Crystal chemistry of ettringite.

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[Taken as read 25 January 1962.]

Summary. Crystal-chemical calculations are based on three chemically analysed samples of ettringite and their respective unit-cell dimensions and specific gravities. The large hexagonal unit cell is deduced to contain 384 oxygen atoms, 64 cations with co-ordination number 6 or more, and 48 cations with co-ordination number 4 or less. Some substitution of cations with co-ordination number 3 apparently takes place, and any excess above 192 H_2O takes place in the form of substitution of (H_4O_4) for XO_4 anionic groups. The isomorphism is extremely complex but can be generalized in simple form as $16[A_4(XO_4)_3(H_2O)_{12}]$, where A represents atoms with six-fold co-ordination (Ca, Na, Al) and X represents atoms with four-fold co-ordination (S, Si, H_4, and possibly some of the Al). It is implied that an isostructural series of silicon-containing calcium aluminium sulphate hydrates might exist, the extreme compositions of which are: $6CaO.Al_2O_3.3SO_3.3SiO_2.24H_2O$ and $6CaO.Al_2O_3.3SO_3.30H_2O$.

The crystal structures of ettringite and thaumasite must be closely related.

ETTRINGITE presents a problem of crystal-chemical interest because of the complexity of its chemical composition. The question can be approached, however, by assuming reasonable co-ordination numbers if, and after, the total number of oxygen atoms has been surmised.

In addition to the occurrence at Ettringen, the mineral has been reported from three other localities: Franklin, N.J. (Hurlbut and Baum, 1960), Scawt Hill, Co. Antrim, Ireland (Bannister, 1936), and Crestmore, California (Murdoch and Chalmers, 1958 and 1960). Excellent X-ray diffraction data are available for materials from each of these three localities, in addition to chemical analyses and optical data. The chemical analyses show several significant differences, as will be discussed in detail, but collectively they indicate at least 2·0 weight per cent of the oxides of each of the following elements: Ca, Na, Al, S, Si, B, and C. An additional complication is the variation of the water content from 40·0 to 48·6 %.

There appears to be little doubt that ettringite is hexagonal or that the correct space group is almost certainly $P6_3/mmc$. The unit cell is large for an inorganic substance—about 9000 Å^3. Details are given in table I, where it is evident that there are variations among the physical properties.

TABLE I. Physical data for ettringite.

Locality and reference	*a.*	*c.*	Sp. gr.
Ettringen (Hurlbut and Baum, 1960)	22·46 Å	21·42 Å	1·750*
Franklin (*idem*)	22·28	21·29	1·770
Scawt Hill (*idem*)	22·47	21·46	—
Scawt Hill (Bannister, 1936)†	22·52	21·48	1·772
Crestmore (Murdoch and Chalmers, 1960) ...	22·33	21·35	1·78
Ettringen (*idem*)	22·48	21·31	—
Synthetic (Swanson *et al.*, 1959)‡	22·46	21·44	(1·754‡)

* Lehmann, 1874.

† Bannister's unit cell dimensions are converted from *kX* units, and the a_0 dimension is doubled.

‡ The a_0 dimension is doubled; the sp. gr. is a calculated value based on the assigned composition $Al_2O_3.6CaO.3SO_3.31H_2O$.

Chemical Data. Hurlbut and Baum (1960) give a formula for the contents of the unit cell for 'Franklin ettringite':

$$Ca_{48}[SiO_3(OH)]_5[Al(OH)_4]_{10}[B(OH)_4]_9[SO_4]_{16}[(OH)_4]_8.208H_2O.$$

In addition to the 192 oxygen atoms (including hydroxyls) used to form anionic groups, they indicate 208 molecules of water, or a total of 400 oxygens in the unit cell.

It is possible to calculate the number of oxygen atoms directly from a knowledge of the specific gravity, unit cell dimensions, and chemical analysis. When the method previously described (McConnell, 1954) is applied to the three recent analyses of ettringite in conjunction with their respective diffraction data and specific-gravity measurements, the calculated numbers of oxygen atoms differ by approximately 9 % (table II). The uncertainty of the calculation is increased to a considerable extent by the possibility of error in the determination of combined water. If it is assumed that the number of oxygen atoms lies somewhere between 368 and 402, a likely number appears to be 384 ($= 2^7 \cdot 3$). This number has much to recommend it in preference to 400 ($= 2^4 \cdot 5^2$) (see comparison with thaumasite, p. 63).

