On Hopeite and other zinc phosphates and associated
minerals from the Broken Hill mines, North-Western
Rhodesia.

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THE new and remarkable mineral locality known as Rhodesia
Broken Hill is situated in North-Western Rhodesia, at a distance
of about 300 miles to the north-east of the Victoria Falls, and at the
present terminus of the Cape to Cairo Railway. The outcrop of lead
and zinc ore which occurs here was accidentally discovered in January,
1902, by Mr. T. G. Davey, while he was prospecting the country for
copper. Rising out of the flat surrounding country is a series of low
hills or kopjes, the largest of them being about 90 feet in height; and
these consist almost entirely of oxidized ore. The surrounding rocks are
mainly crystalline limestones with some beds of sandstone, conglomerate,
and phyllite.

The ordinary type of ore of which the kopjes consist is compact and of
a light yellowish colour. It is composed of an intimate intermixture of
zinc silicate (hemimorphite) and lead carbonate (cerussite) with variable
amounts of interspersed iron hydroxide (limonite). Crystal-lined
cavities are of frequent occurrence in this ore. In the work of explora-
tion, one of the tunnels driven through Kopje No. 1 broke into a large
cavern, measuring about 24 × 80 feet. In this cave were found bones of
recent animals, together with stone implements and other evidences of

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the former presence of man [1]. It is on the bone-breccia in this cave that the crystals of hopeite are found in association with vanadinite. Most of the other crystallized minerals (tarbuttite, parahopeite, descloizite, pyromorphite, &c.) occur in cellular limonite in Kopje No. 2, which is the largest hill of the group. There are thus at this locality two quite distinct occurrences of zinc phosphates.

Most of the specimens which I have examined were very kindly placed at my disposal by Mr. Percy C. Tarbutt, one of the directors of the Broken Hill Exploration Company. Not only has Mr. Tarbutt generously presented the best of his specimens to the British Museum collection and to several other museums, but he has also allowed me the free use of the many specimens which passed through his hands. Another extensive collection of specimens from Broken Hill was acquired for the British Museum from Dr. A. E. Salter, to whom they had been sent by one of his former pupils. Through the kindness of Mr. Alfred Bromwich, I have also been able to examine the specimens exhibited in the Rhodesia Museum at the London offices of the British South Africa Company (the 'Chartered Company'). A few other specimens, independently received by Dr. A. Hutchinson at the Cambridge Mineralogical Museum, and by the Royal Scottish Museum at Edinburgh, have also been submitted to me.

The following is a list of the several mineral species, which I have detected on the specimens :—

Hopeite (p. 3).	Hydrozincite ? (p. 35).
Parahopeite (p. 18).	Cerussite (p. 36).
Tarbuttite (p. 22).	Limonite (p. 37).
Descloizite (p. 31).	Wad (p. 37).
Vanadinite (p. 33).	Quartz (p. 37).
Pyromorphite (p. 33).	Galena (p. 37).
Hemimorphite (p. 34).	Blende (p. 38).
Calamine (p. 35).	

In addition to the minerals mentioned above, there are no doubt others present at the locality. Some of the material is so minutely crystallized and so intermixed that it was not always possible to determine the species satisfactorily. An undetermined mineral, occurring as small, bright-green (monoclinic ?) crystals, appears to be a copper phosphate.

[1] A preliminary account of these remains has been published by F. P. Mennell and E. C. Chubb, Geol. Mag., 1907, dec. 5, vol. iv, pp. 443–448. A paper on the cave deposits prepared by Mr. Franklin White for the Rhodesia Scientific Association was very kindly sent to me by the author in typescript.

HOPEITE.

The mineral hopeite has hitherto been known from only a single locality, namely the zinc-mine of Altenberg or Vieille Montagne in the neutral territory of Moresnet, between Liège and Aachen. It was found here about the year 1820[1], and apparently no specimens have been obtained since that time, although mining operations have been for a long period extensively carried on at the locality.

Specimens submitted to the Abbé Haüy about 1821 were classed by him as a variety of stilbite[2]. In the same year a specimen was sent to Sir David Brewster, and in it he recognized a new mineral species, which he named hopeite, after Dr. Thomas Charles Hope (1766-1844), professor of chemistry at Edinburgh. Very little material was available for examination, although an effort was made to obtain a further supply. It was therefore not possible to determine the chemical composition of the new mineral, but a blowpipe examination by N. G. Nordenskiöld suggested that it was a hydrated phosphate or borate of zinc with an earthy base and some cadmium. A. Lévy (1843) also determined the presence of zinc ; but A. Damour (1879), working on only two milligrams of material, was the first to prove the mineral to be a phosphate of zinc.

In consequence of this determination by Damour, C. Friedel and E. Sarasin, who had previously successfully prepared several mineral phosphates, attempted the artificial preparation of hopeite; they obtained small crystals with the angles of hopeite, which on analysis were found to have the composition $Zn_3P_2O_8.4H_2O$.

Crystalline scales having this composition had indeed been previously prepared by H. Debray[3] in 1861, but as these were not determined crystallographically they were not identified with hopeite. W. Heintz[4] in 1867 had gone a step further, for he had ascertained, under the microscope, that crystals having this composition are orthorhombic. It should also be noted here that W. Skey[5], in 1869, had prepared a crystalline phosphate of zinc, to which he gave the formula $Zn_3P_2O_8.5H_2O$, and which

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[1] A. Des Cloizeaux, 'Manuel de Minéralogie,' 1893, vol. ii, p. 516.

[2] A specimen in the Turner collection was so labelled, with a figure of a crystal, in the handwriting of Haüy (Brewster, 1824) ; and there also is an isolated crystal in the Haüy collection in the Muséum d'Histoire Naturelle at Paris (Des Cloizeaux, 1879). There is no mention of the mineral in Haüy's 'Traité de Minéralogie' (2nd edit., 1822).

[3] H. Debray, Ann. Chimie et Physique, Paris, 1861, ser. 3, vol. lxi, p. 436.

[4] W. Heintz, Ann. Chemie u. Pharmacie, 1867, vol. cxliii, p. 356.

[5] W. Skey, Trans. New Zealand Inst., 1869, vol. ii, p. 146 ; Chem. News, 1870, vol. xxii, p. 61.

he called artificial hopeite; but, as he gives no particulars, it is not clear how he arrived at this conclusion. Quite recently (1904), Baron A. de Schulten has prepared artificial crystals of hopeite measuring $4.4 \times 1 \times 0.6$ mm., from which he was able to determine the crystallographic constants with accuracy.

Several other phosphates of zinc have been prepared in a crystalline condition, and in this connexion mention may be made of those which have been determined crystallographically:—

The anhydrous salt, $Zn_3P_2O_8$, in rhombic prisms.[1]

The acid phosphate, $H_4ZnP_2O_8.2H_2O$, in large, anorthic crystals.[2]

Literature of Hopeite.

D. BREWSTER, 1822. 'New mineral from Aachen, near Altenberg.' Edinburgh Phil. Journ., vol. vi, p. 184.

    (A preliminary note, initialled 'D. B.,' stating the mineral to be distinct from stilbite.)

D. BREWSTER, 1824. 'Description of hopeite, a new mineral, from Altenberg, near Aix-la-Chapelle.' Trans. R. Soc. Edinburgh, vol. x, pp. 107–111. (With crystallographic characters by W. Haidinger, and blowpipe reactions by N. G. Nordenskiöld.)

    The title of this paper, read on June 17, 1823, is quoted in Edinburgh Phil. Journ., 1823, vol. ix, p. 186, where the name hopeite first appears in print. The paper was published in 1824, and was abstracted in various journals of that date, but the date on the title-page of volume x of the Edinburgh Transactions is 1826.

    An account, with slight variations and additions, is given in F. Mohs's 'Grund-Riss der Mineralogie,' 1824, part 2, p. 682, and by W. Haidinger in his English translation of this work (1825, vol. iii, p. 109); also by Haidinger in Ann. Phys. Chem. (Poggendorff), 1825, vol. v, p. 169.

A. LÉVY, 1837. 'Description d'une collection de minéraux formée par M. Henri Heuland, et appartenant à M. Ch. Hampden Turner . . .' London, vol. iii, p. 230, plate LXXIII.

    Description of a single specimen. The prism angle he gives as $mm''' = 59° 45'$.

A. LÉVY, 1843. 'Description de plusieurs espèces minérales appartenant à la famille du zinc.' Ann. des Mines, Paris, ser. 4, vol. iv, pp. 507–520. (Hopeite on pp. 517–520.)

    This paper was read under a slightly different title in 1840 (Comptes Rendus Acad. Sci. Paris, vol. x, p. 197), and extracts only were published after the author's death in 1841.

A. DAMOUR [and A. DES CLOIZEAUX], 1879. 'Nouveaux essais sur la hopéite.' Bull. Soc. Min. de France, vol. ii, pp. 131–135.

    A re-examination of Haüy's crystal.

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[1] A. de Schulten, Bull. Soc. Chim. Paris, 1889, ser. 3, vol. ii, p. 300.

[2] W. Demel, Sitz.-Ber. Akad. Wiss. Wien, math.-naturw. Cl., 1879, vol. lxxix, Abth. II, p. 649 ; Ber. Deutsch. chem. Ges., 1879, Jahrg. xii, p. 1171 ; compare abstract in Zeits. Kryst. Min., vol. v, p. 653.

C. Friedel and E. Sarasin, 1879. 'Sur la composition de la hopéite.' Bull. Soc. Min. de France, vol. ii, pp. 153–156.

G. Cesàro, 1898 'Description des minéraux phosphatés, sulfatés et carbonatés du sol Belge.' Mém. Acad. R. Sci. etc. Belgique, vol. liii, pp. 1–136. (Hopeite on pp. 18–20.)

A. de Schulten, 1904. 'Production artificielle de la hopéite.' Bull. Soc. franç. Min., vol. xxvii, pp. 100–103.

H. Buttgenbach, 1906. 'Hopéite de Moresnet.' Ann. Soc. Géol. Belgique, vol. xxxiii, Mém. pp. 9–11.

In striking contrast to its sparing occurrence at the original locality, hopeite occurs in considerable abundance at the new Rhodesian locality. Almost all specimens of the bone-breccia from the cave in Kopje No. 1 are encrusted with crystals of the mineral.

The brilliant, water-clear crystals, of all sizes up to about a centimetre in length, are scattered singly in great numbers over the surface of the bone-breccia, or are grouped in showy clusters. These crystals are always perfectly colourless and transparent with a bright, vitreous lustre ; and are invariably associated with vanadinite (p. 33). The hopeite crystals rest upon the vanadinite or upon a thin, yellowish-white crust which coats the surface of the bone-breccia. This crust averages about $\frac{1}{4}$ mm. in thickness, and usually consists of two layers ; a lower one of finely fibrous hemimorphite, and an upper one of very minutely crystallized tarbuttite, hemimorphite, or calamine, or of all three of these mixed together (p. 30). On some specimens of this type the more distinct crystals of hopeite are associated with minute tufts of colourless needles of hopeite. Similar tufts of acicular hopeite were also found in some of the cavities in the bone-breccia and inside bones and teeth.

