THE POLYMORPHISM AND HYDRATION CHARACTERISTICS OF HEWETTITE AND METAHEWETTITE

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ABSTRACT

Hewettite and metahewettite, as described by Hillebrand, Merwin & Wright (1914) may be considered as $CaO.3V_2O_5.nH_2O$, where '*n*' depends upon the humidity and varies from a minimum of 3 to a maximum of 9. The crystallographic study of the hydration and dehydration of these minerals is presented here, and leads to several important conclusions.

Weissenberg photographs of the material described by Hillebrand, *et al.* (1914) show that it undergoes very marked changes in its structure during dehydration from $9H_2O$ to $3H_2O$ per molecule. One structure (space group $P2/m$, $Z = 1$) persists from $9H_2O$ down to somewhat above $5H_2O$, at which stage a discontinuous transition takes place to a new structure with space group $A2/m$, $Z = 2$. (This transition is accompanied by strong streaking of some of the spots in the c^* direction.) Following Weeks (Ross, 1959), the two structures are designated as hewettite and metahewettite, respectively. The expulsion of water is at every stage accompanied by a contraction of the unit cell.

All the changes are found to be reversible, in as much as the hewettite structure is regained after hydration; the whole cycle of changes was repeated several times by surrounding the crystal with a special transparent controlled-humidity chamber. General relationships between the structures of the two forms, hewettite and metahewettite, and the Na-analogue of metahewettite, ($NaO.3V_2O_5.3H_2O$), are brought out.

1. INTRODUCTION

In a previous communication (Barnes & Qurashi, 1952) the status of structural data on the vanadium minerals was reviewed, and the relationships between several structural series of these minerals were mentioned. A particularly interesting series is that of the (comparatively simple) hydrous calcium vanadates, whose general formula is $xCaO.yV_2O_5.nH_2O$, where n is sometimes a function of the atmospheric humidity. The value of n for air-dried materials appears to be about $5x/2$, while the variation in n (if any) caused by humidity alone is a function of y, being approximately equal to $2y$. This suggests that the variable water content is primarily associated with the vanadate group. The known members of this series correspond to quite definite values of the ratio x/y, *viz.* 1/3 for hewettite and metahewettite, 2/3 for pascoite, 1/1 for rossite and metarossite, and 2/1 for pintadoite. (At the extremes of the series, we may imagine $Ca(OH)_2$ with $y/x = 0$, and $V_2O_5.nH_2O$ with $x/y = 0$: V_2O_5 is known to take up water to the extent of *at least* 1 H_2O/mol (Huttig &

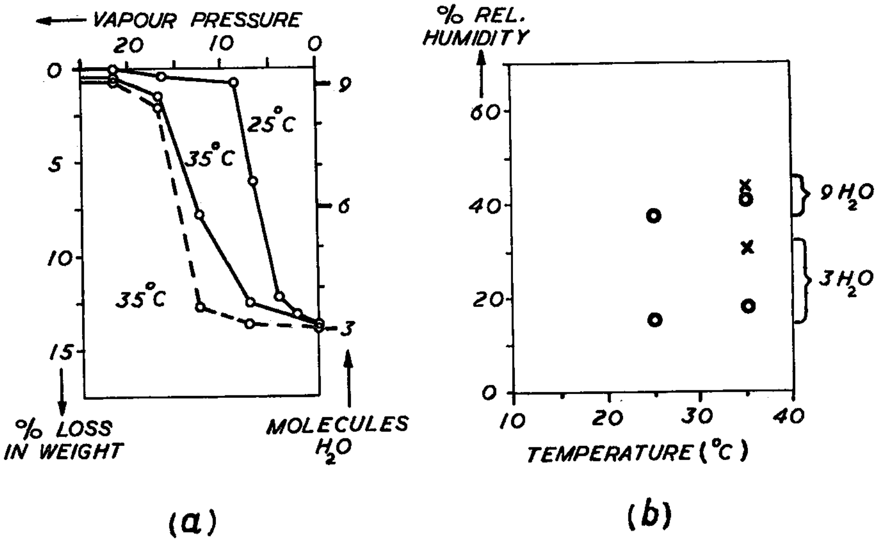


FIG. 1. (*a*) Hydration curves for hewettite (full line) and metahewettite (broken line) (after Hillebrand, Merwin, & Wright, 1914). (*b*) Diagram showing the range of relative humidities corresponding to the min. and max. degrees of hydration: hollow circles for hewettite and crosses for metahewettite.

Konig, 1930).) An interesting feature of this series is the gradual decrease in crystal symmetry as x/y tends to 1, from either end of the series, *viz.* from orthorhombic ($Pmn2_1$, or $Pmnm$) for V_2O_5 to triclinic ($P\bar{1}$) for metarossite. These considerations suggest that a study of this series should be particularly useful in elucidating the structural behaviour of the vanadate groups. Hewettite and metahewettite have the highest symmetry next to V_2O_5 and therefore form the logical starting point for this study.

