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FOSHAGITE: COMPOSITION, UNIT CELL AND DEHYDRATION

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ABSTRACT

Foshagite is confirmed as a mineral species. A new analysis gives the composition $4\text{CaO} \cdot 3\text{SiO}_2 \cdot \text{H}_2\text{O}$; the ionic constitution is probably $\text{Ca}_4\text{Si}_3\text{O}_9(\text{OH})_2$, with infinite metasilicate chains similar to those in wollastonite. The unit cell has been determined from a combination of single-crystal electron diffraction and oriented fibre x-ray methods; it is A-centred monoclinic with a 10.32, b 7.36, c 14.07 Å, β 106.4°, $Z=4$. The crystals are markedly fibrous with length b , and principal cleavage (001). Reflections with k odd are weak and diffuse, and the pseudo-cell is primitive monoclinic with a 10.32, b 3.68, c 7.04 Å, β 106.4°. Foshagite is dehydrated at about 700°, when it undergoes oriented transformation to β -CaSiO₃ and β -Ca₂SiO₄. The relationship of orientations in this transformation has been determined. In conjunction with other evidence, it gives a preliminary indication of the crystal structure.

INTRODUCTION

Foshagite was discovered at Crestmore, California by Eakle (1925). He showed that it was a white, fibrous mineral of approximate composition $5\text{CaO} \cdot 3\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ and concluded from its optical properties that it was probably orthorhombic. Vigfusson (1931) concluded from optical and x-ray powder evidence that it was identical with hillebrandite, as did Berman (1937), but later x-ray powder work (Flint, McMurdie, and Wells, 1938; McMurdie and Flint, 1943; Heller and Taylor, 1956) showed that this was incorrect. Taylor (1952) obtained a fibre rotation pattern which indicated a 7.3 Å repeat distance along the fibre axis, with strong pseudo-halving. In this respect, foshagite resembles several other calcium silicate minerals such as xonotlite, hillebrandite, and tobermorite. Heller (1952) showed that dehydration caused ordered (or partly ordered) transformation to β -CaSiO₃ and β -Ca₂SiO₄. Flint, McMurdie, and Wells (1938) described the synthesis. Jander and Franke (1941) prepared a compound which they considered to be $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$, the powder data for which agreed with those of foshagite. Newman (1956) made a new analysis and determined the heat of solution. The unit cell has not previously been determined.

TABLE 1. CORRELATION OF THE X-RAY POWDER DATA OF HELLER AND TAYLOR (1956) WITH d -SPACINGS CALCULATED FOR THE MONOCLINIC PSEUDO-CELL, WITH k -INDICES DOUBLED. $\text{CuK}\alpha$ RADIATION. CAMERA DIAMETERS 6 CM. AND 19 CM.

X-ray powder data		Monoclinic pseudo-cell	
d -spacings (Å)	k -indices	hkl -indices	d -spacings (Å)
10.0 mw	0	100	9.90
6.8 ms	0	001	6.75
4.95 ms	0	200, 101	4.95, 4.96
3.56 w	0	201	3.55
3.37 ms	0	002, 30 $\bar{1}$	3.37, 3.36
3.25 m	0	202	3.23
2.92 vvs	2	121, 220	2.95
2.79 mw	0	302	2.78
2.68 vw	0	301	2.67
2.48 m	{0 2	202, 400 022, 32 $\bar{1}$, 320	2.48
2.33 vw	0	10 $\bar{3}$, 40 $\bar{2}$	2.33
2.30 ms	0	20 $\bar{3}$	2.30
2.25 vw	2	32 $\bar{2}$	2.22
2.16 ms	2	32 $\bar{1}$	2.17
2.12 w	2	42 $\bar{1}$	2.11
2.09 w	0	302	2.09
2.07 mw	2	222, 420	2.05
1.99 vw	0	500, 50 $\bar{2}$	1.98, 1.97
1.93 vw	2	22 $\bar{3}$, 023	1.95, 1.92
1.86 vvw	2	421, 32 $\bar{3}$	1.86
1.84 ms	4	040	1.84
1.82 vvw	2	322, 123, 52 $\bar{1}$	1.81, 1.80, 1.80
1.77 m	0	402, 501	1.77
1.74 vs/b	{0 2	20 $\bar{4}$, 50 $\bar{3}$, 10 $\bar{4}$ 520	1.75
1.72 vvw	{0 2	30 $\bar{4}$, 60 $\bar{1}$ 52 $\bar{2}$	1.74
1.66 vw	0	303, 600	1.71, 1.72
1.63 mw	2	223	1.65
1.59 m	2	422, 521, 22 $\bar{4}$	1.66
1.57 vw	0	104, 60 $\bar{3}$	1.59, 1.59, 1.58
1.55 vw	2	62 $\bar{1}$, 32 $\bar{4}$	1.59, 1.55
1.53 w	0	502	1.55
1.52 w	2	024, 62 $\bar{2}$	1.53
1.51 vw	2	323, 620	1.53
d -spacings (continued)			
1.47 mw		1.34 vw	1.154 w
1.46 w		1.32 w	1.127 vw
1.42 mw		1.29 vw	1.115 vvw
1.40 vw		1.26 mw	1.107 vw/b
1.39 vw		1.22 vw	1.100 vvw
1.36 vw		1.18 vw	1.077 vvw
1.35 vvw		1.17 vw	1.057 vw
			1.039 mw

