

STUDIES OF MINERAL SULPHO-SALTS: XX BERRYITE,¹ A NEW SPECIES

E. W. NUFFIELD² AND D. C. HARRIS³

ABSTRACT

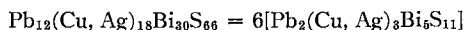
The new species occurs sparsely on the type specimen of cuprobismutite (U.S.N.M. 92902, Missouri mine, Park County, Colorado) as lath-like crystals measuring less than 1 mm. in length. The structural cell is monoclinic $P2_1/m$, with

$$a = 12.72, b = 4.02 \text{ (axis of elongation), } c = 58.07 \text{ \AA, } \beta = 102\frac{1}{2}^\circ$$

A pronounced pseudo-cell has

$$a' = a/3 = 4.24, b' = b = 4.02, c' = c/2 = 29.04 \text{ \AA, } \beta = 102\frac{1}{2}^\circ$$

A second occurrence at the Nordmark mines, Sweden has provided more, although less pure, material for x -ray spectroscopy and density determinations. Based on the available data, the most likely cell contents are



The calculated density 7.11, compares with a measured value of 6.7, corrected for an estimated 10 per cent contamination by quartz.

The name is for Professor L. G. Berry of Queen's University, Canada.

In a study (Nuffield, 1952) which led to the resurrection of cuprobismutite, $12[\text{CuBiS}_2]$, as a valid species, small cavities on the type specimen from the Missouri mine, Park County, Colorado, (U.S.N.M. 92902) yielded a few tiny, prismatic crystals which could not be identified with any known sulpho-salt mineral. The x -ray powder pattern of this mineral resembled that of benjaminite from Nye County, Nevada (Nuffield, 1953), a silver-bismuth sulpho-salt whose precise chemical formula still is not known. However, x -ray single crystal examination showed that the similarity was only superficial. The powder pattern was found to be identical with a pattern in the University of Toronto files, obtained by Professor L. G. Berry in 1939, on material from another locality labelled "galenobismutite, Nordmark mines, Värmland, Sweden," comprising fragments of specimen 125 from the collection of Hj. Sjögren.

The structural cell of the new mineral was investigated by the senior author at this time, but because he was unable to arrange for a micro-chemical analysis of the small amount of material, the study was put

¹The name has been approved by the Commission of New Minerals and Mineral Names, I.M.A.

²Department of Geology, University of Toronto.

³Department of Mineralogy, Royal Ontario Museum.

aside. The development of x -ray spectroscopic methods in this laboratory for analyzing less-than-ten milligram quantities of the ore minerals, has made it possible to return to the problem.

The material at hand was not suitable for undertaking a complete mineralogical study. The U.S.N.M. specimen seemed too precious to section in search of the very sparse, almost microscopic, crystals. The Nordmark Mines material was more plentiful but consisted merely of small unattached grains which furnished only a meagre indication of the mineral's environment in this locality. Galena is common in this ore and an examination of a polished section of three grains showed that small amounts of finely disseminated chalcopyrite, sphalerite and quartz also are present and are intimately associated with the new mineral. The grains are without crystal form and quite unsuitable for single crystal work. However, it has been possible to utilize the two sets of specimens to determine the structural cell, establish the probable chemical composition and unit cell contents, and obtain definitive x -ray powder data to aid in recognizing other occurrences which may prove more fruitful.

Structural crystallography

The mineral occurs sparsely on the Colorado specimen as very tiny prismatic bluish-grey crystals in a few of the numerous cavities, together with three rare bismuth sulpho-salts of copper: aikinite, emplectite and cuprobismutite. The crystals are so rare and difficult to distinguish from these minerals that several days were required to find a number of suitable crystals for the x -ray single crystal study, and enough material for a very small powder specimen.

The crystals, none measuring more than 1 mm in greatest dimension, were mounted with the prismatic axis parallel to the axis of the goniometer head. Weissenberg films showed that the crystals are typically aggregates of two or three not-quite-parallel individuals. However, one of the crystals proved to be eminently favourable and gave sharp reflections.

