

## Stannoidite, $\text{Cu}_5(\text{Fe}, \text{Zn})_2\text{SnS}_8$ , a New Stannite-like Mineral from the Konjo Mine, Okayama Prefecture, Japan

By

**Akira KATO**

Department of Geology, National Science Museum, Tokyo

### Introduction

The occurrences of a copper-iron-tin sulphide mineral optically identified as hexastannite have been reported from the Ashio (NAKAMURA, 1961), Fukoku (SHIMIZU, KATO, and MATSUO, 1966), Tada and Ikuno mines (IMAI, FUJIKI, and TSUKAGOSHI, 1967), all in Japan, from Tingha, New South Wales and Mt. Lyell, Tasmania (MARKHAM and LAWRENCE, 1965), and from Mt. Pleasant, New Brunswick (BOORMAN and ABBOTT, 1967). In spite of such common occurrences, the detailed mineralogical study has not been made mainly because of the finer grain size and intimate association with the other sulphide minerals forming very complex minute textures.

The mineral hexastannite formerly called Zinnkies? I (RAMDOHR, 1944) is very similar to or identical with the present material seeing from the x-ray powder data, optical properties, and the presence of copper, iron, tin, and sulphur as the essential constituents. However, the original description of hexastannite (RAMDOHR, 1960) is not always mineralogically complete (FLEISCHER, 1961), making it difficult to compare the present material with it.

During the observation of many polished sections including the optically identified hexastannites, the author encountered one polished section of the ore from the Konjo mine, Okayama prefecture, including the mineral grains large enough to be taken out for the x-ray single crystal study. Obtaining the mineralogical data for this material required as to the specification, the author inquired the Commission of New Mineral and Mineral Names, I. M. A., about the nomenclature of this mineral. The Commission decided to let the author give it a new name, and to retain the name hexastannite until the full mineralogical study is made along with the original material. Accordingly, the author proposed the name stannoidite in allusion to its similarity to stannite, and this name was approved by the Commission.

Very recently, LÉVY (1967) described a copper-iron-tin sulphide under the name stannite jaune (interpreted as yellow stannite in this paper). Seeing from the x-ray powder data, chemical composition and optical properties, some of his yellow stannites may be stannoidite. The relationship between stannoidite, yellow stannite, and hexastannite are discussed in this paper.

This study was made while the author was in Smithsonian Institution, U.S. National Museum, as a visiting research associate sponsored by National Research Council, U S. A., to which the author expresses his sincere thanks. He is also very much indebted to the advices of Professor Takeo WATANABE, Faculty of Science, Nagoya University, Professor Hideki IMAI, Faculty of Engineering, University of Tokyo, Dr. Brian MASON, Division of Meteorites, Smithsonian Institution, Dr. Yoshio TAKEUCHI, Faculty of Science, University of Tokyo, and Dr. Kin-ichi SAKURAI, Department of Geology, National Science Museum. His thanks are also due to Mr. Yoshinori FUJIKI, Faculty of Engineering, University of Tokyo, who took the photographs of the polished sections.

### Description of the Studied Specimen

The ore deposit of the Konjo mine is of vein type and had been worked for copper and silver for about fifty years ago and now closed. It is situated about 30 kilometers northeast of Okayama, and in Cretaceous rhyolite accompanied by rhyolitic tuff and altered andesite according to KAMBE and HIROKAWA (1963), who reported the occurrences of bornite, chalcopyrite, pyrite, stannite, and quartz in the ores. Also, the occurrence of silver in massive bornite is described by ITO and SAKURAI (1947).

The studied specimen came from the dump of the deposit and has been preserved in Geological Institute, University of Tokyo. It is a small massive sulphide ore containing stannoidite, chalcopyrite, and quartz as the visual constituents. Under the microscope, stannoidite occurs in two different modes of occurrences. One is a mem-

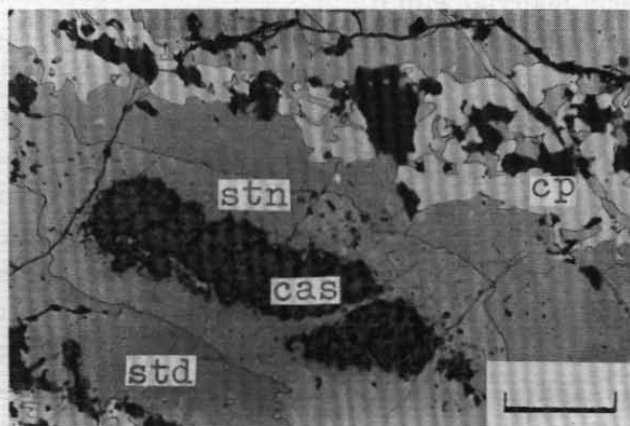


Fig. 1. Stannoidite (std) around stannite (stn) including cassiterite (cas), and in contact with chalcopyrite (cp). A stannite veinlet cuts chalcopyrite and stannoidite. Small bodies with intricate outline against chalcopyrite are stannite. The scale indicates 0.1 mm. One nicol.

