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BIOGENIC MANGANESE OXIDES: Properties and Mechanisms of Formation

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■ **Abstract** Manganese(IV) oxides produced through microbial activity, i.e., biogenic Mn oxides or Mn biooxides, are believed to be the most abundant and highly reactive Mn oxide phases in the environment. They mediate redox reactions with organic and inorganic compounds and sequester a variety of metals. The major pathway for bacterial Mn(II) oxidation is enzymatic, and although bacteria that oxidize Mn(II) are phylogenetically diverse, they require a multicopper oxidase-like enzyme to oxidize Mn(II). The oxidation of Mn(II) to Mn(IV) occurs via a soluble or enzyme-complexed Mn(III) intermediate. The primary Mn(IV) biooxide formed is a phyllomanganate most similar to δ-MnO_2 or acid birnessite. Metal sequestration by the Mn biooxides occurs predominantly at vacant layer octahedral sites.

INTRODUCTION

Mn oxides (a term we use to collectively include oxides, hydroxides, and oxyhydroxides) are highly reactive mineral phases that play important roles in elemental biogeochemical cycles. Mn oxides are some of the strongest oxidants naturally found in the environment, and as such, they participate in a wide range of redox reactions with organic and inorganic chemical species and compounds. Many dissimilatory metal-reducing bacteria can use Mn oxides as the terminal electron acceptor for the oxidation of organic matter or H_2 in the absence of oxygen. Mn oxides also have high sorptive capacities and therefore adsorb a wide range of ions, controlling the distributions and bioavailability of many toxic and essential elements. Indeed, Mn oxides have long been recognized as the "scavengers of the sea" (Goldberg 1954).

Microorganisms, especially bacteria but also fungi, are known to catalyze the oxidation of Mn(II) and the formation of Mn(III,IV) oxide minerals. Biological Mn(II) oxidation is generally fast relative to abiotic Mn(II) oxidation processes, including surface-catalyzed reactions (Hastings & Emerson 1986, Nealson et al. 1988, Tebo et al. 1997, Bargar et al. 2000, Morgan 2000), suggesting that biological Mn(II) oxidation dominates in the environment. A number of investigations at specific field sites have shown that biological processes are responsible for Mn(II) oxidation at those locations (Emerson et al. 1982; Tebo et al. 1984; Tipping 1984; Tebo & Emerson 1985, 1986; Cowen et al. 1986, 1990; Tebo 1991; Mandernack & Tebo 1993; Wehrli et al. 1995; Harvey & Fuller 1998; Marble 1998; van Cappellen et al. 1998; Marble et al. 1999; Fuller & Harvey 2000; Kay et al. 2001). For these reasons, the majority of naturally occurring environmental Mn oxides are believed to be derived either directly from biogenic Mn(II) oxidation processes or from the subsequent alteration of biogenic oxides.

Our knowledge of the properties and structures of Mn(IV) oxide minerals is based largely on studies of oxides made synthetically in the laboratory using extreme conditions of pH, Mn(II) concentration, or temperature. The structures and compositions of biogenic Mn oxides, i.e., Mn biooxides, as well as the mechanisms by which bacteria oxidize Mn(II), have remained largely a mystery. Partly as a result of this lack of information, a number of investigators have sought to interpret the mechanisms of microbial Mn(II) oxidation based on the stability relations known for well-characterized (abiotic) Mn oxides. Ultimately, the thermodynamic relations are expected to play a major role in determining the compositions of biooxides. In the past several years, with the development of good model systems in the laboratory, it has been possible to use Mn(II)-oxidizing bacteria to synthesize Mn oxide minerals under environmentally relevant conditions and to compare their properties to those of synthetic Mn oxides. This review presents general background information on Mn chemistry, mineralogy, sorptive properties, and microbiology. It then summarizes our state of knowledge concerning Mn oxide biogenesis, focusing on the molecular mechanisms of bacterial Mn(II) oxidation and the properties of Mn biooxides. A recent review on the kinetics of Mn(II) oxidation and the scavenging of toxic trace metals by Mn oxides (Nelson & Lion 2003) is available, as are other, somewhat older, but thorough reviews of microbial Mn oxidation (Ghiorse 1984, Nealson et al. 1988, Ghiorse & Ehrlich 1992, Tebo et al. 1997, Tebo & He 1999, Emerson 2000, Brouwers et al. 2000b) and a review of the crystal structures and economic importance of Mn oxides (Post 1999).

Manganese Chemistry

Manganese is Earth's second most abundant transition metal next to iron and resembles iron in several aspects of its geochemistry. This resemblance is due in part to the fact that these metals occur in multiple valence states in the environment and are essential micronutrients for most organisms. Among the various oxidation states of Mn, the +II, +III, and +IV are the most prevalent in nature (Figure 1).

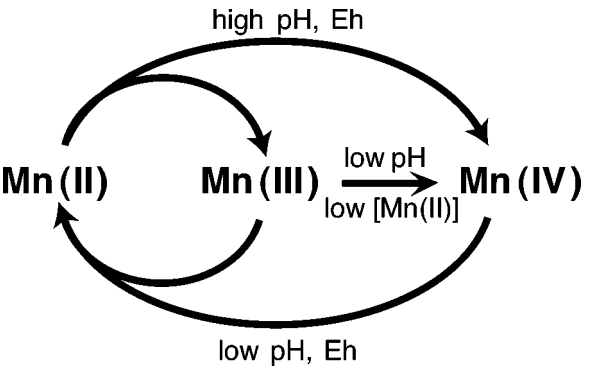

Figure 1 The Mn cycle of oxidation states found in nature. Mn(II) is thermodynamically stable in the absence of O_2 and at low pH, whereas in the presence of O_2, Mn(III) and Mn(IV), which occur primarily as insoluble Mn (oxyhydr)oxides, are favored.

In general, Mn(II) is thermodynamically favored in the absence of oxygen and at low pH, whereas Mn(III) and Mn(IV) are favored in the presence of oxygen and at high pH. Mn(II) occurs as a cation (Mn^{2+}) in solution; as insoluble phosphates or carbonates; and as a minor constituent of other minerals, including Mn(III,IV) oxides. Mn^{2+} can exist at up to millimolar concentrations in natural waters, even in the presence of oxygen. Owing to the high activation energy, the oxidation of Mn(II) to Mn(III) and Mn(IV) is largely catalyzed by microorganisms (bacteria and fungi). Mn(III), which is thermodynamically unstable and disproportionates in aqueous media to yield Mn(II) + Mn(IV), persists only in certain soluble organic complexes (Kostka et al. 1995, Luther et al. 1998, Klewicki & Morgan 1998, 1999; D.L. Parker, G. Sposito & B.M. Tebo, submitted) and in some minerals (e.g., Lanson et al. 2000); Mn(IV) occurs, often with varying amounts of Mn(III), in insoluble oxides, oxyhydroxides, and hydroxides that are important constituents of soils, sediments, and ore-grade deposits. Mn(III) and Mn(IV) are also found in environmentally prevalent ferromanganese (oxyhydr)oxide minerals (Nealson et al. 1988, Nicholson et al. 1997, Tebo et al. 1997). The Mn(III)/Mn(II) and Mn(IV)/Mn(II) couples have particularly high redox potentials, making Mn(III) and Mn(IV) phases some of the stronger oxidants found in the environment. For example, Mn oxides react with the reduced forms of other metals, such as Se, As, and Cr, thereby influencing toxic metal availability by oxidative precipitation or solubilization (Wehrli 1990, Huang 1991, Fendorf et al. 1992, Fendorf & Zasoski 1992, Manceau & Charlet 1992, Scott & Morgan 1995, Nico & Zasoski 2000).

Mineralogy of Mn Oxides

Mn(II) is released through the weathering of igneous and metamorphic rock and is oxidized, forming more than 30 known Mn(III), Mn(IV), or mixed Mn(III,IV) oxide/hydroxide minerals (Post 1999). The Mn(IV) oxides and the mixed Mn

(III,IV) (hydroxy)oxides are termed manganates to emphasize their oxyanion properties (Giovanoli & Arrhenius 1988). Manganates characteristically have open crystal structures; large surface areas with high negative charges; and exchangeable charge-balancing cations, such as Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}, and Mn^{2+}. The basic unit of most Mn oxide minerals is the MnO_6 octahedron, which is generally arranged into either layer structures or chain/tunnel structures. The tunnel structures have single, double, or triple chains of edge-sharing MnO_6 octahedra in which the chains share corners to form tunnels of square or rectangular cross section (Figure 2). The single chain structure (i.e., pyrolusite) differs from the double or triple chains (e.g., todorokite or hollandite) in tunnel diameter and thus surface area, hydration, and accessibility to exchangeable cations.

The layer structures (phyllomanganates) consist of layered sheets of Mn octahedra (e.g., birnessite; Figure 2). Water and various cations are incorporated into

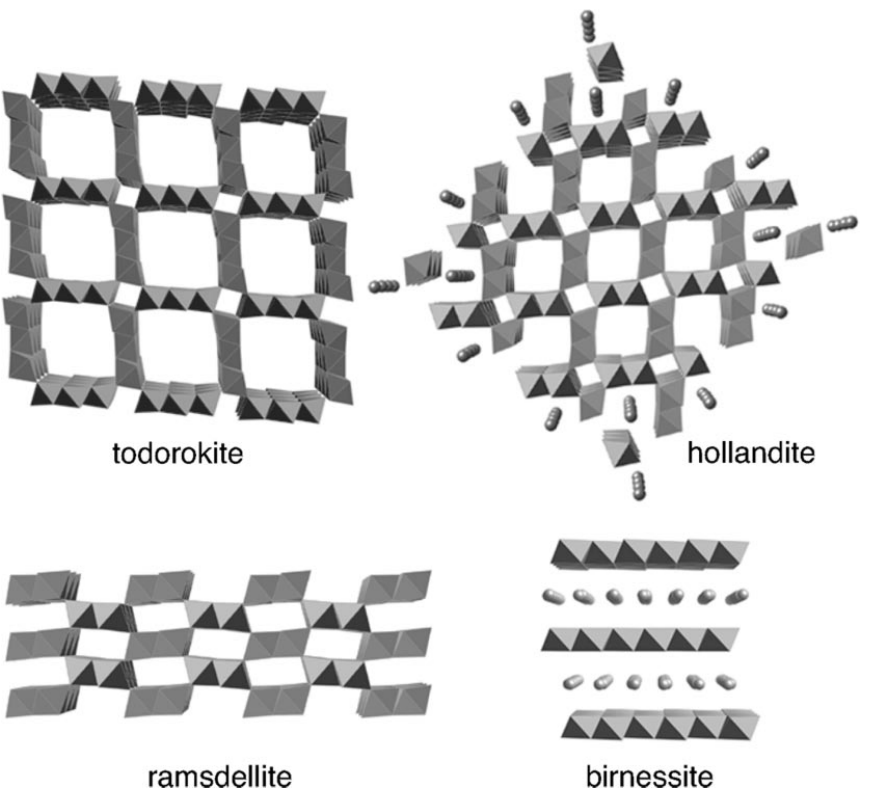

Figure 2 Examples of the chain/tunnel (todorokite, hollandite, and ramsdellite) and layer (birnessite) type crystal structures of Mn oxides. To make the tunnel structures more apparent, the barium cations are not shown in the central tunnels of the hollandite structure and the charge-balancing cations (Ca, Na, and K) are not shown for todorokite.

the interlayer region between the octahedral sheets such that the distance between sheets is affected by the number of interspersed water layers and by counterion size (Giovanoli & Arrhenius 1988). Phyllomanganates with a ca. 10 Å d-spacing (lithiophorite; 10 Å manganate; or buserite, not an official mineral but structurally related to birnessite) contain an extra water layer as compared to those with a ca. 7 Å d-spacing (birnessite, chalcophanite, δ-MnO_2, synthetic 7 Å Na manganate). The precise spacing in 10 Å manganates varies with the interlayer cations (Arrhenius & Tasi 1981, Kuma et al. 1994). Certain 10 Å Na phyllomanganates collapse to 7 Å when dehydrated or protonated, but expand when exposed to large cations like dodecylammonium. This property sometimes distinguishes 10 Å phyllomanganates (i.e., buserite) from tunnel manganates (i.e., todorokite), which are neither collapsible nor expandable (Burns et al. 1983, Usui & Someya 1997). Cations such as Ca^{2+}, Mg^{2+}, Ni^{2+}, and Cu^{2+} stabilize the 10 Å phyllomanganate structure and prevent collapse, whereas others such as H^+, K^+, Pb^{2+}, Ce^{3+}, and Th^{4+} stimulate collapse (Arrhenius & Tasi 1981). K^+, Ba^{2+}, Pb^{2+}, or other large cations can stabilize or promote the formation of tunnel structures (Roy 1981). The structure of synthetic manganates is also influenced by the Mn(II) concentration, pH, and redox conditions during synthesis or subsequent equilibration. For example, triclinic Na-birnessite is formed by alkaline oxidation of Mn(II), acid birnessite by acidic reduction of permanganate, and δ-MnO_2 or c-disordered H^+-birnessite by redox reactions of Mn(II) with permanganate at specific $KMnO_4/Mn^{2+}$ ratios (Villalobos et al. 2003). Triclinic and acid birnessites differ not only in crystal structure but also in Mn(III) content and Mn(III) positioning (Drits et al. 1997; Lanson et al. 2000, 2002a; Villalobos et al. 2003).

