native mercury, one has to postulate the release of mercury from some Hg-rich pre-existing phase(s), for example by some thermal effect. It should be stressed here that, although being very spectacular, the occurrence of Ag–Hg minerals in druses and cavities in the upper parts of the mine is only of minor importance for the total balance of mercury involved in the Sala deposit. The majority of Hg is connected with massive Zn–Pb ores; Tegengren (1924) noted in Zn concentrates a minimum of 100 g mercury per ton and 150–200 g silver per ton. These values can be explained by the occurrence of minute exsolution-like inclusions of amalgam in sphalerite (Fig. 3).

The release of Hg from sphalerite and from a pre-existing amalgam phase of unknown composition produced on the one hand Hg-rich phases as native mercury and moschellandsbergite, and on the other hand Ag-rich phases as native silver and mercurian silver. Theoretically this process could have lead to the formation of paraschachnerite among the Hg-rich phases. In Sala, however, textural evidence (porous appearance and relics of paraschachnerite inside the aggregates) suggests its origin by demercuration directly from moschellandsbergite, or through schachnerite as an intermediate stage. Further demercuration of paraschachnerite resulted in the formation of Hg-rich amalgam.

Acknowledgements. The sample containing the Sala amalgam phases was kindly put at our disposal by Dr B. Lindqvist of the Swedish Natural History Museum at Stockholm. The authors are greatly indebted to Dr C. Kieft for electron microprobe analyses, and for informations about his work on phases in the Ag–Hg–Sb system at Sala. X-ray powder diffraction patterns were made by Mr W. H. Drucker at the Geological Institute of the University of Amsterdam. Facilities for electron-microprobe analyses were provided by the Free University (Amsterdam) and by WACOM, a working group for analytical geochemistry subsidized by The Netherlands Organization for the Advancement of Pure Research (ZWO).

References

Atanasov, V. A. (1979) *Godishnik na Visshiya Minno-Geolozhki Institut Sofiya Svituk*, **26**, 119–29 [MA 84M/0822].

Nordström, Th. (1881) *Geol. Fören. Stockholm Förhandl.* **5**, 715.

Seeliger, E. and Mücke, A. (1972) *Neues Jahrb. Mineral. Abh.* **117**, 1–18.

Sjögren, Hj. (1900) *Geol. Fören. Stockholm Förhandl.* **22**, 187–90.

——(1910) Ibid. **32**, 1363–96.

Tegengren, F. R. (1924) *Sver. Geol. Unders.* Ser. Ca **17**.

[*Manuscript received 4 July 1986;*
revised 25 July 1986]

KEYWORDS: schachnerite, paraschachnerite, amalgam, system Ag–Hg, Sala, Sweden.

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MINERALOGICAL MAGAZINE, JUNE 1987, VOL. 51, PP. 321–5

Chemical variation in a single crystal of chalcophanite

THE non-stoichiometry of chalcophanite was first recognized by Wadsley (1964), who considered it to be $Zn_{1+x}Mn_3O_7.3H_2O, 0 < x < 0.25$. Since then a number of authors (Radtke *et al.*, 1967; Potter and Rossman, 1979; Ostwald, 1985) have shown that the mineral possesses an extremely wide variation in chemical composition associated with a constant X-ray diffraction pattern (JCPDS 15-807). In fact Radtke *et al.* (1967) suggested that the formula of chalcophanite was $(R)\ R_3^1O_7.3H_2O$, where R is commonly Zn but may be Mn^{2+}, Ag, Ba, Ca, Mg and R^1 is Mn^{4+}, Fe^{3+}. Recently a nickel chalcophanite has been recorded (Elias *et al.*, 1981) thus further expanding this list of elements.

Although the writer has not been able to examine specimens of all recorded chemical compositions of this mineral, those examined, including high- and low-Zn chalcophanite, nickel chalcophanite, and manganese-enriched chalcophanite (Ostwald, 1985) have remarkably similar determinative properties (optical properties, reflectivity, microhardness, X-ray '*d*' spacings, infra-red spectra, etc.) which suggests that these properties are a function of the basic 7 Å layer lattice and are little influenced by the widely variable chemistry.

