

## The todorokite–buserite problem: further considerations

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### Abstract

Todorokite has been shown in several recent HRTEM studies to have a tunnel structure analogous to that of romanechite (psilomelane). Further examinations of the structures and crystal chemistry of romanechite and todorokite suggest that lower valence Mn cations occupy larger M2-type  $[\text{MnO}_6]$  octahedra constituting the “walls” of the tunnels, which are distorted as a result of the Jahn–Teller effect in  $\text{Mn}^{3+}$  ions. Atomic substitution of  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Zn}^{2+}$  ions for lower valence Mn cations occur in M2-type sites of todorokite, accounting for the enrichment of Ni, Cu, etc., in many deep-sea manganese nodule deposits. Recent literature is reviewed which identifies asbolan and mixed-layer asbolan–buserite assemblages as additional 10Å manganese (IV) oxide phases occurring in seafloor sediments.

### Introduction

Giovanoli (1985) has pointed to the several areas in which we are in agreement in his discussion of our review of the todorokite–buserite problem. We are now in agreement that todorokite is a valid mineral. Some points of disagreement still remain, however, and are addressed here. We elaborate upon details of the crystal structure and atomic substitution in romanechite (psilomelane) and related todorokite, the nature of lower valence manganese cations in manganese oxide minerals, and recent observations on these phases in the marine environment.

### Structural linkages and cation occupancies of todorokite

As early as 1975, we postulated (Burns and Burns, 1975) that todorokite has structural similarities to minerals of the hollandite and psilomelane (romanechite) groups. Our model then was based on comparable crystal habits, cell parameters, chemical compositions and thermal stabilities of these minerals. We later suggested (Burns and Burns, 1977) that todorokite has a tunnel structure analogous to psilomelane (Wadsley, 1953), and subsequently (Burns and Burns, 1979) classified these minerals as tektomanganates. Recent HRTEM observations not considered by Giovanoli (1985) of todorokites from continental (Turner and Buseck, 1981, and ms.) and marine manganese nodule (Turner and Buseck, 1982; Turner et al., 1982; Siegel and Turner, 1983) deposits have confirmed our structural model. It is now estab-

lished that todorokite does, in fact, possess a tunnel structure consisting of “walls” of triple chains of edge-shared  $[\text{MnO}_6]$  octahedra, and “floors” and “ceilings” of edge-shared  $[\text{MnO}_6]$  octahedra most commonly three octahedra wide. These predominant  $[3 \times 3]$  tunnels often are intergrown with other tunnels ranging in dimension from  $[3 \times 2]$  to  $[3 \times 8]$  and higher. In a typical  $[3 \times 3]$  tunnel the average number of shared edges of the  $[\text{MnO}_6]$  octahedra is 4.67 per unit cell.

Prior to confirmation by HRTEM of the tunnel structure of todorokite, we sought evidence in support of our model, including the infrared spectroscopic data of Potter and Rossman (1979). In their paper, they stated (p. 1215–1216):

“The spectra of todorokite suggest that its structure is based on  $\text{MnO}_6$  octahedral layers. The positions and intensities of the major bands of todorokite samples with the highest crystalline order suggest a polymerization near 5 shared edges per octahedron. This is consistent with a highly polymerized chain or channel structure and with a layer structure containing some vacancies.”

Potter and Rossman drew these conclusions from their Figure 18 which is a plot of major band positions in the  $300\text{--}700\text{ cm}^{-1}$  region versus average number of shared edges per  $\text{MnO}_6$  octahedron in known manganese oxide structures, including manganosite (containing only  $\text{Mn}^{2+}$  ions!) and romanechite (containing two populations of  $\text{MnO}_6$  octahedra with different numbers of edge-shared octahedra). We found that when the todorokite infrared spectral data are plotted on Figure 18 of Potter and Rossman (1979), the average number of shared edges is  $4.7 \pm 0.3$  per  $[\text{MnO}_6]$  octahedron. This corresponds

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exactly to the number estimated for the  $[3 \times 3]$  tunnel structure of todorokite, which is remarkable given the scatter of reference data points and assumptions underlying Potter and Rossman's Figure 18. Note that intergrowths of larger dimension tunnels in todorokite increases the average number to "near 5 shared edges per octahedron" (Potter and Rossman, 1979). Therefore, contrary to Giovanoli's (1985) assessment of the Potter and Rossman data, we maintain that they support the proposed tunnel structure of todorokite.

