

TIN-BEARING CHALCOPYRITE FROM THE IZUMO VEIN, TOYOHA MINE, HOKKAIDO, JAPAN

KATSUO KASE

Department of Earth Sciences, Faculty of Science, Okayama University, Tsushima Naka 3-1-1, Okayama 700, Japan

ABSTRACT

Chalcopyrite containing up to 2.34 wt. % Sn occurs in sphalerite - chalcopyrite - tetrahedrite_{ss} - stannite ores from the Izumo vein of the Toyoha mine, Japan. Microprobe analysis confirms that Sn enters into chalcopyrite as a solid solution toward stannite by the substitution of $\text{Sn}^{4+}\text{Fe}^{2+}$ for $\text{Fe}^{3+}\text{Fe}^{3+}$. The Sn contents are strongly dependent on the orientation of a chalcopyrite crystal, and they are especially high in directions of fast growth. The original composition of the tin-bearing chalcopyrite has been preserved without significant change, owing to quenching of the mineral assemblage from a temperature of approximately 300°C.

Keywords: tin-bearing chalcopyrite, stannite, Toyoha mine, Japan.

SOMMAIRE

De la chalcopyrite dont la teneur en étain s'élève jusqu'à 2.34% (en poids) se présente dans le minerai à sphalérite - chalcopyrite - tétraédrite (solution solide) - stannite du filon Izumo de la mine Toyoha (Japon). L'analyse à la microsonde confirme que l'étain se trouve dans la chalcopyrite à l'état de solution solide en direction de la stannite, par substitution de $\text{Sn}^{4+}\text{Fe}^{2+}$ à $\text{Fe}^{3+}\text{Fe}^{3+}$. La teneur en Sn dépend fortement de l'orientation du cristal de chalcopyrite; elle est particulièrement élevée dans les directions de croissance rapide du cristal. La composition originelle de la chalcopyrite à teneur d'étain a été préservée sans changement notable, grâce à la trempe de l'assemblage minéral à une température d'environ 300°C.

(Traduit par la Rédaction)

Mots-clés: chalcopyrite à teneur d'étain, stannite, Toyoha (mine), Japon.

INTRODUCTION

Small amounts of sphalerite, stannite and tetrahedrite may occur in chalcopyrite as lamellae and star- and dot-shaped inclusions (Ramdohr 1969). They have been ascribed to exsolution, which suggests the incorporation of Zn, Sn, Sb and As in chalcopyrite solid-solution at elevated temperatures. Nondestructive *in situ* analyses of natural chalcopyrite, however, show that this mineral contains

Ag, Zn, Sn and so on, only at levels up to several thousand ppm (Harris *et al.* 1984, Cabri *et al.* 1985). One of the reasons for these low concentrations is that the range of high-temperature solid-solution shrinks quickly with decreasing temperature, as expected from the rapid rate of equilibration of this mineral (Barton & Skinner 1979).

Chalcopyrite with up to 2.34 wt. % Sn in solid solution occurs, however, in the Izumo vein of the Toyoha mine, Hokkaido, Japan. Chalcopyrite containing such high Sn has not been reported previously. This paper describes the mode of occurrence and chemistry of the chalcopyrite.

MINERAL DEPOSITS OF THE TOYOHA MINE

The mineral deposits of the Toyoha mine, situated about 30 km southwest of Sapporo (Fig. 1), are now the most productive Pb-Zn veins in Japan. More than 40 veins occur in altered volcanic rocks and clastic sedimentary rocks of Miocene age; these are correlated with the so-called "Green tuff" formations, the host rocks of the Kuroko-type massive-sulfide deposits. The geology of the Toyoha mining district has been described by many authors (*e.g.*, Hashimoto *et al.* 1977, Kuwahara *et al.* 1983).

