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NEW DATA ON STANNITE AND RELATED TIN SULFIDE MINERALS

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ABSTRACT

Within the system Cu–Fe–Zn–Sn–S, stannite $Cu_2(Fe,Zn)SnS_4$, kesterite $Cu_2(Zn,Fe)SnS_4$, mawsonite $Cu_6Fe_2SnS_8$, stannoidite $Cu_8(Fe,Zn)_3Sn_2S_{12}$ and a number of stannite variants have been studied by Gandolfi X-ray camera and electron microprobe. In all the examined samples, the compounds are stoichiometric with no significant positional disorder, a result confirmed by structure refinements. Despite appreciable (Fe,Zn) and (Zn,Fe) substitutions in stannite and kesterite respectively, observed variations of lattice parameters with composition confirm the miscibility gap. "Zincian stannite" (Berry & Thompson 1962) is a mixture of kesterite with exsolved stannite. The "unknown phase" of Petruk (1973) is a mixture of kesterite and stannoidite. X-ray powder patterns, reflectivity and microhardness data are provided for specimens utilized in the structure refinements of mawsonite (Szymański 1976) and stannite and kesterite (Hall *et al.* 1978).

SOMMAIRE

On a étudié, au moyen de la chambre à rayons X Gandolfi et par microsonde, les phases suivantes du système Cu–Fe–Zn–Sn–S: stannite $Cu_2(Fe,Zn)SnS_4$, kesterite $Cu_2(Zn,Fe)SnS_4$, mawsonite $Cu_6Fe_2SnS_8$, stannoïdite $Cu_8(Fe,Zn)_3Sn_2S_{12}$, ainsi que quelques variantes de stannite. Toutes sont stoechiométriques, pratiquement sans aucun désordre de position, ce que confirme l'affinement des structures. Quoique les substitutions (Fe,Zn) de la stannite et (Zn,Fe) de la kesterite soient considérables, la variation des paramètres réticulaires avec la composition confirme la lacune de miscibilité. La "zincian stannite" de Berry & Thompson (1962) est un mélange de kesterite et de stannite démixée. La phase inconnue de Petruk (1973) est un mélange de kesterite et de stannoïdite. On présente les diagrammes de poudre et des données sur la réflectivité et la microdureté d'échantillons de mawsonite, de stannite et de kesterite qui ont servi à l'affinement des structures (Szymański 1976, Hall *et al.* 1978).

(Traduit par la Rédaction)

INTRODUCTION

The first description of stannite, ideally Cu_2FeSnS_4, is generally credited to Klaproth (1797). Since the recognition of a number of "stannites", as first expressed by Ramdohr (1944), much new information has become available on stannite and related minerals in the system Cu–Fe–Zn–Sn–S that possess tetrahedrally coordinated sulfur atoms. This new information has been summarized by Ramdohr (1960), Moh & Ottemann (1962), Lévy (1967), Springer (1968), Petruk (1973), Kato (1974) and Lee *et al.* (1974). The present paper complements the foregoing with new data obtained in the course of mineralogical studies prior to crystal-structure refinements at CANMET. Specimens suitable for the refinements were obtained: mawsonite (Szymański 1976), stannite and kesterite (Hall *et al.* 1978); however, the mineralogical study was expanded to tackle a number of other problems.

Figure 1a illustrates the variable metal contents and formulae of the minerals in the system Cu–Fe–Zn–Sn–S. The diagram does not show the metal:sulfur ratios; the minerals would not lie in the same plane if a sulfur apex were added. Figure 1b illustrates the ranges in Cu/(Cu + Sn) *vs.* Fe/(Fe + Zn) ratios of the minerals. The most copper-rich mineral is mawsonite $Cu_6Fe_2SnS_8$ (Markham & Lawrence 1965). The original formula, $Cu_7Fe_2SnS_{10}$, was revised on the basis of improved analyses by Lévy (1967), Springer (1968) and Petruk (1973). Although Kachalovskaya *et al.* (1973) reported a mineral with the formula $Cu_{2.86}FeSn_{0.55}S_{4.06}$ under the name mawsonite, the analysis totaled 104.3%; therefore, the analysis likely reflects analytical errors rather than nonstoichiometry. Mawsonite, as noted by Markham & Lawrence and Lévy, is obviously equivalent to the "orange bornite" first described by Murdoch (1916) and to some orange bornites described by a number of later workers.

Stannoidite was originally considered to be $Cu_5(Fe,Zn)_2SnS_8$ or $Cu_5Fe_2SnS_8$ (Kato 1969). Kato also suggested that stannoidite is equivalent

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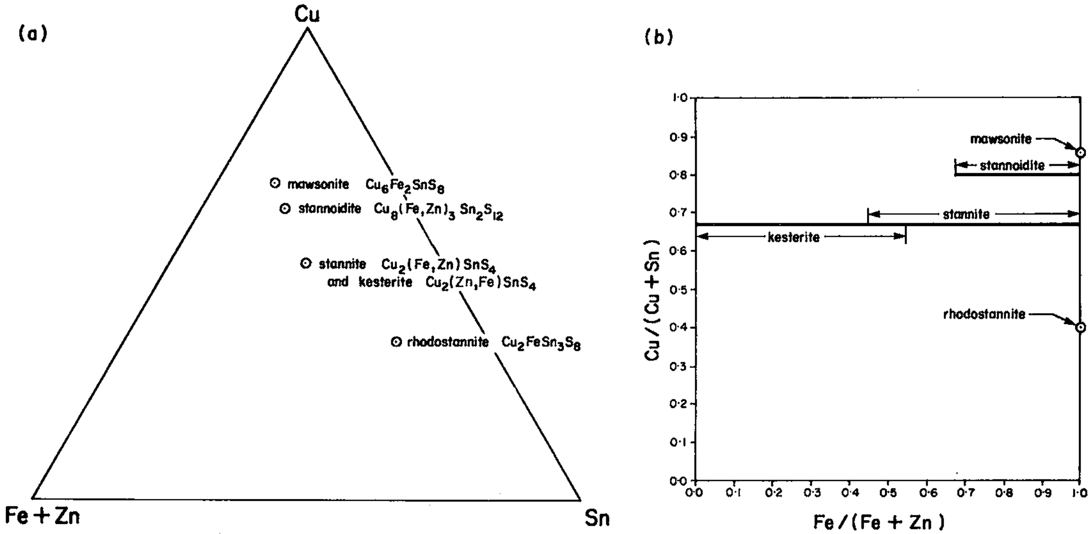

