A review of the todorokite–buserite problem: implications to the mineralogy of marine manganese nodules: discussion

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Abstract

The author agrees that todorokite is a valid mineral species. However, previous comparisons of todorokite and psilomelane (romanechite) are criticized. In addition, the lower-valence manganese ions in psilomelane cannot be Mn^{2+} but must be Mn^{3+} ions, which explains the extraordinary coordination of the position M2 in the psilomelane structure as Jahn–Teller distortion.

Lattice imaging in hollandite and psilomelane on synthetic material is discussed and confirmed as showing the tunnels with Ba^{2+} ions as earlier published. In the case of todorokite, however, the published and accessible data are not convincing and contradict X-ray diffraction and other data. Experimental evidence from the synthesis of hollandite and psilomelane also makes it unlikely that the proposed large tunnels in the previous speculations on the todorokite structure can be stable. The content of these tunnels is also in doubt. It is emphasized that the reduction of $Mn_7O_{13} \cdot 5H_2O$ to γ-MnOOH has been checked by X-ray diffraction methods totally independent from electron microscopy.

Introduction

Todorokite is a manganese oxide phase named after the Todoroki mine (Hokkaido, Japan) that was described by Yoshimura (1934). It was later found in Cuba (e.g., Straczek et al., 1960). More recently, Perseil and Giovanoli (1982) have described a sample from Ambollas (Eastern Pyrénées, France).

Independently of Yoshimura, Wadsley (1950) synthesized a phase by rapid oxidation of a fresh $Mn(OH)_2$ suspension using molecular O_2. This phase showed remarkable ion exchange properties.

Again independently of both Wadsley and Yoshimura, Feitknecht and Marti (1945) synthesized a manganese oxide phase which later turned out to be the dehydration product of Wadsley's phase.

Buser and Grütter (1956) were the first to realize the close relation between Wadsley's phase and one of the constituents occurring in deep sea manganese nodules. Levinson (1960) pointed out that Wadsley's phase produces a powder diffraction pattern which shows a striking resemblance to that of todorokite. Up to that time period the metal scavenging constituent in marine manganese nodules was usually called 10Å-manganate[1] after Buser,

and following Levinson's paper this same constituent was more generally accepted as being todorokite. These relations are listed here in order to clarify the history of todorokite and 10Å-manganate as given by Burns et al. (1983) in a slightly but distinctly different manner. In addition, there are several incorrect statements in their article which I correct here, while fully agreeing with much of the remainder of their text.

Todorokite is a valid mineral species

We entirely agree with Burns et al. (1983) that todorokite is a valid mineral species. Unfortunately, all our samples of todorokite from various origins investigated up to 1978 were not monomineralic. From 1978 to 1980 we have, however, received two samples from Japan and one from the French Eastern Pyrénées which turned out to be almost monomineralic (for the latter sample cf. Perseil and Giovanoli, 1982). I, therefore, withdraw my previous opinion (Giovanoli and Bürki, 1975) that todorokite is not a valid mineral species.

The comparison of todorokite with psilomelane

Burns et al. (1983) devote much of their report to the inferred structure of todorokite as first published (Burns and Burns, 1977) based on morphological similarities. Some occurrences of todorokite are fibrous as is psilomelane (romanechite). Burns and Burns (1977) make the incorrect statement that psilomelane has Mn^{2+} ions in particular structure positions. This has been emphasized

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[1] Feitknecht (1945) had, following Sarkar and Dhar (1921), unfortunately introduced the chemical name "manganite" which created confusion with the mineral name manganite for γ-MnOOH. Buser followed this nomenclature. Feitknecht corrected this in Giovanoli et al., 1970.

by Burns in a discussion remark (Burns, 1979). Picking up this particular point made in 1978 and printed in 1979 we have synthesized psilomelane and verified that no discernible amount of Mn^{2+} can be found in its structure. The lower-valence manganese ions are $\bar{M}n^{3+}$. This explains the coordination of these sites as due to Jahn–Teller deformation. Mn^{2+} ions are much too large to fit into these positions while Mn^{3+} fits very nicely (Giovanoli and Balmer, 1983). It is also noteworthy that in the case of cryptomelane and hollandite the valences have routinely been indicated as Mn^{2+} and Mn^{4+} until Post et al. (1982) showed that the presence of Mn^{2+} ions in these compounds is most unlikely. We have, as early as 1969, rejected the presence of Mn^{2+} as most improbable in synthetic groutite α-MnOOH (Giovanoli and Leuenberger, 1969). Glaunsinger et al. (1979) settled an old controversy by confirming that all Mn ions in γ-MnOOH also are trivalent.

