

## The crystal structure of synthetic chukhrovite, $\text{Ca}_4\text{AlSi}(\text{SO}_4)\text{F}_{13} \cdot 12\text{H}_2\text{O}$

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### Abstract

Synthetic chukhrovite,  $\text{Ca}_4\text{AlSi}(\text{SO}_4)\text{F}_{13} \cdot 12\text{H}_2\text{O}$  crystallizes in the cubic space group  $Fd\bar{3}$ , with  $a = 16.710(2)\text{\AA}$  and  $Z = 8$ . The structure was refined to  $R_w = 0.028$  and  $R = 0.025$ , using 481 nonzero reflections.

Al and Si are statistically distributed at the same site, M [16(d)], which is surrounded by six fluorine atoms to form the octahedral group  $\text{MF}_6$ . The remaining fluoride ion is surrounded by a tetrahedron of Ca ions [ $\text{F}(1)\text{-Ca} = 2.411\text{\AA}$ ] as in fluorite. The overall coordination of Ca is seven with a geometry corresponding to that of a monocapped octahedron. Each corner of the  $\text{MF}_6$  octahedron is linked to a Ca coordination polyhedron and each Ca polyhedron shares three corners with three different  $\text{MF}_6$  octahedra. The  $\text{SO}_4$  ion is surrounded by 12 water molecules, all of which are hydrogen-bonded to  $\text{SO}_4$  oxygens. The most unusual feature of this hydration is that all four faces of the  $\text{SO}_4$  ion are linked to faces of Ca polyhedra *via* hydrogen bonding.

### Introduction

The mineral chukhrovite occurs in the secondary oxidation zone of the Kara-Oba molybdenum-tungsten deposit in central Kazakhstan. These crystals have been described as face-centered cubic with  $a = 16.80\text{\AA}$ , crystal class  $T_h = m\bar{3}$ , and with typical octahedral habit (Ermilova *et al.*, 1960). The chemical composition was given as:  $\text{Ca}_3\text{Al}_2(\text{Y,RE})\text{SO}_4\text{F}_{13} \cdot 10\text{H}_2\text{O}$ , where RE may be a mixture of rare-earth elements.

Crystals of similar composition and X-ray diffraction pattern to that of the mineral chukhrovite often occur in the filter cake during the manufacture of phosphoric acid. Lehr *et al.* (1966) and Coates and Woodard (1966) have published detailed descriptions of this mineral. Coates and Woodard suggested that these octahedral crystals are isomorphous with chukhrovite. They reported a cell parameter of  $16.75(5)\text{\AA}$ , space group  $Fd\bar{3}$ , and gave the chemical composition as:  $\text{Ca}_{4.03}\text{Ba}_{0.04}(\text{Y,La})_{0.09}\text{Al}_{1.31}\text{Si}_{0.75}(\text{SO}_4)_{1.00}\text{F}_{13.0} \cdot 10\text{H}_2\text{O}$ . Meredith (1965), in his studies

of the reaction of hydrochloric acid with phosphate rock, reported a residual crystalline material with the formula  $\text{CaSO}_4 \cdot 1.5\text{CaSiF}_6 \cdot \text{AlF}_3 \cdot \text{CaF}_2 \cdot 12\text{H}_2\text{O}$ . The X-ray diffraction pattern and the differential thermal and thermogravimetric analysis reported by Meredith show that this material is similar to our synthetic chukhrovite. Hájek and Benda (1972) reported a synthetic material with the chemical composition  $\text{Ca}_{12}\text{Al}_2\text{Si}_4(\text{SO}_4)_3\text{F}_{40} \cdot 45\text{H}_2\text{O}$  which corresponds to  $\text{Ca}_4\text{Al}_{0.67}\text{Si}_{1.33}(\text{SO}_4)\text{F}_{13.3} \cdot 15\text{H}_2\text{O}$ . Again, these are octahedral crystals with cubic symmetry and on the basis of the X-ray diffraction pattern appear to be quite similar to our synthetic chukhrovite.