FIG. 1. (a) Triangular Cu–(Fe+Zn)–Sn diagram for minerals in the system Cu–(Fe+Zn)–Sn–S (after Petruk 1973). This diagram displays only the variations among the metals; differences in metal:-sulfur ratios are not shown. (b) Cu/(Cu+Sn) *vs* Fe/(Fe+Zn) for minerals within the system Cu–(Fe+Zn)–Sn–S (after Petruk 1973).

to hexastannite (= stannite I) of Ramdohr (1960), which was given the formula Cu_6FeSnS_8 (details of analyses were not provided), and to some yellow stannites (*stannite jaune*) described by a number of earlier workers. Recalculated analyses of hexastannite by Markham & Lawrence (1965), Lévy (1967) and Boorman & Abbott (1967), together with the hexastannite formula derived by Springer (1968) and the stannoidite formula obtained by Petruk (1973), confirm that the correct formula for stannoidite is $Cu_8(Fe,Zn)_3Sn_2S_{12}$, a composition now accepted by Kato (1974). Kachalovskaya *et al.* (1973) reported finding stannoidite with the formula $Cu_{5.03}(Fe,Zn)_{1.93}SnS_{6.04}$; however, this composition is more likely the result of analytical error, as their analysis totals only 97%. Previous work summarized by Petruk (1973) indicated that stannoidite ranges in composition from $Cu_8Fe_3Sn_2S_{12}$ to $Cu_8Fe_2ZnSn_2S_{12}$.

Petruk (1973) described a mineral from the Mount Pleasant deposit, New Brunswick, with the approximate composition $Cu_{14}Fe_3Zn_3Sn_5S_{24}$ as an "unknown phase". This phase, reexamined in the present study, was found to be a mixture, as discussed below.

Stannite has long been known to contain appreciable zinc, such that its formula might be better written $Cu_2(Fe,Zn)SnS_4$. Petruk (1973) found varieties containing up to 55 at.% Zn in the (Fe,Zn) sites. Kesterite, $Cu_2(Zn,Fe)SnS_4$, named by Orlova (1956), can also contain appreciable iron. Petruk found kesterite with as much as 55 at.% Fe. The problematic structural stability relationships between stannite and kesterite are the subject of much of the present paper.

Isostannite, optically isotropic and possibly a polymorph of stannite (Claringbull & Hey 1955), sakuraiite, the indium analogue of kesterite (Kato 1965) and rhodostannite (Springer 1968) will not be discussed in this paper.

METHODS OF STUDY

Obtaining accurate analyses was initially difficult because the use of binary sulfide or elemental standards often yielded anomalously high or low atomic proportions in analyzed minerals. Improvement over earlier analyses in this laboratory and most literature analyses was attained by production of synthetic Cu_2FeSnS_4 and Cu_2ZnSnS_4 standards. In each case, the stoichiometric proportions of the pure elements were heated for 20 days at 800°C in sealed, evacuated silica tubes. The tubes were then quenched in ice water and the reaction products were ground in a mortar. The products of the initial reaction were then placed in a vertical furnace in sealed, evacuated silica tubes with sufficient flux of NaCl and KCl (1:1 on molar basis) to completely immerse them and heated to 800°C for 4 days. The final quenched products consisted of Cu_2FeSnS_4 and Cu_2ZnSnS_4, with traces of SnS. X-ray powder and single-crystal studies also showed the synthetic products to be structurally identical to the natural minerals. The synthetic materials were compared with natural stannite and kesterite with the microprobe; intensities obtained for $CuK\alpha$, $SnL\alpha$ and $SK\alpha$ peaks were identical.

Specimens examined in this study were analyzed on a Materials Analysis Company (MAC) Model 400 electron microbeam analyzer operated at 25 kV and 0.03 μA specimen current. The compositions and homogeneity of the specimens were determined from data acquired by collecting counts for 10 s periods from 5 to 10 spots on a grain. Stannites and kesterites were analyzed for Cu, Fe, Sn and S by means of the $CuK\alpha$, $FeK\alpha$, $SnL\alpha$ and $SK\alpha$ lines of the Cu_2FeSnS_4 standard and for Zn using the $ZnK\alpha$ line of the Cu_2ZnSnS_4 standard. Mawsonite was analyzed using Cu_2FeSnS_4 and the $FeK\alpha$, $SnL\alpha$ and $SK\alpha$ lines; copper was determined using the $CuK\alpha$ line of Cu_2FeSnS_4 or by averaging the values obtained using Cu_2FeSnS_4, synthetic CuSe, synthetic $CuFeS_2$ and natural chalcopyrite. Copper in stannoidite was determined in the same manner, or by using Cu_2FeSnS_4 alone, as were Fe, Sn and S. The $ZnK\alpha$ peak of synthetic Cu_2ZnSnS_4 or synthetic iron-bearing ZnS was the standard for Zn. Minor Ag, Cd and Mn were determined using $AgL\alpha$, $CdL\alpha$ and $MnK\alpha$ of the pure metal standards. Indium was determined using $InL\alpha$ of synthetic InAs, and Se using $SeK\alpha$ of synthetic CuSe. The data were reduced by means of the EMPADR VII program of Rucklidge & Gasparrini (1969).

All X-ray powder data were obtained by means of a 114.6 mm Gandolfi camera, as its small sample capacity provided the best means of obtaining impurity-free patterns. Filtered $CoK\alpha$ radiation (λ = 1.79021Å) was employed; *d* values were also calculated for resolved $CoK\alpha_1$ (λ = 1.78890Å) and $CoK\alpha_2$ (λ = 1.79278Å) reflections. Relative intensities were estimated visually. Lattice parameters were obtained by means of the PARAM least-squares refinement of Stewart *et al.* (1972).