We can now write a comparatively simple formula for the unit cell in terms of the octahedral cations (*A*) and the tetrahedral cations that make up the anionic groups (X): $16[A_4(XO_4)_3(H_2O)_{12}]$. This formula has in its favour the larger factor, $Z = 16$, and contains 384 hydrogens, or probably more, as well as 384 oxygens. In other words, at least half of the oxygens present in the structure are bonded to hydrogens.

How this structural formula is related to the chemical analyses deserves further consideration, but first it should be pointed out that electron balance does not obtain for this structural formula if A is simply calcium and X is simply sulphur.

TABLE II. Chemical analyses of ettringite.

	I.	II.	III.	IV.	V.	VI.
CaO	30·1	27·3	26·6	27·15	25·40	29·03
Al_2O_3	5·0	5·1	7·0	8·35	8·62	6·09
SiO_2	3·1	3·1	—	—	—	2·39
SO_3	17·1	12·8	18·8	19·12	20·30	22·32
H_2O	40·0	48·6	46·3	45·42	45·68	40·17
Others	5·0	3·2	0·8	0·41	—	—
Sum	100·3	100·1	99·5	100·45	100·00	100·00
Oxygen atoms per unit cell ...	368·3	395·1	401·7	—	384	384

I. Crestmore, California. Analyst: R. A. Chalmers. Others: $CO_2 = 2·7$, $Na_2O = 2·0$, $K_2O = 0·2$, $MgO = 0·1$. Fe_2O_3, BaO, and Li_2O were absent. $H_2O^{-115°}$ 10·7; $H_2O^{115°}$ 27·6; $H_2O^{+115°}$ 1·7. Another determination of Al_2O_3 was 6·7.

II. Franklin, New Jersey. Analyst: Jun Ito. Others are entirely B_2O_3 although a trace of CO_2 was reported. H_2O^- 39·4; H_2O^+ 9·2.

III. Scawt Hill, Co. Antrim, Ireland. Analyst: M. H. Hey. Others are entirely CO_2. (All water is indicated as H_2O^+.)

IV. Synthetic ettringite. Prepared and analysed by Edwin S. Newman. Others are entirely CO_2, but spectroscopic analysis indicated Si and Sr less than 1·0 but greater than 0·1 %, and lesser amounts of other elements. (See Swanson *et al.*, 1959.)

V. Composition of $[Ca_{48}Al_{16}][(S_{24}H_{96})O_{192}][(H_2O)_{192}]$.

VI. Composition of $[Ca_{52}Al_{12}][(S_{28}Si_4H_{64})O_{192}][(H_2O)_{192}]$.

The formula suggested by Hurlbut and Baum (1960) involves a factor $Z = 8$ (rather than $Z = 16$, as above) and is written as

$$8[Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O].$$

Not only does the number 26 times 8 seem improbable as the number of oxygens bonded to two hydrogens, but there is inadequate evidence for assuming that 12 times 8 oxygens are present as hydroxyls. More important, however, is the evidence that there is no constancy (table II) in the ratio of either Al to Ca or of Al to S, as is implied by their formula.

Examination of the chemical analyses implies that variation in the water content must be provided for in the structural formula, and that there are elements with $CN = 3$ present in addition to those with $CN = 4$. The structural substitution of $4(YO_3)$ for $3(XO_4)$ has been discussed in connexion with carbonate apatites (McConnell, 1952 and 1960) and scawtite (McConnell and Murdoch, 1958).

Consideration of the types of co-ordination that are likely to obtain in a structure of this sort gives rise to the following premises:

$$\begin{array}{ll} \mathrm{CN} \geqslant 6\text{: Ca, Na, Al;} & \text{total } 64; \\ \mathrm{CN} = 4\text{: S, Si, } \mathrm{H_4}\text{, (Al?), (B?);} & \text{total } 48\text{-}x; \\ \mathrm{CN} = 3\text{: C, (B?);} & \text{total } 4x/3 \end{array}$$

(neglecting those constituents of ettringite that have been reported as 0·2 % (or less) as the oxide weights).

