

THE RELATIVES OF STANNITE IN THE LIGHT OF NEW DATA

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ABSTRACT

Two new minerals of approximately the same composition as that of stannite but differing crystal structures have been discovered. Ferrokesterite occurs in greisen-bordered sulfide veins in granite from the Cligga mine, Perranzabuloe, Cornwall, England. The mineral is tetragonal with space group $\bar{I}4$, $Z=2$; a 5.433 and c 10.884 Å; D_{calc} 4.490 g cm⁻³. Ferrokesterite has hardness about 4 (Mohs), microhardness (VHN_{100}) 238. Cleavage is distinct parallel to {110}, and parting develops parallel to {001}. Results of an electron-microprobe analysis gave the formula $\text{Cu}_{1.99}(\text{Fe}_{0.67}\text{Zn}_{0.33})_{\Sigma 1.00}\text{Sn}_{0.99}\text{S}_{4.02}$ for the holotype specimen, corresponding to $\text{Cu}_2(\text{Fe,Zn})\text{SnS}_4$ and approaching the end-member $\text{Cu}_2\text{FeSnS}_4$. The strongest reflections in the X-ray powder pattern are: 3.13(10) (112), 1.919(6) (220,024), 1.110(4) (244,228). The mineral is a polymorph of stannite and forms a solid solution with kesterite, of which it is the iron-analog. Petrukite occurs in polymetallic veins associated with granitic plutons at the Herb claim, Cassiar District, British Columbia; the Ikuno mine, Hyogo Prefecture, Japan and the Mount Pleasant mine, Charlotte County, New Brunswick. The mineral is orthorhombic with space group $Pmn2_1$, $Z=2$, a 7.6671, b 6.4399, c 6.2605 Å (Herb); a 7.7050, b 6.4462, c 6.2757 Å (Ikuno) and a 7.6858, b 6.4395, c 6.2947 Å (Mount Pleasant). Microhardness (VHN_{100}) is 319. Results of an electron-microprobe analysis gave the average formula $(\text{Cu}_{1.85}\text{Fe}_{0.95}\text{Zn}_{0.24}\text{Ag}_{0.03})_{\Sigma 3.07}(\text{Sn}_{0.85}\text{In}_{0.05})_{\Sigma 0.94}\text{S}_{3.99}$ for Herb claim specimens, corresponding to the general formula $(\text{Cu,Fe,Zn,Ag})_3(\text{Sn,In})\text{S}_4$ where $\text{Cu} > \text{Fe} > \text{Zn} \gg \text{Ag}$ and $\text{Sn} > \text{In}$. The composition is somewhat variable and can be accounted for by a coupled substitution $\text{Cu} + \text{Sn} \rightleftharpoons \text{In} + \text{Zn}$. Indium substitution appears essential for the stability of the mineral, causing a distortion in a ferrokesterite-like atomic arrangement and resulting in limited disorder between Cu and (Fe,Zn). The strongest reflections in the X-ray powder pattern are: 3.13(10)(002), 1.915(6)(400), 1.106(6)(315), 1.243(5)(151) and 2.712(4)(121) for the Herb claim specimen. Holotype isostannite, as well as toptype occurrences, were investigated and found to be identical to a member of a kesterite-ferrokesterite solid-solution series. Thus, no cubic polymorph of stannite exists, although its as yet unsubstantiated existence is not precluded.

Keywords: new minerals, petrukite, ferrokesterite, isostannite, kesterite, Cornwall, New Brunswick, British Columbia, Japan.

SOMMAIRE

Nous avons découvert deux espèces minérales nouvelles

possédant à peu près la même composition chimique que la stannite mais qui sont distinctes dans leur structure. On trouve la *ferrokesterite* dans des filons de sulfures à bordures greisenisées dans un granite dans la mine de Cligga, à Perranzabuloe, en Cornouaille (Angleterre). C'est un minéral tétragonal, qui cristallise dans le groupe spatial $\bar{I}4$, $Z=2$; a 5.433, c 10.884 Å; Sa densité calculée est 4.490, et sa dureté (échelle de Mohs), 4; sa microdureté (VHN_{100}) est 238. Un clivage distinct est parallèle à {110}; le minéral se sépare le long de {001}. Les résultats d'une analyse chimique à la microsonde électronique mènent à la formule $\text{Cu}_{1.99}(\text{Fe}_{0.67}\text{Zn}_{0.33})_{\Sigma 1.00}\text{Sn}_{0.99}\text{S}_{4.02}$ pour l'échantillon holotypique, ce qui correspond à $\text{Cu}_2(\text{Fe,Zn})\text{SnS}_4$ et qui s'approche du pôle $\text{Cu}_2\text{FeSnS}_4$. Les trois réflexions les plus intenses du cliché de diffraction [d en Å(1)(hkl)] sont: 3.13(10)(112), 1.919(6)(220,024), et 1.110(4)(244,228). La ferrokesterite est un polymorphe de la stannite et forme une solution solide avec la kesterite, dont c'est l'analogue ferrique. La *petrukite* fait partie d'une association polymétallique fissurale liée à des plutons granitiques 1) à l'indice de Herb, dans le district de Cassiar, en Colombie-britannique, 2) à la mine Ikuno, préfecture de Hyogo, au Japon, et 3) à la mine de Mount Pleasant, comté de Charlotte, au Nouveau-Brunswick. C'est un minéral orthorhombique, groupe spatial $Pmn2_1$, $Z=2$, a 7.6671, b 6.4399, c 6.2605 Å (Herb), a 7.7050, b 6.4462, c 6.2757 Å (Ikuno), et a 7.6858, b 6.4395, c 6.2947 Å (Mount Pleasant). La microdureté (VHN_{100}) est de 319. La composition chimique moyenne, d'après une analyse à la microsonde électronique, serait $(\text{Cu}_{1.85}\text{Fe}_{0.95}\text{Zn}_{0.24}\text{Ag}_{0.03})_{\Sigma 3.07}(\text{Sn}_{0.85}\text{In}_{0.05})_{\Sigma 0.94}\text{S}_{3.99}$ pour l'échantillon de l'indice de Herb, ce qui correspond à la formule générale $(\text{Cu,Fe,Zn,Ag})_3(\text{Sn,In})\text{S}_4$, dans laquelle $\text{Cu} > \text{Fe} > \text{Zn} \gg \text{Ag}$ et $\text{Sn} > \text{In}$. La composition varie légèrement selon le couple de substitution $\text{Cu} + \text{Sn} \rightleftharpoons \text{In} + \text{Zn}$. La présence de l'indium serait essentielle pour assurer la stabilité de la petrukite, en causant une distorsion de l'agencement atomique du modèle de la ferrokesterite et un faible désordre impliquant Cu et (Fe,Zn). Les cinq raies les plus intenses du cliché de diffraction (méthode des poudres) sont 3.13(10)(002), 1.915(6)(400), 1.106(6)(315), 1.243(5)(151) et 2.712(4)(121) pour l'échantillon qui provient de l'indice de Herb. L'isostannite holotypique, de même que les échantillons toptypiques, ont été examinés et trouvés identiques à un membre de la solution solide entre kesterite et ferrokesterite. Il est donc clair que l'existence du polymorphe cubique de la stannite n'est pas établie, quoiqu'elle n'est pas exclue.

(Traduit par la Rédaction)

Mots-clés: nouvelles espèces minérales, petrukite, ferrokesterite, isostannite, kesterite, Cornouaille, Nouveau-Brunswick, Colombie-britannique, Japon.

INTRODUCTION

In a previous paper, Kissin & Owens (1979) attempted to summarize the status of tin-bearing sulfide minerals in the system Cu-Fe-Zn-Sn-S. At that time, only one mineral of stannite composition $[\text{Cu}_2(\text{Fe},\text{Zn})\text{SnS}_4]$ was discussed, as we already suspected that isostannite, the purported cubic polymorph of stannite, is in fact identical to kesterite (Kissin & Owens 1975). Continuing work on minerals of this system has not only confirmed the identity of isostannite as kesterite or ferrokesterite, but has uncovered two new minerals of stannite-like composition but differing in structure.

The new mineral *ferrokesterite* $[\text{Cu}_2(\text{Fe},\text{Zn})\text{SnS}_4]$ is the iron analog of kesterite; although of tetragonal symmetry like stannite, it differs in having the space group $\bar{I}4$ of kesterite. Ferrokesterite approaches the iron end-member of a kesterite-ferrokesterite solid-solution series and is a polymorph of stannite. The mineral occurs in the Cligga mine, Perranzabuloe, Cornwall, England. The material is preserved as no. 14747 of the National Reference Collection of the Geological Survey of Canada, which acquired it as a small hand specimen labeled "isostannite" through purchase of the Barstow Collection. Two polished sections labeled A and B and a polished grain mount section were made from material cut from the hand specimen. Polished section A and the grain mount are designated as cotypes and have been deposited with the Geological Survey of Canada, Ottawa (no. 65048) and the British Museum (Natural History), London (no. BM 1984, 844), respectively. The polished section B and the hand specimen are designated metatypes and also were deposited with the Geological Survey of Canada.

