

## Alunogen, $\text{Al}_2(\text{H}_2\text{O})_{12}(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ : Its atomic arrangement and water content

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### Abstract

Alunogen is triclinic, space group  $P\bar{1}$  with  $a = 7.420(6)\text{\AA}$ ;  $b = 26.97(2)\text{\AA}$ ;  $c = 6.062(5)\text{\AA}$ ;  $\alpha = 89^\circ 57(5)'$ ;  $\beta = 97^\circ 34(5)'$ ;  $\gamma = 91^\circ 53(5)'$ ; and  $Z = 2$ . A computer-controlled Buerger-Supper two-circle goniometer (Weissenberg geometry) was utilized for collection of X-ray intensity data. The structure was partially solved by the symbolic addition method and completed by use of Fourier and difference Fourier syntheses. Full-matrix least-squares refinement, with 1675 reflections, led to a final  $R$  index of 0.077.

The structure is built of discrete  $\text{SO}_4$  and  $\text{Al}(\text{Ow})_6$  polyhedra interconnected by a network of hydrogen bonds. Four of the five independent polyhedra are spatially arranged in a manner which gives rise to pseudo-double sheets parallel to (010), thereby accounting for the (010) cleavage and twinning. The fifth polyhedron (an  $\text{SO}_4$  group) is situated between pseudo-sheets and is completely surrounded by the five zeolitic water molecules. Mean Al-Ow and S-O distances are 1.887 and 1.467  $\text{\AA}$ , respectively.

Maximum  $\text{H}_2\text{O}$  content in the alunogen formula was found to be 17 molecules as opposed to the heretofore accepted value of 18. Partial dehydration is accompanied by partial occupancies of zeolitic water sites. That there exists no known aluminum sulfate hydrate other than alunogen is interpreted to be a result of the strong tendency for the  $\text{Al}^{3+}$  ion to form  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  in aqueous solutions.

### Introduction

Recent interest in crystalline hydrates has, as one of its major objectives, the revelation of the general rules of solvation, *i.e.*, an attempt via crystal-structure analysis is being made toward unravelling the relationship between polyhedral clustering in crystalline hydrates and the polyhedra which existed in the solution from which the minerals grew. Despite a considerable amount of existing data, there is little real understanding of the behavior of polyhedra in solution or the multiplicity of their phase formation. In this paper, we report the crystal structure of alunogen, a sulfate hydrate with a very high water content. By virtue of its large number of water molecules, alunogen can be thought of as being closely related to solutions. Thus, its crystal structure is of great interest since it may provide a key to these questions. This study will also settle the question of the exact number of water molecules in the alunogen formula and should also yield considerable information concerning the hydration range in which the alunogen structure can exist. In this paper we extend the conclusions reached by us in connection with the structure of kornelite (Robinson and Fang, 1973).

### Data collection and reduction

Small, transparent laths of alunogen from Königsberg, Schemnitz district, Hungary (now Nova Bana, Czechoslovakia) were kindly supplied by Professor F. Cesbron of the Laboratoire de Mineralogie et de Cristallographie de la Sorbonne, Paris, France. The crystals are stable while in the sample vial. However, if the crystals are exposed to the atmosphere during periods of low humidity, dehydration begins almost immediately, beginning as small cracks visible only under the optical microscope, progressing to tinges of white on the grain edges, and terminating with the entire grain becoming white, translucent, and crumbly. This occurs within a few hours during unusually cold winter days when indoor humidity is very low. However, crystals exposed to the atmosphere for periods of several weeks during the humid summer months showed no deterioration. In addition to the dehydration problem, alunogen is commonly twinned parallel to (010), so considerable time was spent in finding a suitable crystal.

The unit cell parameters, obtained from precession photographs, are  $a = 7.420(6)\text{\AA}$ ;  $b = 26.97(2)\text{\AA}$ ;  $c = 6.062(5)\text{\AA}$ ;  $\alpha = 89^\circ 57(5)'$ ;  $\beta = 97^\circ 34(5)'$ ;  $\gamma =$

$91^{\circ}53(5)'$ ;  $Z = 2$  and space group  $P1$  or  $P\bar{1}$ . This unit cell was chosen so as to conform to the morphological cell of Gordon (Palache, Berman, and Frondel, 1951).

