Acta Cryst. (1963). **16**, 551

The Structure of Bultfonteinite, $Ca_4Si_2O_{10}F_2H_6$

By E. J. McIver*

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 25 *April* 1962)

The structure of bultfonteinite has been determined by two-dimensional Fourier methods, and bond distances are generally correct to better than 0·04 Å. The structural formula has been found to be $Ca_4[SiO_2(OH_{\frac{1}{2}})_2]_2F_2 2H_2O$. It is composed of strips of composition $[Ca_4Si_2O_4]^{8+}$, running along the 5·67 Å *c*-axis, and joined together by Ca–O–Ca, Ca–F–Ca, Ca–H_2O–Ca, and Ca–O–Si bonds. Two-thirds of the hydrogen occurs as water, and the remaining third in short 2·5 Å hydrogen bonds. The silicon occurs in isolated tetrahedra of composition $[SiO_2(OH_{1/2})_2]^{3-}$. The calcium co-ordination is seven-fold, and is derived from a trigonal prism with the seventh atom intruding on one of the square faces.

1. Introduction

Bultfonteinite is a hydrated calcium silicate containing fluorine, which occurs as pale-pink radial spherulites in the Bultfontein mine, Kimberley, South Africa, and at Crestmore, California. The South African material was first described by Parry, Williams & Wright (1932) who found it to be triclinic with composition very close to $Ca_4Si_2O_{10}F_2H_6$. They measured the axial ratios and cell angles with an optical goniometer, and their results, listed in Table 1, show that it is dimensionally pseudo-orthorhombic. These workers also noted the extensive and complicated twinning, but made no attempt to deduce the twin laws. Megaw & Kelsey (1955), made a more detailed study of the twinning of the same material, and found that it could be explained on the basis of two twin laws, whose twin planes were normal to [100] and [010] respectively, the former predominating. They made accurate X-ray measurements of the cell dimensions, quoted in Table 1, which confirm the observation of Parry, Williams & Wright on the mineral's close approximation to an orthorhombic cell. Finally they remarked on the similarity of the 5·67 Å *c*-axis of bultfonteinite to the 5·63 Å *b*-axis of another hydrated calcium silicate mineral, afwillite, $Ca_3Si_2O_{10}H_6$. In both cases these directions are the fibre axes. The structure of afwillite has been solved by Megaw (1952), who showed that the structural formula can be written as $Ca_3(SiO_3OH)_2.2H_2O$, and that the *b*-axis is formed by chains of silicon and calcium co-ordination polyhedra sharing edges. Megaw & Kelsey suggested that similar chains might occur in bultfonteinite, leading to a structural formula $Ca_3(SiO_3OH)_2.2H_2O.CaF_2$. Murdoch (1955) has measured the cell dimensions of bultfonteinite from Crestmore, California, and found it to have dimensions very close to the South African material.

Table 1. *Lattice parameters of bultfonteinite*

	Megaw & Kelsey (1955)	Parry, Williams & Wright (1932)
a	10·992 ± 0·004 Å	—
b	8·185 ± 0·002 Å	—
c	5·671 ± 0·001 Å	—
$a:b:c$	1·3433 : 1 : 0·6930	½(1·3512) : 1 : 0·6873
α	93° 57′	94° 17′
β	91° 19′	91° 59′
γ	89° 51′	90° 44′
α^*	86° 03′ ± 18′	85° 41′
β^*	88° 41′ ± 02′	87° 57′
γ^*	90° 04′ ± 01′	89° 07′

A structure analysis of bultfonteinite was undertaken to discover the extent of the similarity to afwillite. A knowledge of the structure would be valuable since little information is available on the structures of hydrated calcium silicates; apart from afwillite the only other structure which has been fully determined is that of xonotlite, $Ca_6[(OH)_2Si_6O_{17}]$, Mamedov & Belov (1955).

As the bultfonteinite used in the present work was obtained from South Africa, the composition found by Parry, Williams & Wright, and the cell dimensions given by Megaw & Kelsey, have been used throughout this work without modification.

2. Experimental

Because of the extensive twinning it was not easy to select a crystal suitable for a structure determination. The one eventually chosen was a small rectangular plate, 0·16 × 0·09 × 0·04 mm, elongated along [100] and with the plane of the plate normal to [010].

Weissenberg photographs of the *hk*0, *h*0*l*, and 0*kl* reflections were taken with zirconium-filtered Mo $K\alpha$ radiation, which gave reflections out to $(\sin\theta)/\lambda = 1·3$ Å^{-1}. Intensities were measured by visual comparison with an intensity scale; by using the multiple-film technique the intensity range covered was about 500 to 1. No formal correction for resolution of the

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* Present address: Atomic Energy Research Establishment Harwell, Didcot, Berks., England.

