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THE CRYSTALLOGRAPHY OF SAKURAIITE

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ABSTRACT

Sakuraiite from the type locality at the Ikuno mine, Hyogo Prefecture, Japan, was analyzed by electron microprobe and studied by powder and single-crystal X-ray diffraction. The structural formula resulting from the analyses is (Cu,Zn,Fe,In,Sn)S, with $Z = 4$, rather than $(Cu,Zn,Fe)_3(In,Sn)S_4$, with $Z = 1$, as originally announced. Contents of all metals were shown to be highly variable, suggesting a solid solution involving metals in equivalent sites in the structure. Powder patterns are consistent with a cubic cell and $a = 5.4563(24)$ Å; lack of systematic extinctions indicates a primitive cell. Precession photographs confirm the cubic cell and yield diffraction symbol $m3mP$---- with its three possible space-groups. Sakuraiite is the first quaternary mineral with a cubic-P structure somewhat analogous to that of F-centred sphalerite.

Keywords: sakuraiite, Ikuno mine (Japan), sulfide, crystallography, tin, indium.

SOMMAIRE

La sakuraiite du gisement type, mine Ikuno, préfecture de Hyogo (Japon), est analysée à la microsonde electronique et étudiée par diffraction X (poudre et monocristal). Les analyses donnent la formule (Cu,Zn,Fe,In,Sn)S ($Z = 4$), plutôt que $(Cu,Zn,Fe)_3(In,Sn)S_4$ ($Z = 1$), originellement annoncée. On montre que la teneur de tous les métaux est extrêmement variable, ce qui fait penser qu'ils forment une solution solide dans les sites équivalents de la structure. Le cliché de poudre est compatible avec une maille cubique et $a = 5.4563(24)$ Å; l'absence d'extinctions systématiques indique une maille primitive. Les clichés de précession confirment la maille cubique et établissent le symbole de diffraction $m3mP$----, d'où trois groupes spatiaux possibles. La sakuraiite est le premier exemple d'un minéral quaternaire à structure cubique-P ressemblant quelque peu à celle de la sphalérite, cubique-F.

(Traduit par la Rédaction)

Mots-clés: sakuraiite, mine Ikuno (Japon), sulfure (cristallographie d'un), étain, indium.

INTRODUCTION

Sakuraiite $(Cu,Zn,Fe,Ag)_3(In,Sn)S_4$ was first described by Kato (1965), and has proved to be very rare in that no additional occurrences have been reported. Kato concluded that sakuraiite was the indium analogue of kesterite, based on the uncertainty prevalent at the time as to whether the structural formula of kesterite was $Cu_2(Zn,Fe)SnS_4$ or $(Cu,Zn,Fe)_3SnS_4$ (*e.g.*, Ivanov & Pyatenko 1959). The question as to the composition of kesterite has been resolved in favor of the former formula (Kissin & Owens 1979), and its space group is $I\bar{4}$ (Hall *et al.* 1978). Kato (1965) concluded that sakuraiite is tetragonal, and Strunz (1970) assigned the space group $I\bar{4}2m$; however, neither this space group, which is that of stannite, nor that of kesterite is appropriate for sakuraiite, because the metal positions are ordered and metal proportions are stoichiometric within experimental error in stannite and kesterite (Hall *et al.* 1978, Kissin & Owens 1979).

We had the opportunity to reinvestigate sakuraiite in conjunction with other work (Kissin & Owens, in prep.). A study was made on metatype material from the Kanagase vein, Ikuno mine, Hyogo Prefecture, Japan, that had originally been sent to the Mineralogy Section of CANMET some years ago. The geology of the mine was described by Imai *et al.* (1978), and Shimizu *et al.* (1986) described the Kanagase vein in detail. The polished section contains a portion of the banded vein, which appears to have been deposited in open space. Dark, massive sphalerite showing euhedral terminations passes into the succeeding zone of rhythmically banded sakuraiite and a mineral originally identified by Kato (1965) as kesterite. Our work (in prep.) shows that the latter mineral is structurally and compositionally distinct from kesterite. Growth zones in the sphalerite are outlined by trains of micrometre-sized grains of chalcopyrite. Scattered small grains of arsenopyrite also occur in the sphalerite. The rhythmically banded new mineral and sakuraiite also contains bands of sphalerite. Trains of chalcopyrite grains are oriented along crystallographic growth-zones in the sphalerite, but randomly oriented in the new mineral and sakuraiite. The zone also contains irregular areas of gangue and randomly distributed, euhedral crystals of arsenopyrite. Stringers of wormy chalcopyrite also pass through the zone (Fig. 1).

