

Structural characterization of biogenic Mn oxides produced in seawater by the marine *bacillus* sp. strain SG-1

S.M. WEBB,^{1,*} B.M. TEBO,² AND J.R. BARGAR¹

¹Stanford Synchrotron Radiation Laboratory, Menlo Park, California 94025, U.S.A.

²Scripps Institution of Oceanography, University of California San Diego, La Jolla, California 92093, U.S.A.

ABSTRACT

Natural Mn-oxide nanoparticles and grain coatings are ubiquitous in the environment and profoundly impact the water quality and quality of sediments through their ability to degrade and sequester contaminants. These oxides, which are believed to form dominantly via oxidation of Mn²⁺ by marine and freshwater bacteria, have extremely high sorptive capacities for heavy metals. We have used XANES, EXAFS, and synchrotron (SR)-XRD techniques to study biogenic Mn oxides produced by spores of the marine *Bacillus* sp. strain SG-1 in seawater as a function of reaction time under in-situ conditions. An EXAFS model was developed to fully account for the structure and features in the data, providing realistic structural information. The first observed biogenic solid-phase Mn-oxide product is a layered phyllomanganate with hexagonal sheet symmetry and an Mn-oxidation state similar to that in δ -MnO₂, between 3.7 and 4.0. XRD and SEM-EDS data show the biooxides to have a phyllomanganate 10 Å basal plane spacing and an interlayer containing Ca. With time, a phyllomanganate oxide with pseudo-orthogonal sheet symmetry appears. Fits to these EXAFS spectra suggest the octahedral layers have relatively few Mn octahedral site vacancies in the lattice and the layers bend to accommodate Jahn-Teller distortions creating the change in symmetry. A reaction mechanism is proposed to account for the observed products. The phyllomanganate oxides observed in this study may be the same as the most abundant Mn-oxide phases suspended in the oxic and sub-oxic zones of the oceanic water column that are of global importance in trace metal and nutrient cycling.