PIRETITE, $Ca(UO_2)_3(SeO_3)_2(OH)_4 \cdot 4H_2O$, A NEW CALCIUM URANYL SELENITE FROM SHINKOLOBWE, SHABA, ZAIRE

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ABSTRACT

Piretite, ideally $Ca(UO_2)_3(SeO_3)_2(OH)_4 \cdot 4H_2O$, is a new mineral from the Shinkolobwe uranium deposit in Shaba, Zaire, that occurs as crusts in association with an orange masuyite-like U–Pb oxide on the surface of uraninite samples. The crystals are lemon-yellow in color with a pearly luster; they do not fluoresce under ultraviolet light. Cleavage: {001} good. $D_{meas} = 4.00$ g/cm³ and $D_{calc} = 3.87$ g/cm³ (empirical formula), 3.93 g/cm³ (idealized formula); $H_{Mohs} = 2.5$. Optically biaxial negative, $2V = 33(5)°$, α 1.54(calc.), β 1.73(1) and γ 1.75 (1), with optical orientation $X \parallel c$, $Y \parallel a$, $Z \parallel b$. The dispersion $r > v$ is weak, and the crystals are nonpleochroic. Piretite is orthorhombic, space group $Pmn2_1$ or $Pmnm$, with the following unit-cell parameters refined from powder data: a 7.010(3), b 17.135(7), c 17.606(4) Å, V 2114.8(1) Å³, $a:b:c$ 0.409:1:1.027, $Z = 4$. The forms recognized are {100} {010} {001}, tenacity is weak, and the fracture is uneven. The strongest ten reflections of the X-ray powder pattern [d(in Å)(I)hkl] are: 8.79(80)002, 8.56(40)020, 5.57(20)013, 4.43(20)130, 4.30(30)131, 3.51(100)200, 3.24(40)220, 3.093(50)115, 3.032(100)151 and 1.924(40)237. Electron-microprobe and thermogravimetric analyses gave: CaO 3.57, UO_3 72.00, SeO_2 19.29, H_2O 8.00, total 102.86 wt.%. The empirical formula is 0.76 CaO·3.02 UO_3·2.09 SeO_2·5.33 H_2O. Piretite results from the alteration of uraninite and primary selenium-bearing sulfides such as penroseite, in the presence of Ca derived from the host rocks. The name is chosen to honor the Belgian crystallographer Paul Piret. Holotype material is deposited in the mineralogical collection of the Royal Belgian Institute of Natural Sciences, Brussels, Belgium.

Keywords: piretite, new mineral species, calcium uranyl selenite, Shinkolobwe, Shaba, Zaire.

SOMMAIRE

La piretite, de formule idéale $Ca(UO_2)_3(SeO_3)_2(OH)_4 \cdot 4H_2O$, est un nouveau minéral du gîte uranifère de Shinkolobwe, Shaba, Zaïre. Le minéral se présente en croûtes à la surface d'échantillons d'uraninite associée à un oxyde orange d'U–Pb semblable à la masuyite. La couleur des cristaux est jaune citron avec un éclat nacré; il n'y a aucune fluorescence aux rayons ultraviolettes. Le clivage {001} est bon. $D_{mes} = 4.00$ et $D_{calc} = 3.87$ (formule empirique), 3.93 (formule idéale); $H_{Mohs} = 2.5$. Optiquement biaxe négative $2V = 33(5)°$, α 1.54(calc.), β 1.73(1) et γ 1.75(1), avec orientation optique $X \parallel c$, $Y \parallel a$, $Z \parallel b$. La dispersion $r > v$ est faible, et les cristaux sont non pléochroïques. La piretite est orthorhombique, groupe spatial $Pmn2_1$, ou $Pmnm$, avec les paramètres de la maille a 7.010(3), b 17.135(7), c 17.606(4) Å, V 2114.8(1) Å³, $a:b:c$ 0.409:1:1.027 pour $Z = 4$. Les formes des cristaux sont {100} {010} {001}; la ténacité est faible, et la cassure, irrégulière. Les dix raies les plus intenses du spectre de diffraction X (méthode des poudres) [d (en Å)(I)hkl] sont: 8.79(80)002, 8.56(40)020, 5.57(20)013, 4.43(20)130, 4.30(30)131, 3.51(100)200, 3.24(40)220, 3.093(50)115, 3.032(100)151 et 1.924(40)237. Les analyses à la microsonde électronique et thermogravimétriques ont donné: CaO 3.57, UO_3 72.00, SeO_2 19.29, H_2O 8.00, total 102.86%. La formule empirique est 0.76 CaO·3.02 UO_3·2.09 SeO_2·5.33 H_2O. Le minéral résulte de l'altération de l'uraninite et de séléniures primaires, tel que la penroséite; le calcium provient de la gangue du gîte uranifère. Le nom est à l'honneur du cristallographe belge Paul Piret. Le minéral est enregistré dans la collection minéralogique de l'Institut royal des Sciences naturelles de Belgique, à Bruxelles, Belgique.