As discussed by Villalobos et al. (2003), the literature on layer-type Mn oxides is inconsistent with respect to nomenclature of δ-MnO_2, vernadite, birnessite, and hydrous manganese oxide, which should not be used interchangeably. This problem is partially due to difficulties in characterizing Mn oxides with poor crystallinity and is exacerbated by inadequate descriptions of oxide synthesis. Villalobos et al. (2003) have recommended that Mn oxides be designated by unit cell symmetry as an addition to the current nomenclature for these minerals.

Metal and Radionuclide Sorption by Mn Oxides

Based on sequential extraction data (Tessier et al. 1979) and other analyses of diverse samples worldwide, it has become clear that the Fe/Mn oxide component of soils and sediments is an important, even controlling, repository for a wide variety of metals in the majority of these systems (Table 1). Mn oxide minerals can adsorb or incorporate substantial amounts of Cu, Co, Cd, Zn, Ni, Sn, Pb, Ca, Fe, Ra, Hg, U, Pu, Po, As, Se, and Th (Wadsley 1950, Bacon et al. 1980, McLaren et al. 1985, Takamatsu et al. 1985, Todd et al. 1988, Stahl & James 1991, Wei & Murray 1991, Nicholson & Eley 1997, Nicholson et al. 1997, Farrell et al. 1998, Duff et al. 1999, Dong et al. 2000, Foster et al. 2003, Webb et al. 2003, O'Reilly & Hochella

TABLE 1 Examples of studies of metals and radionuclide partitioning to Mn oxides

	Topic/Conclusions	Environments	Reference(s)
Lead	Strong association with the Fe/Mn oxide fraction.	Latvian river sediments	(Klavins et al. 2000)
	Pb binding was dominated by Mn oxides, even in the presence of a 16-fold excess of Fe oxide.	Natural and artificial biofilms from Cayuga Lake and lab studies	(Nelson et al. 1996, 1999a,b; Dong et al. 2000)
	Assimilation of Pb by ryegrass was inhibited by Mn oxides. Sequential extractions of soils confirmed that Mn oxides proved the most effective treatment for reducing the water and acid extractable fractions of Pb.	Contaminated soils	(Mench et al. 1994)
	Assimilation of Pb by wheat was inhibited by Mn oxides. Ca carbonate and zeolite also reduced Pb phytoavailability.	Contaminated soils	(Chen et al. 2000)
	Seasonal cycling of Pb was correlated with Fe cycling, and not with Mn cycling.	Lake Sammamish, WA	(Balistrieri et al. 1995)
	No association of Pb with Fe/Mn oxide fraction.	Lake Baikal sediments	(Müller et al. 2002)
Cadmium	Long-term, but not short-term, Cd partitioning in Mn oxides.	Lake Baikal sediments	(Müller et al. 2002)
	Short-term partitioning in natural and artificial biofilms found Cd bound more to Mn oxides than Fe oxides (mol/mol).	Natural and artificial biofilms from Cayuga Lake and lab studies	(Dong et al. 2000)
	Both ryegrass and tobacco grown in Mn oxide–treated soils assimilated the least Cd. Sequential extractions of soil confirmed that Mn oxides proved the most effective treatment for reducing the water and acid extractable fractions of Cd.	Contaminated soils	(Mench et al. 1994)
	Assimilation of Cd by wheat was inhibited by Mn oxides. Ca carbonate and zeolite also reduced Cd phytoavailability.	Contaminated soils	(Chen et al. 2000)

Mercury	Hg cycling positively correlated with particulate Mn and Fe, and organic C. Total and inorganic particulate Hg correlated most strongly with particulate Mn, whereas particulate monomethylmercury was most strongly correlated with Fe.	Gironde Estuary, France	(Tseng et al. 2001)
	Birnessite added to a laboratory culture sorbs Hg(II) and prevents the bacterial methylation of inorganic mercury.	Lab studies	(Farrell et al. 1998)
Arsenic	Seasonal reduction of groundwater sediments releases Fe(II), Mn(II), and As into the water table. Aeration and sand filtration precipitate Fe and Mn oxides, and concurrently remove As to below 50 μg/L.	Red River delta, Vietnam	(Berg et al. 2001)
	As(III) migrates into Mn oxide pore water, followed by a surface-mediated oxidation to As(V) and absorption.	Lab studies	(Takamatsu et al. 1985)
	A two-step electron transfer creates soluble As(V) from As(III) prior to precipitation in a mixed valence manganese arsenate solid.	Lab studies	(Tournassat et al. 2002)
Cobalt	Specific sequestration of Co with Mn oxides; no correlation between Co and Fe oxides.	Scottish soils	(McLaren et al. 1986)
	Specific sequestration of Co with Mn oxides; no correlation between Co and Fe oxides.	Estuary sediments, Netherlands	(Zwolsman & van Eck 1999)
	Specific sequestration of Co with Mn oxides; no correlation between Co and Fe oxides.	Water column of stratified lake, MI, USA	(Taillefert et al. 2002)
	Oxidation of Co(III) is either by reduction of Mn(III) or by direct Co biooxidation catalyzed by Mn(II) oxidizing bacteria, Co is then sorbed to the Mn oxide.	Lab studies	(Moffett & Ho 1996)
	Biodegradation of Co-citrate complexes in Fe-coated and uncoated quartz sand was quick; in Mn-coated sand acetic acid washes were required to mobilize Co.	Lab studies	(Brooks et al. 1998)

(*Continued*)

TABLE 1 (*Continued*)

	Topic/Conclusions	Environments	Reference(s)
Zinc	Associated with the Fe/Mn oxide sequentially extracted fraction.	Sediments, Pearl River Estuary, China	(Li et al. 2001)
	Associated with the Fe/Mn oxide sequentially extracted fraction.	Freshwater sediments, Domodar River, India	(Singh et al. 1999)
	Associated with the Fe/Mn oxide sequentially extracted fraction.	Weathered soils	(Manceau et al. 2000a)
Chromium	*Soluble when oxidized: mobilized by Mn oxides*		
	First implication of chromium oxidation and mobilization by Mn oxides.	Contaminated soils	(Bartlett & James 1979)
	Showed oxidation of Cr(III) by β-MnO_2 was independent of oxygen; Mn oxide did not act as a catalyst, but was consumed.	Coal fly ash and smelter waste	(Eary & Rai 1987)
Plutonium	Associated with the Fe/Mn oxide sequentially extracted fraction.	Estuarine sediments	(Hamilton 1989)
	Mn oxides and smectites, but not Fe oxides, found to be efficient at Pu immobilization.	Groundwater	(Duff et al. 1999)
Uranium	*Soluble when oxidized: mobilized by Mn oxides*		
	Demonstration of inorganic oxidation of U(IV) by Mn oxides, and a Mn(IV) mediated decrease in the biological reduction of U(VI) by the bacteria *Shewanella putrefaciens*.	Lab studies	(Kennedy et al. 2000)

2003, Tani et al. 2003; S.M. Webb, J.R. Bargar & B.M. Tebo, submitted). These interactions have been reported to decrease dissolved trace metal and radionuclide concentrations by orders of magnitude (Bacon et al. 1980, Todd et al. 1988, Wei & Murray 1991, Fuller & Harvey 2000, Kay et al. 2001) even when only small amounts of Mn oxides are present (Jenne 1968). Some toxic metals are oxidatively precipitated, but notable exceptions to this rule are Cr and U, which are mobilized upon oxidation.

Metal adsorption, ion exchange, and precipitation of metals by Mn oxides are influenced by multiple factors. Those intrinsic to the oxide itself include the strong oxidizing nature of Mn oxide and the Mn(III)/Mn(IV) ratio; the variations in surface areas of Mn oxide particles and coatings; the capacity for cation exchange reactions, some of which exceed that of clays such as montmorillonite (Morgan & Stumm 1965, Post 1999); and crystal structure, crystal size, and degree of crystallinity. For instance, the 7 Å phyllomanganates generally show smaller cation exchange capacities and lower cation exchange rates than do 10 Å phyllomanganates or tunnel manganates (Giovanoli & Brütsch 1979, Crane 1981, Post 1999). Layer and tunnel manganates can differ in their cation replacement series. For example, a replacement series for todorokite (a 10 Å tunnel manganate) was Zn $\gg$ Mg $>$ Co or Ni, whereas that of a 10 Å sheet manganate was Co $>$ Ni $>$ Zn $>$ Mg (Crane 1981).

External factors mediating metal adsorption include pH; Eh; the presence and strength of competing ligands, including organic and inorganic metal-complexing agents; the presence of Fe and Al oxides; biological mediation of oxidation or sorption reactions; and other physicochemical properties, such as water velocity (i.e., exposure time of metal to reactive oxide surfaces), sediment porosity, salinity, and temperature. The combination of these factors complicates predictions of field behavior based on laboratory experiments. An interesting example occurs in Lake Baikal, where massive Fe and Mn oxide concretions have been deposited over millennia, with little human influence (Müller et al. 2002). In Lake Baikal, Mo and Cd are preferentially associated with Mn-rich deposits, whereas P and As are associated with Fe-rich ones. Cd is enriched in aged Mn concretions, but not in young Mn oxides near the sediment-water interface. In direct contrast to many other locales (Table 1), Pb, Zn, and Cu distributions in Lake Baikal are not correlated with either Fe or Mn oxides. Clearly, much remains to be learned about the interactions between metals and metal oxides in complex field environments.

Effects of Mn Oxides on Complex Organics and Organic Pollutants

Mn oxides promote the degradation of a wide array of complex organics, including humic substances, PCBs, phenols and chlorinated phenols, chlorinated anilines, and the ubiquitous pollutant atrazine (Stone & Morgan 1984a,b; Stone 1987; Ulrich & Stone 1989) via multiple chemical mechanisms. These processes

include free radical oxidation (Park et al. 1999), nucleophilic addition of the substrate to *o*-quinones (Park et al. 1999), oxidation and release of CO_2 without organic intermediates (Cheney et al. 1996, Nasser et al. 2000), and dealkylation at Mn oxide surfaces (Cheney et al. 1998). Mn oxides may also function as electron acceptors for bacterial degradation of organic pollutants such as toluene (Langenhoff et al. 1997a,b). Indeed, Mn-, Fe-, S-, and N-reducing bacteria account for $\geq$90% of monoaromatic hydrocarbon biodegradation in some aquifers (Kennedy et al. 1998).

