New occurrences of vanadium minerals (mottramite, descloizite, and vanadinite) in the Caldbeck area of Cumberland.

By ARTHUR W. G. KINGSBURY, F.G.S.,

Dept. of Geology and Mineralogy, University Museum, Oxford,

and J. HARTLEY, B.Sc., F.G.S.,

Dept. of Geology, University of Leeds.

[Taken as read 10 June 1954.]

Summary.—Four new occurrences of vanadium minerals are described. New X-ray powder data are given for descloizite and mottramite, and show appreciable differences. Evidence is brought that the original occurrence of mottramite was not at Mottram St. Andrew, Cheshire, but Pim Hill, Shropshire, and that most if not all specimens labelled Mottram St. Andrew or Cheshire really came from Pim Hill.

VANADIUM minerals are rare in the British Isles, and only two species, mottramite (Cu, Zn)PbVO₄OH and vanadinite Pb₅(VO₄)₃Cl, have so far been recorded from a limited number of localities. We do not include the vanadiferous nodules from Budleigh Salterton in Devon, as the vanadiferous mineral has not been identified. Mottramite, supposedly from Mottram St. Andrew in Cheshire, was first described in 1876,¹ but we have evidence (below, p. 293) that the locality was in fact Pim Hill in Shropshire.² Vanadinite has so far only been found at Leadhills and Wanlockhead in Scotland. Vauquelinite has been described from Leadhills and Wanlockhead,³ but the specimens have since been shown to be mottramite.⁴

As a result of our investigations in the Lake District, we have found several new localities in the Caldbeck area for mottramite, descloizite, and vanadinite.

Higher part of Brandy Gill, Carrock Fell. Mottramite, descloizite, and vanadinite occur here under varying conditions. About three-quarters of the way up Brandy Gill two old trial cross-cuts (now collapsed) have been driven, one on each side of the gill, on an east-west copper-lead

⁴ F. A. Bannister, loc. cit., p. 377.

¹ H. E. Roscoe, Proc. Roy. Soc., 1876, vol. 25, p. 111.

² This locality is mentioned by F. A. Bannister, Min. Mag., 1933, vol. 23, p. 376.

³ T. Davies, Min. Mag., 1877, vol. 1, p. 112.

vein.¹ We found a small specimen, showing minute yellowish-green globular aggregates that proved to be mottramite, on the dump derived from the upper western cross-cut. Shortly after this we located the outcrop of the vein, and by blasting some of this out collected a considerable number of small specimens of mottramite. The primary sulphide minerals in this part of the vein are galena, chalcopyrite, and arsenopyrite; blende seems to be absent. A large amount of massive greyish-brown mimetite is present in certain parts of the vein at the outcrop and it is in cavities in this mimetite that most of the mottramite occurs, forming yellowish-green to dark olive-green crystalline patches and aggregates; other associated minerals are bayldonite, malachite, and yellow mimetite. In other parts of the vein, cavities in quartz contain well-formed but minute olive-green crystals of mottramite; the faces of these crystals, though bright, are rather rounded and striated and it has not been possible to find one suitable for measurement; under the microscope, however, they are seen to be pyramidal in habit and almost certainly of the form o{111}, and while most of them show only this form some appear to have small faces of $M{011}$ and $l{021}$ as well. The other minerals associated with these crystals are bayldonite (in which they are sometimes implanted), beaverite, and beudantite. Mottramite, similar to some specimens from Pim Hill, has been found in other material from this vein, forming dark brown drusy botryoidal aggregates with a fibrous structure and giving a yellow streak.

On the dump from the eastern cross-cut on the same vein, descloizite, a little mottramite, and vanadinite have been found in a spongy quartz matrix which has very different characteristics from the vein-stuff on the western side; copper minerals are uncommon, but small amounts of blende are present. Both the descloizite and the mottramite form aggregates of small greenish-brown, brown, or reddish-brown crystals; mottramite is by far the rarer. Vanadinite sometimes accompanies mottramite or descloizite or occurs alone, forming short prismatic or barrel-shaped crystals or globular aggregates, and ranging from pale buff to reddish-brown; the lighter-coloured crystals are indistinguishable in hand-specimens from mimetite, which is common at this locality. The country-rock is granophyre, which has been much altered near the vein.

