THE STRUCTURES OF THE MINERALS OF THE DESCLOIZITE AND ADELITE GROUPS: III— BRACKEBUSCHITE

D. M. DONALDSON[1] AND W. H. BARNES, *Division of Physics, National Research Council, Ottawa, Canada.*

ABSTRACT

The structure of brackebuschite, $Pb_2(Mn, Fe)(VO_4)_2 \cdot H_2O$, has been determined, although there is still some uncertainty about the location of the water molecule (if it is indeed present). Atoms of Pb, Mn and Fe, and V are in special positions. The coordination of oxygen with vanadium is tetrahedral; it is fourfold or sixfold with manganese depending on the H_2O-sites, and it is eightfold with one lead atom and tenfold with the other. Metal-to-oxygen distances are given and the accuracy of the results is discussed. By comparison with the structure of pyrobelonite it is shown that brackebuschite should not be classified with the minerals of the descloizite and adelite groups.

INTRODUCTION

Several attempts have been made to classify brackebuschite according to the chemical composition deduced from the analyses of Doering (1883) which are the only ones available in the literature. Thus Dana (1892) suggested that the formula is "perhaps $A_3V_2O_8+H_2O$* with $A=Pb$ chiefly, also Fe, Mn", but observed that Damour regarded Mn, Fe, (and Cu) as impurities; these data are repeated by Mellor (1947). Dana also credits Groth with the suggestion that brackebuschite might be the monoclinic equivalent of descloizite.

Strunz (1939) referred brackebuschite to a type $A_2(XO_4)(OH)$,* and, on the basis of x-ray diffraction powder photographs, concluded that it must be completely different structurally from the minerals of the descloizite group. On the other hand, Richmond (1940), without examination of brackebuschite by x-ray methods, assigned it the formula $(Pb, Mn)_2VO_4(OH)$ with $Pb:Mn=2:1$ and suggested that it forms a series with pyrobelonite, which he formulated $(Mn, Pb)_2VO_4(OH)$ (see, Donaldson & Barnes, 1955). He, therefore, placed brackebuschite "tentatively" in the *orthorhombic* section of family $ABXO_4(Z)$ with pyrobelonite, descloizite, higginsite (i.e., conichalcite; Berry, 1951), etc. (Richmond, 1940, pp. 444, 476, 477).

After a careful examination of Doering's analytical results in the light

[1] National Research Laboratories Postdoctorate Fellow, now I.C.I. Fellow, The University, Edinburgh, Scotland.

* The letter R is used by Dana (1892) for the cation whereas it is employed by Strunz (1939) for the metalloid of the anion; in this paper it has been changed to A for the former and X for the latter in conformity with later formulae (Richmond, 1940; Berry & Graham, 1948; Dana, 1951).

of original specific gravity, unit cell, space group ($P2_1/m$), and indexed powder data, Berry & Graham (1948) came to the conclusions that the ideal structural formula of brackebuschite is $2[Pb_2(Mn, Fe)(VO_4)_2 \cdot H_2O]$, that the mineral belongs to the chemical type $A_3(XO_4)_2 \cdot nH_2O$ with $n=1$, and that their investigation had failed to show any relationship with pyrobelonite. These results have been incorporated in the Seventh Edition of Dana's *System of Mineralogy* (1951). The formula of Berry & Graham (1948) is in complete agreement with that suggested by Doering in 1883 and Dana in 1892.

During a recent survey of unit cell and space group data for a number of vanadium minerals in this laboratory (Barnes & Qurashi, 1952), several interesting similarities and differences were observed between precession photographs of brackebuschite on the one hand and those of members of the descloizite and adelite groups on the other (see, Qurashi & Barnes, 1954, Fig. 1). With the information now available on the structures of descloizite and conichalcite (Qurashi & Barnes, 1954) and pyrobelonite (Donaldson & Barnes, 1955) it is of particular interest to compare the atomic arrangement in brackebuschite with that characteristic of the minerals of the descloizite and adelite groups.

Experimental, and Crystal Data

The experimental work was carried out with two crystals from the same (Sierra de Cordoba) specimen (Harvard Museum, 96255) as those examined by Berry & Graham (1948); the crystals had the dimensions $45\times30\times180\mu$ and $50\times35\times80\mu$. Intensities were estimated visually from precession and Weissenberg photographs (MoK_α radiation) using multiple exposure technique for the former and multiple film technique for the latter, and were corrected for the Lorentz and polarization factors. The absorption coefficient for MoK_α ($\lambda=0.7107$ Å) is 535 per cm. and approximate absorption corrections were applied, assuming cylindrical crystals.

Brackebuschite is monoclinic, space group $P2_1/m(C_{2h}^2)$ or $P2_1(C_2^2)$, with $a=7.68_1$, $b=6.15_5$, $c=8.88_0$ Å, and $\beta=111°50'$ (Barnes & Qurashi, 1952). There are $2[Pb_2(Mn, Fe)(VO_4)_2 \cdot H_2O]$ per cell. The calculated density is 6.11 gm. per ml.; observed specific gravity (Berry & Graham, 1948), 6.05 (Doering, 1883, found 5.85 which he acknowledged must be low because the specimen employed contained up to 4 per cent of quartz and ferruginous matter).

In order to facilitate direct comparison with descloizite and pyrobelonite it is convenient to refer brackebuschite to a B-centered cell (see, Barnes & Qurashi, 1952; Qurashi & Barnes, 1954) given by the transformation matrix $\bar{1}00/0\bar{1}0/102$. The dimensions of the new cell are $a'=$

7.68_1, $b'=6.15_5$, $c'=2\times 8.26_2$ Å, $\beta=93°45'$, and the space group is $B2_1/m$ or $B2_1$; coordinates, diagrams, and discussion throughout this paper are in terms of this B-centered cell.