### Experimental

Our crystals of synthetic chukhrovite were prepared as part of a factorial-designed experiment to study the effect of F, Al, and Si on the precipitation of chukhrovite (Frazier *et al.*, 1977). In one of these trials exceptionally large octahedral crystals of chukhrovite were obtained (up to  $200\ \mu\text{m}$  along  $a$ ) by

precipitation from a solution containing 30.0% P<sub>2</sub>O<sub>5</sub>, 3.00% CaO, 1.0% Al<sub>2</sub>O<sub>3</sub>, 1.0% SiO<sub>2</sub>, and 3.8% F, with an excess of solid CaSO<sub>4</sub> · 2H<sub>2</sub>O. The solution was equilibrated for 3 days at 35°C. Traces of gypsum were removed by washing the precipitate with 10% HCl, but a secondary CaF<sub>2</sub> phase was present coating most of the coarse crystals and could not be removed by acid washings. Chemical analyses were therefore carried out on the decanted small crystals which did not have the CaF<sub>2</sub> coating, with the following results (theoretical for Ca<sub>4</sub>AlSiSO<sub>4</sub>F<sub>13</sub> · 12H<sub>2</sub>O in parentheses): Ca, 20.7% (20.7); Al, 3.64% (3.48); Si, 3.69% (3.63); S, 3.37% (4.14); F, 31.4% (31.89).

An X-ray powder diffraction pattern of this synthetic material was recorded on a Philips diffractometer using CuKα (λ = 1.54178Å) radiation (Table 1). This diffraction pattern deviates to some degree from that reported by Ermilova *et al.* for the mineral chukhrovite. Apparently substitution of the rare-earth elements for Al and Si in the structure tends to decrease the unit-cell parameters and shifts the *d* spacings in the powder diffractogram to lower values.

Table 1. Powder diffractogram of synthetic chukhrovite

<i>d</i> <sub>o</sub>	<i>d</i> <sub>c</sub>	hkl	I/I <sub>o</sub>
9.63	9.6458	111	100
5.902	5.9068	220	38
5.036	5.0373	311	16
4.817	4.8229	222	1
4.175	4.1767	400	12
3.834	3.8328	331	7
3.408	3.4103	422	6
3.217	3.2153	333, 511	20
2.955	2.9534	440	3
2.823	2.8240	531	8
2.782	2.7845	442	1
2.642	2.6416	620	7
2.550	2.5478	533	22
2.410	2.4114	444	2
2.340	2.3394	551	4
2.235	2.2326	642	15
2.176	2.1751	553	23
2.0886	2.0884	800	1
2.0264	2.0260	644	2
1.9697	1.9689	660, 822	4
1.9303	1.9292	555, 751	10
1.8680	1.8679	840	1
1.8327	1.8338	753, 911	1
1.8224	1.8229	842	11
1.7809	1.7810	664	3
1.7545	1.7514	931	2
1.7068	1.7051	844	2
1.6799	1.6791	771, 755, 933	3
1.6377	1.6383	862, 1020	2
1.6089	1.6076	666	2
1.5580	1.5579	953	2
1.5063	1.5064	775	5
1.4767	1.4767	880	1
1.4566	1.4542	882, 1044	2
1.4139	1.4171	973	2
	1.4120	1062	
1.3550	1.3551	1064	1

However, the very strong low-angle reflections 111, 220, and 311 are missing in the powder diffraction pattern reported by Ermilova *et al.* (1960). These discrepancies are believed to be due to the limitation of the photographic camera technique they used.

Precession photographs showed *m*3 diffraction symmetry and the systematic absences indicated the space group *Fd*3 (*hkl* reflections present only when *h* + *k*, *k* + *l*, and *l* + *h* = 2*n* and *Ok**l* reflections present only when *k* + *l* = 4*n*).

