STUDIES OF MINERAL SULPHO-SALTS: XVI—CUPROBISMUTHITE

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

Abstract

Study of the type specimen from the Missouri mine, Park county, Colorado (U.S.N.M. 92902) has shown that cuprobismuthite, which has been regarded as a mixture of emplectite and bismuthinite, is a valid species. The unit cell is monoclinic, $C2/m$ with $a=17.65$, $b=3.93$, $c=15.24$ A; $\beta=100\frac{1}{2}°$. Most probable cell contents 12[$CuBiS_2$] and then dimorphous with emplectite.

A "probably new mineral" associated with quartz, chalcopyrite and wolframite at the Missouri mine, Hall's Valley, Park county, Colorado was the subject of a short description by Hillebrand in 1884. The mineral occurred both as dark bluish gray grains in the quartz matrix and as small, deeply striated prismatic crystals in numerous cavities. A specific gravity determination of a quantity of the crystals gave 5.75, recalculated to 6.31 to correct for the presence of 4.43% quartz and 6.97% chalcopyrite. The material offered little opportunity for precise analytical work but two analyses, one of the crystals and the other of the compact material were completed with the following results:

	Bi	Ag	Cu	Fe	Zn	S	Total
I—crystals	60.80	0.89	15.96	2.13	0.10	19.94	99.82
II—grains	63.42	4.09	12.65	0.59	0.07	18.83	99.65

Presumed by Hillebrand to include: I—6.97% chalcopyrite after deducting 4.43% gangue; II—1.91% chalcopyrite after deducting 59.75% gangue. Sulphur content was calculated for each analysis.

The analyses clearly indicated that the mineral was essentially a bismuth sulpho-salt of copper, assuming apart from visible chalcopyrite and nonmetallic gangue, that the analytical samples consisted of one mineral. The relative proportions of the metallic elements led Hillebrand to suggest the composition $3(Cu,Ag)_2S\cdot 4Bi_2S_3$, which is distinct from that of other naturally occurring sulpho-salts of bismuth. He proposed to investigate similar material from other mines in the area before conferring a name upon the mineral or even definitely claiming it to be a new species, but nothing further was forthcoming.

The data of Hillebrand were classified by Dana (1892) in the *System of Mineralogy* without comment except to assign to the mineral the name cuprobismuthite. Scheiderhöhn & Ramdohr (1931, p. 378) reported the occurrence of cuprobismuthite at Arnsberg, Westphalia. However, material from Colorado for comparison purposes was not available to these authors and no chemical evidence was presented to prove that the composition from the new occurrence was identical with that assigned to cuprobismuthite.

The validity of cuprobismuthite as a new species was now seriously questioned by the work of two observers. Short (1931, p. 104) on the basis of a mineragraphic study of specimens from the type locality reported that it was identical with emplectite ($Cu_2S \cdot Bi_2S_3 = CuBiS_2$). Palache (1940) described measurable crystals of bismuthinite (Bi_2S_3) and emplectite in a specimen (U.S.N.M. 92902) which was said to be the one upon which Hillebrand founded the species. He declared that since a mixture of these substances would give the composition revealed by Hillebrand's analyses, the species had no validity. In Dana (1944) cuprobismuthite has been dropped to the rank of a discredited species.

The present author became interested in cuprobismuthite during a study of klaprothite which was supposed to have the composition $3Cu_2S \cdot 2Bi_2S_3 = Cu_6Bi_4S_9$. In an unsuccessful effort (Nuffield, 1947) to locate this mineral, numerous specimens containing Cu-Bi sulphosalt minerals were examined. The type specimen of cuprobismuthite (U.S.N.M. 92902) which had been studied by Palache was at this time on loan to Dr. Charles Milton and his associates of the United States Geological Survey. Through the kindness of Dr. E. P. Henderson and Dr. Milton the specimen was forwarded to me together with 3 x-ray powder spindles obtained from the specimen at the Geological Survey.

The specimen closely resembles Hillebrand's description. Gray metallic minerals, both massive and as prismatic crystals together with scattered chalcopyrite occur in a matrix of quartz. Numerous small cavities were found to be filled with tiny, prismatic crystals. The sparse wolframite mentioned by Hillebrand was located after some effort and identified by an x-ray powder photograph.

The massive, gray metallic material was first investigated. It was found to be composed chiefly of a mineral giving an x-ray powder photograph which could not be matched with patterns from the usual sources. Presumably this is the mineral that yielded the second of Hillebrand's analyses. Minor galena and tetrahedrite were also identified by x-rays.

