Hydrocalumite ($4CaO.Al_2O_3.12H_2O$), a new mineral from Scawt Hill, Co. Antrim.

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IN a further search for portlandite [1] amongst the vug minerals of the Scawt Hill contact-zone, attention was drawn to some in-fillings containing a mineral which had not previously been observed. These infillings, which occur in a larnite-rock carrying melilite-wollastonite aggregates of the hybrid zone of the contact,[2] consist of afwillite, portlandite, ettringite, and aggregates of a mineral, the light-greenish colour of which was conspicuous. This mineral is most intimately associated with afwillite, and examination of it shows it to be a hitherto unrecorded species.

Material isolated from the vugs consists of irregular fragments of colourless to light-green colour showing a perfect cleavage. The lustre is vitreous inclining to pearly on the cleavage surfaces; hardness 3, specific gravity 2·15. No material suitable for goniometrical investigation has been observed. Micro-chemical tests show the presence of abundant calcium and some carbon dioxide. In the closed tube the mineral decrepitates and gives off water. It is alkaline to litmus and dissolves completely in weak hydrochloric acid. Lime, alumina, water, and small amounts of carbon dioxide are proved on quantitative analysis, and these data show that the mineral is a new species. In allusion to its composition as an hydrated calcium aluminate ($4CaO.Al_2O_3.12H_2O$) the name hydro-calumite is proposed.

Cleavage flakes provide excellent material for optical examination. The mineral is biaxial, optically negative, and the cleavage plates

[1] C. E. Tilley, Min. Mag., 1933, vol. 23, p. 419.
[2] C. E. Tilley, Min. Mag., 1931, vol. 22, p. 439.

provide an optic picture with the acute bisectrix standing nearly normal to the cleavage taken as the base c (001); $a : \perp$(001) is less than 3°. As confirmed by X-ray data the symmetry is monoclinic (pseudo-hexagonal). The optic axial plane lies in (010); $\beta = b$. Refractive indices determined with immersion liquids and a stage-goniometer are a 1·535, β 1·553, γ 1·557. Different fragments show some variation in the optic axial angle, but the value determined on the fragments yielding the above values of the refractive indices is 2V 24° $\pm$ 2°. When the mineral is warmed on a heating stage or heated in an oven and examined under the microscope the optic axial angle is seen gradually to decrease and the mineral becomes sensibly uniaxial at 90–95° C. On cooling, it becomes again biaxial, but the original value of the optic axial angle is not reached until some hours have elapsed. Heated to a higher temperature (160° C.), the mineral becomes turbid due to loss of water. Inter-ference-figures obtained on this turbid material show that it is still sensibly uniaxial and only after the lapse of some weeks does it become sensibly biaxial, but the original value of the optic axial angle is not regained. Further data on the dehydration phenomena of this mineral will be given when additional material is available for continuing this interesting study.

On specially selected material Mr. M. H. Hey kindly executed in the Mineral Department of the British Museum two analyses on the small quantities available (analysis I 0·080 gram, analysis II 0·215 gram).

The following figures were obtained:

		I.	Mol. ratios.	II.	Mol. ratios.	Calculated for $4CaO.Al_2O_3.12H_2O$.
CaO	...	41·5	0·740 ...	40·0	0·713 ...	41·33
Al_2O_3	...	18·8	0·184 ...	18·1	0·178 ...	18·82
H_2O	...	38·5	2·137 ...	} 40·3	— ...	39·85
CO_2	...	1·8	— ...		— ...	—
		100·6		98·4		100·00

In I the determination of H_2O and CO_2 was carried out by the Dittler-Hueber method [1] using the Gooch tubulated platinum crucible. In II only the total loss on ignition was determined. Each of the analyses was completed on one portion of material only. MgO, alkalis, TiO_2, P_2O_5, BaO, SrO, and BeO were tested for and found

[1] E. Dittler and H. Hueber, Zeits. Anorg. Chem., 1931, vol. 195, p. 41; 1931, vol. 199, p. 17. [Min. Abstr., vol. 5, p. 141.]

absent. The analytical data given above lead to an empirical formula $4CaO.Al_2O_3.12H_2O$.

