

SAKURAIITE: CHEMICAL COMPOSITION AND EXTENT OF (Zn, Fe)In-FOR-CuSn SUBSTITUTION

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ABSTRACT

Microprobe analyses of sakuraiite and the associated stannite and kesterite from the Ikuno mine, Japan, indicate the following chemical formulae: for sakuraiite, $(\text{Cu}, \text{Zn}, \text{Fe})_3(\text{In}, \text{Sn})\text{S}_4$ with $\text{Cu} > \text{Zn} > \text{Fe}$ or $\text{Zn} > \text{Cu} > \text{Fe}$ and $\text{In} > \text{Sn}$ (In:Sn up to 89:11); for stannite, $(\text{Cu}, \text{Fe}, \text{Zn})_3(\text{Sn}, \text{In})\text{S}_4$ with $\text{Cu} > \text{Fe} > \text{Zn}$ and $\text{Sn} > \text{In}$ (In:Sn up to 40:60), and for kesterite, $(\text{Cu}, \text{Zn}, \text{Fe})_3(\text{Sn}, \text{In})\text{S}_4$ with $\text{Cu} > \text{Zn} > \text{Fe}$ and $\text{Sn} > \text{In}$ (In:Sn up to 46:54). There is a continuous solid solution according to the coupled substitution $(\text{Zn}, \text{Fe})\text{In}$ for CuSn , starting from zincian stannite with $\text{Fe}:\text{Zn}$ about 5:1. A hypothetical formula of the end member is $(\text{Zn}, \text{Fe})_2\text{CuInS}_4$, with $\text{Zn}:\text{Fe}$ about 5:1.

Keywords: sakuraiite, In-bearing stannite and kesterite, coupled $(\text{Zn}, \text{Fe})\text{In}$ -for- CuSn substitution, Ikuno mine, Japan.

SOMMAIRE

Les résultats d'analyses chimiques (microsonde électronique) de la sakuraiite et de la stannite et kesterite qui lui sont associées, de la mine Ikuno, au Japon, indiquent les formules suivantes: pour la sakuraiite, $(\text{Cu}, \text{Zn}, \text{Fe})_3(\text{In}, \text{Sn})\text{S}_4$, avec $\text{Cu} > \text{Zn} > \text{Fe}$ ou $\text{Zn} > \text{Cu} > \text{Fe}$ et $\text{In} > \text{Sn}$ (In:Sn jusqu'à 89:11); pour la stannite, $(\text{Cu}, \text{Fe}, \text{Zn})_3(\text{Sn}, \text{In})\text{S}_4$, avec $\text{Cu} > \text{Fe} > \text{Zn}$ et $\text{Sn} > \text{In}$ (In:Sn jusqu'à 40:60); pour la kesterite, $(\text{Cu}, \text{Zn}, \text{Fe})_3(\text{Sn}, \text{In})\text{S}_4$, avec $\text{Cu} > \text{Zn} > \text{Fe}$ et $\text{Sn} > \text{In}$ (In:Sn jusqu'à 46:54). Il y a une solution solide continue selon la substitution couplée $(\text{Zn}, \text{Fe})\text{In}$ pour CuSn , à partir d'une stannite zincifère ($\text{Fe}:\text{Zn}$ environ 5:1). On propose comme formule hypothétique du pôle zincifère $(\text{Zn}, \text{Fe})_2\text{CuInS}_4$ ($\text{Zn}:\text{Fe}$ environ 5:1).

(Traduit par la Rédaction)

Mots-clés: sakuraiite, stannite et kesterite à contenu d'indium, substitution couplée $(\text{Zn}, \text{Fe})\text{In}$ pour CuSn , mine Ikuno, Japon.

