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## STUDIES OF MINERAL SULPHO-SALTS: XVIII— PAVONITE, A NEW MINERAL

E. W. NUFFIELD, *University of Toronto, Toronto, Canada.*

### ABSTRACT

Alaskaite (benjaminite) from Cerro Bonete, Sur-Lipez province, Bolivia has been found to be a new mineral:  $C2/m$ ;  $a$  13.35,  $b$  4.03,  $c$  16.34 Å,  $\beta$   $94\frac{1}{2}^\circ$ ; probable composition and cell contents  $4[\text{AgBi}_3\text{S}_8]$ .

The species has been named pavonite from the Latin pavo, peacock in honour of the late Professor M. A. Peacock.

Alaskaite was the name proposed by Koenig (1881) for a supposedly new species from the Alaska mine in Colorado. The species was founded on a number of chemical analyses, some partial, which showed considerable variation. In Dana (1944), the formula  $\text{Pb}(\text{Ag,Cu})_2\text{Bi}_4\text{S}_8$  is given as best representing the uncertain results of most of Koenig's analyses. Ahlfeld (1926) announced the discovery of a second occurrence of alaskaite near Cerro Bonete in Sur-Lipez province, Bolivia associated with chalcopyrite and bismuthinite. The identification was based on a chemical analysis by Herzenberg.

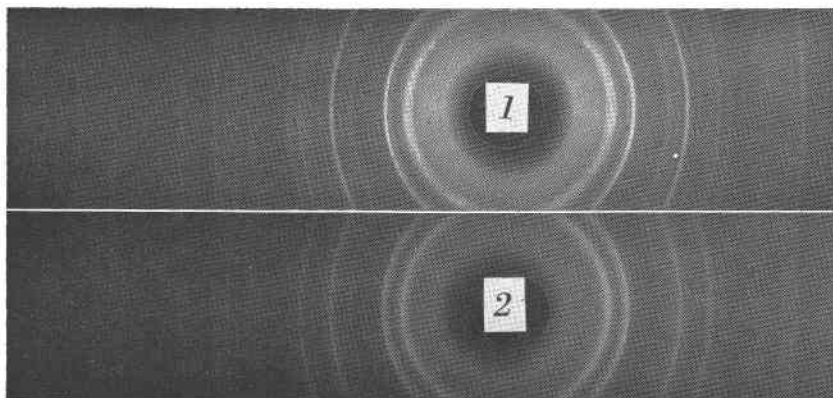
Thompson (1950) examined specimens from the two localities both in polished sections and by means of  $x$ -ray powder patterns. He identified aikinite ( $\text{PbCuBiS}_3$ ), matildite ( $\text{AgBiS}_2$ ) as well as sphalerite, tetrahedrite and galena in the Colorado material. Koenig was not aware of the presence of aikinite and matildite, and it is therefore reasonable to conclude with Thompson that the analyses were made on mixtures and that alaskaite from the type locality must be discredited as a species. On a typical specimen of the Cerro Bonete material Thompson identified benjaminite. Since the composition of benjaminite is given in Dana (1944) as  $\text{Pb}(\text{Cu,Ag})\text{Bi}_2\text{S}_4(?)$ , he surmised that this was the mineral, at least in large part, which had been analyzed by Herzenberg.

### THE BOLIVIAN "BENJAMINITE"

During a recent study of type benjaminite (Nuffield, 1953) from Nye County, Nevada the present writer examined the "alaskaite" from Cerro

Bonete which had been reported as benjaminite by Thompson. The  $x$ -ray powder patterns obtained by Thompson were available for this purpose. A comparison of the patterns of Bolivian material with those obtained from type Nevada benjaminite did indeed show a close similarity. The main difference appeared to be in the quality of the pattern. Several of the diffraction arcs of the type benjaminite are characteristically diffuse while patterns of the Bolivian mineral are sharp suggesting that the latter mineral is more perfectly crystalline.