The structural cell is monoclinic with

$$a = 12.72 \text{ \AA}, b = 4.02 \text{ \AA}, c = 58.07 \text{ \AA}, \beta = 102\frac{1}{2}^\circ$$

(in which [010] is the axis of elongation), but geometrically orthorhombic and then B -centered with $a = 12.72 \text{ \AA}, b = 4.02 \text{ \AA}, c = 113.32 \text{ \AA}$. The systematically-absent reflections conform to the space group $P2_1/m$. Very long exposures are necessary to bring out $h0l$ reflections for which $h \neq 3n$, and only a close scrutiny of zero level films reveals the few weak reflections for which l is odd. Consequently the cell is characterized by a strong pseudo-cell with

$$\begin{aligned}
 a' &= a/3 = 4.24 \text{ \AA} \\
 b' &= b = 4.02 \text{ \AA} \\
 c' &= c/2 = 29.04 \text{ \AA} \\
 \beta &= 102\frac{1}{2}^\circ \\
 V' &= V/6 = 2897/6 = 482.8 \text{ \AA}^3
 \end{aligned}$$

The crystals are invariably twinned, the individuals being related by reflection across (001).

X-ray spectrographic analysis

About 70 mg. of reasonably clean material was obtained from the Nordmark specimen and analyzed in three lots (Table 1). Lot number 1,

TABLE 1. BERRYITE: X-RAY SPECTROGRAPHIC ANALYSIS

Sample Lot Number		1	2	3
Weight of Sample (mg)		12	10	48
Measured weight proportions	Pb	.40	.40	.40
	Cu	.13	.16	.14
	Ag	.15	.11	.17
	Bi	1.00	1.00	1.00
Measured atomic proportions	Pb	.40	.40	.40
	Cu	.44	.53	.46
	Ag	.30	.22	.33
	Bi	1.00	1.00	1.00
	Cu/Ag	1.5	2.4	1.4
Probable atomic proportions	Pb	4		
	(Cu, Ag)	6 ± 1		
	Bi	10		

weighing 12 mg., was obtained from a single grain which was estimated in polished section, to include 5 per cent chalcopyrite, very minor sphalerite, and 15 per cent quartz, much of it in a very finely disseminated state. After removal from the section, the grain was crushed and cleaned by hand-picking the fragments under a binocular microscope. It must be assumed, on the basis of the polished section examination, that not all of the chalcopyrite was removed in the process. Another quantity was obtained by picking a fraction of the ore sample free of extraneous minerals under the microscope, and crushing and re-picking the remaining grains in several stages. In this manner 58 mg. of material were separated. This was broken arbitrarily into a small lot weighing 10 mg. (lot 2, Table 1) and a larger lot weighing 48 mg. (lot 3). Presumably these lots do suffer from some contamination of chalcopyrite.

The three samples were fused with 100 parts of $K_2S_2O_7$ and then

powdered. Qualitative analysis showed that the mineral is a lead, bismuth sulpho-salt of silver and copper. For quantitative analysis, the net peak density ratios $\text{Bi}L\alpha/\text{Pb}L\alpha$, $\text{Cu}K\alpha/\text{Pb}L\alpha$, $\text{Ag}K\alpha'/\text{Pb}L\alpha$ were measured and compared with standard curves for the corresponding ratios, to obtain weight-fraction ratios by interpolation. Finally, the atomic proportions given in Table 1 were deduced.

The atomic ratio, Pb/Bi, is constant at 2/5 for the three samples. The ratios of Cu and Ag to Bi are less certain, however. Although the atomic proportion $(\text{Cu} + \text{Ag})/\text{Bi}$ is virtually the same in the three samples, the agreement is probably more fortuitous than real in view of the variation in the Cu/Ag ratio from one sample to the next. Test analyses of synthetic products of similar (known) composition indicate that the method of analysis is not in error. It is reasonable, in light of the evidence provided by the polished section examination, to attribute the variation to contamination by chalcopyrite and to assume that the sum of Cu and Ag in the structure of the mineral is less than is indicated by the analyses. The statement

$$\text{Pb}:(\text{Cu}, \text{Ag}):\text{Bi} = 4:6 \pm 1:10$$

is an attempt to account for this and probably includes the true atomic proportions.

