

TIN SULPHIDES FROM THE DEPOSIT OF BRUNSWICK TIN MINES LIMITED

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ABSTRACT

The tin sulphides stannite, kesterite, stannoidite, mawsonite, and an unknown phase were found in samples from the deposit of Brunswick Tin Mines Limited, and their properties were used to determine the relationships for these minerals. It was confirmed that stannite and kesterite are members of separate solid-solution series and have different structures. Minerals with the stannite structure have compositions between $\text{Cu}_4\text{Fe}_2\text{Sn}_2\text{S}_8$ and $\text{Cu}_4\text{Fe}_{0.9}\text{Zn}_{1.1}\text{Sn}_2\text{S}_8$, and minerals with the kesterite structure have compositions between $\text{Cu}_4\text{Zn}_2\text{Sn}_2\text{S}_8$ and $\text{Cu}_4\text{Zn}_{0.9}\text{Fe}_{1.1}\text{Sn}_2\text{S}_8$. Extensive substitution occurs in these minerals, particularly in zinc-rich stannite and iron-rich kesterite which contain excesses of iron and zinc, up to 3.8% indium, and have deficiencies of copper and tin.

Stannoidite is associated with kesterite and some is exsolved from kesterite which suggests a stannoidite-kesterite solid-solution. An unknown phase with the composition midway between stannoidite and kesterite was found. This phase could be either an intermediate member in the solid-solution series or a new mineral.

INTRODUCTION

Five tin-bearing sulphides, stannite, kesterite, stannoidite, mawsonite, and an unknown phase have been found in samples from the W-Mo-Bi-Sn deposit of Brunswick Tin Mines Limited (previously Mount Pleasant Mines), located about 35 miles southwest of Fredericton, New Brunswick. Stannite and stannoidite (hexastannite) were reported and described by Boorman & Abbott (1967); kesterite and mawsonite were found during the course of a broad mineralogical study on this deposit (Petruck, in prep.), and the unknown phase was found during the present investigation. These minerals were restudied in detail to provide new data on their properties and relationships.

The minerals in this deposit occur as veins and disseminated grains in intensely silicified and greisenized rock in, and adjacent to, volcanic necks. The ore minerals are associated with fluorite and occur in three assemblages. Assemblage 1 consists of oxides and phosphates of W, Ti, Fe, Nb, Sn, Ta and rare earth elements; assemblage 2

of arsenopyrite, loellingite, molybdenite, and bismuth; and assemblage 3 of sulphides and cassiterite.

The tin-bearing sulphides in this deposit are present as constituents of the sulphide assemblage associated with cassiterite. The main sulphide minerals in the assemblage are sphalerite, chalcopyrite, tennantite, galena, pyrite, arsenopyrite, and tin-bearing sulphides.

METHOD OF INVESTIGATION

The minerals were studied by ore microscopy, x-ray diffraction, and electron microprobe analysed with a Materials Analysis Company (MAC) model 400 electron microprobe, using synthetic SnS, ZnS and InAs, natural chalcopyrite, and cadmium and tin metals as standards. The data were processed with the computer program of Rucklidge (1967). Statistical accuracy of analysis could not be determined because of minor compositional variations in the minerals from spot to spot. It is judged that the results obtained are within 2% of the amount present.

Reflectance and microhardness measurements were made according to the method described by Petruck *et al.* (1970), except that reflectance spectra were obtained by taking a series of

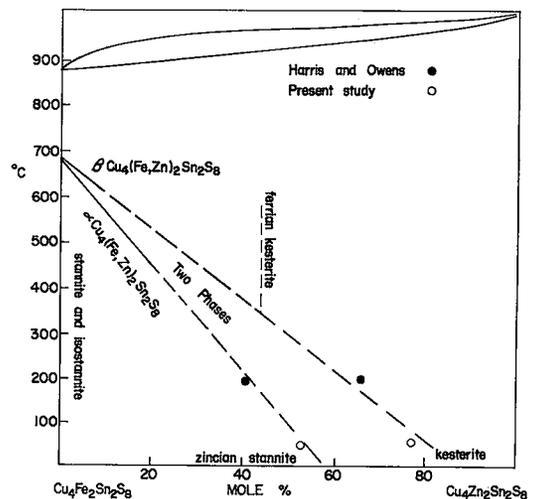


Fig. 1. Provisional phase equilibrium diagram for the $\text{Cu}_4\text{Fe}_2\text{Sn}_2\text{S}_8$ - $\text{Cu}_4\text{Zn}_2\text{Sn}_2\text{S}_8$ system.

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readings at intervals of 20 nm and drawing a line of best fit through them. Values at specific wavelengths were taken from these lines.