Reflectances were measured in air using a Leitz MPE microscope photometer with a silicon reference standard (N 2538.42, issued by the IMA Commission on Ore Microscopy). Microhardnesses were determined on a Leitz Durimet hardness tester using 50 g for 15 s.

STANNITE AND KESTERITE

Stability relationships between stannite and kesterite have an important bearing upon the characterization of the minerals, as it is necessary to know whether composition alone is sufficient to distinguish the two. Experiments by Moh (1960), cited without details but later amplified (Moh 1975), indicated complete solid solution between the two minerals at 700°C in dry systems and at 800°C in NaCl–KCl melts. Springer (1972) confirmed the high-temperature solid solution, but he found a miscibility gap in the Cu_2FeSnS_4–Cu_2ZnSnS_4 pseudobinary system that appeared at 680°C on the iron-rich side and extended to zinc-bearing compositions at lower temperatures. He designated the solid solution above the 680°C inversion β–$Cu_2(Fe,Zn)SnS_4$ and the lower temperature, iron-rich phase α–$Cu_2(Fe,Zn)SnS_4$. In the solid-solution regions of the phase diagram, Springer found that the lattice parameters of the two phases were distinct, with $2a=c$ in β–$Cu_2(Fe,Zn)SnS_4$ and with $2a$ exceeding c by

FIG. 2. Specimen from Oruro, Bolivia (ROM E1769, grain 2R) showing stannite core (lighter, with cleavage) and kesterite rim (darker). Oil immersion.

0.19Å in α–$Cu_2(Fe,Zn)SnS_4$. The β–$Cu_2(Fe,Zn)SnS_4$ phase is apparently isostructural with kesterite; however, the α–$Cu_2(Fe,Zn)SnS_4$ phase, although possessing lattice parameters similar to those of stannite, differs from stannite in that its X-ray powder pattern contains extinctions not permitted in Brockway's (1934) model of the stannite structure. Springer was uncertain whether the lattice parameters of the α and β phases converged near the miscibility gap. If α–$Cu_2(Fe,Zn)SnS_4$ is equivalent to stannite, as was assumed by Harris & Owens (1972), Petruk (1973) and Moh (1975), then Springer's (1972) solvus implies the existence of stannite and kesterite with identical compositions. Petruk (1973) found a range of overlapping compositions with respect to (Fe,Zn) solid solution in the two minerals in his study of natural specimens. The foregoing indicates that differentiating stannite and kesterite would be difficult both on a compositional and structural basis in the absence of additional information.

Stannite and kesterite in a coarsely crystalline core-to-rim relationship (Fig. 2) were used for the structural refinements. Crystal fragments extracted from the field of view in Figure 2 provided Gandolfi X-ray data which clearly differentiated the two minerals, and these fragments ultimately were used in the structural work (Hall *et al.* 1978). The powder patterns are compared with those of synthetic

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR STANNITE AND KESTERITE

	Synthetic Cu_2FeSnS_4 (800°C) a=5.4432 ± 0.0011Å c=10.7299 ± 0.0051Å			Stannite* ROM E1769, Gr 2R(3) a=5.449 ± 0.002Å c=10.757 ± 0.004Å		
hkℓ	$d_{obs.}$	$d_{calc.}$	I/I_{10}	$d_{obs.}$	$d_{calc.}$	I/I_{10}
011	4.89	4.85	3	4.89	4.86	2
012	3.11	3.13	10	3.13	3.13	10
013	3.00	2.99	2	3.01	3.00	1
020	2.723	2.721	3	2.718	2.726	½
004	2.678	2.683	1	2.681	2.689	2
022	2.427	2.427	5	—	—	—
121	2.369	2.374	3	2.336	2.378	2
114	—	—	—	2.202	2.205	½
123	2.006	2.012	2	—	—	—
015	1.983	1.996	1	2.001	2.001	1
220	1.922	1.925	1	—	—	—
024	1.908	1.911	8	1.914	1.914	7
031 006	1.784	1.789 1.788	5	—	—	—
132	1.640	1.639	6	1.643	1.642	5
116 033	1.623	1.622 1.618	6	1.627	1.625 1.620	4
224	1.562	1.564	2	1.563	1.566	1
134	1.449	1.449	½	—	—	—
233	1.389	1.391	1	—	—	—
040	1.359	1.361	4	1.363	1.363	1
008	1.341	1.341	4	1.342	1.344	2
141 226	1.310	1.310 1.310	1	—	—	—
127	1.298	1.297	1	1.303	1.300	½
113	—	—	—	1.273	1.269	½
332	1.249	1.248	1	1.250	1.250	1
136 143	1.240	1.240 1.238	5	1.242	1.243 1.240	6
240 044	1.215	1.217 1.214	1	1.218	1.219 1.215	½
026	1.203	1.203	1	1.209	1.206	½
244 α_1	1.107	1.108	4	1.109	1.110	3
α_2	1.109	1.108	1	1.110	1.110	½
228 α_1	1.100	1.100	2	1.102	1.103	3
α_2	1.101	1.100	½	1.102	1.103	½
129	1.070	1.071	½	—	—	—
152 α_1	1.047	1.047	2	1.048	1.049	1
α_2	1.047	1.047	½			
053 343 α_1	1.043	1.042	1	1.044	1.043	1
α_2	1.042	1.041	½	1.043	1.043	½
1.1.10 α_1	1.034	1.037	2	1.038	1.036	2
α_2	1.033	1.037	½	1.037	1.036	½
0.2.10	0.9987	0.9982	½	—	—	—
253	0.9718	0.9727	½	—	—	—
440 α_1	0.9622	0.9622	½	0.9647	0.9636	2
α_2	0.9617	0.9622	½			
048 α_1	0.9557	0.9552	3	0.9574	0.9571	3
α_2	0.9555	0.9552	2	0.9573	0.9571	1
352 α_1	0.9198	0.9197	3	0.9214	0.9210	2
α_2	0.9200	0.9197	½			
156 α_1	0.9167	0.9166	4	0.9179	0.9182	3
α_2	0.9169	0.9166	2	0.9177	0.9182	2
1.3.10 α_1	0.9105	0.9106	5	0.9125	0.9125	4
α_2	0.9106	0.9106	3	0.9123	0.9125	2
060	—	—	—	0.9087	0.9085	½
444	0.9058	0.9057	2	—	—	—
248	0.9021	0.9013	2	0.9030 0.9032	0.9030 α_1 0.9030 α_2	2 1

