

X-RAY MEASUREMENTS ON BRACKEBUSCHITE AND HEMATOLITE

L. G. BERRY AND A. R. GRAHAM, *Queen's University,
Kingston, Ontario.*

ABSTRACT

New observations on brackebuschite from Sierra de Cordoba, Argentina, and on hematolite from the Moss mine, Nordmark, Sweden, combined with existing chemical analyses yield the following descriptions of these minerals.

Brackebuschite: monoclinic, probable space group $P2_1/m$; the unit cell with $a=8.92$, $b=6.16$, $c=7.69$ Å, $\beta=111^\circ 47'$; contains $2[\text{Pb}_2(\text{Mn,Fe})(\text{VO}_4)_2 \cdot \text{H}_2\text{O}]$. Specific gravity 6.05 (measured), 6.07 (calculated).

Hematolite: hexagonal $-R$; probable space group $R\bar{3}$; the unit cell with $a=8.27$, $c=36.51$, $r=13.07$ Å, $\alpha=36.53'$, $a:c=1:4.415$; contains $\text{Mn}_{10}\text{Mg}_2\text{Al}_3(\text{AsO}_4)_3(\text{OH})_{24}$. Specific gravity 3.49 (measured), 3.48 (calculated). The observed crystal forms are $c(0001)$ and the negative I order rhombohedra $Q(0.2.2.13)$, $P(0115)$ and $S(0112)$.

Brackebuschite and hematolite are two rare minerals, encountered by the authors of volume II of Dana's *System*, on which x -ray observations have not been made. The opportunity to examine these two minerals was provided by typical specimens kindly loaned from Harvard Museum (HM) by Dr. C. Frondel. An additional specimen of each mineral was later borrowed from the United States National Museum (USNM) through the kindness of Mr. E. P. Henderson.

BRACKEBUSCHITE

Brackebuschite, a hydrous vanadate of lead, manganese and iron, occurs at several localities in Sierra de Cordoba, Argentina. On the specimens at hand (HM 96255, USNM C4195), both from the Venus Mine, the mineral occurs in small flattened prismatic crystals, rhombic in cross section and striated parallel to the elongation. The crystals are dark brown to black and transmit red light on thin edges. Excellent x -ray rotation and Weissenberg films were obtained by turning a crystal first about the axis of elongation and later about an axis perpendicular to the elongation. These films indicate monoclinic symmetry with elongation along the 2-fold symmetry axis and yield the cell dimensions:

$$a=8.92, b=6.16, c=7.69 \text{ \AA}; \beta=111^\circ 47'.$$

The systematically missing spectra conform to the conditions: (hkl) present in all orders, $(0k0)$ present only with k even, $(h0l)$ present in all orders. The space group is therefore $P2_1/m$ if the crystals are holohedral. The crystals show the pinacoids $a(100)$ and $c(001)$ in almost equal development. No terminal faces were observed. The measured angle $c \wedge a$ agrees roughly with the β angle determined from x -ray films.

The only available analyses were made by Doering, quoted by Rammeisberg (1880) and again by Dana (1892). The first of the three closely agreeing analyses (1 of Table 1), when combined with the cell volume and measured specific gravity 6.05 (Berman balance) give the empirical cell contents (2) and atomic contents (3). These numbers clearly indicate the ideal structural formula $\text{Pb}_4\text{MnFe}(\text{VO}_4)_4 \cdot 2\text{H}_2\text{O} = 2[\text{Pb}_2(\text{Mn,Fe})(\text{VO}_4)_2 \cdot \text{H}_2\text{O}]$ with the numbers of atoms (4) and the calculated composition (5). The specific gravity calculated for the ideal cell content is 6.07, in close agreement with the measured value.

