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### *Banalsite, a new barium-felspar from Wales.*

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(With Plate IV.)

[Read November 4, 1943, and June 8, 1944.]

IN 1941 the Home Ore Department of Iron and Steel Control, Ministry of Supply, took over the old Benallt manganese mine at Rhiw in the Llyn Peninsula, Carnarvonshire. A new shaft was sunk and a new mine was developed among and mainly below the old workings. It was in one of the old workings of Benallt that Mr. (now Sir) Arthur Russell discovered in 1911 the well-crystallized specimens of celsian and paracelsian recently described by Dr. L. J. Spencer.<sup>1</sup>

Dr. A. W. Groves of the Mineral Resources Department of the Imperial Institute and geologist to the Home Ore Department had had a sharp look-out kept for the reappearance of the barium-felspars in the new workings, and when thin bands of coarsely crystallized but compact, white 'sparry' minerals were found in one of the ore-bodies he sent specimens to the Department of Mineralogy of the British Museum for investigation. His watchfulness for the rare minerals was well rewarded, for the bulk of the white mineral in the specimens he sent proved to be indeed a barium-felspar, but differing quite definitely from any known barium-felspar, and it is in fact a new mineral of very considerable interest.

The name proposed for this mineral is *banalsite*, suggested by its chemical formula  $\text{BaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$ . It is the first example of an aluminosilicate of barium containing sodium as the dominant alkali. Though chemically related to the felspars, X-ray photographs show that its symmetry is orthorhombic. The space-group is either *Iba* or *Ibam*, with cell dimensions,  $a$  8.50,  $b$  9.97,  $c$  16.73 Å., from which may be calculated the axial ratios  $a : b : c = 0.853 : 1 : 1.678$ . The density, corrected for included water and in vacuo, is 3.065, from which the cell contents are calculated to be  $4[\text{BaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}]$ .

The specimens in which the new mineral was discovered came from ore on the foot-wall side of no. 1 ore-body by no. 1 Chute, 50–60 feet west of the main shaft and some 10–20 feet above the 130-foot level. These were found in July 1943.

<sup>1</sup> L. J. Spencer, *Min. Mag.*, 1942, vol. 26, pp. 231–245.

Since then some further specimens have been found forming a thin layer between the 'bedding planes' of no. 2 ore-body towards the foot-wall side. This ore-body lies 40 to 80 feet west of the Court shaft, and dips east at about  $60^\circ$ .

In the original find the material containing the minerals forms a band 1.5 cm. thick, compact and rather coarsely crystalline, traversing dark, spotted manganese ore. Less distinct, narrow, white veins parallel to the main band impregnate the ore for a further thickness of 1–2 cm. and then die out, successive veinlets getting thinner as their distance from the main 'vein' increases.

The main 'vein', broken parallel to its contact with the ore, consists of a compact aggregate of crystals of the new mineral associated with calcite, a few very small patches of baryte, and criss-crossed by dark, narrow, blade-like crystals of tephroite and alleghanyite up to 2 cm. in length and varying in thickness from 2 mm. down to microscopic dimensions.

Included within the 'vein' minerals are some small angular fragments of opaque, black, magnetic ore which prove to be rich in manganese and which are identified from X-ray powder photographs as jacobsite. Small interstices and minute veins are filled by zeolitic material consisting of natrolite with a second zeolite not certainly identified.

The calcite is irregularly distributed. In parts of the specimens it forms visible crystal plates, but in other parts may be found only filling interstices between edges of crystals of the new mineral, which it appears to be partly replacing. Baryte was observed only under the microscope in thin section as relics of a crystal plate surrounded and perhaps partly replaced by calcite. In specimens from the second find mentioned above baryte is quite abundant both as vein material and as a very thin crystallized crust.

Banalsite is pure white in colour and translucent to transparent in thin flakes. On broken surfaces, cleavages show a good pearly lustre and are traversed by fine lines, which are the traces of a second cleavage at right angles to the first. Individual crystal plates, traversed by blades of tephroite and alleghanyite, occasionally measure 1 cm. across, but for the most part they are much smaller (pl. IV, fig. 1). They show no twinning. Minute cavities, many showing a gas bubble and therefore doubtless liquid-filled, are very numerous. It is on account of these that a water determination was made on the second sample analysed and the density was corrected for included liquid. The abundance of these inclusions causes some of the specimens to be opaque and milky in appearance.

The only crystals which were found to show indications of faces were two seen in thin sections. These were measured on the universal stage and the positions of the faces with relation to the principal vibration-directions were plotted and compared on a stereographic projection with the positions of the poles of possible faces of the mineral calculated from the axial ratios obtained by X-ray measurement.

In one crystal three edges are the traces of (110), (112), and (001). The faces (110) and (001) are both parallel to good cleavages. In the second crystal (110) is again represented and is parallel to a cleavage: two other edges correspond very well with (121) and ( $\bar{1}21$ ), a third is clearly (212), and a very narrow face is much less confidently identified as ( $5\bar{1}2$ ).

The only other indications of crystal form are rather well-marked planes of black dusty inclusions which are quite commonly seen within the irregular

boundaries of crystals of the new mineral in fine-grained veins which traverse the ore (fig. 1A). The orientation of these planes in several of the crystals was determined on the universal stage, and comparison with the stereographic projection (fig. 1B) showed that they correspond to planes with indices:

- Crystal 1: (121), (212), ( $2\bar{1}2$ ), and ( $0\bar{1}1$ ).  
 ,, 2: (001), (112), (110), and a steep pyramid, possibly (342).  
 ,, 3: (111), ( $1\bar{1}1$ ).  
 ,, 4: (012), ( $0\bar{1}2$ ).

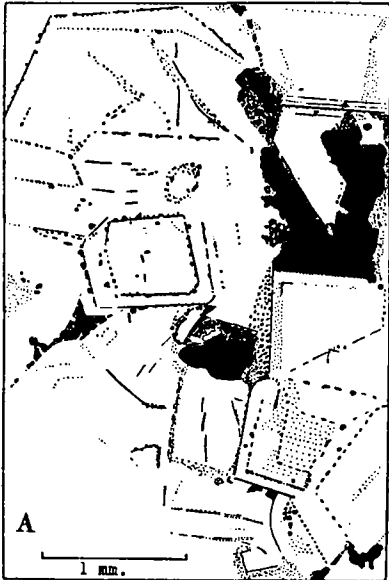


FIG. 1A

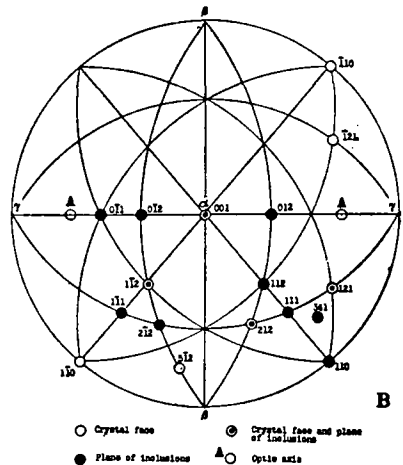


FIG. 1B

FIG. 1A. Thin section of aggregate of banalsite crystals showing zonal inclusions. The black areas are manganese ore.