Most of the veins are composed of sphalerite, galena, pyrite and quartz, with small amounts of chalcopyrite, magnetite, hematite and tetrahedrite-tennantite (described as tetrahedrite_{ss} hereafter). In

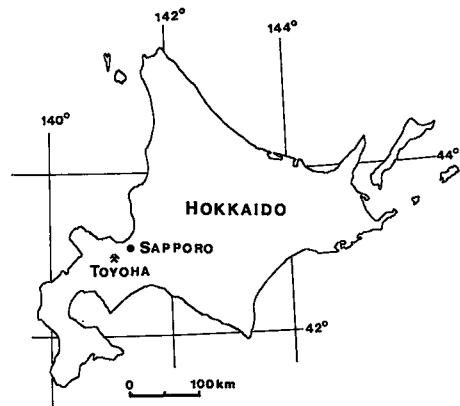


FIG. 1. Location of the Toyoha mine, Hokkaido, Japan.

addition to quartz, rhodochrosite and manganocalcic calcite are the dominant gangue minerals in some veins. Silver minerals, such as acanthite, electrum and pyrargyrite, occur in small amounts (Kojima *et al.* 1979). The Ag content of the ores averages 120 g/t (Kuwahara *et al.* 1983). The veins of the Toyoha mine have been considered to be epithermal (*e.g.*, Shikazono 1975). Tin and W minerals are generally absent in most of the Pb-Zn veins. Yajima (1977) and Yajima & Ohta (1979) have, however, found stannite, cassiterite and wolframite in the Izumo vein of this mine. They pointed out its xenothermal nature, based on the mineralogical characteristics of the Izumo vein, in contrast to other veins of the mine.

Filling temperatures for fluid inclusions in quartz and sphalerite from several Pb-Zn veins of the Toyoha mine are in the range from 150 to 250°C (Tokunaga 1970, Shikazono 1975, Enjoji & Takenouchi 1976, Yajima & Ohta 1979). Filling temperatures of the Izumo vein are somewhat higher than those of other veins, and range from 200 to

300°C (Yajima & Ohta 1979). Mineral deposition at a slightly higher temperature is one of the factors for the unique mineralogical nature of the Izumo vein.

SAMPLE DESCRIPTION

The ore samples in which tin-bearing chalcopryite occurs were taken from drill cores of the Izumo vein. Sphalerite, tetrahedrite_{ss}, arsenopyrite, pyrite, chalcopryite, stannite and quartz are the main constituents. Galena, wolframite, cassiterite, acanthite and loellingite are present in small or trace amounts. Finely banded structures imply the successive deposition of these minerals. Chalcopryite, tetrahedrite_{ss}, sphalerite and stannite are locally intimately intergrown, but no distinct exsolution-intergrowths are observed. Minute grains of tetrahedrite_{ss} occur only along and within chalcopryite grains, suggesting exsolution from that mineral.