An approximately equant octahedral crystal with a mean diagonal of 0.20 mm was used for the measurement of cell constants and intensity data. All measurements were made on a four-circle automatic diffractometer with graphite monochromatized MoKα radiation (λ = 0.70932Å). The diffractometer-controlling programs were those of Lenhart (1975). The cell parameter was obtained by a least-squares fit of the 2θ values of 15 reflections with 39 < 2θ < 45° by automatically centering at both positive and negative 2θ values. Crystal data: *a* = 16.710(2)Å, *V* = 4665.8Å<sup>3</sup>, *Z* = 8, *D* (calc.) = 2.205 g cm<sup>-3</sup>, *D* (meas.) = 2.20 g cm<sup>-3</sup>.

All reflections in the octant with *h* ≥ 0, *k* ≥ 0 and *l* ≥ 0 were measured up to 2θ ≤ 60°, using the θ-2θ scan technique with a scan rate of 0.5° min<sup>-1</sup>. The backgrounds were counted for 40 sec at each end of the scan range. Three reference reflections, monitored periodically during the data collection, did not show significant variation in intensities. The intensities were corrected for Lorentz and polarization effects and for absorption using the program XRAY76 (Stewart *et al.*, 1976). μ(MoKα) was taken to be 12.4 cm<sup>-1</sup>. The maximum and minimum absorption corrections were 1.18 and 1.15 respectively. Equivalent reflections were merged into a set of 575 unique reflections, of which 481, having *F*<sub>o</sub> ≥ 3σ(*F*<sub>o</sub>), were used in the structure analysis and refinements. Symmetrically equivalent reflections agreed within 2% on average.

### Structure solution and refinement

The structure was solved from consideration of the packing and symmetry. Since *Z* = 8, all heavy atoms, Ca, S, Al, and Si, must be in special positions. The origin was chosen to be at the center (3). There are only two 8-fold special positions, [8(a) or 8(b)], one of which could be occupied by the S atom of the SO<sub>4</sub> group, and the other by a fluoride ion. Al and Si atoms would have to occupy one or both of the 16-fold positions [16(c) and 16(d)]. The S atom was assigned the site 8(a), but no assignment was made for

Table 2. Final atomic parameters for chukhrovite. The thermal parameters are of the form  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$  and are multiplied by  $10^4$ . Estimated standard deviations given in parentheses are in the least significant digits. Values without estimates of standard deviations are fixed by symmetry

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ca	.29171 (2)	x	x	217 (2)	$U_{11}$	$U_{11}$	-27 (1)	$U_{12}$	$U_{12}$
M*	.5000	x	x	139 (2)	$U_{11}$	$U_{11}$	-17 (2)	$U_{12}$	$U_{12}$
S	.1250	x	x	172 (3)	$U_{11}$	$U_{11}$	0	0	0
O	.07396 (7)	x	x	233 (4)	$U_{11}$	$U_{11}$	-29 (4)	$U_{12}$	$U_{12}$
F (1)	.3750	x	x	168 (6)	$U_{11}$	$U_{11}$	0	0	0
F (2)	.22049 (6)	.33649 (6)	.45070 (6)	252 (5)	181 (5)	361 (6)	-5 (4)	11 (4)	72 (4)
O (w)	.15481 (8)	.24744 (10)	.30479 (8)	286 (7)	530 (9)	237 (7)	-141 (6)	12 (5)	-39 (6)
H (1)	.126 (1)	.222 (1)	.271 (1)	3.5 (5) <sup>†</sup>					
H (2)	.135 (1)	.231 (2)	.345 (2)	5.5 (7)					

\*M represents the site containing 50% Al and 50% Si.

<sup>†</sup>For hydrogen atoms isotropic thermal parameters ( $\text{\AA}^2$ ) were used.

the fluoride ion. Once the S atom is assigned the site 8(a), it was clear that Al or Si cannot occupy the site 16(c) because of unusually short atomic contacts. Thus the site 16(d) was assigned to Al and Si, statistically disordered with half occupancy of each. The approximate position of Ca along the body diagonal [special position, 32(e)] was calculated on the basis of packing.