OPTICAL AND X-RAY RESULTS

The specimen used was from Eakle's collection at the University of California, collected at the type locality and kindly provided by Professor A. Pabst. It consisted of long white fibres. X-ray examination showed that even small fibres were composed of crystallites that were well-aligned but rotated at random round the fibre axis, and single-crystal patterns were therefore unobtainable. The fibres have parallel extinction with positive elongation. The refractive index is 1.598 ± 0.002 for light vibrating parallel to the fibre direction and 1.594 ± 0.002 for light vibrating across it. Small crystals of thaumasite, identified optically, are distributed fairly evenly in the material and in places were concentrated in yellowish masses up to a few millimetres in each direction. Occasional crystals of calcite are also present. X-ray photographs of fibres taken from different parts of the specimen show that except for one region in which it is intergrown with hillebrandite, the foshagite is free from other known calcium silicate minerals. In all these respects the material agrees closely with Eakle's description, although the latter did not report the presence of hillebrandite.

The x-ray powder and oriented fibre data given by Heller and Taylor (1956) were obtained using this specimen and are reproduced in Table 1. The powder data agree substantially with those of McMurdie and Flint, who however reported moderate reflections at 8.0 and 5.67 Å which were not found in the present experiments.

ELECTRON MICROSCOPE INVESTIGATION

A few fibres were lightly crushed in water and drops of the resulting suspension allowed to dry on specimen grids coated with formvar films.

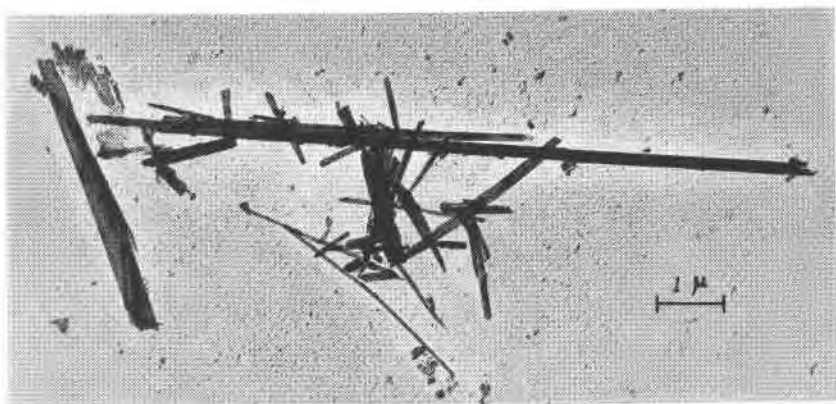


FIG. 1. An electron micrograph of typical fibres of foshagite.

Some of the specimens were shadowcast (Williams and Wyckoff, 1944) with gold palladium alloy at an angle of $\tan^{-1} \frac{1}{4}$. The specimens were examined in a Metropolitan-Vickers EM3 electron microscope. Electron micrographs (Fig. 1) confirmed the fibrous nature of the specimen. Individual fibres had two good cleavages parallel to the fibre axis, and were about 250–4000 Å wide, with thicknesses varying between one-quarter and three-quarters of the width. Electron-diffraction patterns from individual fibres (Fig. 2) showed an orthogonal network of spots with alternate strong and weak layer-lines perpendicular to the fibre axis in

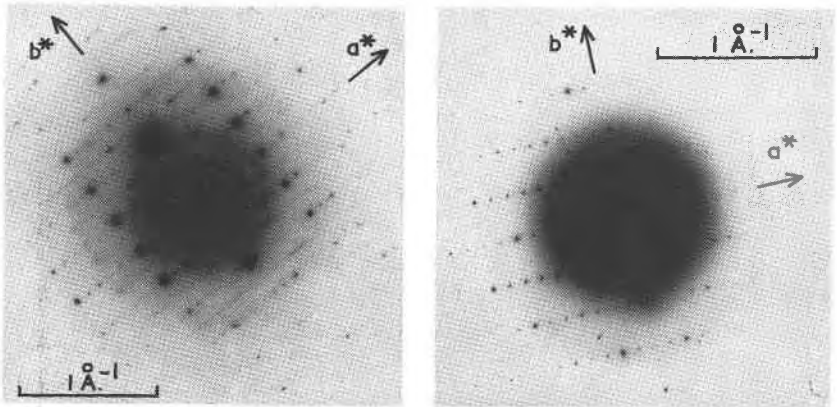


FIG. 2. (left) A typical electron-diffraction pattern from a single fibre of foshagite, with (001) planes normal to the electron beam. There are alternate strong and weak layer lines perpendicular to the fibre direction b . Both strong and weak reflections lie on an orthogonal net, which is divided into Laue zones parallel to b . The maxima of the odd layer lines are halfway between the Laue zones through the strong reflections of the even layer lines.