Specimens of the Bolivian mineral favourable for single crystal studies were now sought in order to explain, if possible, the slight differences in the powder patterns. A Harvard specimen obtained through the kindness of Professor Frondel, labelled "No. 2, benjaminite, pure mass with



FIGS. 1 and 2. X-ray powder patterns; Cu/Ni radiation; camera diameter 57.3 mm.; full size contact prints. 1—Pavanite, Cerro Bonete, Bolivia; 2—Benjaminite, Outlaw Mine, Nye County, Nevada (U.S.N.M. 95058).

bismuthinite and ankerite, Porvenir mine, Cerro Bonete (Aceroduyok), Province Sur-Lipez, Bolivia" offered crystals suitable for single crystal  $x$ -ray studies, and gave powder patterns identical in every detail with Thompson's pattern of the Bolivian mineral. The Weissenberg films which were subsequently obtained proved however, to be different from those obtained on type benjaminite. Measurement of the films indicated that two lattice constants are very similar and this probably accounts for the resemblance between the powder patterns (see Figs. 1 & 2):

$$\begin{array}{l} \text{Benjaminite, Nevada } a' 13.34, b' 4.06, c' 20.25 \text{ \AA}; \beta 104^\circ \\ \text{"Benjaminite," Bolivia } a 13.35, b 4.03, c 16.34 \text{ \AA}; \beta 94\frac{1}{2}^\circ \end{array}$$

The new cell, like the strong pseudo-cell of benjaminite is monoclinic,  $C2/m$ .

The Bolivian mineral is therefore not benjaminite. Its cell constants

and powder pattern cannot be matched with the published data of known sulpho-salt minerals. Consequently a detailed study of the probably new species was undertaken.

#### *Physical properties*

The new mineral occurs abundantly on the Harvard specimen both massive and as tiny bladed crystals elongated parallel  $b[010]$ , which display a highly-reflecting surface. In colour, lustre and hardness it closely resembles bismuthinite with which it is intimately associated. Chalcopyrite and aikinite were also identified.

A polished section of the specimen showed that the bismuthinite, aikinite and non-metallic gangue are so intimately intergrown that it would be impossible to thoroughly clean a large quantity of the mineral. Specific gravity determinations using a Berman balance were made on a number of grains which were subsequently crushed, examined under the binocular microscope and finally used for the preparation of  $x$ -ray powder patterns to ensure a high degree of purity. Three values (6.54, 6.47, and 6.39) measured on three grains weighing between 2.5 and 4.0 mgrs. were obtained in this way. The grains were too small to guarantee high accuracy and from the invariable presence of tiny cavities it might be inferred that the values would tend to be low. A 200 mgr. sample was chosen in much the same way for chemical tests, although with less care since it was obviously impossible to test each grain with an  $x$ -ray powder pattern.

#### *Chemical properties*

A portion of the cleaned material was submitted to Mr. D. A. Moddle of the Ontario Department of Mines for a semi-quantitative spectrographic analysis of the metallic components and the remainder to Mr. E. J. Brooker of the Geological Survey of Canada for an  $x$ -ray fluorescence analysis. Table 1 shows that the results agree within acceptable limits. The table also presents the chemical analysis of Herzenberg for comparison.

The  $x$ -ray fluorescence (IIA) and chemical (III) data cannot be compared directly since elements of atomic number below 22 (S, Si, O, etc.) could not be determined with the fluorescence equipment. However the values for bismuth, silver, lead and copper are compatible. The chief difference lies in the lead content which in the chemical data is proportionately much higher. This difference can safely be attributed to aikinite which had not been recognized by Ahlfeld and was therefore not removed before the analysis. The present polished section study having shown the intimate association of the various minerals in our specimen,

TABLE 1. COMPARISON OF CHEMICAL DATA FOR PAVONITE

I <i>Spectrographic Analysis</i>		II <i>X-Ray Fluorescence</i>		III <i>Chemical Analysis Herzenberg</i>
		A	B	
		Wt. % ratios	Atomic ratios	
Bi	10-100%	53.8%	0.258	56.11%
Ag	5-15	7.8	0.072	9.07
Pb	0.5-5	5.1	0.025	14.41
Cu	1-10	2.8	0.044	2.68
Fe	0.1-1	1.1	0.020	—
Zn	trace	0.3	0.005	—
As	trace	0.2	0.003	—
Sb, Cd	trace	—	—	—