INTRODUCTION

Sakuraiite was originally described by Kato (1965)

from one of the polymetallic Cu-Zn-Pb-Sn-W (-Au-Ag) veins of the Ikuno mine, Hyogo Prefecture, central Japan; it is an indium analogue of kesterite, with the ideal formula $(\text{Cu}, \text{Zn}, \text{Fe}, \text{Ag})_3(\text{In}, \text{Sn})\text{S}_4$, in which $\text{Cu} > \text{Zn} > \text{Fe} > \text{Ag}$ and $\text{In} > \text{Sn}$, according to two slightly different compositions determined by microprobe. However, the empirical formulae derived from these data do not balance electrostatically. New

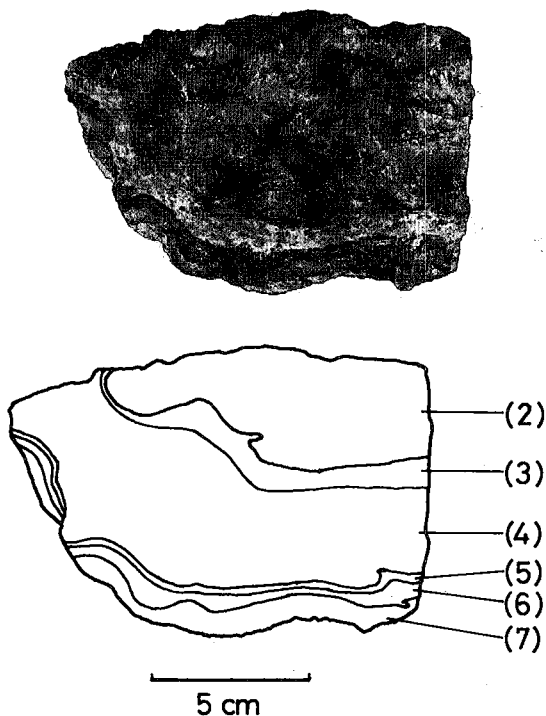


FIG. 1. Photograph of sakuraiite-bearing ore from the Ikuno mine, Japan (sample no. NSM M-15843). The first unit is lacking in the photographed sample. Each unit is numbered.

microprobe analyses of sakuraiite and the associated stannite and kesterite, these three being tetragonal (pseudocubic), indicate that there is a prominent (Zn,Fe)In-CuSn coupled substitution that accounts for the compositional variation, and that the higher Ag contents reported in the original analyses were erroneous.

OCCURRENCE

Sakuraiite was exclusively found in the main adit level of the Senju-hon vein, one of the productive veins in the Kanagase group of veins in the mine. The veins of the group were formed along fractures within the Cretaceous rhyolitic to andesitic volcanic

and pyroclastic rocks of the Ikuno Group (Ichikawa *et al.* 1968). The K-Ar ages of mineralization measured on adularia from the Kanagase group of veins are 63.3 ± 1.9 , 65.6 ± 2.0 and 70.5 ± 2.1 Ma (Metal Mining Agency of Japan 1984).

The vein in which sakuraiite occurs is found in a slightly altered felsic tuff, and has a banded structure composed of at least seven macroscopic units. The following bands are observed from rim to core of the vein where the width of sakuraiite-bearing zone is the widest (Kato 1965) (Fig. 1): 1) sphalerite-chalcopryrite (<5 cm wide), 2) sakuraiite-stannite-kesterite-sphalerite (approximately 2 cm wide), 3) chalcopryrite (<1 cm wide), 4) chalcopryrite-sphalerite-quartz (approximately 5 cm wide), 5)