The crystal selected for data collection was a thin, transparent lath with the dimensions  $0.016 \times 0.010 \times 0.0026$  cm. The shortest dimension very nearly parallels the  $b$  axis about which the crystal was rotated during the intensity gathering process. A total of 2822 raw intensities were collected with a computer-controlled, Buerger-Supper equi-inclination goniometer and Ni-filtered  $\text{CuK}\alpha$  radiation. Scan speed was varied directly with peak intensity in order to minimize variations in counting statistics. Pre-selected standard reflections were manually remeasured between reciprocal lattice levels as a check on system and crystal stability. The system performed normally during the course of the data collection and the crystal remained stable.

All data were corrected for Lp and absorption ( $\mu = 46.06 \text{ cm}^{-1}$ ) using the ACAC program of Prewitt (Wuensch and Prewitt, 1965).

### Structure determination

Normalized structure factors ( $E$ 's) were calculated using the WILNORM program of Fang and Robinson (1969). The strong indication of centrosymmetry indicated by the  $E$  statistics led to adoption of the space group  $P\bar{1}$ .

A modified version of the reiterative Sayre's equation program written by Long (1965) failed to reveal the structure. We then proceeded to perform semi-manual sign prediction with the aid of a symbolic addition program known as SYMBAD, written by Robinson (1974) for our PDP-8/e computer. In this manner we were able to deduce the signs or symbols of 125  $hkl$ 's. This information was then given to the SORTS symbolic addition program of Bednowitz (1970), for extension to  $hkl$ 's with lower  $E$  values. After signs or symbols for 530  $hkl$ 's were determined,  $E$  maps were calculated on the three possible sign combinations that resulted. One set revealed all of the polyhedral atomic sites as well as tentative zeolitic water positions.

All polyhedral atoms were then input to the RFINE least-squares program of Finger (1969) for calculation of structure factors, and the results were passed to a Fourier program known as FORDY (Ohya, 1970) for calculation of an  $F_{\text{obs}}$  Fourier map. The  $F_{\text{obs}}$  map clearly revealed four zeolitic water (Zw) positions. However, the results were inconclusive regarding the remaining two possible zeolitic sites which

would be present if our sample of alunogen contained the full complement of 18 water molecules previously attributed by Palache *et al* (1951) and by Larsen and Steiger (1928) to the fully hydrated mineral.

### Completion and refinement of the structure

The  $R$  index became 0.083 after four cycles of full-matrix least-squares refinement, using atomic scattering factors for  $\text{Al}^{3+}$ ,  $\text{S}^0$ , and  $\text{O}^{1-}$ , from Cromer and Mann (1968) and the 1681 reflections which were considered "observed" after passing the  $\{I-B \geq 4\sqrt{I+B}\}$  test (where  $I$  = total counts accumulated during the scan and  $B$  = total background). During the final cycle,  $\Delta$  values ( $F_o - F_c$ ) were passed to the FORDY program previously mentioned for calculation of a difference Fourier map. The largest peak appeared at a very logical location; however, the low electron density of the peak could only be explained by assuming partial occupancy. Two least-squares calculations were performed in an attempt to fix the occupancy value of this site, herein designated Zw(5). First, a five-cycle run was prepared in which the occupancy factor was given a fixed value for each cycle, beginning with 10 percent occupancy and changing by 10 percent increments for each additional cycle until a 50 percent occupancy value was reached. During each cycle the occupancy value of Zw(5) was locked, but all  $x, y, z$ 's and  $B$ 's were allowed to vary. During the 10%-occupancy cycle the temperature factor became  $-17.0 \text{ \AA}^2$ . As the occupancy was increased, the  $R$  factor decreased and the temperature factor increased until, at 50 percent occupancy, the  $R$  factor again began to increase and the temperature factor became unreasonably high. At 30 percent occupancy the  $B$  for Zw(5) was  $+6.1 \text{ \AA}^2$  while at 40 percent occupancy  $B$  was  $9.1 \text{ \AA}^2$ . The  $R$  index was at its minimum of 0.078 during the 30 and 40 percent occupancy cycles. Thus, it seemed reasonable, in light of the temperature factors of the other zeolitic waters, that the occupancy for Zw(5) was between 30 and 40 percent. Second, attacking the problem from the opposite direction, the temperature factor of Zw(5) was locked at the average  $B$  value of the other four zeolitic water molecules ( $6.2 \text{ \AA}^2$ ) and the occupancy value of Zw(5) was varied, along with all atomic coordinates and  $B$ 's of the other atoms. The occupancy value of Zw(5) refined to a value of 37 percent. It is possible that the Zw(5) occupancy may be slightly higher since the  $B$  of Zw(5) could well be somewhat higher than the average of the full occupancy zeolitic waters. However, we believe our reported value is very close to the true occupancy.

