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Stannite group minerals: investigations on stannite and kesterite

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ABSTRACT. — The optical, chemical and X-ray powder diffraction characteristics of the « stannite group » minerals in the collection of the Mineralogical Museum of the University of Florence are reported.

Stannite and kesterite are the only minerals present. This work has enabled a revised and complete stannite diffraction pattern to be reported, doubt to be shed on the evidence for the existence of isostannite and evidence presented that WANG'S (1982) synthetic product is actually a stannite.

Key-words: stannite, kesterite, X-ray diffraction, chemical composition, optical features.

RIASSUNTO. — Sono stati studiati per via ottica, diffrattometrica e spettrochimica campioni di stannite e kesterite, provenienti da tipiche mineralizzazioni idrotermali a Sn e a solfuri polimetallici, della Cornovaglia, Bolivia e Boemia.

Nel lavoro vengono riportati, accanto alle problematiche inerenti la sistematica e le relazioni di fase dei minerali, i risultati acquisiti che definiscono lo spettro di diffrazione della stannite, non confermano l'esistenza della isostannite e fanno ritenere che il prodotto sintetizzato da WANG (1982) sia in realtà una stannite.

Parole chiave: stannite, kesterite, diffrazione a raggi X, composizione chimica, caratteristiche ottiche.

Introduction

In this paper the results of an optical, diffractometric and spectrochemical study on « stannite group » minerals are reported. The studied samples belong to the collection of the Mineralogical Museum of the University of Florence. Moreover to check our analytical procedures, two samples from the deposit of Brunswick Tin Mines Limited already studied by PETRUK (1973) have been analyzed (samples n. 29-750, 52-523).

Recently several authors (CORSINI & TANELLI, 1984; MOORE & HOWIE, 1984) have pointed out both the uncertainties concerning the mineralogy of the Cu-Fe-Zn-Sn-S (table 1) system and the potential uses of the « stannite group » minerals to improve our knowledge of certain physicochemical features of the hydrothermal environment. For this reason, a research program both on natural and synthetic products is being carried out in the Dipartimento di Scienze della Terra dell'Università di Firenze; this paper represents a contribution to the program.

Analytical methods and experimental results

The only minerals of the stannite group detected in the samples from the Mineralogical Museum of Florence are stannite and kesterite. In table 2, the main optical and textural features of this minerals, together with details of the localities and the mineralogical assemblages in which they occur, are reported.

As a rule, our stannite and kesterite samples have optical features similar to those reported in literature (KISSIN & OWENS, 1979). The only exception is the very weak anisotropy of the sample 17036 (Zn-stannite) from Cligga Head (Cornwall) that makes it similar to kesterite. Usually stannite occurs as an intergrowth of grains with different orientations (fig. 1), but patches of quadrangular net shaped polysinthetic twinning (fig. 2) are also present.

The spectrochemical analyses, carried out using a Cambridge Stereoscan 250 equipped

TABLE 1

« Stannite group » minerals

REPORTED ATTRIBUTIONS IN THE LITERATURE

Stannite I (RAMDOHR, 1980) = Hexastannite = "Stannite jaune" = Stannoidite (YAMANAKA & KATO, 1976)

Stannite II (RAMDOHR, 1980) = Isostannite (CLARINGBULL & HEY, 1956) = Kesterite (KISSIN & OWENS, 1979)

Stannite III (RAMDOHR, 1980)

Stannite IV (RAMDOHR, 1980)

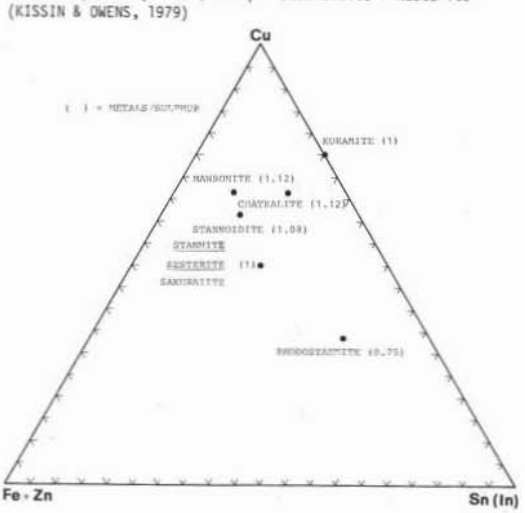
Orange bornite = Brown stannite = Mawsonite (SZYMANSKI, 1976)