I. Spectrographic analysis by D. A. Moddle & W. Taylor, Ontario Dept. Mines. II. X-ray fluorescence analysis by E. J. Brooker, Radioactivity Lab., Geo. Surv. Canada: A. Weight percentage ratios (limit of accuracy: Bi  $\pm 5\%$  of amount present, Ag, Pb, Cu  $\pm 10\%$ , Fe, Zn, As  $\pm 30\%$ ). B. Atomic ratios. III. Chemical analysis by Herzenberg (in Ahlfeld, 1926) recalculated to 100%, S omitted.

suggested that at least a portion of the lead found by the spectrographic and fluorescence analysis was also due to aikinite. Consequently the copper content of a number of grains was next studied in some detail by spectrographic methods. This showed a variation from grain to grain and again suggested that our 200 mgr. sample was contaminated by aikinite.

As a first approximation it was assumed that all of the lead (0.025 of Table 1, column IIB) together with an equal portion of copper and bismuth of the fluorescence analysis was due to aikinite and that the remainder of the copper (0.019) which just matched the iron content (0.020) was due to chalcopyrite. This left 0.233 parts of bismuth and 0.072 parts of silver, giving the ratio Bi/Ag = 0.233/0.072 or 3.24/1. A Bi/Ag ratio of 3/1 seemed more probable and consequently sufficient bismuth (0.017) to reduce the Bi/Ag ratio to 0.216/0.072 or 3/1, was relegated to bismuthinite, another probable component in the sample. Thus the formula  $\text{AgBi}_3\text{S}_5$  or  $\text{Ag}_2\text{S} \cdot 3\text{Bi}_2\text{S}_3$  was derived as representing the ideal composition of the new mineral. The apportioning of the elements as described above is presented in Table 2.

Fusion experiments were now made to test the validity of the above assumptions. Two separate charges were prepared of the elements in the stoichiometrical proportions Ag:Bi:S = 1:3:5. The charges were

TABLE 2. PROBABLE COMPONENTS IN SAMPLE USED FOR X-RAY FLUORESCENCE ANALYSIS

	Bi	Ag	Pb	Cu	Fe
aikinite (PbCuBiS <sub>3</sub> )	0.025		0.025	0.025	
chalcopyrite (CuFeS <sub>2</sub> )				0.019	0.020
bismuthinite (Bi <sub>2</sub> S <sub>3</sub> )	0.017				
AgBi <sub>3</sub> S <sub>5</sub>	0.216	0.072			
	0.258	0.072	0.025	0.044	0.020

inserted in silica glass tubes, the air removed and the tubes sealed off. They were next heated until the constituents melted, held at this temperature for about an hour and then allowed to cool slowly. Polished sections were prepared of various portions of the products and a number of *x*-ray powder patterns made. The polished sections showed that a perfectly homogeneous product had been formed; the *x*-ray powder patterns agreed to the last detail with powder patterns of the natural mineral from Bolivia. It is reasonable to assume therefore that the formula AgBi<sub>3</sub>S<sub>5</sub> represents the ideal composition of the mineral. The calculated specific gravity 6.79, for 4[AgBi<sub>3</sub>S<sub>5</sub>] is in satisfactory agreement with the highest measured value, 6.54, considering the weight and condition of the grains measured. Unfortunately, the fusion products were quite porous and therefore unsuitable for gravity determinations.

The composition of the new mineral is unusual. Although silver is an essential element in many sulpho-salt minerals, hitherto only one mineral, matildite, was known to be composed of only silver, bismuth and sulphur. Furthermore the semi-metal to metal ratio (3/1) is remarkably high. In this respect it is surpassed by only livingstonite (HgSb<sub>4</sub>S<sub>7</sub>) and equalled by only vrbaitite (TlAs<sub>2</sub>SbS<sub>5</sub>).

Since the type alaskaite has been discredited and its name and supposed composition are not applicable to the Bolivian mineral, it is desirable to give the species a new name. The name pavonite (pa/von/it) from the Latin Pavo, peacock, has been selected to honour the memory of the late Professor M. A. Peacock (1898-1950). Professor Peacock devoted himself from 1937 when he joined the Toronto staff until his untimely death, to studies of the mineral sulpho-salts, producing well over a score of published papers. The full scope of his contributions will only be realized when his "Atlas of X-Ray Data for the Ore Minerals" appears as a posthumous work.

