CUPROPAVONITE FROM HALL'S VALLEY, PARK COUNTY, COLORADO

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ABSTRACT

Cupropavonite from Hall's Valley, Park County, Colorado (*USNM* 92902) has a cell with double the *c* edge of pavonite. The cell (*a* 13.40, *b* 4.00, *c* 2 x 16.435 Å, β 93.87°) contains $8[Cu_{1.01}Ag_{0.58}Bi_{2.51}Pb_{0.33}S_5] = 8$ $[Me_{4.43}S_5]$ as compared with $4[Cu_{0.33}Ag_{0.78}(Bi_{2.74}Pb_{0.22}Sb_{0.03})S_5]$ $= 4[Me_{4.10}S_5]$, on the average, for pavonite. The new occurrence has a lower Pb content than type cupropavonite; the ratio Cu:Pb (of the cations that substitute for Ag and Bi in pavonite) is 3:1, as compared with 3:2 in the type material and in average pavonite. The excess of about 0.4 atoms of metal *per* formula unit over the requirement of the ideal pavonite formula ($AgBi_3S_5$) counters a deficiency of about 0.5 atoms of Bi^{3+}, which is presumed to be replaced by Pb^{2+} in type-locality cupropavonite and by Pb^{2+} and Ag^+ in the new occurrence. The excess metal is judged to be Cu and to be accommodated interstitially in the structure, as has been proposed for the excess of 0.1 atom of metal in pavonite. The remaining Cu and Ag are present in about equal amounts. The distribution may be mainly ordered, causing the doubling of the periodicity along [001] and certain distinct differences in intensities compared with pavonite. A general formula based on these assumptions has the form $4[Cu^i_{\geq 0.5y+z}$ $CuAgBi_5(Pb_yAg_z)S_{10}]$, in which Cu^i is interstitial Cu.

Keywords: cupropavonite, Park County, Colorado, pavonite, structural formula, interstitial Cu.

SOMMAIRE

Le paramètre *c* de la maille de la cupropavonite de Hall's Valley, comté de Park, Colorado, U.S.A. (USNM 92902) est double de celui de la pavonite. La maille (*a* 13.40, *b* 4.00, *c* 2 x 16.435 Å, β 93.87° contient 8 $[Cu_{1.01}Ag_{0.58}Bi_{2.51}Pb_{0.33}S_5] = 8$ $[Me_{4.43}S_5]$ au lieu de $4[Cu_{0.33}Ag_{0.78}(Bi_{2.74}Pb_{0.22}Sb_{0.03})$ $S_5] = 4 [Me_{4.10}S_5]$ en moyenne pour la pavonite. Le contenu en Pb de cette nouvelle occurrence est inférieur à celui de la pavonite type. Le Cu et le Pb qui remplacent dans la cupropavonite une partie de l'Ag et du Bi de la pavonite sont ici présents dans un rapport Cu/Pb voisin de 3 alors que ce

rapport est voisin de 3/2 dans la cupropavonite type et dans la pavonite moyenne. L'addition d'environ 0.4 atomes de métal par formule par rapport à la formule idéale de la pavonite $AgBi_3S_5$ compense le retrait d'environ 0.5 atomes de Bi^{3+}. On suppose que Bi^{3+} est remplacé par Pb^{2+} dans la cupropavonite type et par Pb^{2+} et Ag^+ dans la présente occurrence. On estime que le métal en excédent est Cu et qu'il est présent sous forme d'atomes interstitiels dans la structure comme on l'a déjà proposé pour l'excès de 0.1 atome par formule pour la pavonite type. Le Cu restant et l'Ag sont présents en quantités à peu près égales. Leur distribution pouvait être ordonnée le long de [001] causant ainsi le doublement de *c* et des différences d'intensité par rapport à la pavonite. Une formule générale basée sur ces suppositions est: $4[Cu^i_{\geq 0.5y+z}CuAgBi_5(Pb_yAg_z)]$ où Cu^i représente le Cu interstitiel.

(Traduit par la Rédaction)

Mots-clés: cupropavonite, comté de Park, Colorado, pavonite, formule structurale, cuivre interstitiel.

INTRODUCTION

Karup-Møller (1972) discovered that "alaskaite" from the Alaska mine, Colorado, which is known to be a mixture, consists in part of pavonite containing exsolution lamellae of a pavonite variety. He could not distinguish the host pavonite from the lamellae by X-ray diffraction, and detected only one lattice on Weissenberg films, which he interpreted as having a distorted (triclinic) cell with a doubled *c* axis (2 x 16.2 Å). Guinier films failed to reveal either the triclinic geometry or the doubling of the *c* axis. However, microprobe analyses showed that the lamellar phase differs significantly in chemical composition from its host. "Normal" pavonite is a Ag–Bi sulfosalt mineral with subordinate Cu. In the lamellae, Cu proved to be in excess of Ag.