Zn-stannite - $Cu_{2.14}(Zn_{.51}Fe_{.28})Sn_{.97}S_4$ (BERRY & THOMPSON, 1962) = Kesterite (JCPDS n. 21-883) = Kesterite + Stannite (KISSIN & OWENS, 1979)

Zn-stannite - $Cu_2Fe_{.6}Zn_{.4}SnS_4$ (PETRUK, 1973; MOORE & HOWIE, 1984); ? - (KISSIN & OWENS, 1979)

Fe-kesterite (PETRUK, 1973) = Kesterite (KISSIN & OWENS, 1979)

"Unknown phase" (PETRUK, 1973) = Stannoidite + Kesterite (KISSIN & OWENS, 1979)



IMA APPROVED MINERALS (FLEISCHER, 1983 & 1985)

Name	Chemical formula	Space group
Mawsonite	$Cu_6Fe_2SnS_8$	$P\bar{4}m2$
Chatkalite	$Cu_6FeSn_2S_8$	$P\bar{4}m2$
Stannoidite	$Cu_8Fe_2(Fe,Zn)Sn_2S_{12}$	I222
Stannite	$Cu_2(Fe,Zn)SnS_4$	$I\bar{4}2m$
Kesterite	$Cu_2(Zn,Fe)SnS_4$	$I\bar{4}$
Kuramite	Cu_2CuSnS_4	$I\bar{4}2m$
Sakuraiite	$(Cu,Zn,Fe,Ag)_3(In,Sn)S_4$	Tetragonal
Rhodostannite	$Cu_2FeSn_3S_8$	$I4_1/a$

with EDS Link (Si-Li detector) and using a pyrite as standard for S and pure metals for the other elements, are reported in table 3. In table 2 and 3 the characteristics of kesterites determined on the samples from New Brunswick are also reported.

The samples 1494, 1495, 1497, 1498, 1499 and 12917 have chemical compositions typical of stannite, as can be seen from table 3 and fig. 3. On the other hand, samples 17036 and 1496 have a Fe/Zn ratio such that it is not possible to ascribe them, on a chemical basis, to either stannite or kesterite.

The X-ray powder pattern data of stannite 1499 (carried out using a Philips PW 1130 diffractometer and employing CuKα radiation) is reported in table 4. This pattern is almost the same as the stannite of Oruro (KISSIN & OWENS, 1979). Moreover, all of the stannite X-ray powder diffraction patterns examined in this study as well as that of stannite from Dachang (CORSINI & TANELLI, 1984), show at about 5.35 Å and 3.85 Å, two peaks (002 and 110) which are consistent with the $I\bar{4}2m$ space group of stannite. Such peaks are not, however, reported in the Oruro stannite diffractometer pattern, while they are reported in the «cubic phase» of FRANZ (1971), suggested to be the same as isostannite by CLARINGBULL & HEY (1956). CORSINI & TANELLI (1984) suggested, from the presence of these peaks, that the Dachang samples may be either a mixture of stannite and isostannite or a mineral like the synthesized product of WANG (1982). On the other hand, the results of this work suggest that these peaks, always present and in agreement with the $I\bar{4}2m$ space group, belong to stannite.

The X-ray powder diffraction patterns of samples 17036 and 1496 are reported in table 4. These samples, as previously mentioned, have similar optical features and chemical compositions to either stannite or kesterite. On the other hand, the X-ray powder pattern of sample 1496 from Zinnwald, is like kesterite from Oruro (KISSIN & OWENS, 1979). This pattern lacks the typical stannite doublets (004, 020; 034, 220; 116, 132) which are evident, even if very weak, in the sample 17036 from Cligga Head.