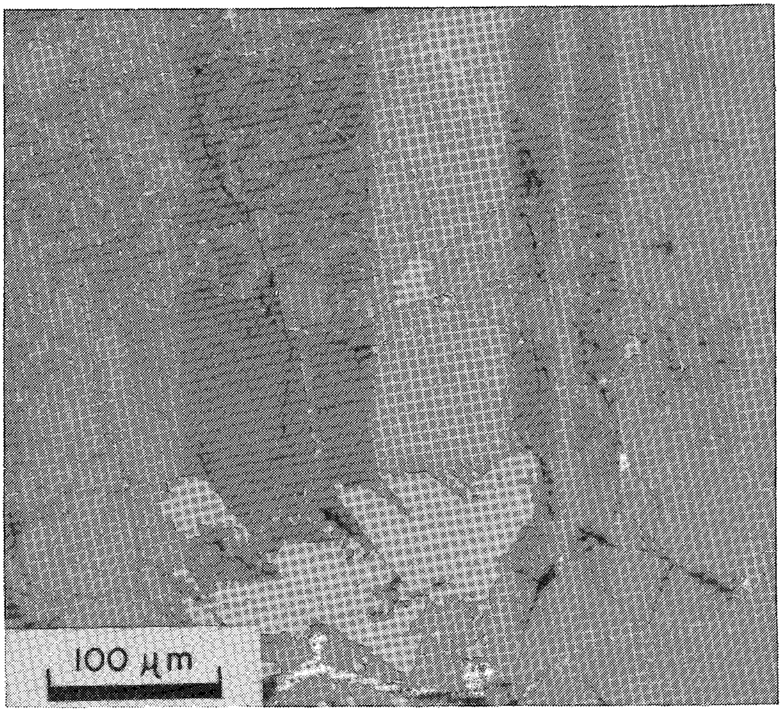

FIG. 1. Photomicrograph illustrating banding of sakuraiite (medium grey) and the new mineral (light grey), with growth zones outlined by trains of chalcopyrite (white). A large grain of sakuraiite surrounds angular chalcopyrite (white) at the bottom centre. Reflected light, oil immersion.

REFLECTANCE AND MICROHARDNESS DATA

Optical properties and microhardness data were not given in the original description of sakuraiite, so we determined these for purposes of completeness. Reflectances were determined with a Zeiss MPC 64 microscope photometer system. The section was freshly polished with 0.5 μm γ-Al_2O_3 prior to measurement, using a halogen lamp, 0.40 field stop and ×16 epi objective. A WTiC reflectance standard was employed. Results are given in Table 1, in which calculated values of color are also given.

The extremely low saturation in terms of the dominant wavelength (λ_d) is seen in a minuscule excitation-purity (P_e%). Thus, sakuraiite is nearly a pure grey, without significant tint.

Microhardness was measured on a Leitz Durimet hardness tester using a 100 g load. A mean (3) of VHN 265 was determined (range 243 - 282). The mineral is therefore significantly softer than the associated new mineral, which has VHN 319 (mean of 3), range 296–353.

CHEMISTRY

We analyzed sakuraiite in two areas of the polished section where it is free of intergrowths with the new mineral. Color variations in the sakuraiite suggest, however, that the mineral is compositionally zoned. Areas selected for analysis, as shown in Figure 1, are unzoned, however.

Analyses were conducted on a Materials Analysis Company (MAC) Model 400 electron-microbeam analyzer operated at 200 kV and 0.028 μA specimen current. The compositions and homogeneity of the specimens were determined from data acquired by collecting counts for 10-s periods (20s for Ag and Cd) from 8 spots on unknowns and standards. The Cu$K\alpha$, Fe$K\alpha$, Sn$L\alpha$ and S$K\alpha$ X-ray emission lines from synthetic Cu_2FeSnS_4, the Zn$K\alpha$ line of synthetic Cu_2ZnSnS_4, the Cd$L\alpha$ line of synthetic CdS, the In$L\alpha$ line of synthetic InAs and the Ag$L\alpha$ of natural argentian pyrite of known composition were used as standards. Sn$L\alpha$ counts were corrected for partial overlap by In$L\alpha$ in the unknowns. The data were reduced by means of the EMPADR VII program of Rucklidge & Gasparrini (1969).