FIG. 1B. Stereographic projection of the crystal-forms and optical orientation of banalsite. (341 in error for 342.)

The cleavages are identified as (110) and (001). The prismatic cleavage seems to be the easier to produce of the two, but it has been noted that in thin section very few crystals indeed develop the cleavages parallel to both the faces of the prism. This general tendency for only one of the two prismatic cleavages to appear gave a false impression that extinction-angles were inclined to the prominent crystallographic planes and masked the orthorhombic symmetry until this was revealed by the X-ray study.

The optical orientation and value of the optic axial angle have been determined by numerous measurements on the universal stage which gave:

$$\alpha = c, \beta = a, \gamma = b. \quad 2V \ 41^\circ \pm 3^\circ, \text{ positive.}$$

The angle between the cleavage (110) and  $\gamma$ , the acute bisectrix, is found to be

50°, agreeing within half a degree of the value, 49° 32', calculated from the cell dimensions.

The refractive indices were measured by the Becke method using a sodium-light lamp. The immersion liquid was changed until the closest possible agreement in refractive index was obtained, and the index of the liquid was measured on a Bellingham & Stanley standard refractometer standing beside the microscope. The objective used was Leitz 3, N.A. 0.25,  $\times 10$ . Measurements were made on each of the two specimens of the mineral which had been used for chemical and X-ray analysis. All (110) cleavages give  $\alpha$ , but only (001) cleavages give  $\gamma$  and  $\beta$ , and this proved to be a difficult cleavage to obtain in fragments suitable for refractive index measurements. Only one set of readings was obtained for  $\beta$ , and this is not considered satisfactory. The average values of the refractive indices obtained at 16–17° C. were:

$$\alpha 1.5695, \beta 1.5710, \gamma 1.5775, \text{ all } \pm 0.0005.$$

The value of  $\beta - \alpha$  calculated from the mean value of 2V, 41°, and of  $\gamma - \alpha$ , 0.008, is 0.001, giving  $\beta 1.5705$ .

The mineral is decomposed by HCl (1 : 1) leaving a colourless residue. The hardness is 6.

TABLE I. Physical properties of barium-felspars compared.

	Hyalophane C, Kaso mine. (Yosimura)	Hyalophane A, Kaso mine. (Yosimura)	Hyalophane, Jakobsberg. (Strandmark)	Banalsite, Wales.	Kasoite, Kaso mine. (Yosimura)	Celsian, Jakobsberg. (Strandmark)	Celsian, Wales. (Spencer)	Paracelsian, Wales. (Spencer)
BaO %	7.60	9.02	12.4	21.99	25.50	36.45	38.94	38.53
Na <sub>2</sub> O %	0.98	1.72	1.5	8.43	1.85	0.77	nil	0.15
K <sub>2</sub> O %	8.80	6.35	9.9	0.66	5.10	0.22	0.18	0.54
Sp. gr.	2.78	2.78	2.756	3.065	3.003	3.384	3.31	3.29
$\alpha$	1.538 <sub>0</sub>	1.537 <sub>8</sub>	...	1.5695	1.564 <sub>4</sub>	1.5835	1.580	1.5702
$\beta$	1.542 <sub>0</sub>	1.542 <sub>5</sub>	...	1.5710	1.568 <sub>8</sub>	1.5886	...	1.5824
$\gamma$	1.544 <sub>5</sub>	1.546 <sub>0</sub>	1.5426	1.5775	1.572 <sub>0</sub>	1.5941	1.590	1.5869
2V	75.0°	75.5°	77.5°	41°	80.5°	86° 22'	near 90°	50° 35'
Sign	negative	negative	...	positive	negative	positive	positive	negative

T. Yosimura, Journ. Fac. Sci. Hokkaido Univ., Ser. 4, 1939, vol. 4, pp. 378, 381. [M.A. 7-412.]

J. E. Strandmark, Geol. För. Förh. Stockholm, 1903, vol. 25, pp. 298-316; 1904, vol. 26, p. 110.

L. J. Spencer, Min. Mag., 1942, vol. 26, pp. 235, 236, and 240.

#### *Composition and unit-cell contents of banalsite.*

Chemical analyses were made of two specimens of banalsite; the first (I) intimately associated with alleghanyite, tephroite, and calcite, was purified by hand-picking, magnetic treatment (the alleghanyite and tephroite are readily attracted by the electro-magnet), flotation with methylene iodide and then with bromoform, extraction with dilute (3 %) acetic acid, and a final hand-picking; the second specimen (II) was part of a cleavage mass, and after removal of manganese oxides by hand-picking was examined microscopically and found to be pure apart from abundant liquid inclusions. Impurities in both specimens (apart from water) are estimated at less than 1 %.

The analyses were made on samples of 20-40 mg. by standard microchemical methods and presented no special difficulties. The portion used for alkalis gave a check determination of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ; in table II, the means of these are given, with the individual determinations below.

The densities of both specimens were determined by the flotation method on the powder used for the analysis; that of the second sample has been corrected for the water found on analysis, but that of the first sample could not be so corrected and is probably low by about 0.02.

The unit-cell contents are given in columns Ia and IIa together with their maximum probable errors. It will be seen that they lead unambiguously to an ideal repeat of  $\text{Ba}_4\text{Na}_3\text{Al}_{16}\text{Si}_{16}\text{O}_{64}$ , with a small but distinct replacement of Si by Al, of Al by Mg, of Na by K, and of Na and Ba by Ca; these substitutions are distinctly greater than the most probable analytical error, though the substitution of Mg for Al is just less than the maximum probable error. It may be noted that while calculation as empirical unit-cell contents, with due allowance for probable error, gives the most positive proof of isomorphous replacements, it is not a very sensitive method for the detection of small, probable replacements; for that purpose, calculations to an assumed integral basis are better suited.

TABLE II. Chemical analyses and unit-cell contents of banalsite. (Analyst, M. H. Hey.)

