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Jeffrey E. Post

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# Manganese oxide minerals: Crystal structures and economic and environmental significance

JEFFREY E. POST

Department of Mineral Sciences, Smithsonian Institution, Washington, DC 20560-0119

ABSTRACT Manganese oxide minerals have been used for thousands of years-by the ancients for pigments and to clarify glass, and today as ores of Mn metal, catalysts, and battery material. More than 30 Mn oxide minerals occur in a wide variety of geological settings. They are major components of Mn nodules that pave huge areas of the ocean floor and bottoms of many fresh-water lakes. Mn oxide minerals are ubiquitous in soils and sediments and participate in a variety of chemical reactions that affect groundwater and bulk soil composition. Their typical occurrence as fine-grained mixtures makes it difficult to study their atomic structures and crystal chemistries. In recent years, however, investigations using transmission electron microscopy and powder x-ray and neutron diffraction methods have provided important new insights into the structures and properties of these materials. The crystal structures for todorokite and birnessite, two of the more common Mn oxide minerals in terrestrial deposits and ocean nodules, were determined by using powder x-ray diffraction data and the Rietveld refinement method. Because of the large tunnels in todorokite and related structures there is considerable interest in the use of these materials and synthetic analogues as catalysts and cation exchange agents. Birnessite-group minerals have layer structures and readily undergo oxidation reduction and cation-exchange reactions and play a major role in controlling groundwater chemistry.

Manganese (Mn) is the 10th most abundant element in the Earth's crust and second only to iron as the most common heavy metal; on average crustal rocks contain about 0.1% Mn (1). Geochemically, Mn behaves like Mg, Fe, Ni, and Co and tends to partition into minerals that form in the early stages of magmatic crystallization. Significant quantities of Mn persist, however, in melts and can be plentiful in late-stage deposits such as pegmatites (2). Mn is readily depleted from igneous and metamorphic rocks by interactions with surface water and groundwater and is highly mobile, as Mn(II), in acidic aqueous systems (2). Near the Earth's surface, Mn is easily oxidized, giving rise to more than 30 known Mn oxide/hydroxide minerals. These oxides are the major players in the story of the mineralogy and geochemistry of Mn in the upper crust and the major sources of industrial Mn.

Most people's introduction to Mn oxides is the messy, black innards of a dry-cell battery. But in fact, Mn oxide/hydroxide (referred to generally as Mn oxide) minerals are found in a wide variety of geological settings and are nearly ubiquitous in soils and sediments. They occur as fine-grained aggregates, veins, marine and fresh-water nodules and concretions, crusts, dendrites, and coatings on other mineral particles and rock surfaces (e.g., desert varnish). Because Mn oxides commonly form at the interface between the lithosphere and hydrosphere, atmosphere and/or biosphere, they can provide environmentally relevant insights into certain types of interactions between these systems and potentially serve as long-term monitors of changes within a system.

As ores, Mn oxides have been exploited since ancient times. In particular, pyrolusite (MnO<sub>2</sub>) was prized as a pigment and for its ability to remove the green tint imparted by iron to glass (3). By the mid-19th century Mn was an essential component in steel making, as a deoxidizer and desulfurizer and for making hard-steel alloys. Mn oxides are the predominant ore minerals in most of today's commercially important Mn deposits, commonly formed by weathering of Mn-rich carbonates or silicates, either by in situ oxidation or by dissolution followed by migration and reprecipitation (4). Approximately 80–90% of the current world production of Mn ore is consumed by the steel industry; on average, steel contains about 0.6 weight percent Mn but may be 10% or more in high-strength steels (5). Other uses include production of special Al alloys, Mn chemicals, catalysts, water-purifying agents, additives to livestock feed, plant fertilizers, colorant for bricks, and in batteries. Natural Mn oxide (primarily nsutite) is used as the cathodic material in zinc-carbon dry-cell batteries. In recent years, however, alkaline batteries, that use synthetic, electrolytic Mn oxide, have increasingly dominated the market (6).