A Fourier synthesis based on the positions of Ca, Al, Si, and S clearly indicated the positions of the remaining non-hydrogen atoms. The presence of an atom (possibly F, OH, or H<sub>2</sub>O) at the special position 8(b) was confirmed in subsequent electron density maps. On the basis of the chemical formula, electro-neutrality, and the type of bonding to four Ca ions, this atom was assigned as a F<sup>-</sup> ion.

All refinements were made by full-matrix least-squares program, RFIN4 (Finger and Prince, 1975). The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w^{-1} = \sigma(F_o)^2 + (0.02F_o)^2$  and  $\sigma(F_o)$  is derived from counting statistics. Corrections for anomalous dispersion were included. The values of  $f'$  and  $f''$  and the scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974).

The structure was refined to  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  of 0.076 using individual isotropic thermal parameters and to 0.058 with anisotropic thermal parameters. The occupancies of Al and Si at site 16(d) were kept at 50% each throughout all calculations. The positions of hydrogen atoms were obtained from a difference Fourier map and their parameters (isotropic) were also refined in subsequent calculations.

In the final cycle of refinement  $R$  was 0.025 and the weighted  $R$  factor  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  was 0.028 for the 481 reflections used in

the refinement. The corresponding values were 0.029 and 0.032 for all reflections. The standard deviation in an observation of unit weight was 0.92 and the maximum shift/error was 0.01. The final difference Fourier map was essentially featureless. Final atomic parameters are listed in Table 2 and the observed and calculated structure amplitudes in Table 3.<sup>1</sup>

### Description of the structure

The structure can be described in terms of a compact assembly of polyhedra consisting of MF<sub>6</sub> octahedra (M = statistically disordered Al and Si), tetrahedral F(Ca)<sub>4</sub> ions and hydrated SO<sub>4</sub> ions (Fig. 1). There is only one independent fluoride ion, F(1), and it is surrounded by the tetrahedron of Ca ions. Selected bond lengths and angles are listed in Table 4.

#### The (Al,Si)F<sub>6</sub> octahedron

Al and Si atoms are bonded to six fluorine atoms forming a nearly regular octahedron. However, Al and Si are statistically distributed at the same set of sites, 16(d), (represented by M) forming an octahedron MF<sub>6</sub>. The M-F(2) bond length of 1.735(1) $\text{\AA}$  is clearly intermediate between those in pure SiF<sub>6</sub> and pure AlF<sub>6</sub> octahedra, as expected, on the basis of an average structure. For example: the Si-F bond length is 1.692(8) $\text{\AA}$  in FeSiF<sub>6</sub> · 6H<sub>2</sub>O (Hamilton, 1962) and the Al-F distance is 1.800(3) $\text{\AA}$  in LiCaAlF<sub>6</sub> (Viebahn, 1971).

All corners of the MF<sub>6</sub> octahedron are linked to different calcium coordination polyhedra (Fig. 2).

<sup>1</sup> To obtain a copy of Table 3, order Document AM-81-149 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, NW, Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

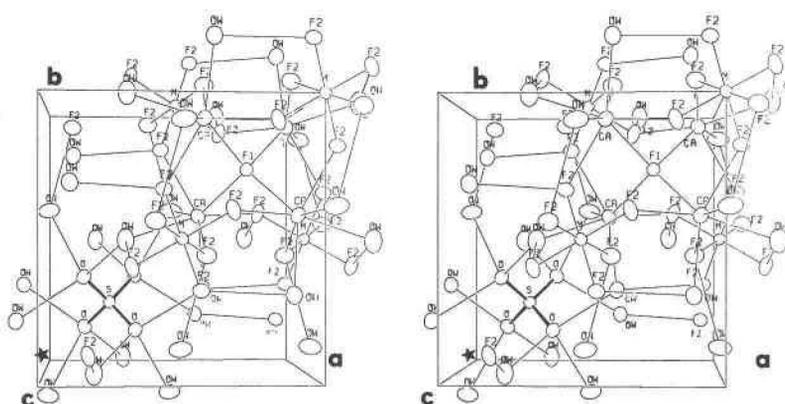


Fig. 1. Stereoscopic illustration of the unit cell in chukhrovite. Only 1/8 of the cell ( $\frac{1}{2}$  along  $a$ ,  $b$ , and  $c$  axes) is shown. The origin is marked by a star (\*).