FIG. 3. (right) An electron-diffraction pattern from a foshagite fibre with its c -axis parallel to the electron beam, so that the $hk0$ Laue zone is almost central. The odd layer lines are very faint streaks, and the spacing of reflections along the even layer lines corresponds to d_{100} . The most intense reflections lie on a slightly distorted hexagonal net with a 3.60 Å.

accordance with the x -ray results. The patterns showed that the fibres were single crystals, of which all but one of those examined lay in the same orientation. The fibre axis will be called b , and the principal cleavage, on which most of the crystals lay, will be called (001). The following discussion relates to the pseudo-cell. The weak, intermediate layer-lines with true k odd, and their connection with the true cell, are discussed later.

The a -axis lies substantially in the plane of the supporting film. As the patterns are orthogonal, it can be chosen normal to b , making $\gamma = 90^\circ$. The mean value found for b was 3.67 Å. This suggests that the 1.84 Å

x -ray reflection, which has true $k=4$, is 020 on the pseudo-cell, giving 3.68 \AA for d_{010} . The agreement between b and d_{010} confirms that $\gamma=90^\circ$ and shows also that $\alpha=90^\circ$. The pseudo-cell is thus geometrically orthorhombic or monoclinic.

Many of the patterns, including that shown in Fig. 2, appeared to be intersected by closely-spaced Laue zones (Brown and Clark, 1952) parallel to the fibre axis. The maximum tilt of the specimen stage (about 7°) was sufficient only in two cases to allow the c -axis to be brought parallel to the electron beam so that the $hk0$ Laue zone was central (Fig. 3).

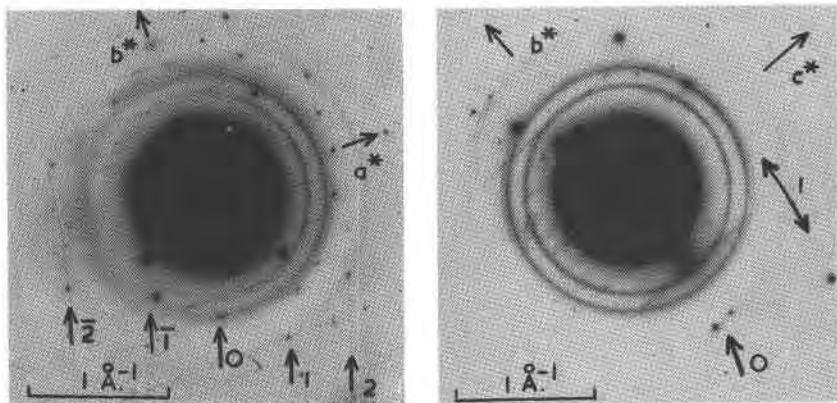


FIG. 4. (left) An electron-diffraction pattern from the foshagite fibre of Fig. 3 after tilting a few degrees from that position. The pattern is now divided into Laue zones arising from the c -axis. The l -values of these zones (indexed on the pseudo-cell) are indicated.

FIG. 5. (right) An electron-diffraction pattern from a foshagite fibre lying on (100), with Laue zones arising from the a -axis; h -values of the zones are indicated. The reflections fall on a face-centred orthogonal net with alternate strong and weak layer lines perpendicular to the b -direction. The reflections on the odd layer lines are joined by streaks, and are not divided into Laue zones. The powder rings are due to the shadow-casting metal.

β therefore probably exceeds 97° . The two exceptional cases presumably occurred with crystals having an initial tilt about the fibre axis, so that their (001) planes were not normal to the electron beam. For both of these patterns with the $hk0$ zone central, d_{100} was 9.95 \AA . All other patterns gave higher apparent values of d_{100} , up to a maximum of about 10.6 \AA . If it is assumed that this maximum value occurs when (001) is exactly normal to the electron beam, it may be taken as a measure of a ; the diffraction conditions are still satisfied because the crystal is necessarily very thin normal to (001). From the relation $d_{100} = a \sin \beta$, β was estimated at about 110° .

Figure 4 shows the effect of tilting the crystal through a few degrees about b on one of the patterns with the $hk0$ zone centred. The pattern is

split into clearly-defined Laue zones for different values of l . By tilting through various angles and applying the procedure due to Gard (1956), c was estimated at about 7.3 \AA from the Laue zone radii. Comparison of reflections in adjacent zones showed the pseudo-cell was primitive. No space-group absences were observed.