Chalcophanite was first described by Moore (1875). It is interesting to speculate how recent knowledge of chemical variation in this apparently discrete mineral would have influenced the early 19th-century dispute between Proust and Berthollet, the former defending the concept of constant composition of compounds while the latter considered that many natural minerals showed widely varying composition. Proust won the argument and we now accept that minerals are essentially daltonides. In spite of the common acceptance of naturally-occurring minerals as daltonides (stoichiometric compounds), Berthollet's concept of variable composition minerals was not completely forgotten. Research in the last four decades, especially in Europe, has shown that non-stoichiometry (berthollide structure) exists in synthetic borides, hydrides, carbides, sulphides and oxides, and may be significant in a range of natural minerals (Wadsley, 1964).

The non-stoichiometric mineral which is the subject of this paper was determined by Wadsley (1955) to be a layer structure, consisting of a stacking of layers of edge-shared $[MnO_6]$ octahedra, with internal sheets of H_2O molecules and Zn^{2+} ions, in the pattern

$$\text{-O-Mn-O-Zn-}H_2O\text{-Zn-O-Mn-O-}$$

Wadsley deduced that the H_2O molecules are grouped in open double hexagonal rings, while vacancies exist in the layers of octahedra, so that 1 in every 7 octahedral sites contained no Mn ion. Zn^{2+} ions occur above and below these vacancies. Each Zn^{2+} ion completed its coordination with three H_2O molecules in the water sheet to form an irregular six-coordination polyhedron.

The present study on chalcophanite derived from an attempt to further investigate the nature of the chemical variability and non-stoichiometry in this mineral, choosing crystals of zinc-chalcophanite from G Quarry, Groote Eylandt manganese ore deposit, for simplicity.

Serial sectioning of chalcophanite. During studies on chalcophanite chemistry (Ostwald, 1985) the writer noted on a number of occasions the existence of an alteration phenomenon in chalcophanite which (1) appeared to develop along the basal plane direction (2) involved a generally higher white light reflectivity than the host mineral and (3) much lower anistropism. Electron probe microanalysis (EPMA) showed generally similar elemental components to the host, but significantly lower totals. However, the latter was not regarded as an artifact resulting from the less-compact nature of the brighter material and resultant epoxy resin infilling during specimen preparation. The phenomena noted may be the same as quoted by Frenzel (1980) as occurring in chalcophanite from the Donaria Mine, Tunisia.

These observations suggested a study of optically homogeneous chalcophanite to determine if chemical variability might exist on the micro-scale in samples from a single locality, a fact apparently not previously documented.

The technique of serial sectioning and investigation used in this study was developed by Lusk and Ostwald (1983) for the study of the transformations of pyrrhotite grain morphologies in metamorphosed nickel sulphide ores. In these sulphide studies, 24 serial sections were produced on a single specimen by successive grinding and polishing, with the depth difference between sections being 0.02 mm. On each section 500–600 measurements were carried out including microanalyses and X-ray diffraction (from powder scrapings from the surface). The present study was much simpler, because it was conducted on a single crystal. It involved 4 serial sections approximately 50 μm in thickness and 40–50 electron probe microanalyses on each section, together with a number of infrared analyses and analytical electron microscope analyses. Since the usual microvolume sampled by EPMA is of the order of $1.5 \times 1.5 \times 1.5$ μm^3 this preliminary investigation was by no means very detailed. Nonetheless, serial sectioning is time consuming and the writer examined a number of chalcophanite occurrences before deciding on a particular crystallized surface encrustation from the Groote Eylandt area. An electron probe microanalysis of the chalcophanite (obtained by averaging six fully ZAF corrected analyses on a single random section) was 67.1% MnO_2, 16.6% ZnO, 0.2% Fe_2O_3, 0.4% Al_2O_3, 0.5% SiO_2, H_2O (by difference) 15.2%. A series of twenty analyses (fully ZAF corrected) on crystals from this locality indicated that the Zn/Mn (wt.%) ratio ranged from 0.2–0.4. As indicated below the analysis is not charac-

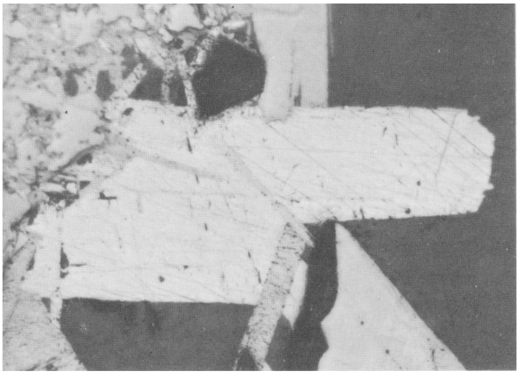

FIG. 1. Single crystal of chalcophanite used for the serial sectioning study. Maximum dimension of the crystal is 60 μm.

teristic of the whole crystal. A value on the basis of Sterling Hill material (Palache *et al.*, 1944) is 0.4.