The new mineral *petrukite* has a composition very similar to that of stannite, but slight nonstoichiometry involving the Cu and (Fe,Zn) sites is present. A small but perhaps essential amount of In is present in the Sn site as well. The symmetry of the crystal structure, however, is decreased to orthorhombic $Pmn2_1$. The mineral was discovered in three localities: 1) the Herb claim, on Turnagain River, Cassiar District, British Columbia; 2) the Mount Pleasant mine, Charlotte County, New Brunswick, and 3) the Kanagase vein, Ikuno mine, Hyogo Prefecture, Japan. Cotypes in polished section from all three localities have been deposited in the National Reference Collection of the Geological Survey of Canada (nos. 65049, 65050, 65051 and 65052, respectively). Metatype specimens in polished section from the Herb claim have been deposited in the American Museum of Natural History (AMNH T98797), British Museum (Natural History) (BM 1987,94), Musée de Minéralogie, Ecole Nationale Supérieure des Mines, Paris (T44352) and the National Museum of Natural History, Smithsonian Institution (NMNH

163779). The mineral is named in honor of William Petruk (b.1930), Canadian mineralogist, who noted the possible existence of petrukite in his study of the Mount Pleasant ores (Petruk 1973).

METHODS OF STUDY

Specimens described in this study were analyzed on a Materials Analysis Company (MAC) model 400 electron-microbeam analyzer operated at 20 or 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. Concentrations of the major components Cu, Fe, Sn and S were measured by means of the $\text{CuK}\alpha$, $\text{FeK}\alpha$, $\text{SnL}\alpha$ and $\text{SK}\alpha$ lines, calibrated against synthetic $\text{Cu}_2\text{FeSnS}_4$, and for Zn using the $\text{ZnK}\alpha$ line of synthetic $\text{Cu}_2\text{ZnSnS}_4$. Synthesis and description of the synthetic standards have been given in our previous papers. Minor Ag, Cd and Mn were determined using $\text{AgL}\alpha$, $\text{CdL}\alpha$ and $\text{MnK}\alpha$ of pure metal standards. Indium was determined using $\text{InL}\alpha$ and synthetic InAs. The data were reduced using the EMPADR VII program of Rucklidge & Gasparrini (1969).

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, although we were not successful in obtaining patterns free of impurities in all cases. Filtered $\text{CoK}\alpha$ radiation ($\lambda = 1.79021 \text{ \AA}$) was employed; d values were also calculated for resolved $\text{CoK}\alpha_1$ ($\lambda = 1.78890 \text{ \AA}$) and $\text{CoK}\alpha_2$ ($\lambda = 1.79278 \text{ \AA}$) reflections. Relative intensities were estimated visually. Cell parameters were obtained by means of the PARAM least-squares refinement program of Stewart *et al.* (1972). Single-crystal studies were carried out using a precession camera and W radiation. Reflectances were measured in air using a Leitz MPE microscope photometer with either a silicon reference standard (N2538.42, issued by the IMA commission on Ore Microscopy) or a silicon carbide standard (Zeiss 474251). Microhardness was determined on a Leitz Durimet hardness tester using a 100-g load for a 15-s duration.

ISOSTANNITE DISCREDITED

Isostannite was described in an abstract only by Claringbull & Hey (1955); it occurs in material from Cligga Head, Perranporth, Cornwall, England. No data were given, but the mineral was described as having the composition of normal stannite, but with a cubic structure. The holotype is deposited in the British Museum (Natural History), no. BM 1955,317. Other localities containing isostannite were indicated by Claringbull & Hey: Zinnwald, Bohemia, Czecho-

slovakia; Via Carmen, Tatasi, Bolivia and Snowflake mine, Revelstoke, British Columbia. The specimens they mentioned were not identified, and we have had no success in locating them.

A polished section containing holotype isostannite, as well as one identified as "isostannite" from the Cligga mine, Perranzabuloe, Cornwall, England, were studied. Topotype material from Zinnwald identified as "stannite" (NMNH C5233) and from the Snowflake mine identified as "zincian stannite" (UT 218) also were studied. The latter is the material collected by Gunning (1929) and described by Berry & Thompson (1962). A specimen from Vita Carmen, Tatasi, Bolivia, could not be located.

The polished section of the holotype consists largely of massive, but polycrystalline, grains of stannite-group minerals that display complex interrelationships, together with minor quartz and small inclusions of chalcopyrite at an arrested stage of alteration to covellite and sphalerite. The chalcopyrite and sphalerite inclusions vary from millimeters to submicrometers in size and in many areas are very abundant in the stannite-group minerals. Optical examinations made with the aid of a 1:1 HNO₃ etch (Harris & Owens 1972) indicate the presence of very complex textures varying from stannite to stannite with exsolved lamellae of kesterite, to kesterite with exsolved lamellae of stannite, to kesterite. Later generations of inclusion-free stannite and kesterite were deposited in very narrow bands along cracks in the original material.

The more inclusion-free areas of the kesterite display very weak reflection pleochroism from medium grey to medium grey with a brownish tinge. Anisotropy is weak but distinct in shades of grey. The optical properties were determined under oil immersion because of the enhanced reflection pleochroism and anisotropy.

Table 1 presents compositions of specimens related to the isostannite question. Composition 1 is the unpublished result of a microchemical analysis of holotype isostannite made by M.H. Hey. Compositions 2 and 3 are the results of microprobe analyses of inclusion-free areas of kesterite and stannite from the holotype specimen. Analysis 4 pertains to a mineral resembling kesterite but with more iron than zinc. As shown later, this mineral is ferrokesterite, a new species. The locality is the same as for the holotype isostannite; the Cligga mine is located at Cligga Head, and Perranzabuloe (C.J. Stanley, pers. comm. 1985). Analysis 5 pertains to massive kesterite, whereas 6 and 7 describe exsolution lamellae of kesterite in stannite, respectively.

The weakly anisotropic material of kesterite composition was extracted from the polished section of holotype isostannite. The powder pattern is compared with that of topotype kesterite in Table 2. The

TABLE 1. COMPOSITIONS OF ISOSTANNITE AND RELATED MATERIALS

	1	2	3	4	5	6	7
wt. %							
Cu	29.72	29.2	29.5	29.2	30.0	29.0	29.3
Ag	—*	—	—	—	—	0.42	0.11
Fe	9.35	4.1	11.3	8.2	6.5	4.4	8.2
Mn	—	—	—	0.1	0.02	n.d.**	n.d.
Zn	2.21	10.9	1.8	5.2	7.8	9.6	5.5
Cd	—	—	—	—	0.17	0.10	0.28
Sn	28.54	26.7	27.9	27.5	26.5	27.0	27.1
In	—	0.04	0.03	—	0.07	0.13	0.12
S	29.58	29.7	29.9	29.6	29.9	29.2	29.5
total	99.40	100.6	100.4	99.8	101.0	99.9	100.1
atomic proportions (8 atoms)							
Cu	2.04	1.98	1.99	2.00	2.03	2.00	2.00
Ag	—	—	—	—	—	0.02	—
Fe	0.73	0.32	0.87	0.64	0.50	0.35	0.64
Mn	—	—	—	0.01	—	—	—
Zn	0.15	0.72	0.12	0.35	0.51	0.64	0.36
Cd	—	—	—	—	0.01	—	0.01
Sn	1.05	0.97	1.01	1.01	0.96	1.00	0.99
In	—	—	—	—	—	0.01	—
S	4.03	4.01	4.01	4.00	4.00	3.99	3.99

* Dash denotes not determined; ** n.d. denotes not detected.

- holotype isostannite
Perranzabuloe, Cornwall, England. B.M. 1955,317; Hey (pers. comm.).
 - holotype isostannite (kesterite)
Perranzabuloe, Cornwall, England. B.M. 1955,317; this work.
 - holotype isostannite (stannite)
Perranzabuloe, Cornwall, England. B.M. 1955,317; this work.
 - "isostannite" (ferrokesterite)
Perranzabuloe, Cornwall, England. G.S.C. 14747; this work.
 - "stannite" (kesterite)
Zinnwald, Bohemia, Czechoslovakia. NMNH C5233, gr. 1; Kissin & Owens (1979).
 - "zincian stannite" (kesterite)
Snowflake mine, British Columbia. UT 218; Kissin & Owens (1979).
 - "zincian stannite" (stannite)
Snowflake mine, British Columbia. UT 218; Kissin & Owens (1979).
- Note: In the above, original identification is in quotation marks; identification according to this work is in parentheses. B.M.: Brit. Museum (Natural History); G.S.C.: National Reference Collection, Geological Survey of Canada; NMNH: National Museum of Natural History, Smithsonian Institution; UT: Department of Geology collection.

pattern cannot be indexed on a sphalerite-like cubic cell; however, it is strongly pseudocubic, with $a = 10.8629(18) \text{ \AA}$. As reflections indicating tetragonal symmetry were not resolved, c is presumed equal to $2a$ within the limitations of the method.

The powder patterns of holotype isostannite and kesterite are clearly those of the same mineral. All reflections in isostannite are indexable on a kesterite cell except for a very weak one at $d = 2.12 \text{ \AA}$, which is attributed to an unknown impurity. Zero-level precession photographs of holotype isostannite were compared with those of kesterite from Oruro, Bolivia. The latter specimen was used in a structure refinement (Hall *et al.* 1978). The photographs are identical and reveal a Laue symmetry of 4 and the diffraction symbol $I4^*/m$, with permitted reflections corresponding to $h+k+l=2n$. Possible space-groups are $I4$, $I\bar{4}$ and $I4/m$; the structure of kesterite was refined in $I\bar{4}$ (Hall *et al.* 1978).

