The Canadian Mineralogist
Vol. 34, pp. 1323-1327 (1996)

PAVONITE FROM THE IKUNO MINE, HYOGO PREFECTURE, JAPAN

MASAAKI SHIMIZU[1]

Department of Petrology and Mineral Deposits, University Museum, University of Tokyo, 7–3–1 Hongo, Bunkyo, Tokyo 113, Japan

AKIRA KATO

Department of Geology, National Science Museum, 3–23–1 Hyakunin-cho, Shinjuku, Tokyo 169, Japan

Abstract

A chemical analysis of pavonite from the Ikuno mine, Hyogo Prefecture, Japan, gives Ag 11.14, Cu 0.40, Fe 0.08, Mn 0.01, Pb 0.16, Bi 69.43, S 18.05, for a total of 99.27 wt.%, corresponding to $(Ag_{0.92}Cu_{0.06}Fe_{0.01})_{\Sigma 0.99}(Bi_{2.95}Pb_{0.01})_{\Sigma 2.96}S_{5.00}$ (basis: S = 5). This allows recognition of $AgBi_3S_5$ as the ideal formula of pavonite, a composition which now acquires "end-member" status. The X-ray powder pattern is identical to those of Cu-Pb-substituted materials, and was indexed on the monoclinic cell with *a* 13.34(1), *b* 4.036(5), *c* 16.42(1) Å, β 94.25(5)°. Pavonite occurs as an accessory member in a ferberite – cassiterite – chalcopyrite – quartz – calcite vein accompanied by microscopic scheelite, bismuthinite, native bismuth, pyrite, and a sulfosalt of approximate formula $Ag_{6.5}Pb_7Bi_{14.5}S_{32}$, a possible derivative of treasurite. This assemblage is different from those in which pavonite had previously been found. The occurrence is near the center of a system of concentrically distributed veins involving Au–Ag, Pb–Zn, Zn, Cu–Zn, Cu, and Sn–W zones; it lies in the Sn–W zone, where neither Ag nor Pb minerals were previously known.

Keywords: pavonite, new association, ideal chemical composition, X-ray powder pattern, Ikuno mine, Japan.

Sommaire

Une analyse chimique de la pavonite de la mine Ikuno, dans la préfecture de Hyogo, au Japon, a donné (en %, poids) Ag 11.14, Cu 0.40, Fe 0.08, Mn 0.01, Pb 0.16, Bi 69.43, S 18.05, pour un total de 99.27%, ce qui correspond à $(Ag_{0.92}Cu_{0.06}Fe_{0.01})_{\Sigma 0.99}(Bi_{2.95}Pb_{0.01})_{\Sigma 2.96}S_{5.00}$ (sur une base de cinq atomes de soufre). Cette découverte nous permet de proposer $AgBi_3S_5$ comme formule idéale de la pavonite pure, c'est-à-dire, non substituée. Le cliché de diffraction (méthode des poudres) en est identique aux matériaux déjà connus, dont la composition dévie vers un pôle riche en Cu–Pb. Le spectre de diffraction X a été indexé avec une maille monoclinique ayant *a* 13.34(1), *b* 4.036(5), *c* 16.42(1) Å, et β 94.25(5)°. La pavonite de la mine Ikuno est un accessoire dans une veine à ferberite – cassitérite – chalcopyrite – quartz – calcite; elle est accompagnée, à l'échelle microscopique, de scheelite, bismuthinite, bismuth natif, pyrite, ainsi qu'un sulfosel dont la formule se rapproche de $Ag_{6.5}Pb_7Bi_{14.5}S_{32}$, et qui serait possiblement un dérivé de la treasurite. Un tel assemblage se distingue des autres dans lesquels on a trouvé la pavonite. Nous l'avons repéré près du centre d'un système de veines concentriques impliquant des zones enrichies en Au–Ag, Pb–Zn, Zn, Cu–Zn, Cu, et Sn–W; la pavonite se trouve dans la zone à Sn–W zone, jusqu'ici sans minéral à Ag et Pb.

(Traduit par la Rédaction)

Mots-clés: pavonite, association nouvelle, composition chimique idéale, spectre de diffraction X, méthode des poudres, mine de Ikuno, Japon.

