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Tin-bearing sulphides from St Michael's Mount and Cligga Head, Cornwall

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ABSTRACT. The result of electron probe microanalyses, along with X-ray and optical data obtained for tin sulphides from two different localities in south-west England indicate that the mineral hitherto described from St Michael's Mount as stannite is in fact kesterite, $Cu_2(Fe_{0.23}Zn_{0.77})SnS_4$. The yellow 'stannite' reported from this locality proved to be stannoidite, $Cu_8(Fe_{2.39}Zn_{0.61})SnS_2S_{12}$. Kesterite, $Cu_2(Fe_{0.09}Zn_{0.91})SnS_4$, and zincian stannite, $Cu_2(Fe_{0.63}Zn_{0.38})SnS_4$, are also reported from Cligga Head. It is suggested that a more cautious approach should be taken in identifying these tin sulphides solely on their optical properties.

IN the system Cu-Fe-Zn-Sn-S, Ramdohr (1960, 1969) recognized four minerals which he subsequently called Zinkies I to IV. However, it was not until the more recent studies by Springer (1972), Petruk (1973), Hall *et al.* (1978), and Kissin and Owens (1979), that the detailed structural, compositional, and optical properties of these minerals were properly documented.

Stannite and kesterite, two of the better-known tin sulphides, are the Fe and Zn end-members, respectively, of the $Cu_2(Fe,Zn)SnS_4$ mineral group. Springer (1972) presented the first phase diagram for this system. His quenching and differential thermal analyses results showed that at above 680 °C a complete solid solution exists between the two minerals, but below this temperature the two are partially immiscible, due to a phase transition in the stannite structure. The immiscibility region starts at 680 °C on the Fe-rich side and extends to the Zn-bearing compositions at progressively lower temperatures. Springer subsequently referred to the two tetragonal stannites separated by the miscibility gap as α and β forms. He also found that these two stannites have distinct lattice parameters, with $2a = c$ in β-stannite and $2a$ greater than c by 0.19 Å in α-stannite. Kesterite is apparently isostructural with the β form.

Moh (1978) showed that the α-β inversion temperature of stannite may vary greatly depending on whether it coexists with chalcopyrite or sphalerite. Petruk (1973), on the basis of chemical analyses of kesterites and ferrian kesterites from the New Brunswick tin mines, Canada, suggested that a wider immiscibility region should be expected between the α and β forms when natural materials are considered, and revised Springer's diagram according to his own data.

Stannoidite is a lesser-known tin sulphide; as a new mineral, it was first described by Kato (1969), but it had been reported previously as yellow stannite by many authors. Ramdohr (1969) gave the name hexastannite to his Zinkies I and suggested the formula Cu_6FeSnS_8 with a hexagonal structure. Kato (1969) proposed the formula $Cu_5(Fe,Zn)_3Sn_2S_{12}$. Kato and Fujiki (1969) found that stannoidite has an orthorhombic symmetry and not a hexagonal one as proposed by Ramdohr (1960); their cell parameter measurements gave $a = 10.76$, $b = 5.40$, and $c = 16.09$ Å. The structure of stannoidite was analysed by Kudoh and Takéuchi (1976), who allocated the formula $Cu_8(Fe,Zn)_3Sn_2S_{12}$, which can be compared with $Cu_6(Fe,Zn)_3Sn_3S_{12}$ for stannite when expressed in terms of the same number of sulphur atoms, i.e. the former has one less Sn^{4+} and two additional Cu^+ atoms. This formula, however, does not balance electrostatically and the problem was only solved by the use of Mössbauer spectroscopy which showed that both ferrous and ferric ions were present and that for Zn-free stannoidite, the content of ferric iron was twice that of ferrous iron (Yamanaka and Kato, 1976). Thus the formula in detail can be stated as $Cu_8^+Fe_2^{3+}(Fe^{2+},Zn^{2+})Sn_2^{4+}S_{12}^{2-}$ and probably indicates that there is a maximum Zn substitution of one Zn per formula unit, i.e. $Zn/(Zn+Fe) \leqslant 0.33$.