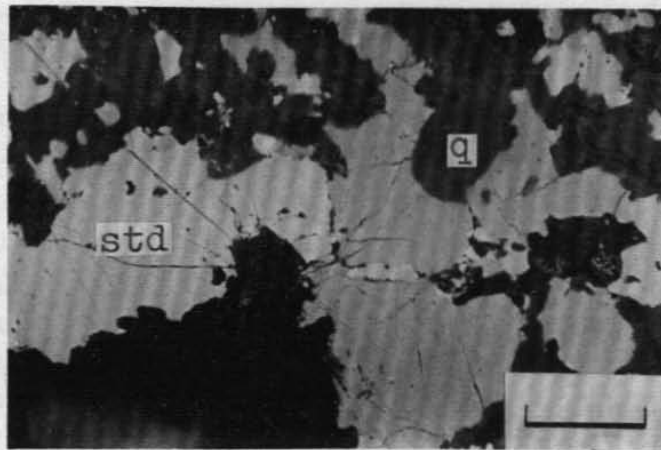


Fig. 2. Coarser-grained part of stannoidite (std) aggregate with quartz(q). The left below part (dark) was cut out for x-ray single crystal study. The scale indicates 0.1 mm. Obliquely crossed nicols.

ber of banded aggregate of sulphides around cassiterite. In the polished surface, there are queues composed of elongated aggregates of cassiterite grains partly replaced and surrounded by stannite. This stannite band reaching 1 mm. in total width is in turn surrounded by stannoidite, which is in the same manner by chalcopyrite (Fig. 1). A small amount of galena is present along the boundary between stannoidite and chalcopyrite or within chalcopyrite grains. There is no direct contact of cassiterite and stannoidite, and stannite and chalcopyrite in this banded aggregate, except where stannite veinlets cut chalcopyrite, which contains minute stannite grains exclusively along the veinlets as seen in Fig. 1. The other one is a member of aggregate outside of this banded aggregate. It occurs in larger grains up to 1.5 mm in maximum interstitial to quartz. The grains are composed of the aggregate of single crystals up to 0.2 mm. across, when surrounded by larger quartz grains. Small amounts of galena, chalcopyrite, tetrahedrite, and cassiterite are included within stannoidite grains, and siderite is within quartz grains. In this assemblage, cassiterite is in direct contact with stannoidite. Some of the larger single crystals were cut out from the polished surface by needle and presented for x-ray single crystal study (Fig. 2). Prior to this procedure, electron microprobe analyses were made along with the coarser-grained stannoidite to know the absence of significant inhomogeneity and the chemical composition itself.

### Physical and Ore Microscopic Properties

Stannoidite is brass brown in colour with metallic luster. That this mineral was at first called brown stannite (YAMAGUCHI, 1939) is due to its colour. Sometimes,

Table 1. X-ray powder data for hexastannite, yellow stannite, and stannoidite.

1		2		3				
$d(\text{\AA})$	$I$	$d(\text{\AA})$	$I$	$d(\text{\AA})$	$I$	$Q_{obs}$	$Q_{cal}$	$hkl$
		11	10					100(?)
		5.4	10	5.40	5	0.034	0.035	200
		5.1	10	5.14	1	0.038	0.038	011
		4.8	20	4.83	10	0.043	0.043	103
		4.1	10	4.13	3	0.059	0.058	112
		3.7	10	3.72	2	0.072	0.073	211
3.08	90	3.1	100	3.11	100	0.103	0.104	213
3.00	10	3.0	10	3.00	2	0.111	0.112	310
		2.80	10				0.127	312
2.67	40	2.69	20	2.70	15	0.137	0.137	020
							0.138	400
							0.139	006
				2.46	2	0.165	0.165	215
2.38	10	2.39	10	2.39	4	0.175	0.174	206
							0.174	305
				2.20	2	0.207	0.207	413
2.08	50			2.12	1	0.224	0.224	017
				2.00	2	0.250	0.251	510
							0.251	503
							0.251	303
1.892	100	1.901	90	1.906	70	0.2756	0.2752	420
							0.2759	026
1.785	30	1.79	10	1.795	2	0.3100	0.3112	600
		1.69	10				0.3493	611
1.618	80	1.621	50	1.621	20b	0.3800	0.3775	233
							0.3785	143
							0.3802	613
							0.3816	219
1.553	20	1.554	20	1.556	3	0.4140	0.4142	426
1.482	20						0.4557	136
		1.344	20	1.346	1	0.5530	0.5534	800
$a_0=3.84 \text{\AA}$		$a_0=10.76 \text{\AA} \pm 0.02 \text{\AA}$						
$c_0=12.6 \text{\AA}$		$b_0=5.40 \text{\AA} \pm 0.01 \text{\AA}$						
		$c_0=16.09 \text{\AA} \pm 0.04 \text{\AA}$						

