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*On Cornetite from Bwana Mkubwa, Northern Rhodesia.*

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*Introductory.*

THE mineral to be described in the following pages was found by Mr. J. L. Popham in 1910 at Bwana Mkubwa, Northern Rhodesia, and was sent by him to Mr. A. E. V. Zealley, at that time Curator of the Rhodesia Museum, Bulawayo. Investigations conducted by one of us (A. M. M.) in Bulawayo showed that the mineral occurred as definite, though minute, orthorhombic crystals and that it consisted in the main of copper and phosphoric acid, but that it differed in many respects from the known hydrated copper phosphates such as libethenite, tagilite, dihydrite, or pseudomalachite. Some specimens were therefore sent to Cambridge for a more detailed examination to be made. A preliminary account of the results of this examination, which confirmed in all respects the work done in Bulawayo, was communicated to the

Mineralogical Society on November 11, 1913, when it was stated that the mineral was probably a new species characterized as follows:<sup>1</sup>

System orthorhombic. Axial ratios  $a:b:c = 0.394:1:1.01$ , forms  $\{110\}$  and  $\{011\}$ . Hardness 4-5; specific gravity 4.1. Chemical composition  
 $2\text{Cu}_3(\text{PO}_4)_2 \cdot 7\text{Cu}(\text{OH})_2$ .

It has recently come to our knowledge that minute crystals having the same crystallographic and optical characters as those examined by us were described by Professor G. Cesàro<sup>2</sup> in April, 1912. The specimens on which these crystals occur were collected by Mr. H. Buttgenbach in 1911 from the copper mine 'L'Étoile du Congo', Katanga, Belgian Congo. Professor Cesàro succeeded in carrying out a remarkably complete crystallographic and optical determination of the material at his disposal and recognized that he was dealing with a new species. He also made some chemical tests but was unable to establish the exact composition of the mineral. He says 'Le minéral est formé essentiellement d'un phosphate de cuivre et de cobalt; j'y ai aussi trouvé de petites quantités d'arsenic et constaté l'absence du vanadium. Il m'est impossible actuellement, avec la petite prise d'essai pure que je possède, de décider s'il s'agit d'un minéral anhydre ou faiblement hydraté, ou fluoré'.

Professor Cesàro did not assign a name to this mineral. This has since been done by H. Buttgenbach,<sup>3</sup> who in 1917 proposed the name Cornetite in honour of the Belgian geologist J. Cornet.

Like Professor Cesàro, we did not at the time of our first communication suggest any name for this mineral. Now, in view of the very close agreement between the physical characters of the crystals from Katanga and from Bwana Mkubwa, and in spite of the fact that our material contains no cobalt, we propose to adopt the name Cornetite, and further, to avoid confusion, we propose also to adopt the orientation of the crystals chosen by Professor Cesàro.

Thus the form taken by us in 1913 to be  $\{110\}$  is  $a^2$  of Cesàro's position and now becomes  $\{102\}$ , while our  $\{011\}$  is Cesàro's  $m$ , and now becomes  $\{110\}$ . The axial ratios originally given by us,  $a:b:c = 0.394:1:1.01$ , become therefore  $0.99:1:0.78$ .

<sup>1</sup> Nature, 1913, vol. 92, p. 364.

<sup>2</sup> G. Cesàro, Sur un nouveau minéral du Katanga. Ann. Soc. géol. Belgique, 1912, vol. 39, Bull. p. 241, and Annexe to vol. 39 (Publ. relatives au Congo Belge), p. 41.

<sup>3</sup> H. Buttgenbach, Les Minéraux et les Roches, Liège, 1917, p. 452.

These figures as well as our final results (see below), which are based on a wider selection of material than was available at first, are in close agreement with those calculated by Cesàro.