We next began a search for evidence of a sixth zeolitic site. We added the partial occupancy Zw(5) position to the list of atoms, refined the structure to an  $R$  index of 0.077, and then calculated a difference Fourier map. The map showed no feasible atomic positions and thus it was concluded that the sixth zeolitic site was non-existent, at least in the crystal under study.

At this point, six  $hkl$ 's, obviously affected by extinction, were removed from the data and two additional least-squares cycles, with 1675 reflections, led to the final  $R$  index of 0.077. Observed and calculated structure factors are given in Table 1<sup>1</sup> while atomic

<sup>1</sup> To obtain a copy of Table 1, order Document AM-75-005 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit in advance \$1.00 for the microfiche.

TABLE 2. Atomic Coordinates and Temperature Factors for Alunogen\*

Atom	x	y	z	B( $\text{\AA}^2$ )
S(1)	.2327(4)	.9390(1)	.4813(6)	1.46(6)
S(2)	.2424(4)	.5607(1)	.4859(5)	1.23(6)
S(3)	.6334(5)	.7470(1)	.4740(7)	2.54(8)
Al(1)	.2803(5)	.0986(1)	.0012(7)	1.27(7)
Al(2)	.7367(5)	.5995(1)	.0029(6)	1.19(7)
O(1)	.374(1)	.9043(3)	.448(2)	2.8(2)
O(2)	.697(1)	.0258(3)	.340(2)	2.3(2)
O(3)	.928(1)	.0886(3)	.457(2)	2.3(2)
O(4)	.175(1)	.9656(3)	.271(2)	2.5(2)
O(5)	.693(1)	.4738(3)	.336(2)	2.3(2)
O(6)	.391(1)	.5955(3)	.447(2)	2.1(2)
O(7)	.908(1)	.4114(3)	.446(1)	2.0(2)
O(8)	.174(1)	.5336(3)	.279(2)	2.2(2)
O(9)	.232(2)	.2814(4)	.387(2)	4.8(3)
O(10)	.604(1)	.7268(4)	.249(2)	3.7(2)
O(11)	.703(1)	.7981(4)	.466(2)	4.2(2)
O(12)	.543(2)	.2528(5)	.437(2)	6.6(3)
Ow(1)	.812(1)	.8415(3)	.113(2)	2.3(2)
Ow(2)	.334(1)	.1254(3)	.289(1)	1.9(2)
Ow(3)	.374(1)	.0379(3)	.112(1)	1.8(2)
Ow(4)	.771(1)	.9304(3)	.285(1)	1.6(2)
Ow(5)	.482(1)	.8829(3)	.053(1)	1.9(2)
Ow(6)	.046(1)	.0774(3)	.062(1)	2.0(2)
Ow(7)	.828(1)	.6603(3)	.128(1)	2.0(2)
Ow(8)	.303(1)	.3725(3)	.282(1)	1.7(2)
Ow(9)	.027(1)	.4179(3)	.047(1)	2.0(2)
Ow(10)	.777(1)	.5696(3)	.287(1)	1.5(2)
Ow(11)	.497(1)	.6145(3)	.052(1)	1.7(2)
Ow(12)	.361(1)	.4622(3)	.121(1)	1.5(2)
Zw(1)	.709(1)	.3249(4)	.201(2)	4.4(3)
Zw(2)	.611(2)	.2101(5)	.043(2)	5.9(3)
Zw(3)	.002(2)	.2164(5)	.101(2)	7.1(4)
Zw(4)	.152(2)	.6965(6)	.229(3)	7.6(4)
Zw(5) <sup>b</sup>	.148(5)	.797(1)	.434(6)	6.2 <sup>c</sup>