Analysis of the Structure

Direct comparison of corresponding zero-level precession photographs of brackebuschite, pyrobelonite, and descloizite (see, Qurashi & Barnes, 1954, Fig. 1) shows that corresponding $hk0$ reflections from the three minerals are almost identical in relative intensities and Bragg angles, corresponding $0kl$ reflections are very similar, but there are important differences between the $h0l$ reflections from brackebuschite and correspond-

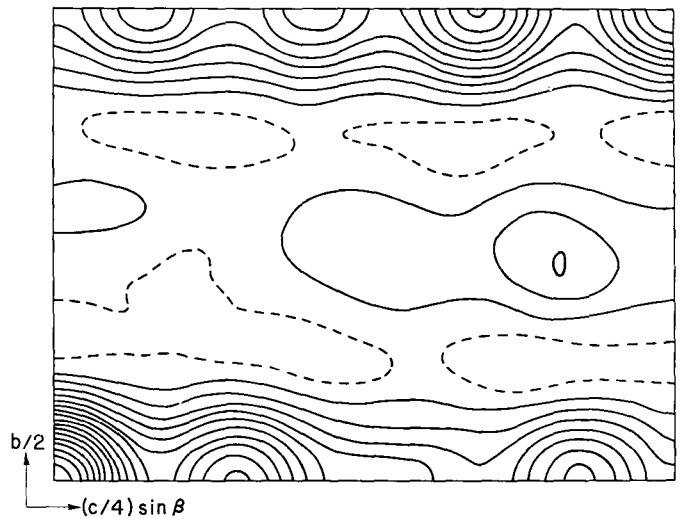

FIG. 1. Patterson map for the $\{0kl\}$ zone of brackebuschite. Contours are regular, but arbitrary, intervals; zero contour broken.

ing ones from pyrobelonite and descloizite. Although it would thus have been feasible to assume that the x and y coordinates of the lead atoms in brackebuschite probably are virtually the same as those in descloizite (Qurashi & Barnes, 1954) and in pyrobelonite (Donaldson & Barnes, 1955) it was decided to start the structure analysis of brackebuschite by computing the (100) Patterson map. The result is shown in Fig. 1 from which it is apparent that the majority of the peaks lie along $y=0$ and $\frac{1}{2}$. These must represent most of the metal-metal vectors. It follows, therefore, that the lead together with some of the lighter metal atoms must lie on, or close to, the same planes which are separated by $b/2$. The positions of the other peaks in Fig. 1 suggest that the remainder of the lighter

metal atoms must be situated on, or near, planes midway between these. If all the metal-atom sites are exactly in the planes specified, they are consistent with space group $B2_1/m$ for the metal atoms, and hence this space group was adopted provisionally as the basis for the structure analysis.

The equivalent positions of $B2_1/m$ are

(*a*) $0,0,0;\ 0,\frac{1}{2},0;\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},\frac{1}{2}$
(*b*) $\frac{1}{2},0,0;\ \frac{1}{2},\frac{1}{2},0;\ 0,0,\frac{1}{2};\ 0,\frac{1}{2},\frac{1}{2}$
(*c*) $x,\frac{1}{4},z;\ \bar{x},\frac{3}{4},\bar{z};\ \frac{1}{2}+x,\frac{1}{4},\frac{1}{2}+z;\ \frac{1}{2}-x,\frac{3}{4},\frac{1}{2}-z$
(*d*) $x,y,z;\ x,\frac{1}{2}-y,z;\ \frac{1}{2}+x,y,\frac{1}{2}+z;\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z;$
$\bar{x},\bar{y},\bar{z};\ \bar{x},\frac{1}{2}+y,\bar{z};\ \frac{1}{2}-x,\bar{y},\frac{1}{2}-z;\ \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z.$

From a detailed interpretation of the (100) Patterson map y, z coordinates were obtained for lead, manganese*, and vanadium, with lead and vanadium at $y=\pm\frac{1}{4}$ (special positions (*c*)) and with manganese in special positions (*a*) or (*b*). In view of the small difference between the atomic numbers of manganese and vanadium, the choice of which should be placed in the available positions was governed by the sites occupied by zinc and vanadium in descloizite. The structure was not prejudged by this selection because an "average" atom X of $f=\frac{1}{2}(f_{\mathrm{Mn}}+f_{\mathrm{V}})$ could equally well have been placed in each of the positions at this stage.

A (100) Fourier synthesis with metal-atom coordinates obtained from the analysis of the Patterson map was then carried out (see Fig. 2). The positions of Pb, Mn, and V were refined and termination-of-series errors were corrected by successive difference syntheses (Cochran, 1951) using coordinates for these atoms alone until those for the oxygen atoms had been determined. After inclusion of the latter only minor shifts in the positions of the metal atoms were required in succeeding difference syntheses.

Examination of the $hk0$ intensities showed that, in addition to the absences characteristic of the B-centering, all reflections for which $h=4n+2$, $k=2n$ and for which $h=4n$, $k=2n+1$ were either unobservable or very weak. On the assumption that this effect must be caused by the positions of the lead atoms, it follows that the x, y coordinates of Pb are $x=\frac{1}{8}$, $y=\frac{1}{4}$, etc. (special positions (c)). Because the lead atoms determine the phases of most reflections, it was possible to carry out a Fourier synthesis for this zone immediately (see Fig. 2) and then to proceed with refinement by successive difference syntheses as in the case of the $\{0kl\}$ zone.

Finally the $\{h0l\}$ zone was refined by the same procedure, commencing

* Since the atoms of Fe in brackebuschite must be occupying some of the Mn-sites, "manganese" refers to both Fe and Mn unless otherwise noted in the text.