Several hydrated calcium aluminates are known as artificial products and have repeatedly been prepared. A summary of the existing data on these artificial compounds is given by Mylius[1] who has also added considerably to our knowledge of these compounds. Mylius has prepared the compound $4CaO.Al_2O_3.13H_2O$ in the form of tabular hexagonal crystals and spherulites whose properties are given as uniaxial negative, ω 1·533, ϵ 1·522 ; while Assarsson[2] prepared a similar product with $13\cdot5H_2O$, the optical properties being given as biaxial negative, 2V 14°, α 1·510, γ 1·538. Mylius's product dried over P_2O_5 gave a product corresponding to $4CaO.Al_2O_3.12H_2O$, losing one molecule of water, and its refractive indices were thereby raised to ω 1·549, ϵ 1·533.

The Scawt Hill hydrocalumite has clearly somewhat different optical properties, for, as noted above, it is biaxial, and the birefringence is considerably greater than that of the Mylius product. The presence of significant amounts of carbon dioxide in the analysis of the natural material is doubtless in part responsible for this divergence.

X-ray analysis.

The composition of hydrocalumite, written for the moment as a hydrated oxide, is $4CaO.Al_2O_3.xH_2O$, where x is found, in two separate analyses, to be 11·6 and 11·8. In the literature, artificially prepared hydroxides of this formula are recorded, in which x varies from 11·5 to 13·5. Mylius (loc. cit.) obtained a compound with $13H_2O$, which, dried over P_2O_5, lost one molecule of water. The variable results obtained by different workers suggest that the structure is based on a composition of $4CaO.Al_2O_3.13H_2O$ and that it may lose a certain amount of water without breaking down. This dehydration may occur in a random manner so that the vacant places left are distributed statistically throughout the structure; or it may be that certain atoms in each cell are more loosely attached than others and are the first to go. Possibly some slight rearrangement of the structure accompanies the loss of water, perhaps causing lower symmetry; this idea is discussed later in the paper. It is, however,

[1] C. R. W. Mylius, Über Calciumaluminathydrate und deren Doppelsalze. Acta Acad. Aboensis, Math. et Physica, 1933, vol. 7, no. 3, 147 pp.

[2] G. Assarsson, Zeits. Anorg. Chem., 1930, vol. 191, p. 333; 1931, vol. 200, p. 391; 1932, vol. 205, p. 338. [M.A. 5–450.]

clear that the actual structure must be closely derived from one containing 13 molecules of water.

The crystal examined consisted of a cleavage flake possessing two well-marked edges parallel to the extinction directions. The cleavage plane was chosen as (001), the optic axial plane being (010). Oscillation photographs were taken about the a- and b-axes and the normal to (001), and Weissenberg photographs of the zone [$h0l$], the layer-line ($h2l$), and the zone whose axis was very nearly normal to (001). The photographs showed unmistakably that the crystal was monoclinic. The c-axis, chosen so as to make the smallest possible cell, gave a β-angle of 69°. The cell-dimensions are a 9·6, b 11·4, c 16·84 Å. (A pseudo-orthorhombic cell could have been chosen, three times the height, in which a and b are as before, c 47·2, β 89°.) Since the density is about 2·15, there are 4 molecules per unit cell. The only true halvings are ($0k0$) absent for k odd, so that the space-group is either C_2^2—$P2_1$ or C_{2h}^2—$P2_1/m$. The fact that the crystal is strongly pyroelectric excludes the latter possibility, thus fixing the space-group as $P2_1$. There are in addition certain well-marked pseudo-halvings. These are: (hkl) very weak for k odd, or $h + k/2$ odd; ($h0l$) very weak for h odd or l odd. Further, the zone [203], whose axis is the normal to (001), shows very conspicuous pseudo-hexagonal symmetry.