Introduction

Descriptions of pavonite exist in the literature; for example, pavonite has been documented from the Porvenir mine, Bolivia (Nuffield 1954, Harris & Chen 1975), the Silver Bell mine (Karup-Møller 1972) and the Alaska mine, Colorado (Karup-Møller & Makovicky 1979). All of them have highly substituted chemical compositions, leading to the proposal of structural formulae such as $[(Bi,Sb)_{1-x}Pb_x]_9 Ag_2CuS_{15-4.5x}$, where $x \leq 0.1$ (Karup-Møller 1972) and $Cu_{3x}Pb_{2x}Ag_{1-y}Bi_{3-y}S_5$, where $5x \approx 2y$ and $0.18 \leq y \leq 0.32$ (Karup-Møller & Makovicky 1979). Type-locality pavonite is a Cu- and Pb-substituted material (Harris & Chen 1975). Although the formula $AgBi_3S_5$ has been assigned to ideal pavonite in light of the

[1] *E-mail address:* mshimizu@um.u-tokyo.ac.jp

results of syntheses (*e.g.*, Van Hook 1960, Makovicky *et al.* 1977), the validity of such a formula has never been tested. The present work reviews this proposal, namely, that pavonite has an "end-member" formula $AgBi_3S_5$; in other words, Pb and Sb would have to be regarded as non-essential if that hypothesis is confirmed.

The first occurrence of pavonite in Japan was reported orally by Kato (1964), who found that its composition is close to the above formula, and its X-ray powder-diffraction pattern agrees closely with that for the synthetic material of Van Hook (1960). The same material is here re-examined in order to document the chemical composition and the refined X-ray powder pattern. In the material examined, we found another Ag–Pb–Bi sulfosalt with an approximate composition $Ag_{6.5}Pb_7Bi_{14.5}S_{32}$, which is derived from the ideal formula of treasurite after substitution of Pb for $Ag_{0.5}Bi_{0.5}$. It is referred to as a "treasurite derivative" in this paper.

Occurrence

The ore deposits of the Ikuno mine, Hyogo Prefecture, Japan, are located approximately at 35°10′N and 134°47′E, and composed of many hydrothermal veins of subvolcanic nature. These are famous for their polymetallic mineralization. The elements present as essential constituents of the ore minerals are Cu, Zn, Pb, Ag, Au, As, Sn, W, Sb, Bi, Co, Ni, In, and Se, in order of decreasing frequency, and their accessory constituents are Cd, Ga, and Te. Two new minerals, ikunolite, $Bi_4(S,Se)_3$ (Kato 1959), and sakuraiite, $(Cu,Zn,Fe)_3(In,Sn)S_4$ (Kato 1965), were found in the ores.

The veins form in basin-structured conformable beds in three main groups, locally called (from west to east), Tasei, Kanagase, and Aokusa (Fig. 1). The distribution of the principal elements in the ore minerals is zonal, with the zones concentrically developed in a mushroom-like structure that has its