	Synthetic Cu_2ZnSnS_4 (800°C) a=5.4339±0.0009Å c=10.8679±0.0018Å			Kesterite* ROM E1769, Gr 2R(2) a=5.427 ± 0.001 Å c=10.871 ± 0.005 Å		
hkℓ	$d_{obs.}$	$d_{calc.}$	I/I_{10}	$d_{obs.}$	$d_{calc.}$	I/I_{10}
011	—	—	—	4.87	4.85	½
012	3.13	3.14	10	3.13	3.13	10
020 004	2.715	2.717	6	2.701	2.712	3
220 024	1.920	1.921	9	1.913	1.918	5
132 116	1.640	1.638	8	1.638	1.636	7
224	1.567	1.569	1	1.571	1.566	½
040 008	1.354	1.359	2	1.358	1.356	1
332 136	1.246	1.247	4	1.245	1.245	3
240 044 028	—	—	—	1.213	1.213	1
244 228	1.110	1.109	5	1.108	1.107	3
152 336 1.1.10	1.047	1.046	5	1.045	1.044	3
440 048	0.9600	0.9605	4	0.9589	0.9589	1
352 156 1.3.10	0.9186	0.9185	6	0.9178 0.9178	0.9169 α_1 0.9169 α_2	2 1

* Lattice parameters from structure refinements of Hall et al. (1978). Error terms in all cases are standard deviations.

TABLE 2. ELECTRON MICROPROBE ANALYSES OF STANNITE AND KESTERITE

Sample and locality	Weight per cent									Total	Atomic proportions							
	Cu	Ag	Fe	Mn	Zn	Cd	Sn	In	S		Cu	Fe	Mn	Zn	Cd	Sn	In	S
STANNITE																		
1. Oruro, Bolivia ROM E1769, Grain 6-2b	29.2	---	11.3	---	1.8	---	28.0	---	29.7	100.0	1.99	0.88		0.12		1.02		4.00
2. Oruro, Bolivia ROM E1769, Grain 2R (3)	29.5	---	10.5	---	2.7	0.43	27.8	---	29.9	100.8	1.99	0.81		0.18	0.02	1.00		4.00
3. Levack West mine, Sudbury, Ont., CANMET concentrate	29.8	---	10.8	---	2.7	0.04	28.0	---	29.7	101.0	2.01	0.83		0.18	0.00	1.01		3.98
4. Oruro, Bolivia GSC 14738, Grain 3	29.6	---	10.8*	---	2.2*	0.11	27.7	0.03	29.7	100.1	2.01	0.84		0.14	0.00	1.01	0.00	4.00
5. Oruro, Bolivia, San José mine, ROM M190349	29.5	n.d.	11.9	---	1.5	---	26.2**	1.33**	30.3	100.8	1.98	0.91		0.10		0.94	0.05	4.03
6. Tam O'Shanter deposit Kootenay, B.C., RM V8.1A	29.1	0.15	11.5	0.10	2.3	n.d.	27.5	n.d.	29.9	100.6	1.96	0.88	0.01	0.15		1.00		4.00
KESTERITE																		
7. Oruro, Bolivia ROM E1769, Grain 2R (2)	29.1	---	3.7	---	11.1	0.22	27.3	---	29.7	101.1	1.98	0.73		0.29	0.01	0.99		4.00
8. Zinnwald, Bohemia, Czech. USNM C5233, Grain 1	30.0	---	6.5	0.02	7.8	0.17	26.5	0.07	29.9	101.0	2.03	0.50	0.00	0.51	0.01	0.96	0.00	4.00
9. Oruro, Bolivia ROM E1769, Grain 2R	29.0	---	3.5	---	11.6	0.27	27.3	---	29.9	101.6	1.96	0.27		0.76	0.01	0.99		4.01
10. Zinnwald, Bohemia, Czech. USNM C5233, Grain A	30.2	---	4.1	0.09	9.8	0.25	26.0	0.11	29.4	100.0	2.07	0.32	0.01	0.65	0.01	0.95	0.00	3.99
11. Zinnwald, Bohemia, Czech. USNM C5233, Grain B	29.7	---	6.3	0.08	7.5	0.17	26.3	0.04	29.6	99.7	2.03	0.49	0.00	0.50	0.00	0.96	0.00	4.01
12. Hugo mine, Keystone, S. Dakota, SDSM&T 5099	29.0	---@	2.3	0.03	10.9	1.67	27.1	---	29.7	100.7	1.99	0.18	0.00	0.73	0.07	1.00		4.04

* Average values; slight variation Zn = 1.7 to 2.7% and Fe = 11.2 to 10.2% wt.
**Average values; slight variation In = 0.54 to 2.04% and Sn = 27.4 to 25.2% wt.
@ Silver could not be determined because of secondary fluorescence from minute inclusions of an unindentified silver-bearing phase.
Specimen no. 5 was taken from the sample used in deriving Berry & Thompson's (1962) pattern for stannite (no. 69). This is the first analysis of this specimen.
n.d. denotes not detected (limit of detection ± 0.02% wt.); ROM = Royal Ontario Museum; USNM = United States National Museum, Smithsonian Institution; GSC = Geological Survey of Canada; SDSM&T = Museum of Geology, South Dakota of Mines & Technology; R.M. = R. Mulligan, GSC.

Cu_2FeSnS_4 and Cu_2ZnSnS_4 from this study in Table 1. Compositional data for the natural specimens are provided in Table 2 and reflectances in Table 3. Microhardness indentations could not be obtained, as grain mounts containing the minerals fractured excessively.