coordinates and temperature factors are presented in Table 2.

### Description of the structure

The structure is composed of isolated  $\text{Al}(\text{Ow})_6$  octahedra and  $\text{SO}_4$  tetrahedra (Fig. 1). However, the polyhedra are not evenly distributed throughout the unit cell as they are, for example, in the alum structure (Cromer, Kay, and Larson, 1967); rather, they form pseudo-double sheets parallel to (010). Between the pseudo-sheets lie the S(3) tetrahedra which are completely surrounded by zeolitic water molecules. In addition, it is interesting to note that the octahedra and tetrahedra lie in separate but parallel sheets normal to (001). This is best visualized in the (100) projection (Fig. 1).

All polyhedra are quite regular (Table 3), as would be expected in an isolated polyhedral arrangement. The mean Al-Ow and S-O distances are 1.887 and 1.467  $\text{\AA}$ , respectively.

### Discussion

#### Hydrogen bonds

A hydrogen bonding scheme, derived from geometrical considerations, is shown in Table 4 (the arrows point toward the acceptor atoms of the H-bonds). It is interesting to note that the only zeolitic water not bonded to a ligand water is Zw(5), the site of partial occupancy. Thus, alunogen owes its existence as a crystalline solid to the extensive three-dimensional network of hydrogen bonds. Table 5 is a summation of donor and acceptor bonds, in support of the proposed hydrogen-bonding scheme. The electrostatic bond strengths and their sums about the anions are shown in Table 6. Anions which have nearly identical environments have been grouped together. We note from the table that, with one exception, the oxygen atoms are undersaturated, and that this imbalance is reflected in the shorter-than-normal Ow-O distances shown in Table 4.

#### Chemical formula of alunogen:

#### Revision of the water content

In the Refinement section, we pointed out that we were unable to locate a sixth zeolitic water from the final difference Fourier map, despite the fact that a sixth site should exist if alunogen contains a total of 18  $\text{H}_2\text{O}$  molecules as reported in the literature. This information was in contradiction with our working hypothesis concerning zeolitic water sites which states that the loss of water in sulfate hydrates does