A re-examination of the specimens led Karup-Møller & Makovicky (1979) to revise the chemical data for the Cu-rich lamellae (Table 1, nos. 1, 2) and their host (Table 2, no. 6). They described the lamellae as a new mineral, cupropavonite, having pavonite-like cell dimensions

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TABLE 1. MICROPROBE ANALYSES AND ATOMIC PROPORTIONS
OF CUPROPAVONITE

			WEIGHT PERCENT				
Analysis	Cu	Ag	Bi	Pb	Sb	S	Total
1	5.7	6.2	56.4	13.5	0.1	18.0	99.9
2	5.9	6.1	56.8	13.4	0.3	17.6	100.1
3	7.26	7.01	59.32	7.65	--	18.10	99.34

	ATOMIC PROPORTIONS (calc. on a basis of S = 5)					
Analysis	Cu	Ag	Bi	Pb	Bi+Pb+Sb	Total Metal
1	0.80	0.51	2.40	0.58	2.98	4.29
2	0.85	0.52	2.48	0.59	3.07	4.44
3	1.01	0.58	2.51	0.33	2.84	4.43

1, 2. Alaska Mine, Colorado; repeat analyses of lam-
ellae within "normal" pavonite. Sample 1124 in Karup-
Møller & Makovicky (1979). The atomic proportions
deduced here differ slightly from the values calculated
by the authors. 3. Hall's Valley, Park County, Col-
orado (USNM 92902); analyst E. Gasparrini. Data
reduction effected by EMPADR VII (Rucklidge & Gaspar-
rini 1969).

TABLE 2. CATION PROPORTIONS (S = 5) FOR MICROPROBE
ANALYSES OF PAVONITE

CATIONS	1	2	3	4	5	6	7
Cu	0.23	0.33	0.37	0.32	0.43	0.27	0.33
Ag	0.90	0.83	0.73	0.75	0.69	0.77	0.78
Bi	2.70	2.85	2.68	2.74	2.71	2.75	2.74
Pb	0.15	0.15	0.21	0.23	0.27	0.32	0.22
Sb	--	0.03	0.07	0.04	0.02	0.01	0.03
Cu+Ag	1.13	1.16	1.10	1.07	1.12	1.04	1.11
Bi+Pb+Sb	2.85	3.03	2.96	3.01	2.98	3.07	2.96
Total Metal	3.98	4.19	4.06	4.08	4.10	4.11	4.07

1. Harris & Chen (1975). 2 - 6. Karup-Møller &
Makovicky (1979).
1. Porvenir Mine, Cerro Bonete, Bolivia (type specimen).
2. Silver Bell Mine, Red Mountain, Colorado (BSF 1821).
3. Old Lout, Ouray, Colorado (# 1139). 4. Gladiator
Mine, Colorado (# 1140). 5. Manhattan, Nevada (ROM
M21003). 6. Alaska Mine, Colorado (# 1124); host of
cupropavonite (analyses 1 & 2, Table 1). Average of
two. 7. Averages of 1 to 6.

but with a doubled c axis (a 13.45, b 4.02, c
33.06 Å, β 93.50°, $C2/m$ or Cm) and cell
contents $Cu_{7.2}Ag_4Bi_{20}Pb_{4.8}S_{40}$.

This paper describes an occurrence of cupro-
pavonite from the Missouri mine, Hall's Valley,
Park County, Colorado, on the type specimen
(USNM 92902) for cuprobismuthite and ber-
ryite. The nature of the occurrence and the
crystallographic properties of the mineral differ
somewhat from those of the Alaska mine min-
eral.

X-Ray-Diffraction Studies

The material available for the present study
consisted of a few, roughly platy crystals measur-
ing less than 0.5 mm across their greatest dimen-
sion after removal from the specimen. Four
crystals were oriented for rotation about b
[010], which lies in the plane of the plates,
and each crystal was used to obtain a set of

Weissenberg films Also, the $hk0^*$ and $0kl^*$
layers were recorded on precession films with the
best crystal.

The X-ray films reveal no departure from
monoclinic symmetry and generally resemble
the films obtained with Cerro Bonete, Bolivia
(type) pavonite and with synthetic Cu- and
Pb-free pavonite. However, there are obvious
differences: (1) The c dimension is doubled
by the presence of additional reflections, as
reported by Karup-Møller (1972). Some re-
flections are as strong as the "normal" reflec-
tions. (2) The films show certain distinct dif-
ferences in the relative intensities of reflections
as compared with pavonite. (3) The $[00l]^*$ row
and all reciprocal rows parallel to it are marked
on the films by discontinuous streaks (although
individual reflections in the rows are generally
sharp), indicating some imperfections in the
structure of these crystals parallel to (001).