Environmental Applications of Mn Oxides

Mn oxides have been used or proposed for many different applications in water and wastewater treatment; soil and sediment remediation (of metals and organics); metal removal and recovery; and as catalysts, sorbents and electrical conductors. For example, a widely used filtration medium for drinking water is manganese greensand (glauconite with Mn oxides of various Mn valence states), designed specifically to remove Mn(II), Fe(II), hydrogen sulfide, and arsenic (Casale et al. 2002). Also, the in situ immobilization of Pb in three types of soil and two mine spoilage samples was strikingly enhanced by the combined addition of phosphorous and the Mn oxide cryptomelane with a roto-tiller (Hettiarachchi et al. 2000). In studies of rye grass grown on Cd-, Pb-, or combined Cd/Pb-contaminated soils, supplementation of the soils with Mn oxide protected the plants from metal uptake to a greater extent than lime, phosphate basic slag, iron oxides, or a modified alumino-silicate (Mench et al. 1994). Similarly, the availability of Pb and Cd to wheat was reduced more by Mn oxides than by phosphate salt, hog composts, or Fe oxides, although calcium carbonate and zeolite had effects close to those of Mn oxides (Chen et al. 2000).

Microbial Mn(II) Oxidation

Microorganisms (bacteria and fungi) that oxidize Mn(II) to Mn(III/IV) oxides are widespread in nature and greatly accelerate the rate of oxidation in many environments (Tebo et al. 1984, 1985; Tipping 1984; Tebo & Emerson 1985, 1986; Cowen et al. 1986, 1990; Nealson et al. 1988; Tebo 1991; Mandernack & Tebo 1993; Wehrli et al. 1995; Harvey & Fuller 1998; van Cappellen et al. 1998; Marble 1998; Marble et al. 1999; Fuller & Harvey 2000; Kay et al. 2001). Although Mn oxide biogenesis has not been well characterized in fungi (Miyata et al. 2003), many phylogenetically diverse Mn(II)-oxidizing bacteria have been described. Based on 16S rRNA gene sequences, all belong to the low (Firmicutes) and high (Actinobacteria) G + C Gram-positive and the α, β, and γ Proteobacteria branches of the Domain Bacteria (Figure 3). Despite the fact that diverse microbes have the ability to oxidize Mn(II), the physiological function of Mn(II) oxidation is unknown. In the final step of Mn(II) oxidation bacteria often become encrusted in Mn oxides, usually at the onset of stationary phase or after sporulation. Although

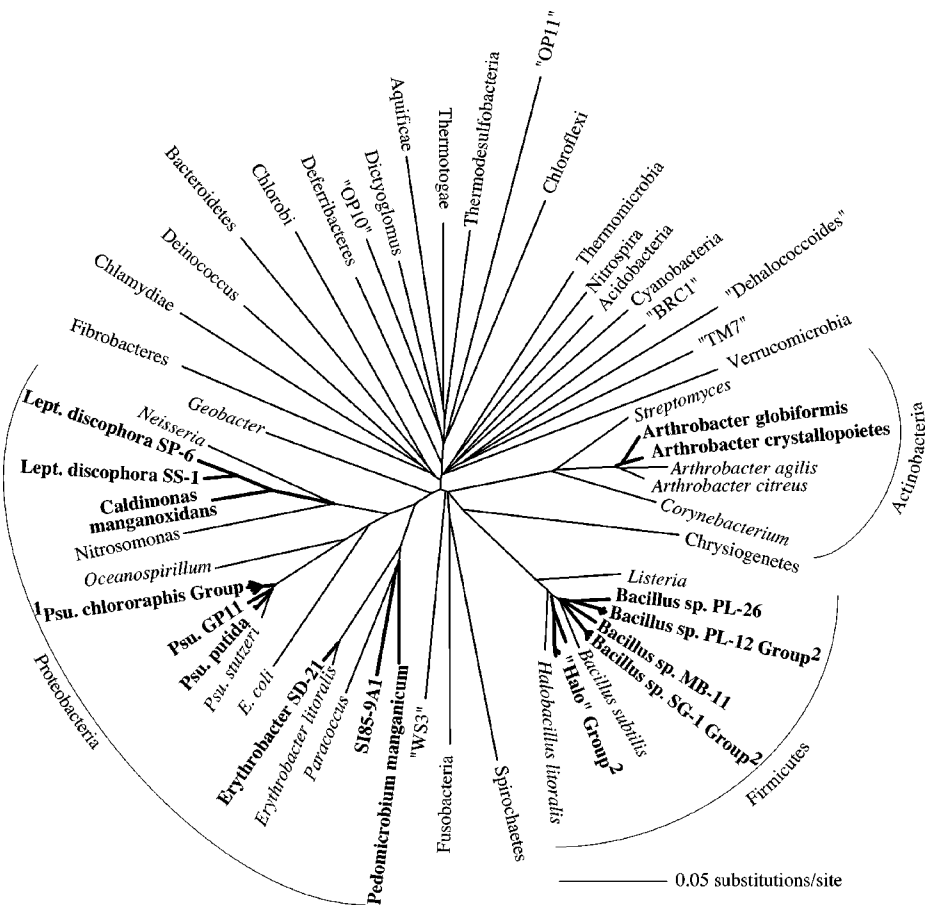

Figure 3 Location of Mn(II)-oxidizing bacteria on a neighbor-joining, unrooted phylogenetic tree of the Domain Bacteria. 16S rRNA sequences aligned over 1536 positions were obtained from the Ribosomal Database Project (RDP, http://rdp.cme.msu.edu) and analyzed using PAUP (ver. 4.0b10). Mn(II)-oxidizing bacterial strains for which sequences appear in the RDP are shown in bold. Sequence similarity is only an estimate of evolutionary relationships and is expressed here as the distance between any two branch tips; sequences that appear next to each other are not necessarily close relatives. Phyla in quotes are considered taxa of uncertain affiliation and have few, if any, cultivated members. Abbreviations: *Lept.*, *Leptothrix; Psu., Pseudomonas*. [1]The *Psu. chlororaphis* group includes the Mn(II)-oxidizing strains ISO1, ISO6, GB-13, MG1, and PCP, but not all similarly close relatives of *Psu. chlororaphis* are known to oxidize Mn(II). [2]*Bacillus* species groups are labeled according to Francis & Tebo (2002).

the oxidation of soluble Mn(II) to Mn(III/IV) oxides is energetically favorable and some evidence suggests that microbes are able to harness and utilize the energy of this reaction (Ehrlich 1983, Kepkay & Nealson 1987, Ehrlich & Salerno 1990), definitive proof remains elusive (Tebo et al. 1997, Brouwers et al. 2000b). One Mn(II)-oxidizing bacterium has even been shown to possess the genes for ribulose-1,5-bisphosphate carboxylase/oxygenase (Caspi et al. 1996), the enzyme responsible for CO_2 fixation in most aerobic chemolithoautotrophs. However, no correlation between Mn(II) oxidation and CO_2 fixation could be demonstrated. Other biological functions of Mn(II) oxidation have been proposed, including protection from toxic heavy metals, reactive oxygen species, UV light, predation, or viruses (Ghiorse 1984, Emerson 1989); storage of an electron acceptor for later use in anaerobic respiration (Tebo 1983); breakdown of refractory organic matter into utilizable substrates (Sunda & Kieber 1994); and scavenging of micronutrient trace metals. These potential biological functions of microbial Mn(II) oxidation are discussed extensively elsewhere (Tebo et al. 1997, Brouwers et al. 2000b).

Bacteria catalyze the oxidation of Mn(II) by direct and indirect processes. Indirect catalysis of Mn(II) oxidation occurs when organisms (*a*) modify the pH and/or redox conditions of the local aqueous environment, or (*b*) release metabolic end products that chemically oxidize Mn(II) (Richardson et al. 1988, Hullo et al. 2001). Bacteria have long been known to oxidize Mn(II) directly via the production of polysaccharides (van Veen et al. 1978, Ghiorse & Hirsch 1979, Beveridge 1989) or proteins (Ehrlich 1968, Jung & Schweisfurth 1979, Douka 1980, Ehrlich 1983, de Vrind et al. 1986, Adams & Ghiorse 1987, Boogerd & de Vrind 1987, Okazaki et al. 1997, Larsen et al. 1999, Francis et al. 2001) that catalyze the reaction, but only recently have the biochemical and underlying genetic details begun to be elucidated. Three model Mn(II)-oxidizing organisms (Figure 4) have been studied extensively using molecular biological techniques: *Leptothrix discophora* SS-1 (Corstjens et al. 1997, Brouwers et al. 2000a), *Pseudomonas putida* strains MnB1 and GB-1 (Caspi 1996; Brouwers et al. 1998, 1999; Caspi et al. 1998; de Vrind et al. 1998, 2003), and *Bacillus* sp. strain SG-1 (van Waasbergen et al. 1993, 1996; Francis et al. 2002; Francis & Tebo 2002). These three Mn(II)-oxidizers are phylogenetically distinct, representing the β-proteobacteria, γ-proteobacteria, and low-GC Gram-positive bacteria, respectively. All three oxidize Mn(II) enzymatically on an exopolymer matrix surrounding the cell: *Leptothrix discophora* on an extracellular sheath (though strain SS-1 is a sheathless mutant that secretes the Mn(II)-oxidizing factor into the medium), MnB1/GB-1 on the outer membrane glycocalyx, and SG-1 on the exosporium (the outermost layer of the spore, Figure 4). Molecular genetic approaches have revealed an exciting connection: All three organisms possess genes that are involved in Mn(II) oxidation and that share sequence similarity with multicopper oxidase enzymes. Biochemical evidence from these organisms and two α-proteobacteria, a *Pedomicrobium* species (Larsen et al. 1999) and the *Erythrobacter*-like strain SD-21 (Francis et al. 2001), is also consistent with the involvement of copper enzymes in Mn(II)

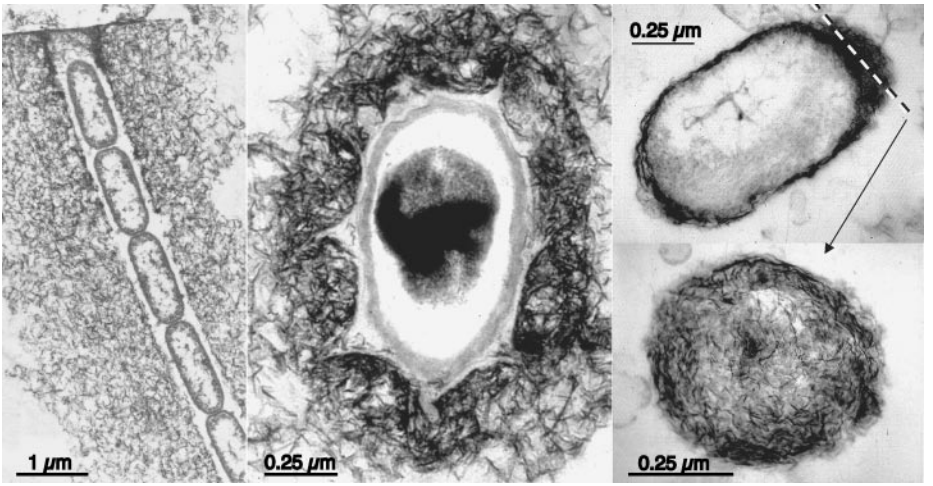

Figure 4 Transmission electron micrographs of representatives of the three Mn(II)-oxidizing bacteria that have been studied in most detail. Left, an unidentified *Leptothrix* sp. from a forest pond near Kiel, Germany (courtesy of W.C. Ghiorse). The flattened top end of the sheath marks the holdfast region at the air-water interface. Center, spores of the marine *Bacillus* sp. strain SG-1 [reproduced from van Waasbergen et al. (1996) with permission from the American Society for Microbiology]. Mn(II) oxidation occurs on the outermost layer of the spores, the exosporium. Right, *Pseudomonas putida* strain MnB1 (courtesy of B. Toner, University of California, Berkeley); Mn oxides accumulate on the extracellular organic matrix (the glycocalyx).

oxidation. In all the organisms tested, copper ions appear to be required for Mn(II) oxidation (van Waasbergen et al. 1996, Larsen et al. 1999, Brouwers et al. 2000a).