Mots-clés : piretite, nouvelle espèce minérale, sélénite d'uranyle et de calcium, Shinkolobwe, Shaba, Zaïre.

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INTRODUCTION

Piretite, ideally $Ca(UO_2)_3(SeO_3)_2(OH)_4 \cdot 4H_2O$, is a new uranyl selenite mineral from Shinkolobwe, Shaba, Zaire. The Shinkolobwe uranium deposit has been exploited for uranium until 1960, and is world-famous for its rich association of secondary minerals. More than forty uranium-bearing species have been identified; twenty-seven were described for the first time from this deposit. This abundance of secondary uranium minerals is mainly due to two factors: (1) the large variety of primary sulfides, selenides and tellurides associated with uraninite, combined with the elements of the host rocks (calcium, barium, magnesium) provide complex chemistry, and (2) the exceptional thickness of the alteration zone, which locally reaches more than 100 meters.

The original sample of piretite was collected at the time of the activity of the mine, and was given to the authors by Gilbert Gauthier. The mineral and the mineral name were approved by the Commission on New Minerals and Mineral Names, IMA. The type specimen of piretite is stored as R.C. 4717 in the mineralogical collection of the Royal Belgian Institute of Natural Sciences, Brussels, Belgium. The mineral is named for Paul Piret, Professor of Crystallography, University of Louvain-la-Neuve, Belgium, who has been involved in the description of thirty-four new mineral species.

MORPHOLOGY, PHYSICAL PROPERTIES AND OCCURRENCE

Piretite occurs as elongate tablets lemon-yellow in color that possess an irregular outline. The streak is pale yellow. The crystals have a mean length of 2–3 mm and a width of around 1 mm, but some crystals are acicular prisms up to 5 mm in length. The mineral is transparent to translucent, with a pearly luster. The tablets are flattened on (001), have a good {001} cleavage, and are in some cases cracked and strongly striated parallel to the elongation. The forms of the crystals are {100}, {010} and {001}. The tenacity is weak, and the fracture is uneven. The photomicrograph (Fig. 1), taken by scanning electron microscopy (SEM), shows a typical association of stacked tablets of piretite. The crystals are generally of poor quality and occur as curved sheets. Figure 2 shows the acicular shape of a hollow crystal with rough faces. The Mohs hardness is 2.5. The density, measured by flotation in Clerici solution at 25°C, is 4.00 g/cm^3. The calculated density based on the empirical formula is 3.87 g/cm^3, and that based on the idealized formula is 3.93 g/cm^3. The higher value of the experimentally determined density may be explained by the presence of some micro-inclusions of uraninite in the crystals. The piretite found in the Shinkolobwe deposit results from the alteration of primary veins of uraninite associated with selenides, such as penroseite, or associated with
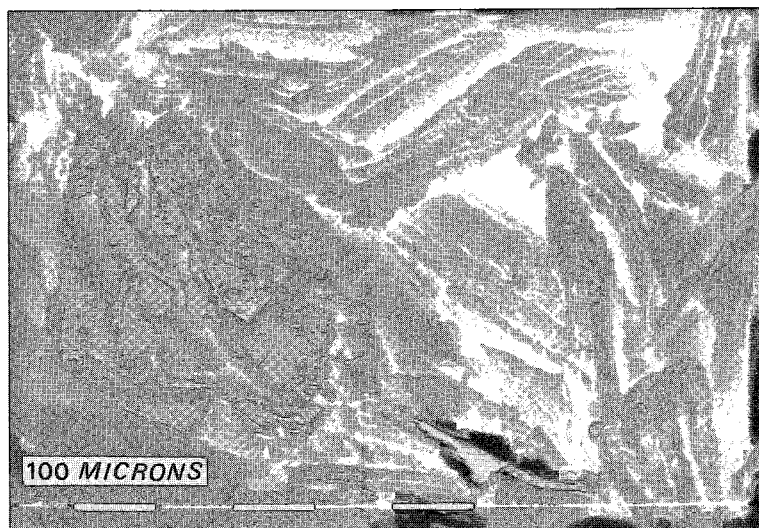