#### **Ocean Mn Nodules**

The most extensive deposition of Mn oxides today occurs in the oceans as nodules, microconcretions, coatings, and crusts (7). Marine Mn nodules were first discovered in 1873 during the voyage of the HMS Challenger (8). Since then, Mn nodules have been found at almost all depths and latitudes in all of the world's oceans and seas (7); it has been estimated, for example, that they cover about 10-30% of the deep Pacific floor (9). Ocean Mn nodules typically are brown-black and subsphericalbotroyoidal and consist of concentric layers of primarily Mn and iron oxide minerals. Other minerals commonly found in the nodules include: clay minerals, quartz, apatite, biotite, and feldspars (10). Most Mn nodules have formed around central nuclei that may be carbonate mineral fragments, pumice shards, animal remains, coral fragments, etc. (11). The nodules range from 0.5 to 25 cm in diameter, with an ocean-wide average of about 4 cm (11). Marine Mn oxide crusts and nodules concentrate at the sediment-water interface (12) but locally are distributed to a depth of 3 or 4 m (13). The nodules are most abundant in oxygenated environments with low sedimentation rates and reach their greatest concentration in deep-water at or below the calcium carbonate compensation depth (11). Accumulation rates range from 0.3 to 1,000 mm/yr in near-shore environments to about 1 cm/million yr in the deep ocean (14, 15). The source of the Mn is thought to be continental runoff and hydrothermal and volcanic activity at midocean spreading centers (16, 17).

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Abbreviation: TEM, transmission electron microscopy.

Research on the complex mineralogy of the Fe and Mn oxides in ocean Mn nodules has been hampered by the fact that the minerals typically occur as thin layers of fine-grained, poorly crystalline mixtures. Previous studies of the mineralogy of ocean nodules concluded that the dominant Mn oxide phases are birnessite (7 Å manganate), todorokite (10 Å manganate), and  $\delta$ -MnO<sub>2</sub> or vernadite (18). Both birnessite and todorokite commonly are found in the same nodule, but birnessite tends to predominate in nodules from topographic highs such as seamounts and ridges, and todorokite is more common in slightly more reducing near-shore and abyssal environments (19, 20).

How ocean Mn nodules grow is a subject of intensive research and some debate. Nodules apparently grow principally by direct precipitation of Mn from seawater, but the types of reactions that occur in the water and at the precipitation surface are poorly known (2, 17). It also has been suggested that some Mn and Fe is supplied by upward diffusion through underlying reducing sediments (2). One scenario suggests that Mn oxide phases in ocean nodule form by catalytic oxidation and adsorption of Mn(II) on suitable substrates, such as mineral and rock fragments and fine-grained MnO<sub>2</sub> and Fe(OH)<sub>3</sub>. Once initiated nodule formation is self-perpetuating because Fe and Mn are autocatalytically precipitated on the surface (2). Indeed Mn oxides, and Mn nodules themselves, have been recommended as oxidation catalysts for automobile exhaust systems (21) and for the reduction of nitric acid pollutants (22). It also has been proposed that in some environments bacteria might be the dominant catalysts for Mn oxide precipitation (7). For example, Mn-oxidizing and Mnreducing bacteria isolated from deep-sea nodules have been shown to increase experimental deposition of Mn onto pulverized nodules (23). More recent studies (summarized in ref. 24) indicate that microorganisms can accelerate the rate of Mn(II) oxidation by up to five orders of magnitude over abiotic oxidation, and thus are likely responsible for much natural Mn(II) oxidation.

Ocean nodules are of potential commercial interest because in addition to Mn they also contain significant amounts (several tenths to more than one weight percent) of Cu, Ni, Co, and other strategic metals (e.g., ref. 25). Laboratory experiments have shown that the sorption capacity of freshly precipitated Mn oxides is extremely high for a variety of metal cations (26-28). Thus in seawater, adsorption by Mn oxide deposits may be the most important mechanism for controlling the concentration of heavy metals (27). The relatively slow accretion rates for deep-sea nodules provide ample opportunity for adsorption of heavy metals and is consistent with observations that more rapidly growing nodules tend to have lower trace metal concentrations (17). It is unclear how the heavy metals are bound in the nodule Mn oxide minerals, or even in which phases they are concentrated. Experiments have demonstrated that adsorption of heavy metals by hydrous Mn oxides is accompanied by release of protons (H<sup>+</sup>), suggesting that the cations are bound into the Mn oxides' atomic structures (27). Additional insights into the nature of the heavy metals likely await a more detailed understanding of the atomic structures and crystal chemistries of Mn oxide minerals in ocean nodules.

