibitors or elemental cofactors) using cell extracts, spent media filtrate, and in-gel protein extracts to delineate the enzymes contributing to Mn oxidation. The speciation, structure, site occupancy and stacking order of the Mn oxide byproducts were determined using X-ray absorption spectroscopy (XAS).

Our study reveals at least 12 different Mn(II) oxidizing Ascomycota species, including members of the Hypocreales, Xylariales, Phyllachorales, Pleosporales, and Capnodiales. Initial results suggest that a few species employ a laccase (multicopper oxidase; MCO) enzyme for oxidation, similar to many Mn(II)-oxidizing bacteria, but additional oxidative mechanisms may be present. Furthermore, Mn XAS analysis demonstrate that these fungi precipitate highly-disordered, reactive oxide phases (e.g. δ-MnO_2 and triclinic birnessite), which are known to be important players in the cycling of contaminants and nutrients in soils and sediments.

Mineralogical characterization of the precipitates developed in a reactive permeable barrier (Shilbottle, NE England)

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In Shilbottle coal mine, a groundwater plume (pH<4, [Fe]>300 mg/L, [Mn]>165 mg/L, [Al]>100 mg/L and [SO_4]>6500 mg/L) was treated with a permeable reactive barrier (PRB, mixture of 50% limestone chips, 25% slurry screening and 25% compost), which transfers alkalinity in anoxic condition.

A mineral characterization of the precipitates developed inside the PRB, was performed by three different techniques: sequential extraction (SE), XRD and E-SEM. The important amount of sulfur and calcium detected in the first step of the SE can be attributed to the presence of gypsum, which was also identified by XRD. The specific steps employed in the SE to differentiate between oxyhydroxides and oxides suggested the presence of different proportions of these Fe-mineral phases inside the PRB, but only jarosite and goethite were confirmed with XRD. Mn release at the SE was linked to the dissolution of the Fe-minerals. This fact could be explained by the presence of Mn-Fe phases or by the adsorption/ coprecipitation of this element in the Fe-minerals. Elevate amount of trace elements were observed after Mn-Fe precipitates dissolution. Concerning to the Al-phases, they were not identified by XRD. However an important amount of Al observed in some steps of the SE could be explained by phases like alunite, basaluminite or jurbanite, which were oversaturated on the pore water of the PRB, according to the hydrochemical model performed with PHREEQC. The presence of pyrite was corroborated by all the techniques employed, being an important evidence of the reducing environment inside the PRB.