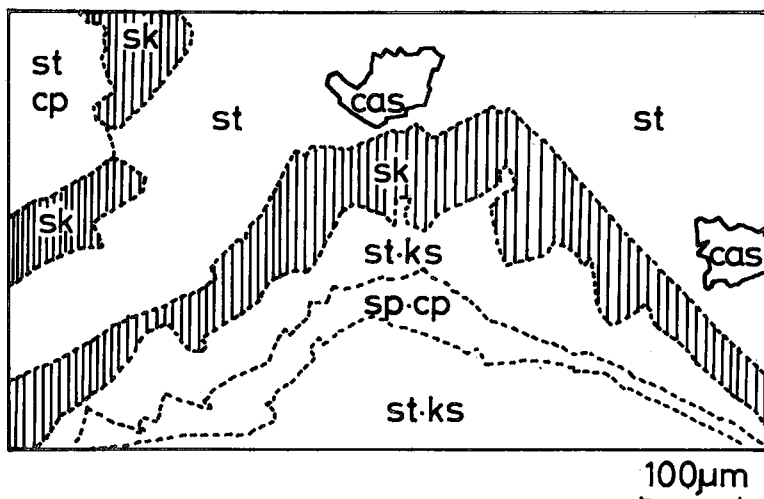


FIG. 2. Photomicrograph of sakuraiite in reflected light, showing the second unit of Figure 1, with a minor portion of the third unit in the upper left corner. A thick line is a trace of step scan of Figure 3. Abbreviations: sk sakuraiite-rich part, cas cassiterite, st stannite-rich part, st.ks stannite- and kesterite-rich part, sp.cp sphalerite- and chalcopryrite-rich part, and st cp stannite and chalcopryrite.