Within the polished specimen a single crystal was chosen for detailed study (Fig. 1). Because of the weak anisotropism of this crystal section, and the presence of broadly-spaced cleavage traces, the serial sections appear to be inclined at a low angle to (0001).

The sampling grid shown in the sketch (Fig. 2) indicates the individual areas of the crystal where microanalyses (EPMA) were carried out. After each group of EPMA determinations were completed the crystal surface was scoured with a steel point and powder collected for infra-red analysis and analytical electron microscopy before re-polishing. While the analytical electron microscopy was not conducted on material *in situ* it did however sample particles of sub-micron size, i.e. producing information on chemical composition variations on a much finer scale than the serial sections and EPMA.

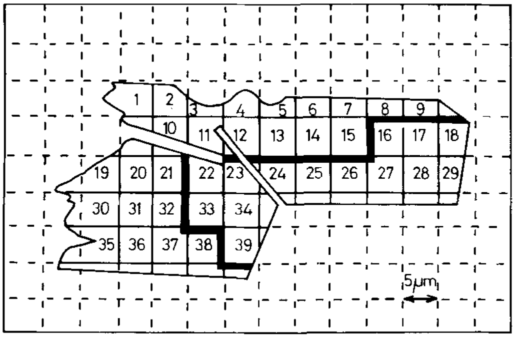

FIG. 2. Schematic showing the areas analysed in each section. The dark line indicates the border of the two compositions in Section C.

Results. Electron probe determined quantitative weight percentage ratios Zn/Mn for the microvolumes defined by the grid pattern in each of four serial sections A, B, C and D (Fig. 3) are listed in Table 1. Analytical totals for all the analyses were in the range 84–87%, indicating generally constant combined water contents. The variation in the Zn/Mn weight ratio thus indicates that the Zn and the Mn content of each analysis is variable. An examination of these values indicates that the ratio Zn/Mn is not random within the volume. In fact Zn/Mn values less than 0.2 definitely concentrate in an area of serial section C, while most of the remaining ratios are more than 0.2.

The presence of lower Zn/Mn in an area of section C with higher Zn/Mn in enclosing serial sections B and D indicates the presence of a 'sheet' of chalcophanite with Zn/Mn < 0.2 enclosed in a matrix of chalcophanite of Zn/Mn = 0.4. The thickness of this sheet is certainly less than 50 μm, but its precise dimensions are unknown. Although electron probe determinations do not allow determination of element valency states the data in Table 1 suggest that the manganese oxides contains both Mn^{4+} and Mn^{2+}, with variable amounts of Zn replacement of the Mn^{2+}, as suggested by Radtke *et al.* (1967).

TABLE 1.

Weight percentage ratio Zn/Mn for points in four serial sections (A B C D) of chalcophanite.

SECTION A

1	0.34	11	0.34	21	0.41	31	0.37
2	0.35	12	0.36	22	0.40	32	0.36
3	0.36	13	0.37	23	0.41	33	0.38
4	0.41	14	0.33	24	0.39	34	0.44
5	0.37	15	0.41	25	0.37	35	0.42
6	0.38	16	0.42	26	0.38	36	0.42
7	0.39	17	0.40	27	0.39	37	0.39
8	0.35	18	0.39	28	0.39	38	0.36
9	0.33	19	0.38	29	0.40	39	0.37
10	0.32	20	0.40	30	0.38	–	–

SECTION B

1	0.28	11	0.38	21	0.40	31	0.40
2	0.36	12	0.44	22	0.40	32	0.40
3	0.37	13	0.41	23	0.40	33	0.40
4	0.41	14	0.40	24	0.40	34	0.38
5	0.38	15	0.41	25	0.39	35	0.38
6	0.34	16	0.40	26	0.37	36	0.40
7	0.36	17	0.38	27	0.36	37	0.41
8	0.37	18	0.36	28	0.40	38	0.38
9	0.33	19	0.37	29	0.40	39	0.36
10	0.32	20	0.40	30	0.37	–	–

