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A low-zinc chalcophanite from Norseman, Western Australia

DURING a recent investigation of Australian specimens of manganese oxide desert varnish the writer noted a specimen of chalcophanite which was deficient in zinc when compared with other specimens previously analysed. This note briefly describes the specimen and discusses its significance.

The specimen consisted of a black encrustation on lateritic clay coating a weathered basic rock, from the gold mining centre of Norseman, Western Australia. An examination of the crust by scanning electron microscopy revealed a mass of randomly arranged hexagonal crystallites, not unlike those of well-crystallized kaolinite. X-ray energy dispersive
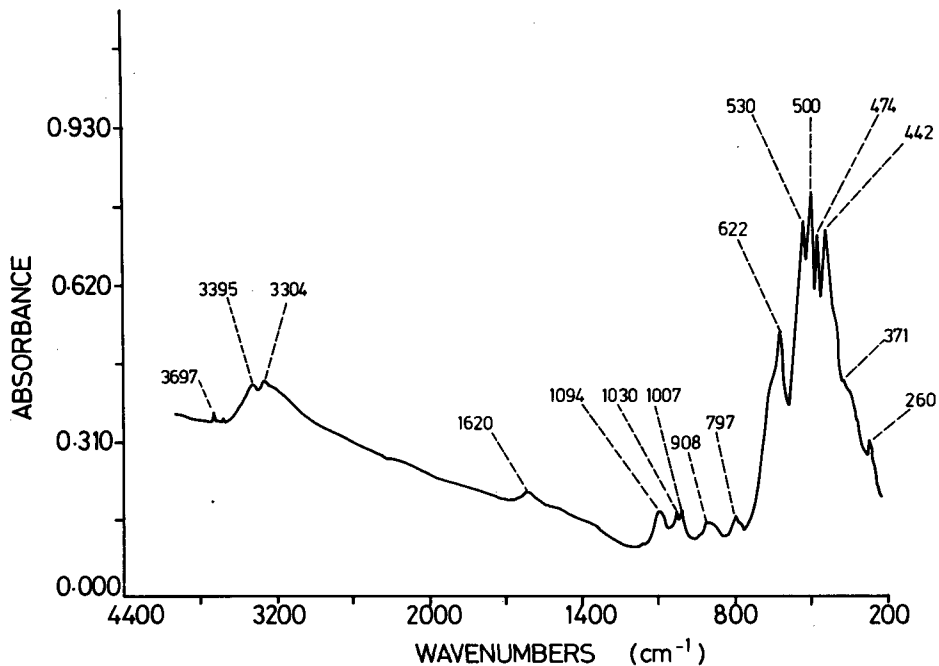

FIG. 1. Infra-red spectrum of chalcophanite and kaolinite from Norseman, Western Australia.

spectroscopy showed that the crystallites contained both Mn and Zn, with traces of Fe, suggesting chalcophanite. This identification was confirmed by mineragraphy, X-ray diffraction, infra-red spectroscopy and electron probe microanalysis.

Mineragraphic examination showed the specimen consisted of densely packed, flattened prismatic crystallites up to 1.0 mm in width, showing the typical strong bireflection and anisotropism. Reddish internal reflections are common.

X-ray diffraction of a powder sample extracted from the polished block showed the following lines: 6.94(100), 4.11(50), 3.45(60), 2.55(50), 2.24(50), 1.88(40), 1.62(40), 1.45 Å (30) which are essentially those of chalcophanite (JCPDS No. 15-807).

The infra-red spectrum of the chalcophanite is shown in fig. 1. This shows the four prominent peaks in the region 400–500 cm^{-1} reported by Potter and Rossman (1979a). The infra-red spectrum in fig. 1 shows the presence of kaolinite (lines at 3697, 1094, 1030, 1007, 908). The chalcophanite lines may be classed as 3395, 3304 (OH-valency vibrations), 1620 (OH-deformation), 797, 622, 530, 500 (Metal-O, (OH)-valency vibrations), 474, 442 (by comparison with data of Frenzel (1980)).

TABLE I. *Chemical analyses of chalcophanite (wt. %)*

	1	2	3	4	5
MnO_2	70.4	72.4	68.3	65.39	59.94
MnO	—	—	—	0.22	6.58
ZnO	9.6	13.4	18.2	18.19	21.7
Al_2O_3	0.4	0.1	—	0.39	—
SiO_2	1.2	0.1	—	1.88	—
Fe_2O_3	0.3	0.2	0.2	0.32	0.25
H_2O^+	18.1	13.8	13.3	13.09	11.58

1. Norseman, Western Australia.
2. Groote Eylandt.
3. Sunny Corner, New South Wales.
4. Buchan, Victoria (Wadsley, 1950).
5. Data from Palache *et al.* (1944).
Analyses 1, 2, 3 by EPMA; 4 and 5 by wet chemistry.