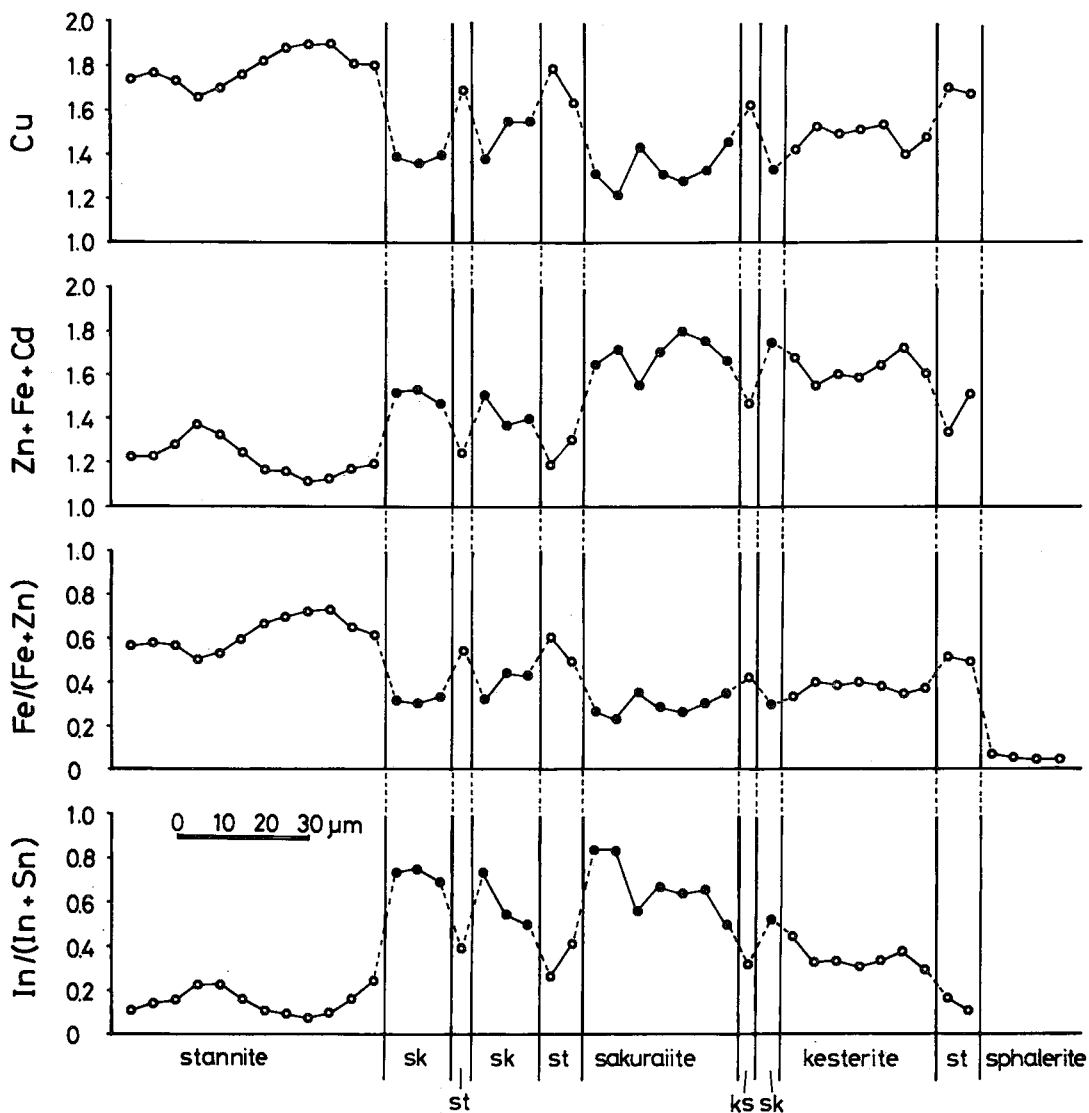


FIG. 3. Step scan of the second unit from bottom to top along the line in Figure 2 (interval $5 \mu\text{m}$). Values plotted are based on a total of 8 atoms.

sphalerite (< 1 cm wide,) 6) sphalerite (< 1 cm wide) and 7) chalcopyrite-pyrite-quartz (approximately 10 cm wide).

The second unit is a brass-grey massive aggregate of very fine-grained sulfide minerals with a smooth fracture. Under the microscope, sakuraiite is seen to be closely associated with stannite and kesterite (Fig. 2). Here, stannite refers to the material with the formula $(\text{Cu}, \text{Fe}, \text{Zn})_3(\text{Sn}, \text{In})\text{S}_4$, in which $\text{Cu} > \text{Fe} > \text{Zn}$ and $\text{Sn} > \text{In}$, and kesterite, to that with the formula $(\text{Cu}, \text{Zn}, \text{Fe})_3(\text{Sn}, \text{In})\text{S}_4$ in which $\text{Cu} > \text{Zn} > \text{Fe}$ and $\text{Sn} > \text{In}$. The other associated

minerals in the above units of the vein are Co-bearing arsenopyrite, cassiterite, bismuthinite, native bismuth, pyrite, galena and calcite (Kato 1965).

The samples used for the present study belong to National Science Museum, Japan and University Museum, University of Tokyo.

ANALYTICAL PROCEDURE

Chemical compositions of sakuraiite, including of the holotype specimen originally examined by Kato,

TABLE 1. REPRESENTATIVE CHEMICAL COMPOSITIONS (ELECTRON-MICROPROBE ANALYSES) FOR COEXISTING SAKURAIITE, STANNITE AND KESTERITE