The general positions in $P2_1$ have the co-ordinates x, y, z; $\bar{x}, y + \frac{1}{2}, \bar{z}$. Since there are four molecules per unit cell, all the atoms may be in general positions; thus there are 52 atoms or ions each to be assigned three independent parameters. It is obvious that this problem cannot be rigorously solved. It is, however, possible to derive a good approximation to the structure by combining the X-ray data with a knowledge of the size and co-ordination of the ions involved.

The problem can be simplified by considering only a quarter of the true cell. This simplification may be made by considering the pseudo-halvings. If (hkl) were absent for k odd, the b-dimension of the cell would be halved; if (hkl) were absent for $h + k/2$ odd, this new cell would be face-centred on the c-face. The absence of ($h0l$) for h odd is implied in this, but if ($h0l$) were absent for l odd, there would also be a c-glide plane. This would make the space-group $C2_1/c$. The top half of the cell would then, by reason of the glide-plane, contain the same atoms as the bottom half. To obtain a first approximation to the structure it is therefore sufficient to deal with a pseudo-cell for which $a = 9·6$, $b = 5·7$, $c \sin \beta = 7·86$ Å.

We have to place in this quarter-cell one molecule of $4CaO.Al_2O_3.$
$13H_2O$, or, as it now becomes necessary to write it, $Ca_4Al_2(OH)_{14}.6H_2O$.
The habit of the crystal and the excellent basal cleavage suggest
that it will be profitable to consider the atoms lying in layers
parallel to the basal plane. There are 24 large ions, viz. 20 oxygens
(diam. 2·70 Å.) and 4 calciums (diam. 1·96 Å.); and these determine
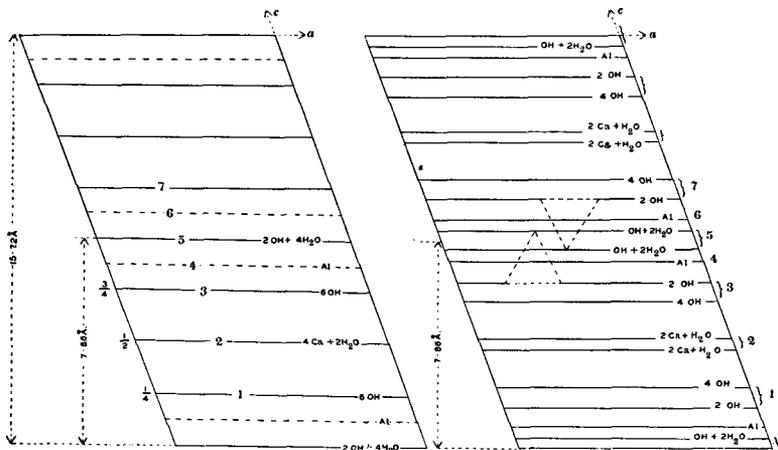
FIG. 1. FIG. 2.

FIG. 1. Projection in the (010) plane, showing the (approximate) arrangement
in layers parallel to (001).

FIG. 2. Projection in the (010) plane, showing the arrangement in layers, with
the parameters given on p. 612.

the structure; the small aluminiums (diam. 1·10 Å.) fit into the
interstices. The face-centring and hexagonal symmetry indicate a
regular hexagonal arrangement with 6 atoms in each layer, and the
cell dimensions permit this, since 6 close-packed oxygens would form
a cell of base 8.1×4.7 Å.[2] There are then four layers in the small
cell, and they must be roughly equally spaced to fit into the cell;
that is, they are at heights 0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$. This is confirmed by the in-
tensities of the orders of the basal plane, (004) and (008) being the
strongest.