	I.	II.	Ia.		IIa.		Ideal.	
$\text{SiO}_2$ ...	35.75	34.74	Si ...	$15.4 \pm 0.7$	} 31.1	$15.2 \pm 0.6$	32.0	16
$\text{Al}_2\text{O}_3$ ...	29.13	31.20	Al ...	$14.8 \pm 0.7$		$\pm 1.1$	$16.1 \pm 0.6$	$\pm 1.0$
BaO ...	22.73	21.99	Mg ...	0.7		0.7		—
CaO ...	1.76	0.81	Ba ...	$3.8 \pm 0.2$	} 12.6	$3.8 \pm 0.2$	} 11.7	4
MgO ...	1.11	1.00	Ca ...	0.7		0.7		—
MnO ...	0.28	0.03	Mn ...	0.1	$\pm 0.7$	0.01		—
$\text{Na}_2\text{O}$ ...	8.92	8.43	Na ...	$7.5 \pm 0.6$		$7.1 \pm 0.6$	$\pm 0.7$	8
$\text{K}_2\text{O}$ ...	0.75	0.66	K ...	0.4		0.4		—
$\text{H}_2\text{O}$ ...	n.d.	1.08	O ...	$62.4 \ddagger$		$63.2 \pm 1.2$		64
	100.43	99.94						

$$D_4^{\text{I}} 3.027 \pm 0.015^* \quad 3.065 \pm 0.005^\dagger$$

Individual determinations in analysis I,  $\text{SiO}_2$  35.58, 35.93,  $\text{Al}_2\text{O}_3$  28.78, 29.48,  $\text{Na}_2\text{O}$  8.90, 8.95; analysis II,  $\text{SiO}_2$  34.11, 35.38,  $\text{Al}_2\text{O}_3$  31.14, 31.26,  $\text{H}_2\text{O}$  1.12, 1.05. \* Not corrected for included water and probably low. † Corrected for water present as inclusions. ‡ Limits, 61.1 to 64.2.

Calculation of the effect on the repeat of a given analytical error is quite a simple matter, but has rarely been attempted, though it is very desirable in tracing isomorphous substitutions of small extent. With essential constituents it is quite straightforward, but where the analytical error may concern an impurity (as in the present instance, absorbed water), it must not be forgotten that the density will be affected, and through it all the unit-cell contents. The necessary calculations have been made for the analyses of banalsite, assuming a possible error of  $\pm 0.5\%$  in the  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , BaO, and  $\text{Na}_2\text{O}$ , and  $\pm 0.2\%$  in the  $\text{H}_2\text{O}$  of analysis II. These figures are probably considerably in excess of the true errors, at least so far as the better analysis (II) is concerned, but it appears best to allow a liberal margin of error. Since water was not determined in analysis I, it is necessary to assume that as much as 1% might have been present. To these analytical errors, which amount to  $\pm 0.9\%$  on the oxygen in analysis II, and

+1.5 to -0.7 % in analysis I, must be added the physical errors in the cell sides and in the density determination (as distinct from the uncertainty in the density correction due to possible error in the water determination): these may amount to  $\pm 1$  % in all constituents in analysis II, and  $\pm 1.3$  % in analysis I. It should be noted that the analytical errors cannot be simply summed, since a loss of  $x$  % of  $A$  causes an apparent increase in the numbers of every other atom in the repeat, and the error in, for example (Si+Al+Mg), is less than the sum of the individual errors.

### *X-ray examination of banalsite.*

It has already been shown that the chemical composition, specific gravity, and optical properties distinguish banalsite without difficulty from the barium-felspars and establish its claim to rank as a new species. An X-ray study was undertaken first of all to determine the symmetry, unit-cell dimensions, and atomic contents, and also to investigate the relationship of banalsite to the felspars.

Cleavage fragments of the mineral selected for optical work yielded two specimens suitable for X-ray photographs. One could be set with the direction of the obtuse bisectrix vertical and the other with the obtuse bisectrix parallel to the X-ray beam. Laue photographs revealed orthorhombic symmetry, the first showing one horizontal plane of symmetry perpendicular to the direction of the obtuse bisectrix, and the second two planes of symmetry at right angles (pl. IV, fig. 2). These photographs were then used to set the fragments for rotation photographs about the three axes  $a$ ,  $b$ , and  $c$  in turn which yielded approximate unit-cell dimensions and served to fix the orientation of the optical indicatrix (fig. 1B). A series of oscillation photographs was next indexed completely. All the diffractions observed obeyed the conditions  $(h+k+l)$  always even;  $(hk0)$  only for  $(h+k)$  even;  $(h0l)$  only for  $h$  even and  $l$  even;  $(0kl)$  only for  $k$  even and  $l$  even. Banalsite therefore possesses a body-centred lattice and may belong to either of the two space-groups  $C_{2v}^{21} = Iba$  or  $D_{2h}^{26} = Ibam$ . Using the higher orders of  $(h00)$ ,  $(0k0)$ , and  $(00l)$  indexed on oscillation photographs, the unit-cell dimensions were found to be  $a$  8.50,  $b$  9.97,  $c$  16.73 Å. The rotation and oscillation photographs about the  $c$ -axis possess weak, odd-number layer-lines with relatively few spots, thus indicating a pseudo-cell of half the size, but possessing the same space-group symmetry.

At first sight there was no very obvious relationship between the unit cells of banalsite and the felspars. In the plagioclase series it is the 7.2 Å. axis which is doubled for the more calcic members. If banalsite is built up on a similar tetrahedral framework then probably the axis 16.73 Å. is the direction of the continuous four-ring chains; in other words, the  $c$ -axis of banalsite corresponds to the  $a$ -axis of sanidine.

In discussing the crystal-structure of sanidine, Taylor<sup>1</sup> makes use of an alternative face-centred unit cell  $a' = [102]$  13.2,  $b' = [010]$  12.9,  $c' = [\bar{1}00]$  8.4 Å.;  $\beta$  100°. A cell of similar dimensions can be derived for banalsite in which  $a' = [110]$  13.1,  $b' = [1\bar{1}0]$  13.1,  $c' = \frac{c}{2}$  8.37 Å.;  $[110] [1\bar{1}0] = 99^\circ$ . This cell, like the larger sanidine cell, would be all face-centred. This dimensional relationship probably indicates the similarity of the silicon-aluminium-oxygen network in the

<sup>1</sup> W. H. Taylor, *Zeits. Krist.*, 1933, vol. 85, pp. 425-442. [M.A. 5-473.]

two structures. A complete crystal-structure investigation would be necessary to confirm this and to discover the positions of the barium and sodium atoms.