STANNITE-KESTERITE

Stannite and kesterite are iron and zinc end-members, respectively, of the $\text{Cu}_4\text{Fe}_2\text{Sn}_2\text{S}_8$ - $\text{Cu}_4\text{Zn}_2\text{Sn}_2\text{S}_8$ mineral group. Springer (1972) prepared the first phase diagram for this system. He showed that material having the stannite composition can occur in two tetragonal forms at 680°C and at progressively lower temperatures as the zinc content in the iron-zinc position increases (Fig. 1). He referred to his forms as α and β $\text{Cu}_2(\text{Fe,Zn})\text{SnS}_4$, respectively, in keeping with the suggestion by Ramdohr (1960) and correlated them with natural minerals found by Harris & Owens (1972). This correlation was extended in this study and used as a basis for

characterizing the minerals from the deposit of Brunswick Tin Mines Limited. The correlation was made by analysing the properties of all the phases, as given below, and the results are summarized in a provisional phase diagram (Fig. 1).

α -form, synthetic tetragonal stannite

The α -form of Springer (1972) applies to synthetic tetragonal material prepared between 300 and 680°C, and its composition ranges from $\text{Cu}_4\text{Fe}_2\text{Sn}_2\text{S}_8$ to the boundary of the two-phase field (Fig. 1). The α -form is assumed to be the same as the synthetic tetragonal stannite of Franz (1971), prepared at 600°C, because the lines 011, 013, 121, 123, and 031 are absent from the x-ray powder patterns of both (see synthetic tetragonal stannite, Fig. 2). These absences indicate that the structure of the α -form is incompatible with the structure of tetragonal stannite

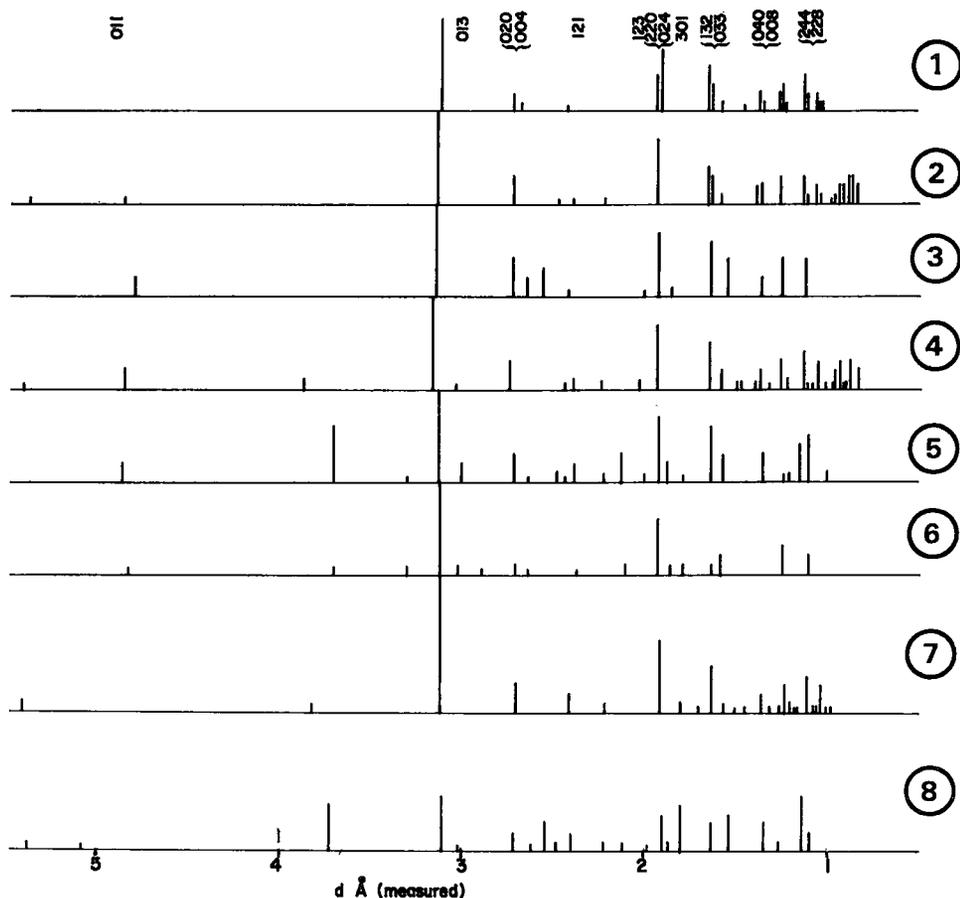


FIG. 2. X-ray powder patterns for tin sulphides: (1) synthetic tetragonal stannite (from Franz 1971), (2) natural stannite (from Berry & Thompson 1962), (3) zincian stannite (sample 4-900), (4) ferrian kesterite (zincian stannite from Berry & Thompson 1962), (5) ferrian kesterite (sample 92-901.5), (6) kesterite (sample 29-750), (7) synthetic cubic stannite (from Franz 1971), (8) stannoidite (sample 29-750).

determined by Brockway (1934). Franz (1971) suggested that his synthetic material has the chalcopyrite structure. Furthermore, the α -form appears to have a different structure from that of natural stannite because natural iron-rich stannite displays the 011 and 121 lines (Fig. 2), and a natural zinc-rich one, found in this study, displays the 011, 123, and 031 lines (see zincian stannite Fig. 2). This apparent structural difference between the α -form and natural stannite suggests that the α -form is not the same as natural stannite even though it has the same composition. It may, however, transform to natural stannite under conditions met in ore deposits.