#### Mn Oxide Minerals and the Environment

The unusually high adsorption capacities and scavenging capabilities of Mn oxide/hydroxide minerals provides one of the primary controls of heavy metals and other trace elements in soils and aquatic sediments (28, 29). Understanding such controls is important for maintaining and improving fertility of soil, mitigating health affects in humans and animals, and for treatment of water for consumption and industrial use. Because Mn oxide minerals commonly occur as coatings and fine-grained aggregates with large surface areas, they exert chemical influences far out of proportion to their concentrations (28). The presence of only tiny amounts (e.g., a fraction of a weight percent of soil or sediment) of Mn oxide minerals might be adequate to control distribution of heavy metals between earth materials and associated aqueous systems (28). Additionally, Mn oxides can act as important adsorbents of phosphate in natural waters and surface sediments (30). Two useful applications of the scavenging ability of Mn oxide minerals are as geochemical exploration tools (25, 31, 32) and purification agents for drinking water (33). Recent studies also indicate that Mn oxide minerals in soils and stream sediments and as coatings on stream pebbles and boulders might serve as natural traps for heavy metals in contaminated waters from mines and other industrial operations (32, 34, 35). Similarly, Mn oxide absorbers effectively recover Ra, Pb, and Po from seawater (36), and it has been shown that the geochemical distribution of several naturally occurring radionuclides (<sup>234</sup>Th, <sup>228</sup>Th, <sup>228</sup>Ra, and <sup>226</sup>Ra) is controlled by Fe and Mn oxides (37, 38).

Hydrous oxides of Mn occur in most soils as discrete particles and as coatings on other mineral grains. Mn is highly mobile in acid, organic soils of the temperate and subarctic zones, but in the more alkaline tropical soils Mn might concentrate with residual laterites (2). It has been noted that frequently observed influences of pH, organic matter, lime, and phosphate on heavy metal availability in soils are understood principally in terms of their influence on the chemistries of hydrous oxides of Mn and Fe (28). The major Mn minerals reported in soils are lithiophorite, hollandite, and birnessite (39, 40); it is more typically the case, however, that because the Mn oxides are fine-grained and poorly crystalline (commonly referred to as amorphous) that no attempt is made to assign mineral designations.

Mn oxides in soils and sediments readily participate in a wide variety of oxidation-reduction and cation-exchange reactions. They exhibit large surface areas and can be very chemically active. Birnessite directly oxidizes Se(IV) to Se(VI) via a surface mechanism (41), Cr(III) to Cr(VI) (42), and As(III) to As(V) (43). Certain Mn oxide minerals easily oxidize arsenate (III), the more toxic form of inorganic As, to arsenate(V), which can more effectively be removed from drinking water by existing water treatment procedures (44). Mn oxide minerals such as birnessite and todorokite readily undergo cationexchange reactions (45), and studies have shown that the cation exchange capacity of Mn dioxide at pH 8.3 (about that of seawater) exceeds that of montmorillanite (46). Clearly, these kinds of reactions profoundly affect the chemistries of soils and associated aqueous solutions.

#### **Mn Oxide Minerals**

What accounts for the complexity and impressive variety of Mn oxide minerals? Mn occurs in natural systems in three different oxidation states: +2, +3, and +4, giving rise to a range of multivalent phases. Mn oxides also display a remarkable diversity of atomic architectures, many of which easily accommodate a wide assortment of other metal cations. Finally, Mn is abundant in most geological systems and forms minerals under a wide range of chemical and temperature conditions, and through biological interactions.

Most Mn oxide minerals are brown-black and typically occur as intimately intermixed, fine-grained, poorly crystalline masses or coatings. Not surprisingly, identifying the particular mineral(s) in a Mn oxide specimen can pose quite a challenge. Hence many scientists report simply "Mn oxide," rather than a particular mineral phase. Geologists have attempted to avoid the problem by simply referring to all soft (i.e., it blackens your fingers), brown-black, fine-grained specimens that were assumed to be Mn oxides as "wad." Similarly, hard (does not blacken your fingers), gray-black, botroyoidal, massive specimens were called "psilomelane." Recent studies have shown that most so-called psilomelane specimens are predominantly the mineral romanechite ( $Ba_{.66}Mn_5O_{10}$ ·1.34H<sub>2</sub>O). There is no comparable correlation between specimens labeled wad and any particular Mn oxide mineral.

Even today identification of the minerals in many Mn oxide samples is not straightforward. In general, powder x-ray diffraction is diagnostic for well-crystallized, monophasic samples. Unfortunately, the crystal structures, and consequently, the powder diffraction patterns are similar for many of the Mn oxide minerals. In many cases, it is necessary to supplement powder x-ray diffraction studies with other techniques, such as transmission electron microscopy (TEM), IR spectroscopy, and electron microprobe analysis.