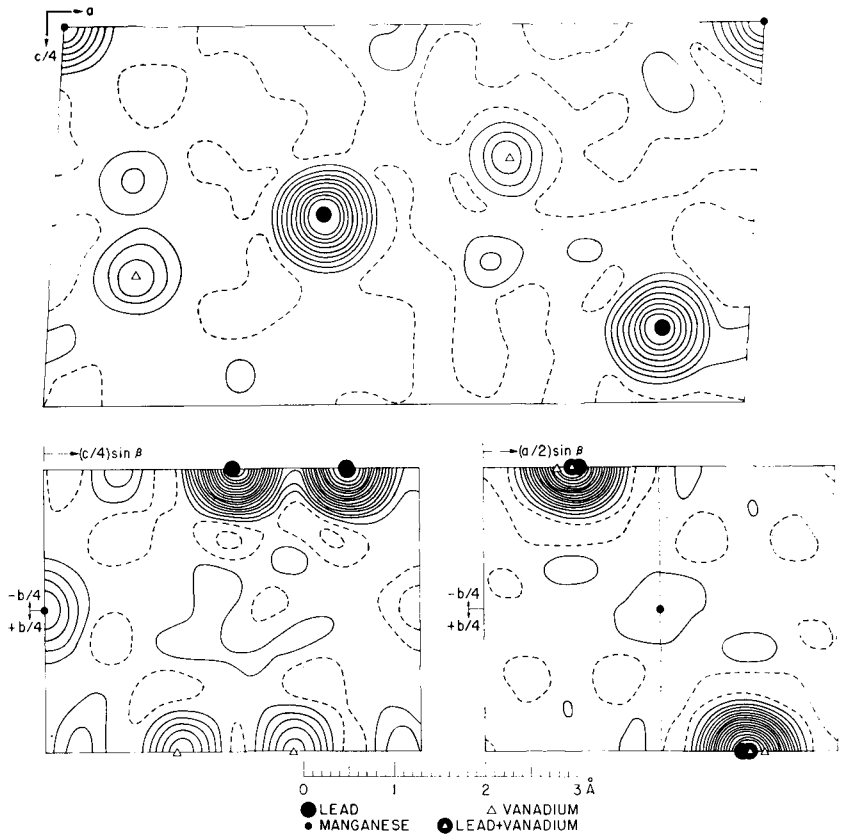

FIG. 2. Fourier maps of the brackebuschite structure. Contours at intervals of $\sim 8e.Å^{-2}$ for (010), $\sim 5e.Å^{-2}$ for (100), $\sim 12e.Å^{-2}$ for (001); zero and negative contours broken.

with metal-atom coordinates derived from the (100) and (001) electron-density maps.

The atomic scattering factors employed for lead and for vanadium were those used in the structure investigation of pyrobelonite (Donaldson & Barnes, 1955).

According to Doering's analyses (1883), manganese and iron are present in approximately equal atomic proportions. The scattering curve for "manganese," therefore, was obtained as the mean of those for the divalent ions, Mn^{2+} and Fe^{2+}, which in turn were derived from the *atomic* scattering curves in the *International Tables* (1935), taking those for Ca and Ca^{2+} as a guide (*International Tables*, 1935).

The three scattering curves were corrected for the temperature factor, $\exp(-B(\sin\theta/\lambda)^2)$, with $B=1.9$ for lead, 0.5 for vanadium, and 1.5 for

TABLE 1. METAL ATOM POSITIONS IN FRACTIONAL COORDINATES

Atom	x	y	z
Pb(1)	0.1149	0.250	0.3745
Pb(2)	0.6233	0.250	0.2989
V(1)	0.6462	0.250	0.0865
V(2)	0.1233	0.250	0.1644
Mn	0	0	0

manganese. These values were obtained qualitatively from the difference syntheses by attempting to reduce the background density around the different atoms to as near zero as possible. It should be noted that the same corrections were applied to the scattering curves for Pb, V, and Mn, respectively, in all three zones, even for non-equivalent atoms.

The final coordinates of the metal atoms are given in Table 1. Values of the structure factors calculated for these atoms alone, $F_{c(m)}$, are listed in Table 3.

POSITIONS OF THE OXYGEN ATOMS, AND THE WATER MOLECULE

There are some indications of the presence of oxygen atoms in the Fourier maps (see Fig. 2), particularly in that on (010), but they are not sufficiently clear for a reliable estimate of the atomic coordinates. The difference syntheses reproduced in Fig. 3 were calculated with the coefficients $(F_o - F_{c(m)})$; they show a set of peaks which, by correlation among the maps for the three zones, were identified as representing the oxygen atoms. The best mean coordinates obtained from these maps are given in Table 2. In view of the poor resolution of the oxygen peaks in the difference syntheses it was not considered profitable to attempt refinement of these values.

Difference syntheses were then computed after subtracting the contributions of all the metal *and* the oxygen atoms. The same scattering curve for the latter ($O^{-1.5}$) was employed as in the case of pyrobelonite

TABLE 2. OXYGEN ATOM POSITIONS IN FRACTIONAL COORDINATES

Atom	x	y	z
O(1)	0.114	0.023	0.104
O(2)	0.114	0.477	0.104
O(3)	0.941	0.250	0.230
O(4)	0.299	0.250	0.247
O(5)	0.632	0.023	0.145
O(6)	0.632	0.477	0.145
O(7)	0.455	0.250	0.017
O(8)	0.846	0.250	0.024