Stannite

The mineral name stannite, as used in this paper, is applied to the naturally-occurring material having the x-ray powder pattern given by Berry & Thompson (1962) and the composition $\text{Cu}_4\text{Fe}_2\text{Sn}_2\text{S}_8$. The name is also applied to material enriched in zinc up to $\text{Cu}_4(\text{Fe}_{1.2}\text{Zn}_{0.8})\text{Sn}_2\text{S}_8$. The x-ray powder pattern (Fig. 2) displays the line pairs 132 and 033, 040 and 088, 244 and 228; in this respect the pattern is the same as that of the synthetic stannite of Franz (1971), although the synthetic one also has 020 and 004, and 220 and 024 line pairs. The mineral is anisotropic, and olive-grey in reflected light.

Only a small amount of stannite, occurring as minute rounded inclusions in galena (Fig 3),

was found in samples from the deposit of Brunswick Tin Mines Limited by microprobe analyses. Its identity was not confirmed by x-ray diffraction because the grains were too small, Microprobe analyses and atomic proportions, calculated on the basis of 8 metal atoms, are given in Table 1 for six stannite inclusions in galena. The results show that the stannite in this deposit has a stoichiometric composition and contains about 0.1% In.

Zincian stannite

The name zincian stannite is used, in the context of this paper, for naturally-occurring material that has the composition of the zinc-rich member in the field containing stannite, but will also be applied to material enriched in iron, up to $\text{Cu}_4(\text{Fe}_{1.2}\text{Zn}_{0.8})\text{Sn}_2\text{S}_8$. A complete solid-solution is assumed between stannite and zincian stannite. The x-ray powder pattern of zincian stannite is approximately the same as that of stannite, but the line pairs are merged. Springer (1972) states that the separation between the line pairs 020 and 004, and 220 and 024, decreases non-linearly as the zinc content in stannite increases, and that the lines merge when the zinc content in the iron-zinc position is about 40%, i.e., when the composition is $\text{Cu}_4(\text{Fe}_{1.2}\text{Zn}_{0.8})\text{Sn}_2\text{S}_8$. This mineral appears to have the same optical properties as stannite.

A significant amount of zincian stannite was found in samples from the Brunswick Tin de-