Multicopper oxidases, a diverse family of enzymes, utilize multiple types of copper ions as cofactors to oxidize a variety of organic and inorganic substrates (Solomon et al. 1996). These enzymes oxidize their substrates in one-electron steps and reduce O_2 to water. Sequence similarity between the putative bacterial Mn(II) multicopper oxidases and more well-studied eukaryotic multicopper oxidases (ceruloplasmin in humans, ascorbate oxidase from plants, and laccase from plants and fungi) is limited to very specific sites within the proteins (the copper binding sites, Figure 5). Beyond what can be inferred from the limited sequence similarity, little is known about the putative bacterial Mn(II) oxidases.

Multicopper Oxidases: The Mechanism of Bacterial Mn(II) Oxidation?

Despite recent advances in identifying proteins involved in bacterial Mn(II) oxidation and in elucidating the mechanism by which it occurs, many central questions remain unanswered. The mere involvement of multicopper oxidases in Mn(II)

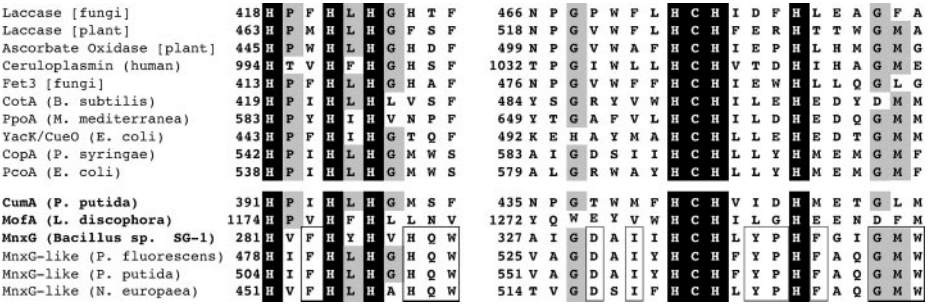

Figure 5 The amino acid sequence alignment of two of the conserved copper binding regions of multicopper oxidases from diverse organisms. Copper ions are typically coordinated at the highly conserved histidine residues. CumA, MnxG, and MofA are the putative multicopper oxidases shown to be necessary for Mn(II) oxidation in *P. putida*, *Bacillus* sp. strain SG-1, and *L. discophora*, respectively. MnxG-like amino acid sequences have recently been found in the genomes of several organisms, including those not known to be Mn(II)-oxidizing bacteria.

oxidation must be distinguished from actual direct catalysis of Mn(II) oxidation by multicopper oxidases. Only in the case of *Leptothrix discophora* has a potential link been made between the Mn oxidase and an underlying multicopper oxidase gene (Corstjens et al. 1997). No bacterial Mn oxidase has been purified in quantities sufficient for detailed biochemical study, and to date, no multicopper oxidase gene thought to encode a Mn oxidase has been successfully expressed to yield active enzyme in a foreign host. Thus the direct role of multicopper oxidases in Mn(II) oxidation remains a hypothesis. Nevertheless, it seems reasonable that multicopper oxidases in bacteria could also directly oxidize Mn(II) because (*a*) genetic and biochemical studies point to the involvement of multicopper oxidases in Mn(II) oxidation in several unrelated bacteria, (*b*) some eukaryotic multicopper oxidases are known to directly oxidize Mn(II) (Höfer & Schlosser 1999, Schlosser & Höfer 2002), and (*c*) multicopper oxidases that oxidize Fe(II) occur in both eukaryotes (Solomon et al. 1996) and bacteria (Kim et al. 2001, Huston et al. 2002).

A general feature of multicopper oxidases is their broad substrate specificity: many are able to oxidize multiple substrates including both metals and organics (Solomon et al. 1996). A low substrate specificity may also be common for Mn oxidases; Francis & Tebo (2001) found that only *Pseudomonas* strains capable of oxidizing Mn(II) could oxidize certain phenolic compounds. Future work is needed to further characterize the substrate specificity of bacterial Mn oxidases. Do Mn oxidases feature a substrate-binding pocket that ensures greater specificity, as in ascorbate oxidase and ceruloplasmin (Solomon et al. 1996), or are they nonspecific, such as the plant and fungal laccases? Perhaps the answers to such questions will shed light on the functional role of bacterial Mn(II) oxidation.

The question of bacterial multicopper oxidase specificity and function has broadened recently as genome sequencing has revealed that multicopper oxidases,

identified by their copper-binding site motifs (Figure 5), are prevalent in bacteria (Alexandre & Zhulin 2000, Claus 2003). Although most of these putative bacterial multicopper oxidases are uncharacterized, results so far indicate that they are involved in a wide range of functions, including copper resistance (Mellano & Cooksey 1988, Lee et al. 1994, Yang et al. 1996, Kim et al. 2001), melanin production/UV protection (Solano et al. 2000, Hullo et al. 2001), and iron oxidation and acquisition (Huston et al. 2002). One study showed that YacK, a multicopper oxidase from *Escherichia coli*, exhibits oxidase activity toward iron and organic compounds, and suggested functional roles for both activities (Kim et al. 2001). However, YacK and another (Hullo et al. 2001) bacterial multicopper oxidase are unable to oxidize Mn(II). Genome sequencing of *Pseudomonas putida* KT2440, *P. fluorescens* strain PfO-1, and *Nitrosomonas europea* has revealed that these organisms contain genes similar to *mnxG*, the gene coding for the putative Mn(II)-oxidizing protein from *Bacillus* sp. strain SG-1, whereas KT2440 also has *cumA*, the gene coding for the putative Mn(II)-oxidizing protein from *P. putida* strain GB-1 (Figure 5). The putative proteins encoded by these three *mnxG*-like genes are from distantly related bacteria and share a high degree of sequence similarity, suggesting perhaps that they represent a distinct class of multicopper oxidases (Figure 5).

MOLECULAR MECHANISMS OF Mn OXIDE BIOGENESIS

The stoichiometry of bacterial Mn(II) oxidation based on measurements of O_2 consumption and H^+ production follows the chemical reaction typically written for Mn(II) oxidation (de Vrind et al. 1986, Adams & Ghiorse 1988):

$$Mn^{2+} + 1/2O_2 + H_2O \rightarrow MnO_2 + 2H^+. \quad (1)$$

Based on laboratory experiments, the abiotic oxidation of Mn(II) to Mn(IV) occurs as a two-step process in which solid phase Mn(III)-bearing oxides (e.g., Mn_3O_4) or oxyhydroxides (e.g., β-MnOOH) are initially formed and then undergo slower disproportionation or protonation reactions, ultimately forming Mn(IV) oxides (MnO_2) (Hem & Lind 1983, Murray et al. 1985). The second step of this process is believed to be the rate-limiting step (Ehrlich 1996) because at pH $>$ 8 and Mn(II) concentrations $> \sim 10^{-6}$ M, the Mn(II,III) minerals are thermodynamically stable with respect to disproportionation. Mn(II) may also be oxidized on mineral surfaces (Sung & Morgan 1981, Junta & Hochella 1994). The primary product formed on hematite, goethite, and albite surfaces in six months in aerated solutions containing 4–26.7 ppm Mn(II) at pH 7.8–8.7 was feitknechtite (β-MnOOH) (Junta & Hochella 1994).

One can envision various scenarios for biologically catalyzed Mn(IV) mineral formation (Figure 6). Because multicopper oxidases all oxidize their substrates via one-electron transfer reactions, it is reasonable to hypothesize that bacteria first oxidize Mn(II) to Mn(III) and then subsequently Mn(III) is oxidized to Mn(IV). The

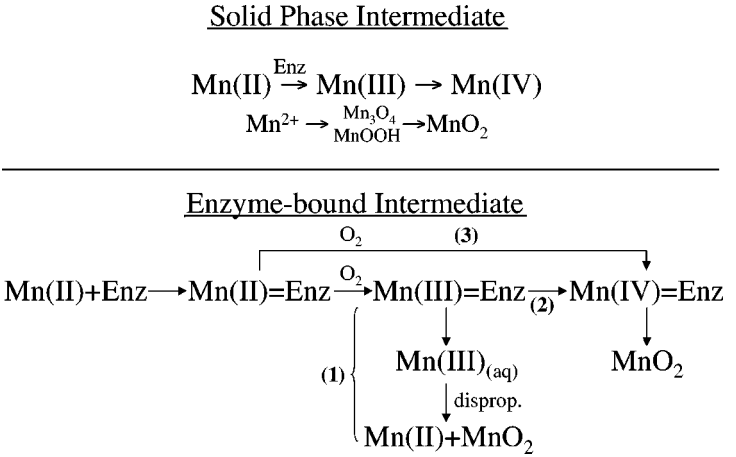

Figure 6 Possible mechanisms of bacterial Mn(II) oxidation. The numbers 1, 2, and 3 in the lower panel indicate different possible pathways for Mn(II) oxidation (see text).

mechanism for Mn(IV) oxide formation may therefore involve enzyme catalysis alone or a combination of enzymatic catalysis and abiotic reactions. The possibility exists that Mn(III) minerals, such as feitknechtite (β-MnOOH) or hausmannite (Mn_3O_4), are the primary product of the enzyme-catalyzed Mn(II) oxidation reaction. These minerals could then transform to Mn(IV) oxides abiotically via disproportionation and protonation reactions (Figure 6, top). Alternatively, Mn(II) to Mn(IV) oxidation could proceed without formation of a solid phase intermediate (Figure 6, bottom). In this scenario, Mn(IV) could form by one of two mechanisms: (*a*) Mn^{3+} could dissociate from the enzyme and, as Mn^{3+} is very unstable in solution, it would rapidly disproportionate to Mn^{2+} and MnO_2 (Figure 6, pathway 1), or (*b*) the enzyme (or enzyme complex) could further oxidize the Mn(III) to Mn(IV) (Figure 6, pathway 2). Finally, Mn(II) may undergo a two-electron transfer and form Mn(IV) directly (Figure 6, pathway 3); however, this type of reaction would be novel for a multicopper oxidase and the two electrons removed from the Mn(II) are not energetically equivalent (Ehrlich 1996).

Several investigations have addressed the mechanisms of biological Mn(II) oxidation and biomineralization, especially concerning the existence of a Mn(III) intermediate, with somewhat conflicting results. Most results involve the marine *Bacillus* sp. strain SG-1. Hastings & Emerson (1986) used SG-1 spores to synthesize Mn biooxides in seawater at pH 7.5 containing moderate amounts of Mn(II) (2 μM). Hausmannite (Mn_3O_4) appeared to form initially and the Mn oxidation state increased slowly with time, consistent with the two-step mechanism involving a solid phase Mn(III) intermediate. Mann et al. (1988) also observed hausmannite as the product of Mn(II) oxidation by purified spore coats from SG-1;

however, these oxides were produced in solutions containing very high concentrations (25 mM) of Mn(II) which would favor the formation of low oxidation state minerals such as hausmannite. In contrast to these studies, Mandernack et al. (1995b), using X-ray diffraction (XRD), demonstrated the formation of Mn(IV) mineral phases by SG-1 spores at moderately high pH and Mn(II) concentrations, where Mn(III) should be thermodynamically stable and only slowly age to Mn(IV) (Hem & Lind 1983, Murray et al. 1985). These results were interpreted as evidence for the oxidation of Mn(II) to Mn(IV) without the formation of lower valence solid phase intermediates. Oxygen isotopic ($\delta^{18}O$) studies of chemically and biologically produced Mn oxides (Mandernack et al. 1995a) provided further evidence supporting this conclusion. Based on reaction stoichiometries for the oxidation of Mn(II) to Mn_3O_4 or to MnOOH,

$$3Mn^{2+} + 1/2O_2 + 3H_2O \rightarrow Mn_3O_4 + 6H^+ \quad (2)$$

$$Mn^{2+} + 1/4O_2 + 3/2H_2O \rightarrow MnOOH + 2H^+, \quad (3)$$

the maximum amount of oxygen in the (oxyhydr)oxides that could be derived from O_2 is 25%. Because no further oxygen is incorporated upon disproportionation of Mn_3O_4 or MnOOH to Mn^{2+} + MnO_2, Mn(IV) oxides formed by one of these solid phase Mn(III)-containing minerals would have at most 25% of the oxygen derived from O_2. In fact, Mn_3O_4 did not have any indication of oxygen derived from O_2. In two different Mn(II)-oxidizing bacteria, *Bacillus* sp. strain SG-1 and the α-proteobacterium strain SI85-9A1, approximately 40%–50% of the oxygen in the Mn biooxide comes from O_2, consistent with the overall stoichiometry of Reaction 1. The work by Mandernack et al. (1995a,b) is still subject to debate because the XRD and $\delta^{18}O$ analyses were performed on minerals that had aged for fairly long periods of time (4 days–1 year) during which the initial Mn(II) oxidation products could have been transformed or present at such minor amounts that they would not have been detected. Furthermore, most of the Mn minerals were poorly crystalline; given the limitations of XRD, the minerals that were found may have represented only a minor fraction of the total Mn oxide.