#### *Lower valence manganese cations in psilomelane and todorokite*

Giovanoli (1985) has addressed an important point about the oxidation state of manganese in psilomelane and todorokite. In our interpretations of the crystal chemistry of manganese cations in these minerals, we utilized published chemical analytical data of psilomelanes (Fleischer, 1960) and todorokites (for example, Frondel et al., 1960) which routinely express manganese proportions as weight percentages of  $\text{MnO}_2$  and  $\text{MnO}$  components, implying coexisting  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$  cations. In his structure determination of psilomelane, Wadsley (1953) assumed "that  $\text{Mn}^{2+}$  together with minor elements substitute for  $\text{Mn}^{4+}$  as they do in hollandite . . ." He also stated: "Some confusion has existed in the past concerning the substantial amount of lower-valency manganese invariably present in psilomelane, and the tendency to regard  $\text{Mn}^{2+}$  as a separate constituent has led to difficulties of formulation. The  $\text{Ba}^{2+}$  ions which are coordinated to the oxygen ions of the stable  $\text{Mn}^{4+}\text{O}_6$  octahedra will upset the charge balance, and for the structure to exist at all, an equivalent number of  $\text{Mn}^{4+}$  ions must be reduced to  $\text{Mn}^{2+}$  ions. These will remain in the  $\text{Mn}^{4+}$  sites as charge deficiencies." Bystrom and Bystrom (1950), in their structure determination of hollandite commented, "Apparently the true oxidation state of the elements in the (hollandite) minerals cannot be deduced from the analyses. The manganese atoms are given as  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$  ions. This is obviously quite arbitrary; they could as well be divided into  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  ions." In recent structure refinements of hollandite and related minerals, Post et al. (1982) state: "This study also indicates that the reduced form of Mn in hollandite is  $\text{Mn}^{3+}$ ; bond lengths calculated from the refinements suggest that  $\text{Mn}^{3+}$  is more easily accommodated in the structures than the larger  $\text{Mn}^{2+}$ ." Post et al. (1982) determined that the average metal-oxygen distances in the  $[\text{MnO}_6]$  octahedra of hollandite and cryptomelane are 1.925 and 1.917Å, respectively, only slightly larger than the 1.88 and 1.89Å distances in the pure Mn(IV) oxide minerals pyrolusite and ramsdellite. Wadsley's (1950) crystal structure determination of psilomelane indicated average metal-oxygen distances for the M1, M3, and M2 sites to be approximately 1.91, 1.91, and 1.99Å, respectively, suggesting to us that large cations are concentrated in the M2 positions. We assumed that  $\text{Mn}^{2+}$  ions occupy

preferentially these larger M2 sites on the basis of chemical analytical data (Fleischer, 1960). Giovanoli (1985) prefers  $\text{Mn}^{3+}$  cations in the structure, and this suggestion may be supported by infrared and X-ray K absorption edge data for romanechite (Yanchuk and Povarennykh, 1975a) which indicate the presence of  $\text{Mn}^{4+}$ ,  $\text{Mn}^{3+}$  and low-valence ions of Mn. We note that the difference between average metal-oxygen distances of the psilomelane M2 site (1.99Å) and a  $\text{Mn}^{4+}$  site in pyrolusite (1.88Å) corresponds exactly to the difference of octahedral ionic radii of  $\text{Mn}^{3+}$  (0.65Å) and  $\text{Mn}^{4+}$  (0.54Å). The  $\text{Mn}^{2+}$  ion (0.82Å) may be, in fact, too large for the M2 positions of psilomelane, as Giovanoli (1985) suggests.

So far as todorokite is concerned, again the infrared and X-ray spectral data of several specimens, including the todorokite from Charco Redondo, Cuba, suggest the presence of  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  ions (Yanchuk and Povarennykh, 1975b). However, chemical analyses of todorokites, including specimens from the type locality, in addition to reporting manganese as  $\text{MnO}_2$  and  $\text{MnO}$  components, also show significant amounts of  $\text{MgO}$  (Frondelet et al., 1960; Straczek et al., 1960). Since  $\text{Mg}^{2+}$  (0.72Å) probably substitutes for lower valence Mn cations in todorokites, so too should  $\text{Ni}^{2+}$  (0.70Å),  $\text{Cu}^{2+}$  (0.73Å),  $\text{Co}^{2+}$ , (0.73Å),  $\text{Zn}^{2+}$  (0.74Å), etc., readily be accommodated in the structure. That is why we continue to propose that atomic substitution of these divalent transition metal cations occurs in psilomelane M2-type sites in the todorokite structure. We again draw attention to the large range of metal-oxygen distances (1.92–2.02Å) in the six-coordinate M2 site of psilomelane (Wadsley, 1953) which we suggest may be the result of Jahn-Teller distortion of the coordination environment induced by the electronic structure of  $\text{Mn}^{3+}$  ions. The existence of a similar distortion of M2-type sites in todorokite would favor the site occupancy of  $\text{Cu}^{2+}$  ions, which also are stabilized by the Jahn-Teller effect, and would be responsible for the anomalously high enrichment of copper in todorokites occurring in cores of manganese nodules (Siegel, 1981; Siegel and Turner, 1983).

