INDIUM IN CO-EXISTING MINERALS FROM THE MOUNT PLEASANT TIN DEPOSIT

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ABSTRACT

Arsenopyrite, pyrite, galena, cassiterite and molybdenite concentrates each contained less than 0.05 weight per cent indium whereas three chalcopyrite concentrates contained 0.98, 0.38 and 0.16 weight per cent. Most of the indium in the chalcopyrite concentrates occurs in stannite and sphalerite impurities. Microprobe analysis indicated that the principal indium carriers at Mount Pleasant are tetragonal stannite, sphalerite, chalcopyrite and digenite, with 2.1, 1.25, 0.19 and 0.11 weight per cent indium respectively. These minerals have a sphalerite-type structure with sulphur atoms in cubic closest packing and indium probably substitutes preferentially for atoms with tetrahedral metal-sulphur bond lengths closest to the tetrahedral In-S bond in stable indium sulphide. Minerals from the Mount Pleasant tin deposit contain more indium than previously recorded from other indium-rich deposits.

INTRODUCTION

The Mount Pleasant deposit which lies about 35 miles south-west of Fredericton, New Brunswick, has mineralogical characteristics similar to Cornwall-type tin deposits (Petruk, 1964). Although a wide variety of minerals are found, this investigation was confined to the most abundant metallic minerals, sphalerite, arsenopyrite, pyrite, chalcopyrite, galena, cassiterite and molybdenite; also to tetragonal stannite, hexastannite and digenite which are less abundant sulphides closely associated with chalcopyrite. Other minerals occurring at Mount Pleasant are wolframite, scheelite, hematite, tennantite, chalcocite, covellite, bismuthinite, wittichenite, glaucodot, marcasite, pyrrhotite, native bismuth, native gold, siderite, goethite, scorodite, arseno-bismite and malachite (Petruk, 1964).

The occurrence of indium at Mount Pleasant is of interest both because of the rarity of this element and the potential economic significance of an ore deposit with a relatively high indium content. Although indium is generally preferentially concentrated in sphalerite, as at Kimberly, B.C., some concentrate analyses of the Mount Pleasant ore indicated that minerals other than sphalerite were good indium carriers. Consequently the electron microprobe study concentrated on the chemistry of chalcopyrite, on tetragonal stannite and sphalerite inclusions within chalcopyrite, and on digenite, hexastannite and cassiterite which are associated with chalcopyrite.

CONCENTRATE ANALYSES

Relatively pure samples of chalcopyrite, pyrite and molybdenite were prepared from material collected at the workings. Samples of arsenopyrite, galena and cassiterite were obtained by purifying mineral concentrates made during beneficiation tests for the Mount Pleasant Company at Warren Springs, England. Sphalerite concentrates were not analysed, as data on the composition were available (Petruk, 1964). The chemical analyses were made by a commercial laboratory in Toronto (Tables 1 and 2).

TABLE 1. ANALYSIS OF MOUNT PLEASANT CASSITERITE
(in weight per cent)

In_2O_3	0.036*
BeO	<0.001
SiO_2	0.55*
TiO_2	0.58*
V	0.005
Mn	0.002
Fe_2O_3	0.58*
Ga	0.003
GeO_2	<0.001
ZrO_2	0.3
Nb_2O_5	0.01*
SnO_2	97.28*
Sb	0.2
Hf	<0.01
Ta_2O_5	0.005
Total	99.56

*Analyses with asterisks are quantitative, others are semi-quantitative.

Cassiterite, arsenopyrite, pyrite, galena and molybdenite concentrates each contained less than 0.05 per cent indium and are unimportant carriers of this element. The three chalcopyrite concentrates contained 0.98, 0.38 and 0.162 weight per cent indium respectively. Two of these values are higher than the maximum amount of indium (0.30 wt. %) Petruk found in Mount Pleasant sphalerite and all are higher than the previous maximum values (0.15 wt. %) recorded for chalcopyrite (Table 10). Chalcopyrite grains from the analysed concentrates contained either sphalerite and minor tetragonal stannite, or tetragonal stannite and minor sphalerite as inclusions. The predominance of one mineral inclusion over the other is reflected in the analyses. Chalcopyrite 3, with much sphalerite, is relatively high in zinc and low in tin, as compared with chalcopyrites 1 and 2, which contain very little sphalerite but instead have tetragonal stannite as the main impurity.

