taux d'occupation par Tl^+ et par H_3O^+ ce qui donne le même pouvoir de diffusant que 0,6 Tl^+). Cette dernière hypothèse est en accord avec la présence de H_3O^+ dans les sites monovalents observés dans les orthophosphates acides de fer, $Fe_3(H_3O)H_{14}(PO_4)_8.4H_2O$ (d'Yvoire, 1962), et d'aluminium, $Al_3(H_3O)H_{14}(PO_4)_8.-4H_2O$ (Brodalla & Kniep, 1980).

Les positions atomiques dans cette dernière structure (monoclinique $C2/c$) ont été entièrement déterminées, y compris celles des atomes d'hydrogène. L'isotypie de $Tl_3\{Tl_{0,5}(H_3O)_{0,5}\}H_{14}(PO_4)_8.4H_2O$ avec $Al_3(H_3O)H_{14}-(PO_4)_8.4H_2O$ est particulièrement frappante, si on décrit la structure du sel de thallium dans le repère monoclinique par la transformation:

$$\mathbf{a}_{mono} = -(\mathbf{a}_{tri} + \mathbf{b}_{tri}), \ \mathbf{b}_{mono} = \mathbf{a}_{tri}, \ \mathbf{c}_{mono} = \mathbf{c}_{tri}.$$

Cette étude montre qu'à côté des orthophosphates de thallium monovalents et trivalents, déjà connus, il existe aussi des orthophosphates de thallium à valence mixte.

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Structure of Dodecacalcium Potassium Fluoride Dioxide Tetrasilicate Bis(sulphate), KF.2[Ca6(SO4)(SiO4)2O]: a Fluorine-Containing Phase Encountered in Cement Clinker Production Process

BY JOSE FAYOS, FREDERIK P. GLASSER, R. ALAN HOWIE, ERIC LACHOWSKI AND MERCEDES PEREZ-MENDEZ

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland

Abstract. $M_r = 1131 \cdot 5$, trigonal, $R\bar{3}m$, $a_H = 7 \cdot 197$ (5), $c_H = 41 \cdot 224$ (28) Å, $V = 1894 \cdot 3$ Å³, $Z = 3$, $D_m = 2 \cdot 92$, $D_x = 2 \cdot 975$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 3 \cdot 06$ mm⁻¹, $F(000) = 1692$, room temperature, final $R = 0 \cdot 046$ for 225 unique reflections; crystal selected from synthetic material. The crystal structure analysis confirms the chemical formula of the phase. The structure is related to that of tricalcium silicate (Ca_3SiO_5) and reveals the presence of rows containing oxide, sulphate, silicate and fluoride anions and six- (or twelve-) coordinate potassium, with seven-coordinate calcium on sites between the rows interconnecting them with Ca—O and Ca—F bonds.

Introduction. The title compound was described by Trivino Vazquez (1982) who isolated it from sedimentary coatings of Dopal kilns and designated it phase *H*. Since phase *H* was encountered in admixture with several other phases during its synthesis in the laboratory, there was some doubt as to its precise chemical composition and even as to its physical properties, *e.g.* density and X-ray powder diffraction pattern. Accordingly phase *H* has been prepared synthetically and an X-ray structure analysis carried out to characterize it more completely.

Experimental. Phase *H* was prepared by heating a stoichiometric mixture of $CaCO_3$, silica gel, K_2CO_3 and CaF_2 together with 6% (by weight) excess of KF and 6% excess of $CaSO_4$ at 1270 K for 1 h followed by crystallization of the melt at 1220 K for 48 h to yield crystals in the form of hexagonal plates suitable for further study. Electron microprobe analysis of the resulting crystals revealed the presence of Ca, K, S and Si in the ratio 1:0·09 (2):0·17 (1):0·32 (3) in agreement, within error, with the values 1:0·083:0·166: 0·333 calculated for the formula $KF.2(Ca_6Si_2SO_{13})$ as proposed for phase *H* by Trivino Vazquez (1982).