Despite the fact that Mn oxides have been extensively studied for the past several decades, the details of many of their atomic structures are poorly understood, and there are several phases for which even the basic crystal structures are not known. This paucity of crystallographic data has greatly hindered research on the fundamental geochemical behaviors of common Mn oxide minerals. In most cases the major limiting factor is the lack of crystals suitable for single-crystal x-ray or neutron diffraction experiments. In the past few years, however, other techniques such as TEM (high-resolution imaging and electron diffraction) and Rietveld refinements using powder x-ray and neutron diffraction data have provided important new insights into the atomic structures of Mn oxide minerals. The Rietveld method (see review in ref. 47) has made it possible to partially solve and refine structures from data collected from even relatively poorly crystalline samples (e.g., refs. 48 and 49). Other methods that have contributed to the understanding of Mn-oxide atomic structures include: IR spectroscopy, extended x-ray absorption fine-structure spectroscopy, and thermogravimetric analysis. The recent application of charge-coupled device imaging plates to singlecrystal x-ray diffraction experiments, particularly at synchrotron sources (50), should open possibilities for detailed studies of extremely tiny crystals of certain Mn oxide phases that were too small for use in conventional experiments.

The basic building block for most of the Mn oxide atomic structures is the  $MnO_6$  octahedron. These octahedra can be assembled by sharing edges and/or corners into a large variety of different structural arrangements, most of which fall into one of two major groups: (*i*) chain, or tunnel, structures and (*ii*) layer structures. The tunnel Mn oxides are constructed of single, double, or triple chains of edge-sharing  $MnO_6$  octahedra, and the chains share corners with each other to produce frameworks that have tunnels with square or rectangular cross sections. The larger tunnels are partially filled with water molecules and/or cations. The layer Mn oxides, sometimes referred to as phyllomanganates, consist of stacks of sheets, or layers, of edge-sharing  $MnO_6$  octahedra. The interlayer regions can host water molecules and a wide range of cations.

One of the complexities of Mn oxide crystal chemistry is the multiple valence states exhibited by Mn, commonly even in a single mineral. It is reasonably straightforward to measure the average Mn oxidation state for a mineral, but it is considerably more difficult to determine the proportions of Mn(IV), Mn(III), and/or Mn(II). In some cases, chemical analyses with bulk oxidation state measurements unambiguously indicate the correct Mn valence state, e.g., pyrolusite  $[Mn(IV)O_2]$  or manganosite [Mn(II)O]. For other minerals, detailed crystal structure studies were able to reveal the valence state information. Manganite (MnOOH), for example, can be chargebalanced assuming all Mn(III) or a half-and-half mixture of Mn(II) and Mn(IV). Crystal structure refinements revealed that the Mn in manganite is in a highly distorted octahedral site, characteristic of the Jahn-Teller effects displayed by Mn(III). The Mn-O bond distances determined by crystal

structure refinements also can provide insights into the Mn valence state(s), e.g., structure studies of hollandite minerals (51), romanechite (52), and todorokite (48) indicate that the reduced form of Mn in these minerals is Mn(III). Studies of Mn oxidation states also have been performed by using x-ray spectroscopy (e.g., ref. 53) and x-ray absorption near-edge structure spectroscopy (54).

Summarized below are descriptions of the atomic structures and other information for some of the most important Mn oxide minerals (for a more in-depth presentation see ref. 55). The minerals and their chemical formulae are listed in Table 1.

#### **Mn Oxide Minerals with Tunnel Structures**

Pyrolusite MnO<sub>2</sub>. There are three known mineral polymorphs of MnO<sub>2</sub>; pyrolusite is the most stable and abundant, the others are ramsdellite and nsutite. In pyrolusite ( $\beta$ -MnO<sub>2</sub>), single chains of edge-sharing Mn(IV)O<sub>6</sub> octahedra share corners with neighboring chains to form a framework structure containing tunnels with square cross sections that are one octahedron by one octahedron (1X1) on a side (Fig. 1). The structure is analogous to that of rutile  $(TiO_2)$ . The chain structure manifests itself in pyrolusite's typically acicular crystal morphology. The tunnels in pyrolusite are too small to accommodate other chemical species, and chemical analyses indicate that the composition deviates at most only slightly from pure MnO<sub>2</sub>. Pyrolusite commonly occurs as lowtemperature hydrothermal deposits or as replacements after other Mn oxide minerals, particularly ramsdellite and manganite. It has long been assumed that Mn oxide dendrites, and other coatings, commonly found on rock surfaces are pyrolusite, but IR spectroscopy studies (70) have revealed that most such deposits are birnessite and/or romanechite, and in no case was pyrolusite identified.