More recently, a variety of synchrotron radiation-based techniques using X-ray absorption spectroscopy (XAS), including bulk and microbeam Mn K-edge X-ray adsorption near edge structure (XANES), extended X-ray absorption fine structure spectroscopy (EXAFS), X-ray emission spectroscopy (XES), and in situ synchrotron radiation-based X-ray diffraction (SR-XRD), have been used to investigate Mn oxide biomineralization (Bargar et al. 2000, Villalobos et al. 2003; J.R. Bargar, B.M. Tebo, U. Bergmann, S.M. Webb, P. Glatzel, M. Villalobos & M.A. Marcus, submitted). These techniques can quantitatively speciate crystalline, amorphous, and soluble forms of Mn and directly probe Mn oxidation states in complex multiphase mixtures or hydrated samples. These qualities are very useful because Mn oxide minerals are often amorphous or poorly crystalline with several minerals intergrown. XANES provides information about Mn oxidation state and local structure surrounding the sorbing atom (i.e., Mn) and is thus a

sensitive probe of phase evolution so long as appropriate model spectra are available. XES is an independent technique for measuring Mn oxidation state based on the fluorescence-yield measurement of the Kβ emission 3p to 1s transition, which is sensitive to the number of unpaired 3d electrons (Bergmann et al. 1998). SR-XRD has several advantages over standard laboratory-based XRD, including the ability to tune energy to penetrate water and minimize sample fluorescence, much higher counting statistics (which translates to lower detection limits and faster data acquisition), and higher angular resolution.

Bargar et al. (2000) used *Bacillus* sp. strain SG-1 spores in batch and continuous in situ flow experiments combined with XANES to measure reaction intermediates and products over very short reaction times (14 min to 9.3 h). The results of the flow experiment with 100 μM Mn(II) are shown in Figure 7. The characteristic absorption maxima for Mn(II), Mn(III), and Mn(IV) are 6553, 6556–6560, and 6562 eV, respectively. The initial spectrum of Mn in the sample gave the characteristic pattern for Mn(II). This was due to the presence of Mn(II) both in solution and in the spores. As the reaction proceeded, a Mn(IV) peak (6562 eV) appeared and grew, whereas the Mn(II) maximum decreased with time. Isobestic points at approximately 6558 and 6584 eV indicate that the system is dominated by two components, Mn(II) and Mn(IV). The data could be fit best using δ-MnO_2 as the only Mn(IV) mineral and model spectra of Mn in the spores, aqueous Mn(II) and adsorbed Mn(II). Batch experiments in 1 mM Mn(II) solutions gave comparable results. Mn(III) intermediates, which have a characteristic absorption in the energy range of 6556–6560 eV, were not detected (detection limit was $\sim$5% of the total Mn) even though Mn(III)/Mn(II,III) (oxyhydr)oxides should have been more stable than MnO_2 at the Mn(II) concentration (100 μM or 1 mM) used. These results, which are also supported by XES and SR-XRD measurements (J.R. Bargar, B.M. Tebo, U. Bergmann, S.M. Webb, P. Glatzel, et al., submitted), indicate that solid phase Mn(III) intermediates are not produced during biological Mn(II) oxidation and that Mn(IV) oxides resembling δ-MnO_2, which form very quickly (14 min), are the primary solid phase product of Mn(II) oxidation by SG-1.

It follows logically that Mn (as +II or +III) must remain complexed to the enzyme before δ-MnO_2 ultimately forms. This leaves three possibilities (Figure 6). To address these possibilities, Webb et al. (Webb et al. 2002; S.M. Webb, J.R. Bargar & B.M. Tebo, submitted) performed experiments using the exosporium of SG-1 and sodium pyrophosphate to "trap" any Mn(III) that would be formed. Because pyrophosphate complexes Mn(III) very tightly and forms a colored complex, Mn(III) formation could be monitored continuously using UV/V is spectroscopy. The results of these trapping experiments demonstrated that the exosporium, which contains the putative Mn(II)-oxidizing protein (Francis et al. 2002), oxidizes Mn(II) forming a Mn(III):pyrophosphate [Mn(III):PP] complex without evidence of solid phase Mn oxides (Figure 8). What was surprising was that after the initial rise in Mn(III):PP, that complex started to disappear concomitant with precipitation of Mn oxides. Additionally, when the exosporium was provided with Mn(III) instead of Mn(II), the Mn(III):PP disappeared at the same rate (Figure 8). Because Mn(III):PP

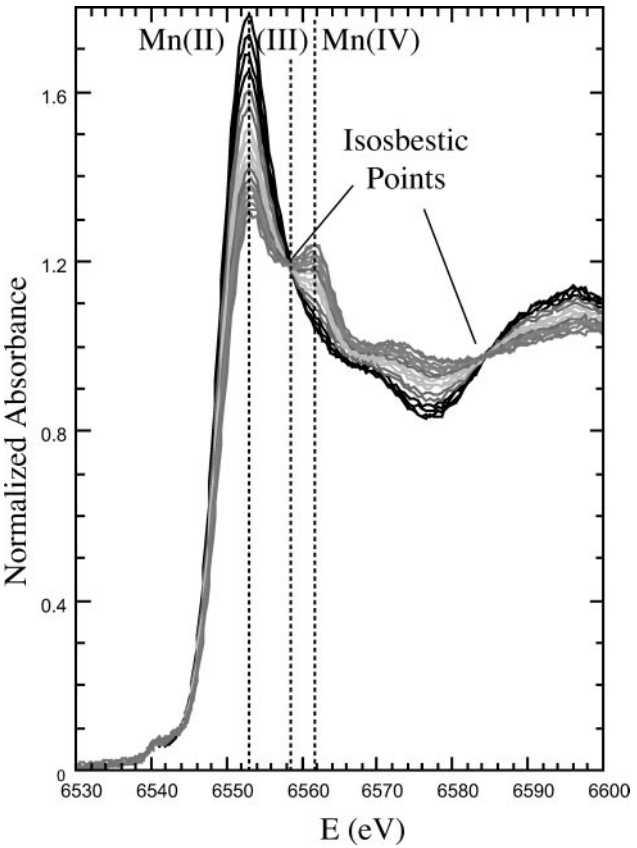

Figure 7 Normalized K-edge spectra as a function of time (up to 9.3 h) for Mn(II) plus *Bacillus* sp. strain SG-1 spores measured in situ using a flow-through cell. The top- and bottom-most curves are the first and last spectra, respectively, for the reaction sequence. The time interval between spectra is about 28 min. The vertical dotted lines mark the approximate expected positions of the Mn(II), Mn(III), and Mn(IV) adsorption edges at 6553, 6558, and 6562 eV, respectively. Reprinted from Bargar et al. (2000), with permission from Elsevier.

is stable over the time course examined in the absence of exosporium (Figure 8), these experiments indicate that Mn(II) oxidation and Mn(IV) biomineralization proceeds via two sequential one-electron steps, both of which are enzymatically catalyzed.

Implications of the Mechanism

As discussed above, most of what we know about the molecular details of Mn(II) oxidation are derived from studies of spores of the marine *Bacillus* sp. strain

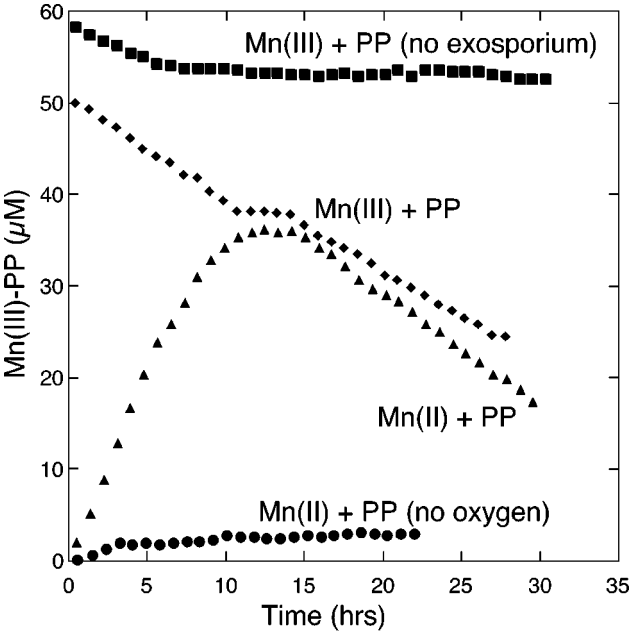

Figure 8 Measurements of Mn(III)-pyrophosphate complexes under various experimental conditions in the presence or absence of an exosporium preparation from spores of the *Bacillus* sp. strain SG-1. Mn(III)-pyrophosphate was detected by its characteristic absorption at 258 and 480 nm (S.M. Webb, J.R. Bargar & B.M. Tebo, submitted).

SG-1. Although different mechanisms for Mn(II) oxidation may be observed in other organisms, there is a common theme of the putative "Mn oxidase" being a multicopper oxidase. It seems likely, therefore, that the Mn(II) oxidation mechanism in other organisms, specifically in relation to the production of a soluble/enzyme-bound Mn(III) intermediate, will be similar.

It is interesting to speculate on the importance of Mn(III) as an intermediate in Mn(II) to Mn(IV) oxidation and draw the analogy to fungal extracellular enzymes (Tebo et al. 1997, Tebo 1998), specifically laccase, lignin peroxidase, and Mn peroxidase in white rot fungi. These enzymes are known to oxidize Mn(II) to Mn(III), which aids in the degradation of lignin (Glenn et al. 1986, Perez & Jeffries 1992, Souren 1998, Höfer & Schlosser 1999, Schlosser & Höfer 2002). Whereas Mn(II) oxidation by lignin peroxidase and laccase may be secondary reactions, Mn peroxidase specifically oxidizes Mn(II) to Mn(III) with hydrogen peroxide (Aitken & Irvine 1990). In these systems, the Mn(III) product is complexed by organic acids and the Mn(III) complex can diffuse away from the active site of the enzyme to act as a diffusible oxidant for a variety of different organic compounds. A more detailed comparison of the bacterial and fungal Mn(II)-oxidizing systems and the potential role of Mn(II) oxidation in bacteria has been presented by Tebo et al. (1997).

Perhaps more relevant to this discussion are the environmental consequences of the production of Mn(III). Mn(III) complexes produced by bacteria may represent an important diffusible oxidant in a wide variety of aquatic and terrestrial environments, where they may participate in redox reactions with organic and inorganic compounds. Mn(III) may also complex to siderophores (Fe-binding ligands) and affect Fe uptake by other organisms (D.L. Parker, G. Sposito & B.M. Tebo, submitted). We speculate that the production of Mn(III), which could compete and exchange with Fe(III) in siderophore binding, may actually help a bacterium acquire Fe from a Fe:siderophore complex it cannot otherwise utilize.