Other specimens, of rather a different type, consist wholly of a close aggregate of hopeite crystals with little or no matrix and no associated minerals. These masses of pure hopeite are of considerable size, and may weigh several pounds. The crystals are of two kinds. The upper portion of the specimens consists of large crystals, measuring up to 2 cm. across, which are white and translucent ; these are pronouncedly tabular in habit parallel to the macropinacoid, on which planes the lustre is markedly pearly. On the free surface of the specimens these large crystals have been considerably corroded, presenting a smooth, rounded surface. The lower portion of the specimens consists of an aggregate of much smaller hopeite crystals of a pale yellowish colour and with a tendency to divergent grouping. Smaller specimens of this type may show only one or other of these two kinds of crystals.

Crystallography.—The crystals of hopeite are orthorhombic, and, as

represented in the accompanying figures (fig. 1), are very simple in habit. According to the greater or lesser width of the faces of the macropinacoid $a\{100\}$, the crystals are tabular or prismatic in habit. Very often the crystals present an unsymmetrical or hemimorphic appearance, owing to the suppression or small development of two adjacent pyramidal planes
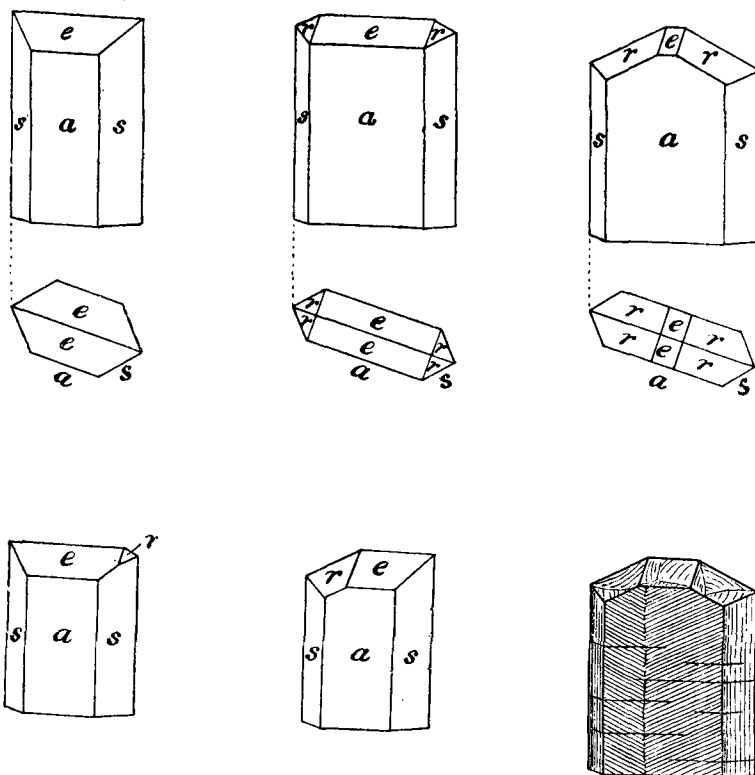

Fig. 1.—Crystals of hopeite from Broken Hill, North-Western Rhodesia.
(Clinographic drawings and plans.)

The crystals are represented as terminated below by the basal cleavage. Two of the lower figures show the irregular development of the crystals, owing to the omission of pyramid-planes ; another shows the surface characters of the faces and the cleavage cracks parallel to the base.

(see figs.), but there is no regularity in this omission of faces. The crystals are usually attached at one end, though this is not always the case, and doubly terminated crystals are not infrequent. There are no indications of twinning.

Although the crystals are so brilliant and their edges so sharp, they are not suitable for very exact measurements. There is a tendency to a sub-parallel grouping of the crystals, and the faces are striated and show uneven, vicinal growths.

The axial ratios calculated from the mean values of the angles $as = 49° 10'$ and $ae = 50° 34'$, measured on fourteen crystals, are:—

$$a : b : c = 0.5786 : 1 : 0.4758.$$

These values are compared below with those obtained by previous observers:—

	a : b : c	$as =$ (100):(120).	$ae =$ (100):(101).
Haidinger (1824)	0.5796 : 1 : 0.4744	49° 13'	50° 42'
Lévy (1843)	0.5723 : 1 : 0.4718	48 51	50 30
Cesàro (1898)	0.5866 : 1 : 0.4838	49 $33\frac{1}{2}$	50 29
Schulten (1904)	0.5759 : 1 : 0.4759	49 2	50 26

The new values are thus closer to the values calculated from Haidinger's early measurements and those of de Schulten for artificial crystals, than to the usually accepted values of Lévy.

The following table gives the measured and calculated angles:—

		Calculated.	Measured.	Limits.		No.
as	$= (100):(120)$	—	*49° 10'	48° 47'	— 49° 44'	22
ss'	$= (120):(\bar{1}20)$	81° 40'	81 41	80 5	— 82	10
sb	$= (120):(010)$	40 50	40 47	40 15	— 40 59	5
ai	$= (100):(5.11.0)$	51 51	$51\frac{1}{2}$	51 5	— 52	4
an	$= (100):(130)$	60 3	60	$59\frac{1}{2}$	— $60\frac{1}{2}$	7
ae	$= (100):(101)$	—	*50 34	49 48	— 51 14	31
ee'	$= (101):(\bar{1}01)$	78 54	78 51	78 13	— 79 10	17
eu	$= (101):(103)$	24 7	$22\frac{3}{4}$	19	— 24	12
uu'	$= (103):(\bar{1}03)$	30 40	$31\frac{1}{2}$	31	— 33	5
ar	$= (100):(111)$	53 24	53 24	53 3	— 53 34	13
rr'	$= (111):(\bar{1}11)$	73 12	73 17	72 9	— 74 56	12
rf	$= (111):(011)$	36 36	36 42	$36\frac{1}{2}$	— 37	8
re	$= (111):(101)$	20 11	20 0	19 48	— 20 11	8

The considerable variations in the readings recorded above are to be accounted for by the vicinal character of many of the faces. Some of the best readings between faces giving single sharp images are: $ee' = 78° 42'$, 78° 48'; $rr' = 73° 10'$, 73° 15'; $re = 20° 11'$, 20° 9', which agree more closely with the calculated values.

The characters of the faces of the forms observed are :—

a {100}.   The largest plane on the crystals, parallel to which they are usually tabular in habit. It often gives scattered images, owing to the sub-parallel grouping and to vicinal faces. Striations arranged in a herring-bone pattern are sometimes present (fig. 1). The lustre on this plane is pearly, owing to the perfect cleavage in this direction.

s {120}.   The predominating prism. Striated vertically.

i {5.11.0}. Observed on only one crystal as four faces quite distinct from s, but inclined to it at only about 2°. Striated vertically.

n {130}.   Usually quite narrow : striated vertically. Observed on four crystals.

b {010}.   Rarely present, as a narrow face.

e {101}.   Largely developed on all crystals. Usually reflects two images at from 3′ to 21′ apart in the zone [100, 001]. Sometimes corroded, and with a surface like ground-glass.

u {103}.   Usually as very narrow planes rounded in the zone [100, 001] and reflecting a faint band of images. Only on one of the fourteen measured crystals were these planes of any appreciable size.

f {011}.   As narrow planes truncating the edges $[rr']$.

r {111}.   Present on most crystals, though not invariably. The faces often show uneven growths and vicinal faces (see fig. 1), and they rarely give single reflected images. The multiple images lie in the zone $[ar]$=[100, 111], and between the outside images of each group the following angles were measured: 12′, 17′, 19′, 54′, 2° 46′. Sometimes the faces are roughened like ground-glass.

q {233}.   As a very narrow plane, together with {011} and {133}, on an edge $[rr']$ of one crystal. Measured to r 10½°. (Calculated, 10° 16′.)

t {133}.   Ditto. Measured to r 23°. (Calculated 22° 42′.)

Crystal-forms of Hopeite.

	Forms.	Haidinger, 1824.	Lévy, 1837.	Lévy, 1843.	Des Cloizeaux, 1879.	Friedel and Sarasin, 1879. (On artificial crystals.)	Cesàro, 1898.	Schulten, 1904. (On artificial crystals.)	Buttgenbach, 1906.	Spencer. (On Rhodesian crystals.)
Pinacoids.	a {100}	d	h^1	h^1	h^1	h^1	h^1	h^1	h^1	a
	b {010}	e	g^1	g^1	g^1	g^1	g^1	g^1	g^1	b
	c {001}	×	—	—	p	p	—	—	—	—
Prisms.	y {310} ?	—	h^2	—	—	—	—	—	—	—
	x {320}	—	—	h^3	—	—	—	—	—	—
	m {110}	—	m	m	—	m	—	—	—	—
	s {120}	b	—	g^3	g^3	—	g^3	g^3	g^3	s
	i {5.11.0}	—	—	—	—	—	—	—	—	i
	n {130}	—	—	g^2	—	—	—	g^2	g^2	n
	k {160}	—	—	—	—	—	—	$g^{\frac{7}{6}}$	—	—
Brachy-Macrodomes.	d {201} ?	—	a^1	—	—	—	—	—	—	—
	e {101}	a	a^d	a^2	a^1	—	a^1	a^1	a^1	e
	u {103}	—	—	a^6	a^3	a^3	a^3	a^3	a^3	u
dome.	f {011}	—	—	—	—	—	—	e^1	—	f
Pyramids.	r {111}	c	b^1	b^1	$b^{\frac{1}{2}}$	—	$b^{\frac{1}{2}}$	—	$b^{\frac{1}{2}}$	r
	q {233}	—	—	—	—	—	—	—	—	q
	t {133}	—	—	—	—	—	—	—	—	t

From this table it will be seen that the common forms of hopeite recorded by almost all observers are only *a b s e u r*. The forms *y* {310} and *d* {201} given by Lévy in 1837 are not included in his list published in 1843 ; and it is possible that they were given in error for the common forms *s* and *u* respectively, but their position as {310} and {201} is clearly indicated on his earlier figure.

Cleavage.—Hopeite possesses three directions of cleavage parallel to

the three axial planes, and the crystals can be broken up into cubical blocks.

a (100) is the direction of the most perfect cleavage, and on this plane the lustre is pearly ; on other faces the lustre is vitreous.

b (010) is a direction of good cleavage, which can be readily developed by placing a knife-edge in the proper direction on a crystal and striking a sharp blow with a hammer. Cleavage-flakes so obtained have smooth, glassy surfaces, and, being perpendicular to the acute optic bisectrix, enable the peculiar optical characters of the mineral to be easily studied. The crystals rarely show any cleavage cracks in this direction, and unless this cleavage is intentionally developed it is not readily noticed.

c (001) is a direction of poor cleavage, but it is a prominent feature in almost all crystals by reason of cleavage cracks (as represented in fig. 1) ; the cleavage surfaces are not very smooth.