X-ray powder patterns were now obtained from crystals within the cavities. Emplectite and aikinite ($PbCuBiS_3$) were readily identified. A third pattern with few diffraction lines resembled that of benjaminite ($Pb(Cu,Ag)Bi_2S_4$) while still another proved to be identical in every respect with the unidentified pattern of the massive material mentioned above. This pattern was obtained several times on carefully chosen crystals and since no variation either in relative intensities or in spacings was observed, it must be assumed that it does not represent a mixture of minerals. The same pattern was obtained from one of the Geological Survey spindles (U.S.G.S. No. 1699) which was labelled as "bright, distinctly anisotropic from polished section 90." It might well be presumed that crystals of this type provided the data of Hillebrand's first analysis.

The crystals which gave the new pattern are very thin blades measuring about 1 mm in greatest dimension. They characteristically show a slight twisting about an axis parallel to the elongation and commonly exhibit a bluish tarnish. They are extremely fragile, shattering at the touch of a needle. Despite the small size and the twisting, a crystal was readily found that gave sharp rotation and Weissenberg films. Projection and measurement of the films led to a monoclinic cell with dimensions:

$$a=17.65, \quad b=3.93, \quad c=15.24\text{ A}; \quad \beta=100\tfrac{1}{2}^\circ$$

In this setting, b is the axis of elongation and a is in the plane of the blades. The systematically missing diffraction spots conform to the extinction conditions (hkl) present only with $(h+k)$ even, $(h0l)$ present only with h even, which are characteristic of the space group $C2/m$.

Attempts to produce cuprobismuthite artificially by fusion of the elements in the stoichiometrical proportions represented by the formula $3Cu_2S \cdot 4Bi_2S_3$ proved unsuccessful. Only two compounds, $3Cu_2S \cdot Bi_2S_3$ (wittichinite) and $3Cu_2S \cdot 5Bi_2S_3$ (Nuffield, 1947), can be formed within the Cu-Bi-S system by this method. My colleague, Dr. F. G. Smith with an active interest in the system undertook to investigate the possibility of producing additional compounds by annealing the fusion products for several days. It was soon established that when fusion products of the elements Cu, Bi and S with Cu/Bi near 1 were annealed at temperatures between 300 and 500° C. for periods upwards of 2 days, a new, nearly homogeneous phase was formed. X-ray powder patterns of this phase proved to be identical in both relative intensities and in spacings with the unknown pattern obtained from the crystals and massive material of the cuprobismuthite specimen. It was thus ascertained that the mineral is a bismuth sulpho-salt of copper very much like Hillebrand's cuprobismuthite in composition.

FIG. 1. X-ray powder contact print of cuprobismuthite from Park county, Colorado. Nickel filtered copper radiation; $1°\theta=1$ mm.

Attempts to determine the exact composition by annealing various proportions of Cu, Bi and S and examining the products in polished sections for homogeneity were not successful. It was evident that the Cu/Bi ratio of the compound was near 1 but in no case was an absolutely homogeneous product produced. A portion of the purest product gave a density of 6.47 grs./cc. on the Berman balance (as compared to Hillebrand's corrected value, 6.31) and this value was used to calculate the approximate weight of the cell contents:

$$\mathrm{MW}\times \mathrm{Z}=\frac{\text{volume of cell}\times\text{density}}{1.6602}=4049.3.$$

The composition $3Cu_2S\cdot 4Bi_2S_3$ or $Cu_6Bi_8S_{15}$ proposed by Hillebrand for cuprobismuthite has a molecular weight of 2534.32, which is clearly incompatible with the calculated value of 4049.3. However, there are three formulas which have a Cu/Bi ratio near 1 and are at the same time compatible with the calculated weight of the cell contents:

Cell Contents	Mol. Weight×Z	Calc. Density
$7Cu_2S\cdot 6Bi_2S_3$ or $Cu_{14}Bi_{12}S_{25}$	4199.48	6.69
$6[Cu_2S\cdot Bi_2S_3]$ or $12[CuBiS_2]$	4040.28	6.44
$5Cu_2S\cdot 6Bi_2S_3$ or $Cu_{10}Bi_{12}S_{23}$	3881.08	6.18

There can be little doubt therefore, that Hillebrand's cuprobismuthite is identical with the mineral studied and described by the present writer, and that it is a valid species with a composition near to that assigned to it by Hillebrand. It is likely that both Short and Palache overlooked it in their studies of type material because of the discovery of the chemically similar mineral emplectite, which had not been noted by Hillebrand.

