

Some observations on the chemical composition of chalcophanite

THE manganese oxide layer-lattice mineral chalcophanite is relatively common in the weathering zones of manganese-containing base metal deposits, and also in soils. The original material, from Sterling Hill, New Jersey, USA, contains appreciable amounts of zinc (Moore, 1875) and Dana's System of Mineralogy (Palache *et al.*, 1944) suggested the formula $(\text{Zn, Mn, Fe})\text{Mn}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, on the assumption that Mn^{2+} substitutes for Zn about $\text{Mn}:\text{Zn} = 1:3$ while Fe^{2+} substitutes for Zn to about $\text{Fe}:\text{Zn} = 2:3$. Wadsley (1950) reported a formula $\text{ZnMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$ for a completely tetravalent chalcophanite from Buchan, Victoria, Australia. A later study (Wadsley, 1955) of specimens of Sterling Hill chalcophanite, containing divalent Mn, indicated a general formula $(\text{Zn, Mn}^{2+})_{1+x}(\text{Mn}_3^{4-x}\text{Mn}_x^{2+})\text{O}_7 \cdot 3\text{H}_2\text{O}$ where x ranges from 0 to 0.25. He found that the structure was composed of layers of edge-shared $(\text{Mn}^{4+}\text{O}_6)$ octahedra and single sheets of water molecules between which Zn^{2+} ions were situated.

The crystal symmetry is triclinic, space group $\text{P}\bar{1}$, $a_0 = 7.54$, $b_0 = 7.54$, and $c_0 = 8.22$ Å, $\alpha = 90^\circ$, $\beta = 117.2^\circ$, $\gamma = 120^\circ$, $Z = 2$. X-ray identification data (JCPDS 15-807) indicate major lines at 6.96(100), 4.08(50), 3.50(60), 2.57(40), 2.24(50), 1.90(30), and 1.59 Å(40).

Later discoveries of chalcophanite have shown even greater chemical variation than indicated by Wadsley's work. These include a chemically complex Ag-Pb-Cu-containing chalcophanite in the Aurora Mine, Nevada with formula $(R)R'_3\text{O}_7 \cdot 3\text{H}_2\text{O}$ where R is commonly Zn but may be Mn^{2+} , Ag, Ba, Ca, Mg, K, Pb, and Cu, and R' is Mn^{4+} , Fe^{3+} and possibly Al and Si (Radtke *et al.*, 1967); chalcophanite deficient in Zn (Radtke *et al.*, 1967) Ostwald (1984b); magnesian chalcophanite of general formula $(\text{Mg}_{0.6}\text{Ba}_{0.1}\text{Fe}_{0.1})(\text{Mn}_{3.0}\text{Al}_{0.1})\text{O}_7 \cdot 2\text{H}_2\text{O}$ in concretions in sediments at Baja, California (Potter and Rossman, 1979), and a nickeliferous chalcophanite, from the lateritic Co-Ni deposits of Kalgoorlie, Western Australia (Elias *et al.*, 1981).

Thus there is abundant evidence that chalcophanite is much more complex than is suggested by the formula recently given in Fleischer (1983), $(\text{Zn, Fe, Mn})\text{Mn}_3^{4+}\text{O}_7 \cdot 3\text{H}_2\text{O}$. Certainly a revised formula is required. The present paper is directed to that end, by presenting electron probe micro-

analyses of chalcophanite from a number of occurrences. No attempt is made to present a new formula for chalcophanite, as electron probe microanalyses do not allow determination of valence states, and water or hydroxyl cannot be directly determined. Moreover, no specimens of high Mg chalcophanite were available for study. The paper does, however, point out some rather unusual features of the chemistry of this mineral which have previously been neglected.

Specimen locations. Specimens of chalcophanite from the following locations were investigated.

(a) Sterling Hill, New Jersey, USA. Specimens from three Australian museum collections, labelled as from the type locality.

(b) Groote Eylandt. Chalcophanite is a rare constituent of the lateritized zone of the manganese ore body (Ostwald, 1980). This occurrence shows textural and microchemical evidence of an origin by metasomatic replacement of kaolinite (Ostwald, 1981).

(c) Norseman, Western Australia. Superficial crusts of manganese oxide associated with lateritized Archaean greenstone proved to be low-zinc chalcophanite (Ostwald, 1984b).

(d) Buchan, Victoria, Australia. Samples from this area, probably equivalent to those studied by Wadsley (1950).

(e) Kambalda area, Western Australia. Specimens of dense black manganese oxide from the area described by Elias *et al.* (1981). This is apparently the first recorded occurrence of nickel-rich chalcophanite (fig. 1).