Hardness.—This may be given as $3\frac{1}{4}$, since the mineral is more easily scratched by fluorite than is calcite by hopeite. The crystals seem to be rather less hard on the pearly *a* cleavage than on the other faces. The hardness as given in the textbooks is clearly too low ; A. de Schulten (1904) gives the value for artificial crystals as a little greater than 3.

Specific Gravity.—Here again the values given in the textbooks are much too low. Brewster (1824) obtained for a single, presumably quite small, crystal the value 2·76, and Lévy (1843) found for three small crystals, weighing together only 10 milligrams, 2·85. A. de Schulten determined for artificial crystals 3·109.

For the Rhodesian crystals I have determined the following values :—

> 3·08, a large white crystal, measuring 2 cm. across and weighing 2·795 grams; by hydrostatic weighing.
>
> 3·06, large white crystals, weighing together 1·989 gram; with a 3 cc. pycnometer.
>
> 3·04, small, clear, glassy crystals, weighing together 0·699 gram; ditto.

By floating a large number of small, isolated crystals in methylene iodide, with indicators of rubellite and spodumene, the specific gravity of the different crystals was found to vary from about 3·0 to 3·1.

As will be described below, the crystals of hopeite consist of a zonal intergrowth of two substances, which differ slightly in specific gravity. With the idea of separating these two modifications of hopeite, 5·6 grams of the large white crystals were crushed to a coarse powder, and the heaviest and lightest fractions separated by means of methylene iodide. The separation was, however, far from complete, as was easily seen on an

optical examination of the fragments of the two lots. The results obtained with the pycnometer were :—

3·04 for the specifically heaviest portion, weighing 1·035 gram.

3·03 for the specifically lightest portion, weighing 1·851 gram.

Optical Characters.—Although some remarkable features are presented by the optical characters of hopeite, yet these are in complete accord with the orthorhombic symmetry of the crystals. On all faces the extinction is uniform and parallel to the crystallographic axes. A cleavage-flake parallel to the brachypinacoid b {010}, perpendicular to which is the acute bisectrix of the optic axes, exhibits, even in ordinary light, a zonal structure, the numerous lamellae being arranged parallel to the faces of the dome e {101} and of the macropinacoid a {100} (fig. 2). This zonal structure is shown most conspicuously when the cleavage-flake is viewed between crossed nicols, since the lamellae polarize alternately in bright colours and in low grey tints. These lamellae are extremely numerous, varying in width from about $\frac{1}{100}$ to $\frac{1}{2}$ mm.; the two sets extinguish simultaneously when the vibration-directions of the nicols are parallel to the a and c edges of the plate. These lamellae mark out the stages of growth of the crystal;

Fig. 2.—Hopeite : cleavage-flake parallel to the brachypinacoid, b {010}, showing zonal interbanding of α-hopeite and β-hopeite, and the interference-figures given by different bands.

sometimes the bands are rather crumpled, or they bear on their upper edges small tufts parallel to the c-axis of the crystal. On no other face of the crystal, nor on a- or c-cleavage-plates, is there the slightest indication of this compound structure.

In convergent light between crossed nicols a remarkable series of changes in the interference-figure is seen as the b-section is moved across the stage of the microscope. The figure continuously and rapidly changes from one with a wide axial angle and several brightly coloured rings, to one with a smaller axial angle and few rings less brightly coloured, and vice versa: further, the plane of the optic axes also changes into positions at right angles, and at certain points the figure is uniaxial. These interference-figures are often considerably distorted; e. g., rings
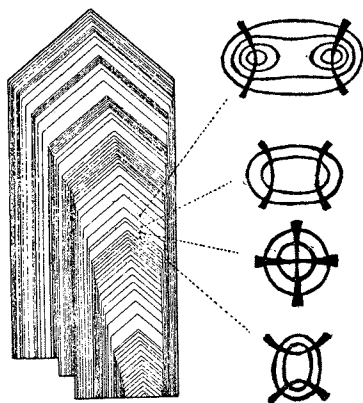
without brushes may be often seen.   This is, however, due to the com-
bined effect of two or more of the very narrow lamellae : when a wider
band is under observation, the figure is perfectly normal.   The optic
sign of these interference-figures is in all cases negative, and the acute
bisectrices are perpendicular to the plane of the plate.

It will be convenient to distinguish the material of which these two
sets of lamellae are composed as α-hopeite and β-hopeite respectively.   The
main optical differences between them may be summarized as follows :—

α-Hopeite.—Higher birefringence, polarizing in bright colours. Acute,
negative bisectrix perpendicular to b (010), and optic axial plane parallel
to c (001).   Wider optic axial angle (2E about $58\frac{1}{2}°$), and the interfer-
ence-figure with several brightly coloured rings.

β-Hopeite.—Much lower birefringence, polarizing in grey tints. Acute,
negative bisectrix perpendicular to b (010) ; optic axial plane sometimes
parallel to and sometimes perpendicular to c (001).   Narrower angle
between the optic axes (2E about $32\frac{1}{2}°$ when the axial plane is parallel
to c (100), and 2E about 20° when perpendicular thereto), and the inter-
ference-figures with very few, less brightly coloured rings.

The uniaxial interference-figures with low birefringence shown by
some portions of the bands of β-hopeite, are doubtless due to the over-
lapping of two biaxial portions the optic axial planes of which are at
right angles.

These two orthorhombic modifications of hopeite differ also in some
other respects.   When a b-section is gently warmed or when boiled in
water, there is no change in the optical characters, but at a temperature
of 105° C. the α-hopeite is destroyed and no longer shows any of the
optical characters above described, either in parallel or in convergent
polarized light.   A plate which has been heated to this temperature
shows, even to the naked eye, alternate bands of opaque, white material,
and of clear, transparent material, the latter being the unaltered
β-hopeite.   The opacity of the bands of altered α-hopeite is seen, under
the microscope, to be due to the presence of vast numbers of minute
spindle-shaped bodies closely arranged side by side parallel to the vertical
c-axis of the crystal, and extending completely across each band.   On
placing the section in water there was no return to the original optical
conditions ; so that in this respect, as also in the absence of any pro-
gressive change in the optical characters with change of temperature,
hopeite behaves quite differently from the zeolites.

When heated to a temperature of 110° C. the bands of β-hopeite still
show the characteristic figures in convergent light, though now perhaps

the axial angle is rather smaller than before, and the birefringence seems also to be less. The plate is now much cracked along cleavages parallel to c (001). Cleavage-flakes parallel to a (100), after being heated to this temperature, still show bright polarization-colours in parallel light. At 139° C. the b-section becomes wholly opaque, and no longer shows the optical characters of β-hopeite. A cleavage-flake parallel to a (100) is, however, still doubly refracting with uniform and straight extinction; and the same was observed in flakes that had been heated even to redness.

There is thus an appreciable difference in the temperature at which water is expelled from a-hopeite and from β-hopeite (see p. 17). There also appears to be a slight difference in their solubility in acid. After a b-section of a crystal of hopeite has been immersed for a short time in a drop of dilute hydrochloric acid the zonal structure may be seen somewhat more distinctly under a hand magnifying lens.

In specific gravity there was also found to be a slight difference between a-hopeite and β-hopeite. On breaking up a b-section and selecting fragments in which one or other modification predominated, it was found that in methylene iodide the fragments in which β-hopeite predominated were lighter than pale-rose tourmaline from Elba (sp. gr. 3·02), and that those in which a-hopeite predominated sank while the tourmaline floated (see p. 10).

An analogous case of the regular intergrowth of two modifications of the same substance is that of zoisite described by P. Termier[1], who distinguishes a-zoisite and β-zoisite by differences in optical characters.

Since all the crystals of hopeite consist of two substances intimately intergrown, and differing widely in their optical characters, it is not possible to make any exact determinations of the optical constants. The values obtained are not concordant, for they result from the combined effect of the two modifications in varying proportions.

Numerous determinations of the *refractive indices* were made by the method of minimum deviation through prisms formed by the natural faces of the crystals. On one crystal, for example, the four prisms formed by the faces of the forms a {100} and s {120}, with refracting angles varying between 48° 58′ and 49° 26′ gave, for sodium-light :—

　　1·593 (mean of 1·5937, 1·5915, 1·5930, 1·5928) for vibrations parallel to the vertical c-axis of the crystal (i.e. the combined effect of the β index of a-hopeite and of the β or γ index of β-hopeite).

[1] P. Termier, Bull. Soc. franç. Min., 1898, vol. xxi, p. 148 ; 1900, vol. xxiii, p. 50 ; abstracts in Min. Mag., vol. xii, p. 215, vol. xiii, p. 207.

1·585 (mean of 1·5862, 1·5843, 1·5829, 1·5856) for vibrations perpendicular to the c-axis (i. e. the combined effect of the α and γ indices of α-hopeite and of the α and γ or α and β indices of β-hopeite).

With the same crystal the refractive indices determined through the two prisms formed by the faces of the forms a {100} and e {101}, with refracting angles of 50° 6′ and 50° 52′, were, for sodium-light :—

1·5903 and 1·6022, for vibrations parallel to the b-axis of the crystal (i.e. the combined effect of the α index of α-hopeite and of the α index of β-hopeite).

1·6024 and 1·6117, for vibrations perpendicular to the b-axis (i. e. the combined effect of the β and γ indices of α-hopeite, and of the β and γ indices of β-hopeite).

With a second crystal the corresponding values were :—

Prism as', 1·5893, for vibrations parallel c-axis.

1·5816, for vibrations perpendicular c-axis.

Prism ae', 1·5806, for vibrations parallel b-axis.

1·5902, for vibrations perpendicular b-axis.

These results are of little value beyond serving to indicate the mean refractive power of the mineral. They are in agreement with Brewster's determination (1824) of 1·601 for the ordinary index measured through the prism ae'. The value $\beta = 1·471$ calculated by Des Cloizeaux (1879) from his measurements of the optic axial angles is clearly too low, whilst the approximate value of 1·666 determined by H. Buttgenbach (1906) by the Duc de Chaulnes's method is too high.

The measurements obtained for the value of the *optic axial angle* are also unsatisfactory ; for, as the section is rotated, different lamellae may come into coincidence with the axis of the instrument. No dispersion of the optic axes could be detected or measured.

For α-hopeite the following values were determined for the angle in air :—

2 E = $55\frac{1}{2}°$, $58\frac{1}{2}°$ (with the axial angle apparatus in sodium-light).

$58°$, $60\frac{1}{2}°$, $63\frac{3}{4}°$ (with the microscope stage-goniometer).

$50°$–$57\frac{1}{2}°$ (with a micrometer-scale in the eye-piece of the microscope).

For β-hopeite when the optic axial plane is parallel to c (001):—

2 E = $30\frac{3}{4}°$, $32\frac{1}{2}$ (axial angle apparatus in sodium-light).

$27\frac{1}{2}°$ (stage-goniometer).

$24°$, $32\frac{1}{2}°$ (micrometer-scale).

For β-hopeite when the optic axial plane is perpendicular to c (001):—
    $2\,E = 18°$, $23°$ (micrometer-scale).
Determinations of the angle in cedar oil ($n = 1.516$) gave:—

        for α-hopeite, $2H_a = 35\frac{1}{2}°$, $36\frac{1}{2}°$, $37°$ (Na).
        for β-hopeite, $2H_a = 21\frac{1}{2}°$–$23\frac{3}{4}$ (Na).