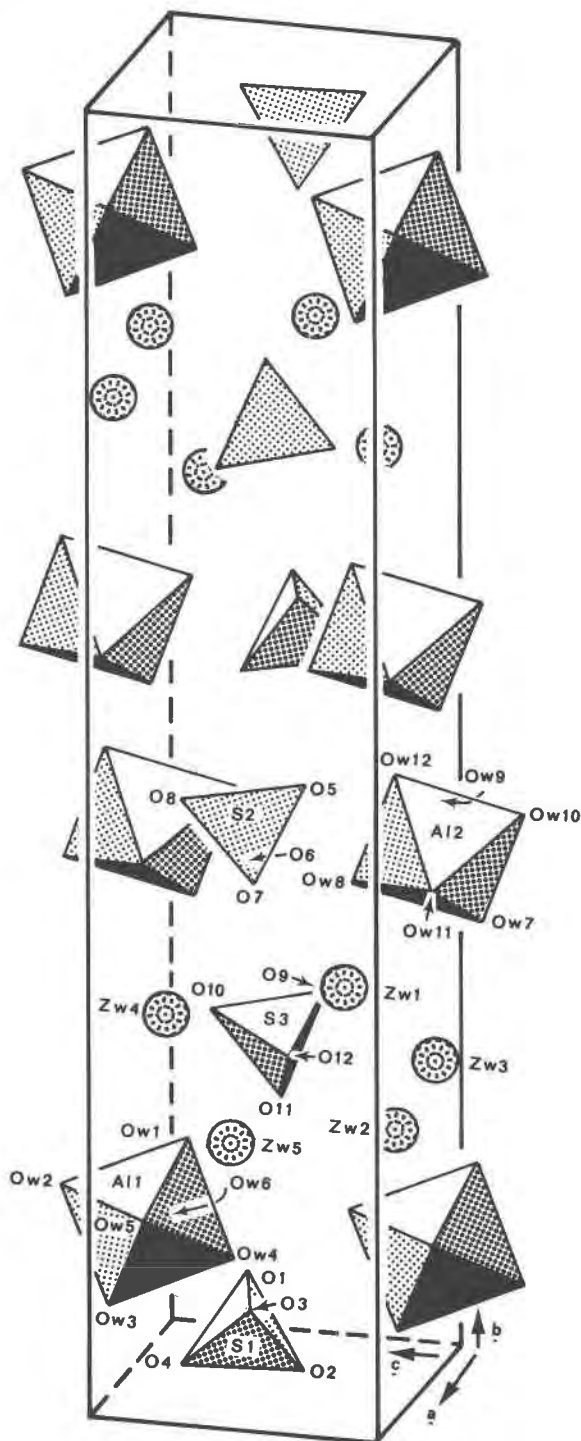


FIG. 1. Polyhedral representation of the alunogen structure.

not cause the disappearance of an entire zeolitic water site, but rather is the result of a decrease in occupancy of one or more sites. In an attempt to discover the source of the difficulty, we recalculated the chemical analyses reported by Dana (Palache *et al.*, 1951,

p. 537). None of the four chemical analyses listed corresponded to 18 H<sub>2</sub>O—they vary from 12.5 to 15.5—and the origin of the 18 H<sub>2</sub>O hydration state was attributed to the work of Larsen and Steiger (1928). However, what Larsen and Steiger stated was that “. . . former contention as to whether alunogen contained 16 or 18 molecules of water has been raised on the incorrect assumption that the water is present in a definite, fixed molecular proportion.” Furthermore, they concluded that their study “indicates a water content of from 15 to 15.5 molecules.” Rather it was Lausen (1928) who actually inferred the water content to be 18, based on his chemical analysis of impurity-containing alunogen from Jerome, Arizona. His calculations showed the molecular ratio of Al<sub>2</sub>O<sub>3</sub>:SO<sub>3</sub>:H<sub>2</sub>O to be 1.0:3.5:18.6. However, it is obvious the ratio must be normalized to 0.9:3.0:15.9, thus indicating a water content of 16. In short, the number 18 was not supported by any published account. Notwithstanding, a survey of the literature on synthetic alunogen proved very enlightening. In his effort to clear up the confusion in the chemical literature regarding aluminum sulfate, Smith (1942) repeated chemical investigations of parts of the system Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O. His summary states “Previous data in the literature have been reviewed and shown to lend little support to the reported formula of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O for hydrated aluminum sulfate.” He further wrote that the compound is either a hexadeca-hydrate or heptadeca-hydrate, the latter favored by him as well as by two other investigators. In a later paper, Henry and King (1949) reported that alunogen is a 16-hydrate. Thus it seems alunogen is either a 16- or 17-hydrate; but which is correct?

As is often the case, the exact chemical composition can only be established via three-dimensional structural analysis. We have demonstrated this in our previous papers, and again emphasize this fact by showing that alunogen is a heptadeca-hydrate when fully hydrated. Further loss of water can be expected to induce further partial occupancies in other zeolitic sites, in order to sustain the alunogen structure.

