UNIT CELL AND SPACE GROUP DATA FOR
CERTAIN VANADIUM MINERALS

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Abstract

The present status of x-ray diffraction data on vanadium minerals is reviewed briefly. Unit cell and space group data for metahewettite, metarossite, melanovanadite, descloizite, pyrobelonite, brackebuschite, and a new (unnamed) iron vanadate are presented. A brief reference to hewettite and some remarks on the structure of metahewettite are included.

Introduction

Although some twenty or thirty minerals containing vanadium as a primary constituent have been reported (for example, see Dana-Ford, 1947, Hey, 1950, or Mellor, 1947), relatively few of them have been satisfactorily characterized crystallographically. This is due primarily to the fact that many, particularly those containing the lighter metals, are so poorly formed that single crystals suitable for goniometric or x-ray investigation are excessively small, rare, or unobtainable, and even their powder diffraction lines often are weak and diffuse. Optical and x-ray studies of the generally better crystallized vanadates of the heavier metals also have been restricted due to the high absorption of both light and x-radiation in many species.

It is not surprising, therefore, that, in spite of the number of simple compounds of vanadium whose structures are known, or for which at least the unit cell constants and space groups have been determined (Lukesh, 1950), very few structural data are available for the vanadium minerals. These do include, however, a suggested structure for vanadinite, $Pb_5Cl(VO_4)_3$, (Hendricks, Jefferson & Mosley, 1931), and one for (synthetic) sulvanite, Cu_3VS_4, (Lundquist & Westgren, 1936). Unit cell data, not always including the space group, have been obtained for ardennite (a vanadio-silicate of Al and Mn, containing As) (Gossner & Strunz, 1932), pascoite, $2CaO \cdot 3V_2O_5 \cdot nH_2O$, (Berman, 1942), descloizite, $(Zn,Cu)PbVO_4(OH)$, (Bannister, 1933), pyrobelonite, $(Mn,Pb)_2 VO_4(OH)$, (Strunz, 1939; Richmond, 1940), brackebuschite, $(Pb,Mn)_2 VO_4(OH)$, (Berry & Graham, 1948), pucherite, $BiVO_4$, (de Jong & de Lange, 1936), hummerite, $Mg_2K_2V_{10}H_{32}O_{44}$, (Weeks, Cisney & Sherwood, 1951; Weeks, 1951), and montroseite, $2FeO \cdot V_2O_3 \cdot 7V_2O_4 \cdot 4H_2O$, (Weeks, Cisney & Sherwood, 1951; Weeks, 1951).

Identical powder photographs have been reported by Bannister (1933) for the zinc-copper-lead hydrous vanadates, descloizite, cuprodescloi-

NRC 2727

zite, psittacinite, eusynchite, deschenite, and mottramite. That from chileite was slightly different but Bannister considers that the specimen probably was not pure. Strunz (1939) has confirmed these results, except in the case of chileite, which he did not examine. Bannister (1933) concludes that a complete isomorphous series exists between descloizite, $ZnPbVO_4(OH)$, and mottramite, $CuPbVO_4(OH)$, in which $Zn+Cu=4$ atoms per unit cell (with some degree of substitution by Fe and Mn), and he recommends that all names be dropped except "descloizite," $(Zn,Cu)PbVO_4(OH)$, for the Zn-rich members of the series and "mottramite," $(Cu,Zn)PbVO_4(OH)$, for the Cu-rich varieties. Strunz (1939) also has pointed out the structural correspondence of aræoxene, ZnPb $(V,As)O_4(OH)$, with descloizite. On the basis of single crystal rotation photographs, Strunz (1939) considers that pyrobelonite, $(Mn,Pb)_2VO_4$ (OH), is isostructural with descloizite, but, from powder photographs, he concludes that brackebuschite, $(Pb,Mn)_2VO_4(OH)$, is completely different. On the other hand, Richmond (1940), who also classifies pyrobelonite with descloizite on the basis of x-ray data, suggests, on chemical grounds, that pyrobelonite and brackebuschite form a series, with which Berry & Graham (1948) are not in agreement.

The status of the copper-calcium hydrous vanadates, calciovolborthite, volborthite, and their varieties (Mellor, 1947; Strunz, 1939) is very confused and their compositions are uncertain. On the basis of powder photographs, however, Strunz (1939) concludes that volborthite probably is identical with tangeite, which is structurally similar to the minerals of the descloizite group. "Tangeite," however, is synonymous with calciovolborthite and Hey (1950) lists it as a member of the descloizite group. He considers it improbable that volborthite should be similarly classified.

In addition to the obvious importance of the structural types, and the coordination number of vanadium, a number of other features of the vanadium minerals are of interest. For example, in the calcium vanadates, $xCaO \cdot yV_2O_5 \cdot nH_2O$, the ratio $x:y$, passes from 1:3 in hewettite and metahewettite (Hillebrand, Merwin & Wright, 1914), through 2:3 in pascoite (Hillebrand, Merwin & Wright, 1914), and 1:1 in rossite and metarossite (Foshag & Hess, 1927), to 2:1 in pintadoite (Hess & Schaller, 1914), with the value of n uncertain in most cases. The water content of hewettite and metahewettite is very sensitive to changes in atmospheric humidity but the two minerals are not interconvertible by this means. On the other hand, metarossite ($n=2$) appears to be a dehydration product of rossite ($n=4$) from which it is obtained on standing in air, while rossite crystallizes from aqueous solutions of either rossite or metarossite.