	WEIGHT PERCENT									ATOMIC PROPORTIONS (TOTAL ATOMS = 8)									
	Cu	Ag	Fe	Zn	Mn	Cd	Sn	In	S	Total	Cu	Ag	Fe	Zn	Mn	Cd	Sn	In	S
SAKURAIITE																			
SK 1	17.71	0.13	5.12	20.26	0.02	0.82	5.61	21.12	28.83	99.62	1.225	0.005	0.403	1.362	0.001	0.032	0.208	0.809	3.954
SK 2	17.72	0.10	5.56	19.44	0.02	0.81	5.12	21.43	29.19	99.39	1.221	0.004	0.436	1.302	0.001	0.032	0.189	0.817	3.987
SK 3	19.69	0.15	6.34	16.73	0.02	0.58	9.12	18.19	29.04	99.86	1.356	0.006	0.497	1.120	0.002	0.023	0.336	0.695	3.965
SK 4	19.38	0.13	6.36	18.08	0.01	0.57	9.64	16.63	29.29	100.09	1.325	0.005	0.495	1.201	0.001	0.022	0.353	0.629	3.968
SK 5	21.03	0.12	7.28	14.40	0.02	0.50	12.01	15.71	29.06	100.13	1.444	0.005	0.569	0.961	0.001	0.020	0.442	0.597	3.955
IN-BEARING STANNITE																			
ST 1	24.64	0.13	8.80	8.11	0.00	0.24	17.62	11.19	29.03	99.76	1.700	0.005	0.690	0.547	0.000	0.009	0.651	0.427	3.969
ST 2	24.19	0.03	8.99	10.31	0.01	0.26	18.94	8.14	29.20	100.07	1.652	0.001	0.699	0.684	0.001	0.010	0.693	0.308	3.953
ST 3	27.68	0.05	10.05	5.15	0.00	0.32	25.64	1.82	29.00	99.71	1.900	0.002	0.784	0.344	0.000	0.013	0.942	0.069	3.943
IN-BEARING KESTERITE																			
KS 1	22.32	0.15	7.50	13.78	0.01	0.38	14.70	11.87	29.04	99.75	1.532	0.006	0.586	0.919	0.001	0.015	0.542	0.451	3.950
KS 2	24.21	0.09	8.95	11.27	0.01	0.29	20.37	5.34	29.57	100.10	1.641	0.004	0.690	0.742	0.001	0.011	0.739	0.200	3.972
Empirical formulas:																			
SK 1	$(Zn_{1.36}Cu_{1.23}Fe_{0.40}Cd_{0.03}Mn_{0.01})_2Zn_{3.03}(In_{0.81}Sn_{0.21})_2Zn_{1.02}S_{3.95}$									ST 1	$(Cu_{1.70}Fe_{0.69}Zn_{0.55}Cd_{0.01}Mn_{0.01})_2Zn_{2.96}(Sn_{0.65}In_{0.43})_2Zn_{1.08}S_{3.97}$								
SK 2	$(Zn_{1.30}Cu_{1.22}Fe_{0.44}Cd_{0.03}Mn_{0.01})_2Zn_{2.99}(In_{0.82}Sn_{0.19})_2Zn_{1.01}S_{3.99}$									ST 2	$(Cu_{1.65}Fe_{0.70}Zn_{0.68}Cd_{0.01})_2Zn_{3.04}(Sn_{0.69}In_{0.31})_2Zn_{1.00}S_{3.95}$								
SK 3	$(Cu_{1.36}Zn_{1.12}Fe_{0.50}Cd_{0.02}Mn_{0.01})_2Zn_{3.01}(In_{0.69}Sn_{0.34})_2Zn_{1.03}S_{3.97}$									ST 3	$(Cu_{1.90}Fe_{0.78}Zn_{0.34}Cd_{0.01})_2Zn_{3.03}(Sn_{0.94}In_{0.07})_2Zn_{1.01}S_{3.94}$								
SK 4	$(Cu_{1.33}Zn_{1.20}Fe_{0.50}Cd_{0.02}Mn_{0.01})_2Zn_{3.06}(In_{0.63}Sn_{0.35})_2Zn_{0.98}S_{3.97}$									KS 1	$(Cu_{1.53}Zn_{0.92}Fe_{0.59}Cd_{0.02}Mn_{0.01})_2Zn_{3.07}(Sn_{0.54}In_{0.45})_2Zn_{0.99}S_{3.95}$								
SK 5	$(Cu_{1.44}Zn_{0.96}Fe_{0.57}Cd_{0.02}Mn_{0.01})_2Zn_{3.00}(In_{0.60}Sn_{0.44})_2Zn_{1.04}S_{3.96}$									KS 2	$(Cu_{1.64}Zn_{0.74}Fe_{0.69}Cd_{0.01})_2Zn_{3.08}(Sn_{0.74}In_{0.20})_2Zn_{0.94}S_{3.97}$								