Further consideration of the quantitative details will permit us to write a specific example of the general structural formula deduced from the crystallographic data:

$$[\mathrm{Ca_{52}Al_{12}}][(\mathrm{S_{28}Si_4H_{64}})\mathrm{O_{192}}][(\mathrm{H_2O})_{192}],$$

the composition of which is compared with those of actual analyses in table II, VI. Admittedly, the sulphur content is high, but the amount of SO_3 would be reduced were CO_2 and B_2O_3 considered. Another example, more comparable with the analysis of synthetic ettringite, is included as V. These examples contain substitution of the type (O_4H_4) for XO_4, as has been postulated for certain phyllosilicates, the hydrogarnets, viséite, coffinite, and others. Postulation of this sort of substitution for ettringite seems reasonable in order to account for variations in the total water content, which ranges from 40·0 to 48·6 %.

Conclusions. Although the isomorphic relationships appear to be very complex in ettringite, it is possible to obtain a simple generalization of the structural formula that is consistent with the recognized principles of crystal chemistry and the available data on the chemical composition of ettringite. The material from Crestmore contains an appreciable amount of carbon dioxide and therefore represents an additional example of the substitution of triangular groups within a structural arrangement that is composed predominantly of tetrahedra. The co-ordination of the boron, present in the Franklin material, cannot be decided from available evidence. It is implied that an isostructural series of silicon-containing calcium aluminium sulphate hydrates might exist, the extreme compositions of which are:

$$6\mathrm{CaO.Al_2O_3.3SO_3.3SiO_2.24H_2O} \text{ and } 6\mathrm{CaO.Al_2O_3.3SO_3.30H_2O}.$$

On the basis of 384 oxygens, it seems likely that the carboaluminate' of Carlson and Berman (1960) has the composition $6CaO.Al_2O_3.3CO_2.33H_2O$ rather than $6CaO.Al_2O_3.3CO_2.32H_2O$ as assigned by them.

The relation of thaumasite and ettringite.

It seems desirable to point out certain similarities in the several properties of ettringite and thaumasite that have been merely alluded to in previous work (Murdoch and Chalmers, 1960). Such comparisons are contained in table III.

TABLE III. Comparisons for ettringite and thaumasite.

Physical properties.	Ettringite.	Thaumasite.
Refractive indices	(1)	(2)
ϵ	1·450–1·470	1·464–1·468
ω	1·465–1·491	1·500–1·507
$\omega-\epsilon$	0·003–0·021	0·036–0·039
Specific gravity	1·75–1·78 (3)	1·84–1·91 (2, 4)
X-ray data		
space group	$P6_3/mmc$ (5)	$P6_3$ (6)
dimensions	(3)	(5)
a_0 (Å)	22·28–22·52	21·90–22·12
c_0 (Å)	21·29–21·48	10·30–10·54
powder pattern	(5)	(7)
$d//I$	9·72//10 5·60//7 3·88//4 2·77//5	9·67//100 5·50//80 3·76//80 2·69//80
Structural data	(8)	(6)
Z-factor	16	2 (9)
Ca atoms	$\sim$ 3	3
Al	$\sim$ 1	0
$O+H_2O$	24	24

Notes: (1) Hurlbut and Baum (1940). (2) Winchell and Winchell (1951). (3) See table I. (4) U.S.G.S. Bull. 591. (5) Murdoch and Chalmers (1960), Cu radiation. (6) Welin (1956). (7) A.S.T.M. card no. 2–0061 (thaumasite from New Jersey), Mo radiation. (8) This work. (9) Using the doubled a (shown above) $Z = 8$.

Nothing is indicated concerning the principal anionic groups in table III. For thaumasite they are approximately equivalent amounts of SO_4^{-2}, SiO_4^{-4}, and CO_3^{-2}. Welin (1956) has indicated that the coordination number for calcium is 6 in thaumasite and this seems to be reasonable for ettringite also. Inasmuch as most of the aluminium of ettringite has $CN = 6$ also, there is justification for writing the formula in such a manner that $\sim 3Ca + \sim Al = 4A$, and this has been done in our most general structural formula. The structures of ettringite and thaumasite must be closely related in several respects.

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