α_1–α_2 doublet was made; the spot area was roughly estimated by eye and an intuitive correction applied at the time of measurement. Corrections were made for the usual Lorenz and polarization effects, and also for absorption, even though the crystal was so small that the maximum absorption was less than 15%.

3. Trial structure

Though bultfonteinite is triclinic, the close approach of the cell angles to 90° suggested the possibility of monoclinic or orthorhombic pseudo-symmetry. A survey of the intensities revealed a pseudo mirror plane perpendicular to [100], together with two classes of systematically weak reflections, namely *h*00 with *h* odd and 0*kl* with *l* odd. Therefore, the space group approximates to the monoclinic space group $P2/c11$ (*i.e.* $\{P2_1/c\}$ with the diad along [100]). A structure with this space group would require γ and β to be 90°, but not α; this fits well with the observed fact that the actual β and γ show a smaller deviation from 90° than does α. This space group has four-fold general positions with co-ordinates $\pm(x,y,z)$; $\pm(\frac{1}{2}-x,y,z+\frac{1}{2})$.

Although the ideal monoclinic space group is centrosymmetric, the distortion required to give a triclinic one would not necessarily preserve the centre of symmetry. To test for centro-symmetry the intensity statistics were examined. The value of the Wilson ratio (Wilson, 1949) for the *hk*0 reflections was 0·76; as the theoretical values for space groups $P1$ and $P\bar{1}$ are 0·79 and 0·64 respectively, the former space group is indicated. However, according to Sim (1958), these theoretical values must be amended when heavy atoms are present, and if calcium is taken to be a heavy atom the theoretical values become 0·82 and 0·68. As the experimental value of 0·76 lies midway between these no firm conclusion could be drawn. The test of Howells, Phillips & Rogers (1950) was applied to the same reflections (Fig. 1). Again the experimental result lies between the two theoretical ones and no conclusion was possible. Neither did tests for piezo-, and pyro-electricity resolve the problem, for the results varied from sample to sample, probably because only very small crystals were available. It was finally decided as a first approximation to assume the space group to be $P\bar{1}$. Subsequent refinement showed this to be fully justified within the accuracy of the data avilable.

The density determined by Parry, Williams & Wright (1932) was 2·73 g.cm.$^{-3}$. If the contents of the unit cell are taken to be $Ca_8Si_4O_{20}F_4H_{12}$ the calculated value of 2·74 agrees well with the experimental one.

Finally, when formulating trial structures no attempt was made to distinguish between the four possible types of anions, namely O^{2-}, OH^-, H_2O, and F^-, and all were considered to be O^{2-}.

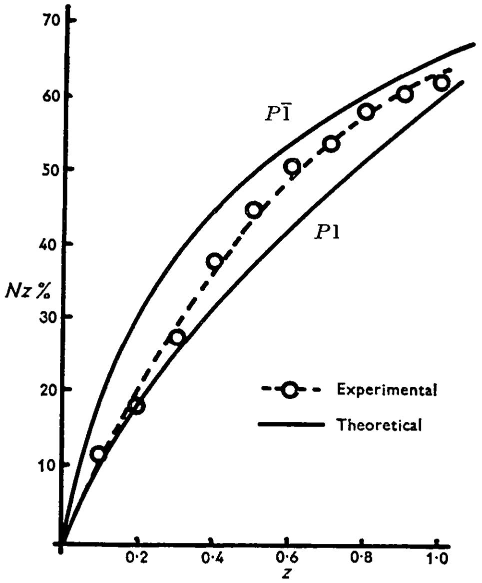

Fig. 1. Result of the Howells, Phillips & Rogers (1950) test on bultfonteinite.

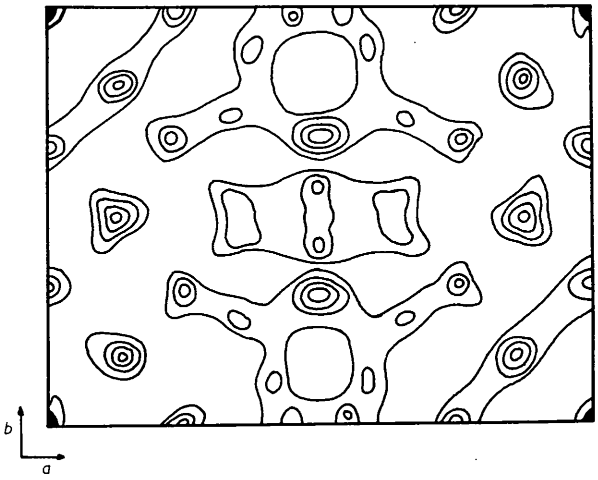

Fig. 2. The *hk*0 Patterson synthesis for bultfonteinite.