The density

The Colorado crystals were much too small to attempt density determinations. The Nordmark material occurs in grains which are large enough for torsion balance trials, but are so consistently and finely contaminated with quartz and chalcopyrite that it is virtually impossible to select a pure grain. A series of traverses under the microscope across the polished surfaces of two seemingly-clean grains indicated quartz contents of 10 and 11 per cent respectively by volume.

Four determinations of the density of grains ranging in weight from 19 to 28 mg. gave values between 5.7 and 6.2. Seven determinations on smaller grains weighing from 8 to 14 mg. ranged over a wider variation (5.5 to 6.3), as might be expected. Assuming that a grain contains 10 per cent quartz and gives a value of 6.2 for the density, the density of the pure mineral is 6.7. When compared with the densities of the established lead-bismuth sulpho-salts of copper and silver (Table 2), this value appears to be small. The table suggests that the true value is near 7.0.

The cell contents

It is possible to deduce a number of cell contents for the large cell of

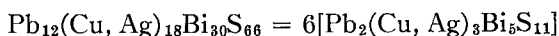
TABLE 2. DENSITIES OF THE ESTABLISHED LEAD-BISMUTH SULPHO-SALTS OF COPPER AND SILVER

Aikinite	PbCuBiS_3	7.22
Gladite	$\text{PbCuBi}_5\text{S}_9$	6.96
Lindstromite	$\text{PbCuBi}_3\text{S}_6$	7.01
Rezbanyite	$\text{Pb}_4\text{Cu}_4\text{Bi}_{10}\text{S}_{21}$	6.24*, 6.9
Un-named†	$\text{Pb}_7(\text{Cu, Ag})_2\text{Bi}_6\text{S}_{17}$	7.11

*Frenzel (1883).

†Alice Arm, B.C., Canada, Priv. comm. Professor R. M. Thompson, University of British Columbia.

the new mineral which are in approximate agreement with the spectrographic analysis. One of the possibilities, namely



appears the most likely. The value of the (Cu, Ag) component stands at the midpoint of the range predicted by the analyses (Table 1). The calculated density is 7.11. The value of Z is compatible with the size of the pseudo-cell which has a volume equal to 1/6 of the volume of the true cell.

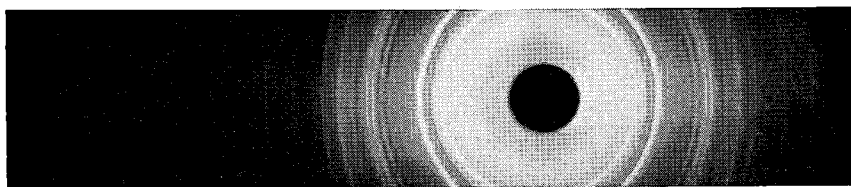


FIG. 1. X-ray powder contact print; Ni filtered Cu radiation; film radius = $180/\pi$ mm. (1 mm. on film = $1^\circ\theta$).

The powder pattern

The powder pattern of the new mineral (Fig. 1), distinguishes it from the lead-bismuth sulphosalts of copper and silver listed in Table 2, and from benjaminite, schirmerite and alaskaite. The only remaining known minerals of this general composition are the three Gladhammar, Sweden species: gladite, hammarite and lindstromite which still rest on the original meagre descriptions of Johansson (1924). No powder data are available for comparison. However, the chemical formulas proposed for these minerals are markedly different from the formula derived for the new mineral:

Hammarite	$\text{Pb}_2\text{Cu}_2\text{Bi}_4\text{S}_9$
Lindstromite	$\text{PbCuBi}_3\text{S}_6$
Gladite	$\text{PbCuBi}_5\text{S}_9$

The powder pattern (Table 3) has been indexed on the basis of the

pseudo-cell $a' = a/3 = 4.24$, $b' = b = 4.02$, $c' = c/2 = 29.04 \text{ \AA}$, $\beta = 102\frac{1}{2}^\circ$ to a d value of 2.18 \AA .