The electron-diffraction pattern from one fibre (Fig. 5) showed that its (100) plane was approximately normal to the beam. Values of $7.0 \pm 0.3 \text{ \AA}$ for c were derived from the spacings of the spots, and of $10.0 \pm 0.8 \text{ \AA}$ for a from the radii of the Laue zones, but the accuracy was poor. These values are in accordance with those already obtained. The electron-diffraction data thus show that the pseudo-cell is monoclinic, with approximate parameters:

$$a \ 10.6, \quad b \ 3.67, \quad c \ 7.0 \text{ \AA}, \quad \beta \ 110^\circ.$$

The structure of the weak intermediate layer-lines perpendicular to b will now be considered. In the electron-diffraction pattern with the $hk0$ Laue zone central (Fig. 3), the weak layers are continuous, very faint streaks. In the patterns from crystals tilted a few degrees from this position (Fig. 4), the streaks have maxima between adjacent Laue zones through the strong spots, and minima on these zones. Each maximum can be resolved into separate reflections with integral h -indices. In the pattern from a crystal lying on (100) (Fig. 5), the intermediate layers consist of spots with half-integral k - and l -indices in terms of the pseudo-cell. These spots are weak and connected by faint streaks parallel to c^* . There is no apparent division into Laue zones for different values of h . This confirms that the weak reflections are streaked parallel to both a^* and c^* , but principally in the former direction. The true cell is thus A -centred monoclinic with the approximate parameters $a \ 10.6$, $b \ 7.34$, $c \ 14.0 \text{ \AA}$, $\beta \ 110^\circ$, with the a , b , and c axes in the same directions as in the pseudo-cell. The principal cleavage is (001) and the secondary cleavage is (100).

Some of the spots on the pattern shown in Fig. 3 are more intense than others. They may be indexed on the pseudo-cell as $0k0$, $4k0$, $7k0$, $11k0$ where k is even, and $2k0$, $5k0$, $9k0$ where k is odd, and thus lie approximately on a face-centred orthogonal network with a mean spacing of 5.6 \AA across the fibre axis. This is a slightly distorted hexagonal network with a about 3.6 \AA .

CORRELATION OF ELECTRON DIFFRACTION AND X-RAY DATA

This provided a check on the pseudo-cell determined above and also a means of refining its parameters. The weak superlattice reflections were visible on the x -ray fibre rotation photographs only as continuous streaks

corresponding to odd values of true k . For convenience, indices were allocated in terms of the primitive monoclinic pseudo-cell, except that, to avoid confusion, the doubled value of b was used. All k -indices are therefore even.

Consideration of the six longest x -ray spacings, all of which have $h0l$ indices, suggests that the 10.0, 4.95, 6.8, and 3.37 Å spacings correspond respectively to 100, 200, 001, and 002. This gives values of 9.90 Å for d_{100} and 6.74 for d_{001} . The $0a^*c^*$ face of the reciprocal lattice was drawn, using these values and assuming $\beta^* = 70^\circ$. It was found that the observed $h0l$ spacing of 3.56 Å could only be 201 and that the one of 3.25 Å could only be $20\bar{2}$. Optimum agreement between calculated and observed values for these spacings was obtained by adjusting β^* to 73.6° . Indices were allotted to all the spacings down to 1.5 Å on the basis of these parameters, taking into account the observed k -indices. Agreement was satisfactory (Table 1). The refined values for the parameters of the monoclinic pseudo-cell are thus

$$a \ 10.32, \quad b \ 3.68, \quad c \ 7.04 \text{ \AA}, \quad \beta \ 106.4^\circ.$$

The corresponding A -centred monoclinic true cell has the parameters

$$a \ 10.32, \quad b \ 7.36, \quad c \ 14.07 \text{ \AA}, \quad \beta \ 106.4^\circ. \dagger$$

The x -ray fibre data show no systematic absences in the $h0l$ reflections, and the electron-diffraction data show no absences in the $0k0$ reflections of the pseudo-cell. The space-group of the latter could therefore be $P2$, Pm , or $P2/m$. The weak reflections corresponding to the true cell were too indefinite to justify any attempt to determine its space-group.

CHEMICAL ANALYSIS AND UNIT CELL CONTENTS

The results of a new analysis made on the present specimen, by Dr. R. A. Chalmers, are given in Table 2 (column 3) with those of Eakle and Newman for comparison. The specific gravity was determined by suspension in bromoform-benzene mixtures after preliminary evacuation to remove air from the mineral. The material analysed contained a small proportion of thaumasite and possibly also a little calcite. An attempt to purify the material by specific gravity separation was unsuccessful, because of the close admixture of the thaumasite and the difficulty of grinding the highly fibrous material. For the same reason the samples taken for the different parts of the analysis were not perfectly representative, and this may explain the slightly low total (99.3%). It was assumed that

† The axes have been chosen in these directions to clarify the relation between the true and pseudo-cells. The conventional true cell would be C -centered monoclinic with $a \ 14.07$, $b \ 7.36$, $c \ 10.32 \text{ \AA}$, $\beta \ 106.4^\circ$.