#### *Crystallization in the Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·nH<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·nH<sub>2</sub>O systems: An interpretation*

One salient objective in crystal-structure analysis is to find or attempt to find a relationship between the crystal structure and the ionic species existing in solutions from which crystalline solids grew. Toward this end, a hydrate of high water content is a good candidate, since it can be thought of as being very similar

TABLE 3. Selected Interatomic Distances and Angles for Alunogen\*

Tetrahedral coordination around S					
S(1)-O(1)	1.462(10)Å	O(1)-O(2)	2.39(1)Å	O(1)-S(1)-O(2)	109.3(5)°
S(1)-O(2)	1.472(9)	O(1)-O(3)	2.40(1)	O(1)-S(1)-O(3)	109.5(5)
S(1)-O(3)	1.474(9)	O(1)-O(4)	2.41(1)	O(1)-S(1)-O(4)	109.7(6)
S(1)-O(4)	1.484(10)	O(2)-O(3)	2.41(1)	O(2)-S(1)-O(3)	109.6(5)
		O(2)-O(4)	2.43(1)	O(2)-S(1)-O(4)	110.9(5)
		O(3)-O(4)	2.39(1)	O(3)-S(1)-O(4)	107.8(5)
MEAN	1.473Å	MEAN	2.40Å	MEAN	109.5°
S(2)-O(5)	1.465(9)Å	O(5)-O(6)	2.39(1)Å	O(5)-S(2)-O(6)	109.5(5)°
S(2)-O(6)	1.467(9)	O(5)-O(7)	2.39(1)	O(5)-S(2)-O(7)	109.0(5)
S(2)-O(7)	1.471(9)	O(5)-O(8)	2.42(1)	O(5)-S(2)-O(8)	110.9(5)
S(2)-O(8)	1.474(9)	O(6)-O(7)	2.40(1)	O(6)-S(2)-O(7)	109.2(5)
		O(6)-O(8)	2.41(1)	O(6)-S(2)-O(8)	110.2(5)
		O(7)-O(8)	2.38(1)	O(7)-S(2)-O(8)	108.0(5)
MEAN	1.469Å	MEAN	2.40Å	MEAN	109.5°
S(3)-O(9)	1.46(1)Å	O(9)-O(10)	2.39(2)Å	O(9)-S(3)-O(10)	110.1(7)°
S(3)-O(10)	1.46(1)	O(9)-O(11)	2.36(2)	O(9)-S(3)-O(11)	108.2(7)
S(3)-O(11)	1.46(1)	O(9)-O(12)	2.43(2)	O(9)-S(3)-O(12)	112.2(8)
S(3)-O(12)	1.48(1)	O(10)-O(11)	2.37(2)	O(10)-S(3)-O(11)	108.8(6)
		O(10)-O(12)	2.39(2)	O(10)-S(3)-O(12)	109.0(7)