TABLE 2

Occurrence, mineralogical assemblages and optical and textural features of the stannite and kesterite samples studied in this work

	SAMPLE	MINERALOGICAL ASSEMBLAGE	OPTICAL AND TEXTURAL FEATURES (°)
1) 1494;	Oruro (Bolivia)	Sphalerite, marcasite, stannite	a) light brown, olive-grey; b) strong: brownish to olive; c) strong: brown-yellowish to olive-greyish; d) polysynthetic twinning
2) 1495;	Animas sur Chicals (Bolivia)	Pyrite, aramayoite, quartz, stannite	a), b), c), d): the same as sample n. 1
3) 1496;	Zinnwald, Bohemia (Czechoslovakia)	Galena, tennantite, aikinite, chalcopyrite, kesterite	a) greyish; b) not present; c) weak
4) 1497;	Illogan, East Pool Mine (Cornwall)	Arsenopyrite, wolframite, chalcopyrite, sphalerite, stannite	a), b), c): the same as sample n. 1
5) 1498;	Redruth, East Pool Mine (Cornwall)	Chalcopyrite, sphalerite, stannite	a), b), c): the same as sample n. 1; d) stannite-chalcopyrite intergrowth
6) 1499;	(Cornwall)	Chalcopyrite, stannite	a), b), c): the same as sample n. 1; d) polysynthetic twinning, quadrangular net shape
7) 12917;	St. Agnes (Cornwall)	Chalcopyrite, bismuthinite, covellite, quartz, stannite	a), b), c): the same as sample n. 1; d) the same as sample n. 5
8) 17036;	Cligga Head (Cornwall)	Sphalerite, chalcopyrite, arsenopyrite, pyrite, Zn-stannite	a) light greyish; b) not present; c) very weak: olive-grey to olive-greenish d) stannite-sphalerite intergrowth
9) 29-750;	Fredericton, New Brunswick (Canada)	Sphalerite, tennantite, cassiterite, arsenopyrite, quartz, fluorite, stannoidite, kesterite	a) greyish; b) not present; c) isotropic
10) 52-523;	Fredericton, New Brunswick (Canada)	Sphalerite, tennantite, stannoidite, kesterite	a), b), c): the same as sample n. 9; d) kesterite-stannoidite intergrowth

(°) a) = Colour; b) = Biriflectance; c) = Anisotropy; d) = Texture

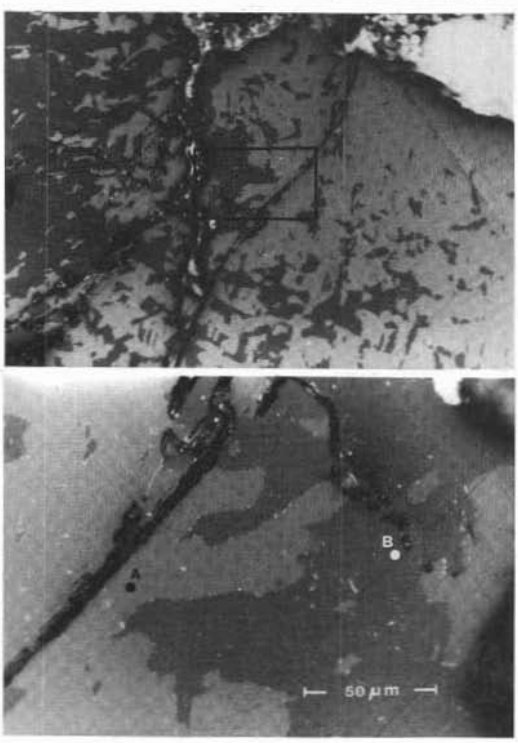


Fig. 1. — Photomicrograph (nearly crossed nicols, oil immersion) of stannite sample 12917. The analyzed points (*A* and *B*) show a same chemical composition.