On the basis of the foregoing evidence, it is clear that all minerals of low anisotropy in holotype or topotype isostannite correspond to kesterite or, in the case of analysis 4 (Table 1), to the new mineral

TABLE 2. X-RAY POWDER DATA FOR ISOSTANNITE COMPARED TO THOSE OF KESTERITE

hkl	holotype isostannite ¹			topotype kesterite ²		
	d(obs)	d(calc)	I/I ₁₀	d(obs)	d(calc)	I/I ₁₀
002	5.41	5.43	1	-	-	-
011	4.85	4.86	2	-	-	-
112	3.13	3.14	10	3.14	3.14	9
013	3.02	3.01	3	-	-	-
020,004	2.72	2.72	4	2.72	2.71	2
022	2.43	2.43	2	-	-	-
121	2.37	2.37	2	2.37	2.37	<1
114	2.22	2.22	1	-	-	-
-	2.12	-	1/2	-	-	-
123,015	2.01	2.02	2	2.02	2.02	<1
220,024	1.920	1.920	8	1.922	1.919	10
132,116	1.638	1.638	7	1.638	1.637	8
224	1.565	1.568	2	1.566	1.567	<1
035	-	-	-	1.390	1.390	<1
040,008	1.356	1.358	4	1.357	1.357	2
141	-	-	-	1.308	1.307	<1
332,136	1.245	1.246	5	1.246	1.245	4
044,028,240	1.213	1.215	2	1.213	1.214	<1
244,228	1.107	1.109	5	1.107	1.108	4
341,051,129	-	-	-	1.081	1.080	<1
152,336,1.1.10	1.044	1.045	4	1.044	1.045	3
251,039	-	-	-	1.004	1.004	<1
055,345	-	-	-	0.970	0.971	<1
440,048	0.961	0.960	2	0.960	0.960	1
352,156,1.3.10	0.918	0.918	3	0.918	0.917	3
248,444,060,0.0.12	.	.	.	0.905	0.904	<1
062	.	.	.	0.891	0.892	<1
260,064	.	.	.	0.859	0.858	3
356,3.3.10	.	.	.	0.828	0.828	2

d-values expressed in Å.

¹ This work a 5.4315, c 10.8629Å; 114.6mm Gandolfi and CoK α .

² Ivanov & Pyatenko (1959) a 5.43, c 10.86Å, 114.6mm Debye-Scherrer and CoK α .

ferrokesterite. The discreditation of isostannite (= a member of a kesterite-ferrokesterite solid-solution series) was approved by the IMA Commission on New Mineral Names. The equivalence to kesterite or ferrokesterite (or both) was specified because of the probable presence of both minerals in the type locality.

OCCURRENCE OF FERROKESTERITE AND PETRUKITE

Ferrokesterite

The mineral occurs in sulfide-bearing veins of tin ore from the 60-m level, Cligga mine, Perranzabuloe, Cornwall, England. The veins occur in the Cligga granite, a small pluton of Permo-Carboniferous age on the north coast of Cornwall (Hosking 1969). The veins in the granite have been classified as greisen-bordered veins by Hosking (1969), who also gave a summary of the tin deposits of Cornwall. The Cligga ores were recently described by Moore & Howie (1984), who presented results of analyses of material they called zincian stannite, which evidently is ferrokesterite.

The hand specimen investigated by us consists of massive ferrokesterite in association with arsenopyrite and quartz, as well as minor cassiterite, chalcopyrite and sphalerite. Cracks and grain boundaries are rimmed by late (supergene?) chalcocite (Fig. 1). Most areas of ferrokesterite contain minute,

round inclusions of sphalerite and chalcopyrite. Some areas of stannite with copious exsolution-lamellae of kesterite occur in grains surrounded by arsenopyrite (Fig. 2A). These grains differ considerably in composition from most of the ferrokesterite and were evidently chemically insulated by the enclosing arsenopyrite. Elsewhere in the same polished section, lamellae of kesterite form a lattice-like array within a stannite host (Fig. 2B). The texture closely resembles that illustrated by Ramdohr (1960, Fig. 398) and attributed to lamellae of isostannite in a host of stannite. The compositions of these intergrowths are given below in Table 4 (analyses 4 and 5; 6 and 7, respectively).

Petrukite

The Herb claim, the first of the three localities, occurs at 58°41'N, 128°10'W, about 8 km northwest of the confluence of the Turnagain and Cassiar Rivers, British Columbia. The claim is described as consisting of galena- and sphalerite-bearing veins in highly kaolinized granite (B.C. Dep. Mines & Petroleum Resources 1970). The veins occur in association with rhyolite and rhyolite porphyry sills and dykes that intrude a granitic stock, an offshoot of the Cassiar plutons (R.G. MacArthur, pers. comm. 1983). Petrukite in the Herb claim occurs as small, round grains (up to 240 μ m in diameter) within massive galena or sphalerite (Figs. 3A, B). The grains are either inclusion-free or occasionally occur as rhythmically alternating concentric growths with sphalerite where enclosed in quartz (Figs. 3C, D). Within the same hand specimens, in order of decreasing abundance, are galena, potosiite (*cf.* Kissin & Owens 1986a), quartz, pyrite, sphalerite and arsenopyrite.

The geology of the Ikuno mine, a xenothermal, polymetallic vein-type deposit, has been described by Imai *et al.* (1978). Petrukite occurs at the type locality for sakuraiite (Kato 1965), in the Senjuhonhi vein of the Kanagase group of veins, in only one of seven symmetrically banded zones of the vein. Details on the occurrence of sakuraiite were recently given by Shimizu *et al.* (1986). Based on the characteristics given, the mineral designated as stannite evidently is petrukite. Petrukite occurs in a 2.54-cm-diameter polished section containing the 2-cm-wide sakuraiite- and petrukite-bearing zone. One edge of the zone consists of massive sphalerite that shows euhedral terminations into rhythmically banded sakuraiite, petrukite and sphalerite (Fig. 4). Each of these bands is a few hundreds of μ m thick. Growth zones in sphalerite are outlined by trains of micrometer-sized chalcopyrite grains. Chalcopyrite also occurs as micrometer-size disseminations in sakuraiite and petrukite and as wormy stringers that cross the growth zones of the section. Irregular areas of gangue and small cassiterite grains, as well as

small, euhedral arsenopyrite crystals, also occur in the section.

The geology of the Mount Pleasant mine has been described recently by Kooiman *et al.* (1986). According to their interpretation, the deposit consists of a tungsten-molybdenum porphyry-style orebody associated with an earlier fine-grained granite and polymetallic vein-type ores associated with a later porphyritic granite phase of an altered Devonian stock. The mineralogy of the entire deposit has been catalogued by Parrish (1977); the mineralogy of tin-bearing sulfides associated with the lead, zinc, copper and tin sulfides in the vein system has been described by Petruk (1973), who first noted the unusual characteristics of the stannite-like material. According to Kooiman *et al.* (1986), Petruk's samples were taken from what is presently known as the Fire Tower North orebody, no. 7 lode. Petrukite occurs in two polished sections used in Petruk's study, nos. MP90.901.5 and MP92.901.5. In these sections, petrukite occurs as irregular, round grains of various sizes contained in quartz. Some grains are rimmed with chalcopyrite, and many contain micrometer-sized inclusions of chalcopyrite.

PHYSICAL PROPERTIES

Ferrokesterite

In hand specimen, ferrokesterite is steel grey with a metallic luster. The mineral has a Mohs hardness of about 4 and yields a black streak. Although no features of crystal morphology are visible, cleavage parallel to $\{110\}$ is distinct, and parting develops parallel to $\{001\}$. Microhardness is given in Table 3.

Petrukite

Macroscopic properties of color, streak and luster were not observable owing to the small grain-size of the material. Grain diameter is a maximum of 240 μm in the Herb claim specimens and 300 to 400 μm in the Mount Pleasant material. Laterally continuous bands that are only about 200 μm thick occur in the Ikuno mine specimen. Crystal forms were not observed; habits are round and anhedral. Distinct cleavages parallel to $\{110\}$, $\{100\}$ and $\{010\}$ were observed, as well as parting parallel to $\{001\}$. Polishing hardness is greater than that of galena and less than that of sphalerite. Microhardness is given in Table 3 for the Ikuno mine specimen.

OPTICAL PROPERTIES

Ferrokesterite

In reflected light (air path), ferrokesterite is medium grey and cannot be distinguished from kesterite. Under oil immersion, reflection pleochro-

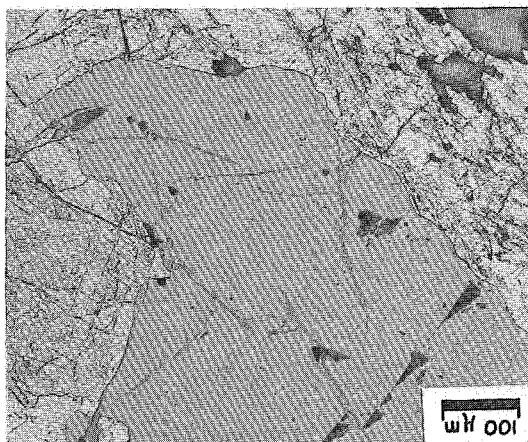


FIG. 1. Ferrokesterite surrounded by arsenopyrite (etched with 1:1 HNO_3). Late (secondary?) chalcocite lines cracks in the ferrokesterite. Note the cleavage trace in the upper left (reflected light). (GSC 65048, section A).

ism is faintly visible in shades of lighter to darker grey. Anisotropy is weak in shades of grey. Bireflectance is weak but measurable; data are presented in Table 3.

Petrukite

Color in reflected light with air path and oil immersion varies somewhat among the specimens, apparently as a function of zinc content. The Herb claim material, with the lowest zinc content, is distinctly brown (air) or greenish brown (oil), but lacks the strong reflection-pleochroism of stannite. Very faint reflection-pleochroism is visible under oil immersion, in shades of greenish brown. The color is increasingly grey with increasing zinc content in the Ikuno mine and Mount Pleasant specimens, and reflection pleochroism under oil immersion is very faint in shades of grey. In these sections, petrukite strongly resembles kesterite and ferrokesterite. Bireflection is weak but measurable; data for the Herb claim specimen are presented in Table 3.

