

Ettringite from Scawt Hill, Co. Antrim.

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British Museum of Natural History.With a chemical analysis by M. H. HEY, M.A., B.Sc.
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(With Plate X.)

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ETTRINGITE was the name given by J. Lehmann¹ in 1874 to minute, transparent, acicular crystals lining the cavities of metamorphosed limestone-inclusions in leucite-nepheline-tephrite from the Ettringer-Bellerberg, near the village of Ettringen (between Mayen and the Laacher See), Rhineland. Lehmann detached sufficient needles from the limestone for chemical analysis, and found that they were not gypsum, as formerly supposed, but a hydrated calcium sulphoaluminate.

Recently Professor C. E. Tilley² recorded ettringite from the contact-zone of Chalk and Tertiary dolerite at Scawt Hill, near Larne, Co. Antrim. There it occurs with three other rare minerals, afwillite, portlandite, and hydrocalumite, as infillings of a larnite rock.³ Sufficient material was isolated to effect a comparison with ettringite from the Laacher See, and to carry out chemical, optical, and X-ray investigations. Thence it was hoped to ascertain the correct chemical formula, and also to explain the dehydration phenomena of the mineral in terms of its crystal-structure.

In addition to the fresh cleavage fragments⁴ of ettringite from Scawt Hill handed to Mr. Hey for chemical analysis, Professor Tilley also succeeded in detaching a comparatively well-formed crystal which was used for determining the optical and X-ray data. This, the largest crystal of ettringite yet found at Scawt Hill, measures

¹ J. Lehmann, Neues Jahrb. Min., 1874, p. 273.² C. E. Tilley and H. F. Harwood, Min. Mag., 1931, vol. 22, p. 444.³ C. E. Tilley, Min. Mag., 1934, vol. 23, p. 607.⁴ Perfect prismatic cleavage (10 $\bar{1}$ 0).

1.1 × 0.8 × 0.5 mm., and has a specific gravity 1.772 ± 0.002 obtained by suspending in a mixture of carbon tetrachloride and bromoform. It possesses five prism faces of the form $m(10\bar{1}0)$ and one small face $a(11\bar{2}0)$; no pyramidal or basal faces, however, can be observed, so that the axial ratio and symmetry could only be obtained by X-ray methods. A Lauegram taken along the c -axis reveals an hexagonal axis and vertical planes of symmetry, showing that the crystal-structure is built upon an hexagonal, not a rhombohedral, lattice. Spots, however, on one side of the photograph reveal a distortion of the crystal. This distortion must be restricted to a twist about the c -axis, since the layer-lines of a rotation photograph about this axis are truly aligned. Owing to this distortion of the crystal, rotation photographs about the $[10\bar{1}0]$ and $[11\bar{2}0]$ axes are slightly mis-set but yield consistent and fairly accurate values for the a -spacing. The unit-cell dimensions obtained from rotation photographs are $a 11.24 \pm 0.02$, $c 21.45 \pm 0.05$ Å. The calculated axial ratio is therefore $a:c = 1:1.908$. The axial ratios obtained from goniometric measurements of ettringite from Ettringer-Bellerberg, Laacher See, by Lehmann and more recently by R. Brauns¹ should be doubled to correspond with the true lattice dimensions. Their values, $c 0.94345$ and 0.9946 , then become $c 1.8869$ and 1.9892 .

The crystal of ettringite used for X-ray work offers two prisms suitable for refractive index measurements. The refracted images of a monochromatic source were, however, too weak to be observed, and the minimum deviation method yielded results only for white light, $\omega = 1.4655 \pm 0.0005$, $\epsilon = 1.4618 \pm 0.0005$, $\omega - \epsilon = 0.0037 \pm 0.0002$. Table I gives all the available optical data and specific gravity determinations of ettringite. Data for artificial ettringite,² a product of interest in the chemistry of Portland cement, are included, although X-ray confirmation of its identity with the natural mineral is lacking.

A chemical analysis of cleavage fragments of ettringite, approximate specific gravity 1.78, from Scawt Hill was then carried out by Mr. Hey giving the results shown in table II. The chemical and optical data so far obtained are in fair agreement with Lehmann's and Brauns's for ettringite from Ettringer-Bellerberg, Laacher See.

¹ R. Brauns, Die Mineralien der Niederrheinischen Vulkangebiete. Stuttgart, 1922, p. 173. [Min. Abstr., 2-24.]

