

Cymrite, a new barium mineral from the Benallt manganese mine, Rhiw, Carnarvonshire.

(With Plate XXXV.)

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Occurrence and optical data (W. C. S.).

AMONG the specimens collected at the Benallt manganese mine in 1944 by Dr. A. W. Groves and myself was one (B.M. 1944,48) from the 60-foot level in no. 1 ore-body which showed on a face of dark, compact manganese ore colourless plates up to 7 mm. across and about $\frac{1}{2}$ mm. thick. These plates proved to be uniaxial and negative with perfect basal cleavage. Heated in an ignition tube the fragments decrepitated, gave off water, and became pearly, white, and opaque. Qualitative tests showed Ba, Al, and SiO_2 to be present. Preliminary X-ray photographs revealed hexagonal symmetry, but could not be matched with those of any known mineral.

Previously an unidentified white mineral had been noticed closely associated with ganophyllite in a specimen collected in 1944 by Dr. Groves from no. 5 ore-body (B.M. 1944,36). The mineral was first studied in thin section where it appears as a colourless mineral with a perfect and very closely spaced cleavage crossed at right angles by a fibrous structure and by a prismatic cleavage (Pl. XXXV, figs. 3-6). Elongation parallel to the fibrous structure and perpendicular to the perfect cleavage is negative, and birefringence moderate. Measurements on the universal stage indicate that the mineral is uniaxial or nearly so. Subsequently a few small white crystals of this mineral were found in cavities on the specimen. These crystals show a satiny lustre and fibrous structure parallel to their length which is crossed by very frequent basal cleavage cracks (pl. XXXV, fig. 3). The best of these little prisms appear to be hexagonal in form, but only two or three good crystals were found and these only about 1 mm. in length.

At first there seemed nothing to connect this mineral with the colour-

less plates from no. 1 ore-body, but when their refractive indices were found to be very close and their densities nearly equal it became a possibility that the two specimens represent different habits of the same mineral. This was promptly confirmed by an X-ray photograph of a small cleavage fragment from the no. 5 ore-body specimen (B.M. 1944,36).

Refractive indices determined by the immersion method for sodium-light are:

B.M. 1944,48: ω 1.6225, ϵ 1.6125, both ± 0.001 . Measurement of the birefringence on a single section whose thickness was accurately determined on the universal stage gave 0.0094 ± 0.0004 for sodium-light.

B.M. 1944,36: the fibrous crystals give lower values, ω 1.6195, ϵ 1.6115 to 1.6140, ϵ varying considerably for different fragments. The birefringence measured directly in white light is 0.008, which agrees with the difference between ω 1.6195 and the lower value of ϵ 1.6115. A single determination for ω (Hg-green) gave 1.624.

With some difficulty sufficient material for a microanalysis was obtained from the colourless plates taken from the specimen (B.M. 1944, 48) from no. 1 ore-body. Part of the face of the specimen carrying the new mineral was cut off closely parallel to the surface. Hand-picking, magnetic and heavy liquid separations, and final hand-picking provided small samples of material of three grades of purity. Two fractions were used for the analyses, one of 20 mg. which still retained a proportion of reddish-brown oxide minerals, and one of 7 mg. almost free from impurities.

The mineral has been named cymrite from the Welsh for Wales, *Cymru* (pronounced kumry).

Chemical analysis (M. H. H.).

Qualitative tests on a few crystals had shown that the mineral is essentially a hydrated aluminosilicate of barium, free from calcium, magnesium, or potassium, but probably containing some sodium; manganese and iron were present in the oxide impurities, but the qualitative analysis had suggested that neither of these was a constituent of the mineral. The quantitative analysis was therefore planned to determine SiO_2 , Al_2O_3 , BaO , MnO , Fe_2O_3 , Na_2O , and H_2O , but in the course of the analysis it became apparent that there was no sodium present, the positive qualitative reaction having been due to an impure sample of perchloric acid.

