The Structure of the Manganese Oxide on the Cell Wall of the Bacterium *Leptothrix discophora*: An XAFS Study

A. Jürgensen, J. R. M. King, R. A. Gordon, L. I. Bendell-Young, M. M. Moore, E. D. Crozier
Simon Fraser University, Burnaby, B.C., Canada

Introduction

In natural waters, manganese oxides (MnO_x) are important in mediating the bioavailability of trace metals such as Ni, Cd, and Pb, because these metals readily adsorb to the MnO_x surface. In the presence of oxygen and under neutral (pH = 7) conditions, soluble manganese (Mn^{2+}) is oxidized to MnO_x. Bacteria such as *Leptothrix discophora* can catalyze this process.

In our ongoing studies[1] of trace metal bioavailability, we grew *L. discophora* in the presence of Mn^{2+} and employed Mn K-edge x-ray absorption spectroscopy to determine the oxidation state (XANES) and coordination (EXAFS) of Mn atoms in the bacterial MnO_x. Our results suggest that this MnO_x has a structure closely related to the mineral birnessite.[2]

Methods and Materials

L. discophora SP-6 was grown for 48 h under controlled laboratory conditions at room temperature.[2] All fluid was removed, and the bacteria were freeze-dried. Mn K-edge absorption spectra were collected using the Si-(111) double crystal monochromator on the Pacific Northwest Consortium Collaborative Access Team undulator beamline.[3] The sample was sandwiched between two layers of adhesive Kapton tape, mounted along the circumference of a Plexiglas disk (3.0" ∅), and rotated at 1200 rpm to minimize radiation damage. The fluorescence spectra were collected using an ion chamber.[4] Spectra of manganese oxide minerals were measured under the same experimental conditions to aid in the structural identification.

EXAFS oscillations were extracted from the spectra using our standard procedures.[2] Fourier transformation into r-space of the k^3-weighted EXAFS spectrum $k^3\chi(k)$ was performed over the k-range from 2.9 to 11.85 $Å^{-1}$ using a 10% Gaussian window. The pre-edge features were isolated from the absorption edge using a background subtraction procedure.[2]

Table 1: The experimental Mn K-edge absorption energies

Name	Oxidation state of Mn	Edge energy (eV)(a)	White-line peak energy (eV)(a)
Mn metal foil	0	6537.7(b)	
MnO_2 (birnessite)	3.77	6548.0	6559.7
Leptothrix discophora	4	6548.4	6560.5
MnO_2 (todorokite)	4	6549.5	6560.9
MnO_2 (powder)	4	6551.4	6559.0

(a) Uncertainty: ±0.5 eV. (b) Calibration standard.[9]

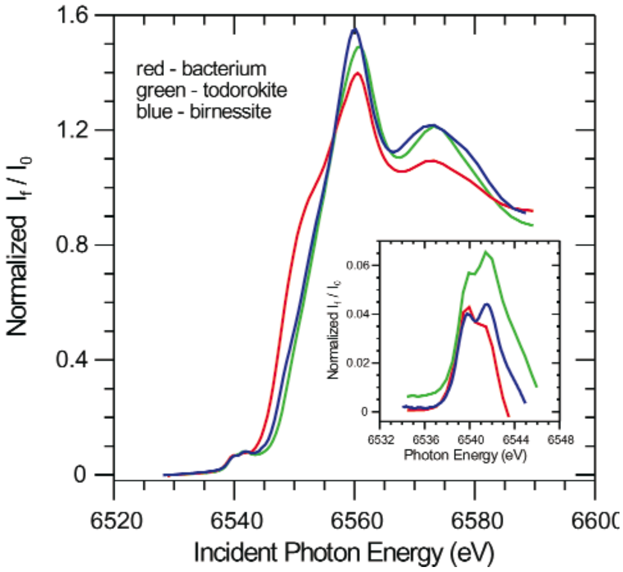

FIG. 1. Mn K-edge XANES spectra.