With fernandinite, $CaO \cdot 5V_2O_5 \cdot V_2O_4 \cdot 14H_2O$, (Schaller, 1915), and melanovanadite, $2CaO \cdot 3V_2O_5 \cdot 2V_2O_4 \cdot nH_2O$, (Lindgren, Hamilton & Palache, 1922), the calcium vanadates become more complex chemically with the appearance of vanadium in two valence states.

The replacement of calcium by copper commences in calciovolborthite and volborthite, lead occurs with copper in mottramite and substitution of zinc for the latter in an isomorphous series is ideally complete with descloizite. In place of copper and zinc, manganese is found with lead in pyrobelonite and in brackebuschite.

The descloizite group of vanadates is linked through the arsenious descloizite, aræoxene, to isomorphous arsenates such as conichalcite (higginsite), $CuCaAsO_4(OH)$, (Strunz, 1939; Richmond, 1940; Berry 1951), thus inviting direct x-ray structural investigation of the tacit assumption sometimes made that certain arsenates and vanadates are necessarily isomorphous and isostructural.

To complete this brief summary, mention must be made of the several interesting uranium vanadates and of a few vanadium minerals that contain cations other than those already mentioned, such as barium, iron, aluminium, and bismuth (for details, see Hey, 1950, Dana, 1947, or Mellor, 1947).

In spite of the unprepossessing nature of much of the available material, a systematic structural examination of vanadium minerals has been started in this laboratory. At present the uranium vanadates are not being included, nor are hummerite and montroseite, which are under study elsewhere (Weeks, 1951).

The present paper covers unit cell and space group data for metahewettite, metarossite, melanovanadite, descloizite, pyrobelonite, brackebuschite, and a new (unnamed) iron vanadate. A few notes on hewettite and a preliminary discussion of the structure of metahewettite are included. A preliminary structure for pucherite, $BiVO_4$, is described in a separate paper (Qurashi & Barnes, 1952).

METAHEWETTITE AND HEWETTITE

Hillebrand, Merwin & Wright (1914) describe metahewettite and hewettite as hydrous calcium vanadates with the same composition, $CaO \cdot 3V_2O_5 \cdot nH_2O$, in which n has a maximum value of 9 and a probable minimum of 3. The water content was found to be very sensitive to changes in atmospheric humidity, and significant differences in the behaviour of the two minerals were observed during progressive dehydration at room temperature and above 100° C. Metahewettite and hewettite apparently are not interconvertible by change in water content. In the absence of crystals suitable for goniometric measurement, Hille-
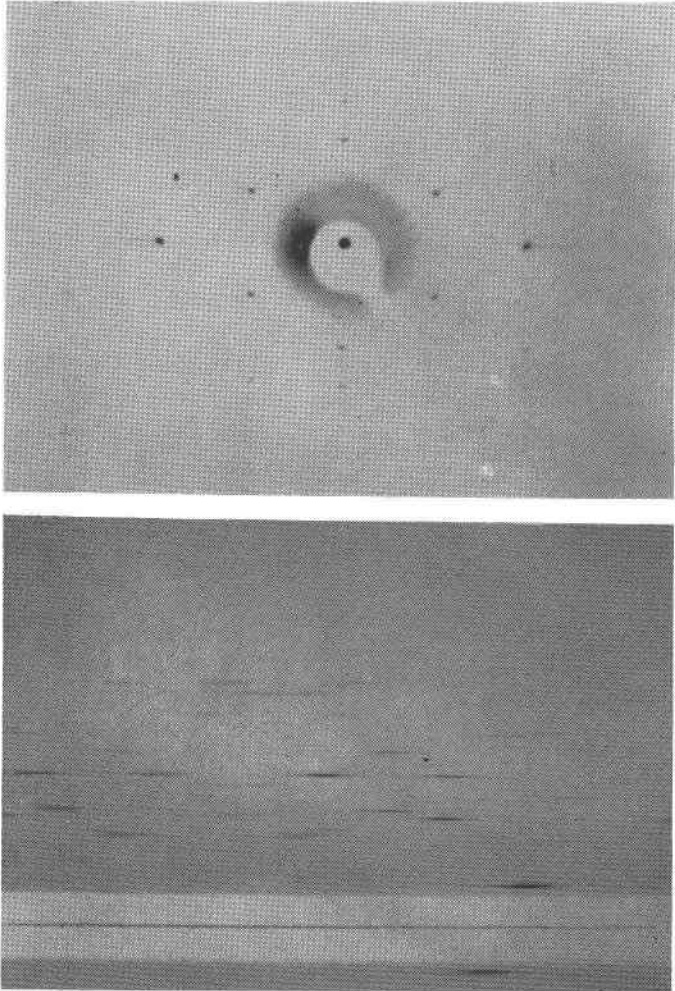
FIG. 1 (top). Metahewettite. Precession photograph of zero level (approximately normal to (101) axis) showing double set of reciprocal lattice points, $(hlh)^*$, $(\bar{h}lh).^*$ (Mo, 36 hrs.)

FIG. 2. Metahewettite, zero level, b axis, Weissenberg photograph. (Cu, 50 hrs.)

brand, Merwin & Wright (1914) concluded from the general outlines and the observable optical properties that both minerals probably are orthorhombic.

The present x-ray investigation of metahewettite is based on material from the Cactus Mine, Yellow Cat District, Grand County, Utah (Harvard No. 98019). The metahewettite cleaves readily to yield lathlike crystals, and sheaves of crystals, of rectangular cross section. Ex.

tinction is parallel to the long axis and the faces of most laths are striated in the direction of this axis. The high negative birefringence, with X perpendicular to the large faces of the laths (Hillebrand, Merwin & Wright, 1914) suggests that the oxygen atoms in the structure probably lie in sheets parallel to these faces.