Hillebrand, Merwin, & Wright (1914), referred to in the following as H.M. & W., have described their samples of hewettite and metahewettite in some detail. Because the crystals are usually very poor, they concluded, from the general outline, and from the optical data, that the minerals are orthorhombic. According to their analyses, the two minerals have the same chemical composition, $CaO.3V_2O_5.nH_2O$, where n varies from 3 in dry air to 9 in a saturated atmosphere. They found the water content to be extremely sensitive to variations of atmospheric humidity; indeed the distinction between the two minerals was made by them partly on microscopic evidence, and partly on the basis of differences in the dehydration characteristics, for example, the distinction observed in the curves of Fig. 1(*a*), which are reproduced from their paper. Figure 1(*b*), which is deduced from Fig. 1(*a*), shows that the fully hydrated state corresponds to about 40% (or more) relative humidity in each case, while the "air-dried" state exists at relative humidities below about 22 ± 8%.

They also concluded from their work that hewettite and metahewettite are not inter-convertible through hydration or dehydration. However, the results of recent investigations have thrown doubt on these conclusions, and it appears probable that H.M. & W.'s hewettite and metahewettite are identical, but that different states of hydration need to be classified separately. In the present communication, the nomenclature suggested by Weeks (Ross, 1959) is adopted; namely that the material with $3H_2O$ be called "metahewettite" and the term "hewettite" be kept for the higher hydrate, which is shown below to possess a different structure.

Some preliminary data on material labelled 'metahewettite' from the Cactus Mine, Yellow Cat District, Grand County, Utah (Harvard Museum, 98019), since identified, however, as the water-insensitive sodium variety (Barnes, 1955), and on material labelled 'hewettite' from Minasragra, Cerro de Pasco, Peru (Harvard Museum, 96258), already have been reported (Barnes & Qurashi, 1952). In the present communication, some *x*-ray data for metahewettite ($CaO.3V_2O_5.3H_2O$) and hewettite ($CaO.3V_2O_5.9\text{–}5(6)H_2O$) are presented and compared with those for the Na-analogue, and the changes occurring during hydration and dehydration are studied.

2. THE RELATIONSHIP BETWEEN METAHEWETTITE AND ITS SODIUM ANALOGUE

Fresh material from Yellow Cat, Utah, and Montrose County, Colorado (specimens 2 and 3, respectively, in Barnes (1955)), was made available through the courtesy of Mrs. A. Weeks of the U.S.G.S. Weissenberg photographs (using filtered Cu*K* radiation) taken with what appeared to be an undistorted single-crystal (about 10 × 40 microns cross section) from this material are reproduced in Fig. 2 (*A*, *B*), and the corresponding reciprocal nets in Fig. 2 (*a*, *b*). Like those of the Na-analogue (Barnes & Qurashi, 1952) the crystals obtainable were poor and fibrous, and the streaky appearance of the reflections in Fig. 2 (*A*, *B*) indicates the presence of a considerable range (about ±15°) of orientations about the needle *b*-axis. However, the comparatively strong spots visible in the middle of this range serve to define the reflections with satisfactory precision.

The cell constants are $a = 12.25$Å, $b = 3.615$, $c = 2 \times 9.27$, $\beta = 118°$; probable space group $A2/m$ ($k + l$ = even for general hkl). The

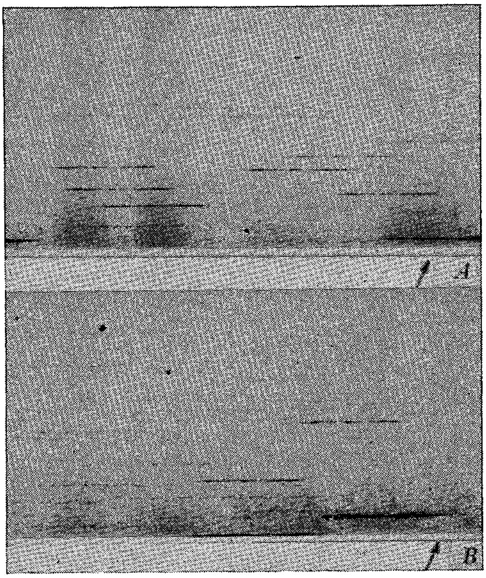


FIG. 2. (*A*) AND (*B*) Zero- and first-level Weisenberg photographs of metahewettite taken with filtered Cu*K* radiation. The arrows indicate the 00*l* and 01*l* reflections.

zero-level is identical with the second-level, and the first-level with the third, after allowing for the Lorentz-polarization factor and the scattering factor, as in the case of the Na-analogue (see Barnes & Qurashi, 1952, p. 414), thus indicating the existence of the approximate mirror plane perpendicular to the short *b*-axis. Half the cell volume is 364Å^3, which agrees very well with the mol-volume (370Å^3) got from H.M. & W.'s density for material with $3H_2O$ per molecule. In the first place, it appears that we are here dealing with a structure closely similar to that of the Na-analogue (Fig. 3), *cf.* the almost identical *a*-, and *b*-axis, and comparable cell volumes. Secondly, the very close agreement between the calculated and observed mol-volumes (370Å^3 against 364Å^3) strongly suggests that the material on which H.M. & W. made their measurements of density is to be identified with metahewettite ($CaO.3V_2O_5.3H_2O$). Since they observed the reversible change $CaO.3V_2O_5$. ($3H_2O \rightleftharpoons 9H_2O$) on the same material, the dehydrated state of our material is to be attributed to the very low humidity prevalent at this time in the Ottawa Laboratory (*cf.* Fig. 1(*b*)).