Powder-pattern differences between stannite and kesterite are subtle but distinct. Both are tetragonal with the same permitted reflections, $h+k+l = 2n$; however, kesterite is strongly pseudocubic. Lattice parameters derived in the structural refinements (Hall *et al.* 1978) show that stannite $2a$ exceeds c by about 0.1Å whereas kesterite c exceeds $2a$ by only 0.01Å. The difference between $2a$ and c in kesterite cannot be determined by powder methods, and its tetragonal symmetry can be determined only by single-crystal methods. For example, (020) and (004) form a closely spaced diffraction couplet in stannite and are unresolved in kesterite. A number of such resolved and unresolved couplets clearly distinguish stannite from kesterite.

TABLE 3. REFLECTANCES AND MICRO-INDENTATION HARDNESS OF STANNITE, KESTERITE AND MAWSONITE

Wavelength (nm)		470	546	589	650
Stannite, Oruro, Bolivia (ROM E1769, grain 2R[3])	R_o	26.1	27.2	27.4	27.4
	R'_e	27.6	28.0	28.2	27.6
Kesterite, Oruro, Bolivia (ROM E1769, grain 2R[2])	R_o	24.3	23.8	23.8	24.7
Mawsonite, Ikuno mine, Japan (NMNH 122102)	R_o	19.5	22.6	24.5	28.3
	R'_e	14.9	20.3	24.9	31.6
Mawsonite, Kidd Creek mine, Ontario (RIT TQ 74-681[1])	R_o	21.2	24.0	25.6	29.6
	R'_e	17.7	22.8	28.3	34.5

Mawsonite, Kidd Creek mine specimen: micro-indenting hardness (mean of three measurements) VHN_{50g} 240 ± 19

To determine the effect of composition on the lattice parameters of stannite and kesterite, carefully selected specimens from worldwide localities were analyzed (Table 2), and X-rayed with a Gandolfi camera. The cell dimensions of kesterite were refined by indexing with a pseudocubic cell of lattice parameter c. This procedure then assumes $2a = c$, so that the results are useful only for comparison with the lattice parameters of stannite. Figure 3 shows $2a$ and c *vs.* composition of the (Fe + Zn) sites in the stannites and kesterites from Table 2. Parameters of the pure, synthetic end-members from this study are also included. Minor amounts of Mn have been added to Fe and Cd to Zn in normalizing the atomic contents of the (Fe + Zn) sites to 1.000.

These studies of well-characterized specimens show that stannite and kesterite are structurally distinct (Fig. 3). Lattice parameters show no tendency to converge as a function of solid solution, although the parameters of stannite increase slightly with increasing solid solution of Zn, and those of kesterite decrease slightly

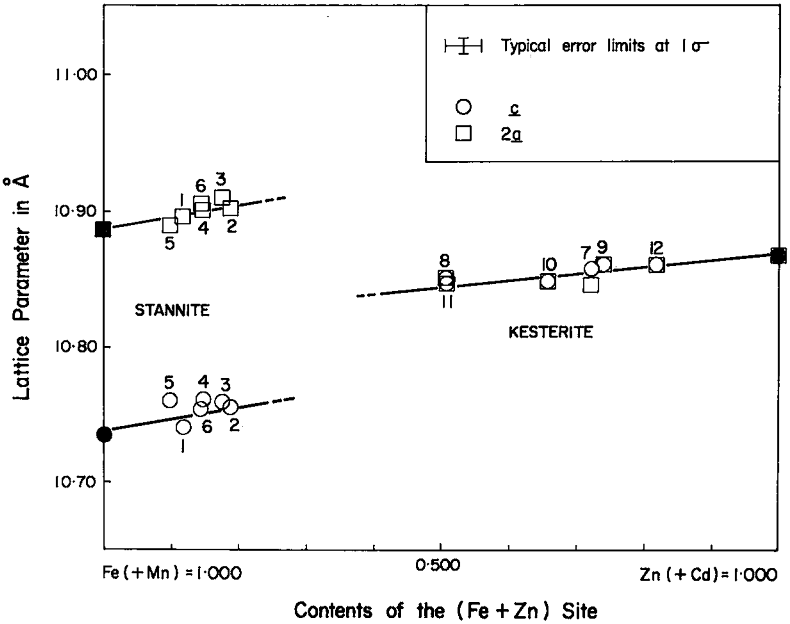

FIG. 3. A plot of $2a$ and c lattice parameters *vs.* the composition of the (Fe+Zn) sites in stannite and kesterite. Sample numbers correspond to those in Table 2; synthetic end-members are from this study. Mn has been added to Fe and Cd to Zn and the atoms in the (Fe+Zn) position have been normalized to 1.000. Solid symbols are the synthetic end-members.

with increased Fe in solid solution. Figure 3 does not purport to illustrate the entire range of solid solution of both minerals; more extensive solubilities of Fe and Zn in kesterite and stannite, respectively, have been reported in the literature. However, the results shown here do indicate a miscibility gap between the two minerals, and suggest that they possess different crystal structures. The latter conclusion has been confirmed by Hall *et al.* (1978), who refined the structure of stannite in space group $I\bar{4}2m$ and kesterite $I\bar{4}$.

Also demonstrated by these well-characterized specimens is that neither stannite nor kesterite exhibits nonstoichiometry beyond ±5% in any atomic position in the idealized formula $Cu_2(Fe,Zn)SnS_4$. The small divergences are attributed to analytical error. These data strongly support the structural model of Brockway (1934) for stannite, *i.e.*, ordered sites in space group $I\bar{4}2m$, and further indicate that the contents of the atomic positions in kesterite are ordered.

The detection of kesterite, often unnoted or misidentified, in a number of museum specimens studied in this investigation indicates that the mineral is probably more common than previously suspected, perhaps nearly as common as stannite. Kesterite should be suspected where isotropic or nearly isotropic "stannites" are noted.