Grainsgill, near the foot of Brandy Gill. Vanadinite has been found

 1 A third cross-cut farther down the gill contains nothing of mineralogical interest. It is desirable to distinguish between the three cross-cuts, which are close together.

290

here in material from an old cross-cut driven close to the point where an east-west copper-lead vein meets an ankerite vein and the Emerson vein, which here lie alongside each other; material from all three veins lies on a small dump, and much of it is iron-stained and gossany. Small



FIG. 1. Powder photographs of mottramite, descloizite, and vanadinite. Camera diameter 9 cm.; Cu-Kα radiation. 1. Mottramite: [labelled] Mottram St. Andrew, Cheshire. 2. Mottramite: higher Brandy Gill, Caldbeck Fells, Cumberland. 3. Descloizite: Venus mine, Sierra de Córdoba, Argentina. 4. Descloizite: higher Brandy Gill, Caldbeck Fells. 5. Vanadinite: McDonal mine, Globe, Arizona, U.S.A. 6. Vanadinite: higher Brandy Gill, Caldbeck Fells.

amounts of vanadinite occur as small stout hexagonal prisms with basal planes, ranging from pale buff to whitish and almost colourless; the two latter colours are most unusual in this mineral. Some of the crystals show a central zone of banding, parallel to the basal plane, of a darker and more brownish colour, a feature present in some very similar pyromorphite crystals from Roughtongill mine, Caldbeck. An interesting feature of the vanadinite from Grainsgill is that it is slightly arsenical. The country-rock here is greisen, but it is close to the gabbro of the Carrock Fell complex.

Potts Gill barytes mine, Caldbeck. Lead minerals are not of frequent occurrence in this mine, but are present in some parts of the old workings in small veins and strings away from the main baryte veins. Vanadinite has been found here, in material on the dumps from the old No. 1 crosscut, as small brown prismatic crystals in cavities in cellular quartz, with baryte and calcite; these crystals, again, are practically indistinguishable in hand specimens from similar crystals of pyromorphite from the Roughtongill area. The country-rock is Borrowdale Volcanic Series.

Netherrow Brow, Caldbeck. Mottramite occurs in small amounts in oxidized material from an unusual vein which carries large amounts of finely disseminated arsenopyrite, with galena, blende, pyrite, and traces of chalcopyrite; this vein strikes approximately north-westsouth-east across Netherrow Brow, on the northern slopes of the Caldbeck Fells north of Potts Gill mine. An old, grassed-over, collapsed level near the farm of Netherrow has a small dump outside its entrance containing a large number of secondary copper, lead, iron, and arsenic minerals, and also a little olive-green mottramite forming small, drusy botryoidal crusts on compact masses of earthy brown beudantite, closely associated with beaverite and a little cerussite: the country-rock is again Borrowdale Volcanic Series.

These occurrences make further interesting additions to the minerals of the Lake District, but the source of the vanadium is a matter for conjecture. It is conceivable that some of the primary sulphides in the veins may have contained small amounts of the element, or that very small quantities of some other vanadiferous sulphide may have been present. The vanadium in vanadinite has been generally considered to be derived from vanadium-bearing sulphides or silicates in the gangue or wall-rock: we do not know which of these possibilities is correct, but it is to be noted that though in two instances the wall-rock is similar, it is different at both the other localities.

The distinction between descloizite and mottramite by X-ray powderphotographs

During the growth of the library of X-ray photographs, in recent years, at the Department of Geology in the University of Leeds, it was noticed that descloizite and mottramite gave different, though similar, powder patterns. The photographs were all taken on cameras of 9 cm.

292

diameter, and since F. A. Bannister¹ considered that the patterns of the two minerals were identical we decided to investigate the matter further. The discovery of mottramite at Brandy Gill provided an additional reason for this investigation, and photographs of material from other collections and localities have all confirmed the differences in pattern. Dr. Bannister kindly examined many of these films, and after re-examining his own films (taken on cameras of 6 cm. diameter) stated in a letter to Hartley that the differences were apparent on his films. Films taken recently at Leeds on a camera of 19 cm. diameter have emphasized the differences.