CHEMISTRY

Ferrokesterite

The ferrokesterite in polished section A (GSC 65048) and grain mount (BM 1984, 844) contains many micrometer-size inclusions; however, clear areas in both specimens were found, and their compositions are given in Table 4 (anal. 1, 2 and 3). The compositions show little variation in the proportion of zinc and iron ($\text{Zn}_{0.67}\text{Fe}_{0.33}$). This composition lies on the iron-rich side of the stannite-kesterite pseudobinary join and thus represents an extension

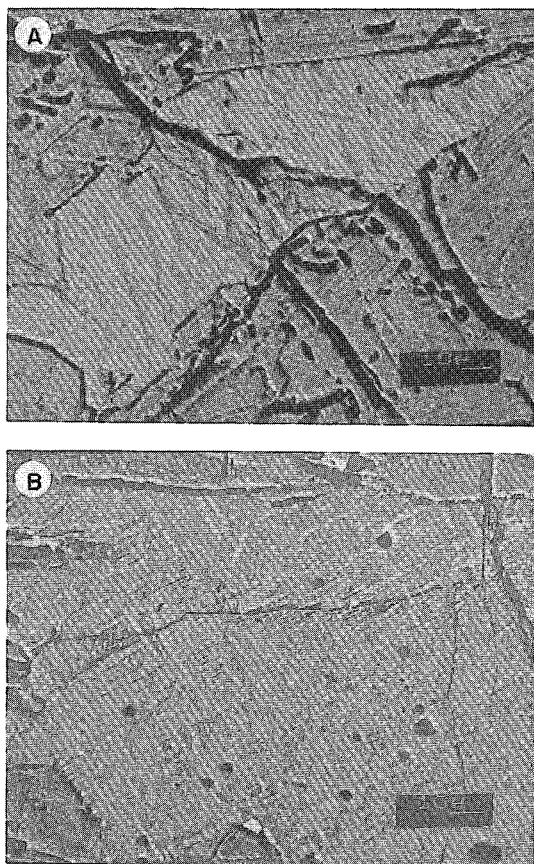


FIG. 2. Back-scattered electron images of stannite-kesterite intergrowth. A. Stannite (darker) containing oriented lamellae of kesterite (lighter). The grain is enclosed in arsenopyrite (GSC 65048, section B, area 2). B. Stannite (darker) with an array of kesterite lamellae. (GSC 65048, section B, area 1).

of the kesterite solid-solution toward an iron end-member (Fig. 5).

Petrukite

Compositional data for petrukite are presented in Table 5. The data from the Herb claim (anal. 1) are given as the mean of eight analyses of various grains, with the corresponding ranges. With the exception of silver, real compositional variations are insignificant. Analyses 2–5 from areas of the Ikuno mine section reveal some inhomogeneity with respect to the distribution of zinc, tin, copper and indium. These areas are richer in zinc and indium and poorer in iron than the Herb claim samples. Analyses 6 through 10 were obtained from Petruk's (1973) section 90.901.5, and analyses 11 through 15, from section 92.901.5. All these compositions are similar, with minor but

significant variations in copper, zinc and indium contents. The Mount Pleasant specimens are poorer in iron, zinc and indium than the Ikuno mine specimens.

The analyses reveal trends illustrated in the atomic proportions column of Table 5. Whereas the sum of the proportions, based on eight atoms, yields $Cu + Fe + Zn \approx 3$ and $Cd + Sn + In \approx 1$ and would be consistent, from this standpoint, with the structural formula $Cu_2(Fe,Zn)SnS_4$, the proportion of Cu is greater than 2, and that of $Fe + Zn$ is less than 1. Thus, a general structural formula for petrukite is $(Cu,Fe,Zn)_3SnS_4$. All analyses reveal a small but significant content of indium. Moreover, the deficit in the proportion of copper appears to be correlated with the proportion of indium.

Compositions 11–15 show a further relationship in that they may be ranked not only in order of decreasing copper and tin and increasing indium contents, but increasing zinc content as well. Iron is nearly constant, which suggests that zinc plays an important role in maintaining charge balance and stoichiometry.

CRYSTALLOGRAPHY

Ferrokesterite

Table 6 compares the X-ray powder-diffraction data for ferrokesterite with those of synthetic $Cu_2(Fe_{0.7}Zn_{0.3})SnS_4$ synthesized at 800°C (Kissin 1989). The agreement between the two patterns is good for the observed reflections in ferrokesterite; however, the pattern for ferrokesterite is weaker than that of its synthetic analog, and only one reflection with $l = 2n + 1$ is observed. The patterns are indexed in the tetragonal system and have permitted reflections obeying $h + k + l = 2n$.

The very small difference in $2a$ compared to c in kesterite leads to the superimposition of pairs of reflections such as 020–004 and 136–332 in the X-ray films, as discussed by Kissin & Owens (1979). However, in ferrokesterite, 1.3.10 is resolved from the pair 156–352, whereas in the synthetic analog, the reflections are superimposed in a single, broad reflection, apparently because of a slightly greater difference in $2a$ versus c than in kesterite. The only surprising feature is the absence of the strong reflection for 132–116 in ferrokesterite. The reflection is present, however, in precession X-ray photographs and in other powder-camera films not included here because of serious problems with reflections from other mineral inclusions. The absence seems to be an aberration in this specimen.

Ferrokesterite can be seen to be an iron-rich member of a solid solution involving the (Zn,Fe) site, by comparison of cell parameters as a function of composition of this site. Figure 5 illustrates such a

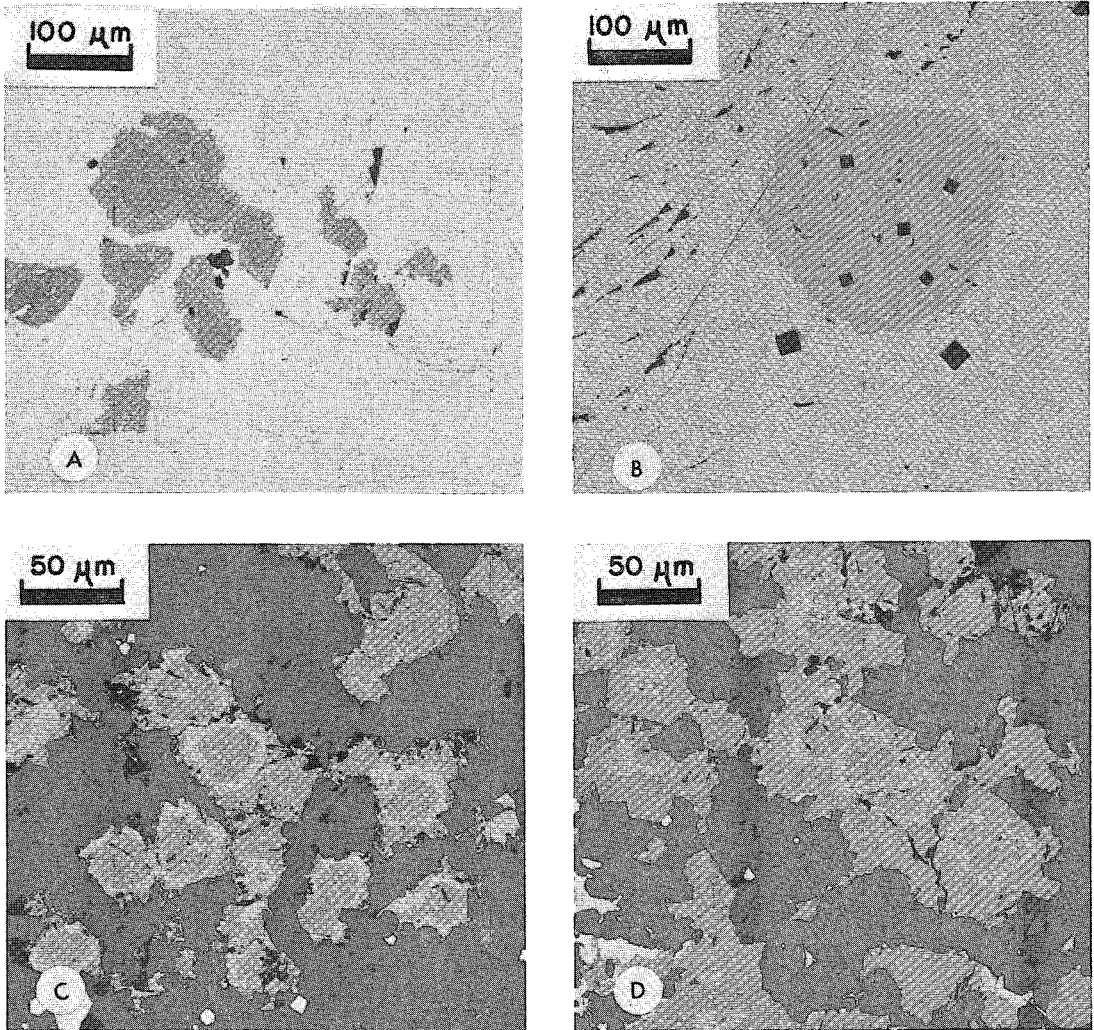


FIG. 3. Textural relationships of petrukite in the Herb claim occurrence (reflected light). A. Petrukite (medium grey) rimming sphalerite (dark grey) in galena (light grey) (oil immersion). B. Anhedral grain of petrukite (medium grey) in galena (light grey) (oil immersion). C. Rhythmic intergrowths of sphalerite (medium grey) and petrukite (light grey) in quartz (dark). D. Rhythmic intergrowths of sphalerite (medium grey) and petrukite (light grey), illustrating two cycles of deposition within a matrix of quartz (dark).

plot, utilizing data from natural stannite and kesterite given by Kissin & Owens (1979). In stannite, $2a$ and c are clearly distinguishable, whereas in kesterite $2a$ and c cannot be distinguished in a powder-diffraction pattern. In the latter case, indices based on a 10.8 Å unit cell were used in the calculation of d -values for a pseudocubic cell, except for sample 7, whose parameters were derived from the structure refinement of kesterite (Hall *et al.* 1978). Figure 5 shows that the cell parameters of kesterite remain essentially constant with increasing iron content in the (Zn,Fe) site, with no tendency to the clear distinction between

$2a$ and c , as shown by stannite. Contrary results reported by Corazza *et al.* (1986) are discussed in Kissin (1989). Ferrokesterite lies near the trend of cell parameters *versus* composition for kesterite, but on the Fe,Zn side of the diagram.