Attempts to measure the obtuse angle between the optic axes through a cleavage-plate parallel to a (100) were made in cedar oil and methylene iodide, but without success, for the axes do not emerge. Through the prism-faces of s {120} two sets of rings, but without brushes, were visible, and gave in cedar oil $2H_a = 43°$ and $33°$ respectively; but these results are not concordant with the other values.

Assuming the β index of hopeite to be 1.59, the axial angles in the crystal are calculated as:—

        for α-hopeite, $2V = 36°$ about.
        for β-hopeite, $2V = 20°$ about.

As is also the case with the refractive index, my determinations of the optic axial angle of hopeite are in closer agreement with the value obtained by Brewster (namely 48°), than with those of Des Cloizeaux ($2E = 78° 35'$, $2V = 54° 44'$, Na) and Buttgenbach [1] ($2E = 149° 32'$, $2V = 70° 47'$).

Des Cloizeaux mentions that the interference-figures are distorted, and he suggests that the distortion is due to twin-lamellae. This suggests that the original hopeite from Altenberg also presents the same lamellar intergrowth as the Rhodesian crystals, but the former I have not been able to examine optically.[2]

Friedel and Sarasin (1879), and de Schulten (1904), say of the artificial crystals that in optical characters they agree with the natural mineral (as previously determined by Des Cloizeaux); they give the optic axial plane as being parallel to c (001). Crystals of hopeite are readily deposited from a solution of zinc phosphate in acetic acid. The crystals which I so obtained are pearly scales flattened parallel to a (100) and with a rectangular outline; they are about $\frac{1}{4}$ mm. in length, and between crossed nicols extinguish parallel to their edges. As these artificial crystals are not flattened parallel to b (010) it is not possible to say whether or not they consist of zonal intergrowths as do the natural Rhodesian crystals.

[1] Buttgenbach's determination was made under the microscope through the prism s and is clearly of no value.

[2] The single specimen of hopeite from Altenberg in the British Museum collection shows only four minute crystals.

Etching.—A cleavage-flake parallel to *a* (100) of hopeite is quickly attacked in even very dilute hydrochloric acid, and the surface becomes dull. Under the microscope, the etched surface shows a shagreen appearance, with no very well-marked corrosion-figures. Under a high power, however, minute six-sided elevations are to be seen; these have their edges parallel to the brachypinacoid and the four adjacent pyramid-planes. The crystals therefore possess holohedral-orthorhombic symmetry.

On a cleavage-flake parallel to *b* (010) the action of the acid is less rapid, and is mostly shown by a rounding of the sides of the flake, due to the more rapid solution on the *a* and *c* faces. No well-marked corrosion-figures were seen, only a few long bars parallel to the vertical -*c*-axis and running across the bands of α-hopeite and β-hopeite. After a *b*-cleavage-flake has been in the acid, the zonal banding is rather more readily seen in ordinary light, indicating that the two constituents have been dissolved in slightly different amounts.

No electrical charge could be detected on crystals of hopeite while they were cooling; the mineral is therefore not pyro-electric.

Chemical Composition.—Owing to the very sparing occurrence of the mineral at the original locality, natural crystals of hopeite have not hitherto been analysed quantitatively. Several analyses have been made, by H. Debray (1861), W. Heintz (1867), C. Friedel and E. Sarasin (1879), and A. de Schulten (1904), of artificial crystals, and these give the formula $Zn_3P_2O_8.4H_2O$.

Heated in a bulb-tube, a crystal of hopeite readily gives off abundance of water. The crystal is then white (both when hot and when cold; compare tarbuttite, p. 27) and opaque with a porcellanous aspect. Before the blowpipe, on a loop of platinum wire, the material readily fuses to a clear, colourless bead, and imparts a pale greenish coloration to the flame. As the bead cools, spherulitic growths rapidly spread over the surface and the bead consolidates partly as crystallized (birefringent) material and partly as a clear, colourless (isotropic) glass. On the final consolidation of a large bead, molten material is violently erupted from the interior to the surface where it consolidates as a glass, leaving pits resembling the craters of volcanoes.

Hopeite is readily soluble in dilute hydrochloric acid. In this solution ammonia produces a bulky white precipitate which is soluble in excess of ammonia, though apparently not so readily as in the case of parahopeite and tarbuttite. Qualitative tests showed the presence of only zinc, phosphoric acid, and water: cadmium was not detected.

A separation of the α-hopeite and the β-hopeite was attempted by crushing 5·6 grams of the large white crystals to a coarse powder and placing in methylene iodide (p. 10). The heaviest (sp. gr. 3·04) and lightest (sp. gr. 3·03) fractions were, however, far from consisting wholly of α-hopeite and β-hopeite respectively, but in the following determinations it will be convenient to refer to them as such.

About a gram of each fraction was taken, and they were heated side by side in an air-oven for one hour at different temperatures. The percentage losses of weight are given below and are also plotted in fig. 3.

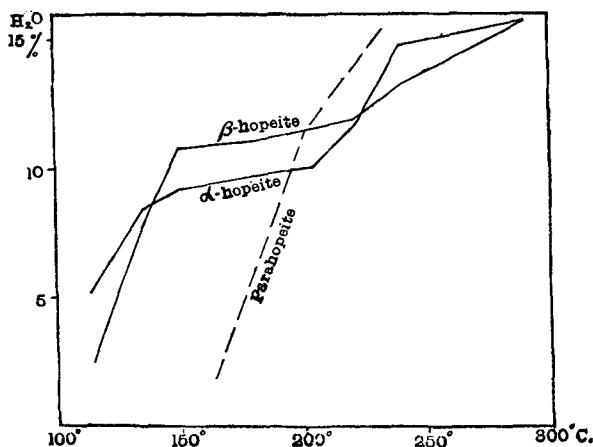|	114°	135°	150°	180°	203°	221°	240°	290°C.	Red-heat.
α-hopeite ...	5·2	8·5	9·2	9·8	10·1	11·8	14·9	15·8	16·1 % H_2O.
β-hopeite ...	2·5	7·9	10·9	11·1	11·7	12·0	13·3	15·8	16·2 % H_2O.

Fig. 8.—Curves representing the rate of loss of water with rise of temperature from α-hopeite, β-hopeite, and parahopeite.

These results show that there is an appreciable difference between α-hopeite and β-hopeite in respect to the temperature at which the water is expelled. The much greater loss from α-hopeite at 114° C. is in agreement with observations made when a section of a crystal perpendicular to the acute optic bisectrix was heated (p. 12).

As may be seen from fig. 3, about half of the water is expelled at 135° C.; and there is much less loss between 135° C. and 221° C. than below and above these points. Other determinations of the loss on ignition were 16·1 and 16·2 per cent., made respectively on 1·990 and 1·108 gram of the large white crystals.

In the quantitative analysis of the two separated portions, the material,

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after ignition, was fused in a platinum crucible with sodium carbonate, and the melt extracted with boiling water; the residue, after ignition, was weighed as zinc oxide ; and from the filtrate, phosphoric acid was precipitated with magnesia mixture and weighed as magnesium pyrophosphate.   The following results were obtained :—

		α-Hopeite.		β-Hopeite.		Calculated for $Zn_3P_2O_8.4H_2O$.
ZnO	...	52·1	...	51·9	...	53·3
P_2O_5	...	31·8	...	$[31·9]^1$	...	31·0
H_2O	...	16·1	...	16·2	...	15·7
		100·0		100·0		100·0
Sp. gr.	...	3·04		3·03		—

The above analyses show that there is no difference in composition between α-hopeite and β-hopeite.   Both of them agree closely enough with the formula $Zn_3P_2O_8.4H_2O$ or $3ZnO.P_2O_5.4H_2O$; but, like almost all analyses of artificial hopeite, they show slight variations from the theoretical values.   The same differences are not shown in the analysis of parahopeite (p. 21), and, as remarked above, there appears to be a difference in the solubility in ammonia of the zinc phosphate from hopeite and that from parahopeite.   In the case of zinc and phosphoric acid it is possible that these differences may be partly due to imperfect separation, but not so with the water.   The same slight excess of water was observed by W. Heintz (1867) and by C. Friedel and E. Sarasin (1879) for artificial hopeite ; the former suggested that it might be due to an admixture of an acid salt $H_2Zn_2P_2O_8.3H_2O$ with the normal salt $Zn_3P_2O_8.4H_2O$ in the proportion of one molecule of the former with four of the latter.

Since α-hopeite and β-hopeite differ neither in chemical composition nor in crystalline form, they cannot be considered as dimorphous modifications in the same sense that hopeite and parahopeite are dimorphous.

PARAHOPEITE.

This name[2] I propose to give to a new species of hydrous zinc phosphate, identical with hopeite in chemical composition, but differing from both α-hopeite and β-hopeite in physical and crystallographic characters.

In external appearance, the new mineral has little in common with hopeite, and, at first sight, it has a striking resemblance to the hydrous

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[1] By difference: the zinc oxide was tested and found to be free from phosphoric acid.

[2] The name parahopeite appeared in the report of the Mineralogical Society's meeting of November 12, 1907, as given in 'Nature', 1907, vol. lxxvii, p. 143.

zinc silicate, hemimorphite. I have been able to find only two specimens on which this mineral is prominently developed, though small, inconspicuous crystals of parahopeite were detected on a few specimens of pseudomorphous tarbuttite (p. 29). On one of the two specimens the platy crystals of parahopeite are thickly grouped together on a layer of colourless tarbuttite crystals, which rest on dark-brown, cellular limonite. On the other specimen the thin, platy crystals are clustered in tufts on nodular, ochreous limonite; on the back of the specimen are a few minute crystals of pyromorphite.

The crystals of parahopeite are colourless and transparent with a vitreous lustre, and have the form of thin plates arranged in divergent or fan-shaped groups. In size they measure 3 to 5 mm. across.