1. Zinnkies? I. Unspecified locality. After RAMDOHR (1944). The original values are given by  $2\theta$  angle with unspecified kind of x-ray. The most reasonable one is  $\text{FeK}\alpha$ , on which the present calculation is based after the removal of  $\text{FeK}\beta$  lines from the original table.
2. Yellow stannite. Vaulry, France. After LÉVY (1967).
3. Stannoidite. Konjo mine, Okayama prefecture, Japan. Cu/Ni radiation. Diffractometer method. b=broad.

iridescence is formed by weathering. The streak is dark brown gray. It has no cleavage and the fracture is uneven to subconchoidal. The hardness is about 4 in Mohs' scale. The specific gravity could not be measured, but the calculated value is 4.29 as  $Z=3[\text{Cu}_5(\text{Fe}, \text{Zn})_2\text{SnS}_8]$  with Fe:Zn=92.6:7.4 in mole ratio.

Under the ore microscope, it is distinctly pleochroic from light salmon brown to brown in air and more distinct in oil without any significant changes in tint. Between crossed nicols, it changes from dark orange red to yellowish gray in air and scarlet to gray-yellow in oil. The reflectivity in air is nearly the same as the associated stannite in the lightest position as well as in oil. The polishing and scratching hardnesses are a little lower than those of the associated stannite. Etching reactions by the ordinary reagents are negative except  $\text{HNO}_3$  (1:1 and concentrated), which forms a brown stain well revealing the internal texture, composed of mosaic aggregate of randomly oriented crystals.

### X-Ray Studies

The precession photographs of the cut-out material were taken about c-axis on zero, first, and second layers of ac and bc planes, employing Mo/Zr radiation. They show orthorhombic symmetry with  $a_0=10.76\pm 0.02\text{\AA}$ ,  $b_0=5.40\pm 0.01\text{\AA}$ ,  $c_0=16.09\pm 0.04\text{\AA}$ . The diffraction spectra appear when  $h+k+l=2n$  to denote the possible space group to be  $I222$ ,  $I2_12_12_1$ ,  $I\text{mmm}$ , or  $I\text{mm}2$ . The photographs also suggest the presence of a pseudocubic subcell with  $a_0'=1/2a_0$ ,  $b_0'=b_0$ ,  $c_0'=1/3c_0$ ;  $a_0'\doteq b_0'\doteq c_0'\doteq 5.4\text{\AA}$ . This subcell is very close to the unit cell of sphalerite,  $a_0=5.4060\text{\AA}$  (SWANSON and FUYAT, 1953), in size and probably structure, as expected from the analogy in the x-ray powder data between stannoidite and stannite, which has double-celled sphalerite structure. Then, the unit cell content of stannoidite is  $3[\text{Cu}_5(\text{Fe}, \text{Zn})_2\text{SnS}_8]$ .

The x-ray powder data were obtained on the grains in association with quartz. They are very similar to those for hexastannite (RAMDOHR, 1944) and yellow stannite (LÉVY, 1967) as compared in table 1.

### Chemical Composition

The chemical analysis made by electron microprobe method is given in table 2, in which it is compared with those of hexastannites from Tingha, New South Wales (MARKHAM and LAWRENCE, 1965), and from Mt. Pleasant, New Brunswick (BOORMAN and ABBOTT, 1967), and of yellow stannite from Vaulry, France (LÉVY, 1967). As discussed by KATO and FUJIKI (1969), the most reasonable calculation base is total metal=8, which gives the empirical formula  $(\text{Cu}_{4.83}\text{Ag}_{0.01})_{4.84}(\text{Fe}_{1.86}\text{Zn}_{0.15})_{2.01}\text{Sn}_{1.15}\text{S}_{8.03}$ . If the deficiency of (Cu+Ag) and excess of Sn are neglected, the ideal for-

Table 2. Chemical analyses of stannoidite, hexastannites, and yellow stannite.