During the course of the chemical analyses by Dr. Hey, samples of both specimens that he analysed were submitted for powder photographs. Table III gives the list of spacings and relative intensities.

TABLE III. X-ray powder data for banalsite. Spacings in Ångström units and estimated intensities. Taken with unfiltered copper radiation  $\lambda$  1.539 Å. in  $\frac{1}{2}$  cylindrical camera, 6 cm. diameter.

6.38	w	2.63	w	1.761	w	1.247	vw
5.64	vw	2.54	m	1.699	m	1.215	vw
5.00	m	2.43	w	1.628	w	1.163	vw
4.21	m	2.36	w	1.588	w	1.096	w
3.77	m	2.28	w	1.546	m	1.074	vw
3.49	s	2.15	m	1.468	mw	1.053	w
3.18	s	2.07	s	1.427	m	1.044	vw
3.06	w	1.983	w	1.391	m (doublet)	1.032	vw
2.98	m	1.948	w	1.343	w		
2.88	m	1.888	w	1.318	w		

#### ASSOCIATED MINERALS.

The chief interest in the associated minerals attaches to the tephroite and alleghanyite. Before describing these in detail a brief account must be given of the second find of banalsite near the foot-wall of no. 2 ore-body referred to above. Here the banalsite is found occurring in thin, flat slabs no more than a centimetre thick. The banalsite is white and opaque; it is associated with baryte in small amount and includes a few small crystals of tephroite. The flat slabs are in places encrusted with a thin, cream-coloured coating on which are minute crystals of baryte and also harmotome, the latter as crystals only 0.03 mm. across. This thin crust is again coated with a film of botryoidal psilomelane, and beads of psilomelane are seen on some of the minute baryte crystals. Specimens found in the same ore-body in November 1943 show a mineralized band in which cleavage plates of baryte pervade the ore. Some pearly cleavages of banalsite can be detected among the baryte crystals and a thin section shows a granular aggregate of banalsite, baryte, and calcite distributed through and including patches of opaque manganese ore with much brown mica and small crystals of tephroite. All the colourless minerals contain abundant hair-like crystals which have not been identified, and both the baryte and banalsite contain abundant liquid inclusions, many of which contain gas bubbles. Flanking the zone with the coarsely crystallized baryte the ore contains several bands 1-2 mm. wide which consist mainly of crystals of tephroite with some banalsite and much opaque ore and brown mica. The tephroite of these bands shows frequent intergrowths of alleghanyite, though less well-developed than in the original specimen. The ore associated with these specimens is dark purplish-brown. Close to the baryte band it is not magnetic, but at 3 cm. from this, where the narrow bands of tephroite are found, it strongly attracts the compass needle.

*Jacobsite*.—In the first specimens received the magnetic property possessed by certain bands and small patches of the ore has been traced definitely to some black, angular patches included in the white minerals of the main 'vein'. Some of the inclusions are 1 cm. in length. The mineral is opaque, streak dark-brown,

strongly ferromagnetic, hardness <6. Material separated with a bar magnet contains much manganese and less iron. The powder photograph of this material taken with iron radiation was indexed as a cubic pattern with unit-cell edge  $a$  8.51 Å. None of the lines shows any departure from a cubic lattice, and the pattern is definitely of the spinel type and distinct from that of hausmannite. The unit-cell dimension of artificial  $\text{MnFe}_2\text{O}_4$  was found by Holgersson<sup>1</sup> to be 8.57 Å., a value not greatly in excess of ours for the Benallt mineral. Moreover, Mason gives eight measurements of the jacobsite phase in vredenburgites from Sweden and India, ranging from 8.48 to 8.50 Å. Since our photograph does not reveal lines of the hausmannite phase we can with some certainty compare our specimen with that from Långban, Sweden, which he describes<sup>2</sup> as containing 55.9 %  $\text{Mn}_3\text{O}_4$ . It is of interest in the absence of a chemical analysis not only to compare the X-ray data, but also to comment on Mason's measurements of magnetic susceptibility on artificial preparations of  $\text{Fe}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4$ . He found that susceptibility increases with increase in  $\text{Fe}_3\text{O}_4$  and that 'the degree of ferromagnetism just begins to decrease rapidly below a content of 40 %  $\text{Fe}_3\text{O}_4$ '.

Jacobsite has not previously been recorded from the British Isles. Its presence with the tephroite and alleghanyite may give an indication of the conditions under which these minerals have been formed from the original manganese ore.

*Biotite*.—A dark-brown mica occurs in the specimens from no. 1 ore-body. The crystals are very small (0.2 mm.). In thin sections they are seen bordering and partly enclosing crystals of tephroite and alleghanyite and also as a border to some of the patches of black magnetic 'ore' (jacobsite). The optical properties are: biaxial, negative,  $2E$  approx.  $16^\circ$ ; pleochroism not strong,  $\alpha$  orange-rufous,  $\beta = \gamma$  burnt Siena (Ridgway), absorption  $\alpha < \beta = \gamma$ ; refractive indices  $\beta$  and  $\gamma$   $1.664 \pm 0.002$ . The refractive index was measured approximately by the Becke line method. The value obtained indicates a biotite high in ferric iron and one would expect a certain content of manganese oxides. The refractive index for  $\beta$  and  $\gamma$  is higher than for recorded manganophyllites and the absorption is normal for biotite, whereas for most manganophyllites the absorption is recorded as  $\alpha > \beta = \gamma$ . However, Dana, quoting Hamberg, notes that in some manganophyllites which contain most manganese the absorption is that normal for biotite, namely,  $\alpha$  red-brown,  $\beta$  and  $\gamma$  dark brown, so that the optical properties recorded may be consistent with a high manganese content.

The ore adjoining the tephroite veins in the specimens from no. 2 ore-body contains a paler brown mica, appearing as flakes and as radiating sheaves of flakes seen on edge. The absorption is  $\alpha > \beta = \gamma$ , the pleochroism being  $\alpha$  amber-brown,  $\beta = \gamma$  light orange-yellow. This second mica resembles in this particular the manganophyllites from Långban described by J. Jakob.<sup>3</sup>

*Tephroite and Alleghanyite*.—The blade-like crystals already referred to as a conspicuous constituent of the specimens from no. 1 ore-body consist of two minerals, one olive-green in colour, the other clove-brown. Both minerals form individual crystals and material for their separate examination could be picked out under a hand-lens, but for the most part they are either in parallel superposition or form composite crystals. Often plates of the brown mineral lie parallel

<sup>1</sup> S. Holgersson, Lunds Univ. Årsskrift, 1927, vol. 23, no. 9.