Crystalline Form.—The crystals are so deeply striated and bunched together with sub-parallel grouping that it is impossible to determine even approximately their crystallographic constants. The appearance of the crystals is approximately represented in the accompanying figure (fig. 4). The faces lettered d and d' are, however, not so definite as represented in the figure, but are merely seen as numerous small spots on the edges and corners of the crystals; on the goniometer these give, like all
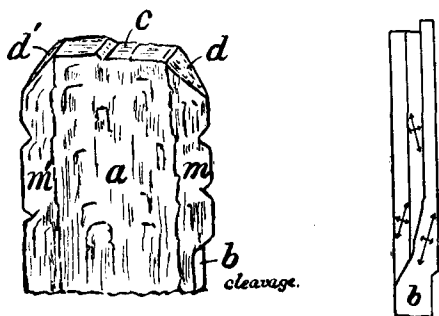

Fig. 4.—Parahopeite crystal : on the right a cleavage-flake parallel to b (010), showing the directions of optical extinction.

the other faces of the crystals, a whole field full of scattered images. Attempts were made to measure eight crystals, which were selected from a large number of crystals detached from the specimens; and the following angles may be given, but they are of little value :—

$$ab \text{ or } a'b \ = \ 88° \ - \ 94°.$$
$$am \text{ ,, } am' \ = \ 33° \ - \ 37°, 42°.$$
$$ac \text{ ,, } a'c \ = \ 85° \ - \ 92°.$$
$$bc \text{ ,, } b'c \ = \ 86° \ - \ 95°.$$
$$bd \text{ ,, } b'd' \ = \ 22°, 34°, 44°, 57°, 66°, 73°.$$

There is a direction of perfect cleavage, on which the lustre is somewhat pearly, parallel to b, i. e. perpendicular, or nearly so, to the large plane a, and parallel to the length of the crystal and to the striations on

a. The cleavage-planes are usually sharply divided parallel to their length into two or more strips, which are inclined to one another at small re-entrant or salient angles. Each of these long, narrow areas gives a single, sharp reflected image, and the angles between them were measured, in the zone [*ab*], as : 52′, 3° 33′, 4°, 5° 19′, 6°, 6½°. The appearance is quite like that shown on the basal (*c*) cleavage of albite-twins of plagioclase-felspar. That parahopeite may be anorthic and twinned like albite is also suggested by the optical characters. It must, however, be noted that the crystals are arranged in fan-shaped aggre-gates with the edges [*ab*] of the several individuals approximately parallel, and this may partly account for the small re-entrant and salient angles measured on the *b*-cleavage.

Optical Characters.—On the large plane *a* the crystals polarize in bright colours, whilst on *b* the double refraction is much lower. The angle of extinction on *a* is 30° with reference to the edge [*ab*]. Through *a*, in convergent light with a $\frac{1}{12}$-inch objective in oil, a somewhat indis-tinct obtuse bisectrix was noted. Cleavage-flakes parallel to *b* show, in parallel light between crossed nicols, quite the appearance of a cleavage-flake of albite twinned according to the albite-law. Two or several lamel-lae may be seen, and these have different directions of extinction, but alternate lamellae extinguish simultaneously (fig. 4). The extinction-angles measured on *b* with reference to the edge [*ab*] vary widely—0°, 8°, 14°, 20°, 25°. In convergent light through *b* is seen a series of coloured rings and a brush around one of the optic axes of a biaxial interference-figure. This is quite near the centre of the field, and has about the same position in different lamellae, though the direction of the optic axial plane varies. The sign of the double refraction is positive. Up to 163° C. there is no noticeable change in the optical characters of parahopeite, though at this temperature the crystals commence to become white and opaque.

A determination of the refractive index, kindly made by Dr. G. F. Herbert Smith with his new model of refractometer, gave the value 1·62 for sodium-light.

Specific Gravity and Hardness.—The crystals just float in pure methy-lene iodide. With the pycnometer, 0·889 gram of crystals gave the value 3·31.

The hardness may be placed at 3¾ ; the crystals easily scratch calcite, and they also are capable of scratching hopeite.

Chemical composition.—Qualitative tests showed the presence of only zinc, phosphoric acid, and water ; cadmium was not detected. The behaviour of parahopeite when heated in a bulb-tube, or before the blow-

pipe on a loop of platinum wire, is exactly like that of hopeite (p. 16). The mineral is readily soluble in dilute hydrochloric acid.

A quantitative analysis[1] was made on 0·885 gram, with the following results :—

	Found.	Calculated for $Zn_3P_2O_8.4H_2O$.
ZnO . . .	53·0 . . .	53·3
P_2O_5 . . .	31·6 . . .	31·0
H_2O . . .	15·6 . . .	15·7
	100·2	100·0
Sp. gr. . .	3·31 . . .	—

Another determination of the water (loss on ignition), made on 0·309 gram, gave 15·8 per cent.

In determining the rate of loss of water with increasing temperature, the behaviour of parahopeite was compared with that of hopeite, the two minerals being heated side by side in an air-oven. The following were the percentage losses of weight during one hour at the different temperatures :—

	113°	139°	163°	201°	233° C.	Red-heat.
Parahopeite ...	nil	nil	1·9	11·6	15·5	15·8 % H_2O
Hopeite ...	1·6	9·2	10·1	10·6	13·5	16·2 % H_2O

The results for parahopeite are plotted in fig. 3 (p. 17), and they show a striking difference in the behaviour of the two minerals.

Comparison of the characters of parahopeite and hopeite.

	Parahopeite.	Hopeite.
Colour	Colourless, transparent.	Colourless, transparent.
Lustre	Vitreous, somewhat pearly on the cleavage.	Vitreous, strongly pearly on the a cleavage.
Crystal-system . .	Anorthic.	Orthorhombic.
Cleavage . . .	b perfect.	a perfect, b good, c poor.
Optical character .	Biaxial, positive.	Biaxial, negative.
Refractive indices .	1·62	1·58–1·60
Hardness . . .	$3\frac{3}{4}$	$3\frac{1}{4}$
Specific gravity . .	3·31	3·0–3·1
Chemical composition .	$Zn_3P_2O_8.4H_2O$	$Zn_3P_2O_8.4H_2O$
Loss of water at 139°C.	nil.	9·2 per cent.
,, ,, 233°C.	15·5 per cent.	13·5 ,,

In this analysis, the water was determined as the loss on ignition; zinc was precipitated from the ammonia solution as sulphide and, after repeated ignitions, weighed as oxide; and in the filtrate the phosphoric acid was precipitated with magnesia mixture.

TARBUTTITE.

For the basic zinc phosphate to be now described I have proposed the name of tarbuttite,[1] after Mr. Percy Coventry Tarbutt, who himself collected, at the Broken Hill mines in Rhodesia, several of the specimens which he has generously presented to the British Museum.

At this locality tarbuttite is found in great abundance, and large, beautifully crystallized specimens are by no means uncommon. Only rarely is a new mineral species found in such profusion. There is also an extraordinary variety both in the character of the specimens and in the appearance of the tarbuttite itself.

The most distinctly crystallized material occurs as an encrustation on masses of cellular or stalactitic limonite, and is often associated with earlier formed crystals of either descloizite or pyromorphite. On the surface of the tarbuttite crystals there are sometimes a few small (1 mm., or less, across), colourless rosettes of hemimorphite crystals. Minutely crystallized crusts of pseudomorphous tarbuttite (p. 28) are also very abundant. These occurrences are in Kopje No. 2, and are not associated with the hopeite in the bone-cave in Kopje No. 1. Tarbuttite was, however, detected in the very thin and minutely crystallized crusts on the hopeite specimens and on some of the bones from the cave (p. 30).

The crystals of tarbuttite are sometimes perfectly colourless and transparent, and have a brilliant, vitreous lustre on their faces. More usually, they are pale shades of yellow, brown, red, or green, with varying degrees of transparency. The green colour is due to the presence of traces of copper, and the other colours to the inclusion of iron hydroxides in the crystals. In size, the crystals vary from about half a centimetre across down to microscopic dimensions.

As a rule, the crystals are thickly clustered together; but sometimes they occur singly on the matrix or attached to crystals of pyromorphite. In the latter case, when the crystals have only a slight point of attachment (for instance, when perched on the top of a crystal of pyromorphite), they may be completely bounded on all sides by crystal-faces.

Crystalline form.—The crystals (fig. 5), invariably show a tendency, which is sometimes very pronounced, to grow in sheaf-like aggregates; and this gives rise to a frequent repetition of the faces in nearly parallel positions. Further, the faces, especially the larger ones, are deeply

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[1] The name tarbuttite first appeared in 'Nature', 1907, vol. lxxvi, p. 215, in the report of the Mineralogical Society's meeting of June 11, 1907; and was also given in my list of new mineral names in Min. Mag., 1907, vol. xiv, p. 411.

striated and are much rounded by irregularities of growth. Some of the smaller faces on the corners of the crystals are perfectly smooth and give single reflected images; but as these small faces are frequently repeated in nearly parallel positions on adjacent portions of the crystal, the measurements from them are confused.

For these reasons only a small number of reliable measurements could be obtained; and the presence of but few well-defined faces in the primary zones on the crystals make the calculations all the more awkward. About a dozen crystals were measured in detail, but the elements given below can only be considered as a first approximation.
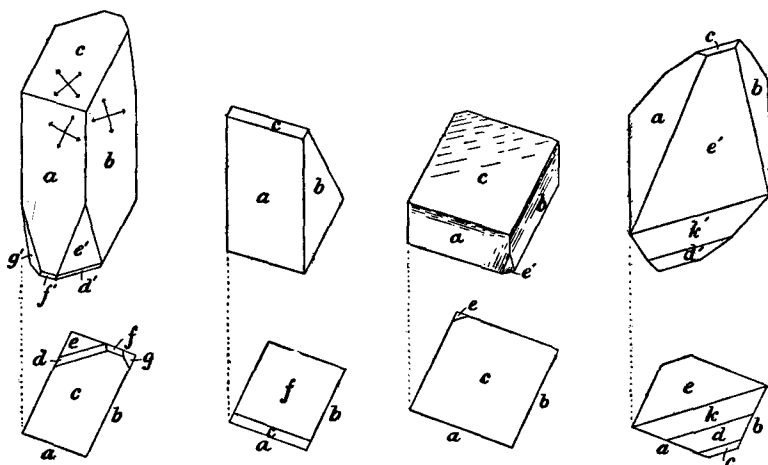

Fig. 5.—Crystals of tarbuttite from Broken Hill, North-Western Rhodesia.
(Clinographic drawings and plans.)
The first figure shows the directions of optical extinction on the faces a, b, c. In the second figure the crystal is terminated below by the cleavage parallel to c (001). The third figure represents the striations on the faces.

The crystals are anorthic with parallel faces; and the elements (calculated from the angles ac, ab and ab', cb and cb', cf, and cd) are :—

$$a : b : c = 0 \cdot 9583 : 1 : 1 \cdot 3204 ;$$
$$a = 102° 37', \beta = 123° 52', \gamma = 87° 25'.$$

The forms determined on the crystals are given below in approximately the order of their relative sizes and frequency of occurrence, and their positions are indicated on the accompanying stereographic projection (fig. 6).

$c\{001\}$, $b\{010\}$, $a\{100\}$, $e\{\bar{2}\bar{2}1\}$, $f\{\bar{1}01\}$, $g\{\bar{2}11\}$, $d\}\bar{2}\bar{2}3\}$, $k\{\bar{1}\bar{1}1\}$, $l\{021\}$, $h\{0\bar{2}1\}$, $i\{\bar{1}22\}$, $r\{\bar{2}\bar{4}3\}$, $o\{1\bar{2}1\}$, $s\{\bar{1}02\}$, $t\{\bar{1}03\}$, $u\{0\bar{1}1\}$, $m\{110\}$.

In addition to these, several other forms are present, either as indefinite, striated faces or as minute faces not lying in the zones actually measured.

Measured and calculated angles of tarbuttite.