Precession X-ray photographs of the first three levels of a single crystal reveal a Laue symmetry of $4/m$ and the diffraction symbol $4/m\bar{1}$, with permitted reflections corresponding to $h+k+l=2n$. Possible space-groups are $I4/m$, $I4$ and $I\bar{4}$; however, in analogy with kesterite, the correct space-group is believed to be $I\bar{4}$ (Hall *et al.* 1978). Z , as well, is taken

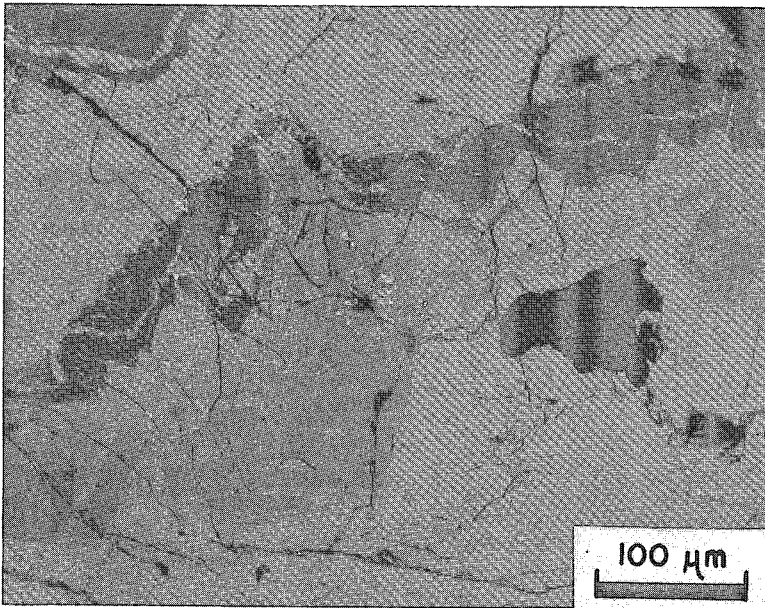


FIG. 4. Photomicrograph (reflected light) of banded ore from the Ikuno mine. Sphalerite (dark grey) shows euhedral terminations into rhythmically banded petrukite (light grey) and sakuraiite (darker grey). Trains of chalcopyrite blebs (white) transect the zones, and an anhedral grain of cassiterite (black) occurs at the right of the photograph (GSC 65052).

TABLE 3. REFLECTIVITY AND MICROHARDNESS OF FERROKESTERITE AND PETRUKITE

Wavelength	ferrokesterite		petrukite	
	R_0	R_{σ}	R_1	R_2
470 nm	23.9	26.8	27.0	27.0
546	26.0	27.0	27.8	27.7
589	26.3	27.3	27.6	27.5
650	26.0	26.8	27.4	27.1
VHN ₁₀₀ mean*	238		319	
range*	228-255		296-353	

* Five rotated indentations

as 2, as specific gravity could not be accurately determined owing to the high content of inclusions in most areas of the specimen. The calculated density is 4,490 g cm⁻³, based on the cell parameters a 5.433(36), c 10.884(89) Å, obtained by a least-squares refinement of the 12 reflections reported in Table 6.

No evidence of twinning was observed in polished section nor in the single-crystal X-ray photographs of ferrokesterite. However, preliminary results of a structural refinement indicate intensity distributions consistent with the presence of twinning.

Petrukite

The X-ray powder-diffraction data for petrukite from the three localities are given in Table 7.

The patterns were indexed on the basis of an orthorhombic unit-cell, with all general reflections hkl permitted, and $h0l$ only for $h+l=2n$. The patterns from the Herb claim and Mount Pleasant specimens contain several reflections from galena and sphalerite, respectively, which are not listed in Table 7. As well, the Herb claim specimen has a weak reflection at $d = 5.46$ Å, which is not indexable in the proposed space-group. The X-ray patterns are very similar to that of kesterite and can be distinguished only by the careful observation of a number of weak reflections. For comparison, the reflections have been indexed on the basis of the tetragonal, pseudocubic cell of kesterite in the right-hand column of Table 7. Asterisks indicate the corresponding reflections of the orthorhombic cell not permitted by the space group of kesterite ($I\bar{4}$). These weak reflections provide the only means of distinguishing the powder patterns of petrukite and kesterite.

The cell parameters derived from the least-squares refinements of the powder data are as follows: Herb claim: a 7.6671(81), b 6.4399(32), c 6.2605(61) Å based on 25 reflections; Ikuno mine: a 7.7050(27), b 6.4421(14), c 6.2757(26) Å based on 26 reflections; Mount Pleasant: a 7.6858(101), b 6.4395(60), c 6.2947(23) Å based on 27 reflections. Axial ratios, calculated from these parameters, are: Herb claim

TABLE 4. COMPOSITIONAL DATA FOR FERROKESTERITE AND ASSOCIATED STANNITE AND KESTERITE

	Cu	Fe	Zn	Mn	Cd	Sn	S	Total	Atomic Proportions						
									Cu	Fe	Zn	Mn	Cd	Sn	S
1. Grain 6 ferrokesterite	29.5	8.7	5.0	0.1	0.1	27.4	30.1	100.9	1.99	0.67	0.33	0.00	0.00	0.99	4.02
2. Sect. A, area 1 ferrokesterite	29.1	7.9	6.0	0.2	n.d.	27.3	29.5	100.0	1.99	0.61	0.40	0.02	-	1.00	3.99
3. Sect. A, area 2 ferrokesterite	29.2	8.2	5.2	0.1	n.d.	27.5	29.6	99.8	2.00	0.64	0.35	0.01	-	1.01	4.00
4. Sect. B, area 1 stannite host	29.1	7.9	5.8	0.1	n.d.	27.4	30.1	100.4	1.97	0.61	0.38	0.01	-	0.99	4.04
5. Sect. B, area 1 kesterite lamellae	28.9	4.6	9.5	0.1	n.d.	27.1	29.9	100.1	1.97	0.36	0.63	0.01	-	0.99	4.04
6. Sect. B, area 2 stannite host	29.1	8.2	5.3	0.2	n.d.	27.6	29.8	100.2	1.98	0.63	0.35	0.02	-	1.01	4.01
7. Sect. B, area 2 kesterite lamellae	28.8	4.4	9.4	0.1	n.d.	27.6	29.9	100.2	1.97	0.34	0.62	0.01	-	1.01	4.05

"n.d." denotes not detected. Ag and In were sought but not detected in all cases. Concentration reported in wt. %.

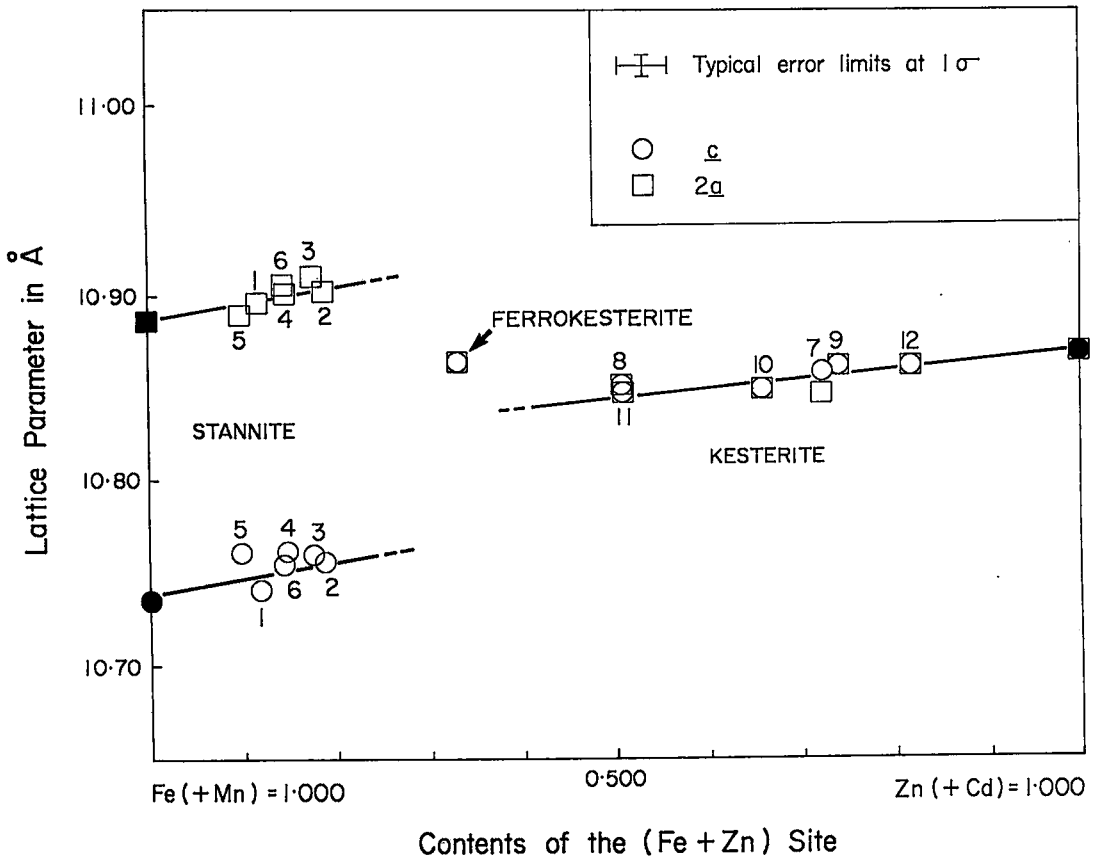


FIG. 5. The dimensions $2a$ versus c in stannite and kesterite as a function of composition, showing the relationship of ferrokesterite to the other two species. Cell parameters were obtained from least-squares refinements of X-ray powder data. The parameters of kesterite and ferrokesterite were refined using indices of a pseudocubic cell. Solid symbols are synthetic end-members synthesized at 800°C. Data from Kissin & Owens (1979).