TABLE 1. CHEMICAL ANALYSES AND CHEMICAL MOLECULAR PROPORTIONS

Sample number	Mineral	Chemical Analyses (wt. %)						Molecular Proportions ^a						Fe/ Fe+Zn			
		Cu	Sn	In	Fe	Zn	Cd	S	Total	Cu	Sn	In	Fe		Zn	Cd	S
1-900 ^{xx}	stannite	29.8	27.6	0.1	10.0	3.9	--	29.5	100.9	3.97	1.98	0.01	1.53	0.51	--	7.84	0.75
1-900 ^{xx}	stannite	29.7	29.0	0.1	11.7	1.4	--	29.5	101.4	4.07	1.94	0.01	1.80	0.18	--	8.02	0.91
1-900 ^{xx}	stannite	29.9	26.9	0.1	9.6	4.5	--	29.8	100.0	4.00	1.94	0.01	1.47	0.58	--	7.93	0.72
1-900 ^{xx}	stannite	29.2	26.5	0.1	8.8	6.2	--	29.1	99.9	3.95	1.90	0.01	1.34	0.80	--	7.77	0.63
4-900 ^{xx}	stannite	29.1	27.2	0.1	9.9	4.3	--	29.6	100.2	3.95	1.97	0.01	1.51	0.56	--	7.97	0.73
4-900 ^{xx}	stannite	29.0	27.2	0.2	9.1	6.6	--	30.1	102.2	3.85	1.92	0.02	1.36	0.85	--	7.90	0.61
4-900 ^x	Zn stan ^b	28.0	25.6	0.3	9.0	8.5	--	29.9	101.3	3.71	1.82	0.02	1.35	1.10	--	7.84	0.55
4-900 ^x	Zn stan	27.4	25.6	0.3	8.7	9.7	--	30.0	102.2	3.66	1.80	0.02	1.29	1.23	--	7.80	0.53
4-900 ^x	Zn stan	27.9	26.1	0.2	8.3	10.4	--	29.9	102.3	3.59	1.83	0.02	1.24	1.32	--	7.77	0.48
4-900 ^x	Zn stan	27.4	26.1	0.2	8.0	11.4	--	30.0	103.1	3.56	1.81	0.02	1.18	1.43	--	7.73	0.45
4-900	Zn stan	27.4	26.1	0.3	9.0	8.3	--	30.2	101.3	3.67	1.86	0.03	1.38	1.06	--	8.01	0.57
92-901.5	Fer. kest ^a	27.8	25.2	1.5	8.0	7.9	0.2	29.0	99.6	3.77	1.83	0.12	1.24	1.03	0.01	7.79	0.54
92-901.5	Fer. kest	26.8	23.4	3.6	7.6	9.4	0.1	29.3	100.2	3.62	1.69	0.27	1.17	1.24	0.01	7.86	0.48
92-901.5	Fer. kest	26.9	23.1	2.6	8.9	8.4	0.1	29.6	99.6	3.65	1.67	0.20	1.37	1.10	0.01	7.93	0.55
6-900	Fer. kest	26.9	26.1	1.3	8.1	8.9	--	29.9	101.2	3.63	1.89	0.10	1.22	1.16	--	7.77	0.51
92-901.5	Fer. kest	25.6	22.4	3.8	7.8	10.5	0.1	29.7	99.9	3.48	1.63	0.29	1.20	1.39	0.01	7.98	0.46
21-750*	Zn stan ^b	27.4	26.0	0.2	7.3	9.1	--	29.3	99.3	3.67	1.86	0.02	1.11	1.34	--	7.78	0.45
21-750*	kesterite	27.0	25.8	0.2	3.7	13.7	--	29.0	99.4	3.70	1.89	0.02	0.57	1.82	--	7.88	0.24
52-523	kesterite	29.7	26.9	n11	1.4	13.8	--	29.7	101.5	4.02	1.94	--	0.22	1.82	--	7.94	0.11
29-750	kesterite	29.5	23.9	0.5	2.5	14.5	--	29.8	100.7	3.97	1.71	0.04	0.39	1.89	--	7.92	0.17
29-750**		31.0	26.4	0.7	2.8	12.1	--	29.1	102.1	4.12	1.88	0.04	0.41	1.55	--	7.67	--
29-750**		32.4	24.3	0.5	3.5	12.0	--	29.6	102.3	4.23	1.64	0.04	0.52	1.52	--	7.61	--
52-523	unknown	34.5	22.6	--	6.4	7.7	--	29.5	100.7	4.69	1.64	--	0.99	1.10	--	7.95	--
29-750	stannoidite	38.5	19.5	--	9.1	5.1	--	29.6	101.8	7.81	2.10	--	2.09	1.00	--	11.87	--
90-1261	mawsonite	43.9	14.4	--	12.7	--	--	29.9	100.9	5.98	1.05	--	1.97	--	--	8.07	--

x-Exsolution in sphalerite xx-Inclusions in galena * Zincian stannite-kesterite exsolution **Bulk composition of kesterite with stannoidite exsolution

^a-Calculated on basis of metals=8.00 in stannite and kesterite, 8.33 in unknown, 13.00 in stannoidite, 9.00 in mawsonite. ^b-Zn stan=zincian stannite ^a-Fer. kest=ferrian kesterite

posit. The mineral occurs as small irregular grains, as exsolution grains from sphalerite (Fig. 4), as rounded inclusions in galena, and as part of a grain composed of exsolved zincian stannite and kesterite (Fig. 5). Six individual microprobe analyses and calculated atomic proportions for zincian stannite in two samples are included in Table 1. The results show that the mineral contains up to 55 at.% zinc ($Fe/Fe + Zn = 0.45$) in the iron-zinc position, and that

zincian stannite containing more than 40% zinc is deficient in copper and tin and has excesses of iron and zinc. Obviously, the iron and zinc replace the copper and tin. The results also show that zincian stannite in this deposit contains up to 0.3% indium, and a plot of atomic proportions of tin versus indium in tin sulphides indicates that indium replaces tin (Fig. 6).

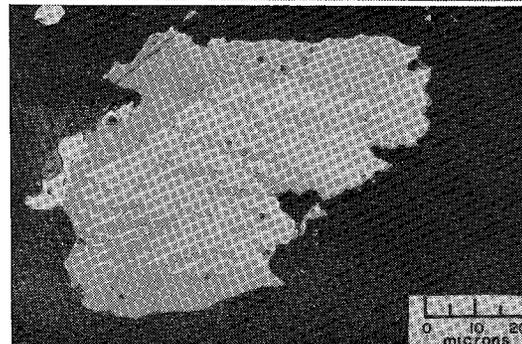
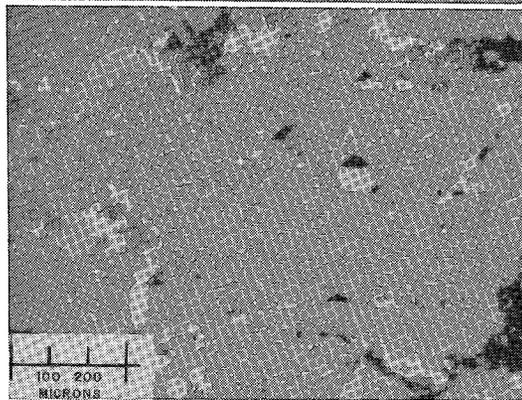
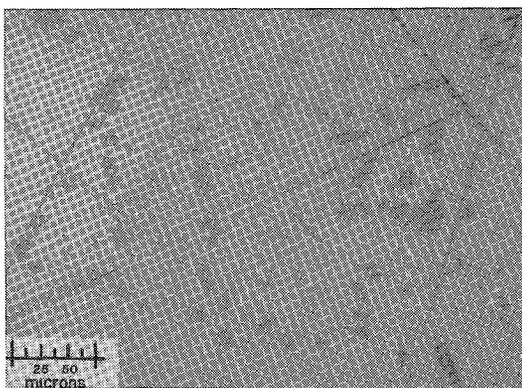