*Descriptive.*

*Occurrence.*—The two specimens received in Cambridge in the early part of 1913 illustrate two slightly different modes of occurrence of the mineral. The first consists of a lump of compact, yellowish, argillaceous sandstone coated with a thin layer of a brownish-black, botryoidal substance which proved to be a hydrated oxide of manganese containing a little copper. Deposited on this, our mineral forms a compact, thin crust of a beautiful peacock-blue colour. Isolated individual crystals do not occur, but under the microscope the crust is seen to consist entirely of a compacted mass of minute crystals of the same habit as are found on the second specimen. The latter consists of a mass of dark shale-like rock shot through with veins and strings of malachite. On its surfaces occur crusts of the blue mineral similar to those just mentioned, while scattered here and there are seen a number of isolated crystals from some of which were obtained the measurements recorded below. On visiting Bwana Mkubwa<sup>1</sup> in the autumn of 1913 the mineral was found plentifully (A. M. M.) lining the cracks in a fissured band some 2 to 10 inches wide which occupies the hanging wall of the lode between 100 and 250 feet below the surface.

*Crystallography.*—The general habit of the crystals suggests orthorhombic symmetry, and so far as measurements are possible, they are in harmony with this view, which is confirmed by the optical evidence. The shape of the majority of the crystals is shown in fig. 1. Doubly-terminated individuals of this aspect are, however, rare, most of the material consisting of a crystalline mass from which project halves of such crystals, a pair of *m* faces meeting in an edge, and portions of *d* planes, usually being visible. The faces of the form *m* are smooth and bright, those of the form *d* are for the most part rounded, though a few

<sup>1</sup> Bwana Mkubwa is situated in latitude 13° 2' S. and longitude 28° 45' E. The mine 'L'Étoile du Congo' lies a few miles north-east of Elisabethville, the capital of the province of Katanga, Belgian Congo. The deposits at these two localities, which are more than 100 miles apart, probably belong to the same formation and have been compared by F. E. Studt, *Geology of Katanga and N. Rhodesia*, Trans. Geol. Soc. S. Africa, 1914, vol. 16, p. 68.

that were fairly flat have been observed. To these two forms the indices  $m = \{110\}$  and  $d = \{102\}$  may be assigned.

A second habit, fig. 2, occurs plentifully on some specimens. It is characterized by the presence of well-developed faces of the form  $v$   $\{221\}$ . The crystals are very small, rarely exceeding 0.5 mm. in their longest dimension and being usually about 0.1 mm. thick. We have not observed any crystals similar to those figured by Cesàro in which  $m$  is very largely developed, nor have we met with any showing a marked development of the fundamental bipyramid  $\{111\}$ , together with  $v$  and  $d$ , a combination likewise figured by Cesàro and Buttgenbach. On a few of our specimens indications of the presence of bipyramids other than  $v$  have been noted, but they are quite subordinate and have not been determined. We have also observed a few crystals which seem to be twinned about a face of a form  $\{0kl\}$ . Cleavage was not observed. On examining under the microscope some crystals mounted for optical

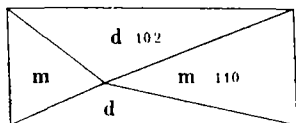


FIG. 1.

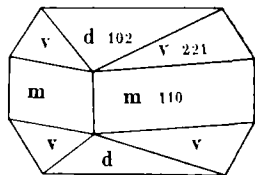


FIG. 2.

Crystals of Cornetite from Rhodesia.

examination in a liquid of high refractive index, well-marked zonal structure was observed. A number of crystals were measured and as will be seen below gave results which agree satisfactorily with those obtained by Cesàro. It was found, however, that angles over similar edges often exhibited somewhat wide variations even on apparently very good crystals and opposite faces of the same form often deviated considerably from parallelism. The crystallographic characters may be summed up as follows:

System. Orthorhombic, bipyramidal class.

Axial ratios (A.H. and A.M.M.)  $a:b:c = 0.9855:1:0.7591$

„ „ (Cesàro)  $0.9844:1:0.7679$

Forms  $m \{110\} = m$ , Cesàro;  $d \{102\} = a^2$ , Cesàro;  $p \{111\} = b^3$ , Cesàro and not observed by us;  $v \{221\} = b^3$ , Cesàro.

Table of Angles.