1.225:1.029:1; Ikuno mine 1.228:1.027:1; and Mount Pleasant 1.221:1:1.023:1.
Precession photographs of the first three levels of

a single crystal from the Herb claim reveal a Laue are $Pmmm$, $Pmn2_1$ and $P2_1nm$; however, $Pmn2_1$ is symmetry of mmm and the diffraction symbol

TABLE 5. COMPOSITIONAL DATA FOR PETRUKITE

	Cu	Ag	Fe	Zn	Cd	Sn	In	S	Total	Atomic Proportions							
										Cu	Ag	Fe	Zn	Cd	Sn	In	S
1. Herb claim, mean	27.4	0.9	12.4	3.6	n.d.	24.8	1.3	29.9	100.3	1.85	0.03	0.95	0.24	-	0.89	0.05	3.99
range	27.3-28.0	0.4-1.2	12.0-12.9	3.1-4.5	-	24.3-25.3	0.9-1.9	29.6-30.3		Cu+Ag+Fe+Zn=3.07							
2. Ikuno mine area 1	26.7	-	9.3	7.6	0.4	22.8	3.4	30.2	100.4	1.80	-	0.71	0.50	0.02	0.82	0.13	4.03
										Cu+Fe+Zn=3.01							
3. Ikuno mine area 2	25.2	-	9.3	9.2	0.3	20.5	5.8	29.9	100.2	1.71	-	0.71	0.61	0.01	0.74	0.21	4.01
										Cu+Fe+Zn=3.03							
4. Ikuno mine area 3	25.9	-	9.7	7.9	0.3	22.9	3.4	30.0	100.1	1.75	-	0.74	0.52	0.01	0.83	0.13	4.02
										Cu+Fe+Zn=3.01							
5. Ikuno mine area 4	27.8	-	9.6	6.2	0.3	25.0	1.9	29.9	100.7	1.87	-	0.74	0.40	0.01	0.90	0.07	3.99
										Cu+Fe+Zn=3.01							
6. Mount Pleasant 90.901.5, gr. 1	28.6	n.d.	8.2	6.6	0.2	25.8	0.6	29.8	99.8	1.94	-	0.63	0.44	0.01	0.94	0.02	4.02
										Cu+Fe+Zn=3.01							
7. Mount Pleasant 90.901.5 gr. 2	28.0	n.d.	8.2	7.9	0.2	25.1	0.8	29.9	100.1	1.89	-	0.63	0.52	0.01	0.91	0.03	4.01
										Cu+Fe+Zn=3.04							
8. Mount Pleasant 90.901.5, gr. 1, area A	27.9	n.d.	8.2	7.3	0.2	25.5	1.2	29.7	100.0	1.90	-	0.64	0.48	0.01	0.93	0.03	4.00
										Cu+Fe+Zn=3.02							
9. Mount Pleasant 90.901.5, gr. 2, area A	28.4	n.d.	8.3	6.8	0.1	25.4	1.2	29.5	99.7	1.94	-	0.65	0.45	0.00	0.93	0.04	3.99
										Cu+Fe+Zn=3.04							
10. Mount Pleasant 90.901.5, area B	28.4	n.d.	8.3	7.5	0.2	25.8	0.7	29.6	100.5	1.92	-	0.64	0.49	0.01	0.93	0.03	3.97
										Cu+Fe+Zn=3.05							
11. Mount Pleasant 92.901.5, gr. 1	28.3	n.d.	8.2	6.5	0.2	26.5	0.7	29.3	99.7	1.94	-	0.64	0.44	0.01	0.97	0.03	3.98
										Cu+Fe+Zn=3.02							
12. Mount Pleasant 92.901.5, gr. 2	27.2	n.d.	8.0	8.2	0.2	25.9	0.8	29.5	99.8	1.86	-	0.62	0.54	0.00	0.95	0.03	4.00
										Cu+Fe+Zn=3.02							
13. Mount Pleasant 92.901.5, gr. 3	26.8	n.d.	8.1	8.4	0.2	24.8	1.1	29.6	99.0	1.84	-	0.63	0.56	0.01	0.91	0.04	4.01
										Cu+Fe+Zn=3.03							
14. Mount Pleasant 92.901.5, gr. 4	26.8	n.d.	8.4	7.9	0.3	24.8	1.0	29.8	99.0	1.83	-	0.66	0.53	0.01	0.91	0.04	4.04
										Cu+Fe+Zn=3.02							
15. Mount Pleasant 92.901.5, gr. 5	26.9	n.d.	8.5	8.7	0.2	24.5	1.1	30.4	100.3	1.81	-	0.65	0.57	0.01	0.88	0.04	4.04
										Cu+Fe+Zn=3.03							

"n.d." denotes not detected. A dash denotes not sought. Mn was sought but not detected in the Mount Pleasant samples. Concentrations reported in wt. %.

TABLE 6. X-RAY POWDER-DIFFRACTION DATA FOR FERROKESTERITE

hkl	ferrokesterite ¹			synthetic ferrokesterite ²		
	d(obs)	d(calc)	I/I ₁₀	d(obs)	d(calc)	I/I ₁₀
112	3.13	3.14	10	3.13	3.13	10
013	-	-	3	3.01	3.01	1
020,004	2.712	2.717	3	2.709	2.711	3
022	-	-	-	2.415	2.425	1
121	2.369	2.371	1/2	2.365	2.366	2
114	-	-	-	2.209	2.214	1
123,015	-	-	-	2.006	2.014	1
220,024	1.919	1.922	6	1.915	1.917	9
132,116	-	-	-	1.632	1.635	8
033,125	-	-	-	1.618	1.617	1
224	1.565	1.569	2	1.566	1.565	2
233,035	-	-	-	1.389	1.388	1
040,008	1.363	1.358	1	-	-	-
332,136	1.242	1.247	3	1.244	1.244	5
240,044, 028	-	-	-	1.212	1.212	1
244,228	1.110	1.109	4	1.106	1.107	6
051,341, 237,129 ¹	-	-	-	1.078	1.079	1
1.1.10	-	-	-	-	-	-
336,152 ¹	1.045	1.047	3	1.043	1.044	5
440,048	0.9603	0.9604	2	0.9584	0.9585	48
1.3.10	0.9206	0.9194	1	-	-	-
156,352	0.9182	0.9187	3	0.9168	0.9165	78

Broad. d-values are expressed in Å. 114.6 mm Gandolfi and CoKa.

¹ GSC 14747, grain 6b a 5.433(36), c 10.884(89) Å.

² Cu₂(Fe_{0.7}Zn_{0.3})Sn₅ a 5.422(1), c 10.884(1) Å.

mmmPn-. All general reflections *hkl* are permitted, as well as *h0l* with *h+l=2n*. Possible space-groups are *Pmnm*, *Pmn*₂ and *P2*₁*nm*; however *Pmn*₂ is

believed to be the correct one, based on the analogy with the enargite structure (Adiwidjaja & Löhn 1970) and other synthetic compounds described by Parthé *et al.* (1969). By analogy with the relationship between the sphalerite and wurtzite structures, the relationship between the structure of stannite and petrukite has been called the stannite - wurtzstannite relationship (Schäfer & Nitsche 1977).

Twinning was not observed in polished section; however, twinning was observed on precession photographs of many grains from the Ikuno mine section (Fig. 6). In the *0kl*^{*} level, the operation of the twin law is evident in the presence of individual crystals I, II and III. The wurtzite-like *c*^{*} axis coincides with the *c*^{*} axis of individual I, and the wurtzite-like *a*^{*} axis coincides with the *b*^{*} axis of individual I. Figure 7 illustrates in detail the formation of the twin cell with symmetry *R3m* and dimensions *a* 3.827 and *c* 9.365 Å, very similar to those of wurtzite-3R (*a* 3.82, *c* 9.42 Å). As the orthorhombic symmetry *Pmn*₂ is a subgroup of the twin symmetry *R3m*, the twin operates so as to produce the higher symmetry. The discovery of this twin law is striking confirmation of the correctness of the space group determined for petrukite on the basis of X-ray diffraction studies.