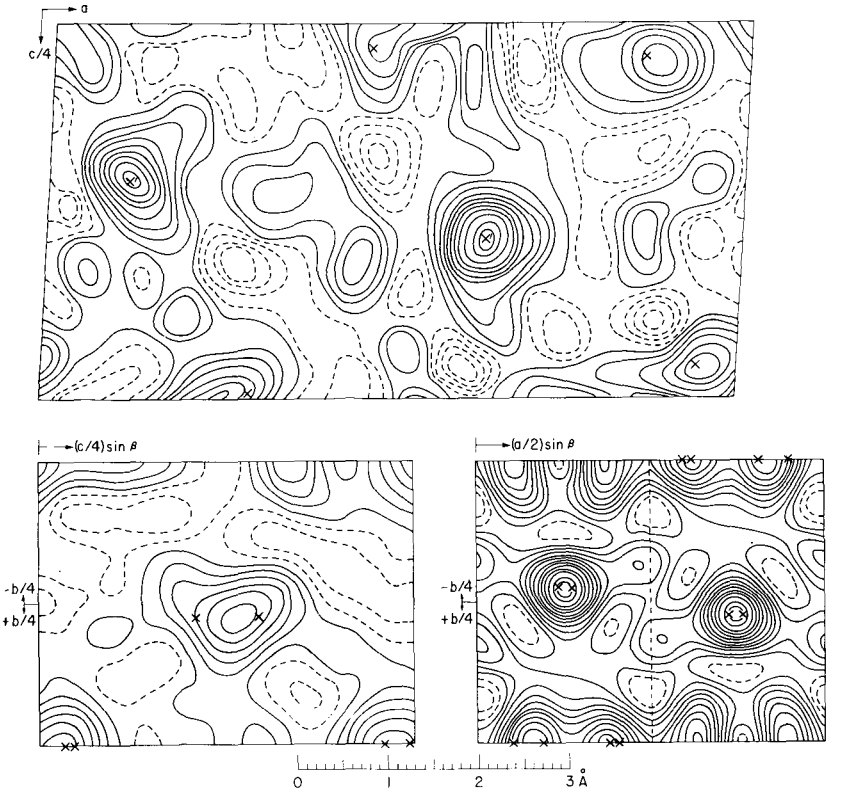

FIG. 3. ($F_o - F_{c(m)}$) maps of the brackebuschite structure. Contours at intervals of $\sim 2e.Å^{-2}$; zero and negative contours broken. Positions of single oxygen atoms indicated by X, and those of two pairs of superimposed oxygen atoms by X′.

(Donaldson & Barnes, 1955). The maps are reproduced in Fig. 4 and it was hoped that some clear indication of the positions of the water molecules might be obtained at this stage. There are a few relatively large peaks in the final difference maps (Fig. 4), generally of 6 to 8 $e.Å^{-2}$ but with two of 14 and 16 $e.Å^{-2}$, respectively, in the (001) map, but none could be correlated through all three zones. On this basis, therefore, it was not possible to fix the position of the water molecule, although a possible site will be discussed later. It should be mentioned that there was originally a peak of approximately 200 $e.Å^{-2}$, representing two lead and two vanadium atoms (see Fig. 2), between the two large peaks (14 and 16 $e.Å^{-2}$) in the (001) map. Thus, although part of either of these residual peaks might be due to the water molecule, both could be accounted for by asymmetric thermal motion of one or both of the crystallographically distinct lead atoms.

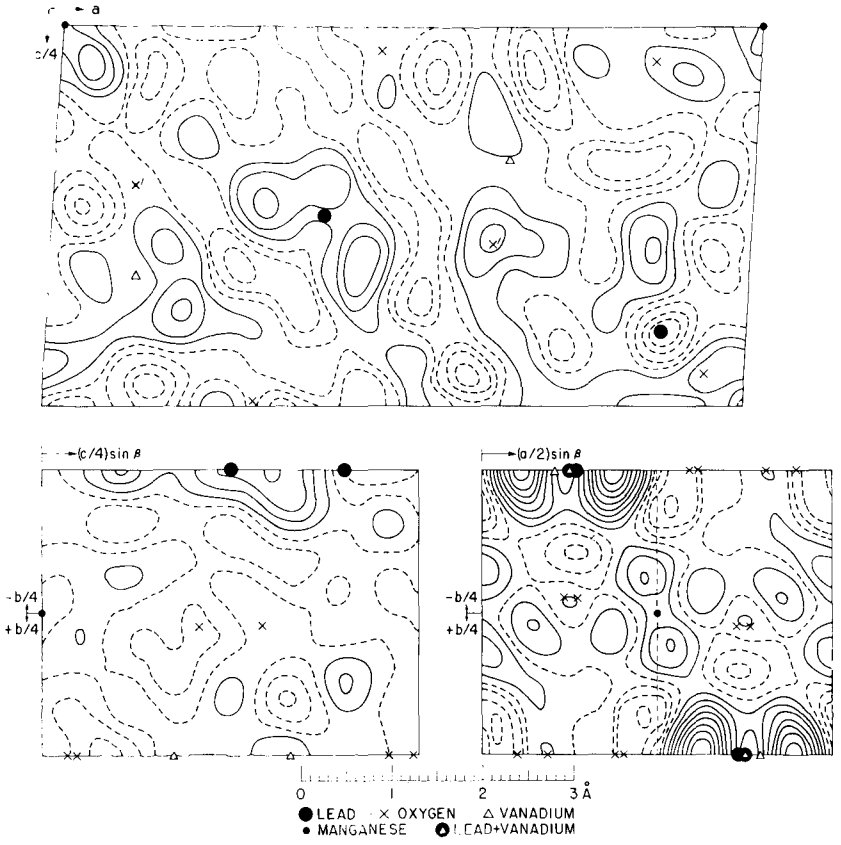

FIG. 4. Final difference ($F_o - F_c$) maps of the brackebuschite structure. Contours at intervals of $\sim 2e.Å^{-2}$; zero and negative contours broken. Positions of two pairs of superimposed oxygen atoms indicated by X′.

ACCURACY OF RESULTS

Values of F_c, $F_{c(m)}$, and F_o are given in Table 3. The reliability index, R, is 0.09 for the $\{hk0\}$ zone, 0.12 for the $\{0kl\}$ zone, and 0.18 for the $\{h0l\}$ zone when the contributions of *the metal atoms only* are included; it is 0.06 for the $\{hk0\}$ zone, 0.08 for the $\{0kl\}$ zone, and 0.12 for the $\{h0l\}$ zone (overall value, 0.10) when the contributions of *the metal and the oxygen atoms* are included.

Standard deviations in the distances between metal atoms were calculated, assuming that the atoms may be considered as symmetrical and independent (Cruickshank, 1949), despite the fact that the criterion of complete refinement has not been met rigidly in the present case.