and the associated stannite and kesterite, were determined using a JEOL 733 electron-microprobe analyzer at Ocean Research Institute, University of Tokyo. The accelerating voltage used was 25 kV. The following standards were used: synthetic $Zn_{0.6}Fe_{0.4}S$ (for Zn and S), natural chalcopyrite of known composition (Cu and Fe), synthetic CdS (Cd), synthetic MnS (Mn), synthetic $CuInS_2$ (In), pure Sn metal (Sn), synthetic Ag_3AsS_3 (Ag and As), synthetic $AgBiS_2$ (Bi), natural galena of known composition (Pb), synthetic $Cu_{10}Zn_2Sb_{1.4}As_{2.6}S_{13}$ (Sb), pure Ge metal (Ge), and pure Se metal (Se). The characteristic X-ray intensities for each point were measured twice for a fixed interval of five seconds. The averaged values were corrected for dead time and background. Quantitative corrections for atomic number, absorption and fluorescence effects were also performed based on the method proposed by Sweatman & Long (1969).

COMPOSITION OF SAKURAIITE

Sakuraiite is compositionally heterogeneous in most cases (Fig. 3). Scanning patterns of sakuraiite demonstrate distinctly positive correlations among Zn, In and Cd, whereas negative correlations were found between In and Sn and between Cu and Zn.

Representative chemical compositions and atomic proportions of sakuraiite are given in Table 1. Besides the tabulated components, Mn, Pb, Bi, As and Se appear in quantities too small to be detected. Gallium is also below the limit of detection, although it was found spectroscopically (Kato 1965). The high

Ag contents reported in the original analyses, 4 and 3.5 wt. % (Kato 1965), were found to be erroneous. The number of sulfur atoms based on a total of 8 atoms can be determined to 0.1 or better, and the other elements can be determined to approximately 0.01.

The analyses yield an ideal formula $(Cu,Zn,Fe)_3(In,Sn)S_4$ in which $Cu > Zn > Fe$ or $Zn > Cu > Fe$ and $In > Sn$, after fulfillment of the charge balance, assuming that Cu, Zn, Fe, Sn and In have the valencies 1 +, 2 +, 2 +, 4 + and 3 +, respectively, as in stannite (Nakai *et al.* 1978, Yamanaka & Kato 1976). The trend of chemical variation in sakuraiite yields compositions between $Cu_2(Fe,Zn)SnS_4$ with Fe:Zn = 5:1 and $(Zn,Fe)_2CuInS_4$ with Zn:Fe = 5:1, approximately (Fig. 4). It is worth mentioning that an unnamed mineral from the Toyoha mine, Hokkaido, Japan, has a composition $(Zn,Fe)_2CuInS_4$, with Zn:Fe = 90:10 and 94:6 (Ohta 1980). If this mineral is approved as a new species and if the formula can be written $(Zn,Cu,Fe)_3InS_4$, where $Zn > Cu > Fe$ and $(Zn + Fe):Cu = 2:1$, a part of the present sakuraiite with $Zn > Cu > Fe$ would be called by the same mineral name, or its tin-bearing variety if precisely specified, unless they are structurally different.

COMPOSITION OF THE ASSOCIATED STANNITE AND KESTERITE

Although the original kesterite was not studied structurally, kesterite from Oruro, Bolivia, was shown to have the space group $I\bar{4}$ (Hall *et al.* 1978),