Other known CuSn sulphides include chatkalite, $Cu_6Fe^{2+}Sn_2O_8$, mawsonite, $Cu_6Fe_2^{3+}SnS_8$, rhodostannite, $Cu_2FeSn_3S_8$ (Springer, 1968), and kuramite, Cu_3SnS_4 (Kovalenker *et al.*, 1979); all are free from appreciable Zn and have not so far been reported from Cornwall.

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Stannite is the only mineral in this group that has been previously reported from south-west England from two specific localities, namely St Michael's Mount (SW 515 299) and Cligga Head (SW 737 538).

Mineralogy and chemistry

In order to study the mineralogy and chemistry of Cornubian tin sulphides, numerous samples were collected from mineralized veins in different parts of the two small granitic plutons of St Michael's Mount and Cligga Head, and in the case of Cligga Head also from all three levels of the abandoned mine. More than 200 polished sections and numerous polished thin-sections (for electron probe microanalysis) were prepared. The results of the detailed X-ray, optical, and chemical studies follow.

St Michael's Mount. Stannoidite was found in abundance at St Michael's Mount. Almost every polished section prepared of the sulphides from the southern flank of the granite contained some stannoidite. Its position in the paragenetic sequence of mineralization is after that of löllingite and arsenopyrite. It is very closely associated with kesterite, either replacing it or exsolving from it (fig. 1). In reflected light it displays a distinct pink colour, very strong bireflection, and conspicuous pleochroism. Hosking (1968) also noticed the presence of stannoidite at St Michael's Mount but, due to lack of chemical and X-ray data, misidentified it, describing it as either a pink variety of stannite or as mawsonite.

The chemical composition and atomic proportions of St Michael's Mount stannoidites are presented in Table I. The mineral is close to stoichiometric $Cu_8(Fe,Zn)_3Sn_2S_{12}$ with $(Fe+Zn)$ ranging between 2.96 and 3.04. The amount of Zn present ranges roughly from 2.5 to 3.5 wt. %. According to Yamanaka and Kato's (1976) Mössbauer spectral studies, Zn^{2+} substitutes Fe^{2+} in the structure; in the St Michael's Mount stannoidite the maximum $Zn/(Zn+Fe)$ ratio is approximately 0.23. Lee *et al.* (1975) showed that the terminal stability of stannoidite varies considerably with the Zn content. Their differential thermal analysis results show that whilst naturally occurring stannoidite (which usually contains 3 wt. % Zn) decomposes to bornite, stannite, and chalcopyrite