**Ramsdellite**  $MnO_2$ . In the ramsdellite structure the  $Mn(IV)O_6$  octahedra are linked into double chains, each of which consists of two adjacent single chains that share octahedral edges. The double chains, in turn, link corners with each other to form a framework having tunnels with rectangular-shaped cross sections that are 1X2 octahedra on a side (57) (Fig. 1). The tunnels are generally empty but chemical analyses commonly reveal minor amounts of water, Na, and Ca that presumably are located in the channels. Ramsdellite is a relatively rare mineral, usually occurring in low-temperature hydrothermal deposits and commonly associated with, and

Table 1. Important Mn oxide minerals

Mineral	Chemical formula	Reference
Pyrolusite	MnO <sub>2</sub>	56
Ramsdellite	MnO <sub>2</sub>	57
Nsutite	$Mn(O,OH)_2$	58
Hollandite	$Ba_x(Mn^{4+},Mn^{3+})_8O_{16}$	51
Cryptomelane	$K_x(Mn^{4+},Mn^{3+})_8O_{16}$	51
Manjiroite	$Na_x(Mn^{4+},Mn^{3+})_8O_{16}$	59
Coronadite	$Pb_x(Mn^{4+},Mn^{3+})_8O_{16}$	60
Romanechite	Ba.66(Mn <sup>4+</sup> ,Mn <sup>3+</sup> )5O10+1.34H2O	52
Todorokite	$(Ca, Na, K)_X(Mn^{4+}, Mn^{3+})_6O_{12} \cdot 3.5H_2O$	48
Lithiophorite	$LiAl_2(Mn_2^{4+}Mn^{3+})O_6(OH)_6$	61
Chalcophanite	ZnMn <sub>3</sub> O <sub>7</sub> ·3H <sub>2</sub> O	62
Birnessite	(Na,Ca)Mn <sub>7</sub> O <sub>14</sub> ·2.8H <sub>2</sub> O	49
Vernadite	MnO <sub>2</sub> ·nH <sub>2</sub> O	63
Manganite	MnOOH	64
Groutite	MnOOH	65
Feitknechtite	MnOOH	66
Hausmannite	$Mn^{2+}Mn_{2}^{3+}O_{4}$	67
Bixbyite	$Mn_2O_3$	68
Pyrochroite	Mn(OH) <sub>2</sub>	66
Manganosite	MnO	69



FIG. 1. Polyhedral representations of the crystal structures of (A) pyrolusite, (B) ramsdellite, (C) hollandite, (D) romanechite, and (E) todorokite, looking approximately parallel to the Mn octahedral chains.

probably altering to, pyrolusite. Ramsdellite is isostructural with goethite (FeOOH) and gibbsite (AlOOH).

**Nsutite MnO<sub>2</sub>.** Nsutite ( $\gamma$ -MnO<sub>2</sub>) is an important cathodic material for use in dry-cell batteries. It is named after the large deposits of the mineral near Nsuta, Ghana. Although classified as a mineral, nsutite is actually an intergrowth between pyrolusite and ramsdellite. TEM images reveal a disordered structure consisting of regions of a ramsdellite-like phase and areas that appear to be ordered intergrowths of pyrolusite and ramsdellite (71). The generally accepted structure model for nsutite is an alternating intergrowth of ramsdellite and pyrolusite (Fig. 1), and therefore, most so-called nsutite samples are, in fact, mixtures of ramsdellite and nsutite. TEM studies

also revealed some tunnels larger than 1X1 (pyrolusite) and 1X2 (ramsdellite), e.g., 1X3 and 3X3, as well as numerous defects and grain boundaries (71). All of these complexities undoubtedly affect the chemical and electrical properties of the material. Chemical analyses of nsutite typically show minor amounts of Na, Ca, Mg, K, Zn, Ni, Fe, Al, and Si, and about 2–4 weight percent water (58). These species probably are accommodated in the larger tunnels or along grain boundaries, and charge balance is maintained by substituting Mn(III) for some of the Mn(IV).

Nsutite has been found in ore deposits worldwide (58), and one occurrence has been reported in ocean Mn nodules (72). It is a secondary, replacement mineral that commonly forms from oxidation of Mn carbonate minerals (58).

Hollandite Group  $R_{.8-1.5}[Mn(IV),Mn(III)]_8O_{16}R = Ba, Pb,$ K or Na. As in ramsdellite, the hollandite structure is constructed of double chains of edge-sharing MnO<sub>6</sub> octahedra, but they are linked in such a way as to form tunnels with square cross sections, measuring two octahedra on a side (Fig. 1). The tunnels are partially filled with large uni- or divalent cations and, in some cases, water molecules. The charges on the tunnel cations are balanced by substitution of lower valence cations [e.g., Mn(III), Fe(III), Al(III), etc.] for some of the Mn(IV). The different minerals in the hollandite group are defined on the basis of the predominant tunnel cation: hollandite (Ba), cryptomelane (K), coronadite (Pb), and manjiroite (Na). Natural specimens having end-member compositions are unusual, and chemical analyses show a wide range of tunnel cation compositions. Hollandite minerals commonly occur intermixed and, in some cases, grade from one to another along a single crystal. They can be major phases in the oxidized zones of Mn deposits and important ores. Consistent with their chain structure, they typically are found as fibrous crystals, usually in compact botroyoidal masses. Less commonly, hollandite minerals form as prismatic crystals in hydrothermal vein deposits.