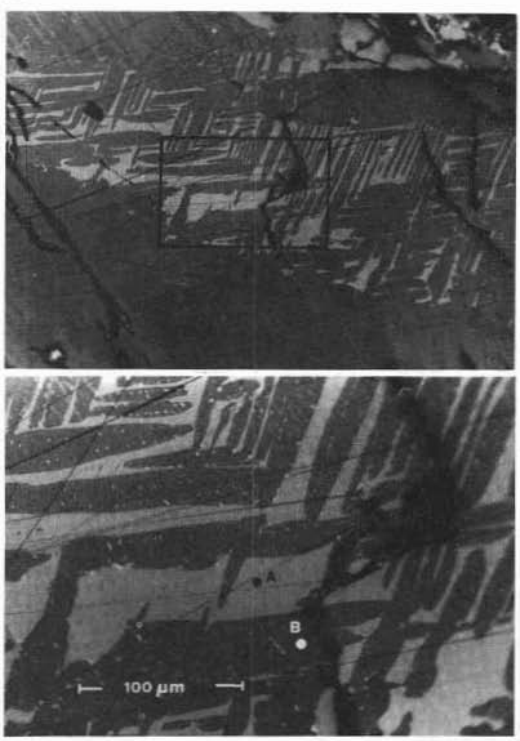


Fig. 2. — Photomicrograph (nearly crossed nicols, oil immersion) of stannite sample 1499, showing twinning fabrics owed to a possible high-low temperature transformation. The analyzed points (*A* and *B*) show a same chemical composition.

TABLE 3
Stannite and kesterite analyses

Sample (°)	Weight % (°°)						Atomic proportions						
	Cu	Fe	Zn	Sn	S	Total	Cu	Fe	Zn	Sn	S	$\frac{Cu}{Cu+Sn}$	$\frac{Fe}{Fe+Zn}$
1) 1494 (5)	29.12	11.98 (11.84) (12.19)	1.59 (.93) (1.97)	28.95	29.23	100.87	1.98	.93	.10	1.05	3.94	.65	.90
2) 1495 (4)	28.89	12.82 (12.61) (13.10)	1.26 (1.13) (1.42)	28.36	29.10	100.43	1.97	.99	.08	1.03	3.92	.66	.93
3) 1496 (5)	29.02	7.03 (6.97) (7.14)	7.90 (7.57) (8.62)	27.74	29.16	100.85	1.98	.55	.52	1.01	3.94	.66	.51
4) 1497 (5)	27.96	10.91 (9.80) (11.57)	3.36 (2.28) (4.25)	28.52	29.03	99.78	1.92	.85	.22	1.05	3.95	.65	.79
5) 1498 (5)	28.01	10.57 (9.88) (11.00)	5.04 (4.73) (5.25)	27.16	29.15	99.93	1.91	.82	.33	.99	3.94	.66	.71
6) 1499 (4)	29.10	10.82 (10.58) (10.96)	2.97 (2.84) (3.10)	28.49	29.56	100.94	1.97	.83	.19	1.03	3.97	.66	.81
7) 12917 (5)	29.60	12.22 (11.74) (12.47)	1.41 (1.13) (1.74)	28.07	29.42	100.73	2.00	.94	.09	1.02	3.95	.66	.91
8) 17036 (5)	28.37	7.42 (7.37) (7.58)	7.40 (7.13) (7.74)	28.46	29.09	100.74	1.94	.58	.49	1.04	3.95	.65	.54
9) 29-750 (6)	29.81	3.08 (2.97) (3.28)	11.72 (11.42) (12.04)	26.00	29.00	99.61	2.05	.24	.78	.96	3.96	.68	.24
10) 52-523 (5)	29.20	2.90 (2.42) (4.05)	12.55 (12.08) (13.09)	26.99	29.10	100.69	2.00	.23	.84	.99	3.95	.67	.21

(°) The number of analyzed points is reported within round brackets.

(°°) Average values; for Fe and Zn the minimum and maximum values are also reported.

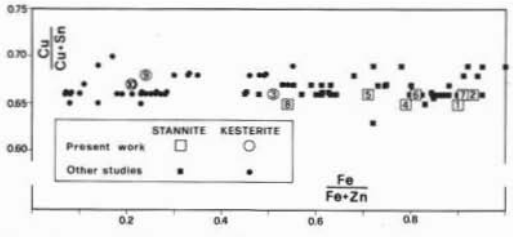


Fig. 3. — Values of Fe/Fe+Zn and Cu/Cu+Sn ratios for stannite and kesterite analyzed in this work (for the identification numbers see table 1) and from the literature (LEVY, 1967; SPRINGER, 1968; HARRIS & OWENS, 1972; PETRUK, 1973; KISSIN & OWENS, 1979; CORSINI & TANELLI, 1984; MOORE & HOWIE, 1984).