<sup>2</sup> B. Mason, Geol. Förh. Stockholm, 1943, vol. 65, p. 152. [M.A. 9-32.]

<sup>3</sup> J. Jakob, Zeits. Krist., 1925, vol. 61, p. 158.



to the tabular face of the olive-green one, while cross-sections under the microscope show brown crystals with pale-green terminations, or, on the other hand, the green blades crossed at right angles by lamellae of the clove-brown mineral.

The olive-green mineral is tephroite. In thin crystals it is transparent, pale olive-green in colour, and feebly pleochroic with absorption  $\alpha > \beta$ . Refractive indices  $\alpha < 1.778$ ,  $\beta$  and  $\gamma > 1.778 < 1.84$ . Measurements of birefringence made on a thin crystal of nearly uniform thickness and by universal stage methods on a thin section gave  $\beta - \alpha 0.026$ ,  $\gamma - \beta 0.014 \pm 0.001$ . The optic axial angle estimated from measurements on rather awkwardly placed sections gave two values for  $2V$ ,  $60^\circ$  and  $72^\circ$ , too far apart to be of more than qualitative value.<sup>1</sup> The optic sign is negative.

As regards crystal habit the long edges of the blade-like crystals, seen in thin section, are parallel to the  $c$ -axis, and the tabular face is (100) and is deeply striated owing to oscillatory combinations of faces of the prism zone.

Optical properties and a qualitative chemical analysis indicated that the mineral was tephroite, and Dr. Brian Mason confirmed this identification by means of an X-ray powder photograph which proved to be identical with the standard one of tephroite from Pajsberg, Sweden. Rotation photographs of a single crystal of the Benallt mineral yielded the unit-cell dimensions  $a 4.90$ ,  $b 10.60$ ,  $c 6.25 \pm 0.02 \text{ \AA}$ . The axial ratios calculated from these measurements are  $a : b : c = 0.462 : 1 : 0.590$ , agreeing closely with those for tephroite given by Hj. Sjögren (1883). Rotation and oscillation photographs were indexed and the space-group found to be  $D_{2h}^{16} = Pnma$ , the same as that of olivine with which tephroite is isostructural.

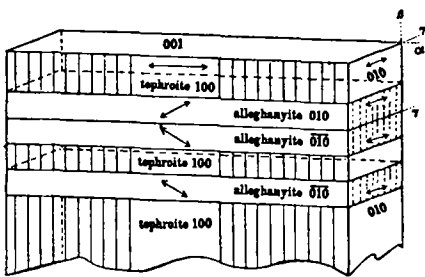
The clove-brown, blade-like crystals closely associated with the tephroite are identified as alleghanyite, though they differ from the mineral of the type locality in colour and in containing a considerable content of titanium. The identification of this mineral is due to Dr. Brian Mason. The qualitative chemical analysis showed it to be a titaniferous silicate of manganese. No titanium-rich manganese silicate was known, but the X-ray powder photograph was recognized by Dr. Mason as identical with that published by C. S. Ross and P. F. Kerr<sup>2</sup> in 1932 for the new mineral alleghanyite from Bald Knob, Alleghany County, North Carolina. This identification is confirmed by the optical properties and later chemical analyses and X-ray photographs. The alleghanyite from Bald Knob occurs as bright pink grains in calcite and contains only 0.15%  $\text{TiO}_2$  according to the latest analysis. Our material is clove-brown in colour, translucent only in very thin plates or sections, and has a vitreous to resinous lustre. Thin sections show twin-lamellae at right angles to the length of the blade-like crystals, and thin plates of the mineral, in parallel growth with tephroite, show oblique extinction often symmetrically inclined in adjacent plates to the edge of the plates (fig. 2A). Symmetrical extinction-angles from the trace of this edge to  $\alpha'$  range from  $19^\circ$  to  $26^\circ$ . Measurements on the universal stage confirm this lamellar twinning and also show that in the intergrowth with tephroite the  $\gamma$  vibration-directions for the two minerals are coincident, and that the  $\alpha$  direction for alleghanyite is inclined at  $28^\circ$  to  $\alpha$  for tephroite and that in the lamellar twins the inclination is symmetrical. Ross and Kerr had observed symmetrical extinctions of  $22^\circ$ , and A. F.

<sup>1</sup> The value calculated from the measurements of  $\beta - \alpha$  and  $\gamma - \beta$  given above is  $71^\circ$ . Direct measurement of the optic axial angle in methylene iodide gave  $2H_O 116^\circ$ ; assuming  $\beta 1.79$ , this leads to  $2V 69^\circ$ .

<sup>2</sup> C. S. Ross and P. F. Kerr, Amer. Min., 1932, vol. 17, pp. 1-18. [M.A. 5-50.]

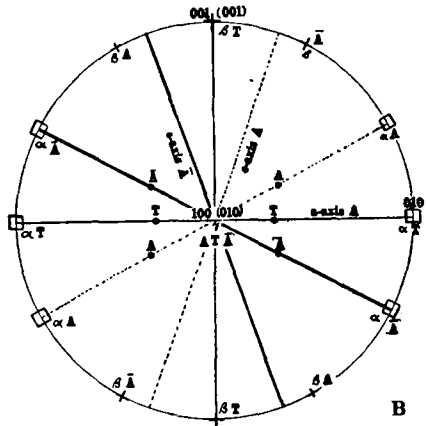
Rogers found a maximum of  $35^\circ$ . Yosimura on material from Kaso mine, Tochigi prefecture, Japan, records  $27^\circ$  (and  $2V\ 75^\circ$ ).<sup>1</sup>

A. F. Rogers<sup>2</sup> concluded that alleghanyite from Bald Knob is monoclinic with  $\beta = 90^\circ$  and the plane of lamellar twinning (001). Following this setting the optical orientation of our mineral is  $\gamma \parallel b$ , plane of optic axis  $\perp (010)$ ,  $u : \alpha = 28^\circ$ . Pleochroism:  $\beta$  amber-brown,  $\alpha$  Dresden brown; absorption  $\beta < \alpha$ . Approximate determinations of the optic axial angle and birefringence by universal stage methods gave  $2V\ 72^\circ$  to  $86^\circ$ , negative,  $\beta - \alpha\ 0.018$ ,  $\gamma - \beta\ 0.014 \pm 0.001$ . Refractive indices  $>1.778 <1.84$ . The specific gravity of analysed material (corrected for



A

FIG. 2A



B

FIG. 2B

FIG. 2A. Parallel intergrowth of tephroite and alleghanyite, the latter showing twin-lamellae. Vertical striations on (100) of tephroite. Optical extinction-directions indicated by arrows.