The less pure sample was divided into two portions. One was gently

ignited, then decomposed with perchloric acid; the filtrate from the silica was precipitated with a small excess of sulphuric acid, and the barium sulphate filtered off, ignited, and weighed; the filtrate was precipitated with 8-hydroxyquinoline (Al+Fe+Mn), and the weighed precipitate dissolved in nitric acid; after destruction of the organic matter, iron and manganese were determined colorimetrically in aliquot parts of this solution, the iron with sulphosalicylic acid and the manganese with periodate. The second portion was treated in the same manner as far as the barium sulphate precipitation, then the filtrate was evaporated to dryness and a sodium determination carried out, as sodium zinc uranyl acetate; sodium was found to be absent.

The purer sample was examined by the first method, but owing to the breakdown of a filter a satisfactory figure for the barium was not obtained, and this constituent is reported by difference.

The density was determined on four carefully selected fragments by suspension in Clerici solution. Owing to the small size of the clean fragments and to the difficulty of wholly eliminating both oxide inclusions and flaws tending to lower the density, the accuracy attained was only about 0.2 %.

TABLE I. Chemical analyses of Cymrite. Col. 1, percentage composition of the purer sample (7 mg.). Col. 2, percentage composition of the second-grade sample (20 mg.). Cols. 1a and 2a, molecular proportions corresponding to Cols. 1 and 2. Col. 3, calculated composition for the formula $\text{BaAlSi}_3\text{O}_8\text{OH}$. Col. 4, empirical unit-cell contents corresponding to Col. 1.

	1.	2.	1a.	2a.	3.	4.
SiO_2	44.8	37.65	0.746	0.627	45.79	2.99 Si
Al_2O_3	10.5	14.94	0.206	0.283	12.95	0.82 Al
BaO	[38.5]	31.50	0.251	0.205	38.97	1.00 Ba
H_2O	3.1	5.31	0.172	0.295	2.29	1.38 OH
Fe_2O_3	2.8	9.26	—	—	—	7.53 O
MnO	0.3	0.86	—	—	—	8.91 O + OH
	<hr/>	<hr/>			<hr/>	
	[100]	99.52	—	—	100.00	—
Sp. gr. (d_4^{16}) ...	3.413	—	—	—	3.46	—
	± 0.005				(calc.)	

X-ray measurements (F. A. B.).

Transparent cleavage flakes of B.M. 1944,48 identical with material used for optical and chemical work were oriented to give rotation and Laue photographs. They show that the mineral is hexagonal with six planes of symmetry parallel to the [0001] axis and the unit-cell dimensions given by rotation photographs about $[10\bar{1}0]$, $[11\bar{2}0]$, and $[0001]$ are $a' 5.33$, $c 7.67 \text{ \AA}$. using copper $K\alpha$ radiation $\lambda 1.5418 \text{ \AA}$. These values

together with the specific gravity and chemical analysis yield as unit-cell contents $\text{BaAlSi}_3\text{O}_8(\text{OH})$ (table I, col. 4).

Well-exposed rotation photographs of the mineral show, in addition to the main layer-lines, additional weak layer-lines that reveal a larger unit cell with $a = 8a' = 42.6 \text{ \AA}$. Additional layer-lines, however, are not found on corresponding photographs about the $[0001]$ axis. The weak layer-lines observed on both $[10\bar{1}0]$ and $[11\bar{2}0]$ photographs are satellites to the main layer-lines and not every level in the reciprocal lattice is represented. Each of the main layer-lines of oscillation and rotation photographs about the $[10\bar{1}0]$ is flanked on both sides by weak layer-lines, the observed sequence corresponding to a 42.6 \AA . being 0, 1, 7, 8, 9, 15, 16, 17, &c., those underlined being the equator, first and second layer-line corresponding to the pseudo-cell with $a' 5.33 \text{ \AA}$. Photographs about the $[11\bar{2}0]$ axis show the sequence 0, 1, 2-6, 7, 8, 9, 10-14, 15, 16, 17, 18, &c., corresponding to the cell dimension $\sqrt{3}a = 73.9 \text{ \AA}$. The larger unit cell appears therefore to possess hexagonal symmetry like the pseudo-cell.