		Calculated.	Measured.	Limits.	No.
⌈ ac =	(100) : (001)	55° 50′	*55° 50′	55° 0′ — 56° 15′	14
| cf =	(001) : (Ī01)	77 38	*77 38	77 30 — 77 55	10
| cs =	(001) : (Ī02)	42 0	42°	—	1
⌊ ct =	(001) : (Ī03)	26 23	26°	25° — 27°	2
⌈ ab =	(100) : (010)	84 34	*⌈ 84 28	84 30 — 84 52	7
| ab′ =	(100) : (0Ī0)	95 26	{ 95 20	95 4 — 95 32	7
⌊ am =	(100) : (110)	37 0	37°	—	1
⌈ cb =	(001) : (010)	76 31	*⌈ 76 24	75 59 — 77°	8
| cb′ =	(001) : (0Ī0)	103 29	⌊ 103 15	102 48 — 103 47	4
| ch =	(001) : (0$\bar{2}$1)	77 7	77½°	77° — 77 44	3
| cu =	(001) : (0Ī1)	55 7	58°	57° — 58 55	2
⌊ cl =	(001) : (021)	54 41	56°	55° — 57½°	2
⌈ cd =	(001) : ($\bar{2}\bar{2}$3)	72 3	*72 3	71 14 — 72 30	10
| ck =	(001) : (Ī11)	90 27	90 35	90° — 91°	4
⌊ ce =	(001) : ($\bar{2}\bar{2}$1)	108 45	108 35	108 14 — 109 4	6
⌈ gf =	($\bar{2}$11) : (Ī01)	43 37	43 59	43 56 — 44 2	4
| fd =	(Ī01) : ($\bar{2}\bar{2}$3)	43 42	44 24	44° — 44 26	4
| di =	($\bar{2}\bar{2}$3) : (Ī22)	18 34	18 38	18 26 — 18 51	4
⌊ dh =	($\bar{2}\bar{2}$3) : (0$\bar{2}$1)	46 1	45 27	45° — 45 58	4

The zones given in the above table of angles are the principal ones on the crystals. Most of the faces were also measured to the three axial planes a, b, and c, and several less important zones might be included in the table. But the calculated and measured angles do not agree as closely as could be wished, and it is unsatisfactory to make tedious calculations when it is clear that the elements are not final. The indices of the remaining faces were determined by the intersection of zones, and the measured angles were checked on the projection with the aid of Penfield's stereographic protractors.

It will be noticed from the above table of angles of tarbuttite that

there is a certain repetition of nearly the same angles in different zones (e. g., *cb*, *cf*, and *ch* about 77°; *a'f* and the angles in the zone [*gh*] about 45°). There is also often an approach in the angles to those of cubic crystals.

In the habit of the tarbuttite crystals there is considerable variation. Some of the more usual forms of crystals are represented in the accompanying figures (fig. 5). Perhaps the most common habit is that shown on the left in fig. 5, where *a* {100}, *b* {010}, and *c* {001} are all large, giving a distorted brick-like shape with small planes on some of the edges and corners.
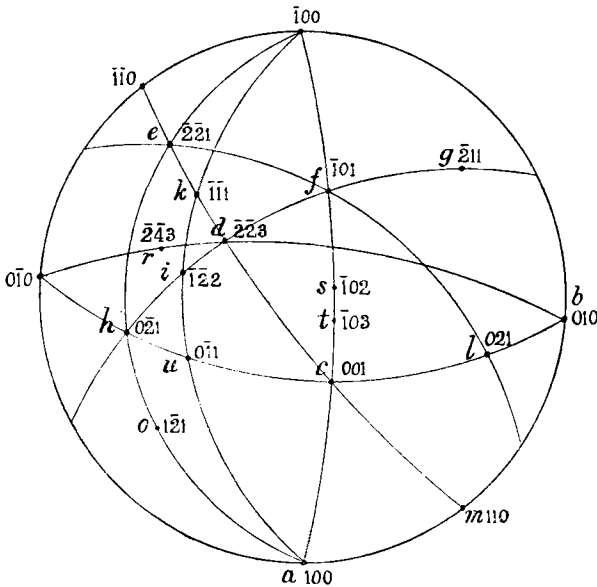

Fig. 6.—Stereographic projection of the crystal-forms of tarbuttite.

Cleavage.—An important feature of tarbuttite is the perfect cleavage parallel to *c* (001). On the cleavage surfaces the lustre is distinctly pearly, though this lustre is often not conspicuous on an uncleaved crystal. The presence of this cleavage helps considerably in the orientation of the crystals, and also in their optical determination. The form *c* {001} is usually prominently developed on the crystals, though sometimes these faces are quite small or altogether absent.

Optical characters.—The directions of optical extinction are oblique on all the faces of the crystals :—

On c (001) at 33° to the edge $[c\,a]$.

     ,,   ,, 35° ,,   ,, $[c\,b]$

     ,,   ,, 10° ,,   ,, $[c\,e]$.

On b (010) ,, 25° ,,   ,, $[b\,c]$.

     ,,   ,, 10° ,,   ,, $[b\,a]$.

On a (100) ,, 26° ,,   ,, $[a\,b]$.

     ,,   ,, 14° ,,   ,, $[a\,c]$.

These extinction directions are shown in fig. 5 ; the angles are related to the axial angles as follows :—

On c (001) . . . $33° + (90° - 35°) = \ \ 88° = \gamma.$

On b (010) . . . $10° + \ \ 25° + 90° \ = 125° = \beta.$

On a (100) · . . $26° + (90° - 14°) = 102° = \alpha.$

The acute, negative bisectrix of the optic axes emerges obliquely through the perfect cleavage c(001). The interference-figure in convergent polarized light appears on the edge of the field of view, and is best seen with a $\frac{1}{12}$-inch objective in oil. The double refraction is strong, and even a thin cleavage-flake shows several coloured rings ; with a thick flake the rings are very small and close together, so that the figure is less readily seen. The trace of the optic axial plane on c (001) is inclined at 33° to the edge $[ca]$, and the acute bisectrix is inclined at an angle of about 40° (in air) to the normal to c (001) towards the face g ($\bar{2}$11). By grinding off the corner formed by the three faces a' ($\bar{1}$00), b (010), and c (001) and the opposite corner of a crystal, a plate was obtained which showed the interference-figure near the centre of the field of view. The axial angle, as approximately measured with the eye-piece micrometer, is about 80° or 90° in air.

The following refractive indices for sodium-light were determined by the method of minimum deviation through prisms formed by the natural faces of the crystals. These are, of course, not the principal indices :—

    1·706 } through a prism of 46° 24′ formed by the faces a (100)
    1·665 }   and f ($\bar{1}$01).
    1·703 } through a prism of 56° 0′ formed by the faces a' ($\bar{1}$00)
    1·672 }   and c (001).

The double refraction is therefore strong.

The sheaf-like aggregation, especially marked in the larger crystals, precluded any possibility of cutting orientated plates and prisms for the exact determination of the optical constants of the mineral.

Specific gravity and hardness.—Crystals of tarbuttite readily scratch calcite and hopeite; the hardness may therefore be placed as $3\frac{3}{4}$. The mineral sinks in methylene iodide. Determinations of the specific gravity made with the pycnometer gave the following values :—

> 4·12, on 1·439 gram of pale greenish material forming a crystallized crust, but quite free from impurity.
>
> 4·12, on 1·308 gram of similar material from another specimen.
>
> 4·15, on 0·847 gram of colourless, transparent crystals associated with pyromorphite (which may account for this slightly higher value).

Chemical composition.—When heated in a bulb-tube, tarbuttite behaves quite differently from hopeite and parahopeite. At a high temperature it decrepitates slightly and gives off only a small amount of water. The material, when hot, is of a bright yellow colour, which changes to pure white on cooling; the crystals are then opaque with a porcellanous appearance. This change in colour indicates that there is a separation of zinc oxide, and that tarbuttite is a basic zinc salt. Heated before the blowpipe on a loop of platinum wire, the mineral readily fuses to a clear, yellow bead, which on cooling crystallizes to an opaque, dark-grey bead ; fragments of this are doubly refracting.

The mineral is readily soluble in dilute hydrochloric acid, and from this solution ammonia produces a bulky white precipitate which is readily soluble in excess of ammonia. Qualitative tests proved the presence of only zinc, phosphoric acid, and water ; cadmium is absent.

A quantitative analysis was made on 1·308 gram of the pale greenish crystalline material, which, after ignition, was fused with sodium carbonate (as described on p. 18). The following results were obtained :—

	Found.	Calculated for $Zn_3P_2O_8.Zn(OH)_2$.
ZnO . . .	66·6 . . .	67·1
P_2O_5 . . .	29·2 . . .	29·2
H_2O · . .	3·8 . . .	3·7
	99·6	100·0
Sp. gr. . .	4·12 . . .	—

Tarbuttite is therefore a basic zinc phosphate with the formula

$$Zn_3P_2O_8.Zn(OH)_2 = Zn_2(OH)PO_4 = 4ZnO.P_2O_5.H_2O,$$
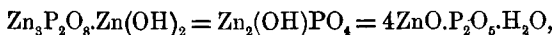
corresponding to, though not isomorphous with, the orthorhombic

adamite $Zn_3As_2O_8.Zn(OH)_2$. Although several zinc phosphates have been prepared artificially, no basic phosphate appears to have been hitherto described.

The water is lost only at a red-heat; there was no loss at 370° C. A second determination of the loss on ignition, made on another sample weighing 1·554 gram, also gave 3·8 per cent. Another analysis, made on slightly impure pseudomorphous tarbuttite, is given below (p. 29).

Pseudomorphous tarbuttite.

With the exception of hopeite and parahopeite, tarbuttite was one of the latest minerals to be formed at the locality, and it has clearly resulted by the action of phosphatic solutions on the earlier formed secondary minerals in the upper, oxidized zone of the deposit of ore. The larger crystals of tarbuttite with the associated crystals of pyromorphite (lead phosphate) must have been formed by the action of such solutions on the mixed zinc and lead ore, which consists of an intimate intermixture of hemimorphite and cerussite with interspersed limonite. · The occurrence of vanadates (descloizite and vanadinite), also of a late date of formation, points to the presence of solutions containing vanadium.

Tarbuttite after calamine.—A form of tarbuttite which is particularly abundant consists of mamillated masses and concentric shells of finely crystalline material. These masses are covered on their free surfaces with small, bright crystals of tarbuttite, and on the fractures they show the sparkling, pearly cleavage characteristic of the mineral; the whole of the material consists, in fact, of an aggregate of crystals or crystalline grains, which measure about $\frac{1}{2}$ to 1 mm. across. This form of tarbuttite has resulted from the alteration of calamine $(ZnCO_3)$. On two specimens some of the unaltered calamine still remained as compact, mamillated masses; and here it was clearly seen that the alteration to tarbuttite had proceeded along the concentric layers of the original mineral.

