American Mineralogist, Volume 91, pages 489–502, 2006

Structural model for the biogenic Mn oxide produced by *Pseudomonas putida*

MARIO VILLALOBOS,[1,3,*] BRUNO LANSON,[2] ALAIN MANCEAU,[2] BRANDY TONER,[3] AND GARRISON SPOSITO[3]

[1]Environmental Bio-Geochemistry Group, LAFQA, Instituto de Geografía, National Autonomous University of Mexico (UNAM), Circuito Exterior, Ciudad Universitaria, Mexico, Coyoacán, 04510, D.F., Mexico
[2]Environmental Geochemistry Group, LGIT, Maison des Géosciences, BP53, University of Grenoble—CNRS, 38041 Grenoble Cedex 9, France
[3]Division of Ecosystem Sciences, University of California at Berkeley, Berkeley, California 94720-3114, U.S.A.

ABSTRACT

X-ray diffraction (XRD) and Mn K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy were combined to elaborate a structural model for phyllomanganates (layer-type Mn oxides) lacking 3D ordering (turbostratic stacking). These techniques were applied to a sample produced by a common soil and freshwater bacterium (*Pseudomonas putida*), and to two synthetic analogs, δ-MnO_2 and acid birnessite, obtained by the reduction of potassium permanganate with $MnCl_2$ and HCl, respectively. To interpret the diffraction and spectroscopic data, we applied an XRD simulation technique utilized previously for well-crystallized birnessite varieties, complementing this approach with single-scattering-path simulations of the Mn K-edge EXAFS spectra. Our structural analyses revealed that all three Mn oxides have an hexagonal layer symmetry with layers comprising edge-sharing $Mn^{4+}O_6$ octahedra and cation vacancies, but no layer $Mn^{3+}O_6$ octahedra. The proportion of cation vacancies in the layers ranged from 6 to 17%, these vacancies being charge-compensated in the interlayer by protons, alkali metals, and Mn atoms, in amounts that vary with the phyllomanganate species and synthesis medium. Both vacancies and interlayer Mn were most abundant in the biogenic oxide. The diffracting crystallites contained three to six randomly stacked layers and have coherent scattering domains of 19–42 Å in the **c*** direction, and of 60–85 Å in the **a-b** plane. Thus, the Mn oxides investigated here are nanoparticles that bear significant permanent structural charge resulting from cation layer vacancies and variable surface charge from unsaturated O atoms at layer edges.

Keywords: Geomicrobiology, *Pseudomonas putida*, Mn oxide, XAS, biogenic Mn oxide, XRD data, crystal structure, new minerals