Measured density from Trivino Vazquez (1982); crystal flake 0·25 × 0·15 × 0·05 mm. Intensities collected on Nicolet *P*3 diffractometer, graphite monochromator, Mo $K\alpha$; unit cell from 14 reflections in range $19 \le 2\theta \le 23°$. No absorption correction. Data collected in range $0 \le 2\theta \le 40°$, $\omega/2\theta$ scan method; h,k,l in ranges $0 \le h,k \le 5$ and $-40 \le l \le 40$; standard reflections 0,0,15 and $20\bar{7}$ showed no significant variation. 364 reflections measured (for Laue group $\bar{3}$); 246 unique (for Laue group $\bar{3}m$); 21 unobserved $[I < 2\sigma(I)]$ not used in calculations. Partial solution of structure from *MULTAN*80 (Main *et al.*, 1980), completed by Fourier methods; block-diagonal least

squares minimized $\sum w(|F_o| - |F_c|)^2$, $w = [1 + \{(F_o - 110)/60\}^2]^{-1}$; in final stages of refinement O and F treated isotropically, all other atoms anisotropic. Final shifts in positional parameters essentially zero and av. $\Delta = 0.1\sigma$ with no feature in difference map exceeding $0.7 \, e^-$. Atomic scattering factors for neutral O, F, S and Si and K$^+$ and Ca^{2+} from *International Tables for X-ray Crystallography* (1974); programs used were *MULTAN*80 (Main *et al.*, 1980), the *NRC* Crystallographic Programs (Ahmed, Hall, Pippy & Huber, 1966), *STRUPLO*82 (Fischer, 1982) for the preparation of Figs. 1 and 2 and *POWD* (Howie & Taylor, 1978) to calculate the theoretical powder pattern.

Intensity data collection was initially confined to the unique reflections appropriate to the Laue group $\bar{3}$. The data showed excellent agreement between the intensities in the reflection pairs hkl and $kh\bar{l}$ consistent with Laue group $\bar{3}m$. The data were averaged on this basis. The space group of phase H must then be one of $R32$, $R3m$ or $R\bar{3}m$. $R\bar{3}m$ was adopted as suggested by the distribution of E values given by *MULTAN*80. This choice was confirmed by the successful outcome of the structure analysis.

The final atomic parameters are given in Table 1 and selected bond lengths and angles in Table 2.*

Discussion. The structure determination of phase H gives an indication of its chemical composition independently of chemical analysis or microprobe results. The distinction between SO$_4$ and SiO$_4$ is readily made on the basis of bond lengths alone (Table 2). There is also evidence confirming the identity of the atom at $00\frac{1}{2}$ as F rather than O. Least-squares refinement with all non-(O or F) atoms correctly identified and all atoms vibrating isotropically but with O at $00\frac{1}{2}$ gave a negative B_{iso} for the atom at this site and $R = 0.054$. Refinement with F at $00\frac{1}{2}$ gave satisfactory B's for all atoms and $R = 0.053$. The cell contents are then $3[KFCa_{12}(SO_4)_2(SiO_4)_4O_2]$, agreeing exactly with the formula given by Trivino Vazquez (1982).

The completed structure of phase H (Figs. 1 and 2) reveals SO$_4$, SiO$_4$ and O^{2-} anions in the $6(c)$ sites of $R\bar{3}m$ with site symmetry $3m$ and K and F in the $3(a)$ and $3(b)$ sites with site symmetry $\bar{3}m$. These components of the structure lie on the rows $00z$, $\frac{1}{3}\frac{2}{3}z$ and $\frac{2}{3}\frac{1}{3}z$ (threefold axes parallel to **c**) and fall in the order

$$\cdots K/Si(1)O_4/Si(2)O_4/SO_4/O/F \cdots$$
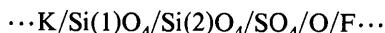
with centres of symmetry at K and F sites. Ca occupies two sets of $18(h)$ sites between the rows and inter-

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Table 1. *Fractional coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($\text{Å}^2 \times 10$) *for* $KF.2(Ca_6Si_2SO_{13})$

Values in parentheses are e.s.d.'s corresponding to the least significant digit.

	Wyckoff notation	x^*	z	B_{iso}
Ca(1)	18(h)	1593 (2)	3978.8 (2)	8.9†
Ca(2)	18(h)	1533 (2)	5324.4 (3)	8.0†
O(1)	18(h)	5564 (6)	−3548.2 (8)	14.7 (7)
O(11)	18(h)	1235 (6)	1946.0 (8)	13.3 (6)
O(21)	18(h)	1261 (5)	728.1 (8)	11.3 (6)
O(2)	6(c)	0	−3604 (1)	10 (1)
O(12)	6(c)	0	−2464 (1)	12 (1)
O(22)	6(c)	0	1233 (1)	8 (1)
O(3)	6(c)	0	4303 (1)	5 (1)
S(1)	6(c)	0	−3243.8 (5)	7.3†
Si(1)	6(c)	0	2064.4 (6)	7.1†
Si(2)	6(c)	0	832.3 (6)	7.8†
K(1)	3(a)	0	0	21.3†
F(1)	3(b)	0	5000	14 (1)

* All atomic coordinates are of the form $x \, \bar{x} \, z$. Only x and z are quoted.