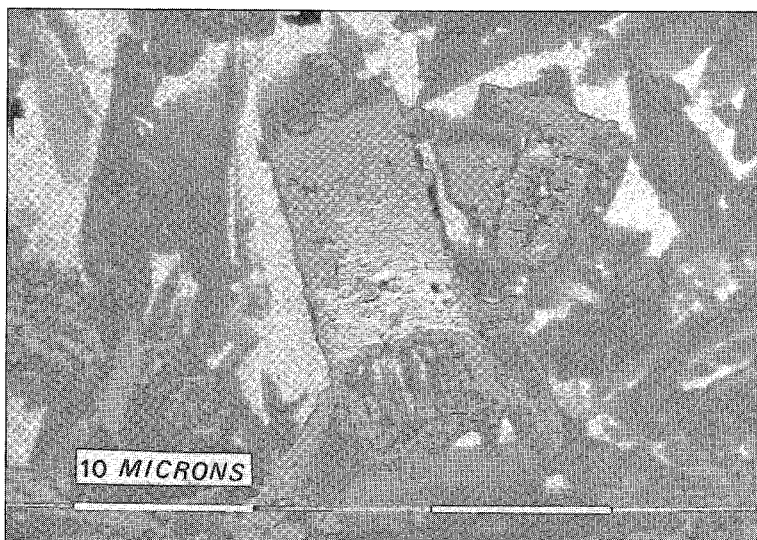FIG. 1. SEM photomicrograph of piretite showing stacked curved tablets. Scale bar: 100 µm.

Fig. 2. SEM photomicrograph of a hollow acicular prism of piretite with rough faces. Scale bar: 10 μm.

selenium-containing sulfides such as linnaeite, siegenite, or vaesite, all in the presence of calcium from the dissolution of the upper Cambrian carbonaceous host-rocks of the Série des Mines. Piretite forms stacked aggregates on the surface of uraninite. An orange uranyl–lead oxide arranged in microcrystalline flecks and veinlets is the only associated uranyl mineral. Its X-ray powder pattern is very near to that of masuyite [$Pb_3U_8O_{27} \cdot 10H_2O$] (PDF 13–408).

OPTICAL CHARACTERISTICS

The mineral is biaxial negative with a measured $2V$ value of 33(5)° (Tobi method). The indices of refraction were determined at 589 nm: α 1.54 (calc), β 1.73 (1) and γ 1.75 (1). The dispersion is weak, and the crystals are nonpleochroic. The optical orientation is $X \parallel c$, $Y \parallel a$ and $Z \parallel b$. Dispersion is weak, $r > v$.