In recent years there has been considerable interest in the hollandite minerals and in the hollandite structure-type in general, both for potential applications as solid ionic conductors (73) and for immobilizing certain radioactive cations as part of a waste storage system (74). Also it has been shown that at high pressures feldspar minerals transform to a hollandite-like structure (75), making this, perhaps, an important structure type in the lower crust and upper mantle.

Romanechite Ba.66Mn(IV)3.68Mn(III)1.32O10.1.34H2O. The romanechite structure is constructed of double and triple chains of edge-sharing MnO<sub>6</sub> octahedra that link to form large tunnels with rectangular cross sections, measuring two by three octahedra (Fig. 1). The tunnels are filled with Ba cations and water molecules in a 1:2 ratio, and the charges on the tunnel cations are balanced by substitution of Mn(III) for some of the Mn(IV). Single-crystal x-ray diffraction studies indicate that the trivalent Mn concentrates on the octahedral sites that are at the edges of the triple chains. Romanechite typically occurs as botroyoidal masses in oxidized zones of Mn-rich deposits. Single crystals, at least those large enough for x-ray diffraction studies, are known only from Schneeberg, Germany. Cross sections of botroyoidal samples typically show very fine concentric layering (layers are tens to hundreds of microns thick). Electron microprobe analyses reveal minor fluctuations in composition among the different layers, mostly in concentration of Ba relative to Na, K, Ca, and Sr. In general, chemical analyses of romanechite deviate only slightly from the ideal formula.

TEM studies have shown that romanechite and hollandite commonly intergrow on a very fine scale (76). The two structures interconnect via the common double octahedral chain. Upon heating above about 550°C, romanechite transforms to hollandite (77).

Todorokite (Ca, Na, K).<sub>3-.5</sub>[Mn(IV), Mn(III), Mg]<sub>6</sub>O<sub>12</sub>·3– 4.5H<sub>2</sub>O. Todorokite is one of the major Mn minerals identified in ocean Mn nodules (10 Å manganate), and the likely host phase for strategic metals such as Ni, Co, etc. It is also a major mineral in the oxidized zones of many terrestrial Mn deposits. For many years the crystal structure of todorokite was a subject of considerable conjecture and controversy. Todorokite occurs with apparent platy or fibrous morphologies, supporting arguments for a tunnel- or layer-type structure (18). Highresolution TEM images (77) confirmed that todorokite has a tunnel structure constructed of triple chains of MnO<sub>6</sub> octahedra. The triple chains share corners with each other to form large tunnels with square cross sections that measure three octahedra on a side (Fig. 1). TEM images also revealed intergrowths with todorokite having tunnels measuring 3X4, 3X5, and up to 3X9 octahedra in cross section (78, 79).

The crystal structure of todorokite recently was refined by using the Rietveld method and powder x-ray diffraction data, revealing for the first time the major water and cation positions in the tunnels (48). Lower valence cations such as Mn(III), Ni(II), and Mg(II), which substitute for Mn(IV) to offset charges on the tunnel cations, appear to be concentrated into the sites at the edges of the triple chains, as in romanechite. Chemical analyses of todorokite show considerable variation in tunnel cation composition (80), and samples from ocean nodules have up to several weight percent Ni, Co, and/or Cu (81). Because of todorokite's large zeolite-like tunnels, there has been considerable interest in recent years in producing synthetic analogues for possible use as catalysts or molecular sieves (82).

Todorokite typically occurs in Mn deposits as an alteration product of primary ores such a braunite. It also seems to be a important phase in many Mn coatings, dendrites, and varnishes (70). In the case of ocean nodules, the mechanism of todorokite formation is not well understood, but some experiments suggest that biological processes might play an important role (83). It has been speculated that nodular todorokite alters from a precursor buserite-like phase (48). Recently, studies have shown that todorokite can be synthesized starting with a Mg-rich birnessite-like phase (45).

**MnOOH Minerals.** There are three natural polymorphs of MnOOH; manganite is the most stable and abundant, the other two are feitknechtite and groutite. The manganite ( $\gamma$ -MnOOH) crystal structure is similar to that of pyrolusite but all of the Mn is trivalent and one-half of the O atoms are replaced by hydroxyl anions. The Mn(III) octahedra are quite distorted because of Jahn-Teller effects. Manganite typically occurs in hydrothermal vein deposits as acicular or prismatic crystals, or as an alteration product of other Mn-bearing minerals. In air manganite alters at 300°C to pyrolusite (84), and many crystals that appear to be manganite, in fact, are pseudomorphs, having been replaced by pyrolusite.