† Equivalent B_{iso} calculated as
$$\tfrac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab/2).$$

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for* $KF.2(Ca_6Si_2SO_{13})$

Values in parentheses are e.s.d.'s applicable to the least significant digit of each entry.

K(1)–O(1^{vi})	2.919 (4) ×6			
O(21)	3.388 (3) ×6			
S(1)–O(1)	1.468 (4) ×3	O(1)–S(1)–O(1)	108.3 (2) ×3	
O(2)	1.484 (6)	O(1)–S(1)–O(2)	110.6 (2) ×3	
O(1)–O(1)	2.381 (5)			
O(2)	2.427 (6)			
Si(1)–O(11)	1.615 (4) ×3	O(11)–Si(1)–O(11)	111.3 (2) ×3	
O(12)	1.649 (6)	O(11)–Si(1)–O(12)	107.6 (2) ×3	
O(11)–O(11)	2.667 (5)			
O(12)	2.634 (6)			
Si(2)–O(21)	1.630 (4) ×3	O(21)–Si(2)–O(21)	113.3 (2) ×3	
O(22)	1.653 (6)	O(21)–Si(2)–O(22)	105.3 (2) ×3	
O(21)–O(21)	2.723 (5)			
O(22)	2.610 (6)			
Ca(1)–O(3)	2.394 (3)	Ca(2)–F	2.332 (1)	
O(2^i)	2.517 (4)	O(3^{ii})	2.452 (3)	
O(1^{ii})	2.601 (4) ×2	O(11)	2.587 (4)	
O(21^{iii})	2.367 (4) ×2	O(21^{iv})	2.620 (4)	
O(12^{iv})	2.357 (2)	O(22^v)	2.289 (2)	
		O(11^{iii})	2.351 (4) ×2	

Symmetry code: (i) $-x, x, -z$; (ii) $2x-1, x-1, -z$ and $1-x, 1-2x, -z$; (iii) $\frac{2}{3}-2x, \frac{1}{3}-x, \frac{1}{3}+z$ and $x-\frac{1}{3}, 2x-\frac{2}{3}, \frac{1}{3}+z$; (iv) $\frac{1}{3}+x, -x-\frac{1}{3}, \frac{2}{3}+z$; (v) $\frac{1}{3}-x, x-\frac{1}{3}, \frac{2}{3}-z$; (vi) as (iii) with $x-\frac{1}{3}, \frac{1}{3}-x, \frac{1}{3}+z$ and three more from $\bar{1}$ at K; otherwise O(1), O(11) and O(21) are replicated as $x, \bar{x}, z; x, 2x, z$ and $2\bar{x}, \bar{x}, z$.

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connects them with Ca–O and Ca–F bonds. K–O bonds also contribute to the interconnection between the rows and possibly to connections within the rows. Viewed in this way there are definite similarities between the structure of phase H and that determined for Ca$_3$SiO$_5$ by Jeffery (1952). In the rhombohedral structure of Ca$_3$SiO$_5$ the rows parallel

to **c** contain alternating sets of three O and three SiO$_4$ groups.

$$\cdots\text{O–O–O–SiO}_4\text{–SiO}_4\text{–SiO}_4\cdots.$$
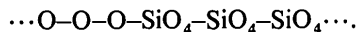
The rows of anions in Ca$_3$SiO$_5$ are again interconnected by Ca—O bonds to Ca in sites between them. Jeffery (1952) pointed out that within any one set of three SiO$_4$ groups one SiO$_4$ is rotated through 60° about the *c* axis relative to the other two. Exactly the same feature is observed in the structure of phase *H* where within any single group of 1 × SO$_4$ and 2 × SiO$_4$ the SO$_4$ is rotated 60° relative to the pair of eclipsed SiO$_4$ ions (viewed along **c**). The main differences between the structures of Ca$_3$SiO$_5$ and phase *H* are: (i) the presence of K in the rows of phase *H*; (ii) F in phase *H* replaces O(5)* in Ca$_3$SiO$_5$; (iii) SO$_4$ in phase *H* replaces Si(1)O$_4^*$ in Ca$_3$SiO$_5$ and (iv) the rows in phase *H* possess centres of symmetry.