The four sets of Weissenberg films show
small variations in intensities. However, the
differences appear to be due, not to intrinsic
differences among the crystals, but to their
poor quality and to the difficulty of mounting
them for a uniform view of the X-ray beam
during oscillation. The films lead to cell dimen-
sions and to a cell volume that are essentially
the same (except for the doubled c edge) as
values recently obtained on natural and syn-
thetic pavonite. This is in contrast to type cupro-
pavonite, for which Karup-Møller & Makovicky
(1979) reported a marked increase in the a and
c dimensions (Table 3). The systematically
absent reflections are compatible with the space
group $C2/m$.

Microprobe Analyses

The microprobe analysis (Table 1, no. 3)
was performed on a polished section of one of
the crystals previously used in the Weissenberg
study. The polished area was of sufficient width
(about 30 x 10 μm) to permit a test of the
chemical homogeneity of the crystal. As far as
can be determined with the microprobe, the
Park County crystals consist of only one phase
and the distribution of elements within the
analyzed crystal is uniform. If some of the odd
diffraction effects noted on the Weissenberg
films are due to chemical or physical inhomo-
geneity, it is on a scale below the resolution
of the microprobe.

The Composition of Pavonite

The composition of pavonite has been dis-

cussed extensively by Harris & Chen (1975), Karup-Møller & Makovicky (1979) and others. The cation proportions derived from recent analyses and collected in Table 2 support the statement of Harris & Chen (1975) that the composition departs significantly from the ideal formula, $AgBi_3S_5$. Substantial amounts of Pb and Cu are reported in the analyses. The values listed in column 7 of Table 2 indicate that the average cell contents are $4[Ag_{0.78}Cu_{0.33}Bi_{2.74}Pb_{0.22}Sb_{0.03}S_5]$ or, in terms of the ideal formula, $4[Ag, Cu]_{1.1}Bi_{2.75}(Pb,Sb)_{0.25}S_5]$. Thus, about one atom of Bi *per* unit cell is replaced, chiefly by Pb. The sum Ag + Cu is in excess of 1 in all the analyses. It averages 0.1 atoms *per* formula unit and represents an additional ½ atom *per* unit cell over that required by the ideal formula. The extra metal is a response to the ubiquitous presence of Pb^{2+} in the Bi^{3+} sites; presumably, it is accommodated interstitially and consists of Cu rather than the larger Ag atoms. The sum of the positive charges of the cations in column 7 is 9.86, assuming the valences Ag^+, Cu^+, Pb^{2+}, Sb^{3+} and Bi^{3+}. The shortfall of positive charges required to balance the charge on S supports the suggestion of Harris & Chen (1975) that the interstitial Cu is present in the divalent state.

An idealized general formula that attempts to show the substitution for Ag and Bi and to separate substituting (Cu^s) from interstitial (Cu^i) copper can take the form $4[Cu^i_{0.5y}(Ag_{1-y}Cu^s_y)Bi_{2.75}(Pb_ySb_z)_{0.25}S_5]$. The values of y (the substitutional coefficient of Karup-Møller & Makovicky 1979), derived from column 7 in Table 2, are Cu 0.22, Ag 0.22, Pb 0.22 for this formula, giving a metal–sulfur composition for the cell of $4[Me_{4.11}S_5]$. These conclusions differ slightly from the composition of "typical" pavonite deduced by Karup-Møller & Makovicky (1979), although they are in agreement with the observation that the Cu:Pb ratio trends to 3:2.

THE COMPOSITION OF CUPROPAVONITE

Type cupropavonite differs from pavonite in having a substitutional coefficient for Ag and Bi of about 0.5 and, as a consequence, a higher metal content. However, the ratio Cu:Pb of the substituting cations remains near 3:2, as in pavonite. The average cell contents derived from the two analyses (Table 1, nos. 1, 2) are $Cu_{6.64}Ag_{4.16}(Bi_{2.44}Pb_{0.59})_8S_{40} = Me_{35.04}S_{40}$. These values differ somewhat from the values calculated from the analyses by Karup-Møller & Makovicky (1979).