TABLE 1. BRACKEBUSCHITE: ANALYSIS AND CELL CONTENT

	1	2	3	4	5
PbO	61.00	3.88	Pb 3.88	4	PbO 62.20
FeO	4.65	.92	Fe .92	1	FeO 5.01
MnO	4.77	.95	Mn .95	1	MnO 4.94
ZnO	1.29	.22	Zn .22		
CuO	0.42	.07	Cu .07		
V ₂ O ₅	25.32	1.97	V 3.94	4	V ₂ O ₅ 25.34
P ₂ O ₅	0.18	.02	P .04		
H ₂ O	2.03	1.60	H 3.20	4	H ₂ O 2.51
			O 17.59	18	
	99.66				100.00

The following table gives the *x*-ray powder pattern of brackebuschite for $\text{CuK}\alpha$ radiation, indexed as far as $\vartheta = 26.6^\circ$.

The close chemical similarity has suggested to some authors that brackebuschite and pyrobelonite may be members of a series. The crystallographic data presented here fail to show any relationship to pyrobelonite which is orthorhombic with a probable structural formula $4[(\text{Mn,Pb})_2\text{VO}_4(\text{OH})]$ (Richmond, 1940). The structural formula of brackebuschite clearly suggests that the mineral belongs to the chemical type $\text{A}_3(\text{XO}_4)_2 \cdot n\text{H}_2\text{O}$. In the classification of minerals of this type given by Wolfe (1940) brackebuschite would belong to a family $\text{A}_3(\text{XO}_4)_2 \cdot \text{H}_2\text{O}$, not recognized by Wolfe. No other mineral representatives of this family have yet been noted.

HEMATOLITE

Hematolite, a basic arsenate of manganese and aluminum, occurs at the Moss Mine, Nordmark, Vermland, Sweden. On the specimens (HM, Boston Society of Natural History, Brigham coll. 396 and USNM C4228) available for this study from the type locality, the mineral oc-

TABLE 2. BRACKEBUSCHITE: $\text{Pb}_2(\text{Mn, Fe})(\text{VO}_4)_2 \cdot \text{H}_2\text{O}$
 Monoclinic, $P2_1/m$; $a=8.92$, $b=6.16$, $c=7.69$ Å; $\beta=111^\circ 47'$; $Z=2$

<i>I</i>	$\vartheta(\text{Cu})$	<i>d</i> (meas.)	(<i>hkl</i>)	<i>d</i> (calc.)	<i>I</i>	$\vartheta(\text{Cu})$	<i>d</i> (meas.)	(<i>hkl</i>)	<i>d</i> (calc.)
1	5.35	8.26 Å	(100)	8.283 Å	2	19.8	2.27 Å	{ (222) (303)	{ 2.282 Å 2.266
8	8.95	4.95	(110)	4.943	4	21.2	2.13	(321)	2.139
2	9.6	4.62	(101)	4.625	4	21.8	2.07	{ (411) (400)	{ 2.090 2.070
$\frac{1}{2}$	10.8	4.11	(200)	4.141	$\frac{1}{2}$	22.2	2.04	(322)	2.042
2	12.1	3.67	(111)	3.699	1	22.9	1.979	{ (031) (131) (123)	{ 1.973 1.966 1.966
2	13.1	3.40	(202)	3.399	3	23.8	1.909	{ (204) (104)	{ 1.918 1.900
10	13.7	3.25	(112)	3.257	3	24.3	1.872	{ (413) (103)	{ 1.872 1.859
5	14.5	3.08	{ (012) (020)	{ 3.089 3.080	3	24.8	1.839	{ (304) (230)	{ 1.843 1.840
6	15.0	2.98	{ (212) (301)	{ 2.976 2.973	3	25.3	1.802	(421)	1.802
8	16.2	2.76	{ (211) (300)	{ 2.780 2.761	6	26.6	1.720	(213)	1.724
1	17.2	2.61	(112)	2.631					
2	17.9	2.51	{ (221) (312)	{ 2.514 2.495					
1	18.9	2.38	{ (122) (003)	{ 2.402 2.380					
2	19.3	2.33	(022)	2.332					