However, a secondary Ca–F(2) contact of 3.00 Å from an adjacent F atom of the  $\text{MF}_6$  octahedron, if taken into account, would make this an edge-sharing linkage. In addition, there are also hydrogen bonds of the type  $\text{O}(\text{w})\text{--H} \cdots \text{F}(2)$  between  $\text{MF}_6$  octahedra and Ca coordination polyhedra, making a very compact assembly.

#### The Ca polyhedron

The primary coordination of Ca ion involves seven atoms, three water molecules,  $\text{O}(\text{w})$ , three fluorine atoms, F(2), from three different  $\text{MF}_6$  octahedra, and the fluoride ion, F(1), with Ca–O or Ca–F distances in the range of 2.361–2.414 Å (Table 4). Three other Ca–F(2) contacts, 3.00 Å, are from adjacent fluorine atoms of the  $\text{MF}_6$  octahedra and do not appear to be involved in any significant bonding. The geometry of the seven coordination around Ca ion can be de-

scribed as a monocapped octahedron with F(1) at the capped position. The  $\text{CaO}_3\text{F}_3$  octahedron is distorted mainly by a spreading apart of the three F(2) atoms defining the capped face. The angles F(2)–Ca–F(2') and F(1)–Ca–F(2) are increased to 114.5 and 76.3° from the ideal values of 90° and 54.7° respectively. These large distortions may also be due to the proximity of the three bulky  $\text{MF}_6$  groups linked to each Ca. One face of the Ca coordination polyhedron (involving the three water molecules) is linked to a face of the  $\text{SO}_4$  ion through hydrogen bonding.

#### The F(Ca)<sub>4</sub> tetrahedron

F(1) ion at the special position 8(b) is coordinated to four Ca ions arranged as a tetrahedron (Figs. 1 and 3). The F(1)–Ca bond length is 2.411 Å. The arrangement is similar to that in fluorite,  $\text{CaF}_2$ , where F–Ca distance is 2.36 Å. Each triangular face of the

Table 4. Bond distances (Å) and angles (°) in chukhrovite

Ca – F(1)	2.411(1)	F(1) – Ca – F(2) <sup>ii</sup>	76.25(3)	O(w) – Ca – F(2) <sup>iii</sup>	79.54(4)
Ca – F(2) <sup>ii</sup>	x 3 2.361(1)	O(w) – Ca – O(w) <sup>i</sup>	79.81(5)	F(2) <sup>ii</sup> – Ca – F(2) <sup>iii</sup>	114.54(4)
Ca – O(w)	x 3 2.414(1)	O(w) – Ca – F(2) <sup>ii</sup>	77.39(4)		
M – F(2) <sup>iv</sup>	x 6 1.735(1)	F(2) <sup>iv</sup> – M – F(2) <sup>v</sup>	88.63(5)	F(2) <sup>iv</sup> – M – F(2) <sup>vi</sup>	91.37(5)
S – O	x 4 1.477(1)	O – S – O	109.47(6)		
Hydrogen bonds					
O(w) – H(1)	0.86(2)	O(w) ... O <sup>vii</sup>	2.807(2)	O(w) – H(2) ... F(2) <sup>viii</sup>	142(3)
O(w) – H(2)	0.80(3)	O(w) ... F(2) <sup>viii</sup>	2.881(2)	Ca – O(w) ... O <sup>vii</sup>	121.13(6)
H(1) ... O <sup>vii</sup>	1.97(2)	H(1) – O(w) – H(2)	99(2)	Ca – O(w) ... F(2) <sup>viii</sup>	97.03(6)
H(2) ... F(2) <sup>viii</sup>	2.21(3)	O(w) – H(1) ... O <sup>vii</sup>	167(2)	O <sup>vii</sup> – O(w) ... F(2) <sup>viii</sup>	130.23(6)

