Heyite and brackebuschite compared

R. F. SYMES

British Museum (Natural History), Cromwell Road, London, S.W. 7

S. A. WILLIAMS

Phelps Dodge Corporation, Douglas, Arizona

SUMMARY. Heyite (see preceding paper) is so strikingly similar to brackebuschite that a close comparison of the two species seemed advisable. Topotype brackebuschite (B.M. 55819) was used for this purpose.

Brackebuschite is a vanadate of lead, manganese, and iron, heyite a vanadate of lead and iron. Both species are monoclinic with diffraction symmetry $P2_1$ or $P2_1/m$. The X-ray cells are remarkably close: $a = 8\cdot810$, $8\cdot910$; $b = 6\cdot155$, $6\cdot017$; $c = 7\cdot651$, $7\cdot734$; $\beta = 111°\ 30'$, $111°\ 53'$ (brackebuschite first). As might be expected, powder patterns are strikingly close as well.

Other than the similarities noted above, the minerals differ so fundamentally that they cannot be the same—they are valid and distinct species. Optic orientations show α: [001] 20° (in acute β) for brackebuschite, 36° (in obtuse β) for heyite. Indices are (brackebuschite first): α 2·28, 2·185; β 2·38, 2·219; γ 2·49, 2·266 for the sodium D line.

Chemical differences are irreconcilable and reaffirm brackebuschite as $Pb_2(Mn,Fe,Zn)(VO_4)_2 . H_2O$ while heyite is $Pb_5Fe_2(VO_4)_2O_4$.

THE striking similarities of the qualitative chemistry and X-ray data of brackebuschite and heyite require some comment if heyite is to be accepted as a new species without reservation. Brackebuschite has had a long but tranquil history since first described from Cordoba, Argentina (Rammelsberg, 1880). This remains the only undisputed locality for brackebuschite, and later workers have never shown evidence of confusion regarding the identity of the mineral. Published data for brackebuschite show good agreement and the mineral is well characterized.

For a complete comparison of heyite and brackebuschite it was necessary to determine some constants for brackebuschite that had not previously been reported. We also performed new chemical analyses. All new information was obtained from one specimen in the British Museum (Natural History), B.M. 55819. This is a type locality specimen purchased by the Museum in 1884, from Mr. Hoseus, and it appears to be of superior quality to material used by previous workers. In this specimen brackebuschite occurs as well-terminated crystals from 0·4 to 1·5 mm in length in cavities with cerussite, descloizite, and vanadinite. The gangue is a sheared granitic rock rich in muscovite and showing replacement by prismatic quartz where it is most severely brecciated.

Morphology. Two terminated crystals were selected for measurement. The crystals were of similar habit showing elongation on [010] and marked flattening on {100}.

Deep striae on {100} are parallel to [010]. Both crystals showed a {100}, c {001}, m {110}, l {$\bar{2}$01}, k {$\bar{3}$01}. Forms found on only one crystal are d {101}, {$\bar{1}$01}, {$\bar{1}$22}, {021}, and {$\bar{1}$25} (?). A typical crystal is shown in fig. 1. Crystals were carefully examined for twinning but no twins were found; heyite commonly shows twinning on {110}. No doubly terminated crystals could be found but crystals appear to be attached to matrix by either $+b$ or $-b$ in roughly equal abundance.

X-ray data. Powder patterns of heyite and brackebuschite are similar. Visual inspection however shows progressive deterioration of line matches and intensities toward larger 2θ values. Indexed patterns of the two species are compared in table I.

TABLE I. *Powder patterns of heyite and brackebuschite, Cr-Kα radiation. Intensities estimated*

Brackebuschite				Heyite			
I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl
4	8·199	8·197	100	2½	8·281	8·270	100
8	4·918	4·922	110	5	4·873	4·868	110
3	4·608	4·604	101	2	4·628	4·635	101
1	4·302	4·298	20$\bar{1}$	½	4·350	4·351	20$\bar{1}$
1	4·090	4·099	200	2	4·134	4·135	200
½	3·821	3·815	10$\bar{2}$	2	3·861	3·859	10$\bar{2}$
3	3·687	3·687	111	4	3·674	3·673	111
1B	3·544	3·559	002	1	3·592	3·590	002
—	—	3·524	21$\bar{1}$	—	—	3·526	21$\bar{1}$
2	3·413	3·411	210	3	3·412	3·409	210
—	—	3·367	20$\bar{2}$	—	—	3·411	20$\bar{2}$
10	3·244	3·243	11$\bar{2}$	10	3·248	3·249	11$\bar{2}$
—	—	3·095	201	1	3·116	3·117	201
5	3·079	3·078	020	3	3·010	3·011	020
—	—	3·081	012	—	—	3·082	012
5B	2·942	2·936	30$\bar{1}$	7	2·970	2·970	30$\bar{1}$
—	—	2·954	21$\bar{2}$	—	—	2·968	21$\bar{2}$
—	—	2·900	102	1	2·916	2·920	102
2	2·880	2·881	120	2	2·825	2·829	120
1	2·822	2·825	021	—	—	2·774	021
6	2·765	2·765	211	6	2·767	2·768	211
1	2·626	2·623	112	3	2·625	2·628	112