It is easy to demonstrate the close structural relationship between the trihydrated Ca- and Na-analogues. If the two zero-level (*h*0*l*) reciprocal lattices are placed with their (almost) equal *c**-axes in coincidence,

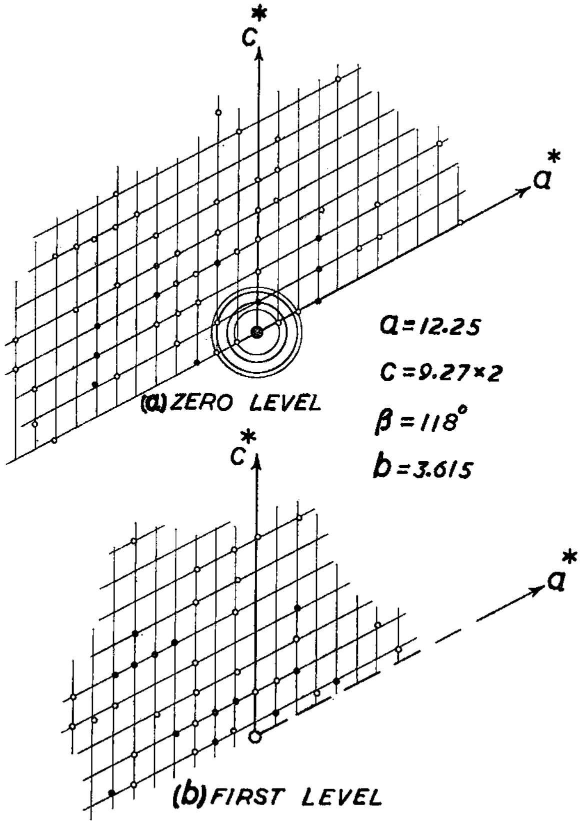
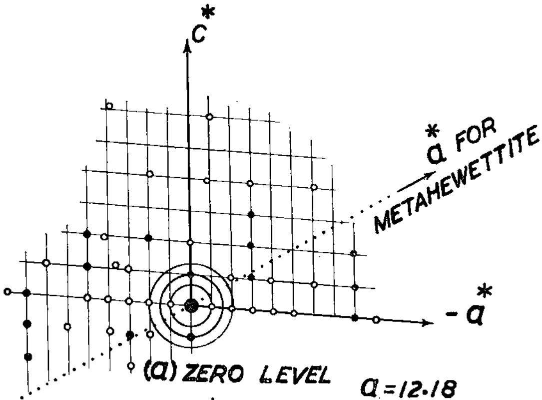
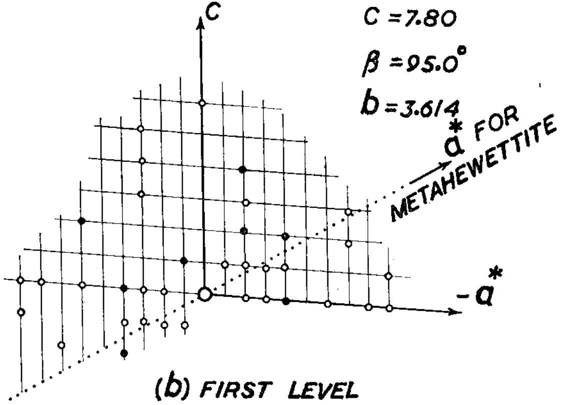


FIG. 2. (*a*) AND (*b*) The reciprocal lattice nets corresponding to Fig. 2(*A*) and (*B*) for metahewettite: circles indicate the observed reflections, the solid circles being for the strong reflections.

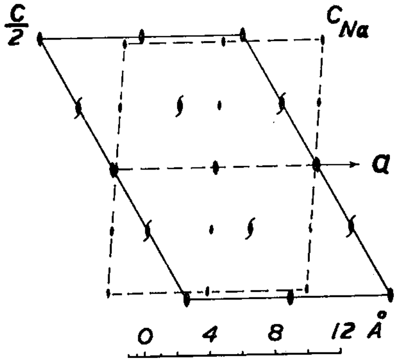
the stronger reflections from the two structures are seen to correspond surprisingly well, *cf.* the lattice nets of Figs. 2 and 3. This intensity coincidence obtained in the case of the first-level reciprocal nets is less striking, which phenomenon is largely due to the *A*-face centring of the lattice of metahewettite. Thus we may expect that these two structures differ from each other in the interchange or displacement of some of the atoms in the unit cells, while the essential features of the structural arrangement remain the same. Figure 3(*c*) shows the structural relationship between the two unit cells, and it follows from the foregoing considerations that all the symmetry elements shown in the composite diagram should be involved in each structure, some exactly and the others only approximately. The V_2O_5 groups, which are common to



(a) ZERO LEVEL



(b) FIRST LEVEL



(C) UNIT CELLS

FIG. 3. (*a*) AND (*b*) Zero- and first-level reciprocal nets for the Na-analogue of hewettite; the solid and hollow circles indicate the strong and weak reflections; the relative direction of the a^*-axis for metahewettite is also shown. (*c*) Structural relationship between the unit cells of metahewettite and its Na-analogue, showing both sets of symmetry elements.

both structures, may therefore be expected to lie along the common *a*-axis.