#### *Manganese oxides in the marine environment*

An aspect of our earlier review (Burns et al., 1983) which deserves further comment concerns the identity of the 10Å phases found in marine manganese nodule deposits. An update of recent studies characterizing manganese oxide phases in seafloor deposits seems appropriate here.

A growing body of evidence from scanning and transmission electron microscope techniques has identified todorokite with tunnel structures inside seafloor manganese nodules from several localities (Burns and Burns, 1978; Chukhrov et al., 1978, 1979, 1981; Turner et al., 1982; Siegel and Turner, 1983). Apart from one report (Arrhenius and Tsai, 1981), there has been no convincing evidence for the occurrence of buserite in the natural environment. Recently, however, Chukhrov et al. (1983)

suggested that mixed-layer asbolan-buserite assemblages occur in oceanic ferromanganese oxide concretions.

Historically, the term asbolan or asbolane referred to a cobalt-rich wad composed of a mixture of poorly defined hydrated manganese oxides (Strunz, 1970; Glossary of Geology, 1972). Chukhrov et al. (1981a, b; 1982) demonstrated that terrestrial Co-Ni and Ni asbolans have hybrid layer structures consisting of two incommensurable hexagonal sublattices I and II with different  $a$  parameters (2.823 and 3.04Å) but identical  $c$  dimensions (9.6Å) which collapse to 9.34Å by dehydration in the vacuum of the electron microscope. Sublattice I was proposed to consist of continuous layers of edge-shared  $[\text{Mn}^{\text{IV}}\text{O}_6]$  octahedra 9.6Å apart and to be interleaved with sublattice II containing discontinuous layers of  $[(\text{Ni},\text{Co})(\text{OH},\text{H}_2\text{O})_6]$  octahedra,  $\text{Ca}^{2+}$  ions and  $\text{H}_2\text{O}$  molecules. Chukhrov et al. (1983) reported that monomineralic asbolans containing  $\text{Mn}^{2+}$  (and/or  $\text{Mn}^{3+}$ ?),  $\text{Ni}^{2+}$  and  $\text{Ca}^{2+}$  in the layers of the defect sublattice II occur in some seafloor Fe-Mn concretions. They also proposed that "todorokite" identified by X-ray diffraction techniques in many Fe-Mn concretions consists of disordered mixed-layer assemblages of asbolan-like and buserite-like components, the latter being readily dehydrated to a birnessite-like (7Å) phase in the electron microscope. Chukhrov et al. (1983) concluded that X-ray diffraction patterns alone containing intense lines at 9.8, 4.9, and 2.44Å can correspond to any one of four phases in manganese nodules: buserite, asbolan, mixed-layer asbolan-buserite, and todorokite.

It becomes apparent from these recent electron microscopy studies that electron beam techniques (selected area electron diffraction and high resolution lattice imaging), perhaps complimented by X-ray energy dispersive analyses, X-ray diffraction, infrared spectra, and ESCA or UV photoelectron spectroscopy, are now necessary to identify unambiguously the manganese oxide minerals occurring in terrestrial and seafloor deposits.

### Conclusions

(1) Todorokite has a tunnel structure analogous to that of romanechite (psilomelane) in which triple chains of edge-shared  $[\text{MnO}_6]$  octahedra constitute the "walls" and predominate in the "floors" and "ceilings" of the tunnels. This  $[3 \times 3]$  tunnel structure of todorokite is consistent with HRTEM and infrared spectral measurements.

(2) Lower valence Mn cations occur in the romanechite and todorokite structures. Although chemical analyses of these minerals express Mn concentrations as proportions of  $\text{MnO}_2$  and  $\text{MnO}$  oxide components, recent X-ray spectral data suggest that  $\text{Mn}^{3+}$  ions may also be present. The lower valence Mn cations are assumed to occupy the larger M2-type sites in the "walls" of edge-shared  $[\text{MnO}_6]$  octahedra.

(3) Atomic substitution in todorokite of divalent Mg, Ni, Cu, Co, and Zn ions for lower valence Mn cations in the M2-type octahedral sites accounts for the high con-

centrations of Ni, Cu, Co, and Zn in many deep-sea manganese nodule deposits.

(4) Recent electron microscopy measurements indicate that, in addition to todorokite, asbolan and mixed-layer asbolan-buserite minerals also occur in marine sediments. X-ray diffraction data alone cannot distinguish between these 10Å manganese oxide minerals.

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