Preliminary precession photographs with the x-ray beam coincident with the long axis of the specimens showed short, diffuse arcs, indicating multiple crystals with a helical twist, or a range of orientation, about this axis.

One of the difficulties in handling metahewettite crystals is longitudinal cleavage into excessively thin specimens when any attempt is made to reduce the length of the laths. A crystal (approximately, $500 \times 40 \times 5\mu$) finally was obtained and mounted on the precession instrument with the long axis horizontal (*i.e.*, at right angles to the direction of the x-ray beam). Precession photographs gave a translation of 3.614A[1] along this (*b*) axis, with $a = 12.18$ A and $c = 7.80$ A, each at 90° to the *b* axis. The c^* axis was found to be perpendicular to the large faces of the laths, thus identifying these faces as {001}. The value of β^*, obtained as the difference between the precession instrument dial readings when the x-ray beam was normal to a^*b^* and when it was normal to c^*b^*, was approximately 90°, high accuracy being impossible due to the diffuse nature of the reflections and the insensitiveness of the a^*b^* and c^*b^* nets on the photographs to small changes in dial setting.

Assuming $\beta^* = 90°$, however, the position of the [101]* axis was calculated and a zero level precession photograph was taken with [101]* vertical and b^* horizontal. This picture is reproduced in Fig. 1. Although some of the spots are very weak and are difficult to observe in the print, the original negative shows two distinct reciprocal lattice nets with a marked difference in the intensities of the spots defining the two nets. The vertical rows are common to both nets but the reciprocal lattice spacings in the vertical direction are not equal. They differ from that calculated for [101]*, on the assumption that $\beta^* = 90°$, by about $\pm 4\%$, which is more than ten times the probable error of measurement, whereas their mean is close to the calculated value. This suggested that the crystal was really monoclinic with $\beta^* \simeq 90°$ and was twinned with c^*(or a^*) common to the two individuals. On this basis the two reciprocal lattice spacings were identified with [101]* and [$\bar{1}$01]*, respectively, and β^* was obtained from the relationship, $(t^*_{101})^2 - (t_{\bar{1}01})^2 = 4a^*b^* \cos\beta^*$. From this, $\beta = 95°15'$.

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[1] All precession photographs of the minerals discussed in this paper were taken with Mo $K\alpha$ radiation ($\lambda = 0.7107$ A), while Cu $K\alpha$ ($\lambda = 1.5418$ A) was employed for the Weissenberg films.
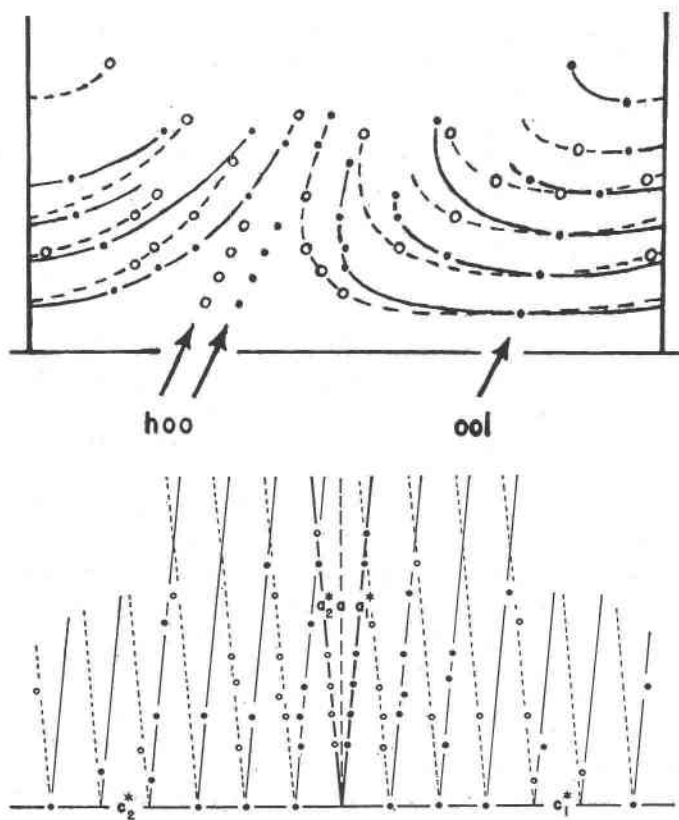
FIG. 3. Metahewettite; a (top), streaks of Fig. 2 reduced to spots; b (bottom) corresponding reciprocal lattice net with points of one twin shown as open circles and points of the other as closed circles.

The crystal was then transferred to the Weissenberg goniometer and a good rotation photograph about the b axis was obtained. The corresponding Weissenberg photographs, however, were comparatively poor, each diffraction spot being drawn out into a streak representing an angular distortion of the crystal of about $\pm 5°$. The upper half of the b axis, zero level, Weissenberg picture is reproduced in Fig. 2. Fig. 3a shows how the same photograph appears when the streaks are reduced to spots at their mid-points. The reciprocal lattice corresponding to these spots is plotted in Fig. 3b from the actual measurements of the Weissenberg film of Fig. 2. Both the twinning with a common a axis and the coincidence of the c^* axes are immediately apparent from these figures. The disentanglement of the streaky reflections due to one twin from

those due to the other in Fig. 2 was aided by the fact that the reflections from one twin are only about 75% as strong as those from the other. The unit cell constants obtained from the Weissenberg photograph agree to within 0.2% with those from the precession pictures.