3. HEWETTITE ($CaO.3V_2O_5.nH_2O$; $3 < n \leqslant 9$)

A freshly received, humidified sample, obtained from the same locality (Montrose County, Colorado), was examined carefully under the microscope, and was found to consist of two distinct types of crystals:

(*a*) Mahogany-red, fine, fibrous needles and very thin blades, which were similar to the material already classified as metahewettite.

(*b*) Beautifully clear, claret-red, plushy, non-fibrous, compact crystals with good faces; some terminal faces meeting in an obtuse angle were frequently observed. These crystals appear so different from the metahewettite that they were provisionally identified as the higher hydrate, hewettite. (It is to be noted that some crystals intermediate in type between (*a*) and (*b*) were also observed.)

Powder patterns taken with material from the above sample showed an anomalous behaviour, which could be interpreted by assuming that hewettite is the fully hydrated form and dehydrates gradually to give metahewettite when exposed to the dry atmosphere of the laboratory. (This is similar to the results reported by Barnes (1955) on his samples 2, 3, 5, 6, and 7.) Sufficient dehydration apparently does occur in the short periods necessary for sample preparation, because the "Duco" cement, which was used for picking up the powdered material, seems fairly impervious to water vapour, especially when it has set.

4. DEHYDRATION OF HEWETTITE

Following upon these observations, a good single crystal of hewettite was mounted with its needle-axis parallel to the axis of the goniometer, and a zero-level Weissenberg photograph was taken using Cu*K* radiation. This photograph, which indicates some distortion of the crystal, is reproduced in Fig. 4(*A*), and is seen to be quite different from the corresponding photographs for metahewettite and its Na-analogue. The cell-dimensions are approximately $a = 12.5$Å, $b = 3.61$, $c = 11.1$, $\beta = 113°$, whence the cell volume is found to be $447Å^3$, lying between the mol-volumes (calculated from H.M. & W.'s data) of $370Å^3$ for $CaO.3V_2O_5.3H_2O$, and $505Å^3$ for $CaO.3V_2O_5.9H_2O$. Thus, from the cell volume, we may infer that the cell contains one molecule of the compound with about $6H_2O$ (at this stage). The most interesting feature of this zero-level Weissenberg photo is that, whereas the majority of the reflections are very sharp, a few of them are somewhat diffuse; these diffuse reflections are distinguished in the reciprocal lattice net (Fig. 4(*a*)) corresponding to this Weisenberg photo. The first-level photograph (taken about 40 hours

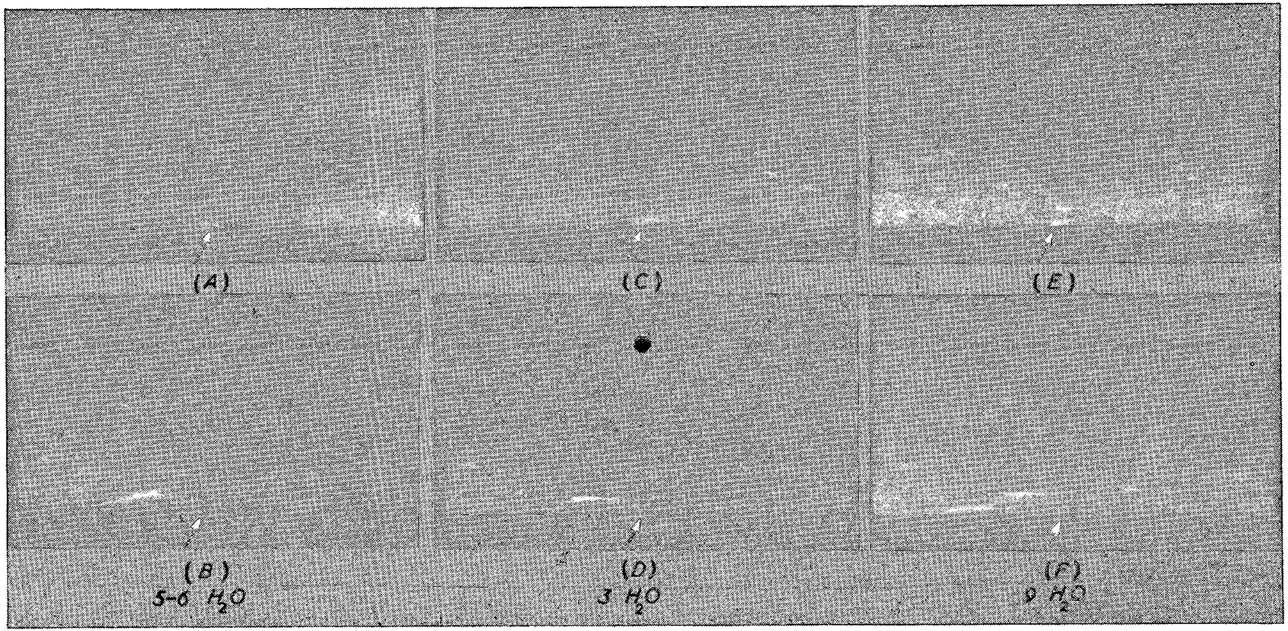


FIG. 4. (*A*) TO (*F*) Zero- and first-level Weissenberg photographs taken with Cu*K* radiation, for various stages of the hewettite $\rightleftharpoons$ metahewettite transformation; the upper and lower arrows indicate the 00*l* and 01*l* reflections, respectively.