X-ray powder data for the mineral are given in table II (pl. XXXV, fig. 1), and it is of interest that all the lines observed can be indexed with certainty with the exception of a very weak one at 2.11 \AA . which presumably is an extra reflection that can be referred to the true unit cell with $a 42.6 \text{ \AA}$. Only photographs of well-oriented single crystals reveal the extra spots of subsidiary layer-lines.

Subsidiary layer-lines corresponding to large unit-cell dimensions have also been observed by one of us for sartorite¹ and by S. H. Chao and W. H. Taylor² for intermediate members of the plagioclases close in composition to labradorite. It is, however, exceptional for the extra layer-lines to be restricted to weak 'ghosts' flanking the equator and main layer-lines of the pseudo-cell. The phenomenon can be resolved into a regular periodic variation of the atomic scattering factor with frequency corresponding to $8a'$ superposed upon the main pseudo-cell repeat of a' . The optical analogy has been already worked out with specially ruled diffraction gratings by Sir Lawrence Bragg and H. Lipson³ who were seeking an explanation of the 'ghosts' observed close to the main powder lines of the alloy Cu_4FeNi_3 .⁴

¹ F. A. Bannister, A. Pabst, and G. Vaux, *Min. Mag.*, 1939, vol. 25, p. 264.

² S. H. Chao and W. H. Taylor, *Proc. Roy. Soc. London, Ser. A*, 1940, vol. 176, p. 76. [M.A. 8-13.]

³ Sir Lawrence Bragg and H. Lipson, *Journ. Sci. Instruments*, 1943, vol. 20, p. 110 (see particularly figs. 5a and 5b, p. 112).

⁴ Vera Daniel and H. Lipson, *Proc. Roy. Soc. London, Ser. A*, 1944, vol. 181, p. 378.

TABLE II. X-ray powder data for cymrite (B.M. 1944,48)

 $a' 5.33, c 7.67 \text{ \AA.}$ (pseudo-cell).