X-RAY CRYSTALLOGRAPHY

The X-ray powder-diffraction data were recorded with a Guinier–Hägg camera using monochromated $CuK\alpha_1$ radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 20 mA. Synthetic fluorphlogopite (SRM–675) was used as a calibrant for the lower θ-values, and silicon powder (SRM–460) was used for the higher θ-values. The relative intensities of the diffraction lines were measured with a Carl Zeiss Jena MD–100 micro-densitometer. The pattern is unique and could not be matched with that of any phase in the ICDD Powder Diffraction File.

Single crystals of piretite were examined using Weissenberg methods employing filtered Cu-radiation. Film data of the 0, 1 and 2 levels for a crystal mounted along the c axis indicate orthorhombic symmetry. Systematic absences give the space groups $Pmn2_1$ or $Pmnm$. The refined unit-cell parameters are: a 7.010(3), b 17.135(7), c 17.606(4) Å, V 2114.8(1) Å^3, a:b:c 0.409:1:1.027, $Z = 4$; they were obtained using the d-values of 32 powder-diffraction lines. The indexing of these lines is conformable with single-crystal Weissenberg data. The program PIRUM (Werner 1969) was used for unit-cell refinement. Figure of merit values are $M(20) = 8$, $F(20) = 14$ (0.0214,70). A fully indexed powder pattern is given in Table 1.

CHEMICAL COMPOSITION

Crystals of piretite were chemically analyzed using a Cameca SX–50 electron microprobe with a beam size of 2 μm operating at 15 kV and a beam current of 20 nA. Except for the major components, no peaks of elements with an atomic number of 6 or greater were significantly above the detection limit, indicating that piretite is essentially a pure Ca–U–Se phase. The

TABLE 1. X-RAY POWDER-DIFFRACTION DATA
FOR PIRETITE

hkl	d_{obs} (Å)	d_{calc} (Å)	I
011	12.30	12.28	10
002	8.79	8.80	80
020	8.56	8.57	40
021	7.73	7.70	5
101	6.52	6.51	5
022	6.15	6.14	20
013	5.57	5.55	20
130	4.43	4.43	20
131	4.30	4.29	30
132	3.96	3.96	5
024	3.92	3.92	10
200	3.51	3.50	100
015	3.45	3.45	5
142	3.38	3.38	5
220	3.24	3.24	40
115	3.093	3.095	50
151	3.032	3.033	100
125	2.952	2.954	20
016	2.895	2.892	20
223	2.841	2.839	5
062	2.715	2.716	10
145	2.535	2.536	5
017	2.487	2.488	5
171	2.291	2.291	5
073	2.257	2.259	5
330	2.162	2.163	10
156	2.124	2.124	10
236	2.093	2.093	5
038	2.053	2.054	10
075	2.009	2.010	5
237	1.924	1.924	40
228	1.821	1.821	5

Guinier–Hägg camera, CuKa_1 radiation. Intensities
measured with Carl Zeiss Jena MD-100 microdensito-
meter.

following standards were used: wollastonite (Ca),
synthetic UO_2 (U), Analytical Reagent selenium (Se).
H_2O content was determined thermogravimetrically. A
thermogravimetric analysis (TGA) reveals a total
weight-loss of 8.00 wt.%. Five electron-microprobe
analyses carried out on each of five different crystals
yield the proportion (wt.%) of major components:
CaO 3.57 [3.07–4.07], UO_3 72.00 [70.60–73.40], SeO_2
19.29 [18.60–20.20]. The oxide formula calculated on
the basis of 14 O atoms is: 0.76 CaO·3.02 UO_3·2.09
SeO_2·5.33 H_2O. The empirical formula, taking into
account electroneutrality, is: $Ca_{0.76}(UO_2)_{3.02}(SeO_3)_{2.09}$
$(OH)_{3.38}$·3.64H_2O. The ideal formula is: $Ca(UO_2)_3$
$(SeO_3)_2(OH)_4$·4H_2O. Piretite is soluble in dilute HCl
without effervescence.

Calculation of the Gladstone–Dale relationship
using the constants of Mandarino (1981) yields a
"good" compatibility index between physical and
chemical data using the measured density [$1 - (K_P/K_C)$
= 0.0567].