FIG. 2B. Stereographic projection of the same on the (100) face of tephroite, showing optical orientation and optic axes of tephroite (T) and of twinned individuals of alleghanyite (A and  $\bar{A}$ ). The faces (010) and (001) of alleghanyite are enclosed in parentheses.

included banalsite) is  $4.088 \pm 0.02$ . Hardness less than 5. Fuses quietly at  $2\frac{1}{2}$  to black enamel. Decomposed by HCl (1 : 1) readily, leaving a silica skeleton. These characters agree with those of alleghanyite from Bald Knob, except that the refractive indices are definitely higher and  $\gamma - \alpha$  slightly lower.

With regard to the orientation of the parallel growths in tephroite,  $\gamma$  directions for the two minerals being coincident the (010) face of alleghanyite is parallel to (100) of tephroite, and the twin-lamellae lie parallel to (001) of tephroite. There are no crystal faces to enable the position of the  $a$ - and  $c$ -axes of the alleghanyite to be fixed.<sup>3</sup>

Taylor and West<sup>4</sup> investigated the crystal-structure of the chondrodite series

<sup>1</sup> T. Yosimura, Journ. Fac. Sci. Hokkaido Univ., Ser. 4, 1939, vol. 4, p. 441. [M.A. 7-412.]

<sup>2</sup> A. F. Rogers, Amer. Min., 1935, vol. 20, pp. 25-35. [M.A. 6-144.]

<sup>3</sup> Ross and Kerr have remarked that a mineral reported as tephroite by A. F. Rogers in 1919 from San José, California, has characters similar to those of alleghanyite, and it is interesting to note that Rogers not only records polysynthetic twinning but adds 'in some areas the twinning resembles an intergrowth of two minerals'. Ross and Kerr, loc. cit., p. 13.

<sup>4</sup> W. H. Taylor and J. West, Proc. Roy. Soc. London, Ser. A, 1928, vol. 117, pp. 517-532. [M.A. 3-528.]

and showed that the chondrodite structure consists of alternate layers parallel to the *c*-face (001) of  $\text{Mg}_2\text{SiO}_4$  and  $\text{Mg}(\text{OH})_2$  in the proportion 2:1 represented by the chemical formula  $2\text{Mg}_2\text{SiO}_4 \cdot \text{Mg}(\text{OH})_2$ . The  $\text{Mg}_2\text{SiO}_4$  portions possess the olivine structure. These authors showed that to make the chondrodite series comparable with olivine it was necessary to make the crystallographic *b*-axis of chondrodite the *a*-axis of the unit cell.

If then Rogers's suggestion that alleghanyite bears to tephroite the same relation as chondrodite does to forsterite is correct, one may expect to find between the structures of the former pair a relation similar to that between chondrodite and olivine. The parallel growths of tephroite and alleghanyite are in exact agreement with such a relation, for the layers of alleghanyite in tephroite are arranged parallel to the (001) face of tephroite and the (010) face of alleghanyite is parallel to the (100) face of tephroite, that is the crystallographic *b*-axis of alleghanyite is parallel to the crystallographic *a*-axis of tephroite exactly as Taylor and West's structure requires.

A. F. Rogers showed that alleghanyite is the manganese analogue of chondrodite with the formula  $2\text{Mn}_2\text{SiO}_4 \cdot \text{Mn}(\text{OH}, \text{F})_2$  and suggested that 'tephroite bears the same relation to alleghanyite that forsterite does to chondrodite'.<sup>1</sup> The parallel growth of the alleghanyite and tephroite in the Benallt specimen is of particular interest in the light of this suggestion.

Rogers based his conclusions on the relationship of alleghanyite to the humite family upon powder data and chemical analyses. It has been possible to isolate single crystal fragments of alleghanyite from Benallt which give Laue and rotation photographs yielding the unit-cell dimensions *a* 4.86, *b* 10.46, *c* 8.3 Å.,  $\beta$   $70^\circ 52' \pm 10'$ , and the axial ratios *a* : *b* : *c* = 0.465 : 1 : 0.794. The cell edges are slightly larger than the corresponding values for chondrodite *a* 4.733, *b* 10.27, *c* 7.87 Å.,  $\beta$   $70^\circ 58'$ , because the divalent manganese ion has a radius of 0.91 Å. compared with 0.78 Å. for magnesium. Hence both the observations on the parallel growth of alleghanyite to tephroite and the unit-cell dimensions of the former mineral confirm unmistakably Rogers's work on Bald Knob material. Alleghanyite is the manganese analogue of chondrodite.

Microchemical analyses were made on carefully selected fragments of tephroite and alleghanyite. Fragments were hand-picked under the microscope and the analysed alleghanyite was believed to be substantially free from tephroite. The intergrowth of the two minerals on a microscopic scale, however, makes an absolutely clean separation impossible. The results of the analysis of tephroite (table IV, column I) show 0.41 %  $\text{TiO}_2$ , suggesting an admixture of 8.5 % alleghanyite. In column II are given the analytical results for alleghanyite. This shows 0.51 %  $\text{Al}_2\text{O}_3$  and 1.12 % BaO. The  $\text{Al}_2\text{O}_3$  found corresponds to 1.75 % of banalsite which would account for 0.40 % BaO, leaving 0.72 % BaO unaccounted for. Deducting 1.75 % banalsite from the results in column II gives the composition of the alleghanyite in column III, and deducting 8.5 % of alleghanyite<sup>2</sup> of this composition from the analysis in column I gives the composition of tephroite in column IV, and these figures are recalculated to total 100 in column V.

<sup>1</sup> A. F. Rogers, loc. cit., p. 31.

<sup>2</sup> In making these adjustments and in calculating the repeats from the results, an unknown though possibly small factor is the proportion of tephroite intergrown with the alleghanyite and inseparable from it, for this cannot be detected by the chemical analysis.

Calculating from the result in column V and using the cell sides and specific gravity recorded above gives for tephroite the repeat (table V, column I) and the atomic ratio to sixteen oxygen in column II. There is a small silica deficiency below that required for the formula  $(\text{Mn,Fe,Ca,Mg})_2\text{SiO}_4$  which would not have been made up even if the small percentage of Ti were counted with the Si.

On calculating the empirical unit-cell contents of the alleghanyite from column III, table IV and the known cell sides and corrected density the (O,OH) content comes to  $20.51 \pm 0.50$  (table V, column III). This is clearly an approach to an integral value of 20 and the empirical repeat is reduced to that basis in column IV.

