

## **Structure of nanocrystalline phylломanganates produced by freshwater fungi**

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### **ABSTRACT**

The crystal structures of biogenic Mn oxides produced by three fungal strains isolated from stream pebbles were determined using chemical analyses, XANES and EXAFS spectroscopy, and powder X-ray diffraction. The fungi-mediated oxidation of aqueous Mn<sup>2+</sup> produces layered Mn oxides analogous to vernadite, a natural nanostructured and turbostratic variety of birnessite. The crystallites have domain dimensions of ~10 nm in the layer plane (equivalent to ~35 MnO<sub>6</sub> octahedra), and ~1.5–2.2 nm perpendicularly (equivalent to ~2–3 layers), on average. The layers have hexagonal symmetry and from 22 to 30% vacant octahedral sites. This proportion likely includes edge sites, given the extremely small lateral size of the layers. The layer charge deficit, resulting from the missing layer Mn<sup>4+</sup> cations, is balanced mainly by interlayer Mn<sup>3+</sup> cations in triple-corner sharing position above and/or below vacant layer octahedra. The high surface area, defective crystal structure, and mixed Mn valence confer to these bio-minerals an extremely high chemical reactivity. They serve in the environment as sorption substrate for trace elements and possess catalytic redox properties.

**Keywords:** Manganese oxide, birnessite, biominerals, phylломanganate, crystal structure