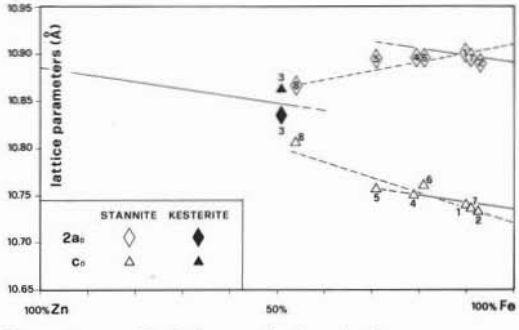


Fig. 4. — Variations of the lattice parameters versus the iron content and the zinc content in the analyzed stannite and kesterite (samples numbered according to table 1). In this figure the continuous lines are those reported by KISSIN & OWENS (1979), correlating stannite and kesterite lattice parameters and chemical composition.

Concluding remarks

According to HALL et al. (1978) stannite and kesterite, although both having a chalcopyrite-like pseudocubic structure, belong to two different space groups: $I\bar{4}2m$ (stannite) and $I\bar{4}$ (kesterite). The prominent structural differences are ascribed to cation packing effects, mainly involving copper. According to KISSIN & OWENS (1979) the correlation between stannite and kesterite

TABLE 4

X-ray powder diffraction patterns (CuKα radiation) of the stannite samples 1499 and 17036 and kesterite 1496

SAMPLE 1499 (STANNITE)			SAMPLE 17036 (Zn-STANNITE)			SAMPLE 1496 (KESTERITE)		
a_o = 5.448 ± 0.001			a_o = 5.433 ± 0.002			a_o = 5.418 ± 0.002		
c_o = 10.761 ± 0.003			c_o = 10.806 ± 0.004			c_o = 10.862 ± 0.005		
hkl	d_{obs}	d_{calc}	hkl	d_{obs}	d_{calc}	hkl	d_{obs}	d_{calc}
002	5.37	5.38	002	5.40	5.40			
011	4.83	4.86	011	4.85	4.85	011	4.85	4.85
110	3.84	3.85	110	3.84	3.84	110	3.83	3.83
112	3.14	3.13	112	3.13	3.13	112	3.13	3.13
020	2.72	2.72	020	2.71	2.72	020	2.71	2.71
004	2.69	2.69	004	2.70	2.70			
022	2.43	2.43	022	2.42	2.43	022	2.42	2.42
121	2.37	2.38	121	2.37	2.37	121	2.36	2.36
114	2.20	2.21	114	2.21	2.21			
220	1.924	1.926				220	1.914	1.915
024	1.914	1.914	024	1.918	1.916			
031	1.791	1.791						
132	1.642	1.641	132	1.637	1.637			
116	1.626	1.626	116	1.631	1.631	116	1.637	1.637
224	1.566	1.566	224	1.566	1.566	224	1.563	1.565
040	1.362	1.362	040	1.358	1.358			
008	1.345	1.345	008	1.350	1.351	008	1.358	1.358
332	1.249	1.249				332	1.244	1.243
136	1.243	1.242	136	1.244	1.243			

lattice parameters and stannite and kesterite chemical compositions leads to a $2a_o - c_o$ difference of about 0.15 for stannite, and near zero for kesterite. Such a correlation does not agree with our results for stannite. In fact, it appears from the data reported in fig. 4, that the lattice parameters converge with an increase in the Zn content.

The other main points of interest resulting from the present work are the following:

a) the stannite diffraction pattern shows two addictional reflections at about 5.35 Å and 3.85 Å compared to the published X-ray patterns (cfr. KISSIN & OWENS, 1979);

b) there is no evidence (in agreement with KISSIN & OWENS, 1979 and MOORE & HOWIE, 1984) of the phase equivalent to isostannite found by CLARINGBULL & HEY (1956), even though the studied samples were collected from Cligga Head and in Zinnwald where this phase was recognized;

c) the close resemblance between the studied stannites and the X-ray diffraction pattern of WANG's (1982) synthesized product leads us to think Wang's product is actually stannite.

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