As in the repeat of tephroite, there is again a deficiency in the amount of Si required by the formula. However, in this case it is possible that part of the Ti present is replacing Si, the main part replacing Mn with a balancing replacement of OH by O. The repeat may then be written  $4\text{Mn}_2(\text{Si,Ti})\text{O}_4 \cdot 2(\text{Mn,Ti})(\text{O,OH})_2$ .

Considering the small amount of material available and the difficulty of obtaining its complete separation from banalsite and tephroite the result shows a convincingly close approach to the composition suggested by A. F. Rogers.

We must await further evidence before the exact role of Ti in the alleghanyite is proved. In the meantime the presence of 4.8% of  $\text{TiO}_2$  is not held to necessitate a new name for this mineral as in every respect other than colour, crystal habit, and its content of  $\text{TiO}_2$ , it agrees in its properties with the alleghanyite of Bald Knob.

TABLE IV. Chemical analyses of tephroite and alleghanyite.

	I		II		III		IV		V	
	Tephroite.		Alleghanyite.		Alleghanyite.		Tephroite.		Tephroite.	
$\text{SiO}_2$	28.90		23.48		22.86		26.94		29.27	
$\text{TiO}_2$	...	...	0.41	4.81	4.81	—	—	—	—	—
$\text{Al}_2\text{O}_3$	...	...	nil	0.51	—	—	—	—	—	—
MnO	...	...	65.71	66.15	66.15	60.03	65.23	65.23	65.23	65.23
FeO	...	...	1.17	0.78	0.78	1.11	1.20	1.20	1.20	1.20
MgO	...	...	1.89	0.85	0.82	1.82	1.98	1.98	1.98	1.98
CaO	...	...	2.21	0.80	0.77	2.14	2.32	2.32	2.32	2.32
BaO	...	...	nil	1.12	0.72	—	—	—	—	—
$(\text{Na,K})_2\text{O}$	...	...	nil	n.d.	—	—	—	—	—	—
$\text{H}_2\text{O}$	...	...	n.d.	2.94	2.94	—	—	—	—	—
F	...	...	n.d.	nil	—	—	—	—	—	—
			100.29	101.44	99.85	92.04	100.00	100.00	100.00	100.00
$D_4^{16}$			$4.024 \pm 0.01$	$4.07 \pm 0.02$	$4.088 \pm 0.02$	4.020	—	—	—	—

TABLE V. Number of atoms per unit cell.

	Tephroite				Alleghanyite			
	I.		II.		III.		IV.	
Si	...	...	3.84	3.87	3.85	3.75	3.75	4.0
Ti	...	...	—	—	0.61	0.25	0.35	
Mn	...	...	7.27	7.32	9.43	9.20	9.20	10.04
Fe	...	...	0.13	0.13	0.11	0.11	0.11	
Mg	...	...	0.39	0.39	0.21	0.20	0.20	
Ca	...	...	0.33	0.33	0.14	0.13	0.13	
Ba	...	...	—	—	0.05	0.05	0.05	20
OH	...	...	—	—	3.30	20.51	3.22	
O	...	...	$15.90 \pm 0.30$	[16]	$17.21 \pm 0.50$	16.78	16.78	

The order of formation of the minerals in the banalsite-bearing 'veins' was apparently: alleghanyite and tephroite, jacobsonite, biotite, banalsite, baryte, calcite, and finally zeolites filling interstices and later veinlets.

In conclusion, we wish to express our thanks to Dr. Brian Mason (now of the New Zealand Government Department of Scientific and Industrial Research) for the initial X-ray work identifying the tephroite and alleghanyite, to Mr. C. M. Richardson, the former manager of the mine, and to Mr. William Campbell, the present manager, for having watched for and found the specimens of the new mineral. Special thanks are due to Dr. A. W. Groves for having sent the material to us for study and for his continued and unfailing interest in the work.

*A brief description of the manganese ore-bodies.*

By A. W. GROVES, D.Sc., Ph.D., M.I.M.M., F.G.S.

The Ordovician manganese ore of the Rhiw district of the Lleyn Peninsula, Carnarvonshire, has been won from a number of mines arranged in two groups separated by a mile of country in which no workable ore has been found. The southern group consists of the Nant mine and several small trials in the Nant y Gadwen. The northern group, in which the present discovery was made, consists of a number of old mines stretching for 2200 feet southwards from the old open-cast 1000 feet SW. of the prominent Clip y Gylfinhir to Tyddyn Meirion on the Rhiw-Aberdaron road. In addition to the open-cast, one (partly open-cast) inclined shaft, and a gloryhole at Tyddyn Meirion, the deposits have been worked all along this 2200 feet from ten principal shafts sunk to depths ranging from 40 to 100 feet.

The geology of the district has been described by Dr. C. A. Matley<sup>1</sup> and the petrography of the ores by Dr. A. W. Woodland,<sup>2</sup> both valuable papers, but, as the mine workings were then inaccessible, and few plans had been deposited with the Mines Dept., these workers could not be expected to throw appreciable light on the geology of the mines themselves, beyond the earlier brief statement in a Geological Survey publication,<sup>3</sup> parts of which have proved to be inaccurate.

The manganese in the undecomposed ore has been described<sup>3</sup> as being 'in the form of carbonate, with a small proportion of silicate'. Dr. Woodland's paper does not include a description of Benallt ore, as the only ore lying about at that time was at Nant. However, his petrographic descriptions of Nant ore indicate that the bulk of the manganese is present as rhodochrosite, with some quite subsidiary psilomelane, and an insignificant amount as manganiferous chlorite. Neither of these mineralogical descriptions fits fresh Benallt ore, of which a typical bulk (bunker) analysis contained (dry): MnO 38.72, MnO<sub>2</sub> 5.52, Fe<sub>2</sub>O<sub>3</sub> 9.52, SiO<sub>2</sub> 21.30, Al<sub>2</sub>O<sub>3</sub> 6.25, CaO 4.64, MgO 1.24, H<sub>2</sub>O(+110°C.) 4.40, CO<sub>2</sub> 4.60, P<sub>2</sub>O<sub>5</sub> 0.332, SO<sub>3</sub> 0.083, K<sub>2</sub>O 0.44, Na<sub>2</sub>O 0.55, BaO 1.86, BaSO<sub>4</sub> 0.52, As trace, CuO 0.005, NiO 0.020, CoO nil, ZnO nil, total 100. (Analyst, G. Watson Gray, Liverpool.) Neglecting MnO<sub>2</sub> in this analysis, there is sufficient CO<sub>2</sub> to satisfy less than one-fifth of the MnO to form rhodochrosite. Actually, the amount of available CO<sub>2</sub> is

<sup>1</sup> C. A. Matley, Quart. Journ. Geol. Soc. London, 1932, vol. 88, pp. 245, 246, 248, 249, 263.