TABLE 2. ANALYSES OF MOUNT PLEASANT SULPHIDE CONCENTRATES (in weight per cent)

	1 Chalcopyrite	2 Chalcopyrite	3 Chalcopyrite	4 Arsenopyrite	5 Pyrite	6 Galena	7† Molybdenite	8 Sphalerite
In	0.98*	0.38*	0.162*	0.005	0.01	0.05	<0.001	0.03–0.30
Li_2O	—	—	—	—	—	—	—	
BeO	—	—	—	—	—	—	—	
S	34.66*	31.81*	33.71*	19.69*	45.51*	14.70*	38.21*	30.70–32.23
TiO_2	—	0.01	0.02	—	0.1	—	0.01	
V	—	—	—	—	0.01	—	0.005	
Cr	—	0.01	0.01	—	<0.005	—	—	
Mn	<0.005	0.005	0.01	—	0.005	0.002	—	0.05–0.08
Fe	29.20*	29.22*	23.49*	34.34*	43.60*	6.43*	0.05	7.8–13.1
Co	0.005	—	—	<0.005	0.01	—	—	
Ni	0.001	0.001	0.001	0.005	—	0.001	—	
Cu	34.12*	34.38*	28.75*	0.20*	0.88*	1.24*	0.02	1.28–5.20
Zn	0.24*	0.75*	8.60*	0.36*	0.88*	1.36*	<0.005	45.20–48.90
Ga	—	0.001	0.001	—	—	0.001	—	
GeO_2	—	—	—	—	<0.001	0.001	—	
As	0.11*	0.09*	0.08*	44.50*	8.50*	7.52*	—	
ZrO_2	—	0.01	0.02	—	—	0.3	—	
Nb_2O_5	—	—	—	—	—	—	—	
Mo	—	—	—	—	0.01	0.2	56.20*	
Ag	0.007*	0.009*	0.005*	0.001	0.003	0.13*	0.005	
Cd	—	—	0.02	—	—	0.01	—	0.12–0.18
Sn	1.5	1.5	0.7	—	—	0.7	0.005	0.14–0.38
Sb	—	—	—	0.05	—	<0.02	—	
Ba	—	—	—	—	—	<0.005	—	
CeO_2	—	—	—	—	—	—	—	
Hf	—	—	—	—	—	—	—	
Ta_2O_5	—	—	—	—	—	—	—	
W	—	—	—	—	<0.01	—	<0.01	
Hg	—	—	—	—	—	—	—	
Tl	—	—	—	—	0.005	0.005	—	
Pb	0.06*	0.05*	0.15*	0.17*	0.08*	67.95*	0.05	
Bi	—	0.002	0.002	0.01	—	2.0	0.04	
ThO_2	—	—	—	—	—	—	—	
U_3O_8	—	—	—	—	—	—	—	
Total	100.89	98.23	95.73	99.43	99.62	102.63	94.61	

—Not detected.
†Contains 4.48% SiO_2
*Analyses with asterisks are quantitative, others are semi-quantitative
1,2 Chalcopyrite from pockets of massive ore in main workings (310E Dr.)
3 Chalcopyrite from disseminated sulphides in porphyry
4 Arsenopyrite purified from a mine concentrate
5 Pyrite from main workings
6 Galena purified from a mine concentrate
7 Molybdenite from Fire Tower Zone
8 Sphalerite (Petruk, 1964). Range of analyses for five samples.

Both sphalerite and stannite are known indium carriers (Anderson, 1953 and Ivanov *et al.*, 1961). Ivanov *et al.* (1961) noted that indium may be favourably partitioned in stannite when sphalerite and stannite co-exist in equilibrium assemblages. The Mount Pleasant concentrates of chalcopyrite (1 and 2, Table 2) in which tetragonal stannite was the main inclusion impurity, contained more indium than did the chalcopyrite concentrate (3, Table 2) which had sphalerite as the principal inclusion. From the early stages of the investigation the good indium-carrying capacity of tetragonal stannite had been suspected as 1.0 per cent indium occurs in cylindrite, a lead-antimony analog of stannite (Brewer & Baker, 1936). In addition, as Moh & Ottemann (1962) were able to synthesize the indium analog, Cu_2InSnS_4, of tetragonal stannite, Cu_2FeSnS_4, stannite could probably also contain large quantities of indium.

ELECTRON MICROPROBE ANALYSES

Three polished sections of sulphides from indium-rich areas within the Mount Pleasant mine were sent for microprobe analyses to a commercial laboratory in Boston.