THERMAL STABILITY

The thermal stability of piretite was studied with
a TGA 2950 thermogravimetric analyzer, TA
Instruments, with a heating rate of 5°C/min and a
constant N_2-flow of 50 mL/min. The TGA curve shows
that dehydration and dehydroxylation do not take place
in distinct steps.

INFRARED SPECTROSCOPY

The infrared spectrum was recorded using the KBr
dispersion technique (1 mg sample in 300 mg KBr)
with an Ati–Mattson Genesis Fourier transform
infrared spectrometer, which covers the range
400–4000 cm^{-1}. The infrared spectrum, presented in
Figure 3, is characterized by the vibrations of H_2O
molecules, OH, UO_2 and SeO_3 groups. The absorption
bands at about 3303 and 1623 cm^{-1} are due to H_2O, and
correspond to stretching and deformation modes,
respectively. The assignment of the absorption bands is
summarized in Table 2.

RELATIONSHIPS TO OTHER SPECIES

In addition to guilleminite, piretite is the second
uranyl selenite to be found at Shinkolobwe. Selenium
in southern Shaba is mainly concentrated in the
Musonoi copper deposit, which also contains localized
uranium mineralization. This deposit, located 200 km
east of Shinkolobwe, is the type locality for four of the
five known secondary uranyl selenites previously
described: demesmaekerite [$Pb_2Cu_5(UO_2)_2(SeO_3)_6$
$(OH)_6$·2H_2O] (Cesbron et al. 1965), derriksite
[$Cu_4(UO_2)(SeO_3)_2(OH)_6$·$H_2O$) (Cesbron et al. 1971),
guilleminite [$Ba(UO_2)_3(SeO_3)_2 O_2(H_2O)_3$]] (Cooper &
Hawthorne 1995) and marthozite [$Cu(UO_2)_3(SeO_3)_3$
$(OH)_2$·7H_2O] (Cesbron et al. 1969). The last secondary

TABLE 2. INFRARED ABSORPTION BANDS OF
PIRETITE

Wavenumber (cm^{-1})	Assignment	
3303 (s,b)	$v_1 H_2O$	*
2927 (w)	$v_2 H_2O$	*
1623 (s)	δH_2O	**
1483 (w)	δH_2O	**
898 (s)	$v_2 UO_2$	*
815 (w)	$v_1 SeO_3$	*
732 (s)	$v_3 SeO_3$	*
468 (m)	$v_2 SeO_3$	*

s: strong, m: medium, w: weak, b: broad
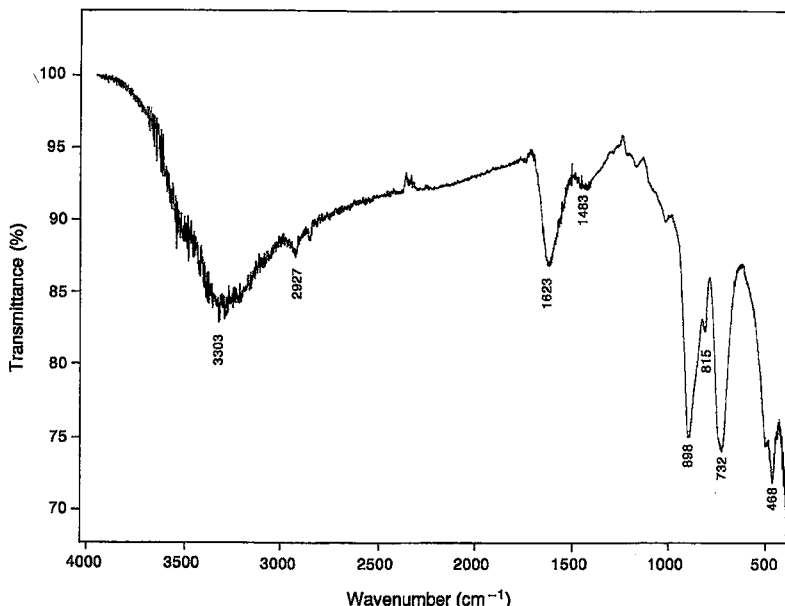* Khandelval & Verma (1976); ** Morris et al.
(1991).