So far the structure has been determined by purely geometrical
arguments; physical considerations must now be introduced. By
analogy with portlandite and gibbsite we may expect to find layers
of cations sandwiched between layers of hydroxyl ions. If we put
two planes of hydroxyl ions at $\frac{1}{4}$, $\frac{3}{4}$, they must, by Pauling's rule,

enclose a plane of cations; and since we have shown that the layer at $\frac{1}{2}$ must consist of large ions, these must be the calciums. There are, however, 6 places in the layer and only 4 calcium ions. The other 2 places might be occupied by aluminium ions; but in that case there are 2 oxygens for which there is no available room, since there are only 6 places in the layer at 0. It seems more reasonable to put 2 water molecules into the layer at $\frac{1}{2}$. For the layer at 0 we have then left 2 hydroxyl ions and 4 water molecules. There are still 2 aluminiums to be placed. Pauling's rule indicates that they must go between the layers at 0 and $\pm\frac{1}{4}$. The probable arrangement of the atoms in their layers will be discussed later. Meanwhile the structure deduced so far is shown in fig. 1.

A quantitative confirmation of the structure, and a value for the c-parameters of the atoms, may be obtained from the intensities of the basal plane (00l). These were estimated by eye on the Weissenberg photograph, and the amplitudes determined from them; the details of the method and corrections to be applied are described in the paper on gibbsite.[1] The experimental amplitudes thus deduced are given in the accompanying table along with those calculated for

| | | | | Intensity. | |
| | | | | Observed | |
Plane.				(in arbitrary units).	Calculated.
(002)	...	...	...	18	26
(004)	...	...	...	46	46
(006)	...	...	...	26	26
(008)	...	...	...	45	54
(0.0.10)	...	...	...	38	58
(0.0.12)	...	...	...	10	14
(0.0.14)	...	...	...	<5	2
(0.0.16)	...	...	...	16	22

a structure with the following parameters (referred to the true cell):

$2Ca + H_2O$, ± 0.235; $4OH$, ± 0.15; $2OH$, ± 0.10; Al, ± 0.05; $OH + 2H_2O$, ± 0.025.

These parameters, of course, are not very exactly determined; as good agreement with the observed values might be obtained by giving individual atoms slight displacements in opposite directions from the positions here assigned to them. It seems unlikely, however, that the good agreement recorded between observed and

[1] H. D. Megaw, The crystal structure of hydrargillite. Zeits. Krist., 1934, vol. 87, p. 185. [M.A. 5–471.]

calculated values could be obtained if the structure were not substantially correct. Fig. 2 shows the projection on the (010) plane of a structure with these parameters.

No attempt has been made to place the atoms more exactly by consideration of the intensities of any other planes. Where there are so many variables the work would have been too laborious, and very possibly no unique solution could have been reached. It is, however, possible to draw certain general conclusions. In the first place, from the fact that the layer of calciums with the layers of hydroxyl on either side form an approximately close-packed structure, it is established that the screw-axes cannot lie in the planes containing the calciums, but must be half-way between them, at 0, $\frac{1}{2}$. The calciums are probably distributed among the six possible positions so as to retain hexagonal symmetry. This is suggested by analogy with gibbsite and all other known AX_3 layer structures; it is confirmed by

O   OH ION OF LAYER 1
●   Ca ION OF LAYER 2
◯   H₂O MOLECULE OF LAYER 2
◎   OH ION OF LAYER 3

FIG. 3. Projection on (001) of layers 1, 2, 3 of fig. 1, showing oxygen octahedra round calciums.

the marked pseudo-hexagonal symmetry of the crystal. It is not so easy to be certain about the positions of the aluminiums. Al can be either 4- or 6-co-ordinated; and it is possible to find an arrangement based on either of these co-ordinations which has hexagonal symmetry. There does not seem to be any good criterion to distinguish between the two possibilities, but on the whole the tetrahedral co-ordination is more plausible. In either case, the arrangement of the hydroxyls and water molecules in the adjacent layer is made so as to satisfy Pauling's rule as well as possible, by placing the hydroxyls in the positions which are nearest to the aluminiums. The two structures are shown in figs. 4 a and 4 b. The hydroxyl ions in layer 5 are probably distributed so as to make all

the Al–OH distances roughly the same ; for tetrahedral co-ordination, the tetrahedra will therefore be imbricated, as shown in section by the dotted lines in fig. 2 (where no attempt has been made to draw them in their right position in the a-direction).