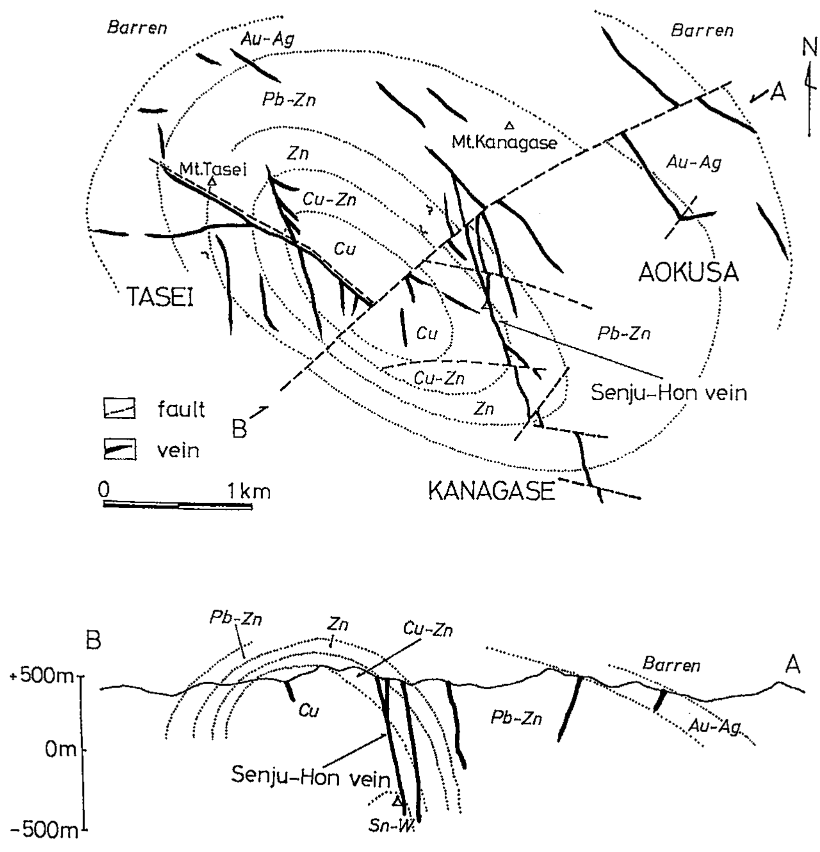

FIG. 1. Distribution of veins and zonal distribution of metals at the Ikuno mine, Japan, mainly after Maruyama (1959). Δ marks indicate the site of occurrence, plotted on plan and in profile, respectively.

geological center at the center of the basin (Maruyama 1957, 1959). From top to bottom (and from margin to center), the zones include: barren, Au–Ag, Pb–Zn, Zn, Cu–Zn, and Cu, with local development of Sn and Sn–W in the central region. Pavonite occurs in the Senju-hon vein of the Kanagase group, approximately 300 meters below sea level, within the Sn–W zone, where neither Ag nor Pb minerals had previously been found. Here, in a well-developed quartz vein, lead-grey minerals appear as visible but minute aggregates adjacent to quartz or chalcopyrite, their maximum dimension being a few millimeters across. Unlike the associated bismuthinite, some grains are devoid of cleavage and were finally identified as pavonite. Ferberite, cassiterite, chalcopyrite, scheelite, native bismuth, pyrite, calcite and siderite are associated minerals in the vein.

Under the ore microscope, all aggregates of pavonite have concave or linear outlines against quartz, the maximum dimension being millimetric (Fig. 2), as well as against bismuthinite, which is optically very similar to pavonite, except for its slightly weak anisotropism and the absence of reflection pleochroism. We also detected another sulfosalt, which is optically indistinguishable from pavonite. The unknown sulfosalt includes minute cubes of pyrite, which serves to distinguish the two minerals. The chemical data allowed us to identify it as a "treasurite derivative", as discussed below.

Sulfur isotopic data for sulfide minerals from the Ikuno mine have been reported in the literature: +1.4‰ (composite: Sasaki & Ishihara 1980), +0.2 to +0.9‰ (sphalerite: Miyoshi *et al.* 1988), +0.3 to +1.2‰ (chalcopyrite: Miyoshi *et al.* 1988) and +0.3‰ (roquesite-bearing ore: Shimizu & Kato 1991). We have no data on fluid inclusions, but Shimizu & Shikazono (1985) estimated the temperature of formation of the boundary between the Cu–Zn and Sn zones to be 270 to 260°C, on the basis of iron and zinc partitioning between sphalerite and stannite.

Chemical Analyses

Electron-microprobe analyses were made on pavonite, the "treasurite derivative" (Table 1), bismuthinite and native bismuth. The latter were found to be nearly pure Bi_2S_3 and Bi, respectively.

Pavonite compositions are all very close to $AgBi_3S_5$. Previously reported compositions have substitutions of 2Pb for AgBi and 3Pb for 2Bi, and, furthermore, a deficiency of S exists, according to Karup-Møller (1972). An example of the latter substitution is seen in material from the Suttsu mine, Hokkaido, Japan (Shimizu *et al.* 1995), the empirical formula being $Ag_{1.01}(Bi_{2.88}Pb_{0.18})_{\Sigma 3.06}(S_{3.57}Se_{1.37}Te_{0.06})_{\Sigma 5.00}$, *i.e.*, a selenium-bearing variety. The results of the present analyses do include minor Cu, ranging from 0.32 to 0.41 wt.%, the figure being fairly definite, despite the