Results of the analyses are presented in Table 1 and compared with the original analyses (Kato 1965). Atomic proportions were calculated on the basis of eight atoms. Some striking differences, which we believe to be real, appear in comparing Kato's and our results. He found significantly higher Ag, somewhat higher Cu, and significantly lower Zn than we did. Analysis No. 3, in fact, yields Fe > Zn, in atomic proportions, such that sakuraiite would seem to be the compositional analogue of both kesterite and stannite, if Kato's conclusions about the structure are correct. Of even greater significance is the result that conflicts with Kato's finding of In + Sn ≃ 1.00. Our results yield no such relationship, and the sole restriction on atomic proportions of metals is that they total 4.00, based on eight atoms total.

CRYSTALLOGRAPHY

X-ray powder data were obtained on a 114.6-mm Gandolfi camera, as its small sample-capacity provided the best means of obtaining impurity-free patterns. Filtered Co$K\alpha$ radiation (λ = 1.79021Å) was employed, and relative intensities were estimated visually. Cell parameters were obtained by means of a least-squares-refinement program written by E.J. Gabe (pers. comm., 1983).

TABLE 1. REFLECTANCE DATA FOR SAKURAIITE

λ(nm)	R(mean of 4)	σ
400	22.5	0.3
420	22.5	0.1
440	22.5	0.1
460	22.6	0.1
480	22.6	0.1
500	22.6	0.1
520	22.6	0.1
540	22 7	0.1
560	22.6	0.1
580	22.5	0.1
600	22.5	0.1
620	22.6	0.1
640	22.6	0.1
660	22.6	0.1
680	22.6	0.1
700	22.4	0.1

Color values relative to the CIE illuminant C

x	0.310
y	0.317
Y%	22.6
λ_d	503
P_e%	0.1

Color values relative to the CIE illuminant A

x	0.447
y	0.408
Y%	22.6
λ_d	508
P_e%	0.1

TABLE 2. COMPOSITIONAL DATA FOR SAKURAITE

Specimen	Weight percent									Atomic proportions (8 atoms)							
	Cu	Ag	Zn	Fe	Cd	In	Sn	S	total	Cu	Ag	Zn	Fe	Cd	In	Sn	S
1. Area A (this study)	19.6	0.2	13.7	6.9	0.6	22.0	7.2	29.1	99.3	1.36	0.01	0.93	0.55	0.02	0.85	0.27	4.01
2. Area B (this study)	18.9	0.1	18.0	4.5	0.7	23.8	4.9	29.0	99.9	1.31	0.00	1.21	0.36	0.03	0.91	0.18	3.99
3. Spec. I (Kato 1965)	23	4	10	9	---	17	9	31	103	1.5	0.2	0.6	0.7	---	0.6	0.3	4.1
4. Spec. II (Kato 1965)	21	3.5	14	5	---	23	4	30	100.5	1.4	0.1	0.9	0.4	---	0.9	0.2	4.1

Note: A dash denotes not sought.

TABLE 3. X-RAY POWDER DATA FOR SAKURAIITE

Tetragonal Indexing (Kato 1965) Diffractometer, Co$K\alpha$				Cubic Indexing (this study) 114.6 mm Gandolfi, Co$K\alpha$			
hkl	d(obs)	d(calc)	I/I_{100}	hkl	d(obs)	d(calc)	I/I_{10}
002	5.47	5.45	5	100	5.47	5.46	1
011	4.87	4.88	2	*	----	----	-
110	3.85	3.86	5	110	3.86	3.86	<1
112	3.15	3.15	100	111	3.15	3.15	10
020 004	2.73	2.73	10	200	2.742	2.728	3
022	2.44	2.44	5	210	2.440	2.440	1
114	2.22	2.23	2	211	----	----	-
220 024	1.927	1.929	40	220	1.932	1.929	6
132 116	1.650	1.645	20	311	1.647	1.645	4
224	1.574	1.575	5	222	----	----	----
040 008	.	.	.	400	1.369	1.364	1
136 332	.	.	.	331	1.251	1.252	2
228 244	.	.	.	422	1.113	1.114	3
152 1.1.10 336	.	.	.	511 333	1.049	1.050	2

* denotes reflection not permitted in 5.455Å cubic cell. Values of d in Å. Cell parameters (Kato 1965); *a* 5.455, *c* 10.91Å; (this study): *a* 5.4563(24)Å.