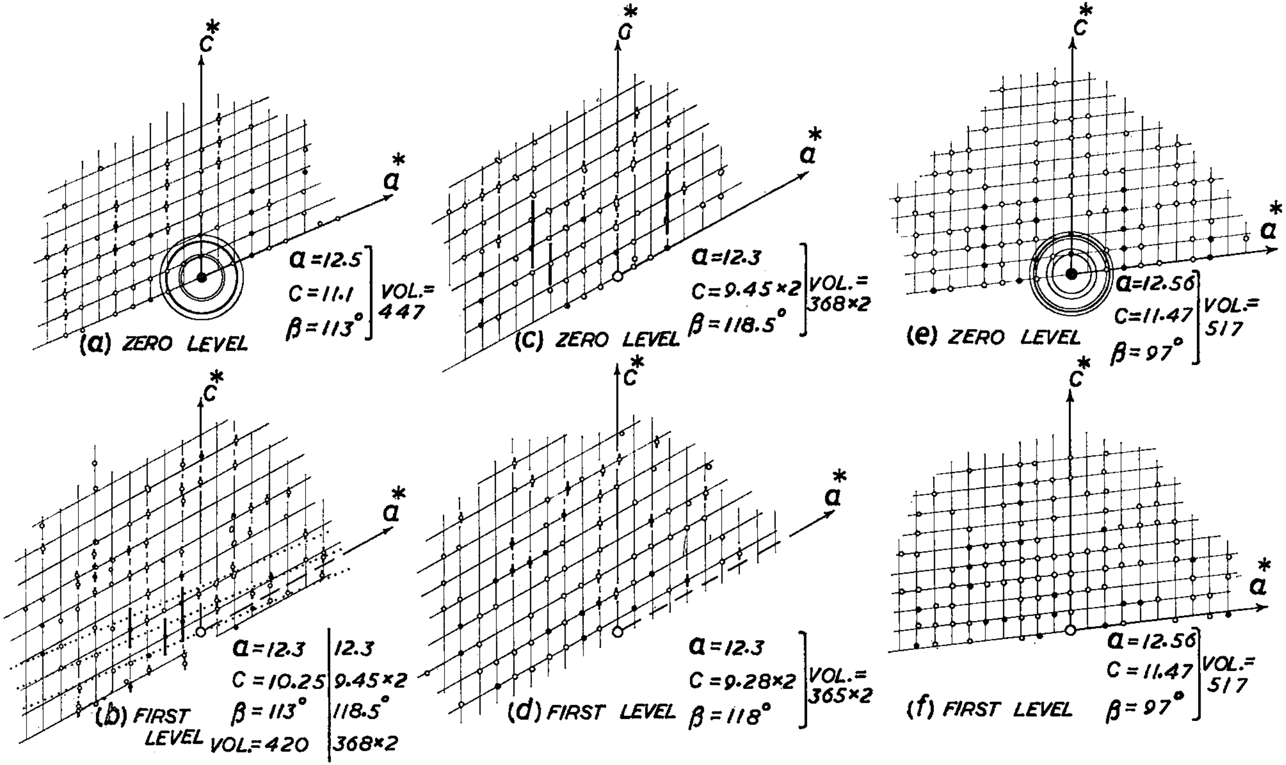


FIG. 4. (*a*) TO (*f*) Reciprocal lattice nets corresponding to Fig. 4 (*A*-*F*), with solid and hollow circles for the strong and weak reflections, respectively. Diffuse reflections are indicated by a line through the circle. (*a*, *b*) are for partially dehydrated hewettite with 6 to $5H_2O$ per molecule, (*c*, *d*) are for completely air-dried material with $3H_2O$, and (*e*, *f*) correspond to fully hydrated hewettite with $9H_2O$.

after the zero-level) is shown in Fig. 4(*B*), and the reciprocal lattice drawing deduced from it is shown in Figure 4(*b*). This picture presents definite evidence that hewettite is indeed transforming by dehydration into metahewettite: two distinct reciprocal lattices are seen intermixed in the picture, in addition to an extraordinary diffuseness and streaking of some of the reflections. (It is well to note here that this streaking is in every case parallel to the c^*-axis, the significance of which will be seen below at the end of Section 7.) The cell dimensions for both lattices, given alongside the figure, are seen to be intermediate between values found above (from the zero-level) and the ultimate values for metahewettite (Fig. 2; also Fig. 4(*c*) and (*d*)). The zero-level Weissenberg photo of the transforming crystal was repeated at this stage (Fig. 4(*C*) and (*c*)); it is different from the previous zero-level picture, and comparison with Fig. 2(*a*) shows that the transformation to metahewettite is nearly complete. This is confirmed by the repeat of the first-level picture shown in Fig. 4(*d*), which is to be compared with Figs. 2(*b*) and 4(*b*). At this stage, about 300 hours had elapsed since the crystal was removed from the main sample and mounted; the passage of more time was found to sharpen up the reflections a little, and to remove the last traces of reflections due to the higher hydrate, but no other lattice changes were observed.