TABLE 3. X-RAY POWDER DATA* FOR BERRYITE $6[\text{Pb}_2(\text{Cu}, \text{Ag})_3\text{Bi}_5\text{S}_{11}]$
NORDMARK MINES, SWEDEN

$a' = a/3 = 4.24$, $b' = b = 4.02$, $c' = c/2 = 29.04 \text{ \AA}$, $\beta = 102\frac{1}{2}^\circ$									
I	2θ	$d(\text{meas.})$	hkl	$d(\text{calc.})$	I	2θ	$d(\text{meas.})$	hkl	$d(\text{calc.})$
$\frac{1}{2}$	24.02°	4.66 Å	006	4.72 Å					
			101	4.23				017	2.85 Å
			102	4.23	2	39.65°	2.86 Å	0.0.10	2.83
$\frac{1}{2}$	26.77	4.18	100	4.14				111	2.83
			103	4.13				106	2.83
$\frac{1}{2}$	27.47	4.06	007	4.05	7	40.53	2.80	114	2.82
$\frac{1}{2}$	29.30	3.83	012	3.87				109	2.82
2	30.35	3.70	013	3.70	$\frac{1}{2}$	41.70	2.72	112	2.75
			008	3.54				115	2.74
$\frac{1}{2}$	31.60	3.56	103	3.52	$\frac{1}{2}$	43.53	2.61	107	2.62
10	32.42	3.47	106	3.51				1.0.10	2.62
1	34.92	3.23	107	3.27				108	2.44
$\frac{1}{2}$	35.42	3.18	009	3.15	$\frac{1}{2}$	47.00	2.43	1.0.11	2.44
$\frac{1}{2}$	36.63	3.08	016	3.06				115	2.43
			105	3.04				118	2.42
$\frac{1}{2}$	37.25	3.03	108	3.04				116	2.31
			111	2.91	1	50.05	2.29	119	2.31
8	39.20	2.89	112	2.91				109	2.28
			113	2.88				1.0.12	2.27
					4	52.75	2.18	117	2.20
								1.1.10	2.19
								0.0.13	2.18
								0.1.11	2.17

I	2θ	$d(\text{meas.})$	I	2θ	$d(\text{meas.})$	I	2θ	$d(\text{meas.})$
3	55.02	2.10	$\frac{1}{2}$	71.35	1.661	$\frac{1}{2}$	94.81	1.316
3	55.92	2.07	2	73.00	1.628	$\frac{1}{2}$	96.36	1.300
4	57.92	2.00	$\frac{1}{2}$	76.97	1.556	$\frac{1}{2}$	97.36	1.290
1	59.00	1.967	2	84.02	1.447	1	99.11	1.273
2	62.65	1.863	$\frac{1}{2}$	85.05	1.433	$\frac{1}{2}$	99.21	1.272
2	64.02	1.828	1	86.61	1.412	$\frac{1}{2}$	111.91	1.169
2	65.37	1.793	1	87.16	1.405	1	114.46	1.152
2	66.70	1.762	$\frac{1}{2}$	90.41	1.365	$\frac{1}{2}$	118.11	1.129
3	67.72	1.738	$\frac{1}{2}$	91.36	1.354	$\frac{1}{2}$	119.16	1.123
$\frac{1}{2}$	69.42	1.701	1	94.11	1.323	$\frac{1}{2}$	121.01	1.113
						$\frac{1}{2}$	121.71	1.109

*Mn filtered Fe radiation; Debye-Scherrer method, camera diameter 114.6 mm.

The name

We propose to name the new mineral berryite for Professor L. G. Berry, who obtained the first powder pattern.

We are indebted to the National Research Council for generous financial assistance (to E. W. N.) to develop x-ray spectroscopy at the University of Toronto and to Dr. George Switzer for the loan of the type specimen of cuprobismutite (U.S.N.M. 92902).

REFERENCES

- JOHANSSON, K. (1924): Bidrag till Gladhammar-gruvornas mineralogi, *Arkiv Kemi, Mineral., Geol.*, **9** (8), 11 (in Dana's System of Mineralogy, **1**, 1944).
- NUFFIELD, E. W. (1952): Studies of mineral sulpho-salts: XIV—Cuprobismuthite, *Am. Mineral.*, **37**, 447-452.
- (1953): Benjaminite, *Am. Mineral.*, **38**, 550-552.

Manuscript received June 9, 1965, emended July 20, 1965