SECTION C

1	0.33	11	0.40	21	0.28	31	0.36
2	0.38	12	0.38	22	0.22	32	0.38
3	0.37	13	0.37	23	0.20	33	0.17
4	0.36	14	0.38	24	0.19	34	0.16
5	0.41	15	0.36	25	0.15	35	0.36
6	0.42	16	0.18	26	0.16	36	0.38
7	0.33	17	0.21	27	0.20	37	0.41
8	0.37	18	0.17	28	0.21	38	0.41
9	0.38	19	0.38	29	0.18	39	0.19
10	0.36	20	0.40	30	0.40	–	–

SECTION D

1	0.32	11	0.37	21	0.34	31	0.36
2	0.33	12	0.36	22	0.32	32	0.37
3	0.38	13	0.34	23	0.33	33	0.38
4	0.41	14	0.38	24	0.41	34	0.33
5	0.44	15	0.44	25	0.33	35	0.39
6	0.33	16	0.41	26	0.37	36	0.44
7	0.37	17	0.37	27	0.36	37	0.40
8	0.38	18	0.38	28	0.31	38	0.41
9	0.39	19	0.34	29	0.33	39	0.42
10	0.38	20	0.41	30	0.34	–	–

Fourier transform infra-red (FTIR) spectra were measured using powder scrapings from each section A, B, C and D. The FTIR spectrum of chalcophanite is very distinctive (among the manganese oxide minerals) because of the presence of four sharp peaks in the region 400–500 cm^{-1} (Potter and Rossman, 1979; Ostwald, 1985). All four spectra could be readily identified. There were some suggestions on the basis of the technique that layer

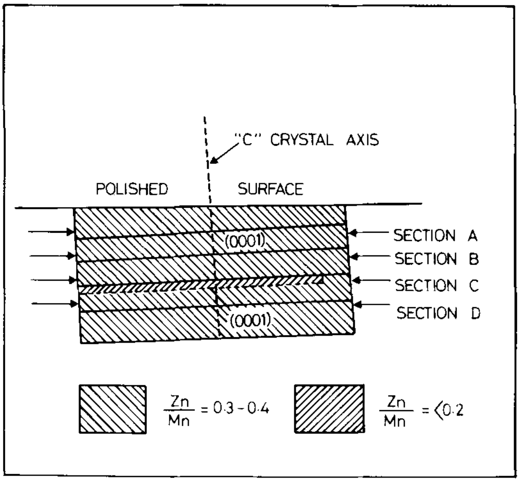

FIG. 3. Schematic showing a section through the smaller dimension of the crystal, indicating possible relationship between the two chemical compositions of chalcophanite and crystal orientation.

TABLE 2. Major Infra-red Peak Positions in Serial Sections A, B, C and D.

Section	Wavenumber (cm^{-1})			
A	442	474	502	530
B	442	476	500	532
C	446	478	505	548
D	445	472	503	534

C was structurally distinct from layers A, B and D. Since the technique of obtaining the sample for FTIR involved scouring the surface after measurement and before re-grinding, the spectrum of section C was based on abundant Zn/Mn < 0.2 material. The evidence for this is seen in Table 2, where IR peak positions for the four major peaks are listed. The highest wave number peak for section C (at 548 cm^{-1}) deviates from the position of equivalent peaks in A, B and D, while the lower peaks are comparable.

Analytical electron microscopy, using X-ray energy spectroscopy, was carried out on dispersions of material essentially equivalent to that studied by FTIR. Counting data were analysed by the method of Cliff and Lorimer (1975) which does not take into account combined water content. Nonetheless the semi-quantitative data presented in Table 3 indicates quite significant variation in Zn/Mn, with 3 of 20 grains analysed being simple manganese oxide, with Zn/Mn of < 0.01.

These grains without zinc also appeared to be too disordered to give an electron diffraction pattern, in contrast to the zinc-containing chalcophanite which readily produces select area electron diffraction (SAED) patterns.

