Electronprobe analyses of stannite and related tin minerals

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Summary. Quantitative electronprobe microanalyses have been made of stannite from various localities. It was found that in general this mineral corresponds in composition to the formula Cu_2FeSnS_4. However, noticeable deviations in the ratio of the metals can occur and considerable concentrations of zinc may be present.

Some tin minerals related to stannite have also been analysed, namely hexastannite, mawsonite, and an apparently hitherto unknown mineral to which the name *rhodostannite* is given.

Zusammenfassung. Quantitative Elektronenstrahl-Mikroanalysen von Zinnkiesen verschiedener Lagerstätten wurden durchgeführt. Es wurde festgestellt, daß sie in ihrer Zusammensetzung gewöhnlich gut der Formel Cu_2FeSnS_4 entsprechen. Es können jedoch merkliche Abweichungen im Verhältnis der Metallgehalte zueinander auftreten, insbesondere können beträchtliche Konzentrationen von Zink vorhanden sein.

Es wurden auch einige dem Zinnkies verwandte Zinnmineralien analysiert nämlich Hexastannit, Mawsonit und ein bisher unbekanntes Mineral, dem der Name *Rhodostannit* gegeben wird.

SINCE the systematic study by Ramdohr (1944) tin minerals related to stannite have received increased interest. Ramdohr recognized at least four different minerals which he called 'Zinnkies? I–IV'. Subsequently, Ramdohr (1960) gave the name hexastannite to 'Zinnkies? I' and suggested for it the formula $Cu_3Fe_2SnS_6$ and a hexagonal lattice structure of the wurtzite type. 'Zinnkies? II' is now known to be identical with the cubic phase isostannite studied by Claringbull and Hey (1955). Ramdohr's phases 'Zinnkies? III' and 'Zinnkies? IV' have so far only been recognized from Carguaicollo in Bolivia. 'Zinnkies? III' is said to be hexagonal and in appearance similar to hexastannite, whilst 'Zinnkies? IV' is cubic with a tetrahedrite lattice. Recently, Markham and Lawrence (1965) have described a tin mineral, mawsonite, with the formula $Cu_7Fe_2SnS_{10}$ and a structure related to that of renierite. It occurs together with hexastannite and is distinct from other stannous minerals previously noted.

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It is clear that this group of tin-bearing phases needs further investigation. In this context it also seems valuable to delimit the compositional range of stannite itself and to clarify its relation to these minerals. As in many cases they are present only in very small amounts the electron-probe microanalyser is ideally suited for their examination.

Experimental. A 'Cambridge Geoscan' microanalyser with a 75° X-ray take-off angle was used. The electron excitation energy was 20 keV for all elements. The characteristic radiations and standards employed were: for As, nickeline (56·1 % As); for Fe and S, pyrite; and for Cu, Sn, Zn, and Sb, the metals; the K_α radiation was used except for Sn and Sb, for which the L_α was used.

Corrections were calculated after a method described by Springer (1967) and are quoted in the Tables as the number added to the uncorrected result. The accuracy of the measurements is estimated at about ± 2 % of the measured value. The figures quoted in the tables are usually the average of measurements on several points within one polished section.

Results

Stannite. The analyses of stannite are listed in Table I. It can be seen that in half of the examples the formula corresponds closely to Cu_2FeSnS_4, which is usually quoted for this mineral. However, it is apparent that considerable amounts of zinc can be present substituting for iron. The other half of the analyses exhibit noticeable deviation from the ideal composition; the atomic ratio $Cu:(Fe+Zn):Sn$ is not always 2:1:1, but the metal:sulphur ratio remains 1:1. Unfortunately not enough material was available to establish whether a complete solid solution exists between pure Fe-bearing stannite and its pure Zn analogue kësterite though a substitution of Fe by Zn to as much as 20 % is documented by closely spaced measured values, and Lévy (1967) reports four analyses with substitutions between 18 and 32 %. On the other hand, that 32 % of the Zn in kësterite can be replaced by Fe is shown by analysis 6, Table I. No significant optical differences could be observed among these stannites. They are all clearly anisotropic so that no confusion with a cubic form of stannite has arisen. Also care has been taken not to analyse portions of crystals that contained exsolution bodies of blende or chalcopyrite. If a ZnS-particle had been included in the analysed volume the Zn concentration would be increased and the Cu and Sn contents would be simultaneously decreased. Similarly, if $CuFeS_2$ were present the amounts of Cu and Fe would be higher

and correspondingly that of Sn lower. It is evident that there is no such trend among the analyses of Table I.