TABLE 3. STRUCTURE FACTOR DATA (F_o, OBSERVED; $F_{c(m)}$, CALCULATED FOR METAL ATOMS ONLY; F_c, CALCULATED FOR ALL METAL AND OXYGEN ATOMS WITH EXCEPTION OF H_2O)

hkl	F_o	F_c	$F_{c(m)}$	*hkl*	F_o	F_c	$F_{c(m)}$
000	—	+1196	+940	0.2.10	<93	−119	−128
200	117	+118	+104	0.3.10	221	−210	−231
400	524	−525	−467	0.4.10	145	+163	+168
600	<46	+1	−1	0.5.10	154	+150	+168
800	261	+279	+274	0.6.10	<75	−61	−64
210	652	−614	−667	0.1.12	<96	+70	+77
220	43	+42	+48	0.2.12	228	+240	+249
230	486	+460	+522	0.3.12	<100	−59	−64
240	73	+66	+61	0.4.12	106	−116	−122
250	376	−355	−355	0.5.12	<90	+42	+46
260	<45	+21	+22	0.1.14	341	−362	−339
270	196	+208	+230	0.2.14	<100	−11	−20
410	47	−34	−38	0.3.14	306	+301	+287
420	511	+480	+527	0.4.14	<93	+65	+71
430	<44	+27	+31	0.5.14	199	−233	−219
440	349	−343	−319	0.1.16	107	+119	+122
450	<46	−18	−19	0.2.16	<99	−64	−56
460	237	+261	+272	0.3.16	97	−103	−105
610	345	+385	+362	0.4.16	78	+83	+90
620	67	+67	+76	0.1.18	<90	+38	+48
630	293	−310	−305	0.2.18	92	+103	+97
640	<45	+4	+3	002	181	−165	−164
650	231	+247	+228	004	204	−182	−186
810	43	+42	+36	006	163	+139	+146
820	138	−176	−200	008	144	+148	+73
830	43	−34	−30	0.0.10	234	+237	+246
020	617	−589	−585	0.0.12	186	−178	−187
040	618	+600	+516	0.0.14	98	+90	+98
060	294	−277	−270	0.0.16	<81	+112	+126
012	312	+295	+336	0.0.18	<73	−57	−49
022	312	+291	+290	101	<37	+28	+30
032	294	−270	−257	103	152	−170	−176
042	95	−104	−104	105	637	+588	+652
052	162	+140	+166	107	<64	−12	−12
062	112	+128	+128	109	217	−263	−318
072	100	−103	−94	1.0.11	210	+230	+226
014	269	−272	−261	1.0.13	<81	+9	+43
024	190	+163	+301	1.0.15	101	+124	+124
034	223	+209	+203	1.0.17	<78	+24	+9
044	145	−114	−121	1.0.19	<58	+3	0
054	108	−139	−136	202	326	+313	+379
064	114	+112	+142	204	145	−178	−190
074	65	+86	+85	206	182	+176	+89
016	<72	−32	+4	208	<70	−34	−44
026	<81	+2	−2	2.0.10	344	+302	+276
036	<90	+41	−3	2.0.12	<80	+86	+84
046	106	+88	+91	2.0.14	253	−276	−289
056	<99	+1	+3	2.0.16	180	+244	+248
066	<94	0	−1	2.0.18	121	+101	+78
018	123	−144	−133	301	<60	+145	+146
028	<87	+36	+44	303	169	−186	−86
038	94	+115	+108	305	<67	+60	+60
048	<99	+81	+45	307	322	+364	+356
058	<99	−78	−74	309	110	−136	−144
068	<88	+21	+27	3.0.11	<80	−31	+23
0.1.10	229	+243	+282	3.0.13	<82	+73	+69

TABLE 3—(*continued*)

hkl	F_o	F_c	$F_{c(m)}$	*hkl*	F_o	F_c	$F_{c(m)}$
3.0.15	81	+106	+93	2.0.$\bar{10}$	242	−198	−202
3.0.17	<71	+93	+86	2.0.$\bar{12}$	<80	−74	−64
402	311	+309	+320	2.0.$\bar{14}$	356	+358	+361
404	322	+287	+250	2.0.$\bar{16}$	<80	−72	−68
406	78	−51	−54	2.0.$\bar{18}$	<69	−27	−14
408	<78	+1	+16	30$\bar{1}$	98	+87	+144
4.0.10	<81	−75	−81	30$\bar{3}$	352	+363	+365
4.0.12	215	+214	+219	30$\bar{5}$	467	−429	−426
4.0.14	<80	−27	−33	30$\bar{7}$	<72	−71	−71
4.0.16	<71	−16	−31	30$\bar{9}$	366	+323	+365
501	<76	+43	+55	3.0.$\bar{11}$	<80	−65	−69
503	<77	+142	+161	3.0.$\bar{13}$	92	+89	+57
505	255	−286	−309	3.0.$\bar{15}$	<81	−60	−66
507	115	+147	+160	3.0.$\bar{17}$	76	+89	+95
509	214	+247	+289	40$\bar{2}$	117	+148	+159
5.0.11	122	−141	−129	40$\bar{4}$	356	+282	+223
5.0.13	<79	+24	+17	40$\bar{6}$	<75	+16	+31
602	<80	−68	−108	40$\bar{8}$	<78	+50	+68
604	205	+211	+208	4.0.$\bar{10}$	107	−137	−129
606	<82	−8	−6	4.0.$\bar{12}$	225	+222	+208
608	<82	+69	+71	4.0.$\bar{14}$	<80	−15	+3
6.0.10	<82	−108	−114	4.0.$\bar{16}$	<71	−58	−64
6.0.12	<76	+38	+42	50$\bar{1}$	198	+161	+169
6.0.14	245	+247	+236	50$\bar{3}$	<77	−1	−16
701	<82	+36	+30	50$\bar{5}$	<78	−91	−93
703	111	+150	+125	50$\bar{7}$	352	+321	+282
705	<81	+77	+73	50$\bar{9}$	<81	−54	−60
707	150	−135	−122	5.0.$\bar{11}$	<82	−25	−17
709	121	+140	+146	5.0.$\bar{13}$	<80	+15	+7
7.0.11	<66	+34	+12	5.0.$\bar{15}$	133	+121	+98
802	111	−133	−142	60$\bar{2}$	183	+211	+238
804	<76	−84	−66	60$\bar{4}$	<81	+34	+26
806	117	+120	+111	60$\bar{6}$	<82	+42	+16
808	75	+47	+47	60$\bar{8}$	<82	−100	−104
901	48	+54	+42	6.0.$\bar{10}$	178	+181	+201
10$\bar{1}$	<37	−57	−64	6.0.$\bar{12}$	111	+144	+141
10$\bar{3}$	258	+219	+229	6.0.$\bar{14}$	131	−193	−186
10$\bar{5}$	299	+274	+266	70$\bar{1}$	<82	−5	−6
10$\bar{7}$	397	−387	−290	70$\bar{3}$	143	−161	−169
10$\bar{9}$	211	+249	+242	70$\bar{5}$	269	+283	+284
1.0.$\bar{11}$	130	+116	+103	70$\bar{7}$	169	+89	+82
1.0.$\bar{13}$	<81	+41	+32	70$\bar{9}$	91	−123	−138
1.0.$\bar{15}$	109	−90	−52	7.0.$\bar{11}$	<66	+75	+72
1.0.$\bar{17}$	<78	−69	−75	80$\bar{2}$	<78	+16	+14
1.0.$\bar{19}$	237	+258	+254	80$\bar{4}$	<76	−73	−37
20$\bar{2}$	133	−148	−249	80$\bar{6}$	<72	−2	−2
20$\bar{4}$	302	+293	+296	80$\bar{8}$	<60	−10	−11
20$\bar{6}$	<64	+6	+79	90$\bar{1}$	63	−36	−32
20$\bar{8}$	204	+205	+213	90$\bar{3}$	27	+33	+31