Two sections, B and C, were prepared from chalcopyrite specimens selected from the pod of massive chalcopyrite (310 Dr.E.) sampled for chalcopyrite concentrates (1 and 2, Table 2). Petruk donated section A which was cut from an ore specimen taken at a mineralized fracture at station 26 + 00 in 303 Dr.E., approximately 200 feet south west of B and C. Two microprobe traverses were run on polished section A and one on each of sections B and C. Traverse A-1 (Figure 1) was across three co-existing minerals, cassiterite, digenite and hexastannite. A-2 (Figure 2) was over cassiterite, hexastannite and chalcopyrite. Traverse B-1 (Figure 3) crossed cassiterite, tetragonal stannite and chalcopyrite, and C-1 (Figure 4) was over sphalerite and chalcopyrite. Analyses (Table 3) for three elements were determined at 0.0001 inch spacings along each traverse. Indium and tin were selected, as these are associated in sulphide minerals (Shaw, 1952). The third element, either zinc or copper, indicated the presence of small inclusions in the various phases. Interpretation of the probe results were complicated by impurities in some of the phases. Sphalerite, whether as large grains or as inclusions in chalcopyrite, contains many orientated "exsolution-type" inclusions of chalcopyrite. As less than 1 per cent copper occurs in solid solution within the sphalerite lattice (Toulmin, 1960), the presence of 6.1 ± 0.5 per cent copper in the sphalerite grain on path C-1 indicates approximately 15 volume per cent included chalcopyrite. Assuming that the chalcopyrite inclusions are in chemical equilibrium with that surrounding the sphalerite, then the

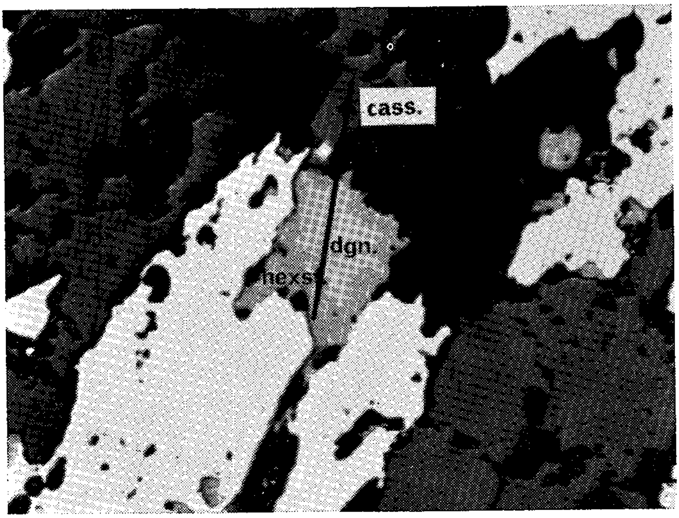

FIG. 1. Microprobe traverse A-1. 400×

hexastannite	hexst.
digenite	dgn.
cassiterite	cass.

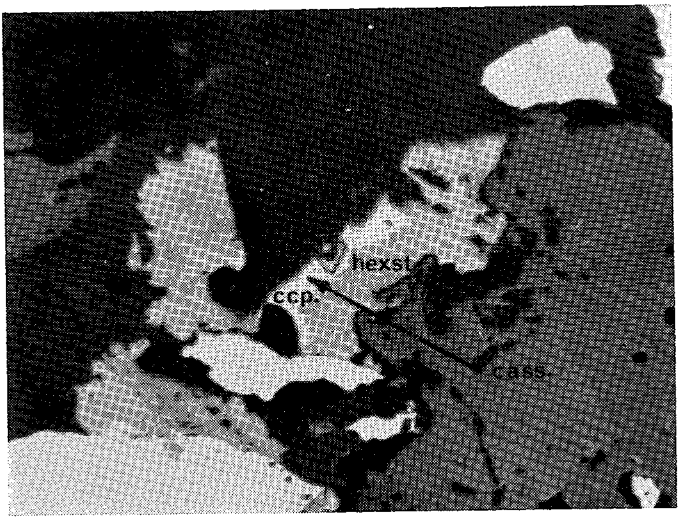

FIG. 2. Microprobe traverse A-2. 400×

cassiterite	cass.
hexastannite	hexst.
chalcopyrite	ccp.