4 a 4 b

⊚	OH IONS IN LAYER 3 AND LAYER 7
×	Al ION IN LAYER 4
⊙	OH ION IN LAYER 5
◯	H₂O MOLECULE IN LAYER 5
+	Al ION IN LAYER 6
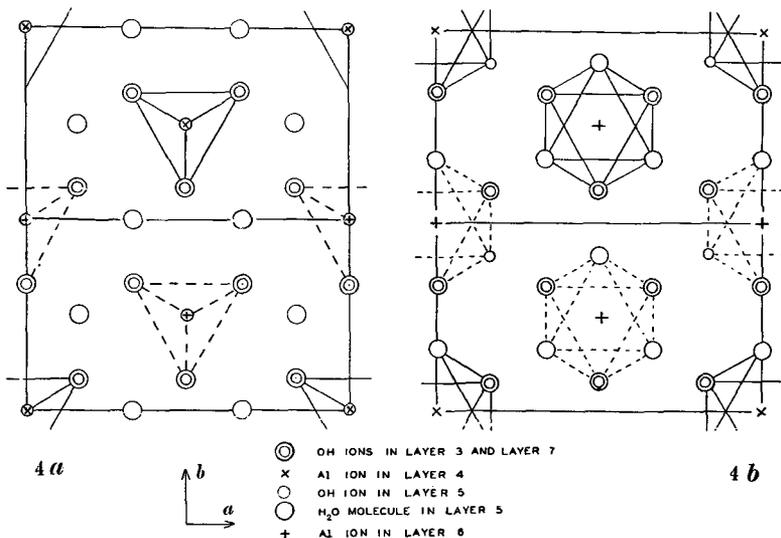
FIG. 4.   Projection on (001) of layers 3–7 of fig. 1.
(a) Al in tetrahedral co-ordination.
(b) Al in octahedral co-ordination.
Full lines indicate tetrahedra and octahedra of layers 3, 4, 5.
Dotted lines indicate tetrahedra and octahedra of layers 5, 6, 7.

The structure thus determined has complete hexagonal symmetry. The actual crystal is, of course, monoclinic, but the lower symmetry can easily be achieved by small displacements of the atoms from their ideal positions.   The structure proposed is in accordance with the evidence available, but it cannot claim any finality.   The general principles determining structures which contain OH groups along with H_2O molecules are not sufficiently well known to provide safe guides when the straightforward determination of parameters be- comes too complicated.   Such general principles must first be found from simpler substances, before it will be possible to make much further progress with this structure.

We may, however, consider how the proposed structure accounts for the physical properties of the mineral.   It cannot be used to

explain its optical properties, because these depend so largely on the polarization of the hydroxyl ions. On the other hand, it accounts satisfactorily for the excellent basal cleavage, and the secondary cleavage at about 60° to (100). It is also easy to see that the structure might lose water without being destroyed. The very varied results obtained by different workers on the artificial hydroxides suggest speculations about their structures and their relations to the natural mineral. Most of the substances are described as uniaxial, while some are biaxial. It seems possible that a uniaxial substance may exist, possessing the ideal structure described above. The change from the ideal hexagonal to the actual monoclinic structure is homeomorphous; and it is possible that as dehydration occurs, the water coming off either statistically or from definite positions in the cell, for certain compositions the stable structure is hexagonal and for other compositions monoclinic pseudo-hexagonal. Or again, even if a monoclinic structure is more stable for a compound with the full amount of water, it is possible that a hexagonal structure is first formed, and that the change to the other only takes place very slowly; or that different rates of crystallization affect the structure assumed. There seems to be definite evidence for this in the case of aluminium hydroxide; it has been shown that the hydroxide obtained by rapid precipitation is not the monoclinic gibbsite, but a less stable form known as bayerite. If a similar process occurs in the calcium aluminium hydroxides, it is to be expected that the naturally occurring mineral should show the stable, less symmetrical form.