<i>I</i>	$\vartheta(\text{Cu})$	<i>d</i> (meas.)	<i>I</i>	$\vartheta(\text{Cu})$	<i>d</i> (meas.)	<i>I</i>	$\vartheta(\text{Cu})$	<i>d</i> (meas.)
3	28.3	1.625	1	34.6	1.356	$\frac{1}{2}$	50.4	1.000
4	30.1	1.536	2	38.4	1.240	$\frac{1}{3}$	51.6	0.982
1	32.1	1.449	$\frac{1}{2}$	45.5	1.080	1	57.1	0.917
2	33.0	1.414	$\frac{1}{2}$	47.8	1.040	$\frac{1}{3}$	59.1	0.898
3	33.9	1.381	$\frac{1}{2}$	49.1	1.019	$\frac{1}{2}$	60.7	0.883

curs as tiny tabular crystals and aggregates in small vugs and fissures in crystalline limestone. The crystals are brownish-red to black in colour and orange to reddish-orange in thin flakes by transmitted light. The perfect basal cleavage shows a pearly lustre.

Sharp rotation and Weissenberg *x*-ray films obtained with FeK radiation by rotating a crystal about *c*, *a* and [2130] indicate an essentially rhombohedral lattice with dimensions:

$$a=8.27, c=36.51; r=13.07 \text{ \AA}, \alpha=36^\circ 53'.$$

The systematically missing spectra conform very closely to the conditions ($hki\bar{l}$) present only with $h+i+l=3n$, characteristic of a rhombohedral lattice. A few weak diffraction spots on the Weissenberg resolution ($h0\bar{h}l$) which do not conform to the above lattice extinction condition indicate a hexagonal superstructure with the dimensions given. The Weissenberg resolution ($hk\bar{i}0$) with diffractions ($30\bar{3}0$), ($11\bar{2}0$), ($22\bar{4}0$) and ($41\bar{5}0$) clearly indicates lack of symmetry about the ($h0\bar{h}0$) rows. On x -ray precession camera films about c with $\text{MoK}\alpha$ and $\text{CuK}\alpha$ radiation, the zero level ($hk\bar{i}0$) shows 6-fold symmetry without planes of symmetry; the levels ($hk\bar{i}1$, 2, 3, 4 and 5) each show 3-fold symmetry without planes of symmetry. Therefore the Laue class symmetry is clearly $\bar{3}$ and the probable space group is $R\bar{3}$.

The geometrical ratio of Sjögren (1885) is related to the structural elements if the c length is multiplied by 5, giving the comparison:

$$a:5c=1:4.4425 \text{ (Sjögren, goniometric)}$$

$$a:c=1:4.415 \text{ (Berry, } x\text{-ray).}$$

The crystals are thick tabular with a triangular basal pinacoid bevelled by I order rhombohedron faces which are striated horizontally. Two circle goniometer ρ angles obtained from 6 crystals are recorded below in comparison with Sjögren's measured and calculated angles and angles calculated from the structural elements. X -ray precession camera films about c on one of the measured crystals clearly indicate that the crystal forms, other than $c(0001)$ are properly negative I order rhombohedra.

TABLE 3. HEMATOLITE: MEASURED AND CALCULATED ρ ANGLES

Sjögren			Berry			
	measured	calc.		measured		calc.
	average			range	average	
—	—	—	(0.1. $\bar{1}$. 29)	8°01'–12°18' (4)	10°04'	9°58'
q (30 $\bar{3}$ 4)	—	37°34½'	Q (0.2. $\bar{2}$. 13)	—	—	38 06
r (10 $\bar{1}$ 1)	45°44'	45°44'	P (01 $\bar{1}$ 5)	43 55 – 50 15 (15)	45 54	45 33
s (20 $\bar{2}$ 1)	64 53	64 01	(02 $\bar{2}$ 5)	—	—	63 53
—	—	68 42	S (01 $\bar{1}$ 2)	64 59 – 70 48 (16)	67 37	68 35

In view of the poor quality of the reflections obtained from the measured crystals the agreement between measured and calculated angles is fair. Sjögren's elements, transformed to the structural setting, appear to fit the measured angles best. The comparison of angles indicates that Sjögren's forms $s(20\bar{2}1)$ and $q(30\bar{3}4)$ are probably equivalent to $S(01\bar{1}2)$