X-ray cells of the two minerals are strikingly similar. Both minerals are monoclinic with parameters:

Brackebuschite	a 8·810±0·005,	b 6·155±0·004,	c 7·651±0·005,	β 111° 30′±4′
Heyite	8·910±0·004	6·017±0·004	7·734±0·004	111° 53′±4′

Barnes and Qurashi (1952) and Berry and Graham (1948) have given very similar data for brackebuschite. Heyite occurs in doubly terminated crystals and shows no evidence that it is not of class $2/m$ symmetry; its diffraction symmetry permits space groups $P2_1$ or $P2_1/m$, and $P2_1/m$ was chosen as more likely. Brackebuschite crystals have not

been found doubly terminated; morphological evidence given by crystals terminated on $-b$ and b suggests $2/m$ symmetry, and since diffraction symmetry permits space groups $P2_1$ or $P2_1/m$, $P2_1/m$ may be preferred as more likely. However, Fanfani and Zanazzi (1967) have suggested $P2_1$ for brackebuschite as more likely on structural grounds.
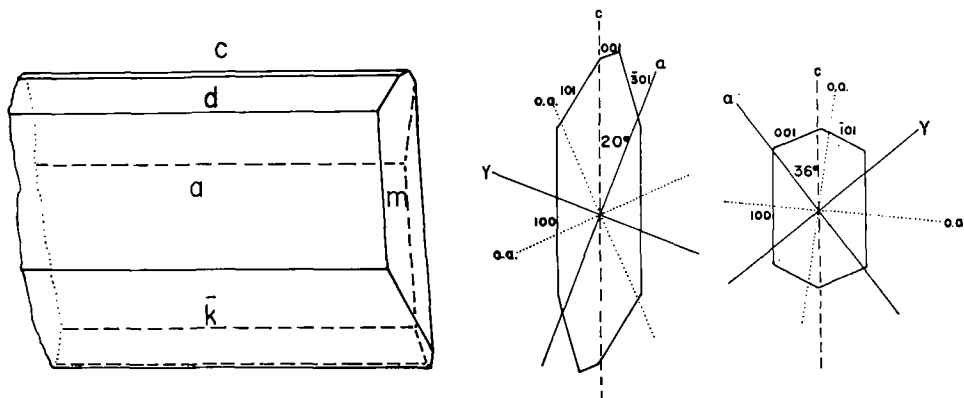
FIGS. 1 and 2: FIG. 1 (left). A typical brackebuschite crystal. FIG. 2 (right). Optic orientations of brackebuschite (left) and heyite (right).

Optics. Although refractive indices for brackebuschite have been reported previously (Larsen and Berman, 1934), redetermination by the identical methods used for heyite seemed desirable. Indices for both minerals were determined in S–Se melts for the sodium D line:

Brackebuschite	$\alpha\ 2\cdot28\pm0\cdot015$,	$\beta\ 2\cdot38\pm0\cdot02$,	$\gamma\ 2\cdot49\pm0\cdot02$
Heyite	$2\cdot185\pm0\cdot01$	$2\cdot219\pm0\cdot01$	$2\cdot266\pm0\cdot01$

Brackebuschite shows strong absorption in the melts for β and γ; heyite does not. Both minerals have a large $2V$; heyite is ($+$) 82° to 89° and brackebuschite is sensibly 90°. The optic orientations of both minerals are presented in fig. 2, and one can see the striking difference. For crystals lying on (100) brackebuschite gives an off-centred optic axis figure and is length-slow with high birefringence. Heyite gives a well-centred optic axis figure and is length slow but with very low birefringence in the same orientation.