Although stannite and kesterite may be distinguished in polished section, particularly in freshly polished sections under oil immersion, the etching technique employed by Harris & Owens (1972) was found to be extremely useful in differentiating the two minerals in intergrowths. A 1:1 solution of HNO_3 etches stannite and attacks kesterite much more slowly. Caution is necessary in interpreting the etched section, as the etchant also attacks twinned crystals differentially.

THE PROBLEM OF STANNITE VARIANTS

Zincian stannite

Berry & Thompson (1962) applied the term "zincian stannite" to a specimen from the Snowflake mine, Revelstoke, British Columbia. They noted that the X-ray pattern (No. 70) of this mineral differed from that of stannite and required different cell dimensions. The PDF listing (21–883) presently applies the

Berry & Thompson data to kesterite, so that identity of zincian stannite and kesterite has been assumed.

The Berry & Thompson specimen (UT R218) that gave pattern No. 70 was found to consist of massive kesterite with copious lamellae of exsolved stannite (Fig. 4). Analyses of the two minerals are given in Table 4. The powder pattern is that of kesterite with several reflections of stannite. The kesterite reflections alone yield lattice parameters intermediate to those of stannite and kesterite, possibly because stannite and kesterite reflections are not resolved in a mixture of the two minerals, even though their lattice parameters differ slightly. The effect on unresolved reflections would be to shift *d* spacings towards a mean value.

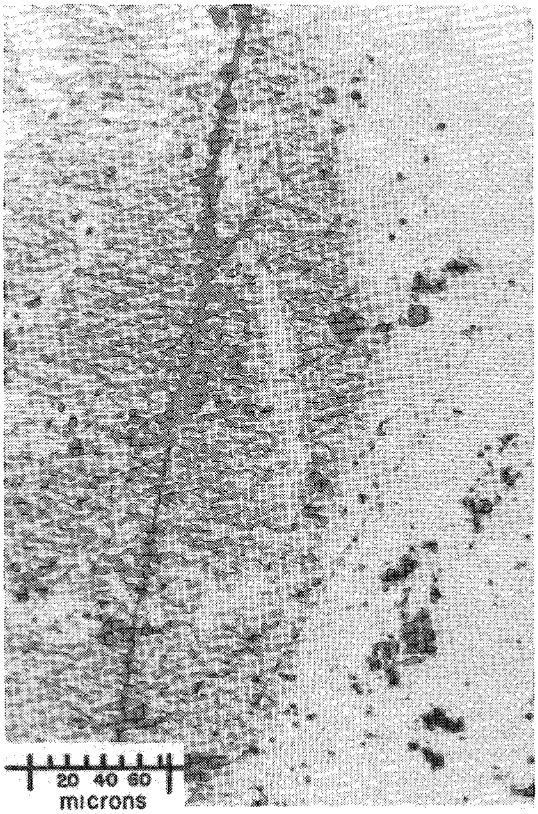

FIG. 4. Specimen from Snowflake mine, Revelstoke, British Columbia (UT R218), identical to zincian stannite of Berry & Thompson (1962). The etched (1:1 HNO_3) left side shows exsolved lamellae of stannite (etched) in a kesterite host (unetched). Crossed nicols, oil immersion.

TABLE 4. ELECTRON MICROPROBE ANALYSIS OF "ZINCIAN STANNITE"†

Element	Kesterite (host)	Stannite (lamellae)
Cu	29.0 wt. %	29.3 wt. %
Ag	0.42	0.11
Fe	4.4	8.2
Zn	9.6	5.5
Cd	0.10	0.28
Mn	n.d.*	n.d.*
Sn	27.0	27.1
In	0.13	0.12
S	29.2	29.5
	99.8	100.1

† University of Toronto collection, UT R218; * not detected (*i.e.*, $\leq$ 0.02 wt. %). Formulae are based on a total of eight atoms. Kesterite host: $(Cu_{2.00}Ag_{0.02})_{\Sigma 2.02}(Zn_{0.64}Fe_{0.35})_{\Sigma 0.99}(Sn_{1.00}In_{0.01})_{\Sigma 1.01}$-$S_{3.99}$; stannite lamellae: $Cu_{2.00}(Fe_{0.64}Zn_{0.36}Cd_{0.01})_{\Sigma 1.01}Sn_{0.99}S_{3.99}$

The Berry & Thompson X-ray powder pattern (No. 70) is therefore suspect, as it may contain reflections attributable to stannite and likely will not yield the correct lattice parameters for kesterite. Preferred data are those obtained either from topotype kesterite by Ivanov & Pyatenko (1959), or from the Oruro (Bolivia) specimen (No. 7) used in this study and in the refinement of the kesterite structure.

Petruk (1973) employed the term "zincian stannite" for stannites containing from 40 to 55 at.% Zn in the (Fe + Zn) sites. This usage is in accord with mineralogical practice but it conflicts with the prior usage of Berry & Thompson (1962). As well, Petruk found significant nonstoichiometry in his specimens in that they contained excess (Fe + Zn) and deficiencies in Cu or (Sn + In) or both. One of us (D.R.O.), who was Petruk's analyst, believes that the deficiencies are analytical and arose principally from the use of binary sulfide and elemental standards. However, if Petruk's zincian stannites are truly nonstoichiometric, they are likely not isostructural with stannite or kesterite and therefore represent some heretofore undescribed species. Unfortunately, Petruk's specimens are too small to be useful for further study. In any event, the term "zincian stannite" probably should be avoided in view of the conflicting usages to which it has been subjected.

Ferrian kesterite

Petruk (1973) applied the term ferrian kesterite to kesterite containing 25 to 55 at. % Fe in the (Fe + Zn) sites. This range seems to be normal, and complete solid solution to the Cu_2ZnSnS_4 end-member is well established. Petruk's ferrian kesterite differs slightly in reflectivity and substantially in microhardness from low-iron kesterite. The most iron-rich kesterites reported in this study (Nos. 8 & 11, Table 2 & Fig. 3) are similar in composition to those reported by Petruk. The problems relating to these high-iron compositions and the role of indium will be treated in a subsequent paper.