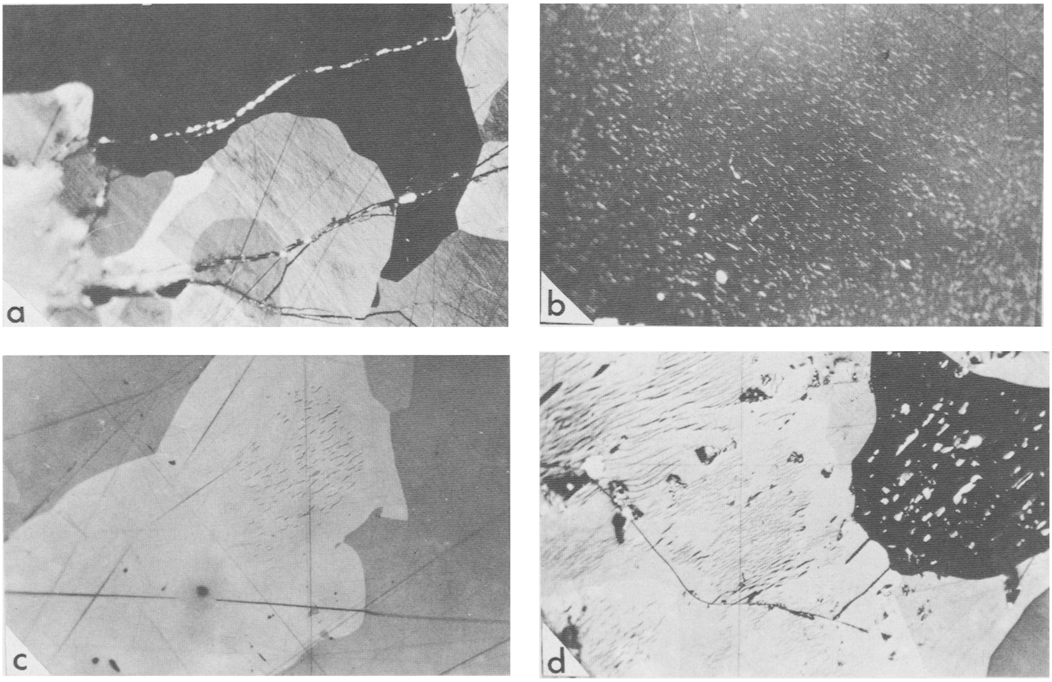

FIG. 1. (*a*) Kesterite (black) and stannoidite from St Michael's Mount (× 800, oil immersion). (*b*) Stannoidite exsolution lamellae in kesterite (× 1050, oil immersion). (*c*) Kesterite exsolution lamellae in stannoidite (× 1050, oil immersion). (*d*) Kesterite and stannoidite from St Michael's Mount, each containing exsolution lamellae of the other (× 800, oil immersion, blue filter).

TABLE I. *Stannoidite analyses from St Michael's Mount*

	STD1	STD2	STD3	STD4	STD5	STD6	STD7	STD8
S	29.60	29.49	29.49	29.18	29.37	29.36	29.63	29.32
Sn	18.50	18.70	18.38	18.66	18.57	18.83	18.47	18.49
Fe	10.72	10.43	10.64	10.27	10.17	9.97	9.85	9.91
Zn	2.79	2.76	2.53	3.12	2.84	3.23	3.43	3.39
Cu	38.87	38.92	39.01	38.52	38.74	38.79	39.02	38.77
Total	100.48	100.30	100.05	99.75	99.69	100.18	100.40	99.88
Atomic Ratios								
S	11.99	11.98	11.99	11.94	12.00	11.97	12.01	11.97
Sn	2.02	2.05	2.02	2.06	2.05	2.07	2.02	2.04
Fe	2.49	2.43	2.48	2.41	2.39	2.33	2.29	2.32
Zn	0.55	0.55	0.50	0.63	0.57	0.65	0.68	0.68
Cu	7.94	7.98	8.00	7.95	7.99	7.98	7.99	7.99
Fe+Zn	3.04	2.98	2.98	3.04	2.96	2.98	2.97	3.00

at 500 °C, the Zn-free synthetic stannoidite is stable up to 800 °C.

When plotted on the triangular (Fe + Zn)–Cu–Sn diagram (fig. 2) St Michael's Mount stannoidites group in the same position as those analysed by Springer (1968) and Petruk (1973) from other localities. This diagram displays only the variations among the metals; differences in metal to sulphur ratios are not shown.

Fig. 3 shows the binary Cu/(Fe + Sn) *vs.* Fe/(Fe + Zn) diagram. Again it can be seen that stannoidite from St Michael's Mount has a similar composition to most published analyses of this mineral.

It proved difficult to obtain powder X-ray diffraction photographs of stannoidite from St Michael's Mount, mainly because of the very small grain size and the existence of intimate intergrowths with kesterite. Nevertheless the (213) and (020) reflections were clearly recorded on several occasions.

On an optical basis it was not possible to determine whether the grey tin sulphide collected from the mineralized veins on the southern flank of St Michael's Mount was stannite or kesterite. The main differences are found in their respective micro-hardness and reflectance values; in the absence of such data the two minerals are almost indistinguishable optically. For this reason many

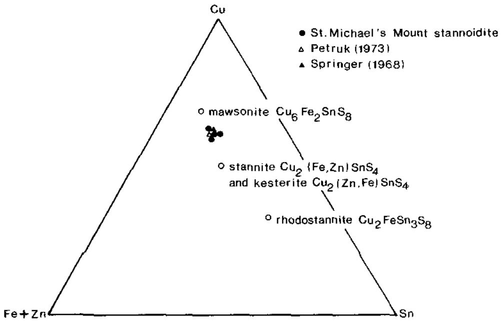

FIG. 2. The position of St Michael's Mount stannoidite on the Cu–(Fe + Zn)–Sn diagram compared with results from other authors.