TABLE 2. CHEMICAL ANALYSES AND UNIT-CELL CONTENTS

	1	2	3	4	5	6
SiO ₂	33.92	36.60	39.8	42.2 Si	12.0	12
Al ₂ O ₃	0.83	0.50	0.6	0.6 Al	0.2	
Fe ₂ O ₃				nil Fe	nil	
MgO	tr	2.61	0.8	0.9 Mg	0.4	
CaO	53.48	48.91	50.7	52.3 Ca	16.1	16
Na ₂ O	n.d.	n.d.	0.1	0.1 Na	<0.1	
K ₂ O	n.d.	n.d.	0.1	0.1 K		
H ₂ O	10.19	8.88	5.7	3.8 H	7.2	8
CO ₂	1.83	2.67	0.8	nil O	44.4	44
SO ₃	n.d.	n.d.	0.65	nil		
	100.25	100.17	99.3*	(100.0)		
Sp.gr.	2.36		2.73	2.79		

* Also: P₂O₅, nil; MnO, tr.

1. A. S. Eakle, 1925. Analyst, C. A. Gentle.
2. E. S. Newman, 1956.
3. This investigation. Analyst, R. A. Chalmers.
4. Analysis 3 after correction for 5% of thaumasite (3CaO·SiO₂·CO₂·SO₃·15 H₂O, s.g. 1.9) and 1% of calcite, and normalizing to 100.
5. Atomic cell contents calculated from 4.
6. Theoretical atomic cell contents for 4[Ca₄Si₃O₉(OH)₂].

all the SO₃ was present as thaumasite and the remaining CO₂ as calcite; on this basis the analysis and specific gravity were corrected for presence of 5% of thaumasite and 1% of calcite (column 4). Atomic cell contents, calculated using these data, are given in column 5. They approximate to 4[Ca₄Si₃O₁₁H₂]. The theoretical specific gravity, corresponding to these idealised cell contents, is 2.74.

DEHYDRATION

A dehydration isobar (Fig. 6, curve A) was kindly determined by Mr. J. W. Howison, B.Sc., using a silica-spring balance. A slow stream of air was passed through the apparatus, after adjustment to 6 mm. humidity and passage over caustic soda and soda-lime to remove carbon dioxide. Constant weight was attained at each temperature before proceeding to the next.

The ignited residue from this experiment contained 1.1% SO₃, indicating that the particular sample used contained about 8% of thaumasite. The presence of 1% of calcite was assumed from the analysis. By analogy with the behaviour on dehydration of the related mineral ettringite (Jones, 1938) it was assumed that water from the thaumasite (3.3%)

accounted for all the loss below 600° and for part of the loss above 600°. It was also assumed that the loss above 600° included the CO₂ both from the thaumasite (0.5%) and the calcite (0.4%). A corrected curve was thus obtained for the foshagite and was normalised to 100% foshagite (Fig. 6, curve B). It shows 3.5% of water, lost mainly within the range 650–750°. The discrepancy from the theoretical value of 4.3% is prob-

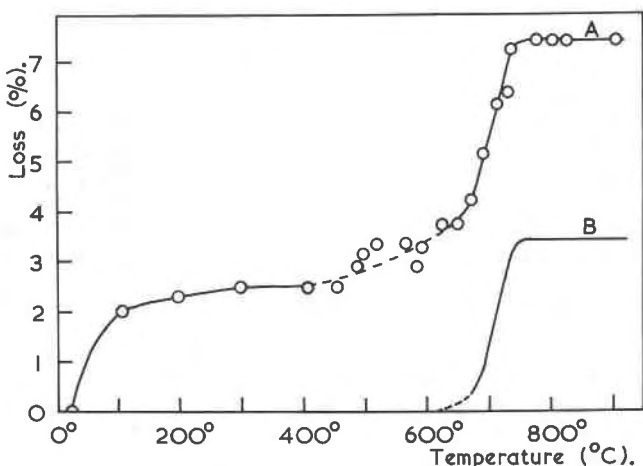


FIG. 6. Curve A. A dehydration isobar for foshagite. Curve B. The dehydration isobar of curve A, after correcting for 8% of thaumasite and 1% of calcite.

ably not significant in view of the assumptions made and the large effect of any small error in the SO₃ determination.

Difficulty was encountered in obtaining steady values with the silica-spring balance at 450–600°, and this part of the experimental curve must be considered uncertain. The effect appears due to some aspect of the behaviour of thaumasite on dehydration and has not been further investigated.