Hillebrand, Merwin & Wright (1914) give the density of metahewettite as 2.942 when there are 3 moles of water per formula unit and 2.511 when there are 9 moles of water. Using the first value, the number of formula units per cell (Z) is 0.93≃1, in agreement with 3 H_2O per formula unit. Although this does not determine the water content precisely, it does fix the maximum for the metahewewttite crystal under investigation. The molecular volumes of $CaO \cdot 3V_2O_5 \cdot 9H_2O$ and $CaO \cdot 3V_2O_5 \cdot 3H_2O$, calculated from the foregoing values for the densities, are 505 A³ and 370 A³, respectively. The difference, 135 A³, represents the increase in molecular volume due to the introduction of 6 H_2O, or about 23 A³ per water molecule. Since this value has been obtained from experimental density data, it seems reasonable to take 25 A³ as a rough estimate of the unit cell volume occupied by one molecule of water in these, and related, minerals, particularly when compared with the molecular volume of liquid water, which is approximately 30 A³.

Comparison of the zero and upper level precession photographs indicates a screw axis (2_1) as the only space group criterion; otherwise the diffraction symmetry is $2/m$ with the diffraction symbol $2/m$ P-/-. However, since the formula unit, $CaO \cdot 3V_2O_5 \cdot 3H_2O$, contains only one Ca and there is only one formula unit per unit cell, the screw axis cannot be a real symmetry element because it would require the presence of at least two atoms of calcium in the unit cell. The extinction, ($0k0$) when k is odd, probably is due to some structural pseudosymmetry, although it should be noted that its recognition, even with a precession angle of 30°, depends on the absence of two reflections, (010) and (030), only, higher orders (with k odd) being beyond the range of the precession instrument even with molybdenum radiation. A statistical survey (Howells, Phillips & Rogers, 1950) of the reflection intensities indicates a centred ($h0l$) zone with possible pseudocentring of the unit cell as a whole. The probable space group of metahewettite, therefore, is $P2$.

These unit cell and space group data for metahewettite, with those for metarossite, are given in Table 1 for comparison with Ketelaar's results (Ketelaar, 1936) on vanadium pentoxide. If the original b and c axes of vanadium pentoxide are interchanged (as they are in Table 1) it will be observed that the unit cell dimensions of metahewettite and of vanadium pentoxide are strikingly similar except for the length of the c axis, which is almost twice as long in metahewettite.

The upper level, b axis, Weissenberg photographs of metahewettite

show the same twinning effect as does the zero level film. Hence b^* (and b), in addition to a, is common to both twins, and (001), therefore, is the composition plane.

An interesting feature of the intensities observed on the upper level Weissenberg films is that $S_{h,k+2,l} \simeq S_{hkl}$ (where $S_{hkl} = F_{hkl}/f_{hkl}$), while no simple relationship exists between $S_{h,k+1,l}$ and S_{hkl}. All atoms, therefore, must have $y \simeq 0$ or $\frac{1}{2}$, which would thus account for the apparent extinction of (0k0) when k is odd. Patterson sections were made at $y = 0$ and $y = \frac{1}{2}$ and some success in their interpretation was achieved by using the structure of V_2O_5 as a guide.

Harker-Kasper inequalities, as developed by Grison (1951), were next applied to the $h0l$ projection and refinement was effected by a special technique applied to the regions of negative electron density. By these means it was possible to identify all peaks in the projection. It is of interest to note that nineteen oxygen atoms can be recognized, in further agreement with three moles of water in the formula unit, $CaO \cdot 3V_2O_5 \cdot 3H_2O$.

At present the structure appears to be made up essentially of sheets of V_2O_5 chains, alternating in the z direction with layers, each composed of atoms of calcium (at $x = \frac{1}{2}$, $z = \frac{1}{2}$) and vanadium (at $x = 0$, $z = \frac{1}{2}$) bonded together through their oxygen atoms and the water molecules. This arrangement is consistent with the optical properties and the cleavage, and is now being refined.

Hewettite is even more difficult to examine than is metahewettite. The material for the present study came from Minasragra, Cerro de Pasco, Peru (Harvard No. 96258). The crystals are microscopically small and, like metahewettite, often consist of multiple growths with the needle axes almost parallel, or they may have a helical twist about the long axis. Precession photographs with the x-ray beam normal to the long axis of one specimen (obtained by cleaving an obviously composite crystal) show that the length of this (b) axis in hewettite is identical (within 0.2%) with the length of the b axis in metahewettite. The largest, apparently single, crystal that was isolated, however, had linear dimensions of only about $100 \times 8 \times 3\mu$. With the x-ray beam again normal to the long axis, no reflections from this crystal could be observed on precession films even after exposures of 10 hours. However, a b axis, zero level, Weissenberg exposure of 70 hours did bring up a few weak, streaky reflections, which correspond with the most intense ones on the corresponding metahewettite film. It is probable, therefore, that hewettite, like metahewettite, is monoclinic with unit cell constants of the same order of magnitude as those of metahewettite.

Powder photographs of different portions of the Utah metahewettite,

taken with several different x-radiations over a period from March to July (*i.e.*, in both dry and damp laboratory atmospheres) show essentially identical d spacings and relative intensities. They can be indexed satisfactorily on the basis of the unit cell constants given in Table 1. Several powder photographs of different portions of the Peru hewettite obtained in August with copper and with cobalt radiation also are essentially identical but the positions and relative intensities of some of the lines show significant differences from the metahewettite pattern. Indexed to correspond with the latter, they indicate that the lengths of the a and c axes of hewettite may differ by 5% or 10% from the corresponding values for metahewettite.

One powder pattern of hewettite, however, which was obtained about five weeks earlier, is not identical with the others, nor does it represent simply a mixture of hewettite and metahewettite. It is possible, therefore, that the cell dimensions, if not the structure, of hewettite may be particularly sensitive to changes in atmospheric humidity.