The simultaneous appearance of two distinct lattice nets in the first-level diagram of Fig. 4(*b*), showing a sudden change in cell volume from about 420Å^3 to about 2 × 368Å^3, provides strong evidence for the presence of a more or less discontinuous transition at this stage. As shown earlier in Section 2, the final cell volume corresponds to two molecules of the air-dried metahewettite, $CaO.3V_2O_5.3H_2O$, so that the above change corresponds to a sudden contraction of 52Å^3 in mol-volume from 420Å^3 to 368Å^3: this is evidence for the abrupt loss of a little more than $2H_2O$/molecule, because the decrease in mol-volume in these minerals is about 23Å^3/H_2O (Barnes & Qurashi, 1952). Such a discontinuous change is supported by the very different space-groups of metahewettite ($A2/m$; $Z = 2$, with $3H_2O$ per molecule) and hewettite ($P2/m$; $Z = 1$, containing from $9H_2O$ down to around $5H_2O$ (*cf.* Section 6), and is also capable of correlation with the slight kink observable at $5.8H_2O$ in H.M. & W.'s hydration curves for hewettite in Fig. 1(*a*).

5. CONTROLLED HUMIDITY CHAMBER FOR THE GONIOMETER HEAD

In order to use *x*-ray photographs to study further the reversibility and other features of the dehydration of hewettite, a rudimentary air-

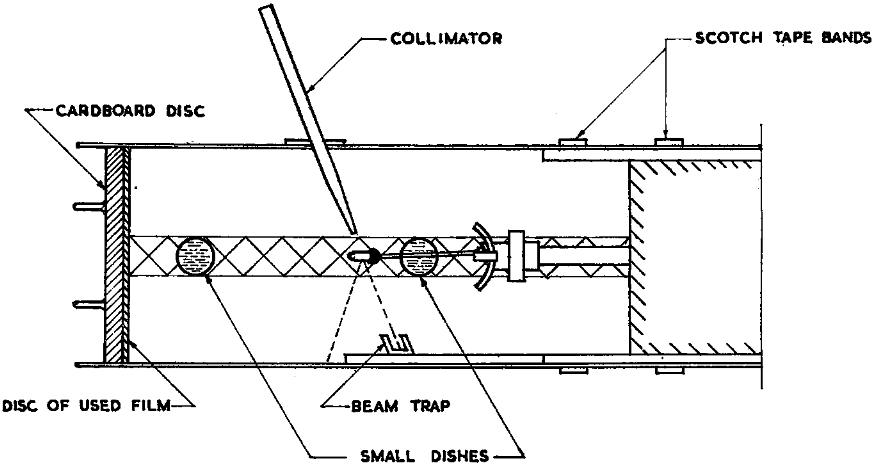


FIG. 5. Diagrammatic sketch of cellophane controlled-humidity jacket for the dehydration-hydration studies of hewettite.

jacket was made as shown in the sketch of Fig. 5. A sheet of cellophane, about 15 × 20 cm., is rolled into a tight cylinder around the sleeve used to support the beam trap when taking oscillation or rotation pictures on the Weissenberg camera. The join in the cellophane cylinder is arranged to lie at the bottom and is fixed securely with cellulose "Scotch Tape", the cellophane cylinder being held fast to the metal sleeve by one or two bands of the same tape. The open end of the cylinder can be closed with a cardboard disc, to the outer face of which a couple of tabs of scotch tape are attached for ease of handling. It was found desirable to attach (again with the scotch tape) a disc of cellophane or used film to the inner face of the cardboard disc to prevent interaction between the moisture in the cardboard and the air within the cellophane jacket. The desiccants or hydrants can be introduced into the jacket by placing them in little dishes, about 15 mm. diameter and 5 mm. high, resting on the reinforced seam in the cellophane cylinder. (Two such dishes are placed one on either side of the crystal to ensure equilibrium conditions in the immediate vicinity of the crystal.)

The collimator is introduced through a $\frac{3}{4}$-cm. diameter hole previously cut in the cellophane with a cork borer; a small collar of cellophane is placed on the collimator and arranged to serve as a gasket by butting on the outside of the cellophane cylinder. In this way, the air surrounding the crystal is virtually isolated, and its humidity is readily controlled by placing a suitable solution (or water–H_2SO_4 mixture) in the small dishes. Best results are obtained with an equi-inclination Weissenberg camera with the inclination angle set at about 30°. This permits simultaneous

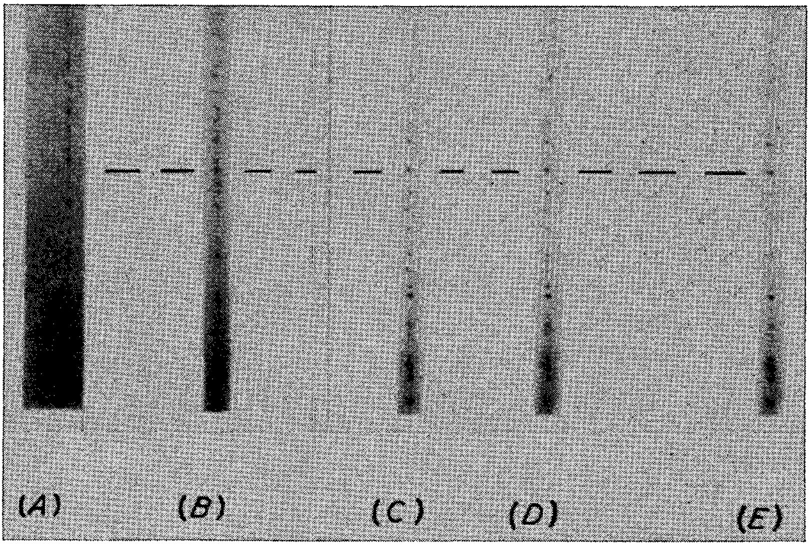


FIG. 6. Successive *hkl* rotation pictures taken with the crystal under various conditions of wetness: (*A*) partially hydrated, (*B*) fully dehydrated, (*C*) to (*E*) fully hydrated.