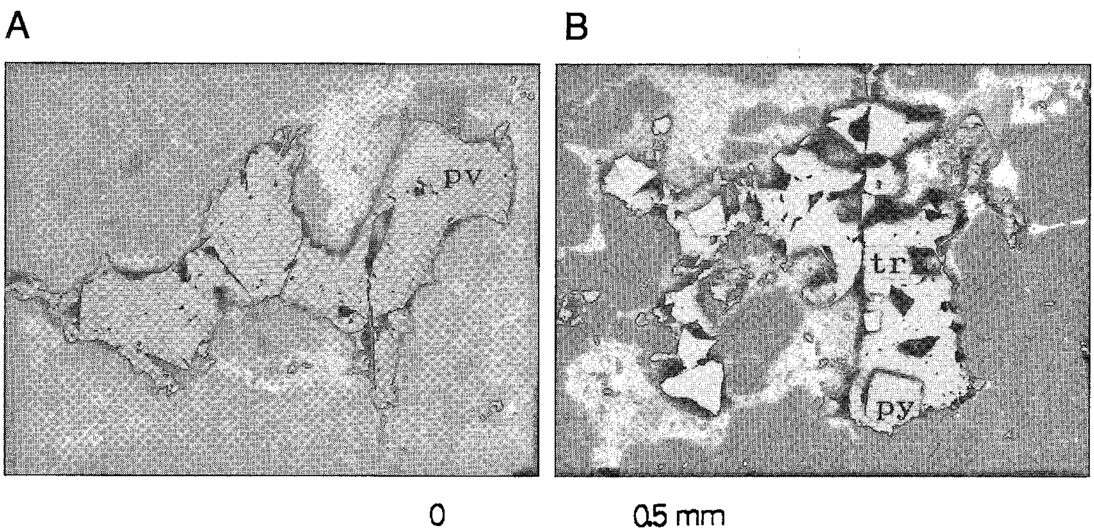

FIG. 2. Photomicrographs of pavonite (A) the "treasurite derivative" (B) from the Ikuno mine, Japan. A: concave outlines of pavonite (pv) against quartz, B: "treasurite derivative" (tr) containing cubes of pyrite (py).

TABLE 1. REPRESENTATIVE CHEMICAL COMPOSITIONS OF PAVONITE AND "TREASURITE DERIVATIVE" FROM THE IKUNO MINE, JAPAN

	1	2	3	4	5
Ag	11.14	12.05	11.02	12.7	12.26
Cu	0.40		0.04		
Fe	0.08		0.04		
Mn	0.01		–		
Cd	–		0.04		
Pb	0.16		23.58	19.6	20.19
Bi	69.43	70.04	48.05	50.5	50.90
S	18.05	17.91	16.29	16.4	16.66
Total	99.27	100.00	99.06	99.2	100.01
Atomic proportions based on S = 9 (for pavonite) or 32 (for treasurite)					
Ag	0.917	1	6.44	7.37	7
Cu	0.056		0.04		
Fe	0.013	0.04			
Mn	0.001		–		
Cd	–		0.03		
Pb	0.007		7.17	5.92	6
Bi	2.951	3	14.48	15.12	15
S	5.000	5	32.00	32.00	32

Columns: 1: Pavonite from the Ikuno mine, Japan. 2: Composition of ideal pavonite ($AgBi_3S_5$). 3: "Treasurite derivative" from the Ikuno mine, Japan. 4: Treasurite from the Treasure Vault mine, Colorado (Karup–Møller 1977). 5: Composition of ideal treasurite ($Ag_7Pb_6Bi_{15}S_{32}$).

close coexistence with chalcopyrite, which is the only Cu mineral in the material examined. Upon close examination, all compositions have a slight excess of (Ag + Cu) after calculation using the basis S = 5, whereas Bi is slightly lower than the theoretical figure. This suggests the existence of a substitution of 3(Ag + Cu) for Bi provided that the relation S = 5 is fixed. Thus, the material from the Ikuno mine is relatively pure, with $x \approx 0$ in the formula proposed by Karup-Møller (1972); Fe as well as Pb appear only in trace amounts; Sb is a minor substituent for Bi.

The chemical composition of other sulfosalts, distinguished from pavonite and bismuthinite by their association with pyrite cubes, indicates a higher Pb content. The stoichiometry obtained, $Ag_{6.5}Pb_7Bi_{14.5}S_{32}$, matches none of known sulfosalts, if critically considered. The closest analogue is treasurite, $Ag_7Pb_6Bi_{15}S_{32}$ (Makovicky & Karup-Møller 1977), from which the present composition is derived by the substitution of Pb for $Ag_{0.5}Bi_{0.5}$. The material thus is here tentatively referred to as a "treasurite derivative". Also, it is worthy of note that the chemical composition of our "treasurite derivative" can be explained by the following reaction: $6.5AgBi_3S_5$ (pavonite) + 7PbS (galena) $\rightarrow$ $Ag_{6.5}Pb_7Bi_{14.5}S_{32}$ ("treasurite derivative") + $2.5Bi_2S_3$ (bismuthinite). However, no proof of the reaction of galena with pavonite could be found. The compositional purity of the associated bismuthinite may be interpreted to indicate that the existence of an Ag–Bi sulfosalt exerts no compositional influence on it. But, if any Pb were present in excess, a significant modification of the phase to be produced may be expected to take place.