Pavonite is almost unique among the new sulpho-salts recently described in that it is probably not a rarity in existing collections. Several

typical specimens were located in the Royal Ontario Museum and it is likely that numerous specimens are housed in Museum and University collections throughout the world under the label of either alaskaite or benjaminite.

#### Polished section studies

Pavonite is white, much like jamesonite, in polished section. It is strongly anisotropic with polarization colours that are pale to intense blue, and light tan to brown. Standard reagents gave the following tests:

40% KOH, 5% HgCl<sub>2</sub>, 20% KCN—negative

20% FeCl<sub>3</sub>—stains light brown but does not etch; easily rubbed off.

1:1 HCl—negative or faint gray stain

1:1 HNO<sub>3</sub>—slowly stains grayish-brown without effervescence; fumes stain

The artificial mineral gives similar reactions.

It is interesting to note that the optical behaviour and etch tests given by Short (1940) for an alaskaite from Silverton, Colorado are almost identical with those he observed on schapbachite (matildite) from Schapbach, Baden. This substantiates Thompson's work which showed that alaskaite from Colorado is a mixture of aikinite and matildite.

#### X-ray powder pattern

The new mineral gives a well-defined powder pattern with numerous diffraction lines. The usual powder data are presented in Table 3, partially indexed to show that the cell constants derived by the Weissenberg study, are compatible with the x-ray powder spacings.

TABLE 3. X-RAY POWDER DATA FOR PAVONITE  
Monoclinic  $C2/m$ ;  $a$  13.35,  $b$  4.03,  $c$  16.34;  $\beta = 94\frac{1}{2}^\circ$

$I$	$d(\text{meas.})$	$d(\text{calc.})$	$hkl$	$I$	$d(\text{meas.})$	$I$	$d(\text{meas.})$	$I$	$d(\text{meas.})$
2	5.36	5.36	( $\bar{2}$ 02)	$\frac{1}{2}$	2.58	$\frac{1}{2}$	1.457	1	0.967
1	4.03	4.07	(004)	3	2.25	2	1.423	2	0.949
$\frac{1}{2}$	3.85	3.86	(110)	2	2.19	$\frac{1}{2}$	1.315	$\frac{1}{2}$	0.919
6	3.58	3.60	( $\bar{2}$ 04)	3	2.10	3	1.272	2	0.901
6	3.44	3.46	(112)	7	2.01	$\frac{1}{2}$	1.201	2	0.860
6	3.33	3.36	(204)	$\frac{1}{2}$	1.963	3	1.162	1	0.790
		3.33	(400)	2	1.893	$\frac{1}{2}$	1.126		
		3.31	( $\bar{4}$ 01)	1	1.753	$\frac{1}{2}$	1.114		
3	2.96	2.96	( $\bar{3}$ 11)	3	1.721	$\frac{1}{2}$	1.100		
		2.94	(403)	3	1.637	1	1.009		
10	2.84	2.85	( $\bar{3}$ 12)	$\frac{1}{2}$	1.484	1	0.987		

Ni filtered Cu radiation;  $\lambda = 1.5418 \text{ \AA}$ .

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## REFERENCES

- AHLFELD, FRIEDRICH (1926): Zinkteallit und Alaskait aus Bolivien, *Cbl. Min.*, A, 388-391.
- DANA, J. D. & E. S. (1944): *System of Mineralogy* 1, ed. 7, by C. Palache, H. Berman and C. Frondel—New York.
- KOENIG, G. A. (1881): On alaskaite, a new member from the series of bismuth sulphosalts, *Am. Phil. Soc., Proc.*, 19, 472-477.
- NUFFIELD, E. W. (1953): Benjaminit, *Am. Mineral.*, 38, 550-551.
- SHORT, M. N. (1940): Microscopic determination of the ore minerals—*U. S. Geol. Surv., Bull.* 914.
- THOMPSON, R. M. (1950): The probable non-existence of alaskaite, *Am. Mineral.*, 35, 456-457.