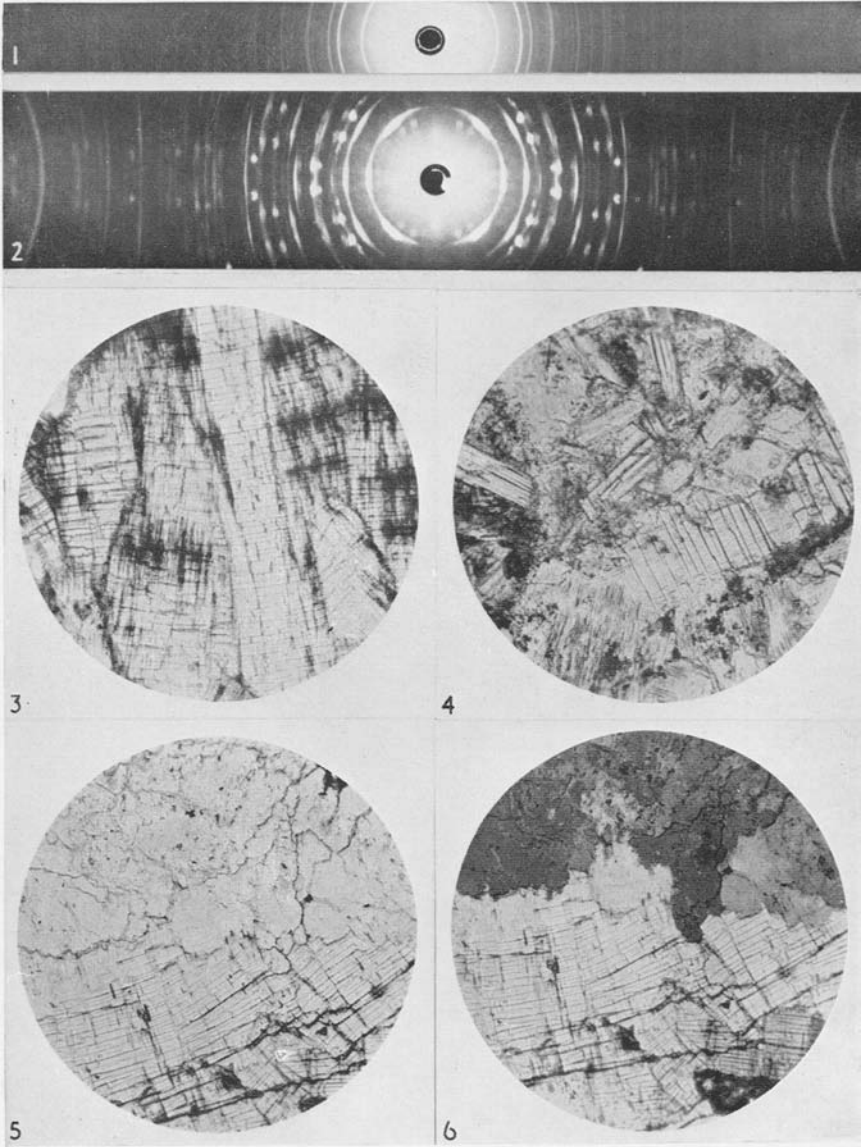
2 θ . cm.	Inten- sity.	Spacing		Index.	2 θ . cm.	Inten- sity.	Spacing		Index.
		Obs. \AA.	Calc. \AA.				Obs. \AA.	Calc. \AA.	
1.20	s	7.7	7.67	0001	6.24	w	1.544	1.539	30 $\bar{3}0$ }
2.00	vw	4.6	4.62	10 $\bar{1}0$	—	—	—	1.534	0005 }
2.35	vs	3.95	3.96	10 $\bar{1}1$	6.64	w	1.468	1.472	10 $\bar{1}5$ }
3.16	vs	2.95	2.95	10 $\bar{1}2$	6.72	vw	1.452	1.441	21 $\bar{3}3$ }
3.50	s	2.67	2.67	11 $\bar{2}0$	7.32	vw	1.341	1.333	22 $\bar{4}0$ }
3.64	vw	2.57	2.56	0003	7.45	vw	1.324	1.319	30 $\bar{3}3$ }
3.70	vw	2.53	2.52	11 $\bar{2}1$	7.73	w	1.283	1.280	3140 \dagger }
4.06	w	2.32	2.31	20 $\bar{2}0$	—	—	—	1.278	0006 }
4.20	m	2.24	2.24	10 $\bar{1}3$	—	—	—	1.277	20 $\bar{2}5$ }
4.25	m	2.21	2.21	20 $\bar{2}1$ }					
—	—	—	2.19	11 $\bar{2}2$ }					
4.46*	vw	2.11	—	—	8.05	vw	1.236	1.233	10 $\bar{1}6$ }
4.76	w	1.990	1.978	20 $\bar{2}2$	8.19	vw	1.219	1.214	31 $\bar{4}2$ }
4.94	mw	1.920	1.918	0004	8.31	vw	1.206	1.200	30 $\bar{3}4$ }
5.14	m	1.849	1.845	11 $\bar{2}3$	8.74	w	1.155	1.154	4040 \dagger }
5.35	vw	1.783	1.772	10 $\bar{1}4$	—	—	—	1.153	11 $\bar{2}6$ }
5.60	mw	1.705	1.701	21 $\bar{3}1$	8.80	vw	1.149	1.152	21 $\bar{3}5$ }
6.04	mw	1.594	1.588	21 $\bar{3}2$	9.02	vw	1.126	1.119	20 $\bar{2}6$ }
6.15	w	1.565	1.557	11 $\bar{2}4$	9.34	vw	1.096	1.096	0007 }
—	—	—	—	—	—	—	—	1.094	2244 }

* An extra reflection from the large unit cell.

 \dagger Spots corresponding to these indices are either very weak or cannot be observed on rotation photographs of cymrite about $[10\bar{1}0]$, $[11\bar{2}0]$, and $[0001]$.