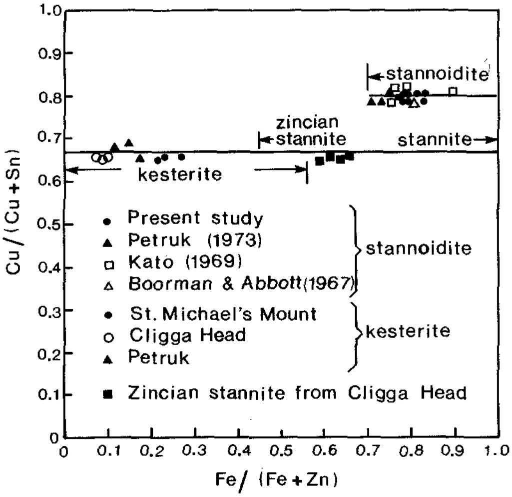

FIG. 3. The position of the analysed tin sulphides from Cornwall on the Cu/(Cn + Sn) *vs.* Fe/(Fe + Zn) diagram compared with results from other localities world-wide.

electron probe microanalyses were carried out on several sections in order to establish the chemical composition. The results all show a homogeneous composition which when plotted on Petruk's Cu/(Cu+Sn) *vs.* Fe/(Fe+Zn) diagram (fig. 3) fall well within the range of kesterite compositions. Table II presents the analyses and atomic proportions of these kesterites. The composition is virtually stoichiometric with Fe ranging from 22 to 25% in the (Zn,Fe) position.

TABLE II. *Kesterite analyses from St Michael's Mount*

	SK1	SK2	SK3	SK4	SK5	SK6	SK7	SK8
S	29.19	29.18	29.56	29.35	29.28	29.49	29.16	29.22
Sn	28.07	27.80	28.17	28.05	27.90	28.14	27.86	27.69
Fe	3.12	2.94	2.82	3.20	3.35	3.08	2.44	2.87
Zn	10.18	11.33	11.23	10.48	10.17	10.73	11.87	11.31
Cu	29.40	29.07	28.36	29.00	29.15	29.08	28.74	29.07
Total	99.96	100.32	100.14	100.08	99.85	100.52	100.07	100.16
Atomic Ratios								
S	4.00	3.98	4.03	4.01	4.01	4.01	3.99	3.99
Sn	1.04	1.03	1.04	1.04	1.03	1.03	1.03	1.02
Fe	0.25	0.23	0.22	0.25	0.26	0.24	0.19	0.23
Zn	0.68	0.76	0.75	0.70	0.68	0.72	0.80	0.76
Cu	2.03	2.00	1.95	2.00	2.01	2.00	1.99	2.00
Fe+Zn	0.93	0.99	0.97	0.95	0.94	0.96	0.99	0.99