² W. Lerch, F. W. Ashton, and R. H. Bogue, Bureau of Standards Journ. Research, Washington, 1929, vol. 2, p. 715.

Tilley's identification of the Scawt Hill ettringite was finally placed beyond doubt by X-ray methods. Fortunately a specimen labelled ettringite, Winfeld stream, Ettringer-Bellerberg, from J. Lehmann's private collection has been preserved in the Mineral Department of the British Museum. Several cavities in the matrix of this specimen

TABLE I. Optical data for ettringite.

	Refractive indices		Birefringence $\omega-\epsilon$.	Specific gravity.	Locality.
	ω .	ϵ .			
Bannister ...	1.4655	1.4618	0.0037	1.772	Scawt Hill
Brauns *	1.4661	1.4612	0.0049	1.791	Ettringen
Lehmann ...	—	—	—	1.7504	Ettringen
Lerch, et al. ...	1.464	1.458	0.006	1.48 †	Artificial

* Values for sodium light; Brauns (1922) also gives ω red 1.4642, ϵ red 1.4590; ω green 1.4726, ϵ green 1.4673.

† Probably a misprint for 1.78.

are lined with minute crystals in various stages of alteration. Most of them are coated with a white opaque substance, and only a prolonged search revealed a few perfectly clear prisms with negative elongation and refractive indices less than olive-oil. The fresh crystals show the forms¹ (10 $\bar{1}$ 0) and (10 $\bar{1}$ 1) or (10 $\bar{1}$ 0) and (10 $\bar{1}$ 2), and one of these yielded a rotation photograph about the *c*-axis

TABLE II. Chemical analysis of ettringite (0.2073 gram) from Scawt Hill, Co. Antrim.

	Percentages.	Mol. parts.	Oxygen %	Calc. comp. % *
CaO ...	26.6	0.474	7.59	26.81
Al ₂ O ₃ ...	7.0	0.069	3.30	8.12
SO ₃ ...	18.8	0.235	11.27	19.14
CO ₂ ...	0.8	0.018	0.58	—
H ₂ O ...	46.3	2.57	41.12	45.93
Total ...	99.5		63.86	100.00

* Calculated for the formula 6CaO.Al₂O₃.3SO₃.32H₂O.

identical with that of the Scawt Hill crystal. Rotation photographs of the altered crystals do not show the characteristic ettringite pattern but broad faint spots due to an oriented pseudomorph of grain-size less than 1×10^{-6} mm.; the *c*-spacing is approximately 11 Å. These have refractive indices near to xyloil. Larsen's values ϵ 1.474, ω 1.488 were probably obtained on similarly altered material. Possibly Brauns's axial ratio, which is considerably higher than

¹ The recorded forms for ettringite are *c* (0001), *m* (10 $\bar{1}$ 0), *r* (10 $\bar{1}$ 1), *p* (10 $\bar{1}$ 2), and *o* (10 $\bar{1}$ 4) [*a* : *c* = 1 : 1.908]; the form *r* was first noted by R. Brauns (1922).

Lehmann's and the X-ray value, was also deduced from measurements on slightly altered crystals.

Having established the identity of ettringite from Scawt Hill with fresh ettringite from the original locality, it is possible to employ Mr. Hey's analysis together with the specific gravity and X-ray data to seek a more correct chemical formula for the mineral than has hitherto been possible. Proceeding in the usual way, the number of oxygen atoms per unit cell (excluding the water content) is 36. Thence the number of atoms of calcium, aluminium, sulphur, and

TABLE III. Atomic contents of the unit cell of ettringite.

	Ca.	Al.	S.	C.	H ₂ .
Hey	12.0	3.5	6.0	0.5	65.1
Brauns	12.0	4.6	5.7	—	62.6
Lehmann	12.2	3.8	6.0	—	63.9
Moses	12.0	4.0	6.0	—	62.3
Artificial*	11.7	4.74	5.75	—	62.6

* Analysis performed in the chemistry division of the Bureau of Standards, Washington.