	1				2	3	4		
	Wt. %	Molecular quotient	Recalculated as total metal=8		Ideal number	Wt. %	Wt. %	Wt. %	
Cu	37.2	0.586	4.83	4.84	5	38.0	36.5	39.5	
Ag	0.1	0.001	0.01			11.2	11.8	13.3	
Fe	12.5	0.286	1.96	2.01	2	4.1	3.6	0.4	
Zn	1.2	0.018	0.15			15.6	17.8	16.4	
Sn	16.5	0.139	1.15				0.04		
In									
S	31.2	0.974	8.03		8	29.2	27.9	32.0	
Total	98.7					98.0	97.64	101.6	
			1a			2a	3a	4a	5a
	Wt. %					Wt. %	Wt. %	Wt. %	Wt. %
Cu	37.7					38.8	37.38	38.9	39.49
Ag	0.1								
Fe	12.7					11.3	12.09	13.1	13.88
Zn	1.2					4.2	3.69	0.4	
Sn	16.7					15.9	18.23	16.1	14.95
In							0.04		
S	31.6					29.8	28.57	31.5	31.88
Total	100.0					100.0	100.0	100.0	100.00

1. Stannoidite. Konjo mine, Okayama prefecture, Japan. The present study.
- 1a. Ditto. Recalculated to 100%.
2. Hexastannite. Tingha, New South Wales. After MARKHAM and LAWRENCE (1965).
- 2a. Ditto. Recalculated to 100%.
3. Hexastannite. Mt. Pleasant, New Brunswick. After BOORMAN and ABBOTT (1967).
- 3a. Ditto. Recalculated to 100%.
4. Yellow stannite. Vaulry, France. After LÉVY (1967).
- 4a. Ditto. Recalculated to 100%.
5.  $\text{Cu}_5\text{Fe}_2\text{SnS}_8$ .

mula becomes  $\text{Cu}_5(\text{Fe}, \text{Zn})_2\text{SnS}_8$ , or  $\text{Cu}_5\text{Fe}_2\text{SnS}_8$ . Since all the available chemical analyses of stannoidites show the presence of zinc (KATO and FUJIKI, 1969), the former formula was preferred for the present time.

### Relation to Hexastannite and Yellow Stannite

The most important points to be here discussed is to make clear the relation to hexastannite and yellow stannite recently described by LÉVY (1967).

The chemical composition of the original hexastannite has been still unknown,

but RAMDOHR (1944) surmised it to be  $\text{Cu}_3\text{Fe}_2\text{SnS}_6$ , seeing from the mode of occurrence that this mineral occurs between stannite and chalcopyrite or the product of addition of  $\text{CuFeS}_2$  to stannite,  $\text{Cu}_2\text{FeSnS}_4$ . MOH and OTTEMANN (1962) synthesized  $\text{Cu}_6\text{FeSnS}_8$ , which is optically similar to hexastannite, and regarded this to be the ideal formula thereof. Also, they knew the possible variation range of the chemical composition of this material from  $\text{Cu}_6\text{FeSnS}_8$  to  $\text{Cu}_{10}\text{FeSnS}_{12}$ . While, the first chemical analysis of optically identified hexastannite from Tingha, New South Wales, was made by electron microprobe method (MARKHAM and LAWRENCE, 1965), to show it about  $\text{Cu}_{4.5}(\text{Fe}, \text{Zn})_2\text{SnS}_7$ .

The unique reliable x-ray powder data for the original hexastannite were given by RAMDOHR (1944), though it required recalculation from  $2\theta$  value to  $d(\text{\AA})$ , assuming that he employed unfiltered Fe radiation. The coincidence with the present material is striking, if some insignificant systematic deviations are neglected. Also, the pseudocubic subcell of stannoidite becomes pseudo-hexagonal by taking [111] as c-axis, giving the new cell constants  $a_0'(\text{pseudo-hex.})=3.82\text{\AA}$  and  $c_0'(\text{pseudo-hex.})=6.21\text{\AA}$  ( $=1/2 \cdot 12.42\text{\AA}$ ) respectively. They are related to those of hexastannite by RAMDOHR (1944),  $a_0=3.84\text{\AA}$  and  $c_0=12.6\text{\AA}$  respectively, obtained by indexing of the x-ray powder data and analogy with wurtzite in them.