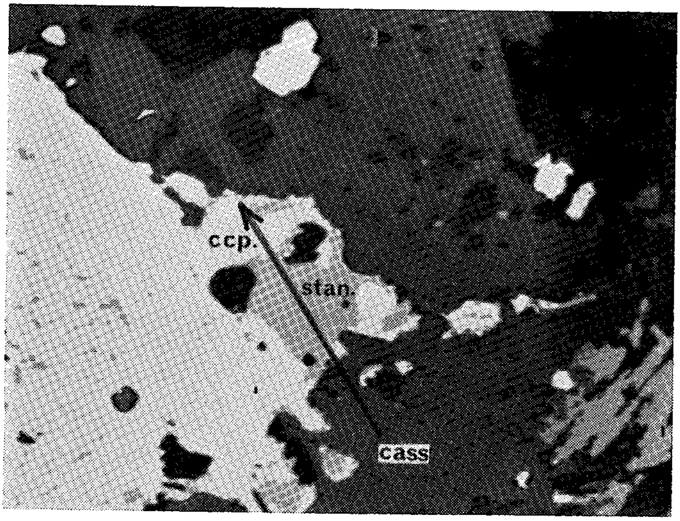

FIG. 3. Microprobe traverse B-1. 400×

cassiterite	cass.
tetragonal stannite	stan.
chalcopyrite	ccp.

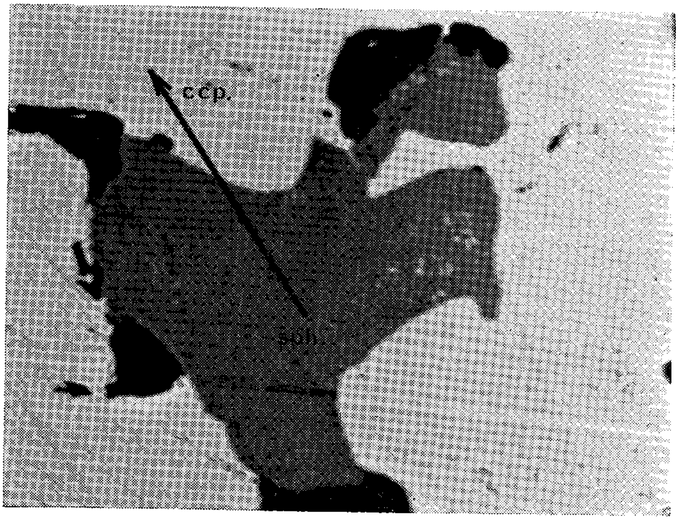

FIG. 4. Microprobe traverse C-1. 400×

sphalerite	sph.
chalcopyrite	ccp.

TABLE 3. ELECTRON MICROPROBE PARTIAL ANALYSES OF SELECTED MOUNT PLEASANT MINERALS (in weight per cent)

Sample Number	Mineral	Points[1]	Indium	Tin	Zinc	Copper
A-1	Cassiterite	6	0.04±0.02[2]	78.3 ±0.7	0.04±0.003	
	Hexastannite	5	0.04±0.01	17.3 ±0.4	3.8 ±0.2	
	Digenite	9	0.11±0.03	0.11 ±0.06	0.8 ±0.3	
A-2	Cassiterite	3	0.03±0.01	78.8 ±0.9	0.14±0.07	
	Hexastannite	5	0.03±0.01	18.3 ±0.3	3.8 ±0.1	
	Chalcopyrite	3	0.13±0.07	0.12 ±0.06	0.08±0.05	
B-1	Cassiterite	8	0.03±0.01	77.1 ±1.1	0.03±0.02	
	Tetragonal Stannite	15	2.1 ±0.2	24.5 ±0.3	6.3 ±0.7	
	Chalcopyrite[3]	5	0.5 ±0.3	3.1 ±3.0	0.06±0.03	
C-1	Sphalerite[4]	13	1.10±0.05	0.009±0.005		6.1±0.5
	Chalcopyrite	17	0.19±0.08	0.11 ±0.02		32.4±0.3

[1] Number of point analyses 0.0001 inches apart.
[2] Standard deviation for given number of analyses.
[3] Contains approximately 14% tetragonal stannite inclusions.
[4] Contains approximately 15% chalcopyrite inclusions.

indium content of sphalerite without chalcopyrite impurities is 1.25 per cent (Table 4).