Thus the final difference maps (Fig. 4) demonstrate that some systematic errors remain. These are due in part to the fact mentioned previously that the same corrections were applied to the scattering curve for a metal atom of a given atomic number regardless of the zone under investigation, even when atoms of that atomic number were crystallo-

graphically non-equivalent. Others arise from the use of final coordinates which are *averages* of the measurements obtained separately from the three zones, thus leaving gradients at some atomic positions in the final difference maps. The calculations, however, should be valid for lead because the peaks in the electron-density maps arising from such very heavy atoms should not be affected appreciably by the presence of the smaller peaks and their associated diffraction ripples. The standard deviation obtained from the Pb-Pb distances was 0.02 Å.

The standard deviation for the Mn-Mn, V-V and Mn-V distances is 0.05 Å, and for the Pb-Mn and Pb-V distances it is 0.04 Å. These values may be low because the precise location of Mn and V will be affected to a greater extent than that of Pb by the incomplete refinement and by the fact that the unresolved oxygen peaks are of comparable size.

The method was useless in the case of oxygen because of the poor resolution and the presence of spurious peaks of similar height (see Fig. 3). Comparison of coordinates from the three zones suggest that errors in the oxygen atom positions may be as high as 0.25 Å. The sites finally adopted, however, are reasonable on chemical grounds and, as stated in connection with Table 3, there is a marked improvement in the reliability index for each zone when the contributions of oxygen atoms in these positions are included.

Description of the Structure, and Discussion

The structure of brackebuschite projected on (100) and on (010) is shown in Fig. 5. The tetrahedral arrangment of oxygen atoms around each of the crystallographically distinct vanadium atoms is the same within the limited accuracy with which the parameters of the oxygen atoms are known, but no definite conclusions can be drawn regarding the regularity of the oxygen tetrahedra. The closest O-O distances in the two non-equivalent VO_4 groups are 2.75 to 3.02 Å in one and 2.79 to 3.01 Å in the other. The V-O distances are given in Table 4.

This tetrahedral coordination of oxygen around vanadium is found also in pucherite (Qurashi & Barnes, 1953), in descloizite (Qurashi & Barnes, 1954), in pyrobelonite (Donaldson & Barnes, 1955), and in V_2O_5(Ketelaar, 1936). In a more recent structure for V_2O_5 proposed by Byström, Wilhelmi & Brotzen (1950) and in the structure of $KVO_3 \cdot H_2O$ (Christ,

Table 4. Vanadium-Oxygen Distances (in Å)

V(2)–O(1), 1.72	V(1)–O(5), 1.71
V(2)–O(2), 1.72	V(1)–O(6), 1.71
V(2)–O(3), 1.83	V(1)–O(7), 1.80
V(2)–O(4), 1.86	V(1)–O(8), 1.90