The above data were obtained from an X-ray photograph of powdered cymrite taken with filtered copper radiation $\lambda 1.5418 \text{ \AA.}$ in a cylindrical camera 6 cm. diameter. Relative intensities are given as vs very strong, s strong, ms medium strong, m medium, mw medium weak, w weak, vw very weak, vvv very very weak.

The chemical composition, unit-cell dimensions, and powder data distinguish the new mineral from all other known barium aluminosilicates: celsian, paracelsian, hyalophane, and the recently described barium-felspar banalsite, from the same locality. The pseudo-cell edge $a' 5.33 \text{ \AA.}$ closely approaches, however, the values of a for certain other substances that crystallize with hexagonal symmetry, particularly barium aluminate BaAl_2O_4 , $a 5.21, c 8.76 \text{ \AA.}$; kalsilite KAlSiO_4 , $a 5.17, c 8.76 \text{ \AA.}$; and β -tridymite, $a 5.03, c 8.22 \text{ \AA.}$ The c dimension of the new mineral is, however, 7.67 \AA. and possibly results from a linking of SiO_4 tetrahedra by edges along the $[0001]$ axis, whereas in all three above-mentioned substances the AlO_4 and SiO_4 tetrahedra have their bases parallel to (0001) . Moreover, no halvings have been observed for X-ray diffractions from single crystals of cymrite, whereas the odd orders from (0001) are missing both for barium aluminate and kalsilite. The new



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mineral has therefore a new crystal-structure probably of a very simple framework type which it is hoped to publish in the near future.

Some X-ray photographs of single-crystal flakes of the mineral before and after heating to known temperatures were also taken to study further the property of decrepitation on heating, already referred to. The white, opaque plates obtained by heating the mineral in a bulb-tube revealed a polycrystalline texture. Each one yields a flecked powder photograph with sharp well-defined (0001) spectra but with all other spots considerably broadened (Pl. XXXV, fig. 2). A single crystal plate heated to 500° C. for three hours still yields single crystal photographs with a small degree of smearing of the spots into powder lines. This heated material had a lower refractive index of 1.61. A single crystal heated to 700° C. for six hours decrepitated into a large number of very thin flakes with n 1.53. Each flake still gives single-crystal diffractions after long exposures and it seems probable that the polycrystalline plates (pl. XXXV, fig. 2) result from a shattering with evolution of water vapour into a large number of subparallel flakes.¹

The chemical analyses are not as good as could be desired, but even with a very wide allowance for analytical error the contents of the pseudo-cell, if integral, cannot be other than $\text{BaAlSi}_3\text{O}_8\text{OH}$. The true cell has a volume 64 times that of the pseudo-cell, and it is possible that this longer periodicity may be associated with a small departure from the simple chemical formula; but the subsidiary layer-lines are so weak that any such departure must be quite small, and it is possible that they may be accounted for by a distinction between O and OH.

EXPLANATION OF PLATE XXXV.

X-ray photographs and photomicrographs of cymrite.

- FIG. 1. Powder photograph of cymrite (table I) taken with filtered copper radiation in a cylindrical camera, 6 cm. diameter. (B.M. 1944,48.)
 FIG. 2. X-ray photograph of cymrite after heating, taken with unfiltered copper radiation. (B.M. 1944,48.)
 FIG. 3. Thin section of specimen from no. 5 ore-body, Benallt mine (B.M. 1944,36), showing basal and prismatic cleavage and opaque oxides. $\times 70$.
 FIG. 4. Thin section of the same specimen showing basal cleavage and vertical fibre or cleavage lines. Ganophyllite in the upper half. $\times 70$.
 FIG. 5. Thin section of the same specimen showing closely spaced basal cleavage and, in the upper half, an approximately basal section. $\times 70$.
 FIG. 6. The same field seen between crossed nicols. $\times 70$.

¹ Flakes after heating to bright redness have n 1.523, a 5.29, c 7.78 Å.; an example of a small change in crystal-structure without change in cell-volume.