The composition of the new occurrence

matches these features except that the principal metal increase occurs with Cu. The ratio of the substituting cations, Cu:Pb, is 3:1. Presumably the deficiency in Bi (compared with the ideal pavonite formula, AgB_3S_5) is made up by Pb^{2+} and Ag^+ in the Park County crystals: $Cu_{0.08}Ag_{3.36}(Bi_{2.51}Pb_{0.33}Ag_{0.16})_8S_{40} = Me_{35.44}S_{40}$.

Despite the high metal content, the cell of the Park County cupropavonite shows no increase in volume, except for doubling, over natural and synthetic pavonite (Table 3). This factor and the similarity in cell dimensions of the two species offer evidence that the excess metal is accommodated interstitially, as in pavonite. The abundance of Cu in the cell and the small radius of its atom imply that the interstitial metal is Cu. When the cell contents are cast into a pavonite-like formula to bring Cu^s + Ag = 1, the excess metal is seen to amount to about 0.4 atoms *per* pavonite formula unit: $8[Cu^i_{0.43}(Cu^s_{0.58}Ag_{0.42})(Bi_{2.51}Pb_{0.33}Ag_{0.16})S_5]$.

The sum of the charges on the cations derived for the Park County material (Table 1, no. 3) is 9.78, accepting the usual valences. It represents a greater shortfall in balancing the charge on S than that occurring in pavonite and supports the view (Karup-Møller & Makovicky 1979) that some, if not all, of the excess (interstitial) Cu in cupropavonite exists in the higher valence state, Cu^{2+}.

A generalized formula to account for the three available analyses of cupropavonite, and to incorporate the chemical characteristics noted above, has the form $8[Cu^i_{>(0.5y+z)}(Cu^s,Ag)_1Bi_{2.5}(Pb_yAg_z)_{0.5}S_5]$. If all the interstitial Cu is divalent, the value of Cu^i in this formula is exactly $0.5y + z$, and the metal–sulfur proportion can range from $Me_{34}S_{40}$ to $Me_{36}S_{40}$, increasing in metal with increasing substitution of Ag for Bi. Table 4 shows the distribution of the cations determined in Table 1 in accordance

TABLE 4. DISTRIBUTION OF CATIONS IN CUPROPAVONITE ACCORDING TO
$Cu^i(Cu^s,Ag)_1(Bi,Pb_yAg_z)_3S_5$

Analysis*	Bi	Pb_y	Ag_z	Ag	Cu^s	Cu^i	(.5y+z)	Total metal	Total x8 charge+
1	2.40	0.58	0.02	0.49	0.51	0.29	0.31	34.3	9.96
2	2.48	0.59	--	0.52	0.48	0.37	0.31	35.5	10.36
3	2.51	0.33	0.16	0.42	0.58	0.43	0.33	35.4	10.21

*From Table 1. +taking Cu^i as Cu^{2+}.

Note: Ag_z = 3-(Bi+Pb), Cu^s = 1-(total $Ag-Ag_z$), Cu^i = total $Cu-Cu^s$.

with the formula. For analyses 2 and 3, the value of Cu^i is greater than the sum $0.5y + z$, and the total positive charge, taking Cu^i to equal Cu^{2+}, is higher than 10. This implies that only some of the interstitial Cu is divalent, and indicates that the total metal content is determined not only by the ratio of Pb to Ag in the Bi sites but also by the valence of the interstitial Cu. Hence, the quantity of Cu^i in the formula is $\geqslant 0.5y + z$. These observations obviously make it difficult to conceive of an "ideal" composition for cupropavonite. The measured metal–sulfur proportions for the three analyses (Tables 1, 4) range from $Me_{34.3}S_{40}$ to $Me_{35.5}S_{40}$.

The distribution of Cu in Table 4 implies that the ratio Cu^s/Ag in the Ag sites is near 1. Cu and Ag exhibit only limited substitution for each other in sulfosalt minerals. Since the high Cu content is the principal chemical difference between cupropavonite and pavonite, it is likely that the two metals are mainly ordered in distinct positions in cupropavonite. This feature accounts for the doubling of the periodicity along [001] and promotes appreciable intensity differences between pavonite and cupropavonite. A general chemical formula for cupropavonite should, therefore, have the form $4[Cu^i_{\geqslant(0.5y+z)}CuAgBi_5(Pb_yAg_x)S_{10}]$, in which z has a maximum observed value of 0.32.

Table 1 shows that the principal difference between the two occurrences of cupropavonite

lies in the ratio Cu:Pb. The lower Pb content of the Park County crystals is presumed to result in the presence of Ag in the Bi sites. This multivalence occupation by Ag^+, Pb^{2+} and Bi^{3+} of the Bi sites is the only apparent source of the disorder in the Park County crystals that is responsible for the streaking observed on the X-ray films.

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