METAROSSITE

Rossite and metarossite have been described by Foshag & Hess (1927), but none of their specimens were suitable for goniometric measurement. Both minerals, however, are soluble in water and good crystals of rossite, $CaO \cdot V_2O_5 \cdot 4H_2O$, were obtained by recrystallization. No pyramid faces were present on these crystals so that the axial ratios could not be determined but Foshag & Hess were able to establish that rossite is triclinic and they measured the axial angles and refractive indices. No optical measurements were possible on metarossite other than the lowest refractive index (α), the other two indices being too high. Foshag & Hess regard rossite and metarossite as distinct hydrates, $CaO \cdot V_2O_4 \cdot 4H_2O$ (rossite) and $CaO \cdot V_2O_5 \cdot 2H_2O$ (metarossite), and they consider that the change from one to the other is a discontinuous process. Rossite transforms gradually into metarossite, the stable form, even on standing under ordinary laboratory conditions. Rossite is obtained from aqueous solutions of either rossite or metarossite.

The specimen of metarossite (Harvard No. 90650) employed in the present investigation came from near Thompson's, Utah. It contains very small platy crystals, lamellar perpendicular to (10$\bar{1}$). Good precession photographs with reasonably sharp spots were obtained. The cell is triclinic and the unit cell constants are given in Table 1. The volume of the unit cell is 324 $Å^3$.

Taking the density of rossite, $CaO \cdot V_2O_5 \cdot 4H_2O$, as 2.45 (Foshag & Hess, 1927), the molecular volume is 210 $Å^3$. Assuming 25 $Å^3$ as the volume of one molecule of water in the unit cell (see section on *Meta-*

hewettite and Hewettite), the volume of a rossite molecule with $2H_2O$ would be approximately $210 - (2 \times 25) = 160$ A^3. If there is similar packing in metarossite, $CaO \cdot V_2O_5 \cdot 2H_2O$, this represents its molecular volume also, and the number of molecules per cell is equal to (vol. unit cell)/(mol. vol.) $= 324/160 = 2.02$. Since the unit cell of metarossite is triclinic and there are two molecules per cell, the probable space group is $P\bar{1}$.

TABLE 1

	Vanadium Pentoxide*	Metahewettite	Metarossite
Cell contents	$2[V_2O_5]$	$CaO \cdot 3V_2O_5 \cdot 3H_2O$	$2[CaO \cdot V_2O_5 \cdot 2H_2O]$
System	orthorhombic	monoclinic	triclinic
a	$11.48 \pm .01$ A	$12.18 \pm .02$ A	$6.21_5 \pm .005$ A
b	$3.55 \pm .005$ A	$3.61_4 \pm .005$ A	$7.06_5 \pm .005$ A
c	$4.36 \pm .005$ A	$7.80 + 0.03$ A	$7.76_9 \pm .005$ A
α	$90°$	$90°$	$92°58' \pm 10'$
β	$90°$	$95°0' \pm 20'$	$96°39' \pm 10'$
γ	$90°$	$90°$	$105°47' \pm 10'$
S.G.	Pmn	$P2$ (probable)	$P\bar{1}$ (probable)

* Ketelaar, 1936, after interchange of a and c axes. A units presumably should be read kX.

A significant feature of the unit cell dimensions is that whereas the c axis is approximately the same in metarossite and in metahewettite, the a axis of metarossite is about one-half the length of the a axis of metahewettite and the length of the b axis of metarossite is almost twice the length of the corresponding axis in metahewettite. In metarossite, extinction is nearly parallel to the b axis; it is parallel to b in metahewettite. There is slight distortion about the b axis of metarossite as shown by short streaks ($\pm 1°$) on the b axis Weissenberg films but it is not so extreme as in metahewettite (Fig. 2). A few weak spots appear on the very long exposure, b axis, Weissenberg films of metarossite, which indicate twinning with $(10\bar{1})$ as the composition plane, compared with (001) in metahewettite.

The most interesting feature of the observed intensities on the metarossite films is that the general (hkl) reflections with k odd are appreciably weaker than are those with k even, indicating considerable structural similarity with metahewettite.

MELANOVANADITE

Lindgren, Hamilton & Palache (1922) assign melanovanadite to the monoclinic system, but optical measurements were difficult due to very strong absorption and goniometric observations were hampered by

curved and striated faces. The original analysis of the material after it had been exposed to warm dry air for several months showed virtually no water content and gave a formula of $2CaO \cdot 3V_2O_5 \cdot 2V_2O_4$. Later, after prolonged exposure to a warm damp atmosphere, a total water content of 16.6% was found, of which 5.9% was retained above 105°C. These percentages correspond to 11 H_2O and 3.5 H_2O per formula unit, respectively.

The present x-ray study has been made on the type material from Minasragra, Peru.

Precession photographs show clearly that the cell is triclinic. The unit cell constants for the primitive cell are $a = 6.36_0 \pm .01$ A, $b = 16.86 \pm .02$ A, $c = 6.27_9 \pm .01$ A, $\alpha = 90°0' \pm 15'$, $\beta = 101°50' \pm 10'$, $\gamma = 93°10' \pm 15'$. The volume of this cell is approximately 658 A³.