A marked compositional zoning is revealed by

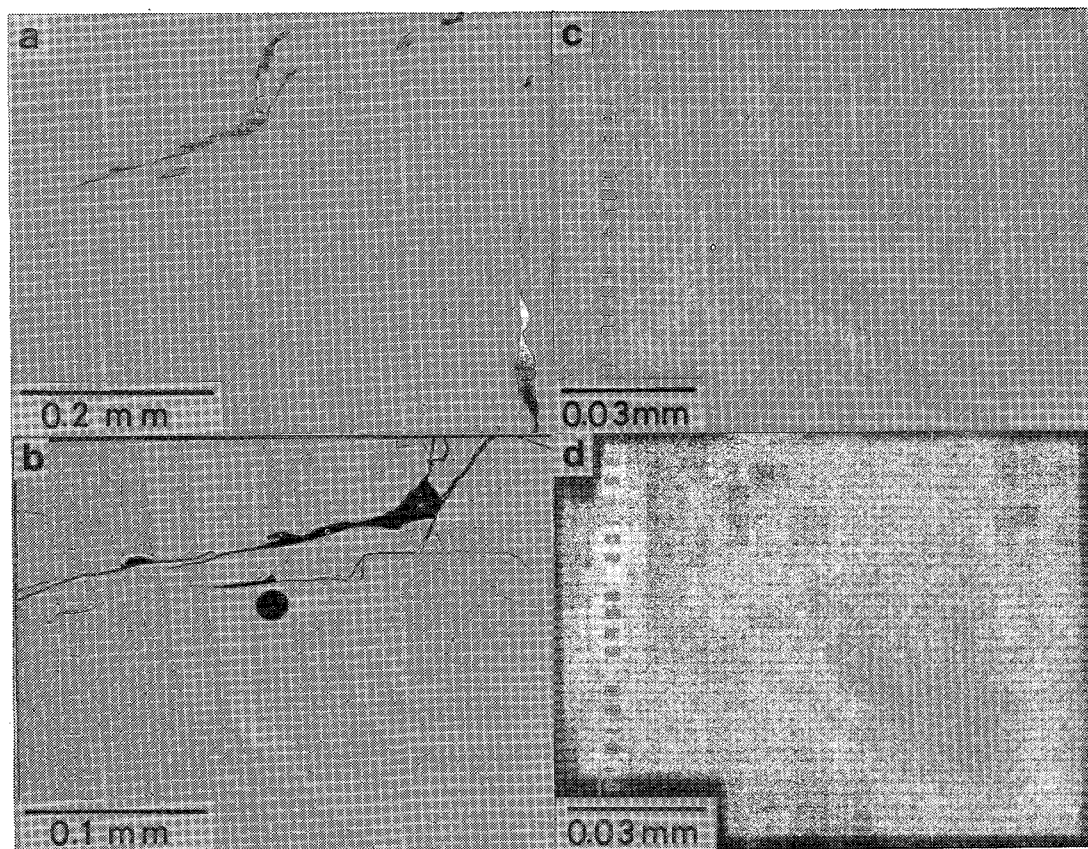


FIG. 2. a. Photomicrograph of tin-bearing chalcopryite. Crossed nicols. Reflected light. Weak anisotropism reveals the banded structure. b and c. Back-scattered electron images of the same area, displaying the distinctly banded structure seen under reflected light. Note that brightest bands coincide with the poorly developed planes. d. SnL α characteristic X-ray scanning photograph taken in the same field as in c.

microprobe analysis in sphalerite and tetrahedrite_{ss}; compositions range from 1 to 6 mole % FeS, and from 10 to 98 mole % tetrahedrite component, respectively. The tetrahedrite_{ss} commonly contains considerable Ag (up to about 13 wt. %). The tin-bearing chalcopyrite displays weak reflection-pleochroism and anisotropism, which permit observation of its internal structure (Fig. 2a).

ANALYTICAL DATA

Back-scattered electron images obtained by using a JEOL electron microprobe reveal a distinct zonal structure in the chalcopyrite (Figs. 2b, c). The lighter domains of the images correspond to higher Sn contents (Figs. 2c, d). Figure 3 shows line profiles for $\text{CuK}\alpha$, $\text{FeK}\alpha$, $\text{SnL}\alpha$ and $\text{ZnK}\alpha$ across the light and dark chalcopyrite bands. An increase in intensity of $\text{SnL}\alpha$ corresponds to a decrease in that of $\text{FeK}\alpha$.

Quantitative analyses mainly were made on the pale domains of the back-scattered electron images. The standards used are chalcopyrite from the Kosaka mine, synthetic ZnS and Sn metal. The measured ratios of intensity were corrected for background and deadtime and then converted into concentrations according to the method of Sweatman & Long (1969). The results are given in Table 1.

The Sn contents increase as the back-scattered elec-

	1	2	3	4	5	6
Cu	34.33	34.31	34.39	34.29	34.08	33.87
Fe	30.52	30.32	30.25	30.40	30.12	29.37
Zn	0.09	0.18	0.14	0.10	0.18	0.29
Sn	0.86	1.12	1.27	1.35	1.50	2.34
S	34.52	34.18	34.03	34.21	34.62	34.40
Total	100.32	100.11	100.08	100.35	100.51	100.27
Number of atoms per formula unit*						
Cu	1.990	1.998	2.007	1.995	1.977	1.977
Fe	2.013	2.010	2.009	2.013	1.987	1.952
Zn	0.005	0.010	0.008	0.005	0.010	0.016
Fe+Zn	2.018	2.020	2.017	2.018	1.998	1.968
Sn	0.027	0.035	0.040	0.042	0.047	0.074
S	3.965	3.947	3.936	3.945	3.979	3.981
Stannite (wt.%)						
	3.11	4.06	4.60	4.89	5.43	8.48