Mn(III) produced as an intermediate in Mn(II) to Mn(IV) oxidation may also impart a co-metabolic activity to the enzyme even in the absence of Mn(III) diffusion. For example, *Bacillus* sp. strain SG-1 spores also catalyze the oxidation of Co(II) to Co(III) (Lee & Tebo 1994) and Cr(III) to Cr(VI) (K.J. Murray & B.M. Tebo, manuscript in preparation) and this could be due to Mn(III). The oxidation of Cr(III) is especially important as Cr(VI) is significantly more toxic than Cr(III). Mn(III) was first implicated in the oxidation of Cr(III) when the effects of oxidized Mn minerals on Cr(III) oxidation were studied (Chung et al. 1994). Examination of Cr(III) oxidation rates by minerals of varied oxidation state showed a correlation between oxidation rate and Mn(III) content. Nico & Zasoski (2000) further investigated this by showing that the addition of sodium pyrophosphate could reduce the rates of Cr(III) oxidation by δ-MnO_2 presumably by binding to and blocking the Mn(III) in the mineral. This result supported the hypothesis that Mn(III) is responsible for Cr(III) oxidation. Recent experiments that show catalysis of Cr(III) oxidation in the presence of SG-1 spores as compared with synthetic and biological Mn-oxides suggest that the Mn(III) intermediate associated with the cells could be an important consideration in determining the fate of Cr in environmental systems. Clearly, future studies in this area of research are required.

Biogenic Mn Oxides

The properties of the Mn oxides produced by *Bacillus* sp. strain SG-1, *L. discophora*, and *P. putida* are being studied in great detail in the laboratory using both standard surface geochemical and X-ray absorption spectroscopic methods. Several recent journal articles and abstracts have been published (Bargar et al. 2000, Pasten et al. 2000, Pasten et al. 2001, Manceau et al. 2002c, Toner et al. 2002, Villalobos et al. 2002, Bargar et al. 2003, Villalobos et al. 2003, Webb et al. 2003; J.R. Bargar, B.M. Tebo, U. Bergmann, S.M. Webb, P. Glatzel, et al., submitted; S.M. Webb, J.R. Bargar & B.M. Tebo, in preparation). These studies have focused on two main aspects of Mn biooxides: the mineralization process and the sorption of other metals.

Mn Biooxide Mineralization

The time course of the evolution of biooxides produced by *Bacillus* sp. strain SG-1 under a range of environmental conditions with differing Mn(II) and O_2

concentration and osmotic strength have been characterized in detail using the complementary techniques of XANES, XES, and SR-XRD (J.R. Bargar, B.M. Tebo, U. Bergmann, S.M. Webb, P. Glatzel, et al., submitted). Based on XANES and SR-XRD measurements of samples prepared with both high and low Mn(II) concentrations, air or pure O_2, and in buffered NaCl or seawater, the initial product was always most similar to δ-MnO_2. XES and XANES measurements of biooxides produced in buffered NaCl indicated that the average oxidation state was close to 4.0. This freshly formed δ-MnO_2-like phase is highly reactive, rapidly scavenging, and oxidizing Mn(II) from solution to form secondary reaction products. SR-XRD measurements clearly indicate that the initial products are amorphous; the secondary reaction products that form are largely dependent on the solute Mn(II) concentration (Figure 9). At low Mn(II) concentration, the dominant secondary product is the hydrated phyllomanganate buserite, characterized by d-spacings of 10.1–10.2 Å. At high Mn(II) concentration, the dominant secondary product is feitknechtite (β-MnOOH). Similar results have been obtained in seawater, except that the reaction proceeds much faster, as expected for a process catalyzed by a marine bacterium, and only traces of feitknechtite are observed. There were no apparent differences between pure O_2 and air.

The visualization and mapping of Mn oxidation states have been determined using scanning transmission soft X-ray microscopy (STXM) (Pecher et al. 2003). STXM combines soft (L-edge) XAS with submicron microscopy thus providing chemical specificity with high spatial resolution. STXM and micro-XANES

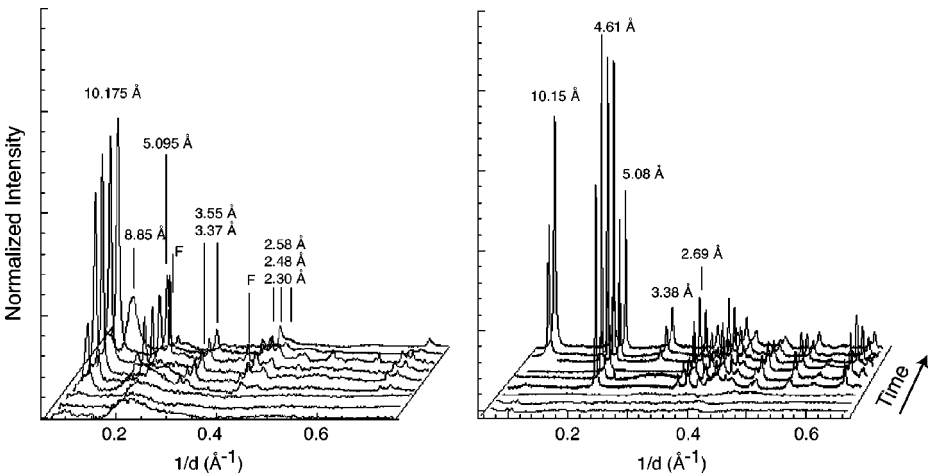

Figure 9 Time-dependent in situ transmission SR-XRD patterns of biogenic Mn(II) oxides formed by reaction of spores of *Bacillus* sp. strain SG-1 with 10 μM Mn(II) (*left*) or 1 mM Mn(II) (*right*). The times represented by the XRD patterns in each figure are approximately 0.25, 0.5, 1, 2, 4, 8, 13, 28, and 77 days.

measurements of the charge state of Mn have been collected for samples of SG-1 spores incubated 5 days in 10 mM Mn(II) solutions without agitation (Figure 10) (Pecher et al. 2003). Different oxidation states of Mn were found associated with different spores in this sample, clearly indicating the heterogeneity of Mn oxidation states associated with the spores. Notable quantities of Mn(II) were found, consistent with the presence of Mn(II) within the spores as shown previously using XANES measurements on bulk samples (see above). Mn(III) was also found in abundance around most spores; only small amounts of Mn(IV) were observed. Given the length of the incubation period combined with the high concentration of Mn(II), it is likely that the Mn(III) detected in this experiment was due to the formation of solid phase Mn(III)-bearing minerals on the surface of the initial Mn(IV) biooxide as opposed to an enzyme-bound Mn(III) intermediate. This result is consistent with the results obtained by bulk analyses (see above).

The secondary Mn oxide products that form following the reaction of primary biogenic oxides with solute metal ions may differ depending on environmental factors other than Mn(II) concentration, such as temperature, presence and concentration of other ions, and aging time. Mandernack et al. (1995b) examined the effects of Mn(II) concentration, temperature, and aging time on the nature of the Mn minerals produced in vitro by spores of SG-1 in buffer (pH 7.4–8.0) or in buffered sea water. For either water type containing 10 mM Mn(II), mixtures of the Mn(III and II,III) minerals γ-MnOOH or β-MnOOH and Mn_3O_4 were initially produced, with Mn_3O_4 being favored at 55–70°C and β-MnOOH being favored at 3°C. After 1 year of aging, γ-MnOOH was the dominant form. Lower Mn(II) concentrations ($<$0.1 mM in buffer and $<$1 mM in sea water) yielded Mn(IV) minerals; a collapsible 10 Å manganate resembling buserite was formed in buffer, whereas a mixture of buserite and a Mg-rich noncollapsible 10 Å manganate (either todorokite or a Mg-stabilized buserite) was made in sea water.

In *L. discophora*, Mn(II) oxidation is catalyzed by a protein that is localized in the sheath of environmental strains but accumulates in the medium of the spontaneous sheathless mutant, strain SS-1. The oxidation state of the Mn biooxide produced by the supernatant activity of SS-1 in a solution containing 200 μM Mn(II) was 3.32 after 11 h of incubation. For cultures, the oxidation state in exponential phase was 3.46 after 15 h and increased to 3.62 after 30 days (Adams & Ghiorse 1988). Electron diffraction patterns indicated that the biooxide was poorly crystalline; faint diffraction patterns seen at 90 days suggested the presence of a layered Mn(IV) phyllomanganate mineral. The oxidation state of this mineral clearly indicates that Mn(II) or Mn(III) exist as a major component of the mineral. The Mn oxides produced by *L. discophora* have a high surface area (224 m^2/g) as determined by N_2 adsorption (the BET method) (Nelson et al. 1999a), which is much higher than that of the synthetic oxide produced by Nelson et al. (1999a) but only 1.4–2 times the values of δ-MnO_2 reported by Villalobos et al. (2003). *L. discophora* strain SP-6 is a sheath-forming isolate for which preliminary studies using XAS and UV-Raman spectroscopy have been reported (Pasten et al. 2000, 2001). The results indicate, in contrast to the earlier oxidation state measurements,

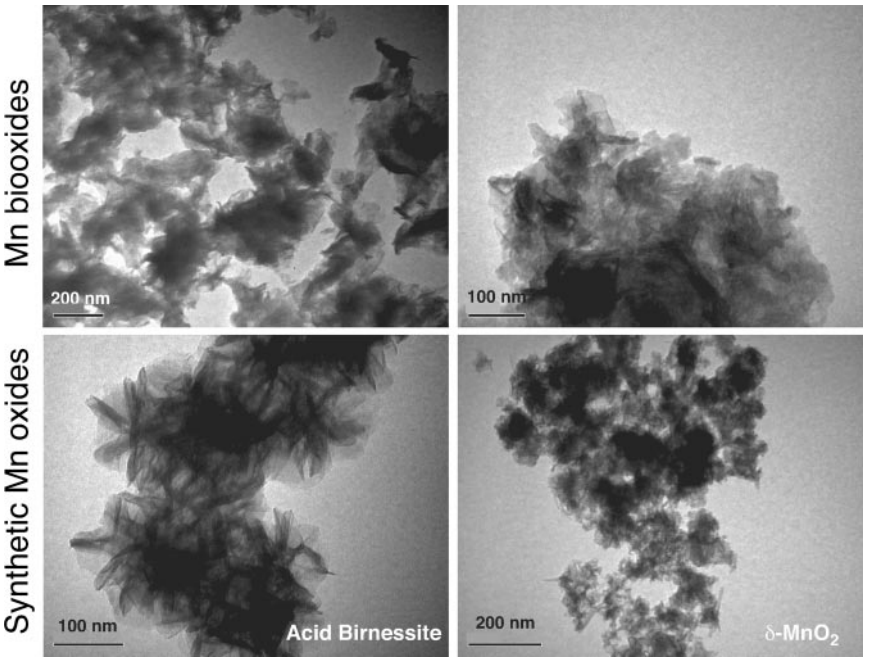

Figure 11 Transmission electron micrographs of synthetic Mn oxides (*lower panels*) and the Mn biooxide produced by *P. putida* strain Mn-B1 (*upper panels*). Reprinted from Villalobos et al. (2003), with permission from Elsevier.

that the product contains primarily Mn(IV); however, no specific mineral could be conclusively identified.

Recently, a comparative study of the Mn biooxide produced by *P. putida* strain MnB1 and synthetic Mn oxides (acid birnessite, δ-MnO_2, c-disordered H^+-birnessite, and triclinic Na-birnessite) was published (Figure 11) (Villalobos et al. 2003). Acid birnessite is a Mn(IV) oxide produced by reducing permanganate with HCl; triclinic Na-birnessite is produced by controlled oxidation of alkaline Mn(II) by O_2, H_2O_2, or MnO_4^- (at a MnO_4^-/Mn^{2+} ratio < 0.4), whereas δ-MnO_2 and c-disordered H^+-birnessite are produced by a more aggressive oxidation of Mn(II) with the redox reaction of permanganate at ratios of 0.67 or 0.52 MnO_4^-/Mn^{2+}, respectively. This research employed electron microscopy, XRD and XANES measurements combined with complementary measurements of the composition, average Mn oxidation state, and N_2-specific surface area to characterize the different oxides. The *P. putida* Mn biooxide (Figure 11) was a poorly crystalline layer-type Mn(IV) mineral with hexagonal sheet symmetry, high average oxidation state (3.9), moderately high surface area (98 m^2/g), and very low Mn(III) content (<10 mol%). It is most similar to δ-MnO_2 and acid birnessite, two synthetic analogs that have the same local molecular structure except in the degree of sheet stacking (Villalobos et al. 2003).