FIG. 3. Fourier-transform infrared spectrum of piretite from 400 to 4000 cm^{-1}.

uranyl selenite described is haynesite [$(UO_2)_3(SeO_3)_2(OH)_2 \cdot 5H_2O$] (Deliens & Piret 1991) from the Repete mine, in Utah. Piretite differs from the other yellow secondary uranium minerals at the Shinkolobwe deposit by its stacking of striated tablets and its pearly luster. Guilleminite, the other uranyl selenite known from Shinkolobwe, occurs as micro-crystalline or powdered amber-yellow-colored crusts on uraninite. The yellow uranyl selenite, haynesite, whose morphology and state of aggregation of crystals resembles that of piretite, has a vitreous luster and is only known from a uranium deposit hosted by the Morrison Formation in Utah, of Upper Jurassic age (Deliens & Piret 1991).

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PAVONITE FROM THE IKUNO MINE, HYOGO PREFECTURE, JAPAN

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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

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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
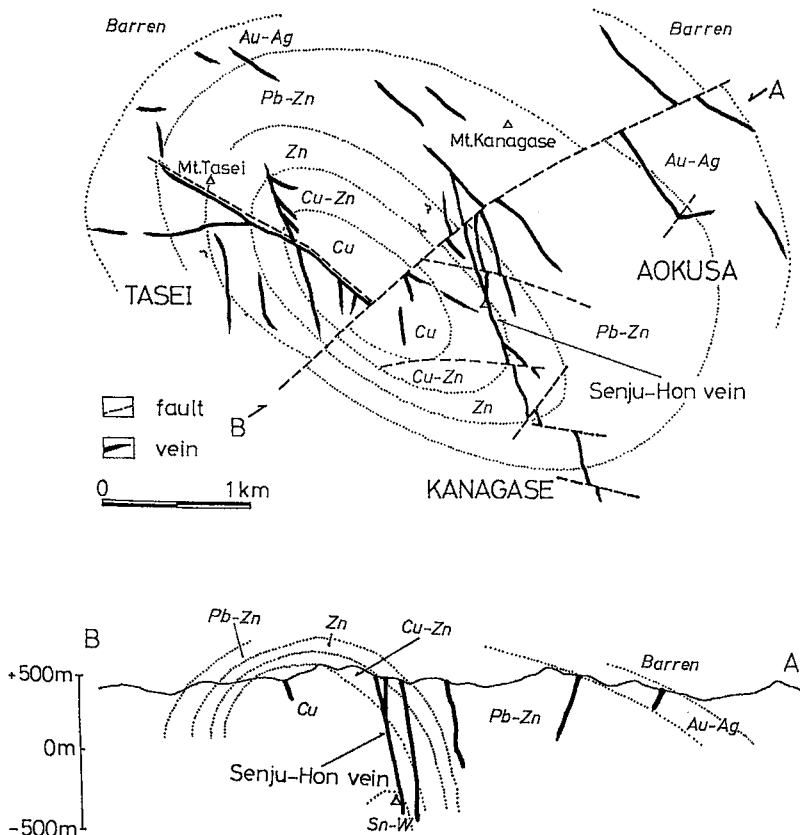

FIG. 1. Distribution of veins and zonal distribution of metals at the Ikuno mine, Japan, mainly after Maruyama (1959). Δ marks indicate the site of occurrence, plotted on plan and in profile, respectively.