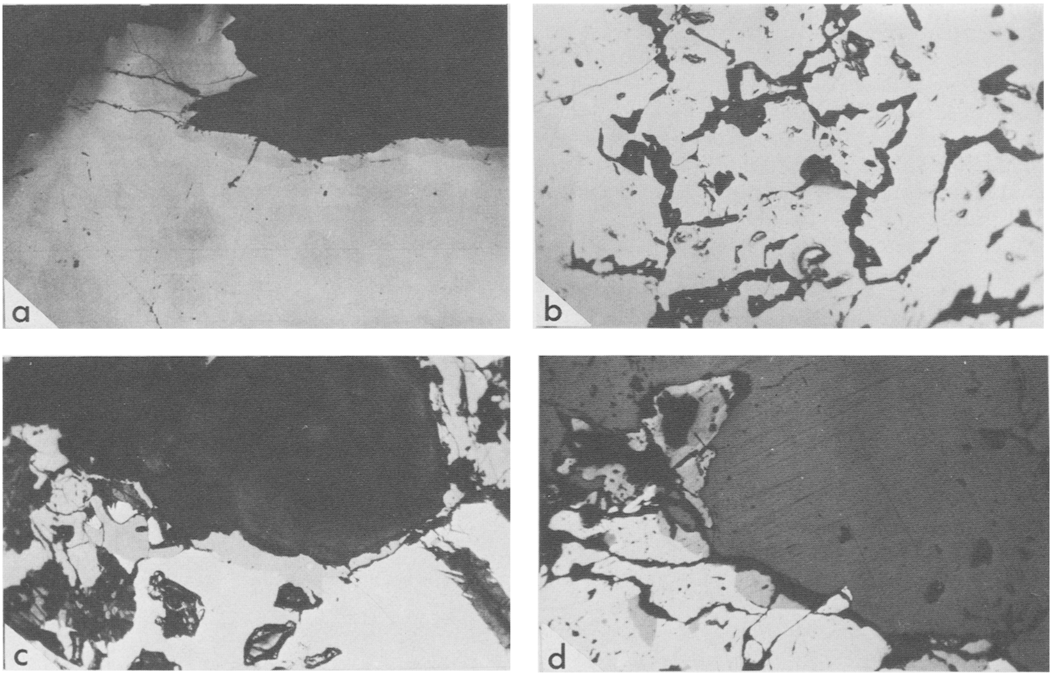

FIG. 4. (*a*) Zincian stannite from St Michael's Mount forming a narrow rim between quartz gangue (dark grey) and kesterite (light grey) (× 600, oil immersion, green and blue filters). (*b*) Late cassiterite filling cracks in stannoidite from St Michael's Mount (× 600, oil immersion). (*c*) and (*d*) Cassiterite (dark grey) being rimmed and replaced by zincian stannite (light grey) from Cligga Head (× 600 and × 800 oil immersion).

Powder X-ray diffraction patterns of stannite and kesterite are very similiar, with the actual differences being in the diffraction lines of low relative intensities. The d_{103} reflection, which is only present for kesterite, represents one such line with a relative intensity of 5. This line was clearly recorded on several diffraction charts prepared from St Michael's Mount specimens.

Stannite was encountered only in two sections (more than 100 polished mounts and polished thin sections were studied from St Michael's Mount for electron microprobe and ore microscopy investigations). In both sections it occurs in a similar way, forming a narrow rim between kesterite and quartz gangue (fig. 4). When analysed it was found to contain between 3 and 4 wt. % zinc and hence should be referred to as zincian stannite.

Cligga Head. The mode of occurrence of stannite and kesterite at Cligga Head is quite different from that at St Michael's Mount. First, these sulphides are paragenetically very closely associated with sphalerite and chalcopyrite (fig. 5). Secondly, some result, at least in part, from replacement of cassiterite (fig. 4), a phenomenon that was not observed in the St Michael's Mount specimens.

Kesterite is not very common at Cligga Head, and has only been detected in one section so far. It displays a dark-grey colour in incident light and is almost isotropic. The presence of exsolution bodies of sphalerite in these kesterites is a common feature (fig. 4). When analysed by electron microprobe kesterite proved to have a stoichiometric composition, with Fe ranging between 7 and 14% in the Zn–Fe position. Table III lists the chemical composition and the atomic proportions of these kesterites.

Stannite is the most abundant tin sulphide at Cligga Head. It displays an olive-grey colour in reflected light with a bluish-grey anisotropy. Almost every grain studied contained exsolution blebs and lamellae of sphalerite or chalcopyrite (fig. 5), and in some cases both. Stannite itself may also occur as an exsolution product in either of these two minerals.