Estimated standard deviations in parentheses refer to the least significant digits. The equivalent positions are designated as superscripts and are (i)  $z, x, y$ ; (ii)  $x, 3/4-y, 3/4-z$ ; (iii)  $3/4-z, x, 3/4-y$ ; (iv)  $3/4-x, 3/4-y, z$ ; (v)  $z, 3/4-x, 3/4-y$ ; (vi)  $1/4+x, 1/4+y, 1-z$ ; (vii)  $x, 1/4-y, 1/4-z$ ; (viii)  $1/2-y, z-1/4, 1/4+x$ .

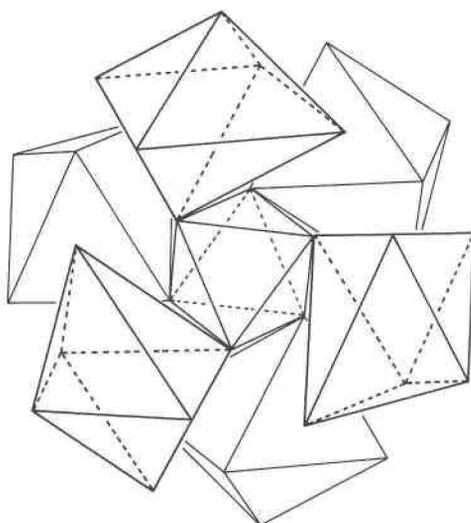


Fig. 2. Corner-sharing linkage of  $MF_6$  octahedra and calcium tetrahedra. F(1) at the capped position is omitted for clarity.

“Ca tetrahedron” is in contact with an  $MF_6$  octahedron (Fig. 3). The environment of F(1) consists of 4 Ca ions in the primary coordination sphere with 12 fluorine atoms in the secondary sphere [F(1)  $\cdots$  F(2) = 2.946Å.

On the basis of the geometry and the strong bonding involving F(1) ions, it is very unlikely that this site will be less than fully occupied. In our synthetic chukhrovite, the amount of  $F^-$  ion is stoichiometric and the Al/Si ratio is 1.0. This would appear to be the most stable composition. Any variation in Al/Si ratio would be restricted by the F(1) content unless other modes of substitutions are invoked. For example, materials with Al/Si ratio greater than 1.0 would imply partial occupancy of the F(1) site if we

Table 5. Comparison of hydrogen bonds in  $SO_4$  ion hydration

Compound	No. of water molecules around $SO_4$ ion	$O \cdots O(w)$ Distances (Å)	
		Range	Mean
$FeSO_4 \cdot 7H_2O^a$	11	2.733–2.950	2.824
$MgSO_4 \cdot 6H_2O^b$	11	2.707–2.934	2.793
$MgSO_4 \cdot 7H_2O^c$	10	2.697–2.978	2.789
Chukhrovite <sup>d</sup>	12	2.807	2.807

<sup>a</sup>Baur (1964a); <sup>b</sup>Zalkin et al. (1964); <sup>c</sup>Baur (1964b); <sup>d</sup>this work.

assume that Al is exclusively at the site 16(d), but substitution of Ca sites by Al is also possible. Materials with an Al/Si ratio less than 1.0 could possibly be accompanied by partial substitution of  $F^-$  by  $O^{2-}$  ions, since no other site is available to accommodate the possible excess of  $F^-$  ions.

#### The $SO_4$ tetrahedron and hydrogen bonds

The  $SO_4$  group has symmetry 23 and therefore all the S–O distances and O–S–O angles are the same. The S–O bond length, 1.477Å, is in excellent agreement with the mean value 1.473Å calculated for several hydrates (Baur, 1964a).

There are only two hydrogen atoms in the asymmetric unit and both are involved in hydrogen bonds (Table 4). Each water molecule is hydrogen bonded to an oxygen atom of the  $SO_4$  ion and to a fluorine atom of the  $MF_6$  octahedron.