* calculated on the basis of 8 total atoms. Composition determined by electron microprobe.

tron images become brighter, with a maximum Sn content measured of 2.34 wt. %. This Sn value is, however, exceptionally high; Sn contents are usually less than 1.5 wt. %. The analyses with unusually high Sn contents were obtained on the poorly developed crystal planes (Figs. 2b, c). In Figure 4, numbers of Fe + Zn ($N_{\text{Fe}+\text{Zn}}$) and Cu (N_{Cu}) atoms are plotted against N_{Sn} , the number of Sn atoms, calculated on the basis of 8 total atoms per formula unit. $N_{\text{Fe}+\text{Zn}}$ decreases monotonously with increasing N_{Sn} , although Zn is restricted to domains with high Sn contents. The relationships between $N_{\text{Fe}+\text{Zn}}$ and N_{Sn}

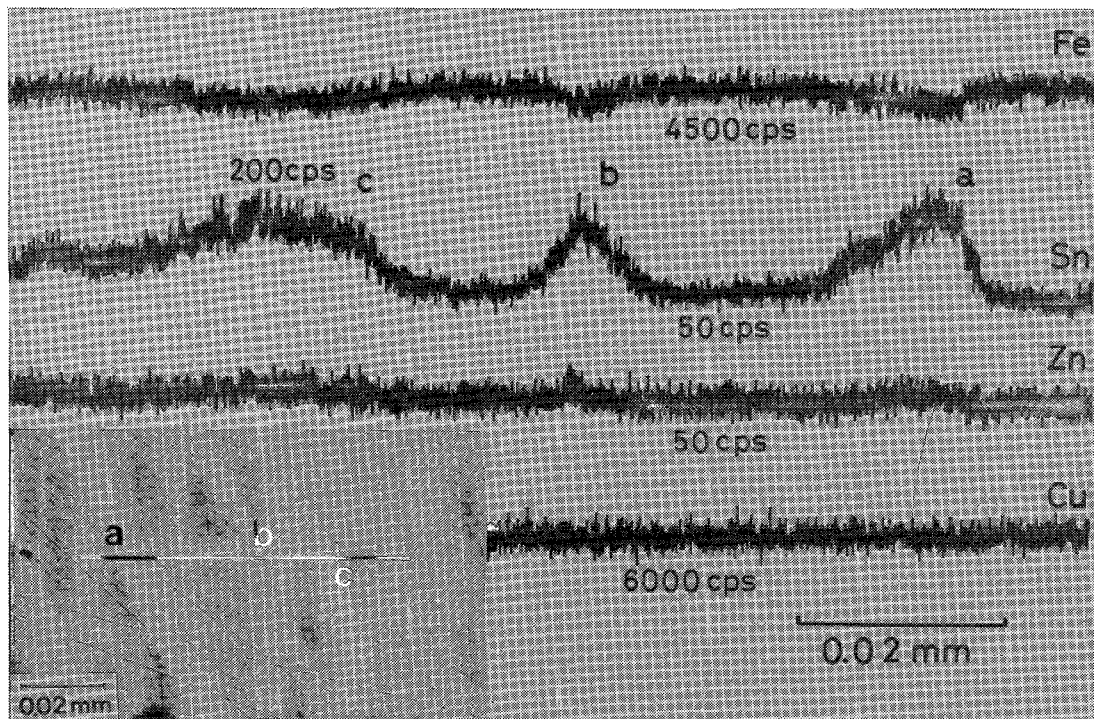


FIG. 3. $\text{FeK}\alpha$, $\text{SnL}\alpha$, $\text{ZnK}\alpha$ and $\text{CuK}\alpha$ scanning profiles across the tin-bearing chalcopyrite, taken along the solid line shown on the back-scattered electron image (inset) (cps: counts per second).