Chemistry. Grains were handpicked from a topotype brackebuschite specimen (B.M. 55819) and ultrasonically cleaned. During this process visible amounts of earthy hematite were removed from innumerable tiny pits in the crystal surfaces. Several of these grains were mounted in an epoxy resin and polished. Twelve of these were then analysed qualitatively and checked for homogeneity before proceeding to quantitative analysis. In all the grains studied lead, zinc, manganese, vanadium, and iron were detected, copper and phosphorus (reported by Rammelsberg and Doering) were sought but not found (i.e. less than 0·05 %). The analyses for both heyite and brackebuschite

were made using a Cambridge Instruments Geoscan, with an accelerating voltage of 20 kV and a current of 0.5×10^{-7} amps. Lead was determined using an analysed anglesite standard from Monteponi, Sardinia; crocoite was used as a secondary standard. Pure Mn, Zn, V, and Fe metal standards were used for the other elements determined. The brackebuschite grains were analysed in the same run as repeat analyses on the heyite grains. Raw data for those elements determined were corrected using the methods described by Sweatman and Long (1969) and the Mason, Frost, and Reed (1969) microanalysis computer programme. At least ten point counts were taken on each of the grains (average largest dimension 250 microns).

TABLE II. *Analyses of brackebuschite and (no. 8) heyite*

	1	2	3	4	5	6	7	8
PbO	61·9	62·1	60·3	61·0	62·6	61·00	58·02	76·3
ZnO	0·52	0·13	0·69	0·66	0·9	1·29	1·23	0·80
FeO	0·20	0·04	2·7	6·8	3·0	4·65	4·46	8·2
MnO	9·5	9·6	6·3	2·5	6·8	4·77	4·56	n.d.
V_2O_5	26·5	25·8	25·2	25·5	27·1	25·32	24·74	12·7
P_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	0·18	0·11	n.d.
CuO	n.d.	n.d.	n.d.	n.d.	n.d.	0·42	0·41	n.d.
H_2O	—	—	—	—	—	2·03	2·43	—
Total	98·62*	97·67*	95·19*	96·46*	100·4*	99·66	100·32†	98·00

* Totals not inclusive of $H_2O = 2.8$ %.   n.d. Not detected.
† Including 3·07 % insol. and 1·29 % $Fe_2O_3 + Mn_3O_4$.

1, 2. Electron probe analyses; R. F. Symes. (Typical analyses of 10 of the 12 grains studied.)
3, 4. Electron probe analyses. (Analyses of the two grains with lower Mn–Fe ratios.)
5. Analysis by atomic absorption: C. J. Elliott (B.M.(N.H.)).
6. Rammelsberg (1880).
7. Doering (1883).
8. Averaged probe analyses of heyite grain, run concurrently with brackebuschite.

Counts for Pb, Zn, V, and Mn showed very little variation within each grain whereas the counts for iron were variable in grains having a low Fe content.

Table II (cols. 1 and 2) shows the analyses of two of the brackebuschite grains, the analyses being typical of the results obtained on ten of the grains selected, and with the best surface polish. Only two of the grains analysed showed any significant variation from these analyses; these analyses are shown in cols. 3 and 4 of table II. The principal differences are in the FeO/MnO ratio. The repeat heyite analyses duplicated those already presented in the previous paper. It is thought that the figures quoted are correct to ± 1 % of the amount present for the major elements.

709 micrograms of the same cleaned sample were dissolved in HNO_3, and Pb, Fe, Mn, Zn, Cu, and V were then determined by atomic absorption spectroscopy by comparison with pure standard solutions. A Perkin Elmer 403 spectrometer was used for the analyses. The analysis is shown in table II, col. 5; Cu was again below detection level.

1·734 milligrammes were found to give 2·82 % H_2O on heating to 550 °C; at lower temperatures (110 °C and 440 °C) no water was released.

Conclusions. Our work on brackebuschite has essentially confirmed older results with but one exception: the formula should be rewritten as $Pb_2(Mn,Fe,Zn)(VO_4)_2$. H_2O. The ratio of Mn:Fe of 1:1 found by older analyses is undoubtedly fortuitous and probably represents the average ratio to be found in brackebuschite with some admixed hematite. Heyite analyses done by the same method give the different and distinct formula $Pb_5Fe_2(VO_4)_2O_4$. The complicated coupled substitutions required to relate brackebuschite to heyite while demanding virtually no change in the X-ray cell stretch credulity too far. The similarity of the X-ray cells is better explained as mere coincidence.

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