Morphologies of fungal Mn oxide biomineralization in southern Appalachian caves

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A common characteristic of southern Appalachian caves are thin, brown-black manganese (Mn) oxide coatings on the walls, on flowstone associated with springs and seeps, and on pebbles and cobbles in streams and pools. These mineral coatings are often associated with bacterial communities, suggesting that microbial activity plays a role in the precipitation of Mn(III/IV) oxides (through catalyzing the oxidation of Mn(II) compounds). Until recently, a fungal contribution to this Mn biomineralization process in caves has been largely overlooked.

In this study, we sought to examine the role of fungi in Mn biomineralization in Daniel Boone Caverns in southwest Virginia and Carter Salt Peter Cave in east Tennessee, all located in the Ordovician Knox Dolomite. Sample locations were chosen based on the presence of black or brownish-black mineral coatings or biofilms on the cave walls and floors, or growing on materials left in the cave by human and animal visitors (tape, socks, feces). X-ray diffraction analyses indicate that the primary cave substrates supporting the Mn oxide coatings was either nontronite clay, dolomite, or anthropogenic materials. Mn oxidation was confirmed in the field using the leucoberbelin blue (LBB) assay, a colorless chemical compound that turns bright blue in the presence of Mn(III) or Mn(IV) compounds. Oxidation was observed in both pristine and agriculturally-contaminated cave systems.

We isolated several different species of Mn(II)-oxidizing fungi from the variety of cave samples. Fungal isolates were analyzed by scanning and transmission electron microscopy (SEM and TEM). TEM imaging with STEM analysis revealed that in several samples, Mn oxidation occurred along the fungal hyphae cells, particularly where new hyphal branches were forming. In other cultures, Mn oxides formed crumpled sheets surrounding the entire exterior of fungal hyphae. In addition to the hyphae-associated oxidation, Mn oxides were produced at the base of fruiting bodies. Interestingly in one culture, fungal spores appeared to be sequestering Mn^{2+} within the spore, but no Mn oxides were present on the cell exteriors.

The Mn oxides produced by fungal cultures were poorly crystalline and amorphous to laboratory-based X-ray sources. Tentative crystallographic identification of Mn oxides by single crystal micro-X-ray diffraction indicate that buserite and todorokite (layer and tunnel structures, respectively) were the dominant Mn oxides present in samples isolated from biofilms in Carter Salt Peter Cave. In the cave environment, the presence of cations, such as Ca^{2+}, may result in the transformation of poorly-crystalline oxide phases to more crystalline and stable forms, such as birnessite and todorokite.

Dynamics of Uranium Release from the Capillary Fringe of Contaminated Hanford Sediments

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Introduction

The fate and transport of radionuclides from contaminated sediments represents a major long-term risk at department of energy (DOE) sites. Waste disposal units at DOE sites have undergone source zone removal, however, a number of persistent subsurface plumes remain. Sediment analysis from these sites suggests the residual contamination has migrated into sediment fractures, pores and pore-throats and is influenced by coupled nanometer scale reactions. These pore scale reactions affect pore-scale contaminant concentrations and control the presence of persistent subsurface plumes. Our objective was to quantify the dynamics of U concentrations in the pore water of micropores compared to large pores.

Methods

We investigated the dynamics of U release to pore water during river stage changes from two contaminated capillary fringe sediments, sampled from 7.0 m and 7.6 m below ground surface (bgs) in the Hanford 300 area. Sediments were packed into columns and saturated with Hanford groundwater for three to 84 days. After specified times, sediment pores > 48 μm radius were drained, followed by draining pores to 15 μm radius.

Results

U release in the first two weeks was similar between sediments and pore sizes with a range of 4.4 to 5.6 μM U in the two-week sample. The 7.0 m bgs sediment U declined steadily in the larger pores to 0.22 μM at day 84, whereas the smaller pores released U to 9.4 μM at day 28 then to 6.7 μM at day 84. The 7.6 m bgs sediment released 6.2 μM U on day 28 and 1.4 μM on day 84, in the large pores. MINTEQ simulations where pH was increased from 8.1 to 8.35 can be used to model the U release and reincorporation into a solid phase. A mineral phase in the sediments was identified as a U-carbonate species, similar to rutherfordine.