FIG. 3. Rounded stannite inclusions in galena.

FIG. 4. Stannite (light grey) and chalcopyrite (white) exsolution in sphalerite (grey).

FIG. 5. A grain composed of exsolved zincian stannite (white) and kesterite (grey).

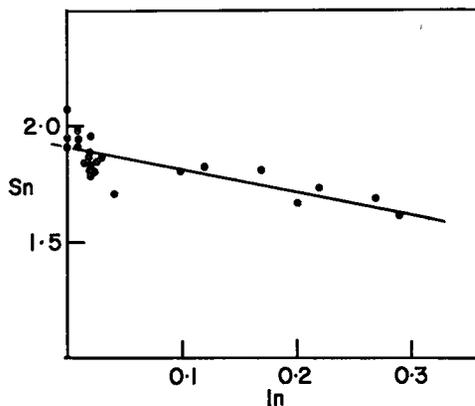


FIG. 6. Relationship between tin and indium in the stannite-kesterite group minerals (in atoms per unit cell).

β -form, synthetic $Cu_4(Fe,Zn)_2Sn_2S_8$

The term β -form is applied to synthetic material within the solid-solution field on the right side of the two phase field (Fig. 1). Its composition ranges from the iron to the zinc end-members. According to Springer (1972) this phase is stable above 680°C for the iron end-members, and at progressively lower temperatures as the zinc content increases. It is assumed to be tetragonal because the x-ray diffraction is similar to the "zincian stannite" of Berry & Thompson (1962). No naturally-occurring equivalents of iron-rich β - $Cu_4(Fe,Zn)_2Sn_2S_8$ have been found to date, but the zinc-rich member (kesterite) is known and intermediate-composition varieties, containing up to 55% iron, were found in this study.

Ferrian-kesterite

For purposes of this paper the name ferrian kesterite is used for material that has the x-ray powder diffraction pattern of kesterite but contains from 25% to 55% iron in the zinc-iron position. This mineral is described separately from kesterite because it is the main tin sulphide in the Brunswick Tin deposit and is the most iron-rich phase of kesterite found to date. It occurs largely as masses containing sphalerite and chalcopyrite inclusions and chalcopyrite

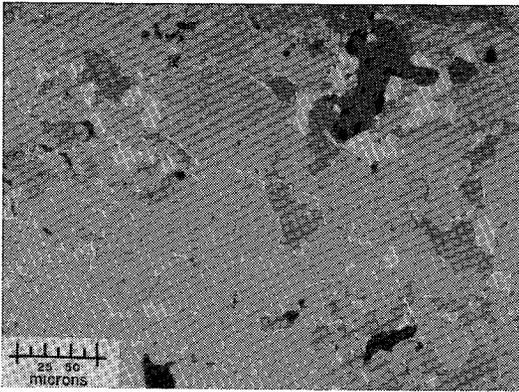


FIG. 7. Massive ferrian kesterite (grey) containing chalcopyrite veinlets and exsolutions (white) and sphalerite inclusions (dark grey).

veinlets (Fig. 7). Ferrian kesterite has the x-ray diffraction pattern (Fig. 2) reported as "zincian stannite" by Berry & Thompson (1962). Five microprobe analyses and calculated atomic proportions for the mineral in two samples are included in Table 1. The results show that ferrian kesterite contains up to 55 wt.% iron ($Fe/Fe + Zn = 0.55$) in the zinc-iron, that the mineral is copper- and tin-deficient, has excesses of iron and zinc, and contains up to 3.8% indium.

Ferrian kesterite appears to have the same optical properties as zincian stannite and stannite, but has a higher reflectivity than kesterite and is not as grey. When etched with HNO_3 , however, ferrian kesterite is a darker grey than stannite. Its reflectance spectrum is shown in Figure 8. The reflectance spectrum for ferrian kesterite has a small hump in the wavelength range of 500 to 600 nm, whereas the kesterite spectrum decreases proportionately with increasing wavelength. These differences in the reflectance spectra account for the different colours

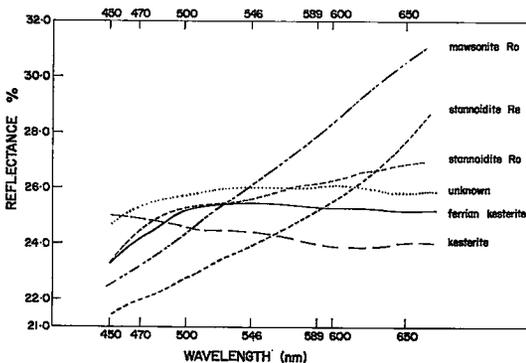


FIG. 8. Reflectance spectra for ferrian kesterite, kesterite, stannoidite, the unknown phase, and mawsonite.

of these minerals. The micro-indentation hardness of ferrian kesterite is included in Table 2.