TABLE I. Microprobe analyses of stannite and kësterite. The corrections range from $+1\cdot3$ to $+1\cdot5$ % in Cu, $+4\cdot4$ to $+4\cdot9$ % in Sn, $-1\cdot1$ to $-1\cdot3$ % in Fe, 0 to $+0\cdot1$ % in Zn, and $+1\cdot3$ to $+1\cdot5$ % in S, except for no. 6, for which they are $+0\cdot9$ % in Cu, $+4\cdot4$ % in Sn, $-0\cdot5$ % in Fe, $+0\cdot3$ % in Zn, and $+1\cdot8$ % in S.

	1	2	3	4	5	6*	7	8	9	10
Cu	29·5	29·2	29·2	29·2	29·3	28·9	28·7	31·0	31·2	29·7
Sn	27·6	27·9	28·1	27·7	27·8	25·5	27·2	26·1	25·7	26·1
Fe	11·1	10·7	12·4	10·5	11·2	4·2	11·7	11·7	11·3	12·9
Zn	1·8	2·1	0·8	3·1	2·0	11·2	2·2	0·7	1·2	1·0
S	30·0	30·1	30·3	30·0	30·3	29·4	29·8	29·7	30·0	29·7
Sum	100·0	100·0	100·8	100·5	100·6	99·2	99·6	99·2	99·4	99·4

Atomic ratios to a total of 8 atoms:

	1	2	3	4	5	6*	7	8	9	10
Cu	2·00	1·98	1·96	1·97	1·97	1·99	1·95	2·10	2·11	2·01
Fe	0·86	0·82	0·95	0·81	0·86	0·32	0·90	0·90	0·86	1·00
Zn	0·12	0·15	0·05	0·20	0·13	0·75	0·15	0·05	0·08	0·06
Sn	1·00	1·01	1·01	1·00	1·00	0·94	0·99	0·95	0·93	0·95
S	4·02	4·04	4·03	4·02	4·04	4·00	4·01	4·00	4·02	3·98
Fe+Zn	0·98	0·97	1·00	1·01	0·99	1·07	1·05	0·95	0·94	1·06

1. No. 12138 ⎫
2. No. 12078 ⎭ San Jose, Oruro, Bolivia.
3. No. 12107 Animas, Ayocha, Bolivia.
4. No. 12079 Wheal Agar, Cornwall.
5. No. 12102 ⎫
6. No. 12105 ⎭ Zinnwald, Bohemia.

7. No. 12074 Uncia, Potosi, Bolivia.
8. No. 12077 ⎫
9. No. 12077 ⎬ Vila Apacheta, Bolivia.
10. No. 12124 ⎭

* Kësterite

From this investigation it appears that the most general stannite formula should be written (Cu, Fe, Zn, Sn)S, although a very common composition is $Cu_2(Fe, Zn)SnS_4$ and deviations from this formula are not large.

Hexastannite[1] *and mawsonite.* Hexastannite has been described by Ramdohr (1960) as looking pinkish-brown in the microscope and being very strongly anisotropic and bireflecting. According to Markham and Lawrence (1965), mawsonite is also very strongly anisotropic and bireflecting and has a brownish-orange appearance. Minerals similar to hexastannite and mawsonite were found in a sample (No. 12077) from Vila Apacheta, Bolivia and in one (No. 12131) from Cholquijirca, Peru. In the former specimen they are imbedded in a matrix of stannite and associated with chalcopyrite and cassiterite. Fig. 1 depicts such an area. The lighter of the two phases in question has an orange tinge and is the more strongly anisotropic with the polarization colours described for

[1] Now renamed stannoidite (Kato, 1968).

mawsonite. The optical characteristics for the other mineral, which is present in somewhat larger quantity, can be matched with those published for hexastannite. In the Cholquijirca specimen the two
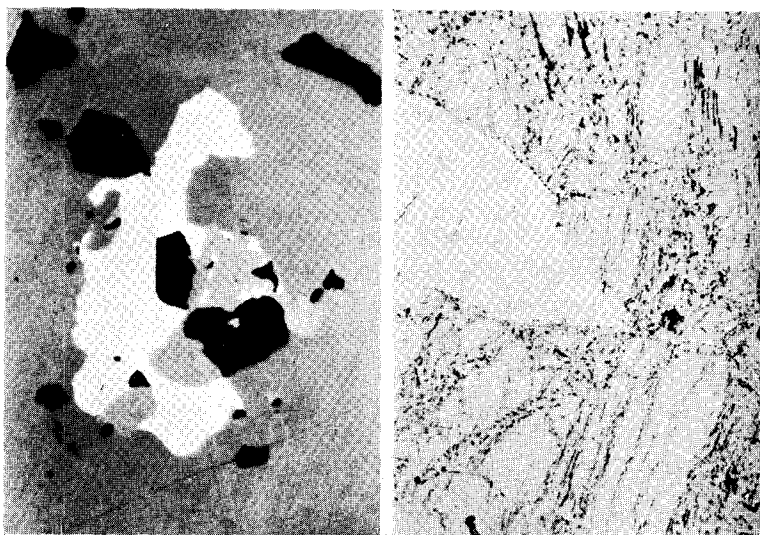
Figs. 1 and 2: Fig. 1 (left). Mawsonite (light grey) and hexastannite (darker grey) surrounding chalcopyrite (white) in a groundmass of stannite (grainy appearance). Cassiterite and holes are black. Magnification 680 ×. Fig. 2 (right). Rhodostannite (dark grey) with wedge-shaped mass of stannite (lighter grey) entering the picture area from left. Magnification 150 ×.