Individual crystals not only were too small for a density determination using the Berman balance but accurate measurements were impossible even by the flotation method. The latter, however, did indicate considerable water content compared with the specific gravity of 3.477 given by Lindgren, Hamilton & Palache (1922) for the original anhydrous material. From this value for the specific gravity the molecular volume of $2CaO \cdot 3V_2O_5 \cdot 2V_2O_4$ is 473 A³. If the present crystals were assumed to be anhydrous, the number of molecules per unit cell (Z) would be 658/473 = 1.39. They must, therefore, contain some water. Hence, assuming one molecule per cell, the difference between the molecular (unit cell) volume actually observed and the molecular volume of anhydrous $2CaO \cdot 3V_2O_5 \cdot 2V_2O_4$ is $658 - 473 = 185$ A³. Again, as in the case of metarossite, if the volume occupied by one H_2O molecule in these minerals is approximately 25 A³, the number of molecules of water per unit cell (and formula unit) of the melanovanadite specimen under investigation is $185/25 \simeq 7$. This is in the middle of the range, $2CaO \cdot 3V_2O_5 \cdot 2V_2O_4 \cdot 3.5$ to 11 H_2O, cal-

TABLE 2. MELANOVANADITE

System	X-ray data (this paper) triclinic	Goniometric data (Lindgren, Hamilton, Palache, 1922) monoclinic
S.G.	$B1$	—
Z	2	—
a	$7.97_0 \pm .015$ A	—
b	$16.86 \pm .02$ A	—
c	$9.81_0 \pm .015$ A	—
a:b:c	0.4727:1:0.5819	0.4737:1:0.5815
α	$87°55' \pm 10'$	$90°0'$
β	$90°45' \pm 10'$	$91°22'$
γ	$92°30' \pm 20'$	$90°0'$

culated from the data of Lindgren, Hamilton & Palache (1922). There is thus one molecule per cell and the space group is probably $P1$.

It is convenient, however, both from the structural point of view and for direct comparison with the results of Lindgren, Hamilton & Palache (1922), to express the cell constants in terms of the centred cell, $B1$, as shown in Table 2.

The difference of approximately $\pm 2°$ in the interaxial angles between the x-ray and goniometric values is not surprising in view of the large dispersion of the ϕ and ρ data reported for the goniometric measurements.

The most interesting feature of the observed intensities is that reflections from $(hk0)$ are either absent or very weak when $h/2+k\neq 2n$, indicating a considerable degree of pseudosymmetry.

Brackebuschite, Pyrobelonite, Descloizite

The minerals of the adelite-descloizite group, $ABXO_4(Z)$, have been discussed in detail elsewhere (Bannister, 1933; Strunz, 1939; Richmond, 1940). There appears to be general agreement that descloizite, (Zn, Cu) $PbVO_4(OH)$, and pyrobelonite, $(Mn, Pb)_2VO_4(OH)$, are closely related, but, whereas Richmond (1940) considers that brackebuschite, (Pb, $Mn)_2VO_4(OH)$ in which $Pb:Mn \simeq 2:1$, forms a chemical series with pyrobelonite, $(Mn, Pb)_2VO_4(OH)$ in which $Mn:Pb \simeq 3:2$, Strunz (1939) concludes that brackebuschite is completely different in structure from the minerals of the descloizite group and Berry & Graham (1948) consider that it belongs to the chemical type $A_3(XO_4)_2 \cdot nH_2O$.

In preparation for structure determinations of the vanadates of the descloizite group, the unit cell constants and space groups of brackebuschite, pyrobelonite and descloizite have been redetermined.

Precession photographs of brackebuschite crystals, from the Sierra de Cordoba, Argentina (Harvard No. 96255), with the x-ray beam normal to the needle axis show clearly that the unit cell is monoclinic, with b coincident with the long axis of the crystals. Zero and upper level photographs with a and c as precession axes were obtained. The a^*c^* nets were photographed by mounting a smaller crystal with b as the precession axis. Measurement of a complete set of zero level films gave the unit cell dimensions, $a = 7.68_1$ A, $b = 6.15_5$ A, $c = 8.88_0$ A, with $\beta = 111°$ 50'. Inspection of zero and upper level photographs shows a 2_1 axis along b but no other characteristic space group extinction. The space group, therefore, is either $P2_1/m$ $(C_{2h}{}^2)$ or $P2_1$ $(C_2{}^2)$. These results are in good agreement with those obtained by Berry & Graham (1948), $a = 8.92$ A, $b = 6.16$ A, $c = 7.69$ A, $\beta = 111°$ 47', after interchanging a and c.

For comparison with pyrobelonite and descloizite it is convenient, however, to choose a B centred cell for brackebuschite by taking the

[102] direction of the primitive cell as the c axis of the centred cell. The dimensions of the new cell are $a = 7.68_1$ A, $b = 6.15_5$ A, $c = 2 \times 8.26_2$ A, with $\beta = 86°15'$ and space group $B2_1/m$ (or $B2_1$).

Richmond (1940) gives the unit cell constants for pyrobelonite as orthorhombic, $a = 7.84$, $b = 9.45$, $c = 6.09$ (no units, but they are probably kX), with space group $D_{2h}^{16} - Pnam$ (no reasons being given for eliminating $C_{2v}^9 - Pna2$) and $Z = 4$. For direct comparison with brackebuschite it is necessary to interchange Richmond's b and c axes, thus making the space group $Pnma$, or $Pn2a$, the former incidentally being the standard structure orientation for D_{2h}^{16}.

Strunz (1939), independently, finds pyrobelonite to be orthorhombic with $a = 6.22$ A, $b = 9.57$ A, $c = 7.74$ A (although it is probable in this

TABLE 3

	S.G.	a	b	c	β
Brackebuschite (B. & Q.)	$B2_1/m$	7.68_1	6.15_5	$2 \times 8.26_2$	$86°15'$
Brackebuschite (B. & G.)	$B2_1/m$	7.69	6.16	2×8.30	$86°20'$
Pyrobelonite (B. & Q.)	$Pnma$	7.66_3	6.19_1	9.52_2	$90°0'$
Pyrobelonite (S.)	$Pnma$	7.74	6.22	9.57	$90°0'$
Pyrobelonite (R.)	$Pnma$	7.84	6.09	9.45	$90°0'$
Descloizite (B. & Q.)	$Pnma$	7.60_7	6.07_4	9.44_6	$90°0'$
Descloizite (B.)	$Pnma$	7.56	6.05	9.39	$90°0'$

case also that the units are kX). He does not mention its space group specifically but apparently assumes that it is the same as that of descloizite, D_{2h}^{16}, determined by Bannister (1933).