When analysed by electron microprobe, Cligga Head stannite was found to contain between 5 and 6 wt. % Zn (Table IV). Hence when plotted on the Cu/(Cu + Sn) *vs.* Fe/(Fe + Zn) diagram (fig. 3) it falls within the region of zincian stannite, cf. Kissin and Owens (1979) and Sugaki *et al.* (1981). Powder

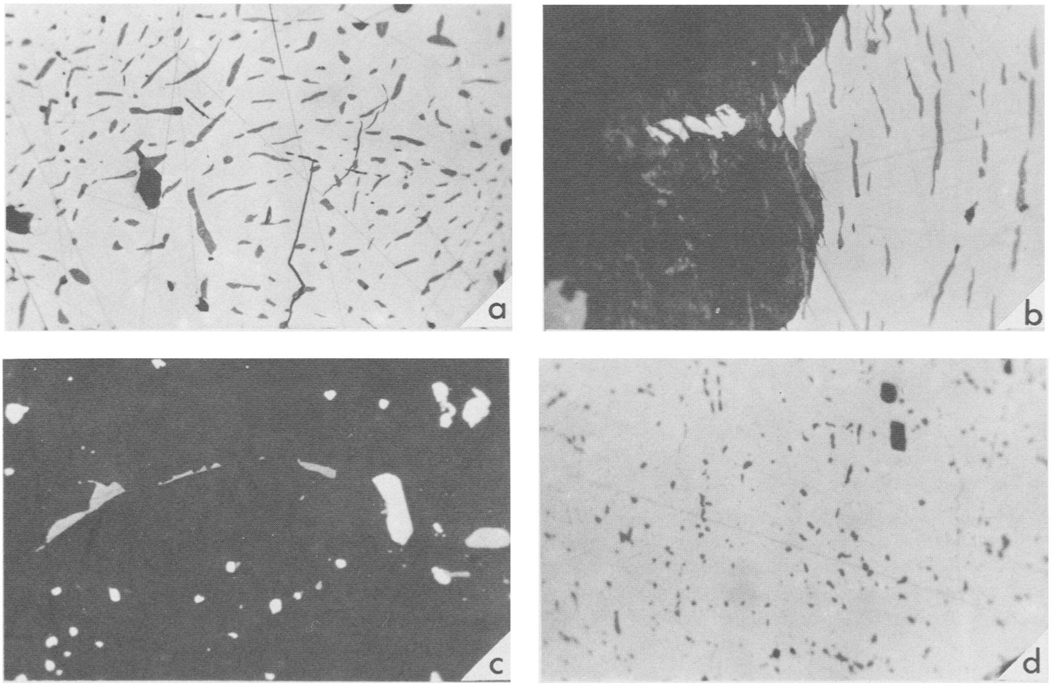

FIG. 5. (*a*) Sphalerite exsolution lamellae in zincian stannite from Cligga Head (×320, oil immersion). (*b*) Stannite exsolution lamellae in chalcopyrite. Note how the lamellae resist the chalcopyrite alteration to covellite (×320, oil immersion, yellow filter). (*c*) Stannite and chalcopyrite exsolution in sphalerite (×600, oil immersion). (*d*) Sphalerite exsolution lamellae in chalcopyrite (×800, oil immersion grey filter).

TABLE III. *Kesterite analyses from Cligga Head, sampled from a complex lode inside the second level of the mine*

	CK1	CK2	CK3	CK4	CK5	CK6	CK7
S	28.89	28.97	29.06	28.87	29.15	28.84	29.21
Sn	28.45	28.32	28.11	28.10	28.04	28.26	27.79
Fe	0.93	1.25	0.91	1.06	1.73	1.00	0.90
Zn	13.75	12.76	13.00	13.83	12.55	13.37	13.69
Cu	28.70	28.83	29.04	28.91	28.35	28.74	28.45
Total	100.70	100.13	100.12	100.77	99.82	100.21	100.04
Atomic Ratios							
S	3.97	3.99	3.99	3.95	4.01	3.97	4.01
Sn	1.05	1.05	1.04	1.04	1.04	1.05	1.03
Fe	0.07	0.10	0.07	0.08	0.14	0.08	0.07
Zn	0.93	0.86	0.88	0.93	0.85	0.90	0.92
Cu	1.98	2.00	2.01	2.00	1.97	2.00	1.97
Fe+Zn	1.00	0.96	0.95	1.01	0.99	0.98	0.99