"Unknown phase"

A mineral compositionally intermediate between stannoidite and ferrian kesterite was reported by Petruk (1973). His polished section, No. 52–523, was borrowed and the grain illustrated in his Figure 11 was relocated. Microprobe analysis yielded results similar to those reported by Petruk and indicated homogeneity with respect to the electron beam. However, in the course of the study, an improved ×100 objective with a flatter field of view was obtained and the grain was re-examined. The grain consists of an extremely fine, oriented, lamellar intergrowth of stannoidite and kesterite (Fig. 5). The apparent composition of the mixture can be represented by the following equation: $Cu_8Fe_2ZnSn_2S_{12}$ (high-Zn stannoidite) + $3Cu_2Zn_{0.67}Fe_{0.33}SnS_4$ (ferrian kesterite) = $Cu_{14}Fe_3Zn_3Sn_5S_{24}$. Ramdohr (1944) shows similar intergrowths, although somewhat coarser, in material from Zinnwald. He identified the two components as stannite I and II. Similar textures were found in material from Zinnwald in the present study. The two minerals are stannoidite and kesterite. The "unknown phase" of Petruk (1973) is an example of a "microprobe-homogeneous intergrowth" that occurs not too infrequently, though rarely expressed as a warning in literature (Scott 1976).

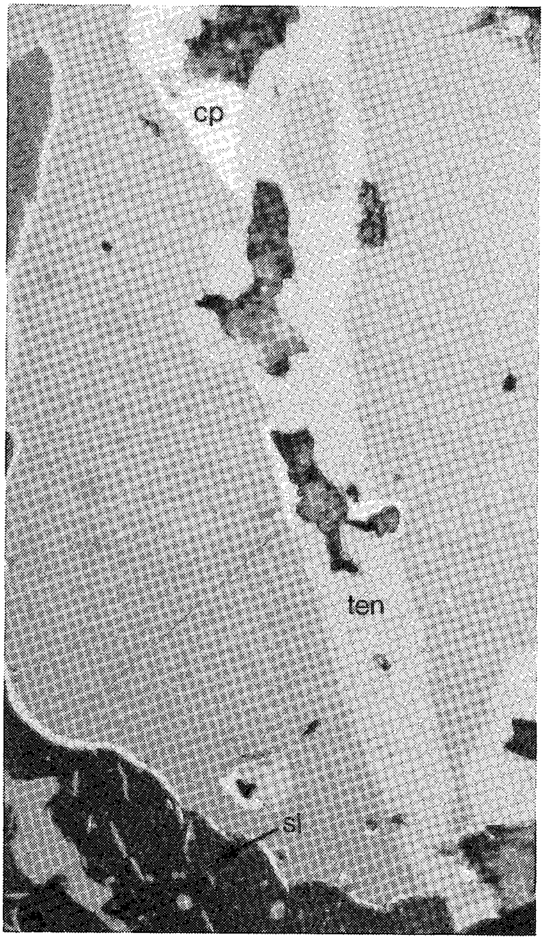

FIG. 5. The "unknown phase" of Petruk (1973), an intergrowth of stannoidite and kesterite (centre). Individual lamellae are less than 1 μm thick. The grain is rimmed by chalcopyrite (cp, white), which also occurs as oriented lamellae in the surrounding sphalerite (sl, dark grey). The light grey mineral is tennantite (ten).

STANNOIDITE

Stannoidite from two localities was analyzed (Table 5). The mineral seems to be stoichiometric $Cu_8(Fe,Zn)_3Sn_2S_{12}$, in agreement with the structural refinement of Kudoh & Takéuchi (1976), who determined that the unit cell of stannoidite contains 25 atoms with the accepted formula. The ratio Fe/Zn in the present analyses ranges from 2:1 to 3:0, in agreement with earlier observations as well as those of Yamanaka & Kato (1976). Their Mössbauer study showed stannoidite to have the ionic formula $Cu^{1+}{}_8Fe^{3+}{}_2Fe^{2+}Sn^{4+}{}_2S^{2-}{}_{12}$. Zinc apparently may substitute only for Fe^{2+}, giving rise to the observed Fe/Zn ratio in the mineral.

TABLE 5. ELECTRON MICROPROBE ANALYSES OF STANNOIDITE

Element	Ikuno mine, Hyogo Prefecture, Japan	Kidd Creek mine, Ontario
Cu	38.5 wt. %	38.8 wt. %
Fe	11.5	8.5
Zn	1.6	4.5
Sn	18.9	18.0
S	29.3	29.1
Se	*	1.1
	99.8	100.0

* Not determined. Formulae listed below are based on a total of 25 atoms. Specimen from the Ikuno mine is NMNH 108319 (Smithsonian Institution collection): $Cu_{7.94}(Fe_{2.69}Zn_{0.33})_{\Sigma 3.02}Sn_{2.08}S_{11.96}$. Specimen from the Kidd Creek mine is TQ 74-560[10] (R.I. Thorpe, Geological Survey of Canada): $Cu_{8.00}(Fe_{2.01}Zn_{0.91})_{\Sigma 2.92}Sn_{1.99}(S_{11.91}Se_{0.18})_{\Sigma 12.09}$.

MAWSONITE

Both the formula, as discussed earlier, and the structure of mawsonite have been subjects of controversy. The formula $Cu_6Fe_2SnS_8$ was confirmed in the present study, analyses having been given previously by Szymański (1976).

The non-cubic structure of mawsonite is indicated by its very strong anisotropy. Attempts by Markham & Lawrence (1965) at indexing the powder pattern led to a pseudocubic solution. Yamanaka & Kato (1976) proposed that the structure was tetragonal with space group $I42m$, $I4mm$, $I422$ or $I4_122$, *a* 10.745, *c* 10.711Å. Szymański (1976), however, refined the structure in space group $P\bar{4}m2$, with *a* 7.603, *c* 5.358Å.