Bannister (1933) reports descloizite as orthorhombic with $a = 6.05$ A, $b = 9.39$ A, $c = 7.56$ A (again, probably kX) and space group $V_h^{16}(D_{2h}^{16} - Pmcn)$ with $Z = 4$. Richmond (1940) interchanged the a and c axes of Bannister, thereby obtaining the orientation $Pnam$, although it appears in his paper (Richmond, 1940, p. 451) as $Pnma$.

As with Richmond's orientation for pyrobelonite, it is desirable to reorientate the unit cells of Strunz for pyrobelonite and of Bannister for descloizite to $Pnma$. This simply involves changing their a, b, and c axes to b, c, and a, respectively.

Precession photographs of crystals of pyrobelonite from Långban, Sweden (Harvard No. 94831), and of descloizite from Los Lamentos, Chihuahua, Mexico (Harvard No. 91040) confirm the orthorhombic cells and the space group ($D_{2h}^{16} - Pnma$, or $C_{2v}^9 - Pn2a$) found by Richmond and Bannister.

The unit cell data are collected in Table 3 where their sources are

identified as B. & Q. (this paper), B. & G. (Berry & Graham, 1948, after interchange of a and c and conversion to $B2_1/m$), S. (Strunz, 1939), R. (Richmond, 1940), B. (Bannister, 1933). It should also be noted that neither the space group $B2_1/m$ nor $Pnma$ has been determined uniquely; they may be $B2_1$ and $Pn2a$, respectively. Axial lengths are in A for B. & Q. data; apparently A for B. & G. data (wave-lengths not given), and probably kX in the others.

The variations in cell dimensions, even after conversion of (S.), (R.), and (B.) data to A, among the values for pyrobelonite and between those for descloizite are not unreasonable, in view of the somewhat variable composition of these minerals.

Very few crystals of brackebuschite were available for the present work and they were too small for an accurate determination of the density. Since the composition and unit cell dimensions, however, are so closely related to those of pyrobelonite and of descloizite it may be assumed that the number of formula units in the primitive cell is the same, namely, $Z=4$, which agrees with the result of Berry & Graham (1948) obtained from a measured specific gravity of 6.05. The B centred cell, therefore, must have $Z=8$.

Not only does the orientation of pyrobelonite and descloizite corresponding to $Pnma$, as in Table 3, emphasize the closeness of their axial lengths (particularly a and b) to the corresponding ones of brackebuschite, but direct comparison of corresponding precession axis reciprocal lattice levels brings out some important relationships.

Thus, the zero level a^*b^* nets of brackebuschite are almost identical (including relative intensities) with the zero level a^*b^* nets of pyrobelonite. The zero level b^*c^* nets of the two minerals are very much alike, but there is only a general similarity between the zero level a^*c^* nets. It is apparent, therefore, that, although the structures of brackebuschite and pyrobelonite cannot be identical, they must be related. The close correspondence of the x-ray diffraction effects is not nearly so apparent in powder photographs on which Strunz (1939) based his conclusions.

Corresponding zero and upper level reciprocal lattice nets along all three principal directions in pyrobelonite and descloizite are so nearly identical as to leave no doubt that the two minerals must have the same structure, at least insofar as the metal atoms are concerned. A general survey of intensities indicates that the coordinates of the heavy Pb atoms in both structures are approximately $\frac{1}{8}$, y, $\frac{1}{6}$; $\frac{7}{8}$, $\frac{1}{2}+y$, $\frac{5}{6}$; $\frac{3}{8}$, $\frac{1}{2}+y$, $\frac{2}{3}$; $\frac{5}{8}$, y, $\frac{1}{3}$. If the space group is $Pnma$ (and not $Pn2a$), then $y=\frac{1}{4}$.

Iron Vanadate

Thin platy hexagonal crystals of an iron vanadate (possibly, $FeO \cdot 2V_2O_4$) from Goldfields, Saskatchewan, have been studied with the pre-

cession instrument. The specimens were collected by Dr. S. C. Robinson, Geological Survey of Canada. The mineral has not yet been described in the literature nor has it been named.

The unit cell is hexagonal with $a = 5.85_4 \pm .005$ A, and $c = 9.29_5 \pm .010$ A normal to the plates. The diffraction symbol is $6/mmmC\text{-}/\text{-}\text{-}c$ so that the space group is $C\bar{6}2c$ ($D_{3h}{}^4$), $C6mc$ ($C_{6v}{}^4$), or $C6/mmc$ ($D_{6h}{}^4$). A piezo-electric test was negative which means that none of these space groups can be eliminated on this basis.