hydrogen in the unit cell of ettringite from Scawt Hill can be calculated. All the available chemical analyses of ettringite have also been recalculated assuming 36 oxygen atoms per unit cell (excluding the water content), table III. Moses has recorded a mineral he identified with ettringite from Tombstone, Arizona.¹ He gives no optical data, and his values of specific gravity 1.37 and 1.55 were perhaps determined on impure material. A specimen of so-called ettringite from Tombstone, Arizona, in the mineral collection of the British Museum has been identified by X-ray and optical methods with halotrichite. Moses's chemical analysis, however, has been included in the present study, and leads to values in agreement with those for ettringite from Ettringen and Scawt Hill. In reviewing the data of table III it must be remembered that no analysis has yet been made on more than 0.4 gram of this rare mineral, so that only round number agreement can be expected. It may, however, be safely concluded that the unit cell of ettringite contains $12\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot 6\text{SO}_3$ and probably $64\text{H}_2\text{O}$ when fully hydrated.

When a rock-slice containing ettringite from Scawt Hill is mounted in Canada balsam and not heated above 110°C . the mean refractive index rises to 1.50 and the material becomes uniaxial positive. The reaction is reversible providing the material is left in moist air

¹ A. J. Moses, Amer. Journ. Sci., 1893, ser. 3, vol. 45, p. 489.

for a sufficiently long period. Lerch, Ashton, and Bogue have followed the dehydration of artificial ettringite and found that the change of optic sign accompanies a change in composition from $6\text{CaO} \cdot \text{Al}_2(\text{C}_3\text{SO}_3 \cdot 31\text{H}_2\text{O})$ to $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$. Table IV shows the calculated percentage of the water lost by ettringite heated to 110°C . and at a red-heat, assuming that fully hydrated ettringite contains 64 molecules of water per unit cell and that dehydration at 110°C . results in a loss of 48 molecules. The experimental values of Lehmann and Moses are in fair agreement.

TABLE IV. Dehydration of ettringite.

% Loss at	Theoretical.	Lehmann.	Moses.		
			(a)	(b)	
110°	...	34.4	—	34.53	32.68
120°	...	—	33	—	—
150°	...	—	34	—	—
200°	...	—	36	—	—
Red-heat	...	45.9	45.8	45.41	48.44

Single crystals of ettringite which have been dehydrated at 110°C . do not yield the distinct X-ray pattern characteristic of the untreated mineral. The diffraction spots are diffuse, showing that the grain-size of the material must be less than 1×10^{-6} mm. The original ettringite has dehydrated to an oriented pseudomorph with approximate cell sides a 8.4, c 10.21 Å. and space-group $C6/mmc$. Thus the c -axis is approximately halved. The odd layer-lines of a rotation photograph of ettringite about the c -axis are weak, so that dehydration corresponds to a sideways shrinkage of the lattice but very little change along the c -axis. It should be noted that the altered crystals of ettringite from Ettringen are not identical with dehydrated ettringite. Neither the optical sign nor the X-ray patterns are the same.