An *x*-ray powder pattern of a specimen of the foshagite after heating at 600° showed no change, thus confirming that the water loss below this temperature is probably attributable to the thaumasite. After heating at 800°, the material is still fibrous. *X*-ray examination of these fibres confirmed Heller's view (1952) that they were composed of β -CaSiO₃ and β -Ca₂SiO₄, with the *b*-axes in each case parallel to the fibre direction. The β -CaSiO₃ was more easily recognized than the β -Ca₂SiO₄. No evidence was found of a CaO-like powder pattern in crystals heated at 550°, as reported in one instance by Heller. It seems possible that this effect also may have been caused by presence of thaumasite.

Electron-micrographs (Fig. 7) of the product obtained by heating at

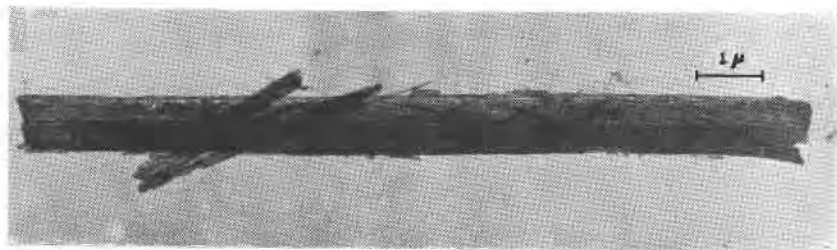


FIG. 7. An electron micrograph of foshagite fibres after heating at 800° . They have split lengthwise into much narrower fibres, and have a fluffy appearance.

800° confirmed that it was a pseudomorph of the foshagite. The fibres had a fluffy appearance and were split lengthwise into much narrower fibres. Electron-diffraction patterns of many of these fibres were those of single crystals (Fig. 8). The spacings and Laue zone radii of the strong reflections indicated a C -centred orthorhombic or monoclinic pseudo-cell with a 15.40, b 3.65, c 6.95 Å, γ 90° , elongation b , cleavage (001). The $hk0$ reflections were strong for $h=6n$ where k was even and for $h=(6n+3)$ where k was odd. These strong reflections form a distorted hexagonal pattern corresponding to an a -axis of about 3.4 Å. These data agree with β - CaSiO_3 (Table 3). This name will be used indiscriminately for wollastonite and parawollastonite, which have identical pseudo-cells, where it is undesirable to distinguish the two. Weak odd layer-lines are present in Fig. 8 corresponding to a doubling of b . The positions of the spots on these layers indicated a mixture of wollastonite and parawollastonite. There was no direct evidence of β - Ca_2SiO_4 .

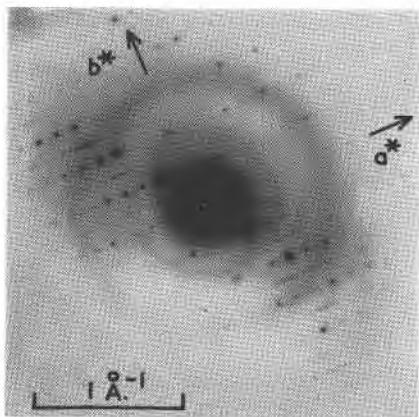


FIG. 8. An electron-diffraction pattern from a foshagite fibre after heating at 800° . The parameters correspond to β - CaSiO_3 lying on (001). The c -axis is at a small angle to the electron beam, so that the zero- and first-order Laue zones can be seen.

TABLE 3. PARAMETERS, ATOMIC CONTENTS, AND VOLUMES OF THE PSEUDO-CELLS OF FOSHAGITE AND β -CaSiO₃ AND OF THE UNIT-CELL OF β -Ca₂SiO₄*

Parameters	Foshagite	β -CaSiO ₃	β -Ca ₂ SiO ₄
<i>a</i>	10.32 Å	15.33 Å	<i>c</i> 9.28 Å
<i>b</i>	3.68	3.64	<i>b</i> 6.76
<i>c</i>	7.04	7.03	<i>a</i> 5.48
β	106°24'	95°24'	94°33'
$\alpha = \gamma$	90°	90°	90°
Atomic contents.	Ca ₄ Si ₃ O ₉ (OH) ₂	Ca ₆ Si ₆ O ₁₈	Ca ₈ Si ₄ O ₁₆
Volume (Å ³)	256	390	342
Volume containing 24 Ca ⁺⁺ (Å ³).†	1536	1560	1026
% change in volume per 24 Ca ⁺⁺ .	—	+1.6	-33.2

* Data for β -CaSiO₃ are from Jeffery (1953). Data for β -Ca₂SiO₄ are from Midgley (1952).

† *i.e.*, volume of six pseudo-cells for foshagite, four pseudo-cells for β -CaSiO₃, and of three unit-cells for β -Ca₂SiO₄.