TABLE 7. X-RAY POWDER-DIFFRACTION DATA FOR PETRUKITE

ortho- rhom- bhc	Herb claim ¹			Ikuno mine ²			Mount Pleasant mine ³			tetragonal indexing	
	hk1	d(obs)	d(calc)	I/I ₁₀	d(obs)	d(calc)	I/I ₁₀	d(obs)	d(calc)	I/I ₁₀	hk1
010	6.13	6.44	1/2	-	-	-	-	-	-	-	*
-	5.46	-	-	-	-	-	-	-	-	-	002
101	-	-	1	4.81	4.87	1	4.78	4.87	1	-	011
111	3.86	3.87	1	3.90	3.88	1	-	-	-	-	110
210	3.33	3.29	1	-	-	-	-	-	-	-	*
020	-	-	-	-	-	-	3.17	3.22	1	-	*
002	3.13	3.13	10	3.12	3.14	10	3.11	3.15	10	-	112
121	2.712	2.682	4	2.709	2.687	3	2.698	2.688	3	-	020,004
112	-	-	-	-	-	-	2.629	2.654	1/2	-	*
202	2.421	2.425	2	2.440	2.433	1/2	2.426	2.435	1/2	-	022
301	-	-	-	2.376	2.377	1	2.361	2.373	2	-	121
311	2.214	2.221	1	2.207	2.230	1/2	-	-	-	-	114
320	-	-	-	2.005	2.009	1/2	2.008	2.005	1	-	123
400	1.915	1.917	6	1.917	1.926	7	1.913	1.921	7	-	220,024
231	1.814	1.794	1	-	-	-	-	-	-	-	222
023	-	-	-	-	-	-	1.761	1.758	1	-	*
123	1.710	1.707	2	-	-	-	-	-	-	-	130
402	1.636	1.635	5	1.636	1.642	5	1.632	1.640	5	-	132,116
421	-	-	-	1.594	1.599	1/2	-	-	-	-	*
004	1.568	1.565	1	1.566	1.569	3	1.568	1.574	1	-	224
501	-	-	-	1.494	1.497	1/2	1.497	1.493	1	-	017,231
241	1.450	1.444	1	1.445	1.447	1/2	-	-	-	-	134
124	-	-	-	-	-	-	1.391	1.391	1/2	-	035
340, 521	**	-	3B	1.363	1.365	3	1.359	1.363	2	-	040,008
242	-	-	-	1.343	1.344	1/2	-	-	-	-	*
224	1.325	1.321	2	-	-	-	-	-	-	-	226,042
151	1.243	1.245	5	1.245	1.246	4	1.241	1.245	4	-	332,136
404	1.210	1.212	2	1.217	1.217	1	1.214	1.217	1	-	240 {044,028 037,019
152	1.180	1.177	1	-	-	-	-	-	-	-	*
343	1.141	1.141	2	-	-	-	-	-	-	-	*
315	1.106	1.108	6	1.109	1.111	5	1.108	1.113	5	-	244,228
630	-	-	-	1.102	1.102	2	1.104	1.100	1	-	*
542	1.047	1.047	1/2	-	-	-	-	-	-	-	*
006	1.044	1.043	3	1.048	1.046	4	1.045	1.049	4	-	{1.1.10 152,336
415	-	-	-	1.037	1.038	1	1.039	1.039	1	-	*
640	**	-	1	-	-	-	1.003	1.002	1	-	039,251
360	0.9882	0.9896	1	-	-	-	-	-	-	-	*
444	-	-	-	-	-	-	0.9714	0.9710	1	-	{0.1.11 055,253
800	0.9599	0.9584	2	0.9636	0.9631	2	0.9629	0.9607	2	-	048,440
316	0.9587	0.9584	1	-	-	-	0.9578	0.9579	3	-	*
070	0.9201	0.9201	2	0.9208	0.9209	2	0.9209	0.9209	1	-	{156 1.3.10,253
236	-	-	-	-	-	-	0.9140	0.9154	2	-	{1.2.11,255
							0.9142	0.9154	1	-	

* Reflections at this d-value not permitted in space group of kesterite.

** Petrukite reflections present but not measured due to interference by galena.

B: broad. d-values expressed in Å. ¹a 7.6771(81), ²b 6.4399(32), ³c 6.2605(61)Å;

²a 7.7050(27), ²b 6.4462(14), ²c 6.2757(26)Å; ³a 7.6858(101), ³b 6.4395(60),

³c 6.2947(23) Å.

The twin law in petrukite is analogous (although not identical) to the twinning in enargite reported by Pauling & Weinbaum (1934). Using a setting in which *a* and *b* are reversed with respect to the setting for petrukite, they determined the triperiodic twin with twin plane (320), equivalent to (230) in petrukite. However, in the orthorhombic system a necessary condition for twinning is that *a*²:*b*²:*c*² approach rational numbers. If the squares of only two of the cell dimensions approach rational numbers, twinning is restricted to the zone containing these axes (Friedel 1926). The Pauling & Weinbaum enargite specimen

has *a*²:*b*²:*c*² = 55.2049:41.7316:38.1924; dividing by a factor of eight yields 6.9006:5.2165:4.77405. Thus, *a*²:*b*² approaches 7:5, and twinning is possible in the zone {*h**k*0}. The Ikuno mine petrukite specimen has *a*²:*b*²:*c*² = 59.3670:41.5007:39.3844; dividing by a factor of eight yields 7.4209:5.1876:4.9231. In this case *b*²:*c*² approaches 5:5, and twinning is possible in the zone {0*k*l}, in accord with the twin law (031) observed in petrukite. It should further be noted that considerable variation in cell dimensions is possible in enargite (cf. Adiwidjaja & Löhn 1970) and in petrukite, and the presence of twinning in either

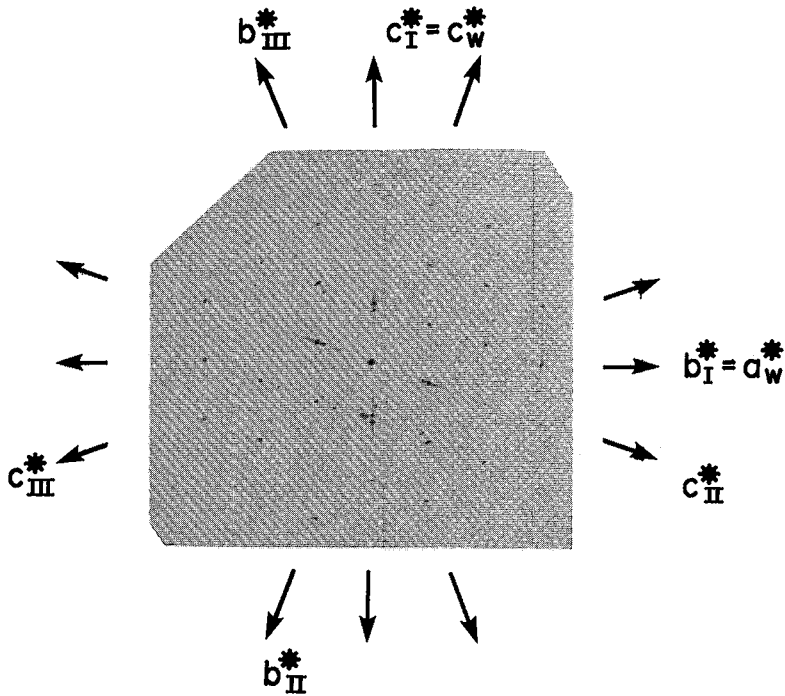
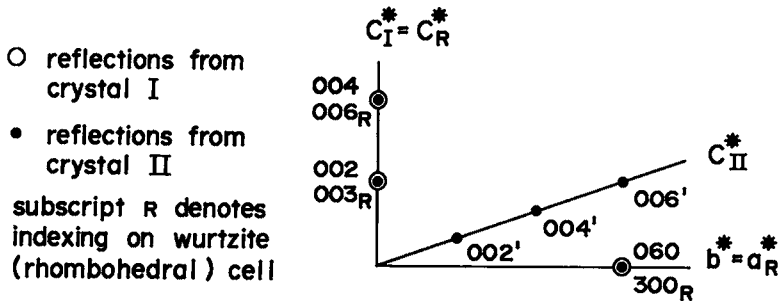


FIG. 6. X-ray precession photograph ($\text{MoK}\alpha$) of the $(0kl)^*$ level of petrukite from the Ikuno mine, illustrating the triperiodic twin it contains. The twin plane is (031) . The twin law operates so as to produce a pseudosymmetry in which the twinned edifice has a rhombohedral, wurtzite-like cell, designated by the subscript w.



Twinning by twin-lattice symmetry (TLS)

twin obliquity (ω) = 0

twin index (n) = 3

twin plane (031)

FIG. 7. Illustration of the operation of the twin law producing a rhombohedral, wurtzite-sized cell. A full description of the twin is given in the figure. The indices $(002)'$, $(004)'$ and $(006)'$ from crystal II have indices (101) , (202) and (303) in the wurtzite cell (using the setting for a hexagonal crystal).

mineral will be dependent upon the proportion $a^2:b^2:c^2$.

The Pauling & Weinbaum enargite crystal has an axial ratio $2a:b=1.739:1$, compared to $2b:a=1.672:1$ in the Ikuno mine specimen of petrukite. As a hexagonal cell would be possible for $2b:a=1.732:1$, (*cf.* Schäfer & Nitsche 1977), a pseudosymmetry is obtained by the operation of the twin law.

STABILITY RELATIONS

Only ferrokesterite will be considered, as petrukite has not been synthesized. The experimental work of Springer (1972) indicates that above 680°C, a complete solid-solution exists between iron and zinc end-members of what he called $\text{Cu}_2(\text{Fe,Zn})\text{SnS}_4$. On the basis of his findings, a solid solution should exist between kesterite and its iron analog, ferrokesterite. A miscibility gap between stannite and ferrokesterite-kesterite opens between 680°C, beginning from the pure iron end-member composition and moving to more zinc-rich compositions with decreasing temperature. The results of Kissin (1989), however, indicate that a miscibility gap between stannite and ferrokesterite-kesterite intersects the solidus of the pseudobinary system. Thus, although iron-rich members of a ferrokesterite-kesterite solid solution exist, the results of this study indicate that the pure iron end-member of ferrokesterite does not exist, at least in the condensed system.