Mechanisms of Metal Sorption by Mn Biooxides

Mn oxides are well known for their cation exchange behavior, metal scavenging or sorption, and redox properties. They influence the movement and distribution of many elements to an extent seemingly out of proportion to their concentration (Post 1999). The sorption of metals to Mn oxides such as buserite and birnessite has been well studied (e.g., Catts & Langmuir 1986; Bendell-Young & Harvey 1992; Paterson et al. 1994; Tu et al. 1994; Appelo & Postma 1999; Nelson et al. 1999b, 2002; Manceau et al. 2000b, 2002a; Drits et al. 2002; Lanson et al. 2002b) and a review of trace metal adsorption to biogenic Mn oxides has also recently appeared (Nelson & Lion 2003). Rather than provide an exhaustive review of this literature, we present an overview and some recent studies of the mechanisms by which metals are sequestered in Mn biooxides.

Negative charges arise in Mn(IV) oxide minerals because of the presence of some Mn(III) [and to a lesser extent, Mn(II) or other heterovalent cations] or vacant sites within the octahedral layers or mineral lattices. As a consequence, protons or alkali, alkaline earth, and transition metal cations are sorbed to compensate the negative charge. Sorption of metals by Mn oxides can occur via (*a*) surface adsorption on layers or edges of MnO_6 octahedra involving the formation of either inner sphere or outer sphere complexes, (*b*) sorption into the interlayer regions or tunnels, and (*c*) incorporation into vacancies or substitution for Mn within the mineral lattice structure.

As described above, synthetic phyllomanganates similar to δ-MnO_2 and birnessite (and probably buserite in marine systems) are good models for biogenic Mn(IV) oxides. Several elegant studies have described the mechanism of heavy metal sorption by these abiotic phyllomanganates (e.g., Drits et al. 2002; Lanson et al. 2002b; Manceau et al. 2002a, 2002b). In one recent publication, EXAFS was used to study the sorption of Zn, Cu, and Pb on birnessite (Manceau et al. 2002a). Metal sorption occurred in the interlayer regions at well-defined crystallographic sites. In this study, no metal was sorbed on layer edges and surface precipitation did not occur. At high surface coverage, Zn formed a tridentate corner-sharing interlayer complex that was octahedrally coordinated with three O atoms at a vacancy site in the layer and three H_2O molecules in the interlayer. At low surface coverage, Zn was tetrahedrally coordinated to three O atoms in the layer and one molecule of H_2O in the interlayer. Cu also formed an interlayer tridentate corner-sharing complex, but with two O atoms and two H_2O molecules in the equatorial plane and one O atom and one H_2O in the axial direction. Studies indicate that phyllomanganates have the highest affinity for Pb, followed by tunnel structure manganates (O'Reilly & Hochella 2003). Pb goes into the structure of both types of manganates (O'Reilly & Hochella 2003). Pb forms both tridentate corner-sharing interlayer complexes and tridentate edge-sharing complexes (Manceau et al. 2002a, Matocha et al. 2001).

One key difference between metal scavenging by biogenic oxides as compared to preformed synthetic Mn oxides is that the former are often actively growing in the presence of contaminant metal ions. This effectively removes or decreases the activation barrier required to incorporate metals into Mn oxide structures,

particularly in the case of tunnel-structure oxides. For example, U(VI) has recently been observed to become structurally incorporated into actively forming biooxides, resulting in the production of a todorokite-like biogenic Mn oxide (Webb et al. 2003). This behavior has never been reported in studies of U(VI) sorption on synthetic phyllomanganates. Sorption of metals to Mn biooxides is likely to include mechanisms that occur on synthetic Mn oxides, with a couple of exceptions. First, the Mn biooxides have structurally less Mn(III); thus, the sorption will occur primarily at tetravalently charged vacancies in the crystal lattice (Villalobos et al. 2003). In fact, the Mn biooxide produced by *P. putida* strain MnB1 seems to be composed purely of Mn(IV) in the layer structure (Manceau et al. 2002c). Second, many Mn(II)-oxidizing bacteria produce extracellular polymeric substances that form biofilms or bacterial sheaths (Figure 12). These materials coat or trap the Mn biooxides, which likely affect the sorptive properties (Toner et al. 2002).

K-edge EXAFS has been used to study the mechanisms of Pb, Zn, and Ni sorption by Mn biooxides of *P. putida* (Manceau et al. 2002c, Toner et al. 2002, Villalobos et al. 2002). Toner et al. (2002) compared Zn(II) and Ni(II) sorption to bacterial cells without Mn oxides, bacterial cells with preformed Mn oxides, and cells actively producing Mn oxide. For the cells alone, Zn was complexed mostly to phosphate groups, whereas carboxyl groups were more important for Ni binding. Both metals showed a high affinity for preformed Mn oxide with little contribution to metal binding by the cells. When metal sorption occurred during Mn(II) oxidation, metal sorption was even more extensive. Measurements of Zn–O and Zn–Mn EXAFS distances indicated a tetrahedrally coordinated tridentate corner-sharing Zn complex at both low and high surface coverage. This suggests a

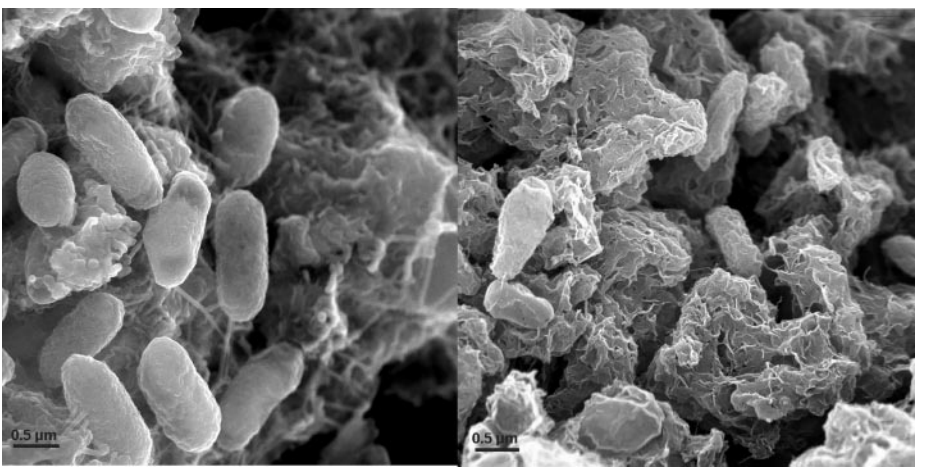

Figure 12 Scanning electron micrographs of cells of *P. putida* with their Mn oxides either sputter coated with carbon (*left*) or gold (*right*). The oxides appear to be encased by the biofilm, which sometimes appears as collapsed "ropes" owing to desiccation of the sample. When coated with gold, the oxide structure seems more apparent. Photos courtesy of Brandy Toner.

fundamental difference between synthetic hexagonal birnessite and the Mn biooxide made by *P. putida*. Similar studies have been conducted for Pb(II) sorption (Villalobos et al. 2002). Pb(II) was also found to associate with organic groups in the absence of Mn oxides, but preferentially bound to Mn oxides, when present. Pb(II) formed a tridentate complex with O atoms at vacancies in the layer.

K-edge EXAFS and XRD have also been used to examine the mechanisms of metal incorporation into biooxides of *Bacillus* sp. SG-1 (S.M. Webb, J.R. Bargar & B.M. Tebo, manuscript in preparation). In these experiments, the contaminant metal was present during the oxidation to simulate conditions that might occur when Mn(II) is oxidized in a contaminated aquifer. These results show that Cu(II), Co(II), and U(VI) all have a high affinity for the oxide. The Mn biooxide was determined to be a poorly crystalline, layered manganate with a high degree of c-axis stacking disorder and a moderate number of vacancies. Cu(II) binds primarily in a tridentate corner-sharing complex over vacancies, similar to that of birnessite (Manceau et al. 2002c). Co(II) is rapidly oxidized and incorporated into the oxide layer structure as Co(III). U(VI) forms a bidentate ternary complex with the oxide surface and the carbonate ion. At high loadings, U(VI) can cause structural changes in the biooxide structure forming pseudotodorokite-like tunnel structures (Webb et al. 2003).

NATURALLY OCCURRING Mn BIOOXIDES

The Mn biooxides produced in the laboratory have features similar to Mn oxides found in the environment, lending further support to the notion that most natural Mn oxides are of biological origin. In many natural waters, microbial activities lead to the formation of particulate Mn oxides with average oxidation states exceeding 3.4 (Kalhorn & Emerson 1984; Tebo et al. 1984; Tipping et al. 1984, 1985; Friedl et al. 1997). Many different mineral forms, including both layer and tunnel structures, have been observed in microbial precipitates in the environment (e.g., Ferris et al. 1987, Takematsu et al. 1988, Mita et al. 1994, Mandernack et al. 1995a, Friedl et al. 1997, Tazaki 2000). This is not surprising, considering the propensity for biooxides to catalyze the formation of secondary minerals or the effects of environmental physicochemical parameters, aging, and perhaps microbial exopolymers. In several cases the tunnel mineral structure todorokite was identified as a mineral of biological origin (Jannasch & Mottl 1985, Ferris et al. 1987, Takematsu et al. 1988, Beveridge 1989, Bilinski et al. 2002). However, in general, Mn oxides formed rapidly in the environment appear to be comparable to those biooxides produced in laboratory cultures, specifically a poorly crystalline phyllomanganate mineral such as δ-MnO_2, acid birnessite, or buserite. For example, Wehrli et al. (1995) analyzed lake sediment using EXAFS and found Mn oxides dominated by vernadite (δ-MnO_2). Friedl et al. (1997) analyzed the Mn biooxides formed at the oxic/anoxic interface in the water column of a eutrophic lake using EXAFS and found the Mn biooxide to be most similar to H^+-birnessite from the presence of Mn in corner linkages. However, they did not perform Mn oxidation state determinations on their natural oxides. Recent evidence suggests that biogenic oxides

contain mainly Mn(IV) in the sheet structure (Villalobos et al. 2003). Therefore, the Mn biooxides may be more similar to acid birnessite with a certain amount of Mn(II) adsorbed at the interlayers (M. Villalobos, personal communication), which was not used as a reference material in the Friedl et al. (1997) study. Our group has made XANES and EXAFS measurements on Mn biooxides produced at the oxic/anoxic interface in the Black Sea and in a seasonally anoxic fjord (Saanich Inlet, British Columbia, Canada) and in both cases the structure was most similar to δ-MnO_2 (Figure 13) (B.M. Tebo, J.R. Bargar & S.M. Webb, in preparation). All of these studies provide evidence that biogenic oxides formed in nature also do not form via a mechanism involving a Mn(II,III) solid phase intermediate.