Kesterite

The mineral name kesterite refers to the zinc end-member of the series ($Cu_4Zn_2Sn_2S_8$), but as used in this paper extends to $Cu_4(Zn_{1.5}Fe_{0.5})Sn_2S_8$ along the solid-solution field towards ferrian kesterite. Kesterite can be distinguished optically from the other three minerals of this group because it is not as strongly anisotropic, is greyer in reflected light (Table 2 and Fig. 8), and has a higher micro-indentation hardness value (Table 2). The mineral was found in the Brunswick Tin deposit where chalcopyrite was rare and where some tennantite and arsenopyrite were present. Kesterite is commonly associated with stannoidite and sphalerite and occurs as irregular grains in tennantite. (Fig. 9), as exsolution gobules from sphalerite, and as exsolution grains from a complex grain containing exsolved zincian stannite and kesterite (Fig. 5). Some kesterite contains narrow exsolution lamellae of stannoidite (Fig. 10). Three microprobe analyses and their atomic proportions are given for the kesterite in this deposit in Table 1. The results show that two kesterite grains have nearly stoichiometric compositions whereas two are deficient in tin and/or copper and have excesses of iron plus zinc. The kesterite studied contains up to 0.5% In.

Isostannite

The mineral name isostannite is applied to cubic stannite, $Cu_4Fe_2Sn_2S_8$. Cubic stannite has been prepared by Franz (1971) at 420°C and a naturally occurring material, referred to as isostannite, has been reported by Claringbull & Hey (1955). This suggests that isostannite may be stable at a lower temperature than the synthetic tetragonal stannite (α -form). Its composition appears to be close to that of tetragonal

TABLE 2. MICRO-INDENTATION HARDNESS AND REFLECTANCE DATA FOR TIN SULPHIDES

Mineral & sample no.	Indentation hardness VHN	Reflectance (%) at: (nm)				
		470	546	589	650	
kesterite 29-750	430±17 mean of 5	Ro	24.9	24.4	24.8	24.0
			24.1	25.4	25.3	25.1
ferrian kesterite 92-901.5	281±15 mean of 5					
unknown 52-523	339 1 reading		25.3	26.0	26.1	25.8
stannoidite 29-750	280 mean of 3	Ro	24.3	25.6	26.1	26.9
		Re	21.9	23.9	25.1	27.7
mawsonite 90-1261	240 mean of 3	Ro	23.1	26.0	27.8	30.5

stannite hence, it is shown on the binary diagram (Fig. 1) in the same position. The x-ray diffraction pattern of cubic stannite, reported by Franz (1971), is included in Figure 2.

Two-phase field (zincian stannite-ferrian kesterite exsolutions)

Springer (1972) has shown that a two-phase field separates the two solid-solution fields containing the α - and β -forms. He defined the boundary between the α -form and the two-phase field for the temperature range 300 to 680°C (Fig. 1), and inferred a boundary between the β -form and the two-phase field. By use of his diagram the compositions of co-existing or exsolved mineral pairs should fall on each side of the two phase field a specific temperatures. An exsolved mineral pair of zincian stannite and ferrian kesterite has been reported by Harris & Owens (1972) (zincian stannite = 59% Fe and 41% Zn, and ferrian kesterite = 35% Fe and 65% Zn), and an exsolved mineral pair of zincian stannite and kesterite were found in this study (Sample 21-750 Fig. 5; zincian stannite = 45% Fe and 55% Zn, and kesterite = 24% Fe and 76% Zn). The zincian stannites from these two mineral pairs, plotted on the extension of the boundary between the α -form and the two-phase field of Springer (1972), give exsolution temperatures of 200°C and 50°C, respectively (Fig. 1). The corresponding ferrian kesterite and kesterite plotted at the appropriate temperatures suggests that a wider two-phase field is expected than proposed by Springer (1972) when natural materials are considered. On the basis of these data Springer's diagram is revised to show the wider two-phase field (Fig. 1).

