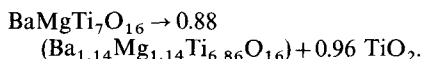


the lower value being adopted by hollandites coexisting with rutile. These non-integral stoichiometries are a necessary consequence of superlattice ordering. Priderite likewise possesses an ordered superstructure and non-integral stoichiometry (Pring and Jefferson, 1983). Dubeau and Edgar (1985) designed their experiments assuming that the most appropriate end-member stoichiometries for magnesian priderites are  $K_2MgTi_7O_{16}$  and  $BaMgTi_7O_{16}$  respectively. However, the latter is not correct. The appearance of rutile in the run products of BP-rich compositions, and its systematically higher abundance with increasing wt. % BP, demonstrates that the Ba end-member has  $x > 1$  and an ordered superstructure. Assuming, for example,  $x = 1.14$  then the bulk composition  $BP_{100}$  disproportionates to yield rutile as follows:



KEY WORDS: priderite, hollandite, system  $K_2MgTi_7O_{16}$ - $BaMgTi_7O_{16}$ .

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## A note on chalcophanite formation in a Recent lake

RECENT mineralogical interest in the nature of manganese oxide particulates in natural marine water (Suess, 1979), natural lake water (Klavness, 1977), and simulated lake water (Giovanoli, 1980), prompted a search for such particulates in a large New South Wales coastal lake. While the investigation revealed the presence of sparse amounts of poorly crystalline particulates in near-surface waters, it did show the existence of manganese oxide replacement phenomena in fragmentary sedimentary rocks near the lake margin.

Mineralogical studies showed this oxide to be chalcophanite. Although this mineral is not uncommon in the weathering zone of ore deposits (Frenzel, 1980) it has not previously been recorded in Recent marine or lacustrine deposits (Glasby, 1977). An occurrence of chalcophanite in fossil manganese nodules in fine-grained argillaceous sandstones, of Permian age, in Montana (Gulbrandsen and Reeser, 1969) is, however, interpreted

by these writers as sedimentary. The absence of chalcophanite from Recent marine and freshwater deposits could possibly be considered unusual, as the apparently similar-structured birnessite (Giovanoli and Stahli, 1970) is an often-reported mineral in Recent manganese nodules and crusts (Burns and Burns, 1977).

*Occurrence.* Lake Macquarie, a large, shallow coastal lake formed by the drowning of coastal lowlands between 20 000 and 6000 BP, is situated to the south of Newcastle, New South Wales. The lake, with a shore line of 180 km and an area of 11 000 ha, is one of the largest salt-water lakes in the world. The salinity is variable, from brackish after heavy rains to very saline after dry periods. Because the lake has limited access to the sea, and because the surrounding area is becoming increasingly populated and industrialized, heavy metal contamination, particularly Pb, Cu, Cd, Se, and Zn is present, particularly in the northern area of the lake

(Crawford *et al.*, 1976). In contrast, Mn tends to be concentrated at the southern area of the lake. This occurrence does not appear to be related to any local source of metal pollution. Maximum recorded levels of Mn in the lake water is 1000 ppm.

The discovery of black crusts of manganese oxide close to the waterline on rocks to the south of the lake is consistent with the researches of Crawford *et al.* (1976). When part of the crust was mounted in epoxy resin, polished and examined optically it proved to be a very fine-grained, structureless material with a poorly defined layering. The identification of this manganese oxide as chalcophanite was based on X-ray diffraction (XRD) analysis and Fourier Transform Infra-red (FTIR) spectroscopy. The FTIR spectrum is very distinctive, with four sharp peaks in the region 400–600  $\text{cm}^{-1}$  and additional peaks at 1630  $\text{cm}^{-1}$  and 3300–3400  $\text{cm}^{-1}$  (Potter and Rossman, 1979a; Ostwald, 1984a). The material showed none of the characteristic optical properties of chalcophanite (Frenzel, 1980) probably because of fine crystallite size.