Discussion. The data presented in the previous section indicates that a single crystal of chalcophanite contains material with a number of chemical compositions—a fact which is contrary to the common definition of a mineral (Berry and Mason, 1959) i.e. a naturally occurring homogeneous solid, inorganically formed with a definite chemical com-

Table 3 Semi-quantitative X-ray energy dispersive analysis* of grains from the low-zinc layer

A. Analyses showing appreciable Zn

	1	2	3	4	5	6	7	8	9	10
MnO_2	85	87	84	80	82	90	83	86	91	86
ZnO	15	13	16	20	18	10	17	14	9	14

B. Analyses with low to zero Zn

	11	12	13	14	15	16	17	18	19	20
MnO_2	98	95	96	97	98	99	100	100	100	98
ZnO	2	5	4	3	2	1	<1	<1	<1	2

* Analyses normalised to 100%.

position and an ordered atomic arrangement. The chalcophanite crystal studied appears to be based on an atomic arrangement sufficiently constant as to produce a recognizable single crystal but the chemical composition is quite variable within the crystal. A possible explanation is that the variation in Zn to Mn stoichiometry is due to some type of metastable growth zoning, as seen in silicates and sulphides, where it results from non-equilibrium growth from melts. In this case, of course, growth was from solution. Wadsley (1964) recognized that chalcophanite showed a definite composition range, and on the basis of the specimens he had studied defined this as $Zn_{1+x}Mn_3O_7 . 3H_2O (0 < x < 0.25)$. He also suggested that wider variations in stoichiometry were theoretically possible. In fact he considered chalcophanite to be an interpolated type of berthollide, in which extra Zn ions were able to be trapped in suitable sites in a basic Mn : Zn = 3 : 1 structure. While such extra Zn ions were restricted to definite sheets in the layer structure Wadsley did not consider that they were especially ordered.

During the decades since Wadsley's studies the possible compositional range in chalcophanite has been enlarged, and the case for berthollide structure strengthened, but the relationship between composition and structure is still obscure. Certainly chemical variation does not greatly influence either X-ray diffraction or infra-red spectra, suggesting that certain structural features of the layer-lattice are not much influenced by the introduction of elements such as Ag, Mg, Ca, Ba, Ni, etc. (Ostwald, 1985).

Chalcophanite is structurally related to the layer-lattice minerals lithiophorite and birnessite, the group termed phyllomanganates by Giovanoli (1985). While most natural occurrences of phyllomanganates are sufficiently constant in composition or in crystal structural characteristics as to be easily identifiable, detailed studies indicate that non-stoichiometry is commonly present. Non-stoichiometry in birnessite and its effect on X-ray diffraction patterns has been researched by Giovanoli (1980) and Perseil and Giovanoli (1983) and that of synthetic lithiophorite by the same author (Giovanoli, 1985). Chalcophanite non-stoichiometry was first recognized by Wadsley (1955) and further investigated in the present paper. These studies therefore suggest that the phyllomanganate minerals as a class may be better considered as berthollides than as daltonides.

References

Berry, L. G. and Mason, B. (1959) *Mineralogy, Concepts, Descriptions and Determinations*, Freeman and Co., 630 pp.

Cliff, G. and Lorimer, G. W. (1975) *J. Microscopy* **103,** 202–4.

Elias, M., Donaldson, M. J., and Giorgetta, N. (1981) *Econ. Geol.* **76,** 1775–83.

Frenzel, G. G. (1980) In *Geology and Geochemistry of Manganese* (I. M. Varentson and G. Gresselly, eds.) 25–158 Stuttgart.

Giovanoli, R. (1980) *Mineral. Deposita* **15,** 251–3.

——(1985) *Chem. Erde*, **44,** 227–44.

Lusk, J. and Ostwald, J. (1983) *Can. J. Earth. Sci.* **20,** 113–19.

Moore, G. E. (1875) *Am. Chem.* **6,** 1–2.

Ostwald, J. (1985) *Mineral Mag.* **49,** 752–5.

Palache, C., Berman, H., and Frondel, C. (1944) *The System of Mineralogy of J. D. Dana and E. S. Dana*, Vol. 1. John Wiley and Son, 834 pp.

Perseil, E. A. and Giovanoli, R. (1983) *Bull. Mus. Nat. Hist. Paris*, Ser. 5, Section C, No. 2, 163–90.

Potter, R. M. and Rossman, G. R. (1979) *Am. Mineral.* **64,** 1227–9.

Radtke, A. S., Taylor, C. M. and Hewett, D. R. (1967) *Econ. Geol.* **62,** 186–206.

Wadsley, A. D. (1955) *Acta Crystallogr.* **8,** 165–72.

——(1964) In *Non-stoichiometric compounds* (Mandelcorn, L., ed.) Academic Press, 98–212.

[*Manuscript received 12 May 1986;
revised 8 July 1986*]

KEYWORDS: chalcophanite, non-stoichiometry, Groote Eylandt, Australia.

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