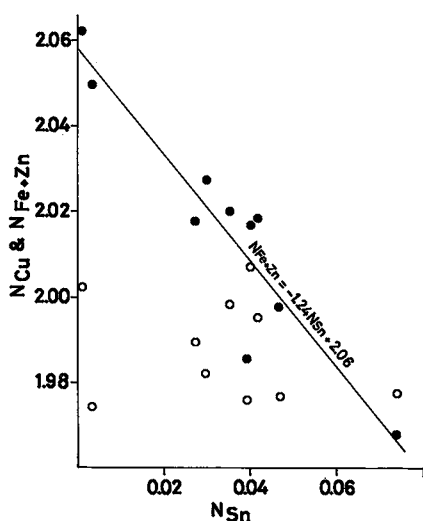


FIG. 4. Relationship between a) number of Fe + Zn atoms ($N_{\text{Fe}+\text{Zn}}$, solid circles) and b) N_{Cu} (open circles), and N_{Sn} in chalcopyrite. Number of atoms is calculated on the basis of 8 total atoms per formula unit.

obtained by least-squares regression is: $N_{\text{Fe}+\text{Zn}} = -1.24N_{\text{Sn}} + 2.06$. No systematic relationship is noticed between N_{Cu} and N_{Sn} .

DISCUSSION

The valence state of Cu in chalcopyrite and stannite is monovalent, according to the X-ray photoelectron spectroscopic data of Nakai *et al.* (1976). Iron in chalcopyrite and Sn in stannite are trivalent and tetravalent, respectively, according to the Mössbauer spectra of Greenwood & Whitfield (1968). The valence state of Fe in stannite may be divalent to maintain a balance of electric charges, thus differing from that in chalcopyrite. Mixing of chalcopyrite and stannite therefore involves coupled substitution of $\text{Sn}^{4+}\text{Fe}^{2+}$ for $\text{Fe}^{3+}\text{Fe}^{3+}$. Zinc may replace Fe^{2+} in Sn-rich compositions. In the Toyoha chalcopyrite, $N_{\text{Fe}+\text{Zn}}$ decreases linearly with increasing N_{Sn} , and the slope for the relationship does not depart much from unity (Fig. 4). Tin enters into chalcopyrite as a solid solution toward stannite by the above schemes of atomic substitution.

Moh (1975), however, showed that only 3 wt. % stannite is soluble in low-temperature (tetragonal) chalcopyrite, which is stable below about 550°C in the system Cu-Fe-S (Yund & Kullerud 1966). For high-temperature (isometric) chalcopyrite, the extent of solid solution is greater (Moh 1975). The maximum Sn content determined in the present study (2.34 wt. %) corresponds to about 8.5 wt. % stannite (Table 1), but the temperature of mineral deposition in the Izumo vein is estimated not to have

exceeded 300°C (Yajima & Ohta 1979). It is thus highly probable that chalcopyrite with unusually high Sn contents has precipitated metastably in the Izumo vein. The observation that the Sn contents are anomalously high on planes characterized by rapid growth supports this idea. In this regard, several grains of chalcopyrite containing symplectitic stannite from the polymetallic veins of the Ikuno mine were analyzed; their Sn contents were found to be below the detection level of the microprobe (ca. 300 ppm). This result indicates that the composition of chalcopyrite changes rapidly during the cooling process. The Toyoha vein system is believed to have formed at very shallow depth (Yajima & Ohta 1979), and therefore quenching of the tin-bearing chalcopyrite can reasonably be inferred.

ACKNOWLEDGEMENTS

The author expresses his sincere gratitude to Drs. Takashi Fujii, Hidehiko Shimazaki and Tsugio Shibata for their critical reading of the manuscript and invaluable suggestions. Thanks are also due to Drs. Robert F. Martin, Alan H. Clark and Louis J. Cabri, who kindly reviewed the manuscript and suggested improvements. The ore samples of the Izumo vein were provided by the staff of the exploration branch of the Toyoha Mining Co. Ltd., through the good offices of Mr. Hiroshi Ogasawara, President of the company. Technical assistance given by Mr. Toshiaki Saito is acknowledged.