Assuming that the fibres of the dehydrated material are pseudomorphs of the original crystals, the electron-diffraction pattern confirms that the foshagite *b*-direction becomes the *b*-direction of the β -CaSiO₃. It shows also that the (001) plane of the foshagite becomes, at least approximately, (001) for the β -CaSiO₃ pseudo-cell.

SYNTHESIS

Synthesis of foshagite was confirmed by treating synthetic rankinite (Ca₃Si₂O₇) with supercritical water at 500° and about 400 atmospheres pressure for 14 days. Apart from some unchanged rankinite, the product consisted mainly of foshagite, which was identified by its x-ray powder pattern. The experiment was originally done in an attempt to confirm Flint, McMurdie and Wells' (1938) observation that a different polymorph of Ca₃Si₂O₇ was formed under these conditions. No product corresponding to their description was detected.

DISCUSSION

Composition and ionic formula

The present results confirm the status of foshagite as a distinct mineral species, and indicate the composition 4CaO · 3SiO₂ · H₂O. The CaO:SiO₂ ratio 4:3 is also supported by Newman's analysis and it seems certain that Eakle's value of 5:3 is too high. It appears likely that both the earlier analyses, like the present one, were made on material containing thaumasite. Exact interpretation of these analyses is difficult because in neither case was SO₃ determined. It is possible to explain Newman's

analysis on the assumption that thaumasite and calcite were present as impurities. The high lime content reported by Eakle cannot be explained in this way; it could possibly have been caused by presence of hillebrandite, which is intergrown with foshagite in parts of the Crestmore specimen, and is hard to distinguish from it by optical methods. The high water contents reported in the earlier analyses could also be attributed to presence of thaumasite. It is significant that synthetic preparations show lower water contents in better agreement with the formula $4\text{CaO} \cdot 3\text{SiO}_2 \cdot \text{H}_2\text{O}$; Flint, McMurdie and Wells reported an ignition loss of 5.7% and Jander and Franke considered their product to be $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$.

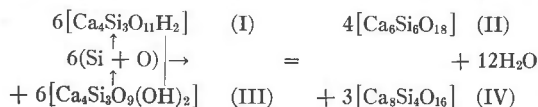
Several lines of evidence suggest the ionic formula $\text{Ca}_4(\text{SiO}_3)_3(\text{OH})_2$. The material is markedly fibrous, and this could be explained by the presence of metasilicate chains of empirical composition SiO_3^{--} . The number (12) of SiO_3 units in the cell is consistent with the hypothesis that it contains four such chains, kinked as in other calcium silicate minerals such as tobermorite (Megaw and Kelsey, 1956) and wollastonite (Buerger, 1956) so as to give a repeat unit of three linked tetrahedra in the space of the 7.3 Å fibre repeat distance. The ordered transformation at about 700° of part of the material into $\beta\text{-CaSiO}_3$ fits in with this view. Presence of hydroxyl ions not directly linked to silicon appears consistent with the conditions of formation and of dehydration. Those calcium silicates which are known to contain hydrogen in the form of water molecules or in Si-OH groups, or both, such as afwillite or tobermorite, are formed hydrothermally at temperatures usually below 200°. They also tend to suffer dehydration at relatively low temperatures, often below 500°. In contrast, xonotlite, which also shows the 7.3 Å fibre repeat distance and contains hydroxyl groups not attached to silicon (Mamedov and Belov, 1955) is formed hydrothermally at temperatures up to 400° and is only dehydrated at about 750°. This is similar to the behaviour of foshagite.

Dehydration

The stoichiometry of the dehydration process is represented by the equation



Consideration of the respective cell contents (Table 3) shows that twelve pseudo-cells of foshagite yield four pseudo-cells of $\beta\text{-CaSiO}_3$ and three unit-cells of $\beta\text{-Ca}_2\text{SiO}_4$. Assuming tentatively that equal numbers of foshagite pseudo-cells are altered to $\beta\text{-CaSiO}_3$ and to $\beta\text{-Ca}_2\text{SiO}_4$, the process could be represented



Formula I represents six pseudo-cells of foshagite which are converted into four pseudo-cells of β -CaSiO₃ (II), and formula III represents six pseudo-cells of foshagite which are converted into three unit cells of β -Ca₂SiO₄ (IV). For this to occur, six silicon and six oxygen atoms must be transferred from III to I, as indicated by the arrow, and twelve molecules of water formed by combination of hydrogen from I with hydroxyl from III. Such a conversion of foshagite into β -CaSiO₃ would entail negligible change in volume, but the corresponding conversion of foshagite into β -Ca₂SiO₄ would cause a 33% decrease in volume (Table 3). The absence of shrinkage in the β -CaSiO₃ would permit some retention of coherence and therefore of orientation, while the considerable shrinkage in the β -Ca₂SiO₄ might cause splitting into very narrow fibres with enough free space to allow random orientation around the fibre axis. The free space might be increased by pressure of escaping steam. Random orientation and small crystal size could explain the failure of electron-diffraction to reveal the β -Ca₂SiO₄. This mechanism would thus explain the experimental findings on the orientations of the products, and is therefore probably correct.