minerals occur in an ore consisting mostly of pyrite with minor amounts of enargite and chalcocite.

Reflectivity measurements have been made with a Zeiss microscope photometer using a carborundum standard of 20·5 % reflectivity, and gave $R = 24 \cdot 1{-}27 \cdot 0$ % for mawsonite and $R = 24 \cdot 6{-}26 \cdot 7$ % for hexastannite for light with a wavelength of 520 nm (mμ). The values for mawsonite are in the same range as those given by Markham and Lawrence (1965).

The electronprobe analyses of the two minerals are listed in Table II together with those quoted by Markham and Lawrence (1965). Mawsonite from Vila Apacheta and from Cholquijirca have almost identical compositions and their formulae approximate well to $Cu_6Fe_2SnS_8$. Though this is at variance with the results of Markham and Lawrence (1965) it is interesting to note than an analysis by Lévy (1967) of

mawsonite from Tingha shows closer agreement, leading to $Cu_{5·94}$ $Fe_{1·89}Sn_{0·98}S_{8·20}$. In the case of hexastannite no good accordance is observed between material from the two localities. The present two analyses of this mineral from Vila Apacheta yield formulae that are equal to $Cu_8(Fe,Zn)_3Sn_2S_{12}$ within the limits of experimental error. In contrast, hexastannite from the other deposit contains considerable amounts of arsenic and antimony and the formula $(Cu,Fe,Zn)_{11}(Sn,Sb,$

TABLE II. Microprobe analyses of hexastannite and mawsonite. The corrections amount to: hexastannite, Cu +2·2, 2·1, 2·2 %, Fe −1·5, 1·4, 1·2 %, Zn 0, Sn +3·3, 3·4, 2·2 %, Sb +0·4 %, As 0, S +1·7, 1·7, 2·2 %; mawsonite, Cu +2·5, 2·6, 2·5 %, Fe −1·9, 1·7, 1·7 %, Sn +2·4, 2·4, 2·5 %, S +1·9, 1·9, 1·9 %.

	Hexastannite				Mawsonite				
	1	2	3	4	5	6	7	8	9
Cu	38·2	39·1	43·8	38·0	43·0	43·6	42·9	44·3	45·0
Fe	11·9	11·5	8·5	11·1	12·8	12·4	12·5	12·5	11·8
Zn	0·8	1·0	0·8	4·1	—	—	—	—	< 0·1
Sn	18·7	19·0	12·2	15·6	13·6	13·6	13·8	10·4	11·8
S	29·9	29·8	30·0	29·2	29·4	29·9	29·5	33·0	30·3
Sum	99·5	100·4	99·9*	98·0	98·8	98·5	98·7	100·2	98·9

Atomic ratios to a total of 25 atoms in hexastannite and 17 in mawsonite

Cu	7·83	7·99	8·88	7·8	5·94	5·97	5·93	6·0	6·1
Fe	2·76	2·66	1·94 ⎫		2·01	1·92	1·96	1·7	1·7
Zn	0·18	0·21	0·17 ⎬ 3·5		—	—	—	—	—
Sn	2·06	2·08	1·31†	1·7	1·01	1·00	1·02	0·8	0·9
S	12·17	12·06	12·05	12·0	8·04	8·11	8·09	8·5	8·3

* Also 2·5 % Sb and 2·1 % As.   † Also 0·28 atom Sb and 0·37 atom As.

1. No. 12077 ⎫ Vila Apacheta, Bolivia.
2. No. 12077 ⎭
3. No. 12131 Cholquijirca, Dept. Junin, Peru.
4. Tingha, New South Wales (Markham and Lawrence, 1965).
5. No. 12077 ⎫ Vila Apacheta, Bolivia.
6. No. 12077 ⎭
7. No. 12131 Cholquijirca, Dept. Junin, Peru.
8. Mt. Lyell, Tasmania (Markham and Lawrence, 1965).
9. Tingha, New South Wales (Markham and Lawrence, 1965).