		O(11)-O(12)	2.38(2)	O(11)-S(3)-O(12)	108.4(7)
MEAN	1.46Å	MEAN	2.39Å	MEAN	109.5°
Octahedral coordination around Al <sup>3+</sup>					
		Ow(1)-Ow(2)	2.70(1)Å	Ow(1)-Al(1)-Ow(2)	91.9(4)°
		Ow(1)-Ow(4)	2.66(1)	Ow(1)-Al(1)-Ow(4)	89.9(4)
		Ow(1)-Ow(5)	2.71(1)	Ow(1)-Al(1)-Ow(5)	92.1(4)
Al(1)-Ow(1)	1.873(9)Å	Ow(1)-Ow(6)	2.68(1)	Ow(1)-Al(1)-Ow(6)	90.5(4)
Al(1)-Ow(2)	1.878(9)	Ow(2)-Ow(3)	2.64(1)	Ow(2)-Al(1)-Ow(3)	88.9(4)
Al(1)-Ow(3)	1.885(9)	Ow(2)-Ow(5)	2.64(1)	Ow(2)-Al(1)-Ow(5)	89.1(4)
Al(1)-Ow(4)	1.889(9)	Ow(2)-Ow(6)	2.68(1)	Ow(2)-Al(1)-Ow(6)	90.6(4)
Al(1)-Ow(5)	1.891(9)	Ow(3)-Ow(4)	2.65(1)	Ow(3)-Al(1)-Ow(4)	89.2(4)
Al(1)-Ow(6)	1.896(9)	Ow(3)-Ow(5)	2.61(1)	Ow(3)-Al(1)-Ow(5)	87.6(4)
		Ow(3)-Ow(6)	2.67(1)	Ow(3)-Al(1)-Ow(6)	89.7(4)
		Ow(4)-Ow(5)	2.69(1)	Ow(4)-Al(1)-Ow(5)	90.8(4)
		Ow(4)-Ow(6)	2.66(1)	Ow(4)-Al(1)-Ow(6)	89.4(4)
MEAN	1.885Å	MEAN	2.67Å	MEAN	90.0°
		Ow(7)-Ow(8)	2.69(1)Å	Ow(7)-Al(2)-Ow(8)	91.5(4)°
		Ow(7)-Ow(9)	2.68(1)	Ow(7)-Al(2)-Ow(9)	90.6(4)
		Ow(7)-Ow(10)	2.66(1)	Ow(7)-Al(2)-Ow(10)	89.9(4)
Al(2)-Ow(7)	1.877(9)Å	Ow(7)-Ow(11)	2.70(1)	Ow(7)-Al(2)-Ow(11)	91.3(4)
Al(2)-Ow(8)	1.878(9)	Ow(8)-Ow(9)	2.67(1)	Ow(8)-Al(2)-Ow(9)	90.2(4)
Al(2)-Ow(9)	1.888(9)	Ow(8)-Ow(11)	2.68(1)	Ow(8)-Al(2)-Ow(11)	90.5(4)
Al(2)-Ow(10)	1.895(9)	Ow(8)-Ow(12)	2.65(1)	Ow(8)-Al(2)-Ow(12)	89.0(4)
Al(2)-Ow(11)	1.896(9)	Ow(9)-Ow(10)	2.65(1)	Ow(9)-Al(2)-Ow(10)	89.1(4)
Al(2)-Ow(12)	1.908(8)	Ow(9)-Ow(12)	2.70(1)	Ow(9)-Al(2)-Ow(12)	90.6(4)
		Ow(10)-Ow(11)	2.68(1)	Ow(10)-Al(2)-Ow(11)	90.1(4)
		Ow(10)-Ow(12)	2.68(1)	Ow(10)-Al(2)-Ow(12)	89.7(4)
		Ow(11)-Ow(12)	2.63(1)	Ow(11)-Al(2)-Ow(12)	87.5(4)
MEAN	1.890Å	MEAN	2.67Å	MEAN	90.0°