X-Ray Powder-Diffraction Study

The X-ray powder pattern (Table 2) is essentially identical to that of highly substituted pavonite (Karup-Møller 1972). A critical comparison reveals a very slight contraction of *a*, which may be ascribed to the influence of Cu substituting for Ag. The unit-cell parameters calculated from the indexed pattern are:

TABLE 2. X-RAY POWDER-DIFFRACTION PATTERN OF PAVONITE FROM THE IKUNO MINE, JAPAN

1		2			
I	*d*(Å)	I	*d* obs.	*d* calc.	*hkl*
10	16.401	<5	16.41	16.37	001
		<1	8.200	8.187	002
40	6.615	<5	6.661	6.652	200
30	5.436	15	5.453	5.458	$\bar{0}03$
50	5.344	19	5.361	5.361	$\bar{2}02$
10	4.369	<5	4.382	4.382	$\bar{2}03$
50	4.070	24	4.084	4.094	004
				4.074	203
40	3.866	12	3.864	3.852	$\bar{1}10$
90	3.594	85	3.604	3.608	$\bar{2}04$
10	3.525	18	3.528	3.522	$\bar{1}12$
100	3.464	59	3.463	3.464	112
70	3.368	73	3.373	3.376	204
70	3.323	40	3.326	3.326	400
20	3.262	14	3.273	3.275	005
40	3.214	13	3.211	3.213	$\bar{4}01$
30	3.177	12	3.186	3.185	$\bar{1}13$
40	3.122	13	3.123	3.121	$\bar{1}13$
10	3.073	<5	3.060	3.028	$\bar{2}05$
50	2.987	26	2.984	2.985	$\bar{3}10$
70	2.962	30	2.961	2.963	$\bar{3}11$
40	2.897	10	2.901	2.911	311
100	2.849	100	2.850	2.855	$\bar{2}05$
				2.850	$\bar{3}12$
50	2.759	16	2.759	2.760	312
10	2.713	<5	2.728	2.729	$\bar{0}06$
30	2.582	13	2.592	2.593	$\bar{2}06$
30	2.562	<5	2.566	2.566	313
20	2.488	<5	2.494	2.493	404
10	2.423	11	2.462	2.462	206
10	2.356	<5	2.356	2.357	314
		<5	2.339	2.339	$\bar{0}07$
50	2.246	31	2.253	2.252	$\bar{1}16$,405
40	2.202	13	2.206	2.207	$\bar{1}16$
40	2.182	11	2.188	2.191	$\bar{4}06$
				2.183	511
10	2.149	<5	2.154	2.153	315
40	2.110	18	2.111	2.111	512
30	2.079	<1	2.078	2.066	316
20	2.047	16	2.046	2.047	008
20	2.036				
50	2.022	62	2.015	2.018	020
70	2.012			2.014	$\bar{5}13$
50	2.002	13	1.983	1.984	407,117
30	1.9622	11	1.966	1.966	316
10	1.9515	<1	1.953	1.959	022
		<5	1.918	1.917	208
50	1.8900	17	1.892	1.893	023
10	1.8434	<5	1.850	1.850	$\bar{4}07$
		<5	1.824	1.825	$\bar{1}18$
20	1.7932	10	1.803	1.804	$\bar{4}08$
20	1.7739	<5	1.776	1.778	$\bar{5}16$
40	1.7600	10	1.760	1.761	$\bar{2}24$
30	1.7321				
20	1.7274	18	1.726	1.725	420
10	1.7210				
10	1.7059	<5	1.707	1.709	421
		<5	1.673	1.673	$\bar{5}16$
		<5	1.663	1.663	$\bar{5}17$
40	1.6397	11	1.648	1.648	225
		<5	1.564	1.563	$\bar{5}17$
10	1.5023	<5	1.513	1.505	$\bar{2}27$
20	1.4813	<5	1.483	1.484	426

1: Pavonite from the Silver Bell mine, Colorado (Karup–Møller 1972). Guinier camera method.
2: Pavonite from the Ikuno mine, Japan. Cu/Ni radiation. Diffractometer method.

a 13.34(1), *b* 4.036(5), *c* 16.42(1) Å, β 94.25(5)°. The unit cell contains 4[$AgBi_3S_5$], giving the calculated density 6.74 g/cm^3. These values are similar to those obtained by Makovicky *et al.* (1977).