TABLE 4. HEMATOLITE: ANALYSES AND CELL CONTENT

	1	2	3	4	5	6	7		8	
MnO	46.86	50.98	10.33	10.67	10.50	Mn	10.50	10	MnO	47.17
MgO	6.66	5.38	2.58	1.98	2.28	Mg	2.28	2	MgO	5.36
CaO	0.66	0.71	0.18	0.19	0.19	Ca	0.19	—	—	—
Al ₂ O ₃	6.39	8.61	0.98	1.25	1.19	Al	2.38	3	Al ₂ O ₃	10.17
Fe ₂ O ₃	1.01		0.15							
As ₂ O ₅	21.55	22.54	1.47	1.46	1.47	As	2.94	3	As ₂ O ₅	22.93
H ₂ O	13.93	14.02	12.09	11.55	11.87	H	23.74	24	H ₂ O	14.37
Insol.	0.64					O	35.76	36		
	97.70	102.24								100.00

and $Q(0.2\bar{2}.13)$, respectively, in the structural setting. Likewise the form $t(70\bar{7}3)$, observed by Lorenzen (1884) is equivalent to $S(01\bar{1}2)$. The new form $(0.1\bar{1}.29)$ recorded here, was observed on two crystals as a very narrow face bevelling the edge of $c(0001)$.

TABLE 5. HEMATOLITE: $(\text{Mn,Mg})_4\text{AlAsO}_4(\text{OH})_8$
Hexagonal, $R\bar{3}$; $a=8.27$, $c=36.51$; $r=13.07\text{\AA}$; $\alpha=36^\circ53'$, $Z(r)=3$

<i>I</i>	$\vartheta(\text{Fe})$	$d(\text{meas.})$	(hkl)	$d(\text{calc.})$	<i>I</i>	$\vartheta(\text{Fe})$	$d(\text{meas.})$	(hkl)	$d(\text{calc.})$
8	9.1°	6.12Å	(0006)	6.085Å	10	23.9	2.39Å	{(2137) (3030)}	{2.403Å 2.387}
3	9.9	5.63	(10T4)	5.634	3	24.6	2.33	(1238)	2.328
5	10.7	5.20	(01T5)	5.114	1	26.5	2.17	(2.1.3.10)	2.177
8	13.5	4.14	(1120)	4.135	2	27.6	2.09	{(1.1.2.15) (1.2.3.11)}	{2.098 2.098}
2	13.8	4.06	(0009)	4.057	2	29.8	1.948	{(2.1.3.13) (1344)}	{1.949 1.941}
3	14.4	3.89	(1123)	3.915	4	31.0	1.880	{(3.0.3.12) (1.2.3.14)}	{1.878 1.878}
4	16.5	3.40	(1126)	3.420	4	33.7	1.745	(2.1.3.16)	1.745
4	17.4	3.22	{(1.0.1.10) (2025)}	{3.253 3.215}	1	37.2	1.601	(4.0.4.10)	1.607
2	18.6	3.03	(0.0.0.12)	3.042	9	38.3	1.562	(4150)	1.563
3	19.0	2.97	(0227)	2.952	2	39.8	1.512	(0.2.2.22)	1.506
1	19.6	2.89	(1129)	2.896	1	45.0	1.369		
3	20.1	2.82	(2028)	2.817	1	47.8	1.307		
1	21.0	2.70	(2131)	2.700	1	52.6	1.218		
4	21.9	2.60	(2134)	2.595	1	57.9	1.143		
1	23.4	2.44	{(0.0.0.15) (2.0.2.11)}	{2.434 2.434}					

The two available analyses of hematolite by C. H. Lundstrom (1 of Table 4) and A. Sjögren (2) (Sjögren, 1885) when combined with the rhombohedral cell volume and the measured specific gravity, 3.49, give the cell contents (3) and (4) and the average cell content (5). The average atomic content of the rhombohedral cell (6) indicates the ideal structural formula $Mn_{10}Mg_2Al_3(AsO_4)_3(OH)_{24}$ with the numbers of atoms in column (7). The total number of metal atoms is undoubtedly 15 but the numbers of each are uncertain. The formula above has been written with 12 divalent and 3 trivalent metals. The latter, shown as all Al in the formula probably includes both Fe^{III} and Mn^{III} . For this reason the calculated specific gravity, 3.48, for this structural formula, is low although