Hillebrand's results from the analysis of the crystals are in fair agree-

TABLE 1. COMPARISON OF WEIGHT PERCENTAGES

	I	II	III	IV	
Cu	21.19	18.88	16.38	14.58	15.54
Ag	—	—	—	0.96	
Zn	—	—	—	0.11	
Bi	59.72	62.08	64.62	65.50	
S	19.09	19.04	19.00	18.85	
	100.00	100.00	100.00	100.00	

I–III. Calc. weight percentages. I. $Cu_{14}Bi_{12}S_{25}$. II. $CuBiS_2$. III. $Cu_{10}Bi_{12}S_{23}$. IV. Cuprobismuthite crystals; anal. Hillebrand. Fe deducted as $CuFeS_2$ and analysis recalc. to sum 100%.

ment with the latter two of the three suggested formulas. Table 1 compares the calculated weight percentages for the three formulas with the weight percentages of this analysis, summed to 100% after deducting iron as chalcopyrite. But because of the impure nature of the material, the analysis does not lend itself to the calculation of the exact formula. However the possible cell contents $6[Cu_2S \cdot Bi_2S_3] = 12[CuBiS_2]$ are worthy of further consideration. The cell contents of emplectite are $2[Cu_2S \cdot Bi_2S_3]$ (Hofmann, 1933) and its cell while orthorhombic in symmetry, has dimensions remarkably similar to those of the monoclinic cell of cuprobismuthite:

	a	*b*	*c*	*β*	Cell Volume	Density
Emplectite[1]	6.14	3.90	14.54	—	348.2	6.43 calc.
Cuprobismuthite	3×5.88	3.93	15.24	100½°	3×346.5	6.47 meas.

[1] The cell constants of Hofmann have been converted to Angstrom units.

The *b* and *c* dimensions compare directly while the *a* dimension of emplectite is roughly ⅓ that of cuprobismuthite suggesting similar structural arrangements. The cell volumes are almost exactly in the proportions of 1 to 3. Furthermore, the densities of the two minerals are almost identical. Since it is known that cuprobismuthite has a Cu/Bi ratio of near 1, it is not unreasonable to suggest that its chemical formula is in fact $Cu_2S \cdot Bi_2S_3$ and that the mineral is therefore dimorphous with emplectite. Since it is produced artificially by annealing the constituents, it is evidently the form which is stable at high temperatures. Emplectite cannot be produced by simple fusion or by annealing and may therefore represent the variety which is formed at low temperatures in nature. The final proof of the composition must however, wait on the results of fu-

TABLE 2. CUPROBISMUTHITE, $12[CuBiS_2]$—*X*-RAY POWDER DATA[1]

Monoclinic, *C2/m; a*=17.65, *b*=3.93, *c*=15.24 A, *β*=100½°

I	*d* meas.	*I*	*d* meas.	*I*	*d* meas.	*I*	*d* meas.
2	6.15	10	3.07	½	2.49	3	1.957
2	4.32	½D	2.95	½D	2.30	½	1.877
3D	3.64	½D	2.86	2	2.17	½	1.829
½	3.46	6	2.73	2	2.09	3	1.719
4	3.25	½	2.59	½	2.00		

D—diffuse line.

[1] For Ni filtered, Cu radiation (Cu $K\alpha_1$=1.5405 A).

ture analyses of pure material. It is hoped that the *x*-ray powder data of Table 2 will aid in the discovery of more favourable occurrences.

REFERENCES

DANA, E. S. (1892): *System of Mineralogy,* ed. 6, New York.

DANA, J. D. & E. S. (1944): *System of Mineralogy* **1,** ed. 7, by C. Palache, H. Berman and C. Frondel, New York.

HILLEBRAND, W. F. (1884): A probably new mineral, *Am. Journ. Sci.,* **27,** Third Series, 355–357.

HOFMANN, W. (1933): Strukturelle und morphologische Zusammenhänge bei Erzen vom Formeltyp ABC_2, *Zeit. Krist.,* **84,** 177–203.

NUFFIELD, E. W. (1947): Studies of mineral sulpho-salts: XI—Wittichenite (Klaprothite), *Econ. Geol.,* **42,** 147–160.

PALACHE, C. (1940): Cuprobismuthite—a mixture, *Am. Mineral.,* **25,** 611–613.

SCHNEIDERHÖHN, H. & RAMDOHR, P. (1931): *Lehrbuch der Erzmikroskopie,* **2,** Berlin.

SHORT, M. N. (1931): Microscopic determination of the ore minerals, *U. S. Geol. Survey, Bull.* **825.**