Optical microscopy of polished sections indicated that the manganese oxide was not simply encrusting the rock substrate, as a layer of finely mixed manganese oxide and weathered rock material existed between the rock and the chalcophanite. An X-ray diffraction analysis showed that the weathered rock layer consisted of kaolinite and traces of quartz and hematite in addition to chalcophanite. A more complex zonation was revealed by electron probe microanalysis (EPMA) line scans for  $\text{SiO}_2$ ,  $\text{MnO}_2$ , and  $\text{ZnO}$  from the rock substrate to dense chalcophanite. These reveal the existence of at least three layers (fig. 1).

Layer A, adjacent to the rock, is composed essentially of kaolinite, of weathering origin, together with low levels of manganese oxide without detectable Zn.

Layer B, a manganese oxide layer containing admixed kaolinite and low amounts of Zn.

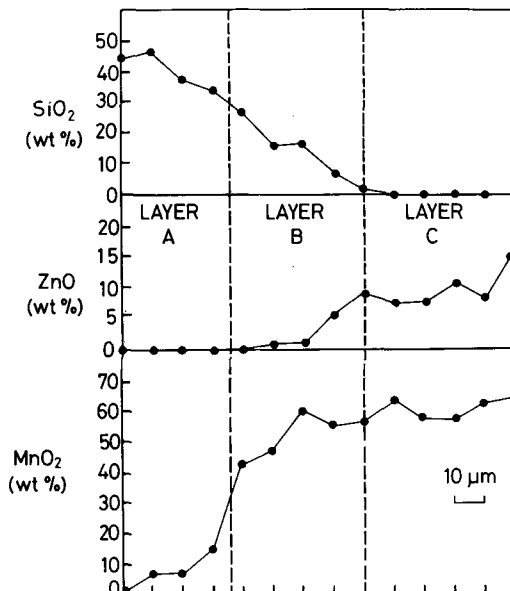


Fig. 1. Electron probe microanalysis (EPMA) line scans for silica, manganese oxide, and zinc oxide across layering in the chalcophanite.

Layer C, chalcophanite containing 10–15% ZnO.

Quantitative microanalyses on ten areas of layer C are listed in Table I. As chalcophanite was the only manganese oxide determined by XRD and FTIR and EPMA line scans suggest that the manganese oxide of layer B is chalcophanite.

*Discussion.* The origin of terrestrial chalcophanite, by weathering of manganeseiferous rocks, has been discussed by Ostwald (1984b). There is evidence that chalcophanite develops in weathering profiles by the structurally guided (topotactic) replacement of kaolinite, so that the kaolinite unit layer (7.13 Å) becomes the manganese-oxygen octahedral unit layer (7.16 Å). The initial stage of

TABLE I. MICROANALYSES OF CHALCOPHANITE (WTS)

	1	2	3	4	5	6	7	8	9	10
MnO <sub>2</sub>	70.6	72.0	70.2	70.7	67.5	69.2	72.4	67.7	71.3	69.4
ZnO	16.3	14.2	17.1	15.6	17.3	16.5	12.8	18.3	15.6	17.3
Fe <sub>2</sub> O <sub>3</sub>	0.3	0.3	0.6	0.2	0.1	ND	ND	0.4	0.6	ND
Al <sub>2</sub> O <sub>3</sub>	ND	0.2	0.3	0.3	1.1	1.3	0.6	0.4	0.1	0.2
SiO <sub>2</sub>	0.6	ND	ND	ND	1.4	1.6	ND	ND	0.1	0.7
H <sub>2</sub> O*	12.4	13.3	11.8	13.2	12.6	11.4	14.2	13.2	12.3	12.4

N.D. not detected

\* by difference from 100%.

chalcophanite crystallization is thus not nucleation from a liquid but is topotaxy and metasomatism of a degrading kaolinite crystal structure. (The fan-like crystallized crusts so often observed in chalcophanite are not kaolinite pseudomorphs—these represent normal grain growths on finer-grained primary chalcophanite substrates.)