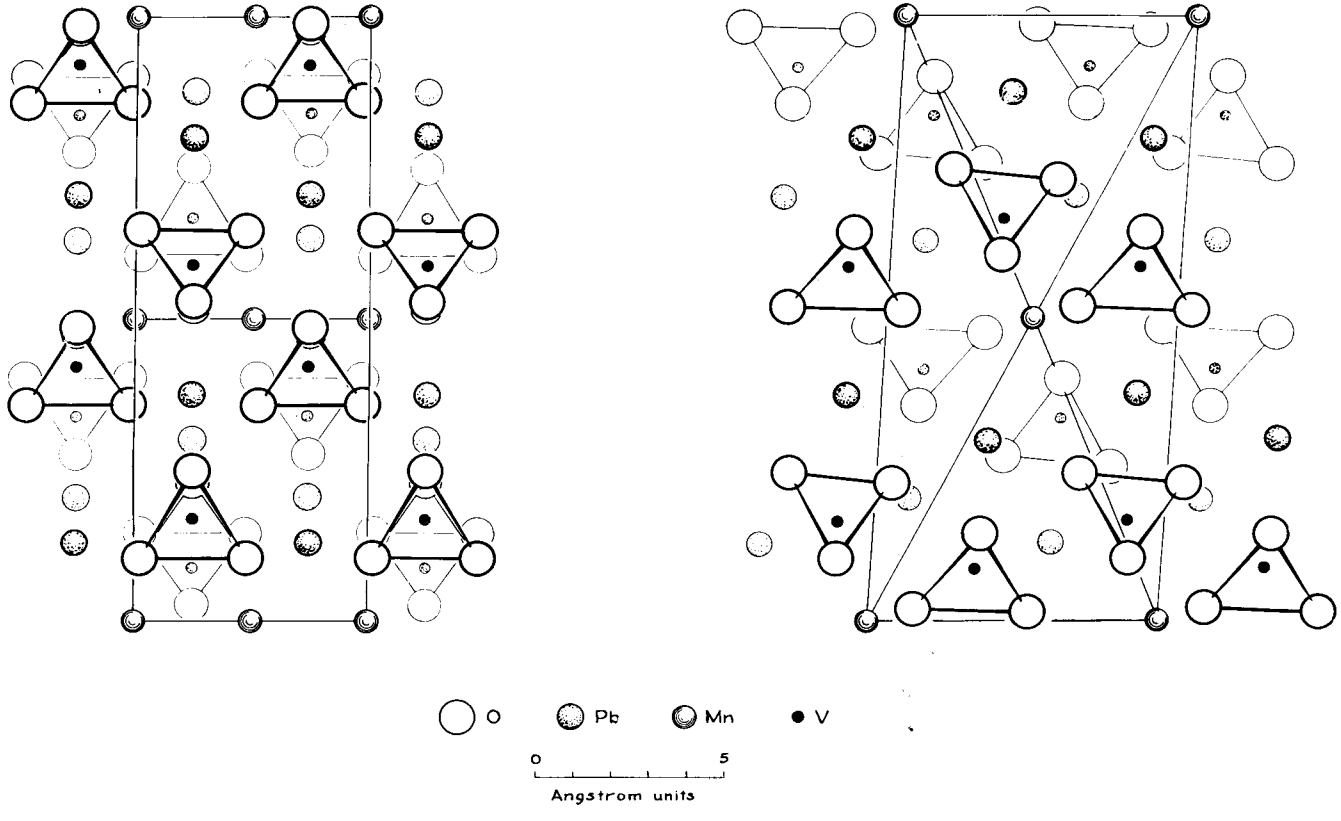

FIG. 5. Projection of the structure of brackebuschite (left) on (100), and (right) on (010); c vertical in each case.

Clark & Evans, 1953) there is fivefold coordination of oxygen around vanadium, the oxygen atoms forming a system of linked distorted trigonal bipyramids. This arrangment, however, also may be considered as made up of distorted tetrahedral VO_4 building units (see Fig. 3*a* of Byström, Wilhelmi & Brotzen, 1950, and O_I, O_{II}, O'_{III} in Fig. 2 of Christ, Clark & Evans, 1953).

The coordination of oxygen with manganese is square within the limits of experimental error. The Mn-O distances are 1.88 Å and 2.00 Å (the manganese atoms are at centres of symmetry) and the distances between oxygen atoms are 2.73 Å and 2.75 Å, respectively. The plane of the square is tilted at an angle of 50° to (010) about one of the diagonals, and the structure around manganese consists of these square arrays of oxygen atoms, sharing a corner, and running in a zig-zag along the *b*-axis with the manganese atoms at the centres of the squares.

The initial distinction between the vanadium and manganese positions is thus confirmed by the coordination of the oxygen atoms around these sites. Interchanging the manganese atom and one of the vanadium atoms would result in a most improbable configuration for the VO_4 group.

Although no coordinates have been assigned to the water molecules, the most reasonable positions for them on spatial grounds are above and below the centre of the plane of the four oxygen atoms around the manganese atom. This would not affect the coordination around any of the other metal atoms but would make the oxygen coordination sixfold around manganese with tetragonal bipyramidal polyhedra of oxygen atoms sharing edges. The environment of the manganese atoms would then resemble that of the metal atoms in the structures of MnO and FeO (Wells, 1945, p. 312). One of the extraneous peaks on each of the (100) and (001) electron-density maps is consistent with such a position for the water molecule, but no confirmation is obtained from the (010) map. It is possible, of course, that the chemical analysis (Doering, 1883) may be in error. Unfortunately, brackebuschite is a rare mineral but, if sufficient pure material could be collected, a new analysis would be highly desirable. No clear indication of whether the H_2O should be included or not can be obtained from comparison of the observed and calculated densities although it may be noted that the value calculated on the basis of $Pb_4MnFe(VO_4)_4 \cdot 2H_2O$ is slightly higher than that observed by Berry & Graham (1948). It is interesting to note that the oxygen coordination around each Mn in pyrobelonite (Donaldson & Barnes, 1955) is sixfold, and it may be significant that the positions of the OH groups in that structure correspond to those now suggested for the H_2O molecules in brackebuschite.

Different arrangments of oxygen atoms occur around each of the two

non-equivalent lead atoms. One of these, Pb(1) has eight nearest oxygen neighbours at distances of 2.54 to 2.95 Å. Within this octahedron, the closest O-O distances vary from 2.58 to 3.36 Å. The other lead atom, Pb(2), has ten nearest oxygen neighbours at distances of 2.58 to 3.02 Å, and the closest approach of oxygen atoms within this polyhedron is 2.75 Å. There appears to be no resemblance between either of these polyhedra and the arrangment of the seven nearest oxygen atoms around the lead in pyrobelonite (Donaldson & Barnes, 1955).

The two lead atoms, Pb(1) and Pb(2), are 4.18 Å apart, but the shortest Pb-Pb distance is between Pb(2) and its equivalent through the centre of symmetry at $\frac{3}{4}, \frac{1}{2}, \frac{1}{4}$ where the distance is 4.04 Å. The nearest Mn is 3.82 Å from Pb(1) and 3.84 Å from Pb(2). The closest approach of vanadium and lead is 3.48 Å between Pb(1) and V(2); other Pb-V distances are 3.53, 3.75, and 3.97 Å. The manganese atoms are separated by 3.08 Å, and they are at distances of 3.21 and 3.51 Å respectively, from the nearest two cystallographically distinct vanadium atoms. V(1) and V(2) are 4.30 Å apart.