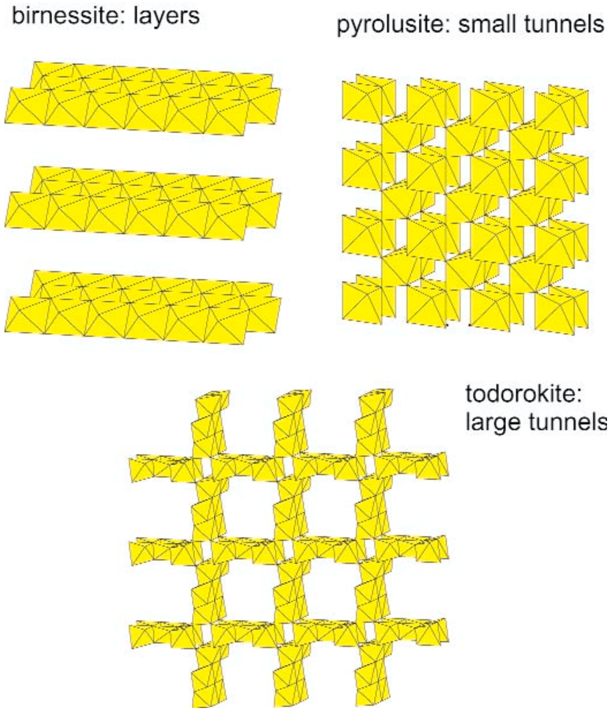

FIG. 2. Some MnO_2 crystal structures.

Results and Discussion

The edge energy and the white-line energy for the bacterial MnO_x are between those of birnessite and todorokite (Table 1), suggesting a formal oxidation state close to 4.0 (Mn^{4+}). The spectral features resemble those of birnessite and todorokite, but there is a shoulder preceding the white line observed in neither mineral (Fig. 1). There is one low-intensity pre-edge feature peaking at 6539.6 eV with a high-energy shoulder caused by a peak at 6541.5 eV. The relative intensities of these peaks are reversed in both minerals (Fig. 1, inset).

MnO_2 has a variety of different stable crystal structures,[5,6] composed of MnO_6 octahedra forming layers or tunnels (Fig. 2). The Fourier transform of $k^3\chi(k)$ of all manganese dioxides has

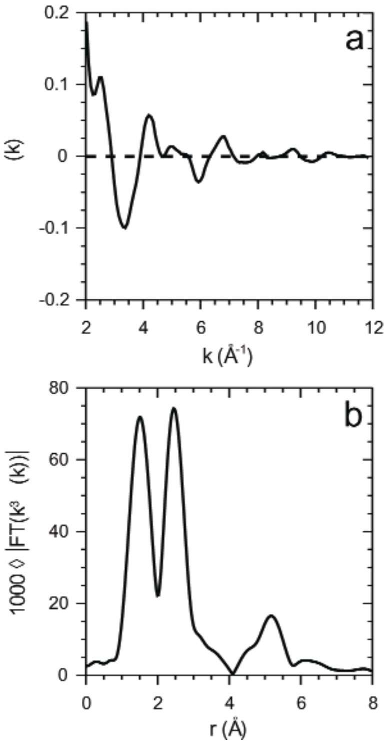

FIG. 3. (a) Mn K-edge XAFS spectrum of the bacterium and (b) its Fourier transform.

two fairly high intensity peaks corresponding to the Mn-O distance of 1.9 Å in the first coordination shell and the edge-sharing Mn-Mn distance of 2.9 Å in the second shell. A peak at 3.4 Å, corresponding to the Mn-Mn distance of corner-sharing octahedra, is only observed for the tunnel structures.[5,7]

The Fourier transform of the EXAFS interference function $\chi(k)$ [Fig. 3(a)], weighted by k^3 of the bacteria sample has two high-intensity peaks corresponding to the Mn-O distance of 1.9 Å and the Mn-Mn distance of 2.9 Å [Fig. 3(b)]. A peak at 3.4 Å is not observed, indicating a layered structure. The peaks in the figure appear at shorter distances because of the EXAFS phase shift, which has not been removed. Fits using spectra calculated with FEFF7[8] suggest that the bacterial MnO_x is composed of microcrystals having a structure related to birnessite.[2]

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