recording of rotation diagrams for all levels that have $\zeta < 2 \sin 30° = 1$ without producing great obliquity of the diffracted beams, so that the upper level spots are not unduly diffuse. (With some Weissenberg cameras this necessitates improvization of a beam trap, because the one supplied is useful for normal-beam rotation photographs only.) By taking short rotation photographs with different solutions in the dishes, the dependence of the structure on humidity can be followed rather nicely. This method is naturally more powerful than the use of a powder sample, because the different levels perpendicular to the rotation axis are separated. If it is necessary to take Weissenberg photographs under conditions of controlled humidity, the crystals can be kept completely enclosed by covering the slots in the layer-line screen with cellulose scotch tape. When investigating crystals with a nearly fixed value of ζ (as in the hewettites), it is moreover possible to record two (or more) levels simultaneously on the top and bottom halves of the film with a specially constructed screen.

6. HYDRATION-DEHYDRATION STUDY OF METAHEWETTITE $\rightleftharpoons$ HEWETTITE

The investigation of the hydration-dehydration transformations in hewettite was commenced by mounting, as shown in Fig. 5, a hewettite crystal, completely dehydrated and thus converted into metahewettite.

A rotation exposure was given for about five hours (Fig. 6(*B*)). The dishes inside the cellophane jacket were then filled with water at room temperature (24° C) by means of a small dropper, and the open end of the jacket was again closed. Several five-hour rotation exposures were given in succession, the camera being translated a small distance between exposures. The results for the first level are shown in Fig. 6 alongside the very first rotation picture (Fig. 6(*A*)) taken with this particular crystal (that is, before the Weissenberg Fig. 4(*A*) was taken). Two facts stand out:

(*a*) The metahewettite crystal has transformed (into hewettite);

(*b*) This transformation is essentially completed in *much less* than five hours, since all the successive rotation pictures taken after the introduction of the water inside the cellophane jacket are identical with each other.

Also, these rotation photographs show no observable diffuseness or doubling of spots, such as would occur if the time of transformation were comparable with the exposure time for each picture. This checks with the experiments of H.M. & W., who found that their samples took up atmospheric moisture rapidly, and attained absolute equilibrium in controlled atmospheres well within 24 hours. The extremely slow rate of dehydration observed in the pictures of Fig. 4 is due to the segregation of the crystal in the camera and to the humidity remaining around 20% to 30%.

Zero-, and first-level Weissenbergs of the fully hydrated crystal are shown in Fig. 4(*E*) and (*F*) together with the reciprocal lattice nets deduced from them (Fig. 4(*e*) and (*f*)). The cell dimensions are: $a = 12.56$ Å, $b = 3.615$, $c = 11.47$, $\beta = 97.0°$; cell volume = 517Å^3, which is to be compared with the mol-volume of 505Å^3 for material containing 9H_2O. The probable space group is $P2/m$ (contrast $A2/m$ for metahewettite). Comparison in Fig. 4 of (*e*) with (*a*) shows that, although the crystal was not fully hydrated when the first Weissenberg photograph (Fig. 4(*A*)) was taken, it did show the same space group and intensity pattern, thus pointing to a continuous transformation at least from 9H_2O to 6H_2O. This is supported by the observation that in Fig. 4(*b*) the coexisting $P2/m$ lattice leads to a water content of a little more than 5H_2O per molecule. As a final check, the process of dehydration of the crystal was again followed by means of rotation and Weissenberg photographs; the same structural changes were observed as in Fig. 4. It was further noted that the hydration-dehydration cycle could be repeated several times before the internal stresses produced an incipient splitting of the crystal into thin laths, which probably explains the distortion observed in the Weissenberg of Fig. 4(*A*) for hewettite.

7. DISCUSSION

These observations confirm the identity of this particular material with that on which H.M. & W. performed their dehydration and density measurements. It is interesting to note here that in their section on the characterization of metahewettite, they actually have descriptions of the material from Thompson's, Utah, and from Paradox valley, Montrose County, Colorado, which do in fact correspond to the characteristics of metahewettite and hewettite (*cf.* page 36, para 3 and 4 respectively of H.M. & W.'s paper).

The single crystal data for the three modifications of hewettite are collected in Table 1.

TABLE 1.
SINGLE CRYSTAL DATA FOR THE THREE MODIFICATIONS OF HEWETTITE

Label	Cell dimensions				Cell volume	Probable space	Comparison with previous work of
	a(Å)	*b*(Å)	*c*(Å)	*β*(°)	(Å³)	group	H.M. & W.
Na-analogue of metahewettite	12.18	3.614	7.80	95.0	343	*P*2/*m*	Insensitive to humidity; not recognized by H.M. & W.
Metahewettite	12.25	3.61_5	2×9.27	118	2×364	*A*2/*m*	*cf.* mol-volume of 370 Å³ got from H.M. & W.'s density for material with $3H_2O$.
Metahewettite ⇌	12.3	3.61_5	2×9.45	118.5	2×368	Co-existent *A*2/*m* & *P*2/*m* lattices	*cf.* mol-volumes of 370 and 415Å³ estimated for material with $3H_2O$ & $5H_2O$ respectively
Hewettite	12.3	3.61_5	10.25	113	420		
Hewettite	12.56	3.61_5	11.47	97.0	517	*P*2/*m*	*cf.* mol-volume of 505 Å³ got from H.M. & W.'s density for material with $9H_2O$.