There appears to be no reason to differ from Bannister's original conclusion that descloizite and mottramite are the respective zinc and copper end-members of a series, but no mineral so far examined has given an intermediate pattern. Measurements of powder photographs of the two minerals show close agreement down to 1.652 Å., but the smaller spacings differ markedly. In view of these differences in pattern it seems advisable to give new powder data obtained from recent photographs, and these are set out in table I. Powder photographs of mottramite, descloizite, and vanadinite from some of the new Lake District localities are given in fig. 1, together with photographs of corresponding material from other localities.

A note on the origin of mottramite from Mottram St. Andrew [A. W. G. K.]

As we have already mentioned (p. 289), there is good reason to suppose that the original occurrence of mottramite was at Pim Hill and not Mottram St. Andrew; the evidence for this is partly historical and partly based on the nature of the specimens. Although Roscoe obtained his original material from Mottram St. Andrew, from piles of ore awaiting treatment, the ore was probably not mined there. Most specimens of mottramite in collections are labelled 'Mottram St. Andrew', or simply 'Cheshire', but there is no record of its being found *in situ*; 'vanadium ore' has been reported from Alderley Edge.

Roscoe,² in his original description of mottramite, says that it 'occurs as a crystalline incrustation on Keuper sandstone found at Alderley Edge and at Mottram St. Andrew in Cheshire, and at other places', but these localities clearly refer only to the Keuper sandstone. Vanadium certainly occurred at Alderley Edge, and Roscoe³ states that he obtained a supply of vanadium from a precipitate which was a by-product of the

¹ Loc. cit., p. 378. ² Loc. cit., p. 111.

³ H. E. Roscoe, Phil. Trans. Roy. Soc., 1868, vol. 158, p. 4.

TABLE I. X-ray data for descloizite and mottramite in Å.; 9 cm. camera, Cu-K α radiation; broad lines are asterisked: descloizite, P. 1140¹: Venus Mine, Sierra de Córdoba, Argentina; mottramite, P. 1566¹: Mottram St. Andrew (B.M. specimen).

Descloizite.		Mott	Mottramite. ²		Descloizite.			Mottramite. ²	
Ι.	d (obs.).	Ι.	d (obs.).		Ι.	d (obs.).	I.	d (obs.).	
\mathbf{vs}	5·12 Å.	vs	5·07 Å.		vvw	2·37 Å.	vvw	2·39 Å.	
m	4.75	m	4 ·66		s	2.30	s	2.30	
s	4.25	s	4.24		$\mathbf{m}\mathbf{w}$	2.24	∫mw	2.24	
\mathbf{m}	4.00	\mathbf{m}	3.99				∫mw ∣	2.22	
m	3.54	\mathbf{m}	3.54		s	$2 \cdot 10$	∫ms	2.10	
$\mathbf{m}\mathbf{w}$	3.34	$\mathbf{m}\mathbf{w}$	3.31				շ) ms	2.08	
vvs	3.23	vvs	3.24		$\mathbf{m}\mathbf{w}$	1.975	mw	1.967	
\mathbf{m}	3.04	\mathbf{m}	3.03		mw	1.898	w	1.912	
	_	vvw	3.02		\mathbf{m}	1.866	mw	1.871	
vs	2.90	\mathbf{vs}	2.87				vvw	1.837	
vs*	2.69	(vs	2.68		\mathbf{ms}	1.787	ms^*	1.782	
_	_) vs	2.66		\mathbf{m}	1.757			
vs*	2.62	vs	2.59				vvw	1.721	
w	2.55	w	2.54				w	1.657	
w	2.44	vvw	2.47		\mathbf{vs}	1.652	\mathbf{vs}	1.648	
_		vvw	2.41						

To this point the spacings show close agreement. Smaller spacings are different.