Angles measured.	Mean		No. of edges.	Limits	Calculated Cesàro.	Observed Cesàro.
	Calculated A.H. and A.M.M.	observed A.H. and A.M.M.				
$m_1 m_3 = (110) : (\bar{1}10)$	*	90° 50'	18	89° 52' - 91° 50'	*	90° 54'
$d_1 d_2 = (102) : (\bar{1}02)$	42° 8'	42 9	14	41 8-43 2	42° 37'	42 22-42'
$m_1 v_1 = (110) : (221)$	*	24 48	17	24 22-25 25	*	24 33
$v_1 p_1 = (221) : (111)$	17 56½	—	—	—	17 52	17°-18°
$v_1 v_1 = (221) : (\bar{2}21)$	79 11	79 21	1	79° 21'	79 18	—
$v_1 v_2 = (221) : (\bar{2}21)$	80 33	80 20	2	80 15-80 25	80 49	—
$m_1 d_1 = (110) : (102)$	75 10	74 53	4	74 26-75 14	74 59½	74° 51'
$v_1 d_1 = (221) : (102)$	51 24½	51 13	8	50 49-51 32	51 29½	50½°-52°
$p_1 d_1 = (111) : (102)$	34 47½	--	—	—	34 57½	35°-35½°

*Physical properties.*—The specific gravity was determined on a small quantity of the carefully selected material subsequently used for analysis. The substance was weighed in a small glass tube, first in air, and then in carbon tetrachloride. The procedure adopted, which was similar to that recommended by Penfield, renders good service in the case of substances of which only small quantities are available and which are too dense for determination by suspension in a liquid, while the substitution of carbon tetrachloride for water greatly increases the delicacy of the method. Two determinations were carried out on the same sample.

- I. Weight of substance 0.2553 gram. Sp. gr. at 18.8° = 4.01
  - II. " " 0.2538 " " " 3.99
- } Mean 4.00

When the sample used for this determination was dissolved in hydrochloric acid a siliceous residue amounting to 4.03 per cent. was left behind. The specific gravity given above is therefore too low. If, however, we assume that the specific gravity of the residue was 2.6, a correction can easily be applied. The resulting corrected specific gravity is 4.10. The hardness<sup>1</sup> was found to be 4-5.

The colour of the crystalline crusts is a fine peacock-blue, the depth of colour varying with the thickness of the crust and the nature of the underlying matrix. Some of the darker portions resemble clinoclase in tint. Isolated individual crystals and fragments are seen to be transparent and greenish-blue by transmitted light, the colour being very similar to that exhibited by clinoclase fragments of similar thickness. The crystals are not appreciably pleochroic. The optic axial plane is parallel to *c* (001), the acute negative bisectrix is perpendicular to *a* (100). The optic axial angle is small. The indices of refraction are

<sup>1</sup> Cesàro gives 5.5, but our specimen failed to scratch apatit.

high and the double refraction is strong. Determinations of the indices of refraction by the immersion method showed that for green light  $\alpha = 1.765$  (about), while  $\gamma$  was considerably greater than 1.78. The angle between the optic axes was found to be  $32^{\circ} 40'$  for green light in the case of a crystal exhibiting good  $m$  faces and rotated in a liquid of refractive index 1.785. This angle is approximately equal to  $2V$ , though probably somewhat too low.

*Chemical composition.*—Considerable difficulty was experienced in obtaining pure material for analysis. The crystalline crust was for the most part very thin and adhered tenaciously to the matrix. It was removed by careful chiselling, reduced to a coarse powder, passed through wire sieves to obtain a product of even grain from which the blue particles were picked out by hand under a lens—a very long and tedious process. In this way a fairly pure sample weighing 0.29 gram was obtained, but under the microscope some grains were seen to be contaminated with malachite and particles of matrix. The latter were removed so far as possible by hand and an attempt was made to get rid of the former by washing the grains with a cold concentrated ammonia solution in which malachite dissolves fairly easily and quickly, while the blue mineral is but slowly attacked.