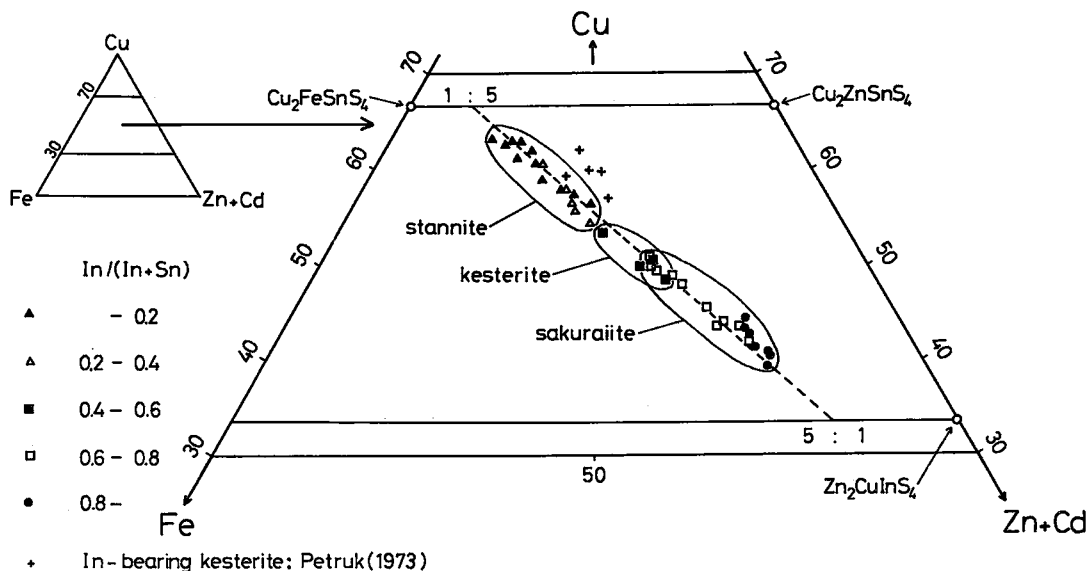


FIG. 4. Cu - Fe - (Zn + Cd) plot showing compositions of sakuraiite and the associated In-bearing stannite and kesterite.

which is distinct from that of stannite, $I\bar{4}2m$. Kesterite is optically similar to stannite, but the intensity of anisotropism is weaker (Kissin & Owens 1979). This helps to distinguish between the two, though their In contents are significantly high. Indium-bearing stannite examined shows discernible anisotropism, but In-bearing kesterite and sakuraiite are apparently isotropic. The name *stannite* is here conventionally used for $Fe > Zn$ material, and *kesterite* for $Zn > Fe$ material, and this agrees with the optical distinction.

As given in Table 1, stannite and kesterite compositions are nearly stoichiometric $(Cu, Fe, Zn)_3(Sn, In)S_4$, with a coupled substitution of $ZnIn$ [more correctly $(Zn, Fe)In$] for $CuSn$. Figure 4 illustrates the compositional variations of stannite, kesterite and sakuraiite, together with In-bearing kesterite from Brunswick Tin Mines Ltd., New Brunswick (Petruk 1973), which has a variation trend parallel to the present one.

THE EXTENT OF $(Zn, Fe)In$ -FOR- $CuSn$ SUBSTITUTION

A continuous substitution of In for Sn is seen in sakuraiite and the associated stannite and kesterite (Fig. 4). Because Cd contents of the minerals are very low (Table 1), a regular increase in Zn or $Zn/(Zn+Fe)$ values with the increase in In or $In/(In+Sn)$ in the minerals implies that Zn is preferentially incorporated into sulfides with a stannite or kesterite structure over Fe, if their crystallochemical behaviors are similar to those of In,

i.e., both of (Zn, Fe) and In are incorporated into a single phase in which they occupy nearly equivalent atomic sites.

Figure 4 demonstrates well the $(Zn, Fe)In$ -for- $CuSn$ coupled substitution in stannite, kesterite and sakuraiite. This means that sakuraiite is compositionally a ZnIn-substituted kesterite rather than a mere In analogue of kesterite, and that the present In-bearing kesterite assumes an intermediate position between In-bearing stannite and sakuraiite.

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