Along with yellow stannite, LÉVY (1967) presented nine chemical analyses including variable contents of copper and tin giving the general formula  $\text{Cu}_{2+x}\text{FeSn}_{1-x}\text{S}_4$ , with  $0 < x < 0.44$ . The present material has  $x=0.42$ , if the above formula is applied. Among yellow stannites, the material from Vaulry, France is poorest in tin, with the composition  $\text{Cu}_{4.96}(\text{Fe}_{1.90}\text{Zn}_{0.05})_{1.95}\text{Sn}_{1.10}\text{S}_{7.95}$  based on total metal=8, which agrees very well with the formula of stannoidite.

Also, the x-ray powder data for yellow stannite are virtually the same as those for stannoidite, except the lines of  $11\text{\AA}$ ,  $2.80\text{\AA}$ , and  $1.69\text{\AA}$ . All of them are reasonably indexed with the unit cell constants of stannoidite, but the first one requires the index (100), which is excluded by the possible space group known from the precession photographs. The indices of the other two fit the extinction rule thereof. If this  $11\text{\AA}$  diffraction is due to an impurity, the substantial identity between this x-ray studied yellow stannite and stannoidite will be established with certainty.

The present author inclines to identify some yellow stannite with stannoidite. As to hexastannite, the lack of chemical analysis of the original material impedes the substantial comparison as well as the final identification. However, it seems that the name hexastannite should be retained until the detailed studies will be made along with the original material.

## References

- BOORMAN, R. S., & D. ABBOTT, 1967. Indium in co-existing minerals from the Mount Pleasant tin deposit. *Can. Mineral.*, **9**: 166-179.
- FLEISCHER, M., 1961. New Mineral Names. *Am. Mineralogist*, **46**: 1204.
- IMAI, H., Y. FUJIKI, & S. TSUKAGOSHI, 1967. Late Mesozoic to early Cenozoic metallogenic province in western Kinki District. *Kozan Chishitsu (Mining Geology)*, **17**: 50. (Abstr.) (In Japanese.)
- ITO, T. & K. SAKURAI, 1947. Minerals of Japan, 3rd Ed. 25-27. Chubunkan. (In Japanese.)
- KAMBE, N. & O. HIROKAWA, 1963. Geological map of Sayo (1:50,000) and the explanatory text. *Geol. Surv. Japan.* (In Japanese.)
- KATO, A., & Y. FUJIKI, 1969. The occurrence of stannoidites from the xenothermal ore deposits of the Akenobe, Ikuno, and Tada mines, Hyogo prefecture, and Fukoku mine, Kyoto prefecture, Japan. *Miner. Jour.*, **6**. (in press)
- LÉVY, C., 1967. Contribution à la minéralogie des sulfures de cuivre du type  $Cu_3XS_4$ . *Bur. Rech. Géol. Min., Mém.* (54): 1-178.
- MARKHAM, N. L. & L. J. LAWRENCE, 1965. Mawsonite, a copper-iron-tin sulphide from Mt. Lyell, Tasmania and Tingha, New South Wales. *Am. Mineralogist*, **50**: 900-908.
- MOH, G. & J. OTTEMANN, 1962. Neue Untersuchungen an Zinnkiesen und Zinnkiesverwandten. *N. Jb. Miner. Abh.*, **99**: 1-28.
- NAKAMURA, T., 1961. Mineralization and wall-rock alteration at the Ashio copper mine, Japan. *Jour. Inst. Polytech. Osaka Univ.*, (G), **4**: 53-127.
- RAMDOHR, P., 1944. Zum Zinnkiesproblem. *Abh. Preuss Akad. Wiss. Math.-naturw. Kl.* (4): 1-30.
- RAMDOHR, P., 1960. Die Erzminerale und ihre Verwachsungen, 514. Akademie Verlag, Berlin.
- SHIMIZU, T., A. KATO, & G. MATSUO, 1966. Minerals from the Fukoku mine, Kyoto prefecture, with special reference to cosalite, boulangerite, hexastannite and some secondary arsenic minerals. *Chigaku Kenkyu (Earth Science Studies)*, **Masutomi Vol.** 201-209. (in Japanese.)
- SWANSON, H.E., & R.K. FUYAT, 1953. Standard x-ray diffraction powder patterns. National Bureau of Standards, Circular 539, **2**: 16-18.
- YAMAGUCHI, K., 1939. Ore deposits of the Ikuno mine and their zonal arrangement. *Jour. Jap. Assoc. Miner. Petro. Econ. Geol.*, **21**: 257-275. (In Japanese.)