REFERENCES

- BARTON, P.B., JR. & SKINNER, B.J. (1979): Sulfide mineral stabilities. *In* *Geochemistry of Hydrothermal Ore Deposits* (2nd edition, H.L. Barnes, ed.). John Wiley & Sons, New York.
- CABRI, L.J., CAMPBELL, J.L., LAFLAMME, J.H.G., LEIGH, R.G., MAXWELL, J.A. & SCOTT, J.D. (1985): Proton-microprobe analysis of trace elements in sulfides from some massive-sulfide deposits. *Can. Mineral.* **23**, 133-148.
- ENOJII, M. & TAKENOCHI, S. (1976): Present and future researches of fluid inclusions from vein-type deposits. *Mining Geol. (Japan), Spec. Issue* **7**, 85-100 (in Japanese).
- GREENWOOD, N.N. & WHITFIELD, H.J. (1968): Mössbauer effect studies on cubanite (CuFe_2S_3) and related iron sulfides. *J. Chem. Soc. (A), Inorg. Phys. Theor.*, 1697-1699.
- HARRIS, D.C., CABRI, L.J. & NOBILING, R. (1984): Silver-bearing chalcopyrite, a principal source of silver in the Izok Lake massive-sulfide deposit: confirmation by electron- and proton-microprobe analyses. *Can. Mineral.* **22**, 493-498.

- HASHIMOTO, H., ISHIZUKA, T. & ICHINOSE, T. (1977): Recent exploration for the Izumo vein of the Toyoha mine. *Mining Geol. (Japan)* 27, 87-97 (in Japanese).
- KOJIMA, S., KAWAZUMI, T., TAKEYAMA, T. & MIYAISHI, O. (1979): The modes of occurrences and mineralogy of silver minerals from the Toyoha mine. *Mining Geol. (Japan)* 29, 197-206 (in Japanese).
- KUWAHARA, T., MIYAZAKI, T., TANI, T. & IIDA, K. (1983): A characterization of the vein mineralizations at the Motoyama mine from the view point of their tectonic setting and ore assays. *Mining Geol. (Japan)* 33, 115-129 (in Japanese).
- MOH, G.H. (1975): Tin-containing mineral systems. II. Phase relations and mineral assemblages in the Cu-Fe-Zn-Sn-S system. *Chem. Erde* 34, 1-61.
- NAKAI, I., IZAWA, M., SUGITANI, Y., NIWA, Y. & NAGASHIMA, K. (1976): X-ray photoelectron spectroscopic study of copper minerals. *Mineral. J. (Japan)* 8, 135-138.
- RAMDOHR, P. (1969): *The Ore Minerals and Their Intergrowths*. Pergamon Press, Oxford, England.
- SHIKAZONO, N. (1975): Mineralization and chemical environment of the Toyoha lead-zinc vein type deposits, Hokkaido, Japan. *Econ. Geol.* 70, 694-705.
- SWEATMAN, T.R. & LONG, J.V.P. (1969): Quantitative electron-probe microanalysis of rock-forming minerals. *J. Petrology* 10, 332-379.
- TOKUNAGA, M. (1970): Lead-zinc veins of the Toyoha mine. In *Volcanism and Ore Genesis* (T. Tatsumi, ed.). Univ. Tokyo Press, Tokyo, Japan.
- YAJIMA, J. (1977): New occurrence of tin minerals from the Toyoha mine, Hokkaido, Japan. *Mining Geol. (Japan)* 27, 23-30 (in Japanese).
- _____ & OHTA, E. (1979): Two-stage mineralization and formation process of the Toyoha deposits, Hokkaido, Japan. *Mining Geol. (Japan)* 29, 291-306.
- YUND, R.A. & KULLERUD, G. (1966): Thermal stability of assemblages in the Cu-Fe-S system. *J. Petrology* 7, 454-488.

Received October 18, 1985, revised manuscript accepted May 28, 1986.