Descloizite.		Mottramite. ²		Descloizite.		Mottramite. ²	
Ι.	d (obs.).	Ι.	d (obs.).	Ι.	d (obs.).	Ι.	d (obs.).
\mathbf{m}	1·604 Å.	\mathbf{m}	1·615 Å.	vvw	1.095 Å.	vvw	1·050 Å.
\mathbf{ms}	1.565	vvw	1.552	vvw	1.080	vvw	1.032
mw	1.517	m	1.544	w	1.068	vw	1.018
w	1.507	$\mathbf{m}\mathbf{w}$	1.497	vvw	1.048	vw	0.990
vw	1.466	$\mathbf{m}\mathbf{w}$	1.483	vvw	1.034	VW	0.977
vvw	1.446	w	1.454	vvw	1.022	vw	0.970
s	1.409	w	1.409	vvw	1.009	vvw	0.950
$\mathbf{v}\mathbf{v}\mathbf{w}$	1.392	w	1.391	vvw	0.982	vvw	0.940
vvw	1.370	vw	1.370	$\mathbf{m}\mathbf{w}$	0.971	vvw	0.930
$\mathbf{m}\mathbf{w}$	1.360	\mathbf{ms}	1.336	vvw	0.955	vvw	0.923
mw	1.334	vvw	1.306	vvw	0.944	vvw	0.907
w	1.309	vvw	1.286	$\mathbf{m}\mathbf{w}$	0.931	vvw	0.895
vvw	1.287	\mathbf{ms}	1.251	$\mathbf{m}\mathbf{w}$	0.921	vvw	0.888
vvw	1.268	vw	1.205	vvw	0.913	vw	0.878
w	1.241	vw	1.200	vvw	0.906	vw	0.861
vw	1.209	$\mathbf{v}\mathbf{w}$	1.184	w	0.896	vw	0.852
vw	1.201	vw	1.165	vw	0.885	$\mathbf{v}\mathbf{w}$	0.845
mw	1.178	w	1.148	vw	0.878		
w	1.160	vw	1.135	vvw	0.863		
vvw	1.152	$\mathbf{m}\mathbf{w}$	1.117	w	0.853		
vvw	1.130	vvw	1.089	w	0.848		
m	1.112	VW	1.078	w	0.837		
vvw	1.107	vvw	1.067				

¹ Number of film in X-ray Film Library, Dept. of Geology, University of Leeds. ² Identical pattern and spacings are given by mottramite from Pim Hill, Shropshire, collected by A. W. G. Kingsbury.

294

extraction of cobalt at Mottram St. Andrew (by the Alderley Edge Copper Mining Co.) from 'cobalt-bed sandstone'; he refers to the succession of beds containing this sandstone as that described by Hull,¹ which is the succession at Alderley Edge and not Mottram St. Andrew. In the same paper² Roscoe describes this sandstone, and states that it 'possesses a light colour and contains 0.1 to 0.3 per cent. of the oxides of cobalt, nickel and copper disseminated as small black, green and red specks throughout the mass' and that the vanadium probably occurs as vanadinite; he goes on to say that the mine at Mottram St. Andrew had by then (1867) stopped working, preventing him from getting further supplies of the material from which the vanadium precipitate was prepared, and so it seems unlikely that the specimens of mottramite he obtained in 1875-6 were mined there. Moreover, since most of the known specimens of the mineral are on a matrix unlike that from Alderley Edge and Mottram St. Andrew (the ore-bearing beds are conglomerate at the latter³), the historical evidence against either locality being the correct one is fairly strong. The mine at Pim Hill was working for a short period around 1875, and the ore is known to have been transported elsewhere for treatment; this constitutes the only positive historical evidence for Pim Hill as the correct locality.

Both Sir Arthur Russell and I have collected mottramite in situ at Pim Hill in the parish of Preston Gubbals some 6 miles north of Shrewsbury: the matrix here is a compact fine-grained Keuper sandstone, light cream when fresh and often with small reddish-yellow streaks, which bounds a fault running along the crest of the hill. This sandstone is identical with the matrix of nearly all the specimens reputed to come from Cheshire, and moreover the habits of the mottramite itself are the same, being a botryoidal or drusy crystalline coating on the sandstone (as described by Roscoe), only rarely occurring in the sandstone and then not as a cementing medium; in all cases where mottramite is present other minerals are conspicuously absent.

In most cases the similarity of the 'Cheshire' specimens with those from Pim Hill would seem to put their origin beyond doubt. Thus, while there is no direct evidence, the historical and other data strongly suggest that the specimens reputed to come from Mottram St. Andrew and Cheshire really come from Pim Hill. This view is also held by Sir Arthur Russell, who agrees with the substance of this note.

¹ Mem. Geol. Surv.: E. Hull, Geology of Stockport, &c., 1866, p. 39; see also R. Hunt, British Mining (London, 1884), p. 260. ² Loc. cit., p. 5. ³ This is confirmed by all accounts.