The SO$_4$ and SiO$_4$ ions of phase *H* have bond distances and angles in the usual range (Table 2). Both
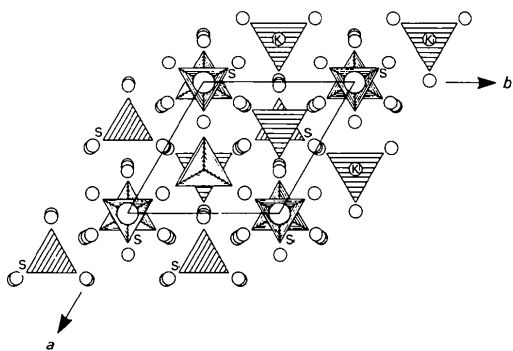
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* Atom numbering according to Jeffery (1952).

Fig. 1. Projection of one half of the unit cell of KF.2(Ca$_6$Si$_2$SO$_{13}$) ($z = 0$–$\frac{1}{2}$) on (001). SiO$_4$ and SO$_4$ (marked S) are shown as tetrahedra. F and Ca are shown as large and small circles. O is not visible in this representation.
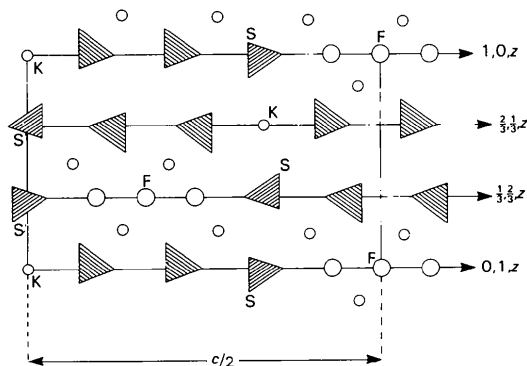

Fig. 2. Section of the structure of KF.2(Ca$_6$Si$_2$SO$_{13}$) close to (110). SiO$_4$ and SO$_4$ (marked S) are shown as tetrahedra. F (marked) and O and K (marked) and Ca lying on the plane of the section are shown as large and small circles respectively.

Ca atoms are seven-coordinate (Table 2) and the coordination is in each case that of a pentagonal bipyramid and includes an edge shared with a tetrahedral ion. Ca(1) is coordinated only to O with Ca—O in the range 2·357–2·601 Å; O(12^{iv}) and O(2^i) are the apical atoms. The other atoms lie close to a plane at right angles to the crystallographic mirror plane passing through Ca(1); the out-of-plane distances for the O atoms defining the plane (mean value) and for Ca(1) are 0·05 (6) and 0·28 (6) Å respectively. The two O(1^{ii}) define an edge of an SO$_4$ tetrahedron, which is thus bidentate with respect to completing the Ca coordination. Ca(2) is coordinated to O (Ca—O 2·289–2·620 Å) and to F (Ca—F 2·332 Å). The apical atoms are O(11^{iii}) (twice) and the pentagonal base of the pyramid lies in the crystallographic mirror plane passing through Ca(2). O(21^v) and O(22^v) define the edge of an SiO$_4$ tetrahedron. K has six nearest-neighbour O(1) at 2·919 Å (Table 2) distributed over the apices of a rather flattened trigonal anti-prism. The next-nearest atoms are six O(21) at 3·388 Å belonging to SiO$_4$ groups above and below K and in the same row parallel to **c**. This rather distorted coordination may account for the relatively high thermal vibration parameter for K.

The X-ray powder diffraction data observed for phase *H* by Trivino Vazquez (1982) are in good agreement with values calculated from the final parameters of the structure analysis.* No spacing is found on the calculated pattern to match those observed at 1·885, 1·797, 1·592, 1·505, 2·051 and 1·589 Å. However, each of the first four 'missing' spacings corresponds in position and intensity to the α$_2$ component of an adjacent reflection and the program *POWD* (Howie & Taylor, 1978) is designed to delete such lines from the calculated pattern. Only the last two weak spacings cannot be accounted for and presumably arise from impurity phases.

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* See deposition footnote.

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