The relatively high standard deviations of indium (0.5 ± 0.3%), tin (3.1 ± 3.0%) and zinc (0.06 ± 0.03%) analyses in the chalcopyrite on traverse B-1, reflect the presence of small tetragonal stannite inclusions. These values can be contrasted with the low standard deviations of indium (0.19 ± 0.08%) and tin (0.11 ± 0.02%) analyses from the inclusion free chalcopyrite on path C-1. Tetragonal stannite (2.1 ± 0.2% In) which tends to be free from mineral impurities, was found as inclusions in chalcopyrite. The largest concentrations of this mineral occurred near rounded grains of inclusion-free cassiterite. The hexastannite phase in polished section A forms small grains with inclusions of chalcopyrite, tetragonal stannite and a copper sulphide mineral which is blue-grey under reflective light and is isotropic. It is tentatively identified as digenite rather than

TABLE 4. ELECTRON MICROPROBE PARTIAL ANALYSES OF SELECTED MOUNT PLEASANT MINERALS WITH CORRECTIONS MADE FOR INCLUSIONS (in weight per cent)

Mineral	Indium	Tin	Zinc	Copper
Tetragonal Stannite	2.1 ±0.2	24.5 ±0.3	6.3 ±0.7	
Sphalerite	1.25±0.06	0.0		3.4±2.1
Chalcopyrite	0.19±0.08	0.11±0.02	0.07±0.04	32.4±0.3
Digenite	0.11±0.06	0.11±0.06	0.8 ±0.3	
Hexastannite	0.04±0.01	17.8 ±0.03	3.6 ±0.1	
Cassiterite	0.03±0.01	78.5 ±0.8	0.03±0.02	

chalcocite (Buerger, 1941) and has an indium content of 0.11 ± 0.03 weight per cent.

There are areas both rich and poor in indium within the Mount Pleasant deposit (Petruk, 1964). However, because chalcopyrite from the two stopes sampled, has similar indium and tin values, within limits of random error, both zones could constitute an indium-rich equilibrium assemblage. Table 4 illustrates the analyses, corrected for inclusion impurities for this assemblage.

THE STANNITE PROBLEM

In addition to tetragonal stannite, two hexagonal and two isometric forms were recognized by Ramdohr (1944). Claringbull (Hey, 1962) proposed the name "isostannite" for minerals II and IV, Ramdohr's two isometric stannites. Moh & Ottemann (1962) used the term "hexastannite" for the two hexagonal stannites, minerals I and III. Moh & Ottemann showed that mineral IV, which has the tetrahedrite structure (Ramdohr, 1944), contains much silver, antimony and arsenic, whereas mineral II, for which Ramdohr did not supply *x*-ray data, has essentially the same composition as the tetragonal stannite ($Cu_2(Fe,Zn)SnS_4$) and is characteristically devoid of antimony and arsenic.

Hexastannite is rose-brown and strongly anistropic and thus distinguishable from tetragonal stannite which is greenish brown-grey and apparently isotropic. Initially the *x*-ray powder patterns (11.46 cm camera, 20 minute exposure, iron filtered cobalt radiation) of tetragonal stannite appeared similar to the sphalerite pattern because the weak reflections, distinctive of tetragonal symmetry, were not recorded. Thus we initially assumed that this isotropic mineral was an "isostannite", possibly Ramdohr's mineral II. As 24-hour exposures with a large powder camera (11.46 cm) revealed the weak and very weak reflections 121, 123, 033 and 315, this was later reidentified as the tetragonal variety (Table 5). The unit cell parameters are $a = 5.42$ Å, $c = 10.88$ Å and the pattern is similar to the pattern indexed by Berry & Thompson (1962).

Some difficulty was experienced in excavating hexastannite grains free of other mineral impurities from polished sections. *X*-ray powder mounts always consisted of mineral composites of hexastannite, tetragonal stannite, cassiterite and chalcopyrite. However, a number of wurtzite-type reflections could be resolved from the complexed *x*-ray patterns and these are similar to corresponding lines in Ramdohr's mineral I ($a = 3.84$ Å; $c = 12.6$ Å).

A complete electron microprobe analysis of the Mount Pleasant tetragonal stannite supplied by J. Rucklidge (University of Toronto) is shown in Tables 6 and 7. A comparison of the two Mount Pleasant

TABLE 5. *X*-RAY POWDER DIFFRACTION DATA FOR TETRAGONAL STANNITE

Mount Pleasant. Tetragonal; a = 5.42 Å, c = 10.88 Å (approx.) 114.6 mm. Debye-Scherrer camera iron filtered cobalt radiation; Kα = 1.79021