(f) Lake Macquarie, New South Wales. Chalcophanite was identified in a black crust on a boulder at the edge of the lake (Ostwald, in press).

Results. Representative samples from the six localities were examined by XRD and by Fourier Transform Infra-Red (FTIR) spectroscopy, and all showed chalcophanite characteristics. The FTIR spectrum of chalcophanite is very characteristic, with four sharp absorption peaks in the region $400\text{--}500\text{ cm}^{-1}$, and OH peaks at 1620 cm^{-1} and at $3300\text{--}3400\text{ cm}^{-1}$ (Potter and Rossman, 1979).

The constancy in the IR spectrum irrespective of quite gross changes in chemical composition is shown by the spectra in fig. 2, which represent normal zincian and nickeliferous chalcophanite. Electron probe microanalyses (EPMA) on 30 areas

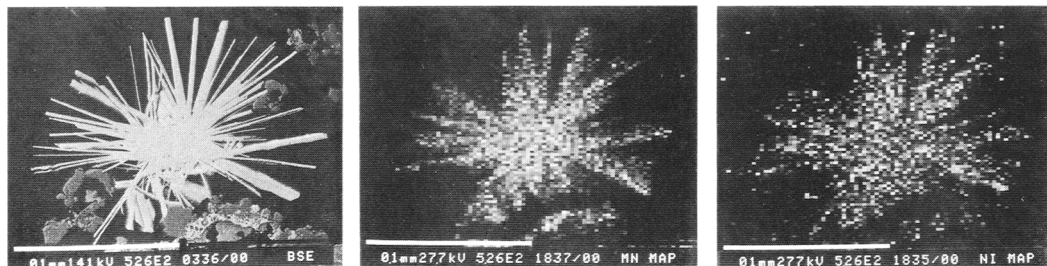


FIG. 1. Back-scattered electron (BSE) image of Kambalda chalcophanite, and X-ray scans for Mn and Ni.

of chalcophanite are listed in Table I. All analyses are fully ZAF corrected; the water content is by difference.

Discussion. The data presented in Table I indicate that the simple formula $ZnMn_3O_7 \cdot 3H_2O$, often given for chalcophanite, can no longer be considered valid. While they are not sufficient to allow the derivation of a more appropriate formula, for reasons given above, they suggest that certain aspects of chalcophanite mineralogy need further consideration.

First, the EPMA analyses, though carried out on grains are areas of optically homogeneous chalcophanite, often show amounts of Al and/or Si. This feature was previously noted by Potter and Rossman (1979) and by Radtke *et al.* (1967). Both groups of researchers accepted that these elements were chemical components of the chalcophanite, not extraneous silicate contamination.

In the specimens investigated the chalcophanite crystals were often associated with clays and quartz, as indicated by the FTIR spectra and by XRD. Nevertheless, the areas analysed by EPMA, with spot size of the order of 1–3 μm , were typically (100

sections, of width 20–50 μm . Basal sections, which could have contained clays, etc. in cleavage planes less than 3 μm beneath the polished surface were rarely analysed.

In an attempt to resolve this matter the writer examined powder from the polished sections by transmission electron microscopy, and carried out semi-quantitative analysis using an X-ray energy dispersive spectrometer attached to the microscope. Under these circumstances the area analysed is larger than the dispersed mineral particle, and the data analysis used (Cliff and Lorimer, 1975) does not take into account water content. None the less no discrete particles of clay (Al+Si) or quartz (Si) were identified by the analyses, but these elements appeared to be only associated with the manganese oxides. Results on ten areas of chalcophanite from the Norseman district are listed in Table II. (The actual results of the data analysis procedure have been multiplied by 0.87 on the assumption that chalcophanite contains 13% H_2O , to make them more directly comparable with the analyses of Table I.)