STANNOIDITE

Stannoidite was first described as a new mineral by Kato (1969), but it had been reported previously as hexastannite and yellow stannite (Nakamura 1961; Shimizu *et al.* 1966; Markham & Lawrence 1965; Levy 1967; Boorman & Abbott 1967). Kato (1969) proposed the formula

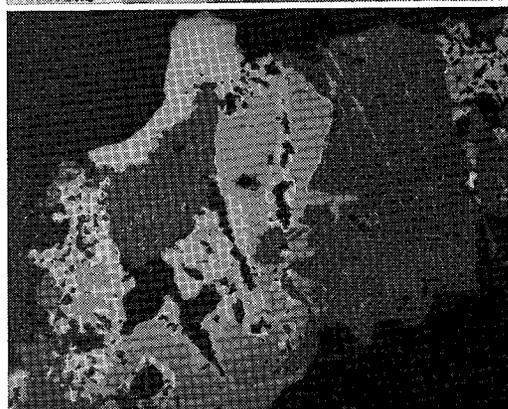
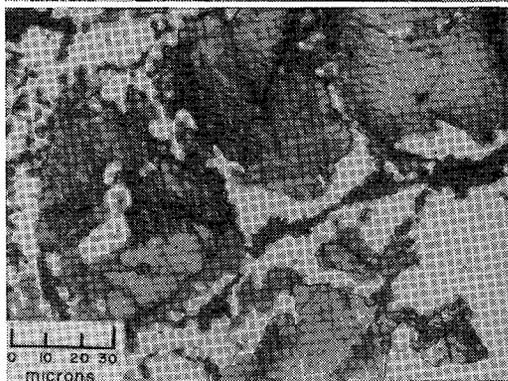
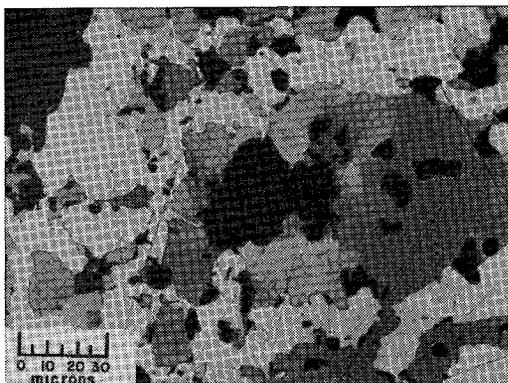


FIG. 9. Kesterite (grey) intergrown with stannoidite (light grey). The kesterite and stannoidite grains occur as inclusions in tetrahedrite (white). The black areas represent pits on the polished surface.

FIG. 10. Kesterite with finely laminated exsolved stannoidite (etched with HNO_3 to bring out exsolution).

FIG. 11. The unknown phase (grey with square pit) in a complex grain composed of chalcopyrite (light grey) with exsolved kesterite and stannoidite, and tennantite (white).

FIG. 12. Mawsonite (grey) intergrown with arsenopyrite (white), all in gangue (black).

$\text{Cu}_5(\text{Fe,Zn})_2\text{Sn}_2\text{S}_8$, but chemical analyses of hexastannite by Boorman & Abbott (1967), Springer (1968), and Markham & Lawrence (1965) are close to $\text{Cu}_8(\text{Fe,Zn})_3\text{Sn}_2\text{S}_{12}$. This composition corresponds closely to the composition of stannoidite studied from this deposit (Table 1). Kato (1969) determined that stannoidite has orthorhombic symmetry $a = 10.76$, $b = 5.40$, and $c = 16.09 \text{ \AA}$. The x-ray diffraction pattern is included in Figure 2. The stannoidite in this deposit occurs primarily as small irregular grains in sphalerite and tennantite and is commonly associated with kesterite as intergrowths (Fig. 9), and as exsolution lamellae from kesterite (Fig. 10), and some surrounds kesterite grains. This stannoidite-kesterite relationship agrees with observations made by Oen (1970). Reflectivity and micro-indentation hardness data for the mineral studied are included in Table 2.

UNKNOWN PHASE

An unknown phase was found in a complex grain as an intergrowth with sphalerite, chalcopyrite, and tennantite (Fig. 11) in a sample containing significant amounts of kesterite and stannoidite in sphalerite and tennantite. The composition, reflectance, and micro-indentation hardness of this phase fall midway between those of kesterite and stannoidite (Tables 1 and 2). This phase could either be a new mineral or could represent part of a solid solution between kesterite and stannoidite. The grain is too small to x-ray.

MAWSONITE

Mawsonite, $\text{Cu}_6\text{Fe}_2\text{Sn}_1\text{S}_8$, was found only in one sample from this deposit. This sample contained arsenopyrite, tennantite, and wolframite, with the mawsonite occurring as irregular grains in tennantite, arsenopyrite, and gangue (Fig. 12). The wolframite in this deposit contains about 20% FeO (Petruk, in prep.).

The composition, reflectance, and micro-indentation hardness for the mineral are given in Tables 1 and 2. The mineral is brownish-orange in reflected light, is strongly anisotropic, and is somewhat similar to stannoidite although it is lighter orange and more anisotropic. The shape of the reflectance spectrum (R_o) for mawsonite is similar to that of stannoidite (R_e) (Fig. 8), which explains the similar colour for these two minerals in reflected light.