Groutite ( $\alpha$ -MnOOH) is isostructural with ramsdellite, but, as in manganite, with all Mn(III) and one-half of the O anions replaced by hydroxyl anions. Groutite is not a common mineral, but sometimes is intimately mixed with pyrolusite, to which it is probably altering.

In 1945 a hydrous Mn oxide was synthesized that yielded an x-ray diffraction pattern identical to that of hausmannite with the exception of a strong extra reflection (d = 4.62 Å) and a general weakening of the remaining reflections, and it was given the name hydrohausmannite (85). Later a mineral was described from Franklin, NJ that gave an identical x-ray diffraction pattern to that of hydrohausmannite (86). Eventually it was determined that the original hydrohausmannite actually was a mixture of two phases: hausmannite and  $\beta$ -MnOOH (87). Electron micrographs showed that the  $\beta$ -MnOOH crystallized as hexagonal plates. It was assumed that all so-called hydrohausmannite mineral specimens were also mixtures, and the name feitknechtite was proposed for naturally occurring  $\beta$ -MnOOH (66). Feitknechtite is known only in very fine-grained mixtures, and consequently, its crystal structure has not yet been determined.

#### Mn Oxide Minerals with Layer Structures

**Lithiophorite LiAl<sub>2</sub>[Mn(IV)<sub>2</sub>Mn(III)]O<sub>6</sub>(OH)<sub>6</sub>.** The lithiophorite structure consists of a stack of sheets of  $MnO_6$  octahedra alternating with sheets of  $Al(OH)_6$  octahedra in which one-third of the octahedral sites is vacant (Fig. 2). In the ideal formula, Li cations fill the vacant sites in the Al layer, and charge balance is maintained by substitution of an equal number of Mn(III) for Mn(IV) cations (61). The layers are cross-linked by H bonds between hydroxyl H on the Al/Li layer



FIG. 2. Polyhedral representation of (A) lithiophorite showing alternately stacked layers of  $MnO_6$  (blue) and (Al, Li)(OH)<sub>6</sub> (red) octahedra, (B) chalcophanite with Zn cations (green octahedra) occupying positions above and below vacancies in the Mn octahedral layers, and (C) Na-rich birnessite-like phase showing disordered H<sub>2</sub>O/Na sites (yellow) sandwiched between the Mn octahedral sheets.

and O atoms in the Mn sheet. Lithiophorite commonly is found in weathered zones of Mn deposits and in certain acid soils, but also has been reported from low-temperature hydrothermal veins (88). It typically occurs in finely crystalline masses, but in Postmasburg, South Africa is found as large (1–2 cm) hexagonal plates. Chemical analyses show that the Li content of lithiophorite ranges from 0.2 to 3 weight percent and that transition metals such as Ni, Cu, and Co commonly substitute into the structure (89, 90). Extended x-ray absorption fine-structure spectroscopy suggest that Ni and Cu concentrate in the Al-OH sheets and Co in the Mn layers (91). Materials known as asbolanes are important components of certain Mn ore deposits and are thought to have a crystal structures similar to that of lithiophorite but with Al replaced by transition metal cations (92).

**Chalcophanite ZnMn<sub>3</sub>O<sub>7</sub>·3H<sub>2</sub>O.** Chalcophanite is a common weathering product in many Mn-bearing base metal deposits. Its structure consists of sheets of edge-sharing  $Mn(IV)O_6$  octahedra that alternate with layers of Zn cations and water molecules (Fig. 2). One of seven octahedral sites in the Mn layer is vacant, and the Zn cations are above and below the vacancies (62). The water molecules form a hexagonal close-packed layer with one of seven molecules absent. Minerals recently have been described with the same structure as chalcophanite but with Mg (93) and Ni (94) instead of the Zn cations. The crystal structure of chalcophanite has been of interest because it is similar to, and, therefore, can serve as a model for, that of the more abundant and environmentally important birnessite, which has not been found in crystals suitable for detailed structural studies.

**Birnessite Group** [Na,Ca,Mn(II)]Mn<sub>7</sub>O<sub>14</sub>·2.8H<sub>2</sub>O. Birnessite was first described as a natural phase from Birness, Scotland (95), and since then it has been recognized that birnessite and birnessite-like minerals occur in a wide variety of geological settings. As was mentioned above, it is a major phase in many soils and an important component in desert varnishes and other coatings and in ocean Mn nodules. It is also commonly found as an alteration product in Mn-rich ore deposits. It readily participates in oxidation-reduction and cation-exchange reactions and therefore might play a significant role in soil and groundwater chemistry.