Lattice imaging

When Turner and Buseck (1979) produced high resolution electron micrographs of natural samples of psilomelane it was obvious that the contrast lineages correspond to the Ba^{2+} in the tunnels of this structure. Occasionally intergrowth with hollandite was observed. We could reproduce these results on a large variety of synthetic psilomelane and hollandite phases and also found frequent intergrowth (Giovanoli and Balmer, 1983). We have, however, also found similar transmission microscope images in 7Å-phyllomanganate (Giovanoli and Arrhenius, 1985) and the high resolution electron micrographs are therefore not unambiguous. Turner and Buseck later investigated todorokite and also interpreted the lineages found as tunnels. They inferred, therefore, that todorokite is a tektomanganate with large tunnels, an assumption that fitted nicely into the speculations of Burns and Burns. It is possible that this is indeed the case and that—except for hollandite and psilomelane tunnels—larger tunnels also exist, at least as isolated defects. Potter and Rossman (1979) who have thoroughly studied the infrared spectra of Mn–O phases discuss this point at great length on the grounds of Weissenberg X-ray diffraction patterns they have also taken of todorokite. Their text which is only partly quoted by Burns et al. (1983) says:

"... No chain or channel manganese oxides composed of such large units are known to exist, although isolated quadruple chains have been observed in hollandite in electron microscope images (Turner and Buseck, 1979). It appears that for highly polymerized structures a layer structure is preferred. [...]Weissenberg single-crystal X-ray diffraction indicates that the sample is ordered in the same plane as the plates but disordered in planes perpendicular to them. This suggests that it consists of a random superposition of single-crystal

todorokite plates and eliminates the possibility that it is a mass of needles that appear morphologically as a plate."

The content of such large tunnels as proposed by Burns and Burns has also never been established. All known tunnels in Mn–O phases contain tightly fitting large cations; e.g., Ba^{2+}, K^+ and others. Until these questions are answered, and as long as no diffraction evidence is put forward, the structure drawings as shown in Figures 2 and 3 in Burns et al. (1983) must be regarded as being speculative.

The reduction of 7Å-manganate to γ-MnOOH

On p. 975 ff. Burns et al. discuss at great length a reaction we have undertaken (Giovanoli et al., 1971) in the context of other topotactical transformations. No simulation of natural geochemical environments has been intended (as Burns et al. suggest); only the process as exclusively taking place under a particular redox potential is implied. Burns et al. claim that the structural interpretation of this reaction was wrong. They refer to Figure 1 (in Burns et al., 1983) where we have indeed drawn the left-hand side incorrectly. The figure is also not to scale. Since its purpose was to show that starting and end products have virtually identical Mn–Mn distances only in one structure direction, this error in a purely schematic drawing—although deplorable—is of little importance in the context.

Burns et al. (1983), however, go still further in their deductions from the error in Figure 1. They question that the reduction product was γ-MnOOH. I completely reject this interpretation since it has been shown beyond doubt through X-ray diffraction patterns (in Giovanoli et al., 1971) that γ-MnOOH is the end product which can easily be reproduced.

Conclusions

(1) Naturally occurring todorokite is a valid mineral species.

(2) The structure of todorokite is unknown and Figures 2 and 3 in Burns et al. (1983) are speculative.

(3) Psilomelane contains Mn^{3+} ions, not Mn^{2+}.

(4) Larger tunnels than those in psilomelane could not be produced hitherto and the possibility of their existence as a structural unit is remote. However, they may occur as isolated lattice defects.

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