Prior to Szymański's structural refinement, the specimen [RIT, TQ74-681(1)] from the Kidd Creek mine was examined mineralogically. The microhardness and reflectivity of the mineral were measured and the latter property compared with that of mawsonite from the Ikuno mine (Table 3). Szymański (1976) provided a calculated powder pattern of mawsonite; an indexed measured pattern given in Table 6 is compared with data obtained previously by Markham & Lawrence (1965) and Yamanaka & Kato (1976). Although the agreement among the patterns is good, Szymański (1976) questioned whether some of the reflections observed by Yamanaka & Kato (1976) were perhaps due to impurities. Although Yamanaka's & Kato's reflections at *d* = 7.62, 1.318 and 1.302Å are indexable in Szymański's cell as (010), (014) and (441,152), respectively, Szymański concluded from his structural work that the intensities of these reflections should be too weak to be observed. However, comparison of intensities on the Gandolfi film with those of Szymański indicates that all but (014) are observable. The intensity of (014) is very weak according to Szymański's data; but the observed reflection reported by Yamanaka & Kato is too close to the calculated *d* value to be fortuitous. The (012) reflection, as well, was observed in this study, although Szymański omitted this reflection as too weak to be observed. The 2.462Å reflection observed by Yamanaka & Kato does not agree well with any observed in this study or with the data of Szymański, although it is nearest to (012). The (230) reflection was not reported by Szymański, nor was a correlative one found by Yamanako & Kato, although Markham & Lawrence reported one at *d* = 2.098Å. The $CoK\beta_1$ reflections for (040) and (222) could have produced the *d* = 2.098 Å reflection noted here, but filtration problems were not previ-

TABLE 6. POWDER X-RAY DIFFRACTION DATA FOR MAWSONITE

1 Mawsonite		2 Mawsonite		3 Mawsonite			
d_{obs}	I/I_{100}	d_{obs}	I/I_{100}	d_{obs}	I/I_{10}	d_{calc}	hkℓ
-	-	7.62	3	-	-	7.6	010
5.37	20	5.38	10	5.3	1	5.4 5.4	110 001
4.37	20	4.38	15	4.38	4	4.38	011
3.80	10	3.80	8	3.70	½	3.80 3.80	020 111
3.34	10	3.378	4	-	-	3.40	120
3.09	100	3.099	100	3.10	10	3.10	021
2.875	10	2.868	10	2.88	4	2.87	121
2.680	50	2.684	25	2.69	6	2.69 2.68	220 002
-	-	2.462	3	2.52	½	2.53	012
2.395	10	2.401	8	2.41	3	2.40 2.40 2.39	130 221 112
2.287	10	2.291	5	2.30	2	2.29	031
2.185	5	2.192	3	2.19	1	2.19	022
2.098	5	-	-	2.09	½	2.11	230
1.959	5	1.962	3	1.958	½	1.962	231
1.895	80	1.899	75	1.899	7	1.901 1.898	040 222
1.788	5	1.791	3	1.790	2	1.792 1.789	330 132
1.739	2	1.742	3	1.741	2	1.744	141
1.618	80	1.620	40	1.618	6	1.621 1.617	241 023
-	-	-	-	1.584	½	1.581	123
1.547	10	1.549	7	1.552	3	1.550	042
1.460	5	1.463	3	1.462	2	1.463 1.463 1.460	051 341 033
-	-	-	-	1.438	½	1.435	242
-	-	1.366	3	1.362	½	1.365 1.363	251 233
1.343	20	1.344	15	1.338	5	1.344 1.340	440 004
-	-	1.318	3	-	-	1.319	014
-	-	1.302	4	-	-	1.304 1.303 1.300	530 152 114
1.232	30	1.233	10	1.213	½	1.233 1.231	061 243
1.201	5	1.201	5B	1.201	3	1.202 1.201 1.199	260 442 224
.....		-	-	1.155	½	1.159 1.158 1.158 1.146	451 343 053 062
.....		1.096	15	1.095	7	1.097 1.095	262 044
.....		.....		1.032	5	1.035 1.034 1.031	461 063 025
.....		.....		1.023	½	1.025 1.024 1.022	271 163 125
.....		.....		0.9967	½	0.9983 0.9979 0.9954	370 172 225
.....		.....		0.9567	½	0.9570 0.9553	363 235
.....		.....		0.9491	5	0.9504 0.9488	080 444
.....		.....		0.9360	1	0.9355	372
.....		.....		0.9291	2	0.9288	471
.....		.....		0.9079	2	0.9079	463
.....		.....		0.9066	4	$0.9065\alpha_1$	245
.....		.....		0.9068	3	$0.9065\alpha_2$	245

1. Mawsonite, Mt. Lyell, Tasmania, Australia,(Markham & Lawrence 1965), Debye-Scherrer (Co)
2. Mawsonite, Akenobe mine, Hyogo Prefecture, Japan, (Yamanaka & Kato 1976), Diffractometer (Cu/Ni)
3. Mawsonite, Kidd Creek mine, Kidd Township, Cochrane District, Ontario, Canada [TQ 74-560 (10)]*

a = 7.603±0.002Å , c = 5.358±0.001Å

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* Lattice parameters from structure refinement of Szymański(1976). Error terms are standard deviations.

ously observed with our X-ray camera. As well, the reflections appear in other powder patterns and in the calculated pattern using Cu$K\alpha$ radiation (J. T. Szymański, pers. comm.). Markham & Lawrence and Yamanaka & Kato observed a weak reflection at d = 3.34 and 3.378Å, respectively. Szymański stated that this reflection could not be indexed on his cell, although the calculated value of d = 3.40Å for the (120) reflection is closest to their values. Although (120) was not observed in the present study, it seems possible that it is an X-ray reflection of mawsonite and that neither the pattern of Markham & Lawrence nor that of Yamanako & Kato contains reflections attributable to impurities.

The strongly pseudocubic X-ray powder pattern of mawsonite is explicable if $a^2 \simeq 2c$ in terms of the unit cell and space group given by Szymański (1976). Thus, for reflections such as (110) and (001) in which $(h^2 + k^2)_{(110)} = 2l^2_{(001)}$ and $(h^2 + k^2)_{(001)} = 2l^2_{(110)}$, the two reflections will be nearly superimposed and unresolved. Although $P\bar{4}m2$ has no extinction requirements, the previous condition greatly reduces the number of discretely observable reflections.

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