American Mineralogist, Volume 95, pages 1608–1616, 2010

Structure of nanocrystalline phyllomanganates produced by freshwater fungi

Sylvain Grangeon,[1,*,†] Bruno Lanson,[1,*] Naoyuki Miyata,[2,3] Yukinori Tani,[2] and Alain Manceau[1]

[1]Mineralogy and Environments Group, Laboratoire de Géodynamique des Chaines Alpines, Université J. Fourier, CNRS, F-38041 Grenoble Cedex 9, France
[2]Institute for Environmental Sciences, University of Shizuoka, Shizuoka 422-8526, Japan
[3]Department of Biological Environment, Akita Prefectural University, Shimoshinjo-Nakano, Akita 010-0195, Japan

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^{2+} 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_6 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^{4+} cations, is balanced mainly by interlayer Mn^{3+} 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, phyllomanganate, crystal structure