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 $Ag_{1.01}(Bi_{2.88}Pb_{0.18})_{\Sigma3.06}(S_{3.57}Se_{1.37}Te_{0.06})_{\Sigma5.00}$, 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
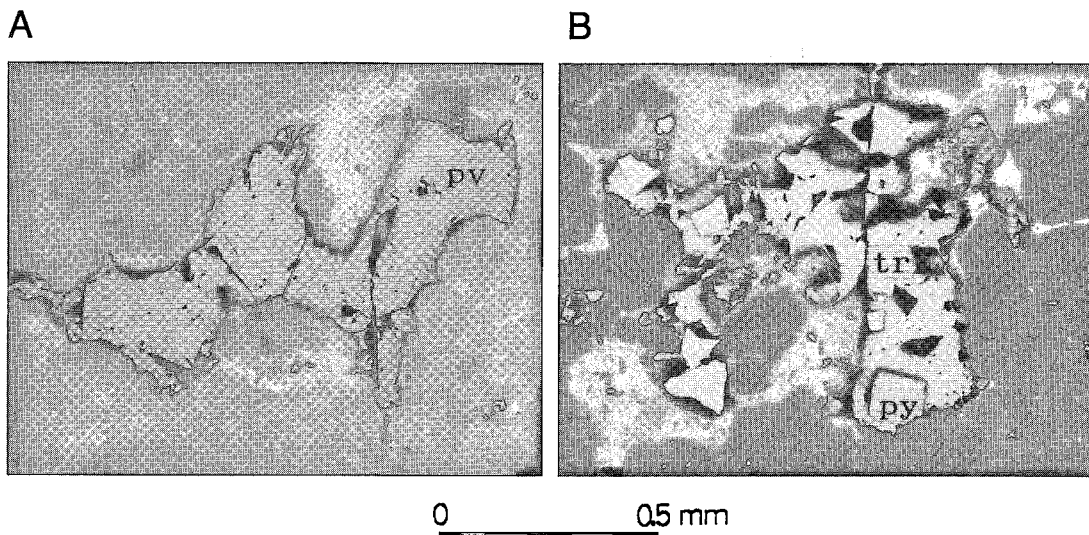

Fig. 2. Photomicrographs of pavonite (A) the "treasurite derivative" (B) from the Ikuno mine, Japan. A: concave outlines of pavonite (pv) against quartz, B: "treasurite derivative" (tr) containing cubes of pyrite (py).

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)

	1	2	3	4	5
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$_3$S$_5$). 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$_7$Pb$_6$Bi$_{15}$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$_7$Bi$_{14.5}$S$_{32}$, matches none of known sulfosalts, if critically considered. The closest analogue is treasurite, Ag$_7$Pb$_6$Bi$_{15}$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$_3$S$_5$ (pavonite) + 7PbS (galena) → Ag$_{6.5}$Pb$_7$Bi$_{14.5}$S$_{32}$ ("treasurite derivative") + 2.5Bi$_2$S$_3$ (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	003
50	5.344	19	5.361	5.361	202
10	4.369	<5	4.382	4.382	203
50	4.070	24	4.084	4.094	004
				4.074	203
40	3.866	12	3.864	3.852	110
90	3.594	85	3.604	3.608	204
10	3.525	18	3.528	3.522	112
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	401
30	3.177	12	3.186	3.185	113
40	3.122	13	3.123	3.121	113
10	3.073	<5	3.060	3.028	205
50	2.987	26	2.984	2.985	310
70	2.962	30	2.961	2.963	311
40	2.897	10	2.901	2.911	311
100	2.849	100	2.850	2.855	205
				2.850	312
50	2.759	16	2.759	2.760	312
10	2.713	<5	2.728	2.729	006
30	2.582	13	2.592	2.593	206
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	007
50	2.246	31	2.253	2.252	116,405
40	2.202	13	2.206	2.207	116
40	2.182	11	2.188	2.191	406
				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	513
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	407
		<5	1.824	1.825	118
20	1.7932	10	1.803	1.804	408
20	1.7739	<5	1.776	1.778	516
40	1.7600	10	1.760	1.761	224
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	516
		<5	1.663	1.663	517
40	1.6397	11	1.648	1.648	225
		<5	1.564	1.563	517
10	1.5023	<5	1.513	1.505	227
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$_3$S$_5$], 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$_3$S$_5$ 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$_3$S$_5$ with respect to naturally occurring pavonite.

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