These results indicate that the aluminium and

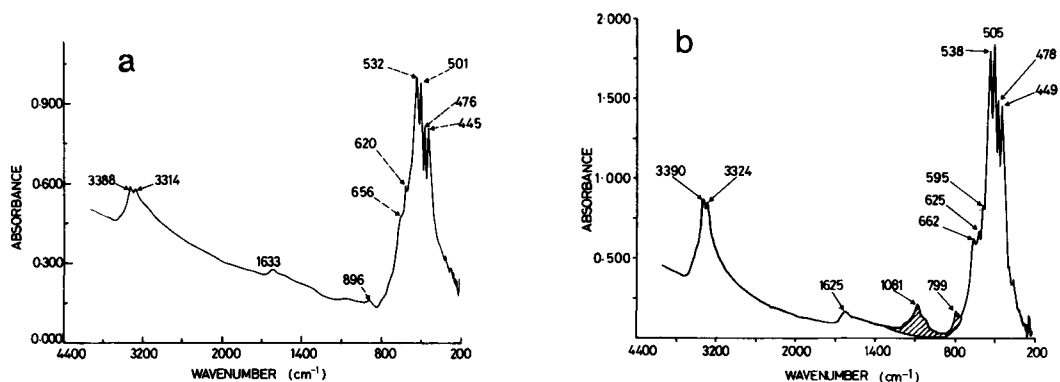


FIG. 2. Infra-red (IR) spectra of normal zincian chalcophanite (Sterling Hill) (a) and nickeliferous chalcophanite (Kambalda) (b). The shaded area represents quartz.

TABLE I. ELECTRON PROBE MICROANALYSES OF CHALCOPHANITE (WT %)

No.	MnO ₂	Fe ₂ O ₃	ZnO	NiO	CuO	CoO	CaO	MgO	K ₂ O	BaO	Al ₂ O ₃	SiO ₂	H ₂ O ^a
1	65.3	0.1	21.6	nd	nd	nd	nd	nd	nd	nd	nd	nd	13.0
2	64.7	0.2	21.2	nd	0.1	nd	0.1	0.5	0.1	0.3	0.3	0.1	12.4
3	63.9	0.3	22.1	nd	0.2	0.2	0.3	nd	nd	nd	nd	nd	13.0
4	62.3	nd	20.1	nd	nd	nd	nd	nd	nd	nd	nd	0.4	17.2
5	64.2	nd	21.3	nd	nd	nd	0.2	0.2	0.3	nd	nd	nd	13.8
6	63.8	nd	22.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	14.1
7	65.2	0.1	21.8	nd	nd	nd	nd	nd	nd	nd	nd	nd	12.9
8	64.3	0.3	22.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	13.3
9	69.7	0.4	15.6	0.1	nd	0.1	nd	nd	0.7	0.6	0.1	0.1	12.6
10	69.5	0.7	14.6	nd	nd	0.2	nd	nd	0.4	0.1	0.1	0.1	14.3
11	72.8	0.8	9.4	nd	0.2	nd	nd	nd	nd	0.1	0.4	nd	16.3
12	71.2	1.2	12.6	nd	nd	nd	nd	nd	0.1	nd	nd	0.1	14.8
13	73.7	0.3	10.7	nd	nd	nd	nd	nd	nd	nd	0.1	nd	15.2
14	72.2	0.8	13.4	nd	nd	nd	nd	nd	nd	nd	0.2	nd	13.4
15	68.9	0.3	11.3	0.2	nd	nd	nd	nd	0.1	0.6	3.6	0.7	14.3
16	67.4	1.2	8.4	1.3	0.2	0.4	0.8	1.2	0.3	1.6	1.7	3.3	12.6
17	56.5	2.3	14.2	0.1	nd	0.1	1.2	0.4	1.2	1.3	4.3	4.2	14.2
18	74.3	0.1	9.6	nd	nd	nd	nd	nd	0.4	0.8	0.7	0.8	13.3
19	63.4	0.7	15.4	nd	nd	nd	0.7	nd	0.2	nd	nd	3.2	15.4
20	65.2	0.3	18.7	nd	nd	nd	0.3	1.2	0.7	nd	nd	0.7	12.9
21	64.1	0.2	22.3	nd	0.1	nd	nd	1.4	nd	nd	0.4	1.1	10.3
22	64.8	1.1	18.8	nd	nd	nd	nd	nd	nd	nd	nd	0.2	15.1
23	63.5	nd	nd	17.6	nd	nd	nd	0.9	nd	nd	nd	nd	18.0
24	64.3	nd	nd	17.8	nd	nd	nd	1.2	nd	nd	nd	nd	16.7
25	64.8	nd	nd	15.2	nd	nd	nd	3.1	nd	nd	nd	nd	16.9
26	64.2	nd	nd	15.9	nd	nd	nd	2.4	nd	nd	nd	nd	17.5
27	68.2	nd	nd	14.9	nd	nd	nd	2.7	nd	nd	nd	nd	14.2
28	66.5	nd	nd	19.0	nd	nd	nd	0.9	nd	nd	nd	nd	13.6
29	60.9	0.4	17.5	0.4	0.3	nd	nd	nd	nd	nd	3.6	2.7	14.2
30	67.4	0.3	4.2	0.3	1.2	nd	nd	nd	nd	nd	4.7	8.6	13.3

Analyses 1 - 8, Sterling Hill, New Jersey; 9 - 14, Grootte Eylandt; 15 - 18, Norseman, Western Australia; 19 - 22 Buchan, Victoria; 23 - 28, Kambalda, Western Australia; 29 - 30, Lake Macquarie, New South Wales.

nd = not detected by EPMA

* by difference

TABLE II. Semi-quantitative X-ray energy dispersive analyses of chalcophanite.