Advantage was taken of this difference of solubility to prepare a second sample of the mineral from the powder which had passed the finest sieve and of which the particles were too small to make hand-sorting possible. In spite of the fact that some of the blue mineral dissolved, its rate of solution proved so much slower than that of the malachite that a considerable quantity of it persisted after the latter had entirely disappeared. This sample was further purified by suspension in methylene iodide when a considerable amount of siliceous matter was removed. In the purified blue material both brown and colourless particles could be seen under the microscope, though most of these remained in the insoluble portion when the mineral was warmed with dilute hydrochloric acid, in which the blue material is very easily soluble. This sample, amounting to about 0.25 gram, was used for a preliminary qualitative-quantitative examination, as a result of which it was found that the mineral consisted essentially of copper, phosphoric acid, and water. Arsenic was tested for with especial care but could not be detected. No metal other than copper could be found in groups I and II. Traces of iron and manganese were found in the solution after the removal of the copper, but no cobalt, nickel, or calcium could be detected, nor were chloride or sulphate observed. In the

light of these results the analysis of the main sample was conducted as follows.

The air-dried material was heated for an hour to  $190^{\circ}$  in an air-bath—the loss of weight under these conditions was almost inappreciable and the appearance of the mineral was quite unchanged. The mineral was next heated to redness in a porcelain boat placed in a tube of silica-glass traversed by a current of dry air and the water given off was collected in a small U-tube containing sulphuric acid. The ignition loss proved to be slightly greater than the weight of water collected. The material in the boat which had turned black was then dissolved in warm dilute hydrochloric acid, when a small insoluble residue remained which was filtered off, ignited, and weighed; it amounted to 4.03 per cent. Copper was precipitated from the solution by hydrogen sulphide and weighed as cuprous sulphide. To the filtrate from the copper, ammonia was added, after removal of the hydrogen sulphide, when a very small precipitate, consisting mainly of iron phosphate, came down. It was collected, dried, weighed, fused with sodium carbonate and silica, and the phosphate it contained added to the main portion. Phosphoric acid was estimated by the molybdate method according to the instructions given by Woy. The results are as follows:—

Weight of substance taken	...	...	0.2803	...	Per cent.
Insoluble residue	...	...	0.0113	...	4.03
Loss at $190^{\circ}$	...	...	0.0005	...	0.18
Ignition loss	...	...	0.0246	...	8.77
[Water	...	...	0.0231]	...	—
Copper oxide	...	...	0.1886	...	67.28
Ferric oxide	...	...	0.0015	...	0.53
Phosphorus pentoxide	...	...	0.0528	...	18.83
Total	...	...	0.2793	...	99.62
Unaccounted for...	...	...	0.0010	...	0.38

In interpreting these results we need only take into consideration copper, water, and phosphoric acid. From the weight of these constituents given in column I on p. 232, the percentages in column II are calculated, as also the molecular ratios, column III, which reduced to their simplest terms give the numbers under IV. These lead to the formula  $13\text{CuO} \cdot 2\text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ , which may also be expressed in the form  $2\text{Cu}_3(\text{PO}_4)_2 \cdot 7\text{Cu}(\text{OH})_2$ . The percentage composition calculated from this formula is given under V, while that corresponding to the somewhat simpler formula  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{Cu}(\text{OH})_2$  is quoted under VI.

	I.	II.	III.	IV.	V.	VI.
CuO ...	0.1886	71.30	0.8961	6.38	71.60	70.88
P <sub>2</sub> O <sub>5</sub> ...	0.0528	19.96	0.1405	1.00	19.67	21.10
H <sub>2</sub> O ...	0.0281	8.73	0.4847	3.45	8.73	8.02

Although the exact formula to be assigned to this mineral must remain a little uncertain till larger quantities of pure material are available for analysis, the results so far obtained are sufficient to confirm the individuality of the species and to differentiate it from libethenite with which it shows certain crystallographic analogies, as has been pointed out by Cesàro. It differs entirely in its crystallographic and optical properties from the minerals of approximately similar composition which have been placed in the pseudomalachite group, nor does it resemble clinoclase, save in colour. There can be little doubt that the material from Katanga only differs from that from Bwana Mkubwa in containing a small quantity of cobalt replacing some of the copper, and that both are essentially basic copper phosphates.

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