The data on the lacustrine chalcophanite described in this paper is consistent with the kaolinite-replacement theory for terrestrial chalcophanite. Moreover, the pattern of Zn occurrence revealed by the line scans suggests that the early stages of replacement, as shown by Layer B, were not necessarily accompanied by zinc fixation. It would appear that the 7 Å manganese oxide layer lattice developed by manganese oxide pseudomorphism of the kaolinite where the argillaceous weathering surface of the boulder was in contact with oxic lake water. The common occurrence of Zn in this manganese oxide in weathering zones suggests that the element may have a stabilizing effect on the structure. Possibly the diffusion of Zn into the layer lattice may have been necessary for its preservation.

This concept of kaolinite replacement is validated by a consideration of the chalcophanite occurrences described by Renard *et al.* (1978), Gulbrandsen and Reeser (1969), and Potter and Rossman (1979b).

A recent report (Renard *et al.*, 1978) on the development of manganese oxide minerals on granite substrate in intertidal areas at Belmont, in France, is significant in relation to the Lake Macquarie chalcophanite. At Belmont a variety of manganese oxides including todorokite, rancieite, cryptomelane, and amorphous manganese oxide are developing preferentially on the mica minerals of the granite. The writers consider the rancieite (calcium-rich birnessite) and todorokite to have developed epitaxially on and between the cleavages of the micas. Assuming that micas in saline intertidal outcrops would be altering to complex mixtures of layer-lattice minerals including montmorillonite, vermiculite, kaolinite, and illite, such an environment would be ideal for structurally guided crystallization of certain manganese oxides (Ostwald, 1984a, b).

Permian age manganese concretions occur at Sheep Creek, near Dillon, Montana, USA, in fine-grained, argillaceous sandstone (Gulbrandsen and Reeser, 1969). The investigators noted that the major clay mineral present with chalcophanite was kaolinite. At adjacent locations where the clay mineral was illite or montmorillonite, chalcophanite was not observed. Thus the association kaolinite-chalcophanite is further established.

Although the chemical composition of the Sheep

Creek chalcophanite was not investigated in detail, Gulbrandsen and Reeser consider that the Zn ions in the structure were in part replaced by  $Mn^{2+}$ , Ni, Cd, and Co ions. The mineral classed as chalcophanite by Potter and Rossman (1979b) which occurs as concretions in the sediments of Baja California, Mexico, is unusual in being magnesium rich, with a formula  $(Mg_{0.6}Ba_{0.1}Fe_{0.1})(Mn_{3.0}Al_{0.1})O_7 \cdot 2H_2O$ . Nevertheless it shows the typical XRD and IR characteristics of 'normal' zincian chalcophanite. The occurrence of this mineral in a matrix of quartz, clay, mica, and calcite suggests that, as in the Montana nodules, clay replacement by Mn may have produced the initial manganese oxide layer lattice, with subsequent incorporation of  $Mg^{2+}$  (possibly from magnesian calcite) to stabilize the structure.

The Lake Macquarie chalcophanite occurrence on clay substrate raised the query as to whether any Zn-Mn oxide occurred in the amorphous (non-electron diffracting) particulates initially detected in the lake water. An analysis of particulates by transmission electron microscopy and X-ray energy dispersive spectroscopy showed that the particulates collected were all Mn + Fe or Mn + Fe + Al + Si with no detectable Zn. Analyses for the water containing these particulates ranged from 50 to 400 ppm.

It is possible to speculate whether the absence of chalcophanite from Recent marine manganese nodules where the structurally related layer lattice mineral birnessite occurs is due rather to the lack of kaolinite than to other factors. Red clay, the typical substrate for marine manganese nodules, is essentially illite and montmorillonite (Jenkyns, 1978). Thus, there is evidence that chalcophanite is not a simple manganese oxide crystallization from  $Mn^{2+}$  in aqueous solution. In the cases examined a kaolinite crystal structure is required to produce the basic 7 Å manganese oxide layer lattice mineral, and additional elements, commonly Zn but sometimes Mg, Ag, Ba, Ca, K, etc., then become incorporated in the chalcophanite structure, apparently to increase stability.

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