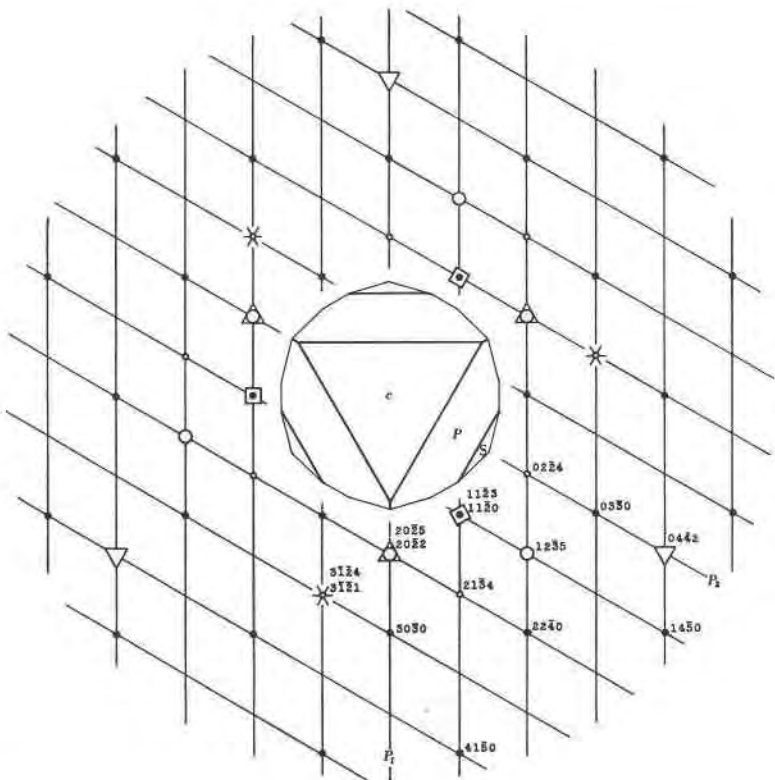


FIG. 1. Hematolite, Nordmark, Sweden: Idealized plan drawing of a typical crystal with $c(0001)$, $P(01\bar{1}5)$ and $S(01\bar{1}2)$ superimposed on the reciprocal lattice projection of diffractions observed on x -ray precession camera films about c (observed diffractions shown as follows: $(hk\bar{i}0)$ as solid circles, $(hk\bar{i}l)$ as small open circle with six rayed star, $(hk\bar{i}2)$ as triangles, $(hk\bar{i}3)$ as squares, $(hk\bar{i}4)$ as small open circles and $(hk\bar{i}5)$ as large open circles. $(41\bar{5}0)$ and $(14\bar{5}0)$ diffractions appear with distinctly different intensities.

it agrees well with the measured value; and the calculated composition differs somewhat from the analyses, principally in the percentage of alumina.

The x -ray powder pattern of hematolite for $\text{FeK}\alpha$ radiation, indexed as far as $\vartheta = 39.8^\circ$, is given in Table 5.

REFERENCES

- DANA, E. S. (1892), *System of Mineralogy*, ed. 6. New York.
LORENZEN (1884), *Öfv. Ak. Stockholm*, **41** (4), 95.
RAMMELSBERG, C. (1880), *Zeits. deutsche geol. Ges.*, **32**, 711.
RICHMOND, W. E. (1940), Crystal chemistry of the phosphates, arsenates and vanadates of the type $\text{A}_2\text{XO}_4(\text{Z})$: *Am. Mineral.*, **25**, 441.
SJÖGREN, H. (1885), Ueber die Manganarseniate von Nordmarken in Wermland: *Zeits. Kryst.*, **10**, 111.
WOLFE, C. W. (1940), Classification of minerals of the type $\text{A}_3(\text{XO}_4)_2 \cdot n\text{H}_2\text{O}$: *Am. Mineral.*, **25**, 738 and 787.