DISCUSSION

The findings of this work have important implications for long-standing notions regarding the stability field of minerals with compositions similar to that of stannite. Firstly, the concept of a stannite-like mineral with a cubic structure has a long history extending at least to stannite II of Randohr (1944). The isostannite of Claringbull & Hey (1955), here discredited, seemed to bear out this concept. It is noteworthy that there have been few reports of occurrences of isostannite, a recent one by Corsini & Tanelli (1984) notwithstanding. Significantly, Corazza *et al.* (1986) subsequently discounted the existence of isostannite. However, in most cases, earlier reports of isostannite occurrences were based only on optical identification of an isotropic-looking mineral. The few instances of X-ray-diffraction identifications were indeterminate as to whether the mineral was ferrokesterite or a truly cubic mineral (*e.g.*, Corsini & Tanelli 1984).

On the other hand, some evidence for a cubic polymorph of stannite has emerged in experimental work. Franz (1971) synthesized a cubic phase of stannite composition at 500 and 420°C, a result duplicated by Wang (1982). However, the phase was indexed on a 10.85 Å cell, which cannot be distinguished by

powder-diffraction approach from a pseudocubic cell of ferrokesterite. Whereas some question thus remains as to the symmetry of the purported phase, several investigators have reported that a phase transition occurs in stannite at high temperatures. Bernhardt (1972) determined that an inversion occurs in $\text{Cu}_2\text{FeSnS}_4$ at 706°C on the basis of DTA experiments. Duplication of this result was reported by Lee (1972) and Bente (1974), and the latter demonstrated that a cubic structure was present at 800°C in high-temperature X-ray-diffraction studies. A recent re-investigation of the pseudobinary join $\text{Cu}_2\text{FeSnS}_4\text{-Cu}_2\text{ZnSnS}_4$ by Kissin (1989) also provides indirect support for the existence of a high-temperature polymorph of stannite; however, it is evidently not quenchable to room temperature.

The foregoing comments suggest that although the type specimen of isostannite of Claringbull & Hey (1955) has here been shown to be kesterite or ferrokesterite, the possible but as yet undemonstrated existence of a cubic polymorph of stannite is not precluded. Studies of material such as that from the Dachang mine, Peoples' Republic of China, described by Corsini & Tanelli (1984), may yield this proof; however, the mineral must be characterized by single-crystal X-ray diffraction and compositional data.

The existence of ferrokesterite was predicted on the basis of experimental work by Springer (1972), and its discovery does not present any surprises from this standpoint. Moreover, its discovery, together with the recognition in the West of the existence of kesterite, discovered earlier in the USSR, explain the otherwise mystifying results of Koucky (1959). Koucky found "isostannite" to be tetragonal by single-crystal X-ray techniques and, as well, to be rather zinc-rich, with $\text{Fe:Zn} \approx 1:1$. His results, which could not be interpreted at that time, anticipated by nearly thirty years the discreditation of isostannite and the discovery of ferrokesterite.

Although here reported from three different localities, petrukite appears to be a rare mineral. Apart from instances of possible misidentification, only one other occurrence of petrukite is known to us. Ohta

<u>ferrokesterite ($I\bar{4}$)</u>			<u>petrukite ($Pmn2_1$)</u>		
(Fe,Zn)	2d	}	(Fe,Zn)	} 4b	
Cu (1)	2a		Cu (1)		
Cu (2)	2c	→	Cu (2)	2a	
Sn	2b	→	Sn	2a	
S	8g	→	{	S (1)	4b
				S (2)	2a
				S (3)	2a

FIG. 8. Hypothetical positions of atoms in petrukite, as derived by distortion of those in ferrokesterite.

(1980) reported on analyses of two varieties of stannite from the Toyoha mine, Japan. Although X-ray-diffraction data were not given, the structural formula of his "stannite II" is $(\text{Cu}_{1.83}\text{Fe}_{0.66}\text{Zn}_{0.50})_{\Sigma 2.99}(\text{Sn}_{0.99}\text{In}_{0.03})_{\Sigma 1.02}\text{S}_{3.99}$, very similar to those reported for the petrukite from the localities studied here. This composition is contrasted to that of "stannite I", a normal, stoichiometric stannite. Within the Toyoha mine, several indium-rich minerals, including sakuraiite and a previously unreported AgInS_2 mineral, also were described (Ohta 1980). The deposit appears to be similar to the Ikuno mine on this and numerous other criteria; these xenothermal veins associated with granitic plutons appear to be the characteristic mode of occurrence of petrukite.

The stability relations of petrukite are unknown, but compositional relationships suggest that indium substituting for tin is essential to ensure its stability. The compositional data of Table 5 suggest that the coupled substitution $\text{Cu} + \text{Sn} = \text{In} + \text{Zn}$ is the charge-balance mechanism and ensures stoichiometry of the mineral, a relationship also suggested by Shimizu *et al.* (1986) in their study of the ores from Ikuno mine; however, they identified petrukite as stannite.

The incorporation of indium in the tin site of petrukite may further be responsible for the reduction in symmetry from tetragonal for stannite and kesterite to orthorhombic. Distortion of bond symmetry about the tin atom could produce the slight modification necessary to obtain an orthorhombic structure. This process may be demonstrated by the following hypothetical illustration.

If ferrokesterite, with a structural formula $\text{Cu}_2(\text{Zn},\text{Fe})\text{SnS}_4$ ($Z=2$) is considered (Fig. 8), (Fe,Zn) and Cu(1) are in distinct sites, according to the structural refinement of Hall *et al.* (1978). Chichagov *et al.* (1986) suggested an alternative ordering scheme within this space group; however, neither their evidence nor the refinement of Hall *et al.* (1978) seem to provide a definitive answer to the question of ordering. Distortion of the ferrokesterite structure due to substitution of a small amount of In in the Sn site could produce the enargite structure, in which Cu(1) and (Fe,Zn) occupy the same site. As Cu(1) and (Fe,Zn) are located in equivalent sites, a departure from the stoichiometry of ferrokesterite is possible, and the structural formula of petrukite becomes $(\text{Cu},\text{Fe},\text{Zn})_3(\text{Sn},\text{In})\text{S}_4$.

Shimizu *et al.* (1986) also described a "kesterite" with the structural formula $(\text{Cu},\text{Zn},\text{Fe})_3(\text{Sn},\text{In})\text{S}_4$. This variant appears to be petrukite, with $\text{Zn} > \text{Fe}$. However, it is found in close proximity to, if not actual contact with, petrukite. Thus, the minerals may not be members of a solid solution; this "kesterite" merits full characterization by an X-ray-diffraction study, as does holotype sakuraiite from the same locality, as noted by Kissin & Owens (1986b).

CONCLUSIONS

This study has demonstrated that three minerals of stannite-like composition exist. Aside from stannite of composition $\text{Cu}_2(\text{Fe},\text{Zn})\text{SnS}_4$ and space group $I42m$, there are the new minerals: 1) *Ferrokesterite*, $\text{Cu}_2(\text{Fe},\text{Zn})\text{SnS}_4$, the composition of which falls within the compositional range of stannite; however, its X-ray powder pattern is strongly pseudocubic. Single-crystal studies reveal that it is tetragonal ($I4$). *Ferrokesterite* forms a solid solution, $\text{Cu}_2(\text{Zn},\text{Fe})\text{SnS}_4$, from which its name is derived, at high temperatures. *Ferrokesterite* evidently is a polymorph of stannite. 2) *Petrukite* is similar in composition to stannite; however, careful analyses reveal that stoichiometric coefficients for Cu are less than 2.0, and for (Fe+Zn), greater than 1.0, with $\text{Cu} + \text{Fe} + \text{Zn} = 3.0$, and that In, although present in minor amounts, apparently is an essential component. Careful X-ray-diffraction studies also reveal that petrukite is orthorhombic ($Pmn2_1$). The mineral is believed to owe its stability to the distortion of the tetrahedral bonds surrounding Sn due to substitution by In.

Studies of holotype isostannite, the purported cubic high-temperature polymorph of stannite, reveal that it is a member of a kesterite-ferrokesterite solid-solution series. The as-yet unproven existence of a cubic polymorph of stannite is not precluded.

ACKNOWLEDGEMENTS

This research was aided by technical assistance from the following at CANMET: E.J. Murray (powder X-ray diffraction), the late J.M. Stewart (single-crystal X-ray diffraction) and J.H.G. Laflamme (preparation of polished sections). At Lakehead University the following are thanked for their assistance: T.J. Griffith (single-crystal X-ray diffraction), S.T. Spivak (drafting) and W.C. Bons and S.E. Millar (manuscript preparation). Reflectivity measurements were carried out by L.J. Cabri at CANMET (petrukite) and J. Guha at Université du Québec à Chicoutimi (ferrokesterite). Sample materials were obtained from H.G. Ansell and R. Mulligan, Geological Survey of Canada, A.J. Cridle, British Museum (Natural History), and W. Petruk (CANMET). Valuable discussions were held with W. Petruk and H.D. Grundy, who is also thanked for his hospitality at McMaster University, where some of the final details of the work were completed. F. Corsini, an anonymous referee and R.F. Martin provided valuable suggestions for improvement of the manuscript. This work was supported initially by a National Research Council of Canada postdoctoral fellowship and later by a Natural Sciences and Engineering Research Council of Canada Operating Grant (A3814) to S.A.K.

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Received January 4, 1989, revised manuscript accepted July 8, 1989.