DISCUSSION

The compositions of the tin-bearing sulphides are plotted on a ternary (Sn + In)-Cu-(Fe + Zn) diagram (Fig. 13) to show their inter-

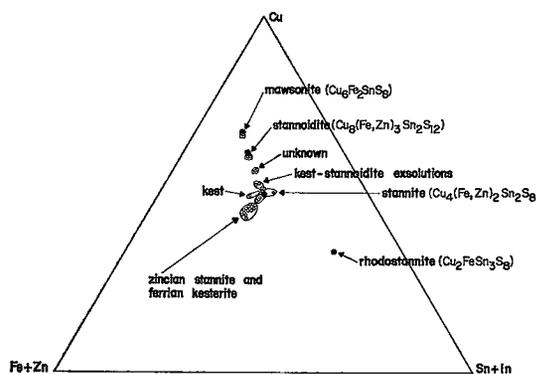


FIG. 13. Ternary (Fe + Zn) - Cu - (Sn + In) diagram showing positions for theoretical compositions of tin sulphides (solid dots) and for data on samples from the Brunswick Tin deposit (open circles). The diagram does not allow for variations in sulphur content.

relationships. This diagram, however, disregards sulphur and could, at a glance, give the false impression that the metal : sulphur ratio is constant in all minerals. It is, therefore, supplemented by Table 3 which shows that the tin-

TABLE 3. METAL:METAL AND METAL:SULPHUR RATIOS OF THE TIN SULPHIDES

Mineral	Cu:Sn	Metal:Sulphur	Fe/Fe+Zn
mawsonite	6:1	9:8	1.00
stannoidite	4:1	8.667:8(13:12)	1.00 to 0.67
unknown phase	3:1	8.33:8(25:24)	0.50
stannite and zincian stannite	2:1	8:8	1.00 to 0.45
kesterite and ferrian kesterite	2:1	8:8	0.0 to 0.55
rhodostannite	2:3	6:8	1.00

bearing minerals have specific metal : sulphur and Cu : Sn ratios. The iron and zinc contents, on the other hand, are variable in some minerals and constant in others. Figure 14 shows that the iron : zinc ratios for the stannite-zincian stannite solid solution series ranges from the iron end-member to $\text{Fe/Fe} + \text{Zn} = 0.45$; for the kesterite-ferrian kesterite solid solution series it ranges from the zinc end-member to $\text{Fe/Fe} + \text{Zn} = 0.55$; for stannoidite it ranges from the iron end-member to $\text{Fe/Fe} + \text{Zn} = 0.67$. Furthermore, the unknown phase contains equal quantities of iron and zinc, and only iron-bearing varieties have been found for mawsonite and rhodostannite.

The synthetic tetragonal stannite (α -form), stannite, zincian stannite, and isostannite have different x-ray diffraction powder-patterns, but

all appear to lie within the same compositional field. This suggests that the differences may be temperature-dependent. On the other hand, because precise compositions of these phases are not established, the differences in powder patterns may be dependent on composition, particularly on the metal: sulphur ratio. It is also significant that the structures of these phases are not well established, thus the differences among the powder patterns cannot be defined with a large degree of confidence.

A characteristic that may be significant is that iron and zinc in zincian stannite and ferrian kesterite in the deposit of Brunswick Tin Mines Limited, substitute for copper and tin to an excess of 30% from stoichiometry. The reason for this is not apparent.

The unknown phase found in this study has a composition midway between that of stannoidite and kesterite. This phase could either be a new mineral or part of the solid solution between stannoidite and kesterite. Grains of kesterite with exsolved stannoidite have been found in this ore (Fig. 10) which indicates that at least some solid solution exists between stannoidite and kesterite. The solid-solution field could extend to the composition of the unknown phase or even to stannoidite. On the other hand, the bulk composition of the kesterite with exsolved stannoidite is similar to that of kesterite; thus, the solid-solution field could be limited near kesterite, and the unknown phase would then be a new mineral. The existence of such a new mineral, however, cannot be readily explained because kesterite co-exists with stannoidite and the position of tie lines to such a mineral cannot be envisaged.

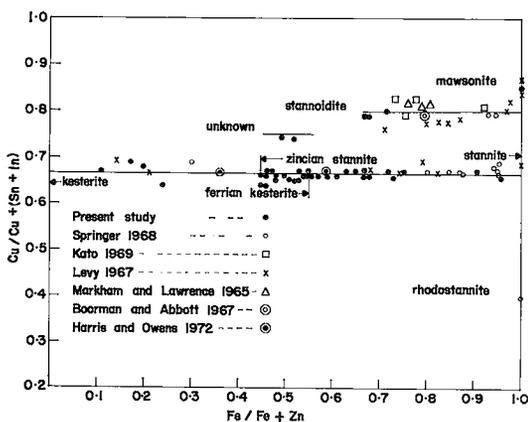


Fig. 14. Binary Cu/Cu + Sn + In vs. Fe/Fe + Zn diagram showing compositional variations of tin sulphides found in this study as well as those reported in the literature. This diagram does not allow for variations in sulphur content,

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