"End-Member" Pavonite

Although studies of the synthetic products prove $AgBi_3S_5$ to be the ideal formula of pavonite, no natural material had been reported to substantiate this composition. The compositions of pavonite in the literature are derived from the above formula, principally as a result of two kinds of substitutions, as stated above. The results presented here confirm that the term "end-member" may truly be applied to the formula $AgBi_3S_5$ with respect to naturally occurring pavonite.

Acknowledgements

We thank Dr. Sadao Maruyama for helping the second author collect the studied materials, and the late Dr. Kin-ichi Sakurai, the original owner of the Sakurai Mineral Collection, currently held by National Science Museum, from which a part of the studied material was also included. We also thank Drs. Robert F. Martin, Alfonso G. Trudu, and two anonymous referees for incisive criticism and helpful suggestions. This study was partly supported by Ministry of Education, Science, Sports and Culture of Japan (Nos. 06302030 and 07304044) and the Japan Mining Promotive Foundation.

References

Harris, D.C. & Chen, T.T. (1975): Studies of type pavonite material. *Can. Mineral.* **13**, 408-410.

Karup-Møller, S. (1972): New data on pavonite, gustavite, and some related sulphosalt minerals. *Neues Jahrb. Mineral. Abh.* **117**, 19-38.

________ (1977): Mineralogy of some Ag–(Cu)–Pb–Bi sulfide associations. *Bull. Geol. Soc. Denmark* **26**, 41-68.

________ & Makovicky, E. (1979): On pavonite, cupropavonite, benjaminite and "oversubstituted" gustavite. *Bull. Minéral.* **102**, 351-367.

Kato, A. (1959): Ikunolite, a new bismuth mineral from the Ikuno mine, Japan. *Mineral. J.* **2**, 397-407.

________ (1964): Pavonite from the Ikuno mine, Japan. *J. Mineral. Soc. Japan* **7**, 77 (abstr. in Japanese).

________ (1965): Sakuraiite, a new mineral. *Geosci. Mag., Sakurai Vol.*, 1-5 (in Japanese).

Makovicky, E. & Karup-Møller, S. (1977): Chemistry and crystallography of the lillianite homologous series. I. General properties and definitions. *Neues Jahrb. Mineral. Abh.* **130**, 264-287.

________, Mumme, W.G. & Watts, J.A. (1977): The crystal structure of synthetic pavonite, $AgBi_3S_5$, and the definition of the pavonite homologous series. *Can. Mineral.* **15**, 339-348.

Maruyama, S. (1957): The relation between ore veins and igneous intrusives. *Mining Geol.* **7**, 281-284 (in Japanese).

________ (1959): Zonal distribution of ore deposit and prospecting at the Ikuno mine, Japan. *J. Mining Metall. Inst. Japan* **75**, 673-677 (in Japanese).

Miyoshi, T., Nakamura, T. & Kusakabe, M. (1988): Sulfur isotopic study of vein deposits in the Kinki district, Inner Zone of southwest Japan. *Mining Geol.* **38**, 323-333 (in Japanese with English abstr.).

Nuffield, E.W. (1954): Studies of mineral sulphosalts. XVIII. Pavonite, a new mineral. *Am. Mineral.* **39**, 409-415.

Sasaki, A. & Ishihara, S. (1980): Sulfur isotope characteristics of granitoids and related mineral deposits in Japan. *Proc. 5th IAGOD Symp.* **1**, 325-335.

Shimizu, M. & Kato, A. (1991): Roquesite-bearing tin ores from the Omodani, Akenobe, Fukoku, and Ikuno polymetallic vein-type deposits in the Inner Zone of southwestern Japan. *Can. Mineral.* **29**, 207-215.

________, Schmidt, S.Y., Stanley, C.J. & Tsunoda, K. (1995): Kawazulite and unnamed $Bi_3(Te,Se,S)_4$ in Ag – Bi – Te – Se – S mineralization from the Suttsu mine, Hokkaido, Japan. *Neues Jahrb. Mineral. Abh.* **169**, 305-308.

________ & Shikazono, N. (1985): Iron and zinc partitioning between coexisting stannite and sphalerite: a possible indicator of temperature and sulfur fugacity. *Mineral. Deposita* **20**, 314-320.

Van Hook, H.J. (1960): The ternary system Ag_2S–Bi_2S_3–PbS. *Econ. Geol.* **55**, 759-788.

Received May 14, 1996, revised manuscript accepted August 15, 1996.