The most interesting feature of the c axis, zero level, photographs is the appearance of an hexagonal "sub-cell" whose a axes coincide with or-thohexagonal (b) axes of the true cell and have a length $\frac{1}{6} b$ (*i.e.*, $1/2\sqrt{3}$ a). Furthermore, from the intensities of the general ($hk \cdot l$) reflections it appears that $S_{hh.l} \simeq S_{h+2, \ h+2,..l}$ from which it can be shown that all, or most, of the atoms must be at the corners of the "sub-cell," which con-stitute twelve points in the true cell. Considering only the c glide (which is common to all three possible space groups) there are four sets of equiv-alent points as follows: (a) two-fold: $00z$; 00, $\frac{1}{2}+z$, (b) two-fold: $\frac{1}{3} \frac{2}{3} z$; $\frac{2}{3} \frac{1}{3}$, $\frac{1}{2}+z$, (c) six-fold: $0 \frac{1}{2} z$; $0 \frac{1}{2}$, $\frac{1}{2}+z$; $\frac{1}{2} 0 z$; $\frac{1}{2} 0$, $\frac{1}{2}+z$; $\frac{1}{2} \frac{1}{2} z$; $\frac{1}{2} \frac{1}{2}$, $\frac{1}{2}+z$. (d) six-fold: $\frac{1}{3} \frac{1}{6} z$; $\frac{1}{6} \frac{1}{3}$, $\frac{1}{2}+z$; $\frac{\bar{1}}{6} \frac{1}{6} z$; $\frac{1}{6} \frac{\bar{1}}{6}$, $\frac{1}{2}+z$; $\frac{\bar{1}}{6} \frac{1}{3} z$; $\frac{\bar{1}}{3} \frac{1}{6}$, $\frac{1}{2}+z$.

The $h0 \cdot l$ projection offers the best hope of resolution of the atoms and is now under investigation.

ACKNOWLEDGMENTS

REFERENCES

BANNISTER, F. A. (1933): The identity of mottramite and psittacinite with cupriferous descloizite, *Min. Mag.*, **23**, 376–386.

BERMAN, H. (1942): private communication from Dr. C. Frondel.

BERRY, L. G. & GRAHAM, A. R. (1948): X-ray measurements on brackebuschite and hematolite, *Am. Mineral.*, **33**, 489–495.

DANA, E. S. (1947): *Textbook of Mineralogy*, ed. 4, revised by W. E. Ford, New York. The best general reference undoubtedly is Dana's *System of Mineralogy*, vol. 2, 1951, a copy of which, however, had not been received when this paper went to press.

DE JONG, W. F. & DE LANGE, J. J. (1936): X-ray study of pucherite, *Am. Mineral.*, **21**, 809.

FOSHAG, W. F. & HESS, F. L. (1927): Rossite and metarossite; two new vanadates from Colorado, *Proc. U. S. Nat. Museum*, **72**, art. 11.

GOSSNER, B. & STRUNZ, H. (1932): Über strukturelle Beziehungen zwischen Phosphaten (Triphylin) und Silikaten (Olivin) und über die chemische Zusammensetzung von Ardennit, *Zeit. Krist.*, (A) **83**, 415–423.

GRISON, E. (1951): De l'usage des inégalités de Harker-Kasper, *Acta Cryst.*, **4**, 489, 490.

HENDRICKS, S. B., JEFFERSON, M. E. & MOSLEY, V. M. (1931): The crystal structures of some natural and synthetic apatite-like substances, *Zeit. Krist.*, (A) **81**, 352–369.

HESS, F. L. & SCHALLER, W. T. (1914): Pintadoite and uvanite, two new vanadium minerals from Utah, *Jour. Wash. Acad. Sci.*, **4**, 576–579.

HEY, M. H. (1950): *Chemical index of minerals*, London.

HILLEBRAND, W. F., MERWIN, H. E., & WRIGHT, F. E. (1914): Hewettite, metahewettite and pascoite, hydrous calcium vanadates, *Proc. Am. Phil. Soc.*, **53**, 31–54.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950): The probability distribution of x-ray intensities. II. Experimental investigation and the x-ray detection of centres of symmetry, *Acta Cryst.*, **3**, 210–214.

KETELAAR, J. A. A. (1936): Die Kristallstruktur des Vanadinpentoxyds, *Zeit. Krist.*, (A) **95**, 9–27.

LINDGREN, W., HAMILTON, L. F. & PALACHE, C. (1922): Melanovanadite, a new mineral from Mina Ragra, Pasco, Peru, *Am. Jour. Sci.*, Ser. 5, **3**, 195–203.

LUKESH, J. S. (1950): The crystal chemistry of the vanadium compounds, Schenectady. Private communication, manuscript. This useful compilation brings together data scattered through Wyckoff's *The Structure of Crystals* (vols. 1 & 2) and *Crystal Structures*, the *Strukturbericht* (vols. 1 to 7), and *Chemical Abstracts* (through 1948).

LUNDQUIST, D. & WESTGREN, A. (1936): The crystal structure of Cu_3VS_4, *Svensk. Kem. Tidskr.*, **48**, 241–243.

MELLOR, J. W. (1947): *A comprehensive treatise on inorganic and theoretical chemistry*, vol. 9, London.

QURASHI, M. M. & BARNES, W. H. (1952): A preliminary structure for pucherite, $BiVO_4$, *Am. Mineral.*, **37**, 423–426.

RICHMOND, W. E. (1940): Crystal chemistry of the phosphates, arsenates, and vanadates of the type $A_2XO_4(Z)$, *Am. Mineral.*, **25**, 441–479.

SCHALLER, W. T. (1915): Four new minerals, *Jour. Wash. Acad. Sci.*, **5**, 7.

STRUNZ, H. (1939): Mineralien der Descloizitgruppe, *Zeit. Krist.*, (A) **101**, 496–506.

WEEKS, A. D., CISNEY, E. A., & SHERWOOD, A. M. (1951): Hummerite and montroseite, two new vanadium minerals from Montrose County, Colorado, *Am. Mineral.*, **36**, 326, 327.

WEEKS, ALICE D. (1951): private communication.