TABLE IV. *Chemical composition of zincian stannite from Cligga Head*

	CS1	CS2	CS3	CS4	CS5	CS6
S	29.08	29.37	29.33	29.31	29.36	29.33
Sn	27.82	27.66	27.63	27.92	27.76	27.65
Fe	8.38	8.07	8.17	8.32	7.83	7.96
Zn	5.81	5.97	5.68	5.48	6.07	6.02
Cu	29.19	29.06	29.10	28.99	29.14	28.81
Total	100.28	100.13	99.91	100.02	100.16	99.77
Atomic Ratios						
S	3.94	3.98	3.98	3.98	3.98	3.99
Sn	1.02	1.01	1.01	1.02	1.02	1.02
Fe	0.65	0.63	0.64	0.65	0.61	0.62
Zn	0.37	0.40	0.38	0.36	0.40	0.40
Cu	2.00	1.99	1.99	1.99	1.99	1.98
Fe+Zn	1.02	1.03	1.02	1.01	1.01	1.02

X-ray diffraction patterns revealed a structure similar to that of stannite. However, the lattice parameters of stannite and zincian stannite are very similar and only slight shifts in the positions of the powder film lines occur. Furthermore none of the weaker lines (020), (004), (220), and (024) which should be present in stannite was recorded. This is in agreement with Springer's results (1972) which showed that the separation of these lines decreases non-linearly as the Zn content of the stannite increases, and that they merge when the composition is $Cu_2Zn_{0.4}Fe_{0.6}SnS_4$, a composition similar to that of Cligga Head's zincian stannite.

No stannoidite was detected in the Cligga Head specimens.

Discussions and conclusion

The similarity in the optical properties of stannite and kesterite, and in their powder patterns, has caused kesterite, being relatively uncommon, to be misidentified as stannite on many occasions, in the absence of chemical data. This even includes a number of museum specimens (Kissin and Owens, 1979). The present study indicates that the same may also hold in south-west England for those tin sulphides that, on an optical basis alone, have previously been called stannite. St Michael's Mount is well known in south-west England as a stannite locality. Many authors, including Davison (1920), Hosking (1953, 1968), and Jackson (1976), have studied the St Michael's Mount stannite. However, in view of the above-mentioned compositional and X-ray data, it may be that the majority of the so-called stannite reported from St Michael's Mount is misidentified kesterite. Hosking (1968) also describes a pink variety of stannite from St Michael's Mount which, as was explained in the previous section, proved to be stannoidite.

The subtle difference in the powder pattern of stannite and kesterite has caused many authors to use the single-crystal diffraction methods in order to differentiate between the two. Hall *et al.* (1978), using such a method, showed that kesterite and stannite have distinct structures. According to these studies the principal difference is in the cation ordering of the unit cell, especially the positioning of the Cu ions. Their results ascribe stannite to the $I\bar{4}2\,m$, and kesterite to the $I\bar{4}$ space group. Kissin and Owens (1979) have also shown that stannite and kesterite are structurally distinct; their comparison of unit cell parameters and chemical composition of these minerals from world-wide localities showed that there is no tendency for the cell parameters to converge as a function of solid solution (increase or decrease in Fe and Zn contents).

The Zn enrichment of Cligga Head stannite is not surprising as it has been known for a long time that the association of stannite with sphalerite generally leads to enrichment of Zn in stannite. Nekrasov *et al.* (1975) indicated that such an enrichment may even reach the point of kesterite formation according to the equation:

$$Cu_2FeSnS_4 + ZnS \rightarrow Cu_2ZnS_4 + FeS$$

Whether Cligga Head kesterites are the result of such a reaction is not known, since such a conclusion can only be reached when sufficient data on partition of Zn and Fe between sphalerite and stannite at different temperatures and pressures are available.

No isostannite (cubic stannite) similar to that reported by Claringbull and Hey (1955) was found. Hosking (1968) also stated his disappointment in failing to detect such a mineral in his specimens from Cligga Head. The presence of such a mineral and its relation to stannite and kesterite merits further investigation.

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