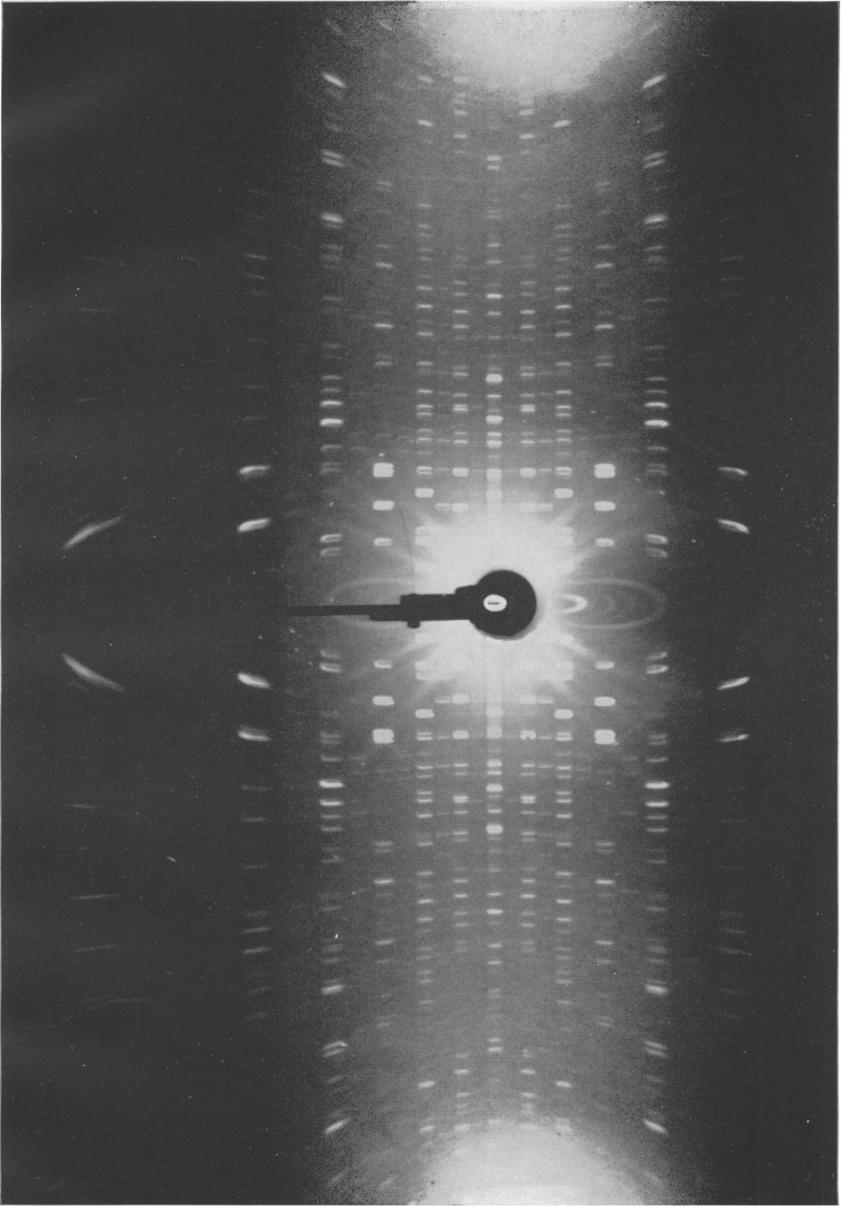
The rotation photograph of ettringite reproduced in plate x is a good example of arrangement of diffraction spots in row-lines as well as layer-lines, and was readily indexed. The missing spectra are of the type $(h h \bar{2}h l)$ when l is odd, and a photograph about the a -axis reveal that odd orders of $(000 l)$ are also missing. Assuming the presence of a plane of symmetry parallel to (0001) the space-group is therefore $C6/mmc = D_{6h}^3$. The contents of the unit cell, a 11.24, c 21.45 Å., are shown from table III to be $12\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 64\text{H}_2\text{O}$. It is natural to assume that the crystal-structure of ettringite will contain SO_4 groups, and that the aluminium atoms will be enclosed in octahedral groups $\text{Al}(\text{OH})_6$. The structural formula of ettringite

would then be written $\text{Ca}_{12}\text{Al}_4(\text{OH})_{24}(\text{SO}_4)_6 \cdot 52\text{H}_2\text{O}$. Mr. Bernal has proposed a structure of 'zeolitic' type for ettringite based upon the space-group $C6/mmc$. Approximate atomic co-ordinates have been suggested for all the atoms compatible with their ionic radii and 48 water molecules are located in the channels parallel to the c -axis [0001]. Such a structure on dehydration would change to $\text{Ca}_{12}\text{Al}_4(\text{OH})_{24}(\text{SO}_4)_6 \cdot 4\text{H}_2\text{O}$, the zeolitic channels would collapse sideways, but the structure would preserve essentially the same pattern along the c -axis. Preliminary calculations of structure-factors for diffractions of the type $(000l)$ and $(h h \bar{2}h 0)$ are not, however, in satisfactory agreement with the observed intensities, suggesting that the contributions of the zeolitic water molecules cannot be neglected. It is hoped to carry out shortly a more rigorous X-ray analysis of ettringite by the Weissenberg method. When this is completed a more detailed discussion of the structure will be given.

EXPLANATION OF PLATE X.

Rotation photograph of a crystal of ettringite from Scawt Hill, Co. Antrim, about the c [0001] axis (set horizontally on the page); taken with filtered copper radiation $\lambda = 1.539 \text{ \AA}$., and with a cylindrical camera, diameter 6.04 cm. Actual size. Note the regular arrangement of spots in vertical rows and horizontal lines.

A portion of this photograph was reproduced for the first time in Sir W. H. Bragg and W. L. Bragg, *The Crystalline State*, London, 1933, vol. 1, plate IV facing page 30.



F. A. BANNISTER : X-RAY PHOTOGRAPH OF ETTRINGITE