$Cu_2(Fe,Zn)_{1.25}SnS_4$

hkl	I(est.)	d(meas.)	d(calc.)
110	w	3.84	3.833
112	s	3.13	3.133
004	mw	2.71	2.720
020			2.710
022	w	2.42	2.426
121	w	2.37	2.366
114	w	2.218	2.218
123	vw	2.015	2.015
024	ms	1.914	1.920
220			1.916
116	ms	1.637	1.639
132			1.635
033	w	1.620	1.617
224	w	1.572	1.567
017	vw	1.494	1.494
134	vw	1.451	1.450
008	w	1.360	1.360
315	vw	1.348	1.346
136	mw	1.243	1.246
228	mw	1.106	1.109
244			1.107
336	w	1.042	1.044
343			1.039
053			1.039

San Jose mine, Oruro, Bolivia (ROM, M19349) (Berry & Thompson, 1962) Tetragonal; a = 5.47 Å, c = 10.746 Å

Cu_2FeSnS_4

hkl	I(est.)	d(meas.)	d(calc.)
002	vw	5.37	5.373
011	vw	4.85	4.876
112	s	3.12	3.139
020	mw	2.71	2.735
004			2.687
022	vw	2.46	2.438
121	vw	2.38	2.386
114	vw	2.21	2.206
024	ms	1.922	1.917
132	mw	1.642	1.646
116	mw	1.626	1.625
033			1.625
224	w	1.570	1.570
040	w	1.368	1.368
008	w	1.347	1.343
143	mw	1.245	1.244
136			1.244
235			1.239
244	mw	1.114	1.113
228	w	1.105	1.103
336	w	1.048	1.046
343			1.046
053			1.046

TABLE 6. ELECTRON MICROPROBE ANALYSES OF THE THREE MAJOR INDIUM CARRIERS AT MOUNT PLEASANT (in weight per cent)

Traverse	B-1	B-1	C-1	C-1
Mineral	Tetragonal Stannite	Chalcopyrite	Chalcopyrite	Sphalerite
Cu	27.5	34.2	34.2	5.7
Sn	26.1	0.13±0.02*	0.15±0.14*	0.0±0.0*
Fe	11.0	29.4	31.5	5.5
Zn	5.1	0.16	0.48	56.4
S	27.9	34.2	34.6	32.8
In	1.95±0.21*	0.05±0.04*	0.15±0.21*	1.1±0.1*
Ag	0.19	0.0	0.0	0.0
Total	99.74	98.14	101.08	101.5

*Analyses with asterisks represent the average of more than one point analyses. The associated precision is given as a standard deviation. "The accuracy of analyses is estimated at ±10% at concentrations lower than 1 wt. per cent, and improving to ±2% at concentrations around 30 wt. per cent".

Analyst: John Rucklidge (University of Toronto).

TABLE 7. COMPARISON OF COMPOSITIONS OF STANNITE, HEXASTANNITE AND MAWSONITE
(Analyses with asterisks are from Mount Pleasant)

	Tetragonal Stannite				Hexastannite		Mawsonite
	1	2*	3	4	5	6*	7
Cu	31.52	27.5	31.56	26.69	38.0	36.5	44.3
Sn	27.83	26.1	26.65	31.80	15.6	17.8	10.4
Fe	12.06	11.0	3.65	2.62	11.1	11.8	12.5
Zn		5.1	7.72	10.32	4.1	3.6	
S	28.59	27.9	29.76	27.58	29.2	27.9	33.0
In		1.95		0.02		0.04	
Ag		0.19		0.49			
Insol				0.36			
Total	100.00	99.74	99.34	99.88	98.0	97.64	100.2

1. Tetragonal stannite (Cu_2FeSnS_4). Oruro, Bolivia (Palache *et al.*, 1961).
2. Tetragonal stannite ($Cu_2(Fe,Zn)_{1.25}SnS_4$). Mount Pleasant, electron microprobe analysis by J. Rucklidge, University of Toronto.
3. Zincian stannite ($Cu_{2.2}(Zn,Fe)_{0.8}SnS_{4.1}$). Snowflake mine, B.C. (Berry & Thompson, 1962).
4. Kesterite ($Cu_{1.98}(Zn,Fe)_{0.95}Sn_{1.25}S_4$). Kester deposit, Yakutsk A.S.S.R. (Ivanov & Pyatenko, 1959).
5. Hexastannite ($Cu_{4.5}(Fe,Zn)_2SnS_7$). Tingha, New South Wales (Markham & Lawrence, 1965).
6. Hexastannite ($Cu_{3.79}(Fe,Zn)_{1.78}SnS_{5.85}$). Mount Pleasant. Cu, Fe and S are qualitative estimates (see text).
7. Mawsonite ($Cu_7Fe_2SnS_{10}$). Mt. Lyell, Tasmania (Markham & Lawrence, 1965).

stannites with analyses of other copper-tin sulphides is shown in Table 7. Data on the hexastannite represent a partial microprobe analysis for tin, zinc and indium, combined with a qualitative estimate for copper, iron and sulphur, calculated from the intensities of the hexastannite microprobe spectral pattern relative to those of the analysed tetragonal stannite. Hexastannite contains more copper and iron but less indium, tin and zinc, than the tetragonal stannite.