Powder-diffraction data are presented in Table 2, where they are compared with Kato's (1965) original data. Kato's tetragonal indexing is retained for his pattern, whereas cubic indexing is employed for our data. Kato's indexing yields two rather disturbing results: (1) the pattern is very sparse, with many permitted reflections absent, and (2) with one exception, *hkl* lines with *l* odd are absent, even though for the $I\bar{4}2m$ or $I\bar{4}$ space groups, all reflections with $h+k+l=2n$ are permitted.

Our data, on the other hand, are entirely consistent with a primitive cubic cell with a = 5.4563(24) Å. The crystal that provided the Gandolfi pattern was found to be single, with only minor spurious reflections due to the presence of smaller crystal fragments. Precession photographs of the first three levels along [001] confirmed the primitive cubic cell. Photographs of the first and second levels for a tetragonal 10.9 Å *c*-repeat yielded no reflections. The diffraction symbol *m3mP---* was determined, corresponding to possible space-groups $P432$, $P\bar{4}3m$ and $Pm3m$. Axial reflections of the type (h00) with

$h = 2n$, as well as those of the type $(hk0)$ with $h = 2n$ and $k = 2n$, are much stronger than other reflections.

DISCUSSION

Our determination of a cubic structure for sakuraiite is consistent with our compositional data, which show a lack of stoichiometry in atomic proportions of metals, implying that metal sites in the structure are in equivalent positions. No other mineralogical examples of quaternary sulfides with a sphalerite-sized cell (*a* 5.4 Å) are known.

Our findings are in conflict with the original results of Kato (1965) in that his reflection at $d = 4.87$ Å is not indexable on a 5.45-Å cubic cell (Table 2). Moreover, the structural formula he determined, $(Cu,Zn,Fe,Ag)_3(In,Sn)S_4$, suggests other possible structures. Two possibilities seem to exist: (1) the 4.87 Å reflection is due to an impurity, and the atomic proportion In + Sn = 1 is fortuitous. The weak (101) reflection of the new mineral (Kissin & Owens, in prep.), which is intimately intergrown with sakuraiite in this section, occurs at this approximate spacing. Most other stronger reflections in the new mineral occur at similar values of *d* as those in sakuraiite. (2) The symmetry and structural formula of holotype sakuraiite are actually different from the material we investigated. The question can be resolved only by additional studies of the holotype material.

The space groups $P\bar{4}3m$, $P432$ and $Pm3m$ bear direct relationships to the space group of sphalerite, $F\bar{4}3m$. In sphalerite, metals are located at the equivalent positions (000, 0½½, ½0½, ½ ½0), *i.e.*, in 4*a*. However, in the primitive space-groups, 1*a* is at (000), whereas 3*c* has equivalent positions (0½½, ½0½, ½½0). The latter arrangement is therefore consistent with the structural formula $(Cu,Zn,Fe)_3InS_4$, as originally proposed (Kato 1965). Shimizu *et al.* (1986) have confirmed the original structural formula in more extensive recent analyses of sakuraiite; however, their finding disagrees with ours.

The structure of synthetic $CuZn_2InS_4$ has been determined to be cubic, $F\bar{4}3m$, by Parthé (1964) and Parthé *et al.* (1969). In this structure, identical to that of sphalerite, all metals are randomly distributed among equivalent sites (disorder of metals). It may be conjectured that in sakuraiite, the metals in the *P* cell are partly ordered, yet the cell retains cubic symmetry. Such a hypothesis fits the Shimizu *et al.* (1986) data, not ours, and further suggests the possibility that the two minerals in question are actually different.

The suggested relationships between the space groups of sphalerite and sakuraiite may not, however, be as simple as outlined above. The mineral sulvanite Cu_3VS_4 is also cubic, $P\bar{4}3m$ (Pauling & Hultgren 1933), where *V* occupies the 1*a* site and three Cu atoms occupy the 3*c* sites. The resulting structure, in which sulfur occupies approximately the same sites as in sphalerite, leaves V with three nearest-neighbor Cu atoms. Pauling (1965) later explained the structure in terms of electronegativity differences in a comparison of the sulvanite structure with that of enargite Cu_3AsS_4. However, V–Cu hybrid bonds are a factor mentioned by Pauling and are to be expected in the case of the two transition metals involved. However, as indium is not a transition metal, it does not seem likely that sakuraiite has the same structure as sulvanite.

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