$As)_2S_{12}$ can be suggested for it. However, a close compositional relationship is evident between the two kinds of hexastannite: arsenic and antimony substitute for some of the tin and the combined total of copper, iron, and zinc is the same although the relative proportions of these elements are different.

Recently, Lévy (1967) has pointed out that hexastannite ('stannite jaune') and mawsonite ('bornite orange') are possibly part of a solid-

solution series extending between $Cu_3(Fe,Zn)S_4$ and $Cu_2(Fe,Zn)SnS_4$ (stannite). However, it should not be overlooked that the present investigation and also the analyses by Lévy (1967) and by Markham and Lawrence (1965) clearly show that the metal:sulphur ratio is larger than 1:1 in both these minerals, and it is also distinctly different for each phase. Furthermore there are structural differences: Kato (1968) has shown that hexastannite is in fact orthorhombic, whereas stannite and perhaps also mawsonite are tetragonal.

Rhodostannite. In one specimen from Vila Apacheta (No. 12124) a reddish variety of 'stannite' was found associated with ordinary stannite. The mode of occurrence of these two minerals is illustrated in fig. 2.

TABLE III. Analytical and X-ray data for rhodostannite, No. 12124, Vila Apacheta, Bolivia. The corrections for the microprobe analyses amount to: Cu, $+0.4$, 0.4 %, Fe -0.5, 0.4 %, Sn $+7.4$, 7.4 %, S $+0.5$, 0.5 %. X-ray powder data by diffractometer, Cu/Ni radiation, internal quartz standard.

	1	2	1a	2a	d	I	d	I
Cu	16.0	15.9	2.03	1.98	6.09 Å	40	1.993 Å	10
Fe	6.8	6.5	0.98	0.92	5.93	60	1.917	4
Sn	45.5	45.4	3.10	3.02	3.64	15	1.837	20
S	31.3	32.8	7.89	8.08	3.12	100	1.819	30
Sum	99.6	100.6			2.99	6	1.755	2
					2.58	50	1.637	2
					2.37	4	1.583	2
1, 2, percentages.					2.31	2	1.498	2
1a, 2a, atomic ratios to a total of 14 atoms				2.12	4		

The reddish phase gives the appearance of being an alteration product of the normal stannite. The replacement is apparently accompanied by a shrinkage in volume, which explains the porous texture of the new mineral. In this respect it resembles 'Zinnkies? III' of Ramdohr (1960) but the isotropic 'Zinnkies? IV', which this mineral is said to replace, was not observed in the present case and the X-ray pattern is not that of 'Zinnkies? III'. Two independent analyses of the reddish 'stannite' have been made and are listed in Table III. It is evident that the mineral corresponds very closely to the formula $Cu_2FeSn_3S_8$. In composition it can therefore be considered as ordinary stannite, Cu_2FeSnS_4 with two additional molecules of SnS_2 per unit formula.

The mineral is anisotropic and has polarization colours ranging from bluish-grey to dark brown. The anisotropic behaviour is not as pronounced as in ordinary stannite. The material from Vila Apacheta is extremely fine grained so that even with the smallest available field aperture (2.5 μ diameter) of the Zeiss microscope photometer the

bireflectance could not be recorded quantitatively. A mean reflectivity of 27·8 % was measured at λ 520 nm using a carborundum standard of 20·5 % reflectivity. In comparison, the ordinary stannite of the same specimen gave values ranging from 27·5 to 28·6 %.

Hardness determinations were carried out with a Leitz Durimet tester. Vickers Hardness Numbers lying between 243 and 266 kg/mm² were obtained for a load of 100 g. In comparison stannite gave Hardness Numbers ranging from 242 to 283 kg/mm². It should be noted that whereas the impressions on stannite were quite well-shaped, those on the reddish mineral were rather ruptured, which is probably due to its porous texture.

Sufficient material was available for an X-ray diffraction powder pattern (Table III). No known substance with these lattice spacings could be found. A. Kato (National Science Museum, Tokyo; priv. comm.) has kindly made some suggestions on the symmetry and unit cell of the new mineral. He proposes a hexagonal cell with a 7·27 Å and c 18·07 Å. The majority of the diffraction lines can be satisfactorily indexed on this basis, the two or three exceptions being very weak. Assuming D 4·79 g.cm^{-3}, the unit cell would contain 3 $Cu_2FeSn_3S_8$.

The mineral is clearly a new species, and the name *rhodostannite*, referring to its reddish colour compared to stannite, has been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

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