to a solution. Now that we have elucidated the structure of a heptadeca-hydrate, have we shed any light in this regard? The answer is a qualified yes. The nucleation of alunogen crystallites was probably initiated when the solution became oversaturated with respect to the composition— $\text{Al}_2(\text{SO}_4)_3(\text{H}_2\text{O})_{12} \cdot 1.5\text{H}_2\text{O}$ —because  $1.5\text{H}_2\text{O}$  is the minimum amount of zeolitic water required to build up the alunogen structure (if

0.3 occupancy in each zeolitic site is taken to be the minimum). As crystallization progressed, the up-take of zeolitic water was increased, varying from the initial  $1.5\text{H}_2\text{O}$  to  $5\text{H}_2\text{O}$ , when all zeolitic-water sites were filled. The most outstanding feature of the  $\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  system, when compared with the analogous  $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  system, is the fact that a multiplicity of phases occurs in the latter (at least

TABLE 4. Probable Hydrogen Bonds in Alunogen

Donor	Acceptor	Distance(Å)	Angle(ADA)
Ow(1)	→ 0(11)	2.644	112.3°
	→ Zw(3)	2.574	
Ow(2)	→ 0(1)	2.660	93.3
	→ 0(11)	2.586	
Ow(3)	→ 0(2)	2.637	102.0
	→ 0(4)	2.662	
Ow(4)	→ 0(2)	2.679	120.4
	→ 0(3)	2.621	
Ow(5)	→ 0(1)	2.689	108.2
	→ Zw(2)	2.625	
Ow(6)	→ 0(3)	2.637	119.2
	→ 0(4)	2.666	
Ow(7)	→ 0(10)	2.651	107.0
	→ Zw(4)	2.562	
Ow(8)	→ 0(6)	2.732	118.2
	→ 0(9)	2.592	
Ow(9)	→ 0(7)	2.688	106.7
	→ 0(8)	2.679	
Ow(10)	→ 0(5)	2.665	115.0
	→ 0(7)	2.694	
Ow(11)	→ 0(6)	2.663	104.7
	→ Zw(1)	2.630	
Ow(12)	→ 0(5)	2.639	104.7
	→ 0(8)	2.665	
Zw(1)	→ 0(12)	2.771	122.5
	→ Zw(4)	2.987	
Zw(2)	→ 0(10)	2.831	97.3
	→ 0(12)	2.765	
Zw(3)	→ 0(9)	2.832	127.3
	→ Zw(2)	2.880	
Zw(4)	→ Zw(1)	2.987	125.1
	→ Zw(5)	2.983	
Zw(5)	→ 0(12)	2.719	113.1
	→ Zw(4)	2.983	

TABLE 5. Summation of H Bonds in Alunogen

	D	A	S	D	A	S
Ow(1)	2	-	2	0(1)	-	2
Ow(2)	2	-	2	0(2)	-	2
Ow(3)	2	-	2	0(3)	-	2
Ow(4)	2	-	2	0(4)	-	2
Ow(5)	2	-	2			
Ow(6)	2	-	2	0(5)	-	2
				0(6)	-	2
Ow(7)	2	-	2	0(7)	-	2
Ow(8)	2	-	2	0(8)	-	2
Ow(9)	2	-	2			
Ow(10)	2	-	2	0(9)	-	2
Ow(11)	2	-	2	0(10)	-	2
Ow(12)	2	-	2	0(11)	-	2
				0(12)	-	3
Zw(1)	2	2	4			
Zw(2)	2	2	4		25	25
Zw(3)	2	2	4		34	43
Zw(4)	2	2	4			
Zw(5)	2	1	3		34	68
	34	9	43			

carries the same charge. The smaller the ion, the stronger its polarization power and, in the presence of a polar aqueous solution, the aluminum ion has a much stronger tendency than the ferric ion to be enveloped by water, forming  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  groups. This phenomena precludes the possibility of aluminum bonding directly with sulfate oxygens, and the resultant crystalline solid is a completely isolated polyhedra of  $\text{SO}_4$  and  $\text{Al}(\text{H}_2\text{O})_6$ , linked only by H bonds to yield coherence. This may serve to explain the fact that the highest  $n$  in the  $\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  system is 17, whereas in the  $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  system it is only 11 (Thomas, Robinson, and Fang, 1974), with no insular polyhedra.

From these observations and inferences we feel that further structural studies of other crystalline hydrates are of significance if we are to bring progress and new vista to the study of minerals.

five), and yet there is *only* one aluminum sulfate hydrate. This is especially puzzling when a limited Al→Fe substitution is found in coquimbite (Fang and Robinson, 1970). An apparent answer would be the non-availability of  $\text{Fe}^{3+}$  during the mineralization of alunogen, but then, why have no lower hydrates of aluminum sulfate been found? We propose that the reason may be found in the different ionic sizes of the two otherwise similar ions. The aluminum ion is nearly 30 percent smaller than the ferric ion, yet it

TABLE 6. Electrostatic Bond Strengths and Their Sums about the Anions in Alunogen\*

Anion/Cation	Al	S	H(a)	H(d)	$p_o$
0(1 to 11)		1.5	2 x 1/6		1.83 v.u.
0(12)		1.5	3 x 1/6		2.00
Ow(1 to 12)	0.5			2 x 5/6	2.17
Zw(1 to 4)			2 x 1/6	2 x 5/6	2.00
Zw(5)			1 x 1/6	2 x 5/6	1.83

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