

## Biomineralization of Mn oxides by Mn(II)-oxidizing fungi

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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. The majority of studies thus far have focused on the contributions of bacteria to the biogeochemical cycling of Mn, however recent studies have suggested that fungi may substantially contribute to the biomineralization of Mn oxide minerals in some environments. Understanding the environmental impact of these fungally precipitated mineral phases requires detailed analysis of their size, composition, and structure.

Several species of Mn(II)-oxidizing Ascomycete fungi were isolated from metal-contaminated and freshwater environments. A microscopic examination of these fungi revealed that the patterns of Mn oxide deposition varied amongst the different species. In this study, representative Mn(II)-oxidizing fungi were grown under the same chemical and physical conditions to determine if the species of fungus impacts the size, morphology, or structure of Mn biooxides. A combination of electron microscopy and synchrotron radiation X-ray absorption spectroscopy (SR-XAS) were utilized to characterize the Mn oxide phases produced by these representative fungal species.

Our study reveals that the initial phase produced by different species of Mn(II)-oxidizing fungi grown under the same conditions is a highly disordered, nanocrystalline phyllo-manganate similar to  $\delta$ -MnO<sub>2</sub>. Amongst the different species, however, differences in mineral size, morphology, and secondary products are observed. Changes in solution chemistry (e.g. Mn concentration) further impacts the structure of these biominerals, which could translate to large influences on biogeochemical processes in the environment.

## Changes in the Fe(II)/Fe(III) ratio by bacterial activity according to dynamics of an acid pit lake

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Nuestra Señora del Carmen acidic pit lake (Iberian Pyrite Belt) generally presents a chemical stratification, differentiating two layers: 1) a thin upper layer of ~2 m depth, pH between 2.5-2.7, EC from 2 to 8 mS/cm and Eh 820 mV, which corresponds to oxic conditions where iron is predominantly Fe(III), and 2) a thick bottom layer from 2 m to 35 m depth, homogeneous in depth, with pH ~2.5, EC 9 mS/cm, anoxic (<0.2 mg/L) and Eh between 640-680 mV, where Fe is both Fe(II) and Fe(III). Microbial community composition was analyzed by 16S and 18S rRNA gene cloning and sequencing in this layer, detecting oxidising bacteria (*Leptospirillum*) and the facultative iron-reducing bacteria such as *At. ferrooxidans* and *At. ferrivorans*.

Occasionally at the beginning of some winters, a period of mixing and total homogenization was observed in entire water column, being this process favoured by dry autumns. The pit lake recovered the chemical stratification after intense episodes of rainfall (strong inflow of runoff). An unusual mixing process happened during summer 2009 as a result of intense evapoconcentration that took place in the upper layer.

High average concentrations of SO<sub>4</sub> (8.5 g/L), Mg (1.0 g/L) and metals (Fe 760 mg/L, Al 230 mg/L, Mn 88 mg/L and Cu 29 mg/L) were measured in the homogeneous pit lake during the winter mixing. In this process the dissolved oxygen is introduced from surface to depth, but it is rapidly consumed by the bacterial oxidation of ferrous iron, decreasing the Fe(II)/Fe(III) ratio. This ability is normal in these types of microorganisms as could be checked during the winter mixing of entire water column in November 2008 or partial mixing of summer 2009, in which had a decrease of the Fe(II) and a increase of the Fe(III) as a result of aerobic bacterial oxidation. These bacterial species have revealed metabolic versatility, being able to reduce ferric iron in anoxic conditions. This ability is less common but it was registered in the anoxic bottom layer during stratification periods (Fe(II) increased and Fe(III) dropped). Extremophile bacteria respond to changes in environmental conditions and its versatility seems to control the evolution of the redox species of iron in the bottom layer of this pit lake.