Electron probe microanalyses of the Norseman chalcophanite are listed in Table I, together with analyses of chalcophanite from Groote Eylandt (Ostwald, 1981) and for Sunny Corner, New South Wales, and analyses taken from Wadsley (1950) and Palache *et al.* (1944). These data show that the Norseman chalcophanite is notably deficient in Zn. Low Zn varieties of chalcophanite have been previously noted by Radtke *et al.* (1967) but these writers presented no analyses. The chalcophanite structure was originally described by Wadsley (1955) as a stacking of layers of edge-shared [MnO_6] octahedra and sheets of water molecules between which Zn^{2+} ions were located. The sequence normal to the c axis is -O-Mn-O-Zn-H_2O-Zn-O-Mn-O-, with the distance between successive manganese-oxygen octahedra of 7.16 Å. Wadsley (1955) gave the formula for the mineral as $ZnMn_3O_7 \cdot 3H_2O$ but this has been modified by later researches, and formulae such as $Zn_2Mn_6O_{12} \cdot 6H_2O$ (Burns and Burns, 1979) (Zn,Mn,Fe)$(Mn_{3-x}^{4+}Mn_x^{2+})O_7 \cdot 3H_2O$ (Frenzel, 1980) exist for normal chalcophanite. Two examples of more exotic compositions have also reported. These are the silver-containing chalcophanite (aurorite) of formula $(Ag_2,Ba,Ca,Pb,K_2,Cu,Mn^{2+})Mn_3O_7 \cdot 3H_2O$ (Radtke *et al.*, 1967) and $MgMn_3O_7 \cdot 3H_2O$ (Potter and Rossman, 1979b). This range of formulae suggests that chalcophanite may be highly variable in nature, not only in the nature and proportion of its cations but also in the structural water content.

The writer has suggested (Ostwald, 1981) the chalcophanite structure may represent a structurally guided replacement of kaolinite by manganese oxide. If this is the case, Zn may be less essential to the structure than considered previously. When the mineral develops during the weathering of manganese- and zinc-containing deposits, such as those of Franklin, New Jersey (Frenzel, 1980) Zn is a common constituent. Weathering of chemically complex manganese oxides in carbonates at the Aurora mine, Nevada (Radtke *et al.*, 1967) produced a chalcophanite structure containing a range of cations including Ag, Ba, Ca, Pb, K, and Cu, but no Zn. When, however, the mineral develops as a desert varnish or soil concretion, such elements may be in very low concentration or completely lacking, resulting in chalcophanites containing quite low levels of these cations, such as the Norseman chalcophanite, or chalcophanites containing none of these elements. These facts suggest that it is the manganese-oxygen layer-lattice with basal spacing of about 7.1 Å which constitutes the mineral chalcophanite, not the presence of inter-layer Zn ions.

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Hematite-pyrophanite intergrowth in gondite, Chikla area, Sausar Group, India

PYROPHANITE ($MnTiO_3$, ilmenite-type structure; Lindsley, 1981) has been reported as a minor constituent of some metamorphosed manganese deposits (Lee, 1955; Zak, 1971; Sivaprakash, 1980) and exsolution lamellae of pyrophanite in jacobsite (Sivaprakash, 1980) and in magnetite and franklinite (Ramdohr, 1980, pp. 922, 997) have been described. But there is, as yet, no record of crystallographically oriented intergrowth of pyrophanite and hematite. This paper presents data on the textural relationship and chemistry of pyrophanite and hematite forming such intergrowths in gondites of Chikla area (Maharashtra State, India) in the Precambrian Sausar Group.

The gondites are manganese silicate–oxide rocks produced by metamorphism of manganiferous noncalcareous sediments (Roy, 1966, 1981). This rock occurs in India mainly in the Precambrian Sausar Group. In the Chikla area, the gondites have been metamorphosed to staurolite–kyanite grade as determined from the enclosing co-metamorphosed pelites (Mitra, 1965; Roy, 1966). These consist of spessartine, quartz, rhodonite, braunite, jacobsite, hematite, tirodite, apatite, K-feldspar, and minor pyrophanite. The gondites are interbanded with metamorphosed ferromanganese ores containing braunite, hollandite, hematite, bixbyite/jacobsite and hausmannite and both have identical thermodeformational history (Roy, 1966). Hematite mainly occurs as minute specks in the oxide ores but in gondite it forms coarse sub-idioblastic grains. The hematite grains in gondite often contain tiny blebs and spindles of pyrophanite arranged along the (0001) plane of the host (fig. 1). Occasionally, however, pyrophanite occurs

as sub-equant grains, but in such cases also it is always confined to the grain limits of hematite.

The chemical composition of coexisting hematite and pyrophanite was determined by Electron Probe Microanalyzer JEOL/JXA-5A model at the Geology Department, Kyushu University, Japan. Carbon-coated surfaces were analysed with accelerating voltage of 15 kV, specimen current of 0.020 μA and 1 to 2 μ electron beam diameter. The standards used were natural MnO and synthetic $CaSiO_3$, Fe_2O_3, Al_2O_3, and TiO_2. For matrix correction the Bence and Albee (1968) method was adopted. Beam drifting was checked at regular
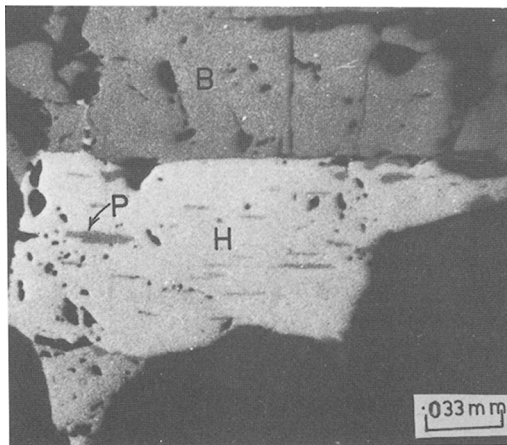

FIG. 1. Blebs and spindles of pyrophanite (P) oriented along the (0001) plane of hematite (H). Associated phases: braunite (B), spessartine and quartz (black).