Between the concentric shells of tarbuttite there is often a free space, and both surfaces of the shells are encrusted with crystals. These shells of tarbuttite do not exceed a few millimetres in thickness, and the material of adjacent layers may differ slightly in colour; for instance, pale green in one layer and colourless or grey in the next, and often reddish on the top layer. Sometimes these thin, curved layers of tarbuttite are found quite separated from other layers. The fact that spaces are left between the shells indicates that some of the zinc must

have been removed in solution, for the molecular volumes of calamine ($113 \cdot 6 = 28 \cdot 4 \times 4$) and of tarbuttite ($117 \cdot 5$) are practically identical.

On these specimens of tarbuttite pseudomorphous after calamine no other mineral but tarbuttite could, as a rule, be detected under the lens; but on some of them small crystals of parahopeite, calamine, &c., were found (see below). The following analysis was made on 0·984 gram of material from one of the mamillated specimens, which was at first believed to consist wholly of tarbuttite:—

$$
\begin{array}{lr}
\text{ZnO} & 65\cdot3 \\
\text{P}_2\text{O}_5 & 30\cdot2 \\
\text{H}_2\text{O} & 4\cdot1 \\
\text{CuO} & \text{trace} \\
\hline
& 99\cdot6 \\
\text{Sp. gr.} & 4\cdot06
\end{array}
$$

At 220°C. there was a loss in weight of 0·2 per cent. These values are near to the corresponding values for tarbuttite; but the slight excess of water and phosphoric acid, and the slight deficiency of zinc, as well as the slight loss of water at 220°C. and the low specific gravity, all point to the presence of a small proportion of parahopeite intermixed with the tarbuttite.

On one or two specimens of a similar character a few minute crystals of parahopeite were afterwards detected. These were found resting on the shells of tarbuttite, and they have, no doubt, resulted from the subsequent alteration of the tarbuttite.

On other specimens of rather a different character, but also probably pseudomorphous after calamine, the crystalline crusts showed minute crystals of hemimorphite and calamine side by side with crystals of tarbuttite. Fragments of the crust when examined chemically were found to contain zinc and water, with phosphoric, silicic, and carbonic acids. Even when examined under a high-power lens there was little or nothing to suggest but that the minute, water-clear crystals were all of the same kind. But on heating a fragment in a bulb-tube a difference in behaviour was at once apparent: spike-like crystals of calamine became bright yellow in colour and remained yellow after cooling; the tarbuttite was bright yellow when hot and white when cold; and the hemimorphite was faintly yellow when hot and white on cooling. The microscopical examination of fragments of the crystalline crust crushed in oil also confirmed these results: through the cleavage-flakes of tarbuttite was seen a negative biaxial interference-

figure at the edge of the field; the calamine cleavages gave a negative uniaxial figure, also at the edge of the field; and the cleavage laths of hemimorphite gave straight extinction and no optic figure, or when viewed through b (010) the obtuse negative bisectrix.

Some of these pseudomorphous specimens showed indications of many complex stages of alteration, and could not always be satisfactorily made out. On some of them the tarbuttite crystals themselves are white and opaque on their surfaces, due to the alteration of tarbuttite to perhaps parahopeite or hydrozincite.

Tarbuttite after descloizite.—On the pseudomorphs of tarbuttite after calamine, above described, there are no indications of any crystalline form of the original mineral; only the mamillated surfaces of the massive calamine are represented. Specimens of tarbuttite pseudomorphous after descloizite, on the other hand, clearly show the outlines of the original crystals of descloizite. These are lenticular or tabular in habit, exactly like the large crystals of unaltered descloizite found at the locality (fig. 7 c, p. 32). These pseudomorphous crystals are hollow, and they measure up to about a centimetre across; their surface is minutely crystalline, and they consist wholly of a granular aggregate of. very small crystals of tarbuttite. The few specimens of this kind which I have seen are of a bright reddish colour; the tarbuttite crystals being tinged, on the surface of the pseudomorphs, with iron hydroxide.

Tarbuttite after hemimorphite (?).—On one specimen, granular aggregates of reddish tarbuttite have the form of flat prisms, about $\frac{1}{2}$ cm. in length, standing out from the surface of tarbuttite pseudomorphous after calamine. The appearance of these pseudomorphous crystals rather suggested that the original mineral might have been hemimorphite, but there was no means of proving this. On the surface of this specimen the granular tarbuttite is also aggregated in arborescent forms.

Tarbuttite from the Bone-cave.

The description of tarbuttite so far given is based solely on material from Kopje No. 2. The mineral, however, also occurs in association with hopeite, in the bone-cave in Kopje No. 1, but only as very minute (about $\frac{1}{10}$ mm. across) and obscure crystals. Indeed it would have been impossible to determine this material had not the characters of the mineral been previously made out on the larger crystals.

As mentioned on p. 5, tarbuttite forms a skin of minute crystals

on the thin crust of hemimorphite which coats the surface of the bone-breccia. The material is also mixed with calamine, and it was almost impossible to isolate the mineral free from impurity. The fragments collected sank in methylene iodide; and when heated in a bulb-tube they behaved like tarbuttite. Dissolved in a drop of hydrochloric acid on a microscope-slide, the solution gave with ammonia a white precipitate, which was soluble in excess, and from this, ammonium sulphide gave a white precipitate; the latter was dissolved in a drop of nitric acid and a yellow precipitate was produced with ammonium molybdate. Zinc and phosphoric acid are therefore present: in larger fragments, silicic and carbonic acids were also detected. Fragments when crushed in oil gave cleavage-flakes with an extinction angle of 34° and showed the characteristic interference-figure of tarbuttite.

In the same way, the minutely crystallized encrustation on one of the bones was identified as tarbuttite (p. 38).

DESCLOIZITE.

Descloizite occurs in large quantities, and I am informed that several tons of it were thrown away on the dumps. It forms more or less cavernous masses mixed with limonite. Usually it is associated with yellowish crystals of tarbuttite, or less frequently with crystals of pyromorphite or quartz; all these minerals being of later date than the descloizite. The material is crystallized, and on the free surfaces is developed as somewhat rough crystals. Some of the specimens consist wholly of an aggregate of descloizite crystals each measuring a centimetre across. On one specimen a few small crystals of descloizite are implanted on the mamillated surface of calamine.

The crystals are dark brown in colour and have a bright, sub-metallic lustre; sometimes the crystals are partly altered and are dull on the surface. On the fractured surfaces the colour is lighter and the lustre resinous in character. The streak is yellowish-brown or buff-coloured. The mineral is brittle, and there is no cleavage. Chemical tests showed the presence of vanadium, lead, zinc, and a little water and copper; and the absence of arsenic, phosphoric acid, and chlorine.

The crystals exhibit a sub-parallel grouping of individuals with frequent repetition and rounding of the faces. Only approximate goniometric measurements could therefore be obtained, but sufficiently close to identify the forms. Three habits of crystals may be distinguished :—

(i) Pyramidal (fig. 7 a), with the forms[1] b {010}, s {310}, m {110}, l {130}, u {011}, v {021}, o {111}, ϵ {211}.

(ii) Prismatic (fig. 7 b), with the same forms as in habit (i), and differing only from this in the greater width of faces in the zone [100].

(iii) Tabular or lenticular (fig. 7 c), with the forms a {100}, s {310}, m {110}, u {011}, o {111}. The large face a is often much rounded, giving rise to lenticular forms.
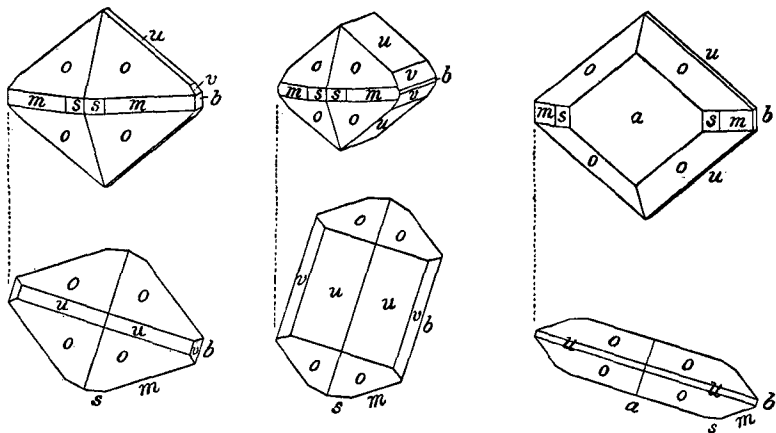

Fig. 7 a.   Fig. 7 b.   Fig. 7 c.
Crystals of descloizite from Broken Hill, North-Western Rhodesia.

The new form s {310} was present on five of the seven crystals which were measured; the angles are:—

		Calculated.	Measured.
ss'''	$= (310):(3\bar{1}0)$	$24° 30'$	$22° - 24°$
sm	$= (310):(110)$	$20\ 14\frac{1}{2}$	$19 - 21$

The distribution of the faces and the measurements accord with orthorhombic symmetry, as also do the optical characters, so far as these could be determined. Light is transmitted through the thinner crystals of tabular habit, and on the face a the direction of optical extinction bisects the angle between the edges of o {111}. No optical interference-figure was visible through a with a $\frac{1}{12}$-inch oil immersion. The dichroism on this face is distinct, being reddish-brown for vibrations

[1] Letters and indices as given in Dana's 'System of Mineralogy', 6th edit., 1892.

parallel to the b-axis and yellowish-brown for vibrations parallel to the c-axis. Small irregular fragments crushed in oil were seen to be even more strongly dichroic.

VANADINITE.

This is present on almost all the hopeite specimens in the form of botryoidal masses of a light-brown colour. The small globules often form branching aggregates somewhat resembling moss or broccoli. The surface is quite smooth without any indication of crystallization. The material is very brittle. When crushed under the microscope the globules show a radiated structure, and, being birefringent, they give a black cross parallel to the vibration-directions of the crossed nicols. Chemical tests showed the presence of vanadium, lead, and chlorine; and the absence of phosphoric acid.

The mineral is of quite recent formation. It is anterior to the hopeite crystals, but posterior to the thin crust of hemimorphite and tarbuttite which coats the bone-breccia; and it is often seen encrusting small bones which project from the surface.

In appearance the mineral is very like some of the vanadinite from Wanlockhead in Scotland: but its occurrence as a mineral of recent formation on bone-breccia seems to be unique.

PYROMORPHITE.

Small crystals of pyromorphite occur in association with tarbuttite, descloizite, and limonite in Kopje No. 2. Nearly all the specimens with the larger tarbuttite crystals show crystals of pyromorphite resting on the cellular limonite; the tarbuttite crystals rest on the pyromorphite when they are not in contact with the limonite. The association of pyromorphite with descloizite is less frequent. Some specimens consist wholly of a loose aggregate of small yellowish crystals of pyromorphite.

The crystals vary from a fraction of a millimetre up to about a centimetre in length. The smaller crystals are almost, or sometimes quite colourless and transparent, while the large ones are usually pale green and nearly opaque. The long-prismatic habit of the crystals is without variation; and the only forms present are the hexagonal prism m $\{10\bar{1}0\}$ terminated, often at both ends, by the low hexagonal pyramid x $\{10\bar{1}1\}$. The angle mx was measured as 49° 29′–49° 40′, and the angle xx in the same zone over the apex of the crystal as 80° 10′–80° 48′. The faces though bright are slightly hummocky.