All known natural birnessite samples are fine-grained and relatively poorly crystalline. Consequently, it has not been possible to perform detailed studies of the crystal structures of these materials. The crystal structures of synthetic Na-, K-, and Mg-birnessite-like phases, however, recently were determined by using TEM and powder x-ray diffraction (49). The study confirmed that the basic structural unit is a sheet of  $MnO_6$ octahedra and revealed that the interlayer cations and water molecules occupied different positions in each of the three phases (Fig. 2). Powder x-ray diffraction patterns of the minerals ranceite and takanelite suggest that they are isostructural with birnessite, but with the dominant interlayer cations being Ca and Mn(II), respectively.

The reported cation-exchange capacity of a synthetic Nabirnessite-like phase is 240 meq/100 g, with a preference for Ni and Ba over Ca and Mg (45).

**"Buserite."** When Na-birnessite is prepared synthetically, the initial precipitate yields a powder x-ray diffraction pattern similar to that of birnessite but with a 10 Å interlayer spacing, which upon drying collapses to the typical 7 Å birnessite spacing. The collapse presumably involves the loss of a water layer and is irreversible. The natural phase that is the presumed analogue of the synthetic 10 Å material has been called buserite (not an approved mineral name) (96–98) and might be a common component of ocean Mn nodules before they dry out (99, 100). Cations such as Ni(II), Mg(II), Ca(II), and Co(II) tend to stabilize the buserite structure against collapse (101, 102).

Vernadite MnO<sub>2</sub>·nH<sub>2</sub>O. Vernadite is a fine-grained poorly crystalline natural Mn oxide phase characterized by a powder x-ray diffraction pattern with broad XRD lines at 2.46, 1.42, and rarely at 2.2 Å. Vernadite appears to be analogous to the synthetic phase δ-MnO<sub>2</sub>. Chemical analyses of vernadite samples commonly show minor amounts of K, Mg, Ca, Ba, and Fe (63) and 15-25 weight percent water. The crystal structure of vernadite is not known, but it has been proposed that vernadite is a variety of birnessite that is disordered in the layer-stacking direction (103, 104), thereby accounting for the absence of a basal reflection in the x-ray diffraction pattern. The lack of a basal reflection also could be the result of individual vernadite crystallites that are extremely thin plates, perhaps less than 100 Å thick, such that there is no Bragg diffraction arising from the stacking direction. (66, 103). Vernadite is found in the oxidized zone of Mn ore deposits and might be a major phase in ocean Mn nodules and other Mn oxide crusts and coating.

#### **Other Mn Oxide Minerals**

Hausmannite  $[Mn(II)Mn(III)_2O_4]$  has a spinel-like structure with Mn(II) in the tetrahedral and Mn(III) in the octahedral

sites. It and Bixbyite  $[(Mn,Fe)_2O_3]$  typically are found in hydrothermal or metamorphic deposits. The amount of Fe that can be accommodated into the bixbyite structure is a function of temperature (105), and therefore the mineral is an important geothermometer in some ore deposits. The crystal structure of pyrochroite  $[Mn(OH)_2]$  consists of stacked sheets of  $Mn(II)(OH)_6$  octahedra, and manganosite (MnO) is isostructural with halite. Both minerals are relatively rare, typically occurring in low-temperature hydrothermal veins in Mn-rich deposits.

#### Summary

There are more than 30 Mn oxide/hydroxide minerals, and many of them occur abundantly in a wide variety of geological settings. In addition to being important as ores of Mn metal, they also play an active role in the environmental geochemistry at the Earth's surface. Mn oxides are ubiquitous in soils and sediments, and because they are highly chemically active and strong scavengers of heavy metals, they exert considerable influences on the compositions and chemical behaviors of the sediments and soils and associated aqueous systems. The ability to successfully model and predict the chemical and thermodynamic properties of Mn oxide minerals and to prepare synthetic analogues depends to a large degree on a detailed understanding of their crystal structures. Unfortunately, many Mn oxide minerals occur only as fine-grained, poorly crystalline aggregates and coatings, making crystal structure studies extremely challenging. In recent years, however, an arsenal of new techniques, such as TEM, Rietveld refinements using powder diffraction data, extended x-ray absorption fine-structure spectroscopy, and single-crystal studies using charge-coupled device detectors and synchrotron sources, have slowly started and are continuing to unravel many of the inner secrets of Mn oxide minerals. Given the already considerable interest in Mn oxide minerals by geologists, soil scientists, microbiologists, chemical and environmental engineers, ceramicists, etc., the future for this group of characteristically dark minerals looks very bright.

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