<sup>2</sup> A. W. Woodland, Proc. Geol. Assoc. London, 1939, vol. 50, pp. 205-222. [M.A. 8-250.]

<sup>3</sup> Tungsten and manganese ores. Mem. Geol. Surv., Special Reports on the Mineral Resources of Great Britain, 3rd edit., 1923, p. 71.

somewhat less than this, for calcite veins are often seen, and a small amount of  $\text{CO}_2$  is probably combined with the collophane that occurs in nearly all the ore.

A thin section of the spotted manganese ore attached to the specimens found in no. 1 ore-body shows the largest and palest nodules in the ore attached to this specimen to consist of collophane; other and smaller pale patches consist of feldspar and epidote, either separately, or as mixtures of both. The whole of the groundmass is heavily impregnated with opaque ore material in which only some minute veins of reddish-brown manganese chlorite and detrital grains of feldspar largely replaced by chlorite and epidote are to be seen. The collophane nodules are quite unaffected by the metasomatism, which has converted nearly all the rest of the material into ore.

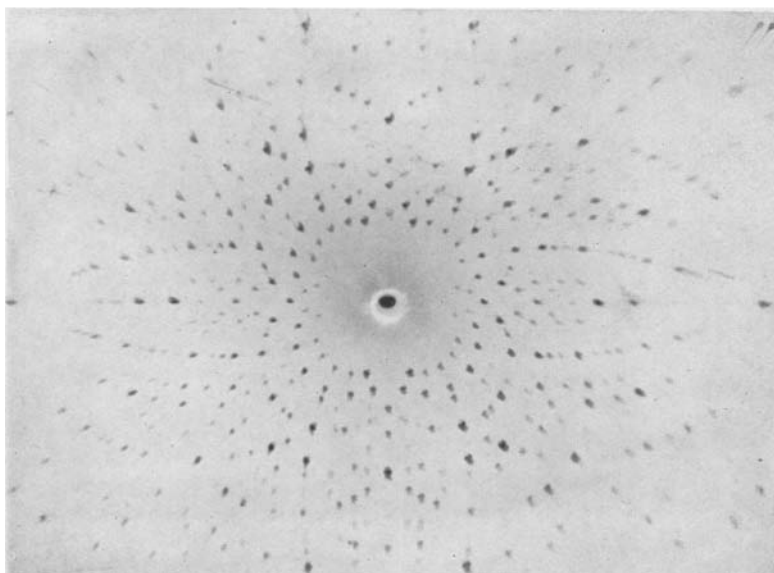
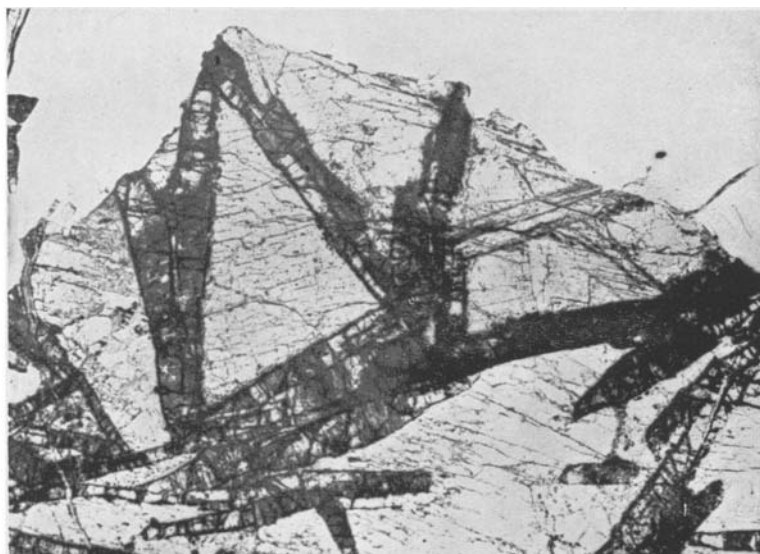
As the modern mine developed, Benallt was found to have perhaps the most complex structural geology of any British metalliferous mine now operating. In brief, the ore occurs in lenticles of all sizes from 10 or 20 tons up to 30,000 tons. The ore lenticles, enclosed in mudstone, run for the most part in a disconnected manner parallel to and along the very centre of a belt of strata contained between the foot-wall sill (an albitic dolerite) and the lower Clip lava [of Clip y Gylfinhir]. They are usually elongated N-S., dip at angles of about  $60^\circ$  to the E. (but the dips tend to flatten out towards the upper and lower terminations), and may occur en echelon or one behind the other. The structure generally within the mudstone is imbricate and there are innumerable thrusts and faults. The N. and S. ends of ore-bodies are often terminated by curving thrust-faults. As our knowledge of these ore-bodies has grown, certain of the larger ore-bodies have been found to be a complex in themselves containing one or more bands of included mudstone and clear evidence of overriding within themselves. By means of overriding, an ore-bed, originally 8-10 feet thick in all probability, has been built up into a massive lenticle 30 feet thick measured horizontally in the dip direction, and having anything from 30 to 60 feet inclined height. It is when ore overrides ore that mineralized veins are usually observed cementing the ore together again.

The mineral association described in the foregoing paper suggests a certain degree of metasomatism at an elevated temperature, subsequent to the formation of the ore by metasomatism of a bedded deposit and subsequent also to the formation of lenticular ore-bodies therefrom. The source of this latest metasomatism is not evident, though the foot-wall sill of albitic dolerite, believed to be of considerable thickness, may well have been intruded along a major thrust-plane towards the close of the period of imbrication and so metamorphosed the newly formed ore-bodies, particularly along fractures where late readjustment was taking place. The fact that so far the minerals have all tended to be located in the foot-wall side of the ore-bodies, i.e. on the side towards the sill and distant only 100 feet or so from it, lends some support to this tentative explanation.

#### *Explanation of Plate IV.*

FIG. 1. Photomicrograph of thin section showing banalsite (with some calcite at the top right-hand corner), and intercrossing blades of alleghanyite (dark); light patches in the alleghanyite are tephroite. Magnification  $\times 6$ . (Photo. W. H. T. Tams.)

FIG. 2. Laue photograph of a banalsite cleavage prism along the *c*-axis with *a*-axis horizontal. Tungsten radiation. Plate to crystal 3.5 cm. (Photo. F. A. Bannister.)



W. CAMPBELL SMITH, F. A. BANNISTER, AND M. H. HEY: BANALSITE,  
A NEW BARIUM-FELSPAR