	1	2	3	4	5	6	7	8	9	10
MnO ₂	61.9	67.0	63.6	79.1	75.5	72.7	66.6	67.4	67.1	65.5
Fe ₂ O ₃	1.2	0.5	0.4	1.6	0.2	n.d.	n.d.	1.2	0.9	n.d.
ZnO	20.2	18.4	19.2	5.5	6.2	12.6	18.4	15.2	17.6	20.3
Al ₂ O ₃	1.4	0.3	2.4	n.d.	2.7	0.4	1.6	2.0	n.d.	1.2
SiO ₂	2.3	0.8	1.4	0.8	2.4	1.3	0.4	1.2	1.4	n.d.

Normalized results corrected by the method of Cliff and Lorimer (1975) and multiplied by 0.87 on the assumption of 13% combined water content.

n.d. = not detected.

silica reported in analyses of chalcophanite are probably not clay and quartz contaminants.

Secondly, the analyses cast doubt on the explanation that chemical variations in the mineral are the result of isomorphous substitution (Frenzel, 1980). In view of the fact that the zinc-containing chalcophanite was the first variety to be discovered, and

because this was the structure investigated by Wadsley, there is a natural tendency to assume that the later discovered varieties (zinc-deficient, argentiferous, magnesian and nickeliferous) are the results of isomorphous replacement of either Mn⁴⁺, Mn²⁺, or Zn²⁺ ions. Certainly replacement of Zn²⁺ by Ni²⁺, Mg²⁺, or Mn²⁺ is in accord with

accepted ideas on isomorphous replacement. How Ag^+ (radius 1.26 Å) could replace Zn^{2+} (radius 0.74 Å) and the location of such elements as Cu, Pb, K, Ba, and Ca in the structure, if these are simply replacements, is not obvious. Also, if Al and Si are actually constituents of chalcophanite, even at low concentration, it is difficult to see how these elements could be isomorphous replacements of the above elements.

Thirdly, Table I, analyses 11–14, 18 suggest that deficiencies in Zn may be made up by replacement by Mn^{2+} , as the Zn-deficient analyses show 6–8% more manganese oxide than 'normal' chalcophanite analyses. If this is so, it is interesting to speculate whether a purely manganese variety of chalcophanite could exist. Some evidence for such compositions is given by analyses 4 and 5, Table II, which show Zn/Mn of < 0.1.

Thus, analyses of chalcophanite cause difficulties in terms of Al and Si content; in the mechanism of isomorphous replacement of certain elements in the layer-lattice and in relation to minimum levels of non-manganese elements in the manganese oxide structure.

A possible explanation for the above is that chalcophanite may not be a single structure mineral in the currently accepted sense but a hybrid composed of irregular mixed layers of a well-defined tetravalent manganese oxide layer lattice with 7.1 Å basal reflection, and one or more series of 'islands' of other structures. Such a concept has been investigated in depth by Soviet researchers, especially in the case of terrestrial Co–Ni asbolane (Chukhrov *et al.*, 1982). The possibility that Co–Ni-containing lithiophorite is structurally similar has been discussed by the writer (Ostwald, 1984a). The existence of even more complex mixed-layer hybrids in marine manganese nodules has been deduced by Chukhrov *et al.* (1983). In these, chalcophanite-like structures are a prominent feature.

Additional evidence in favour of this concept comes from the conclusion of the writer (Ostwald, 1981) that chalcophanite may result from the topotactic metasomatism of kaolinite by manganese ions. Incomplete replacement could result in the occurrence of relicts of Al–Si lattice coherently intergrown with the host manganese oxide. Such relict would not be gangue inclusions, but actual components of a hybrid mineral.

The existence of such a hybrid structure in

chalcophanite would explain the constant X-ray diffraction and IR characteristics of the mineral (derived from a well defined 7 Å manganese oxide layer structure) and also its variable chemistry (irregularly distributed structural 'islands' of variable chemistry and of limited extent which would not produce X-ray maxima). Such a mineral could contain Al, Si, Ag, etc. as specific lattices not as individual atomic replacements. High resolution transmission electron microscopy (HRTEM) and select area electron diffraction (SAED) studies may hold the key to elucidating currently unsuspected complexity in the common manganese oxide minerals.

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