Each oxygen atom of the  $SO_4$  ion is the acceptor in three hydrogen bonds from three different water molecules. The  $O(w) \cdots O(SO_4)$  distance, 2.807Å, is in good agreement with the mean value in other hydrated sulphates (Table 5). The environment of the  $SO_4$  ion consists of 12 water molecules arranged approximately at the vertices of an icosahedron (Fig. 4).

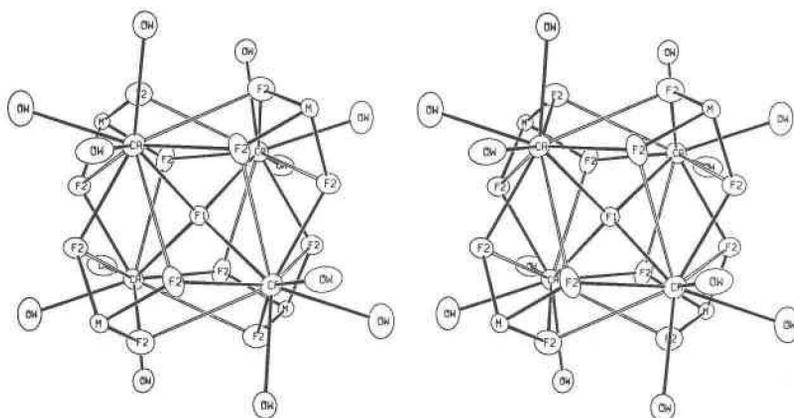


Fig. 3. The environment of F(1) ion consisting of the tetrahedron of Ca ions and the 12 fluorine atoms from 4  $MF_6$  octahedra. Bonds shown by double lines represent the longer Ca–F(2) contacts of 3.00Å.

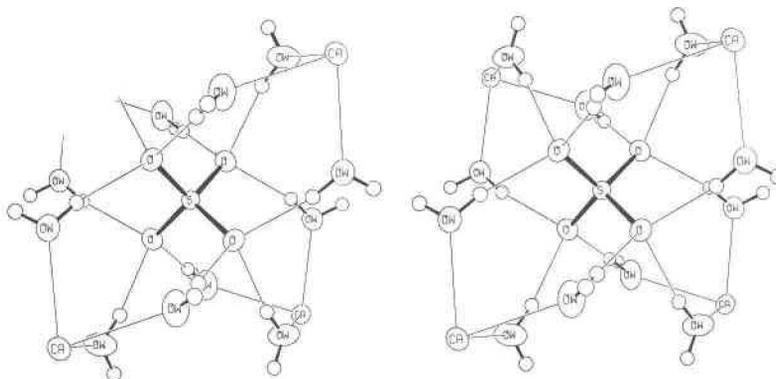


Fig. 4. The configuration of the water molecules around the  $\text{SO}_4$  ion showing the face-sharing of  $\text{SO}_4$  with Ca polyhedra.

Although complete hydration of the  $\text{SO}_4$  ion has been observed in several hydrates (Table 5), this appears to be the first example of hydration number 12 observed for the  $\text{SO}_4$  ion in the crystalline state. Another unusual feature of the structure is that all four faces of the  $\text{SO}_4$  ion are linked to faces of four different calcium polyhedra *via* hydrogen bonds (Fig. 4). Hydration number 12 and different types of face sharing (2, 3, or all 4 faces) involving the isoelectronic  $\text{PO}_4$  ions are known in several magnesium phosphates (Schroeder *et al.*, 1978; Mathew *et al.*, 1980).

In summary, the chukhrovite structure consists of an assemblage of  $\text{F}(\text{Ca})_4$  units, statistically disordered  $\text{AlF}_6$  and  $\text{SiF}_6$  octahedra, and completely hydrated  $\text{SO}_4$  ions,  $\text{SO}_4 \cdot 12\text{H}_2\text{O}$ .

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