DISCUSSION

Several Russian writers, including Ivanov *et al.* (1961), have postulated an Fe^{2+} and In^{3+} diadochy as the mechanism for indium substitution in sulphides. As the hexagonal stannite of Mount Pleasant contains considerably less indium than the tetragonal form, even though both have similar iron content, some mechanism other than, or perhaps in addition to, In^{3+} substitution for Fe^{2+} is operative.

Bonding forces in sulphide minerals are predominantly covalent and/or metallic and substitution is not so much governed by the electrostatic balancing and atom size restrictions that apply to ionic crystals as by limits on the size of the tetrahedral or octahedral bonds (Anderson, 1953). Consequently the substitution of indium should be facilitated in sulphide structures which have metal to sulphur bonds of the same type and length as the In—S bonds in the indium sulphides with which the host sulphide would be in equilibrium. Stubbs *et al.* (1952) described four indium sulphides, β-In_2S_3, In_3S_4, In_5S_6, and InS, which they believed to be stable phases in the In—In_2S_3 system. Miller & Searcy (1965) have since disproved the existence of In_3S_4 and the composition of In_5S_6 has been changed to In_6S_7 by Duffin & Hogg (1965). The sulphur atoms in InS and β-In_2S_3 are in cubic closest packing. Indium is tetrahedrally surrounded by three S and one In in the InS structure, which has the *Pmnn* space group (Schubert *et al.* 1954) and is in both octahedral and tetrahedral co-ordination in the spinel structure ($I4_1/amd$) of β-In_2S_3 (Steigmann *et al.*, 1965). The octahedral In—S bond-lengths in β-In_2S_3 vary from 2.54 Å to 2.68 Å. The tetrahedral In—S bond-lengths for InS and β-In_2S_3 are given in Table 8.

TABLE 8. TETRAHEDRAL METAL-SULPHUR BOND LENGTHS IN PRINCIPAL INDIUM CARRIERS COMPARED WITH IN-S TETRAHEDRAL BONDS IN INDIUM SULPHIDES

Compound	Bond	length Å	Reference
Tetragonal stannite (Cu_2FeSnS_4)	Sn-S Fe-S Cu-S	2.43 2.36 2.31	Anderson (1953) (after Brockway, 1934)
Sphalerite (ZnS)	Zn-S	2.35	From cell edge 5.4093 Å
Chalcopyrite ($CuFeS_2$)	Cu-S Fe-S	2.28 2.28	Berry (1965)
Digenite ($Cu_{9-x}S_5$)	Cu-S	2.40	From cell edge 5.552 × 5 Å (Morimoto & Kullerud, 1963)
β-In_2S_3	In-S	2.44 2.48	Steigmann *et al.* (1965)
InS	In-S	2.56 2.58	Schubert *et al.* (1954)

The four principal indium carriers at Mount Pleasant, tetragonal stannite (2.1%), sphalerite (1.25%), chalcopyrite (0.19%), and digenite (0.11%) have structures with metal atoms tetrahedrally bonded to cubic close packed sulphur. The similarities between these minerals extend to a common zinc blende-type structure. Although tetragonal stannite and chalcopyrite have tetragonal symmetries, the structures may be considered to be derivatives of the sphalerite lattice (Buerger, 1947) as shown in Table 9. Morimoto & Kullerud (1963) reported four different superstructures in synthetic digenites. Three are metastable at room temperature and the fourth is stable low temperature digenite with the isometric space group *Fd3m*. This is the "diamond" lattice which is similar to the sphalerite structure. The sulphur atoms are arranged in a slightly distorted cubic close packing with 1 copper atom in an octahedral hole, 6 in tetrahedral holes and 2 with a triangular co-ordination (Hellner, 1958).