Two, but only two, instances were found in which two crystals were grown together nearly at right angles and with one pair of prism-faces coincident. Twinned on {33$\bar{6}$4} the angle between the principal axes would be 95° 40′. The angle, as measured under the microscope, between the prism-edges of one crystal and those of the other was 97° in one instance and 90° in the other. These, therefore, are probably only accidental attachments of crystals and not regular twin intergrowths.

Chemical tests of the pyromorphite crystals showed the presence of lead, phosphoric acid, and chlorine. Three crystals were separately tested for arsenic, but this was not detected.

HEMIMORPHITE.

Zinc silicate is one of the most abundant of the minerals at this locality, but only rarely is it distinctly crystallized, and finely crystallized specimens were not seen. The bulk of the oxidized ore consists of an intimate mixture of hemimorphite and cerussite with variable amounts of interspersed limonite. Thin sections of this ore show, under the microscope, radiating groups of hemimorphite needles with grains and indistinctly bounded crystals of cerussite. On the walls of cavities are small radiating tufts of indistinct crystals. Even on larger specimens of this character the crystals are much intergrown and very indistinct. Small tufts of more freely developed crystals of hemimorphite, about $\frac{1}{2}$ to 1 mm. in length, are thickly clustered on almost all the crystals of cerussite on those specimens in which the latter is distinctly crystallized. On one specimen, with crystals of cerussite, a loose, confused (not radiating) aggregate of minute crystals of hemimorphite had quite the appearance of drifted snow.

The crystals of hemimorphite are tabular in habit parallel to the brachypinacoid, and show the forms b {010}, m {110}, s {101}, and sometimes c {001}. In all cases the crystals are colourless and transparent.

Mamillated crusts of hemimorphite with a pale bluish tint also occur, but appear to be rare. Compact, dark-brown material mixed with much limonite, and sometimes containing a little phosphoric acid (probably as tarbuttite), was also represented in the various collections.

Crystals of hemimorphite belonging to a later period of growth also occur. For instance, minute rosettes of colourless or reddish hemimorphite crystals are sometimes to be seen on the larger crystals of tarbuttite; and a similar group was noted on a crystal of quartz. As mentioned above (p. 29), minutely crystallized hemimorphite occurs in the pseudomorphous crusts of tarbuttite after calamine.

Hemimorphite is also present in the crystallized crusts on the bones and on the bone-breccia in the cave in Kopje No. 1 (pp. 5, 38). On the bone-breccia, the lower part of the crust usually consists of finely fibrous hemimorphite, and amongst the minute ($\frac{1}{10}$ to $\frac{1}{4}$ mm.) crystals on the surface, pale yellowish crystals of hemimorphite were detected, together with crystals of tarbuttite and calamine (p. 30). Similar pale yellowish crystals were present in abundance on two of the bones examined: these crystals have not at all the appearance of hemimorphite, being quite short and of a thick-tabular, rhombic habit; further, they show no radial grouping, but are confusedly aggregated. On one of the larger of them, measuring about $\frac{1}{2}$ mm. across, the forms, as determined on the goniometer, are b {010}, m {110}, t {301}, h {021}.

CALAMINE.

Zinc carbonate appears to occur quite apart from the ordinary type of ore, no trace of it being detected in the mixture of hemimorphite and cerussite. It forms mamillated masses with a concentric structure and a smooth or indistinctly crystallized surface; the colour is white, pale yellowish, or brown. A mass weighing several hundredweights is exhibited in the Rhodesia Museum at the London offices of the British South Africa Company. Dark brown or dark grey, friable to compact masses, mixed with much limonite, also occur; and in one instance a light-grey marly material proved, on examination, to be calamine.

The mamillated calamine has been in many cases partially or completed altered to tarbuttite; and on the surface of this pseudomorphous material, either mixed with the tarbuttite crystals or resting on them, there is sometimes a later growth of a few small ($\frac{1}{2}$–1 mm.) crystals of calamine. These crystals are transparent with a pale yellowish colour; they are of an acute, spike-like habit, and their faces are rough and drusy. Goniometric measurement of one crystal proved the forms to be the scalenohedron v {$20\bar{1}$} = {$21\bar{3}1$} and the acute rhombohedron s {223} = {$05\bar{5}1$}; while on another measured crystal only s was developed.

HYDROZINCITE (?).

On the surface of those crusts of tarbuttite pseudomorphous after calamine which are intermixed with hemimorphite and calamine (p. 29) there are a few minute hemispherical masses which are white and earthy and quite soft. This material was found to contain zinc, carbonic acid, and water, and is therefore probably hydrozincite. It was the last

mineral to be formed. On the same specimen there is, however, an opaque, white crust, beneath the surface crystallized layer, which also contained zinc, carbonic acid, and water, together with some phosphoric acid; this is also possibly hydrozincite, but may be earthy calamine, mixed with tarbuttite or parahopeite.

CERUSSITE.

Cerussite not only forms a large part of the massive ore (p. 34) but is also of common occurrence in cavities of the ore as fine groups of magnificent crystals. Perfectly colourless and transparent crystals bounded by a profusion of brilliant faces reach a size of $1\frac{1}{2}$ cm.; while still larger crystals with a slightly yellowish tinge and drusy surfaces measure up to 7 cm. in length. These cerussite crystals are almost invariably encrusted with tufts of minute crystals of hemimorphite.

The crystals are elongated in the direction of brachyaxis a [100], and are either prismatic in habit, or are tabular parallel to the brachy-pinacoid b {010} or to the basal pinacoid c {001}. Twinning on m (110) is frequent, giving rise to the six-rayed groups of crystals so characteristic of cerussite. On one twinned crystal, consisting of two individuals, the following forms[1] were determined :—

$a\{100\}$, $b\{010\}$, $c\{001\}$; $m\{110\}$, $r\{130\}$; $y\{102\}$; $x\{012\}$, $q\{023\}$, $k\{011\}$, $i\{021\}$, $t\{061\}$; $p\{111\}$, $o\{112\}$; $s\{121\}$.

On another measured crystal the forms were $a\,b\,c\,m\,r\,y\,k\,i\,p$ and $z\,\{041\}$; and on a third $b\,c\,m\,y\,x\,i\,p\,o$.

A very curious and remarkable form of cerussite is represented by some short stalactitic growths, which, I am told, are being formed at the present day on the walls of the bone-cavern. One of these stalactites, which I examined, has a length of $2\frac{1}{2}$ inches and a diameter of $1\frac{1}{2}$ inch; and shows transverse corrugations or flutings on the surface. On the upper surface of these flutings there is a slight yellow stain of iron hydroxide, but the remainder of the stalactite is pure white, with somewhat the texture of snow. The material is loose and friable, and consists of an aggregation of minute crystals without any definitely orientated directions. When a fragment of the stalactite is crushed in oil and examined under the microscope, vast numbers of isolated crystals are seen. These have the form of short needles or rods, measuring about $\frac{1}{5}$ mm. in length and $\frac{1}{30}$ mm. in thickness, and extinguishing between crossed nicols parallel to their length. Sometimes, though rarely, the

[1] Letters and indices as in Dana's 'System of Mineralogy', 6th edit., 1892.

rods are arranged in stellate groups and show other indications of twinning. A chemical examination of the material proved it to be lead carbonate.

LIMONITE.

Limonite is of common occurrence with all the secondary minerals in Kopje No. 2. It forms cellular or stalactitic masses; it may be hard and dark brown in colour, or soft and ochreous. A bright yellow, ochreous deposit on the surface of some crystals of hemimorphite at first suggested cadmium-ochre (greenockite), but on examination it proved to be only limonite.

WAD.

A soft, powdery form of manganese oxide sometimes occurs as a thin coating on the mamillated surfaces of tarbuttite pseudomorphous after calamine ; so that the specimen as a whole rather resembles psilomelane. Very small nodular masses with a concentric shelly structure, and consisting of soft, black wad, occur in the limonite of one or two of the tarbuttite specimens.

QUARTZ.

The common mineral quartz is conspicuous by its rarity at this locality : only on three specimens was it detected. Silicate of zinc (hemimorphite) is, however, of abundant occurrence.

Small, rounded grains of yellowish quartz were found in a clayey matrix on one of the hopeite specimens. A crust of small quartz crystals (*m r z*), of a pale yellowish colour and transparent, is present on one of the descloizite specimens; at first sight this looked very like the crust of yellowish tarbuttite which is usually associated with descloizite. Small crystals of quartz were also found on the surface of a specimen of compact ferruginous hemimorphite; on the surface of one of the quartz crystals a small tuft of colourless crystals of a later growth of hemimorphite was noticed.

Flakes of opaque, white quartz, which have been worked by the hand of man, are found embedded in the bone-breccia of the cave.

GALENA.

A few specimens of galena in ordinary cleavage masses were seen. On one of them, small crystals of cerussite are attached. Mr. Franklin White mentions the occurrence of small nodules of galena embedded in the clay of the bone-cavern, and he expresses the opinion that they have been formed in situ (possibly by the reducing action of animal matter).

BLENDE.

Massive zinc-blende with yellow cleavage surfaces was seen embedded in pieces of a very fine-grained, crystalline limestone of a bluish-grey colour.

All the secondary zinc and lead minerals described above have without doubt resulted from the alteration of blende and galena, which as yet have been met with in only small quantities.

APPENDIX.

REPLACEMENT OF THE BONES BY ZINC AND LEAD MINERALS.

A few of the bones from the hopeite cave were examined to ascertain how far their material had been replaced by zinc phosphates. One bone, which showed no crystalline structure, was found to consist mainly of calcium phosphate and carbonate, with a little zinc and lead, and practically no organic matter: the specific gravity was about 2·85. Another bone, which had evidently been more altered and was thickly encrusted with minute crystals, both on the exterior and in interior cavities, was found to consist, in the compact portions, of calcium phosphate and carbonate with considerable amounts of zinc and lead: the specific gravity of the compact portion was in this case 3·25.

The crystallized crusts on and in the bones consist of very minute (about $\frac{1}{10}$ mm. across) crystals closely and confusedly aggregated; and it was not always possible to determine the mineral-species to which they belong. In similar crusts on the surface of the bone-breccia, hemimorphite, tarbuttite, hopeite, calamine, and vanadinite were determined. On one or two specimens, minute tufts of colourless, acicular crystals of hopeite were present in the cavities of bones and teeth. The larger and more distinctly developed crystals of hopeite are never in contact with the bones, but always separated from them by the crusts of hemimorphite, vanadinite, &c. In the crystallized crust on one bone minute yellowish crystals of tarbuttite (p. 31) were detected; and on two others yellowish crystals of hemimorphite (p. 35). Hemimorphite appears to be the most frequent of the crystallized minerals replacing the bones. Small bones projecting from the surface of the bone-breccia are sometimes completely enveloped by vanadinite (p. 33). This was the only lead mineral found in association with the bones, but it is probable that most of the lead which they contain is present as carbonate, though crystals of cerussite could not be detected.