Mn oxides in the environment act as natural traps for heavy metals and have been the subject of numerous investigations. Rarely, however, are the sorptive properties of the natural Mn oxides characterized with respect to mineralogy and properties

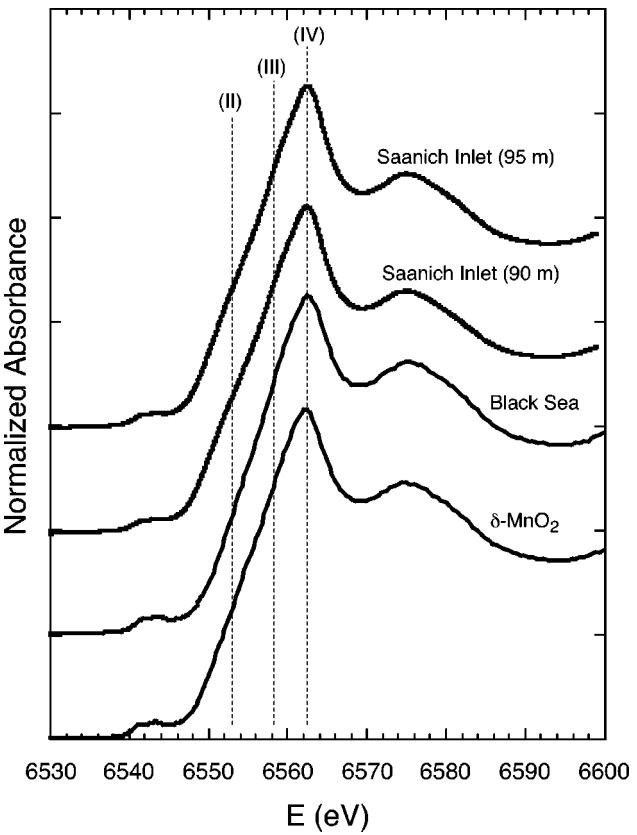

Figure 13 X-ray absorption near edge structure (XANES) spectra of Mn oxides collected from the particulate Mn maxima in the Black Sea and the seasonally anoxic fjord, Saanich Inlet, British Columbia, Canada. For comparison, the spectrum for δ-MnO_2 is shown.

of the minerals or to biogenic origin. Pinal Creek, Arizona, is a perennial stream impacted by groundwater contaminated from copper mining operations. In this system, dissolved Mn(II) enters the stream at the leading edge of an acidic groundwater plume and is microbially oxidized (Marble et al. 1999, Kay et al. 2001). The resulting Mn biooxides sorb Co, Ni, Zn, and other metals in the hyporheic zone (zone in which surface water penetrates the underlying sediments) (Harvey & Fuller 1998, Fuller & Harvey 2000, Kay et al. 2001), thereby retarding and limiting the downstream transport of metal contaminants. These oxides occur as non-cemented particulates and coatings on streambed material and as cemented black crusts having the appearance of asphalt. A number of different Mn oxide minerals have been identified in Pinal Creek based mostly on XRD (Lind & Hem 1993, Bilinski et al. 2002). Although various 7-Å phyllomanganates (e.g., rancieite and takanelite) as well as tunnel forms (todorokite) were observed, it was difficult to assign any particular mineral as being a primary biogenic oxide. Our group has recently made XANES measurements on Mn oxides freshly precipitated on glass beads incubated in Pinal Creek (kindly provided by Martha Conklin and Tim Corley at the University of Arizona). Like the biogenic oxides from the Black Sea and Saanich Inlet, these oxides were most similar to δ-MnO_2. These results suggest that the other minerals observed in Pinal Creek are secondary reaction or alteration products.

There are many types of environments where Mn oxide deposition may be microbially mediated. However, one cannot necessarily conclude from the identification of a specific mineral alone that it was biogenic in origin. Manceau et al. (2000b), studying the speciation of Zn in soils contaminated by smelter operations, identified a birnessite as one of the phases controlling Zn speciation in the system. This result suggests that birnessite is a good model for natural Mn oxides in soils, but doesn't establish its origin. Bilinski et al. (2002) have also studied Mn oxides in hot-spring deposits from Yuno-Taki Falls, Hokkaido, Japan. Three different types of samples were examined using a suite of techniques, including XRD and differential scanning calorimetry, but not XAS. Interestingly, the sample that was freshly deposited on a piece of polyvinyl chloride pipe was identified as a very pure buserite. One sample removed from the surface of a waterfall was a more aged buserite that would collapse upon drying but could not be expanded. The third sample, from a dried Mn deposit downstream from the waterfall, was a 7-Å phyllomanganate. Interestingly, a buserite-like phyllomanganate was also identified in microbial mats, which formed a characteristic banded zebra pattern in hot springs on the volcanic island of Satsuma-Iwo Jima in southern Kyushu, Japan (Tazaki 2000). More work needs to be done to determine whether buserite-like Mn oxides in these hot-spring environments are of biogenic origin.

Microorganisms may also contribute significantly to the formation of several other types of Mn deposits. Rock varnishes are dark-colored Mn- and Fe-rich coatings that form on rock surfaces exposed to the atmosphere. They are particularly abundant in deserts and are believed to form, at least in part, through microbial activity (Dorn & Oberlander 1981, Dorn 1991, Nagy et al. 1991). The color of rock varnish is largely dependent on the Mn oxide content. Recently, McKeown & Post (2001) have used XANES and EXAFS to characterize the Mn oxide mineralogy

of rock varnishes and also of Mn dendrites, which, like varnishes, occur as coatings, but mostly on sedimentary rocks. XANES spectra indicate that the average Mn oxidation state is between +III and +IV; the oxidation state of the varnishes was close to +IV, whereas those of the dendrites were somewhat lower. Both layer-type minerals (the birnessite group) and tunnel structures (todorokite or romanechite) were found in both types of deposits. Ferromanganese nodules and crusts found in lakes and in the ocean are similar to rock varnishes in the sense that they formed over long periods of time (years to millions of years) and possess mixtures of fine-grained poorly crystalline Fe and Mn minerals (Post 1999). The main minerals that have been identified in oceanic nodules are birnessite, todorokite, and vernadite (δ-MnO_2) (Burns & Burns 1979); however, to our knowledge, synchrotron-based XAS measurements have not yet been employed on nodules [although, the speciation of Zn and Ni in soil ferromanganese nodules has been reported (Manceau et al. 2002b, 2003)]. Given the age and weathering of rock varnishes and nodules, it is difficult to link the potential microbial origin of the Mn oxides with any defined mineral phase.

Hydrothermal vents and plumes and metalliferous deposits adjacent to the ridge flanks of the oceanic spreading centers are also environments where microbial oxidation is important. Although some information is known about Mn mineralogy in preserved hydrothermal deposits (e.g., Lalou 1983, Lalou et al. 1983, Hodkinson et al. 1994), to our knowledge the mineralogy of fresh precipitates and deposits has not been systematically investigated. Clearly, a more detailed understanding of the types of minerals formed in these environments is needed.

SUMMARY AND CONCLUSIONS

The mechanism of bacterial Mn(II) oxidation in most environments is enzymatic, and, although bacteria that oxidize Mn(II) are phylogenetically diverse, a common feature of the well-studied organisms is the involvement of a multicopper oxidase-like enzyme in Mn(II) oxidation. In *L. discophora*, some evidence exists that the multicopper oxidase is directly involved in Mn(II) oxidation, but this direct link has not been established for other Mn(II)-oxidizing bacteria. Mn(II) oxidation proceeds as two sequential one-electron oxidation reactions with the occurrence of a short-lived soluble or enzyme-complexed Mn(III) intermediate. Solid phase Mn(II,III) minerals do not occur as intermediates as they do in abiotic Mn(II) oxidation. Both steps of the two-electron oxidation of Mn(II) to Mn(IV) are enzymatically catalyzed. Thus, if a multicopper oxidase is indeed the catalyst for both steps, this would represent a novel type of multicopper oxidase. Alternatively, different enzymes may catalyze the Mn(II) to Mn(III) and Mn(III) to Mn(IV) steps. Further insights into the mechanism of Mn(II) oxidation have been hampered by the inability to obtain sufficient protein.

That Mn(III) is produced as an intermediate during Mn(II) oxidation and can exist in a soluble form complexed with inorganic and organic ligands suggests that soluble Mn(III) species may be more important in the environment than generally

believed. Mn(III) is a strong oxidant that can impact the cycling of many other elements, including carbon, oxygen, iron, and sulfur (Kostka et al. 1995; Luther III et al. 1998; Klewicki & Morgan 1998, 1999).

To date, several criteria have emerged to help assess whether a Mn oxide is biogenic. The primary products of microbial Mn(II) oxidation are layer-type (phyllomanganate) Mn oxides with high surface area and principally Mn(IV) as the structural Mn. Their mineral structure contains very little Mn(III), is poorly crystalline, and is most similar to δ-MnO_2 (the synthetic analog of vernadite) (Post 1999) or acid birnessite in terms of the relatively high Mn oxidation state and the relatively low defect levels in the octahedral Mn layer. In the presence of calcium, a biooxide is produced having somewhat higher crystallinity and a 10 Å basal plane spacing. Negative charges in the mineral arise from vacancies in the octahedral sheets where Mn is absent. Tetravalent charge at these vacancies may be balanced by hydrated cations and protons in the interlayer, depending on pH (Villalobos et al. 2003), or the layers may complex or structurally incorporate other metals. The Mn biooxide is a highly reactive catalyst for further Mn(II) oxidation reactions. Diverse secondary reaction products can form depending on the physicochemical conditions [Mn(II) concentration, temperature, other ions]. Todorokite and buserite are frequently observed in natural Mn oxide deposits that are believed to have formed microbially. Whether these are secondary reaction products, alteration products, or produced directly by microbes under specific physicochemical conditions needs to be investigated.

It is now possible to routinely synthesize Mn oxides using Mn(II)-oxidizing bacteria to catalyze Mn(II) oxidation under physicochemical conditions closely representing those found in the natural environment. Comparative studies of these Mn biooxides with abiotically synthesized and natural Mn oxides holds promise for providing new insights into the sorptive and redox capacities of Mn oxides and the role of Mn oxides in the environmental chemistry of soil and aquatic ecosystems. Understanding the properties of Mn biooxides at the atomic and molecular level may provide the impetus to explore the synthesis of Mn biooxides useful for environmental and materials science applications.

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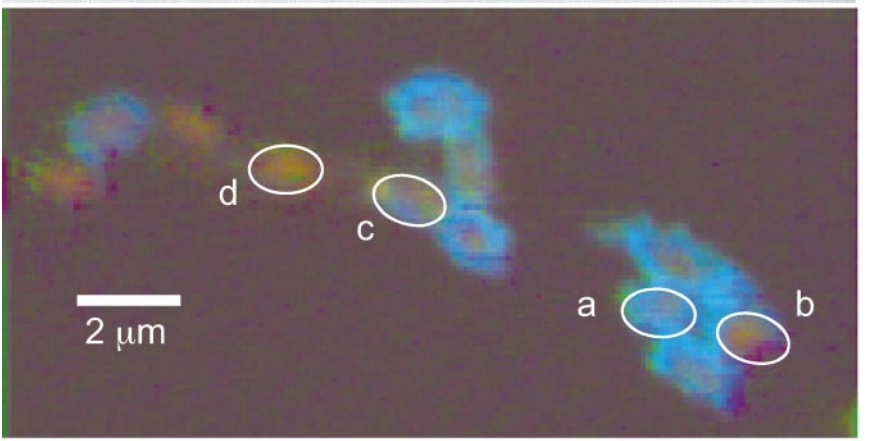

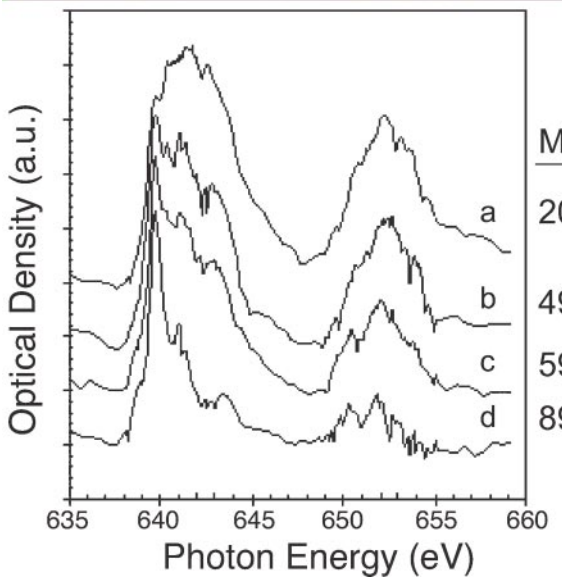

	Mn(II)	Mn(III)	Mn(IV)
a	20%	62%	18%
b	49%	49%	2%
c	59%	41%	–
d	89%	11%	–

Figure 10 Scanning transmission X-ray microscopy (STXM) images and area averaged X-ray absorption near edge structure (XANES) of *Bacillus* sp. strain SG-1 spores incubated for 5 days in 10 mM Mn(II). Top: STXM image of contrast at 639.5 eV. Middle: Red [Mn(II)], Green [Mn(III)], Blue [Mn(IV)] charge state composite image. Labeled areas correspond to L-edge XANES in the lower panel. The percentages of Mn(II), Mn(III), and Mn(IV) is given on the right in the lower panel based on fitting the XANES spectra with spectra from model Mn compounds [$MnSO_4$ for Mn(II), Mn_2O_3 for Mn(III), and commercial grade MnO_2 for Mn(IV)]. Reprinted from Pecher et al. (2003), with permission from Elsevier.

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