Throughout the structure investigation it has been assumed that the space group of brackebuschite is $B2_1/m$ and not $B2_1$. The primary object of the present study has been to establish the features of the brackebuschite structure in sufficient detail to determine its relationship to that characteristic of the minerals of the descloizite and adelite groups. No attempt has been made to attain very high accuracy in the determination of interatomic distances which would have required three-dimensional treatment of the observed data because of the overlapping of oxygen atoms. The accuracy attained, however, is sufficient to show that if the space group is in fact $B2_1$, only minor displacements of the metal atoms from the special positions of $B2_1/m$ could be involved, although the sites of the oxygen atoms and of the water molecules (if present) are somewhat more flexible.

Relationship between Brackebuschite and the Minerals of the Descloizite and Adelite Groups

In assessing the structural relationship of brackebuschite to the minerals of the descloizite and adelite groups, it is appropriate to select pyrobelonite as a typical example of the latter. Its structure, which is essentially the same as those of descloizite and conichalcite, has been refined with satisfactory accuracy (Donaldson & Barnes, 1955), and the suggestion has been made (Richmond, 1940) that pyrobelonite actually forms a chemical series with brackebuschite.

The three principal projections of the structures of both minerals are shown schematically in Fig. 6. In the study of pyrobelonite (Donaldson

& Barnes, 1955) the origin chosen was not the most suitable for such direct comparison but this has now been adjusted. It should also be noted that $c/2$ in brackebuschite corresponds to c in pyrobelonite.

The major differences between the structures of the two minerals appear to be due to the presence of the additional manganese atoms in pyrobelonite, the accommodation of which requires some alteration in the lattice of the lead and vanadium atoms from brackebuschite to pyrobelonite (see particularly the projections on (010)). The changes are primarily along the direction of the c-axis, which increases from 8.26 Å for $c/2$ in brackebuschite to 9.52 Å for c in pyrobelonite.

The reasons for the interesting similarities and differences between corresponding precession photographs of brackebuschite and pyrobelonite (Barnes & Qurashi, 1952; Qurashi & Barnes, 1953, Fig. 1) are now evident from Fig. 6. The projections on (001) are almost identical except for very slight displacements of lead, vanadium, and oxygen atoms in brackebuschite which are superimposed in pyrobelonite, thus accounting for the almost identical precession photographs of the $\{hk0\}$ zones. Additional manganese atoms in pyrobelonite, and changes in the z-coordinates, are the principal differences between the projections on (100), but the similarity is still sufficiently close to explain why corresponding $0kl$ reflections are so much alike. Because of different symmetry elements, in addition to the presence of additional manganese atoms and different positions for the lead atoms in pyrobelonite, the projections on (010) are quite different, and thus very little resemblance would be expected between corresponding $h0l$ reflections, as is indeed found to be the case.

It is clear from Fig. 6 that, although the structures of brackebuschite and pyrobelonite are similar in some respects, the relationship is not of the type suggested by Richmond (1940), who implied that the two minerals were isostructural, differing only in the Pb:Mn ratio. The present results are in complete agreement with the contents of the unit cell derived from chemical analysis (Doering, 1883) except perhaps for the water-content, and with the observed specific gravity (Berry & Graham, 1948). They substantiate the conclusion of Berry & Graham (1948) that brackebuschite probably belongs to a chemical type $A_3(XO_4)_2 \cdot nH_2O$, and they demonstrate clearly that brackebuschite should not be classified with the minerals of the descloizite and adelite groups.

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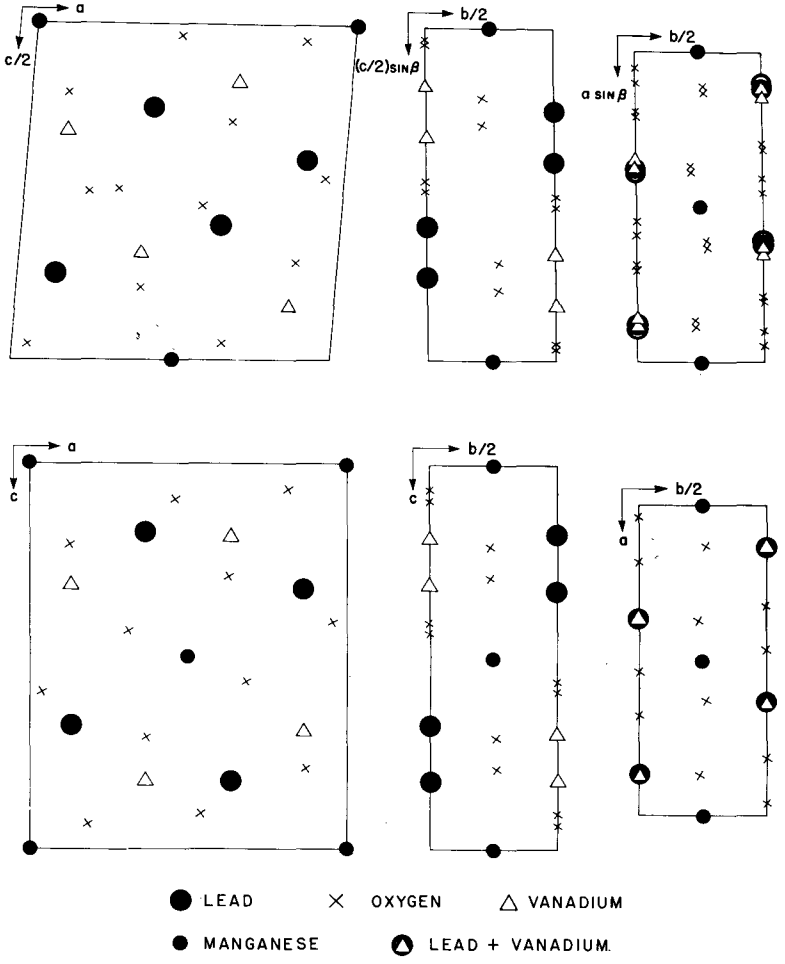

FIG. 6. Projections on (010), (100), and (001) of (top) brackebuschite and (bottom) pyrobelonite (possible H_2O sites not shown in former; OH sites not shown in latter).

with the structure factor and Fourier calculations. We are indebted especially to Dr. Howard T. Evans for his kindness in preparing Fig. 5.

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