The proposed dehydration mechanism would entail acceptance of silicon and oxygen atoms by the foshagite converted into β -CaSiO₃, but no change in the number of calcium ions. It resembles that of xonotlite (Dent and Taylor, 1956), although it is more complex. Xonotlite is dehydrated to β -CaSiO₃ at about 750°, and the process seems to involve the breaking of Si-O rather than Ca-O bonds. This suggests that the Ca-O skeleton in foshagite may be closely similar to that in wollastonite. There may also be a more distant structural similarity to β -Ca₂SiO₄.

Structure

The detailed structure remains to be determined but the present results give some strong indications. As already stated, there is evidence that the unit-cell is traversed in the *b*-direction by four metasilicate chains kinked similarly to those in wollastonite, and that the calcium-oxygen skeletons of the two minerals may be very similar. This is supported by other evidence:

(i) In the electron-diffraction patterns both of foshagite and of β -CaSiO₃, the strongest *hk0* reflections fall on distorted hexagonal nets similar to that of calcium hydroxide. In β -CaSiO₃, this is attributable to the arrangement of the relatively heavy calcium ions, which in (001) projection closely resembles that of calcium hydroxide. A similar arrangement may therefore occur in foshagite.

(ii) If only calcium ions are considered, and slight movements of some calcium ions are allowed, β -CaSiO₃ can be described in terms of a pseudo-cell almost identical with that of foshagite (Fig. 9), with the (100) planes

common to both pseudo-cells. This relation between the pseudo-cells is consistent with the dehydration evidence and appears too marked to be explained by coincidence. It is therefore suggested that the four calcium ions in the pseudo-cell of foshagite are approximately in the positions shown in Fig. 9. This could be compatible with any of the possible space

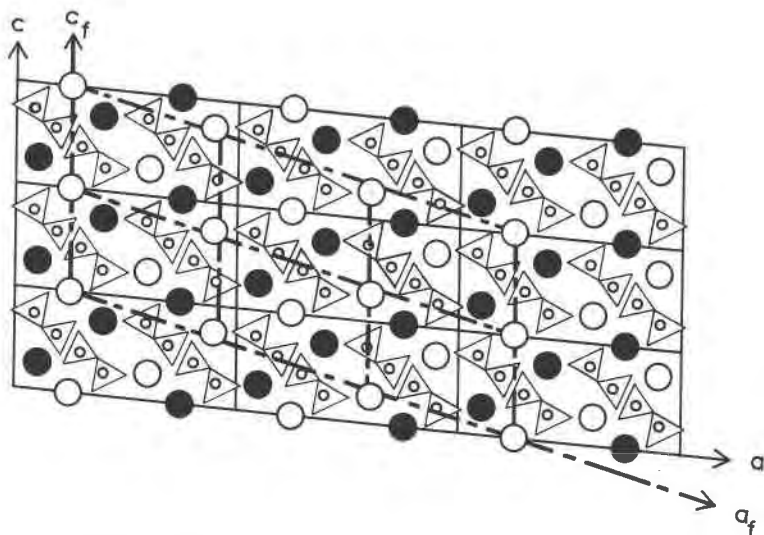


Fig. 9. Nine pseudo-cells of β - CaSiO_3 , looking down the b -axis.

The black and large open circles represent calcium ions at heights 0 and $\frac{1}{2}$ in the pseudo-cell respectively, and the double triangles represent projections of the metasilicate chains. The thick broken lines show the probable outlines of foshagite pseudo-cells before dehydration, with the calcium ions occupying slightly different positions. Three pseudo-cells of foshagite could accept one silicon and one oxygen atom each and change into two pseudo-cells of β - CaSiO_3 with negligible volume change, and preservation of the b - and c -axes. An equal number of adjacent foshagite pseudo-cells could donate silicon and oxygen atoms, and change into β - Ca_2SiO_4 with considerable shrinkage, causing disintegration into very narrow fibres with random orientation round the fibre axis.

groups ($P2$, Pm , or $P2/m$). The present evidence is inadequate to locate the metasilicate chains or the hydroxyl groups, though both are probably placed symmetrically relative to two-fold axes. Further work is in progress to complete the structure determination.

A structure of the type suggested would explain the extreme weakness and streaking of reflections with true k odd. The weakness is partly explained by the fact that the pattern of calcium ions repeats at intervals of $b/2$ along the fibre direction. Random displacements of $b/2$ in the placing of the metasilicate chains would enhance the effect and also

cause the streaking. This effect is observed with xonotlite (Mamedov and Belov, 1955) and with other fibrous calcium silicates.

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