Table 1 shows clearly that the differentiation already made between hewettite and metahewettite on morphological grounds is real indeed, because there is a change in space group from a primitive lattice to an *A*-centred one with twice the *c*-axis, quite apart from the large contraction in the cell volume due to the removal of the water. As the dehydration of hewettite proceeds in the range from $9H_2O$ to $6H_2O$ per molecule, the lattice dimensions (mainly *c* and *β*) seem to change continuously without any change in the space group but with certain changes in the relative intensities of the reflections. However, when a water content of about $5H_2O$ (actually 5.5 ± 0.3)* is reached, the change becomes discontinuous, and there appears another lattice (with space group *A*2/*m*)

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*This is the mean of the values estimated from Fig. 4 (*b*) and the kink in Fig. 1 (*a*). Further work is in hand to determine more precisely the minimum water content of hewettite.

with a very much smaller volume per molecule, and therefore a smaller water content. This new lattice already has the minimum water content of $3H_2O$ per molecule, and the structure becomes that of metahewettite. The two lattices are seen to coexist in Fig. 4(*b*). Although the reciprocal nets of metahewettite and hewettite differ radically, two important relationships stand out:

(1) The *a*-axis and the *b*-axis remain practically constant in length (and of course in direction) throughout the whole dehydration,

(2) Inspection of the intensity distribution of the reflections in the two structures shows that the Fourier transform of the unit cell contents is similar and similarly oriented in the two forms. This second feature readily follows from the regions of strong intensity falling in the same positions when the two lattices are oriented with *a*-axes parallel. It follows of course that the main part of the structure (that is, the $CaO.3V_2O_5$ layer) should remain essentially unchanged in position and orientation.

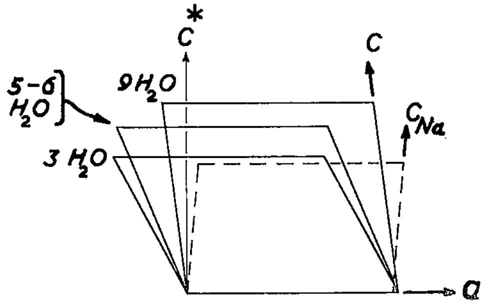

FIG. 7. Progressive changes in the unit cell of hewettite during dehydration to give metahewettite: the broken-line cell is for the Na-analogue of metahewettite.

The progressive changes in the unit cell during dehydration are shown in Fig. 7, from which it appears that the six removable water molecules fit in between the layers of $CaO.3V_2O_5$, which are (probably) arranged along the fixed *ab*-plane. As these water molecules are progressively removed, the lattice contracts perpendicular to this plane (that is, in the c^*-direction); the increasing obliquity of the cell is to be associated with the inclined direction of the bonds holding the water molecules in place. The discontinuous transformation from hewettite with about $5H_2O$ to metahewettite (with $3H_2O$) is naturally accompanied by a rather large sudden contraction in the c^*-direction. It appears reasonable that this should be preceded and accompanied by large thermal motions of the atoms along this direction, which serves to explain the very marked streaking parallel to c^* observed in the photographs of Fig. 4.

8. Relationship with Powder Data

In order to correlate the single-crystal data with the powder work of Barnes (1955), who found that the patterns are particularly sensitive in the low-angle region, circles have been drawn through the low-angle reflections in the zero-level nets of Fig. 4. Since the *b*-axis is so much shorter than the *a*- and *c*-axes, these circles give an exact picture of the low-angle portion of the corresponding powder pattern. Particularly remarkable is the variation in *d*-value of the innermost and strongest powder line, which corresponds to the 001 reflection (002 in metahewettite). During the transformation from the completely hydrated hewettite to metahewettite, the *d*-spacing corresponding to this line changes by about 25%, due to the shortening of the *c*-length (in the *h*0*l* level) from 11.47Å to 9.27Å, together with the increase in angle β from 97° to 118°. On the other hand, in the powder patterns of the Na-analogue and metahewettite this line occupies practically the same position, because of the almost identical values of c^* for these two forms. Both these deductions from the reciprocal lattice nets are borne out by the powder patterns of the various samples examined.

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References

Barnes, W. H. (1955): "Hewettite" and "metahewettite", *Am. Mineral.*, **40**, 689–691.

Barnes, W. H., & Qurashi, M. M. (1952): Unit cell and space-group data for certain vanadium minerals, *Am. Mineral.*, **37**, 407–422.

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

Huttig, G. F., & Konig, A. (1930): Hydrated Oxides, XXXII: The vanadium pentoxide – water system, *Z. anorg. allgem. Chem.*, **193**, 81–92.

Ross, M. (1959): Mineralogical applications of electron diffraction. II. Studies of some vanadium minerals of the Colorado plateau, *Am. Mineral.*, **44**, 322–341.