TABLE 9. DERIVATIVE STRUCTURES OF SPHALERITE
(after Buerger, 1947)

		Space group
Basic structure, sphalerite	$\left|\mathrm{Zn}\right|\mathrm{S}$	$(F\bar{4}3m)$
Derivative structure, chalcopyrite	$\left|\begin{matrix}\mathrm{Cu}_{\frac{1}{2}}\\ \mathrm{Fe}_{\frac{1}{2}}\end{matrix}\right|\mathrm{S}$	$(I\bar{4}2d)$
Derivative structure, stannite	$\left|\begin{matrix}\mathrm{Cu}_{\frac{1}{2}}\\ \mathrm{Fe}_{\frac{1}{4}}\\ \mathrm{Sn}_{\frac{1}{4}}\end{matrix}\right|\mathrm{S}$	$(I\bar{4}2m)$

The In—S tetrahedral bond-lengths in β-In_2S_3 and InS are closest to the Sn—S bond in tetragonal stannite. This stannite contains more indium than any of the other Mount Pleasant minerals (Table 10). The Cu—S tetrahedral bond in digenite is longer than the metal-sulphur bonds in sphalerite and chalcopyrite, yet indium substitutes to a greater extent in the latter two minerals. Apparently univalent copper ions are less favourable substitution sites for trivalent indium, than are divalent zinc ions. Octahedral and triangular Cu—S bonds in digenite could also diminish the indium carrying capacity of digenite.

Hexastannite which has the "wurtzite" structure with sulphur atoms in hexagonal closest packing is a poor indium carrier (0.04%) relative to the tetragonal stannite (2.1%) with the "sphalerite" structure and cubic close packed sulphur atoms. Both minerals have similar compositions (Table 7). Fleischer (1955) also noted that indium occurs in higher concentrations in sphalerite than in wurtzite. The tetrahedral Zn—S bond-lengths in wurtzite are the same as those in sphalerite, and similarly the tetrahedral metal-sulphur bond-lengths in hexastannite and the tetragonal stannite (from lattice parameter measurements) are also comparable. The substitution of indium in sulphide structures, therefore, seems to be governed more by the type of sulphur packing than by suitable bond-lengths.

Anderson (1953) noted that although indium can occupy octahedral as well as tetrahedral positions in β-In_2S_3 the ground-state configuration

TABLE 10. COMPARISON OF MOUNT PLEASANT INDIUM CONTENTS WITH PREVIOUS RECORDED VALUES (in weight per cent)

Mineral	Mount Pleasant	Recorded Maximum	Reference
Tetragonal Stannite	2.1 ±0.3	0.1	Ivanov *et al.* (1961)
Sphalerite	1.25±0.06	1.0	Fleischer (1955)
Chalcopyrite	0.19±0.08	0.15	Ivanov *et al.* (1961)
Cassiterite	0.03±0.01	0.009	Zabarina *et al.* (1962)
Galena	0.05[1]	0.001	Anderson (1953)

[1] Spectrographic analysis of galena concentrate.

of the indium atoms is KLMN $5s^25p$, and the formation of tetrahedral In—S covalent bonds using ($5s5p^3$) orbitals is preferred energetically as compared with octahedral bonds which also require the use of 6*d* levels. However, Nitsche & Merz (1962) synthesized $ZnIn_2S_4$ crystals in which indium occurs in octahedral as well as tetrahedral co-ordination with cubic packed sulphur atoms. Thus the possibility of indium substitution in octahedrally co-ordinated sulphides cannot be completely dismissed.

Herzenbergite (SnS), alabandite (MnS), and hauerite (MnS_2) have structures with sulfur atoms in cubic closest packing, and octahedral metal-sulphur bond-lengths of 2.62–2.68 Å, 2.61 Å and 2.55 Å respectively (Troshin, 1965). These values are comparable with octahedral In—S bonds (2.54–2.68 Å) in β-In_2S_3; therefore these three sulphides are also potential indium carriers. Alabandite has the galena (NaCl) structure, herzenbergite the same structure as teallite (a deformed galena-type lattice) and hauerite has the pyrite structure.

Among the sulphides identified at Mount Pleasant (Petruk, 1964) only galena and pyrite have sulphur atoms in cubic closest packing with octahedral metal-sulphur bonds. However, the Pb—S bondlength (2.96 Å) in galena is considerably greater, and the Fe—S bondlength (2.27 Å) in pyrite is much less than the octahedral In—S bond (2.54–2.68 Å) in β-In_2S_3. Thus it is not surprising that indium substitution in these minerals is limited (Table 2).

In summary then, indium substitutes most favourably in sulphide structures which have sulphur atoms in cubic closest packing with metal-sulphur tetrahedral and possibly octahedral bonds comparable in length with In—S bonds in stable indium sulphides. The valency and size of the metal atoms replaced are of secondary importance.

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