The Patterson function of the *hk*0 intensities is shown in Fig. 2. All the strong peaks lie on the intersections of a grid formed by the (430) and $(\bar{4}30)$ planes and form a face-centred square network with a 2·7 Å side. This implies that in this projection the cell edges are approximately integral multiples of 2·7 Å. In addition it was noted that the third cell edge, which is perpendicular to the other two, is also almost an integral multiple of 2·7 Å:

$$a=10\cdot99=4\times2\cdot75,\ b=8\cdot18=3\times2\cdot73,$$
$$c=5\cdot67=2\times2\cdot84\ \text{Å}\,.$$

As the diameter of an O^{2-} ion is about 2·7 Å, it was inferred that the structure is composed of a simple cubic array of anions with the cations in the 8-co-ordinated interstices.

From these ideas 'Trial Structure I' was formulated (shown in Fig. 3). All the anions were given *z*-co-

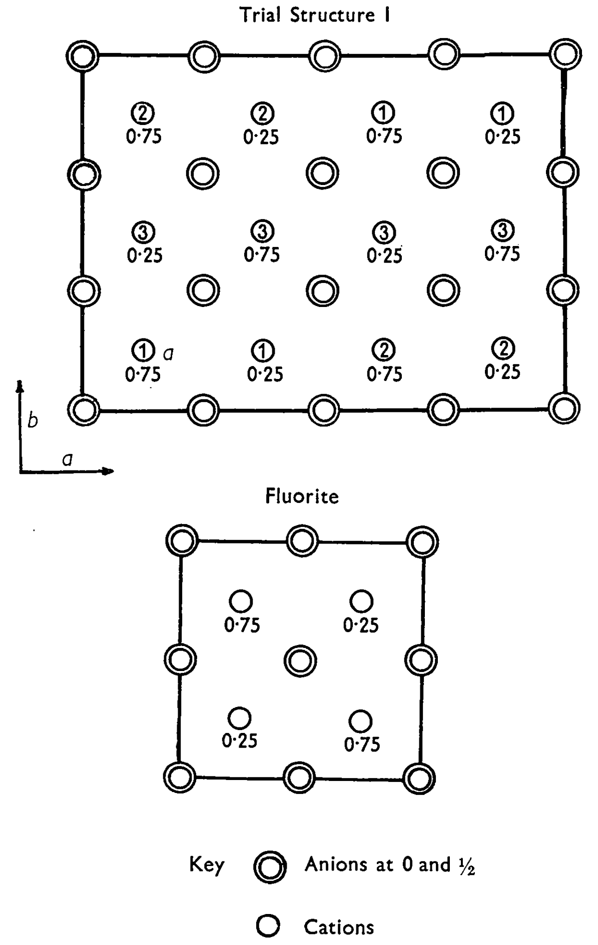

Fig. 3. Trial Structure I, showing the similarity to fluorite. The three sets of cation sites are denoted by 1, 2, 3.

ordinates of 0 or $\frac{1}{2}$, and all the cations $\frac{1}{4}$ or $\frac{3}{4}$. In this array, all cations are at least 3·9 Å apart, except those between adjacent unit cells along the b-axis, which are 2·7 Å apart. There are, of course, other ways of placing the cations in the 8-co-ordinated interstices, but all of these result in more cations being within 2·7 Å. This structure is almost identical with that of fluorite (shown in Fig. 3) which is cubic with $a = 5{\cdot}45$ Å, and has its anions in exact simple cubic packing, but no cations less than 3·9 Å apart.

Trial structure I is an oversimplification, for in the first place it does not distinguish between the calcium and silicon atoms. The next step was to choose from among the cation sites those most likely to be occupied by the silicon atoms, and then to distort the regular anion array so as to give them tetrahedral co-ordination. It was assumed that the cations would be related by the monoclinic symmetry, and so there were only three sets of independent 4-fold sites to be considered, denoted by 1, 2 and 3 in Fig. 3. As sets 1 and 2 are essentially the same, the four silicon atoms must occupy either set 1 or 3. Of these set 1 seemed more likely since all calcium–calcium distances would then be about 3·9 Å, as in fluorite, while all the calcium–silicon distances would be 2·7 Å. To see how the probable displacements of the silicon atoms and their associated oxygens were derived, consider the silicon atom at position $1a$ (Fig. 3). Its displacement is likely to increase the short calcium–silicon distance, and also to bring one of its associated oxygens between it and the calcium as a shield. Moreover if, as in afwillite, the structure contains isolated silicon tetrahedra, the silicon atoms will tend to move away from one another. These conditions can all be realized if Si$1a$ is moved from its mean position along $[\bar{3}40]$, and the tetrahedron arranged as in Fig. 4, which will be referred to as 'Trial Structure II'. In it the monoclinic symmetry has been maintained, and the anions and cations have the same z-co-ordinates as in trial structure I, with the exception of $O_{3,4,5,6}$ which form part of the $[SiO_4]^{4-}$ tetrahedra and have z-co-ordinates of $\frac{1}{4}$ and $\frac{3}{4}$ instead of 0 and $\frac{1}{2}$.

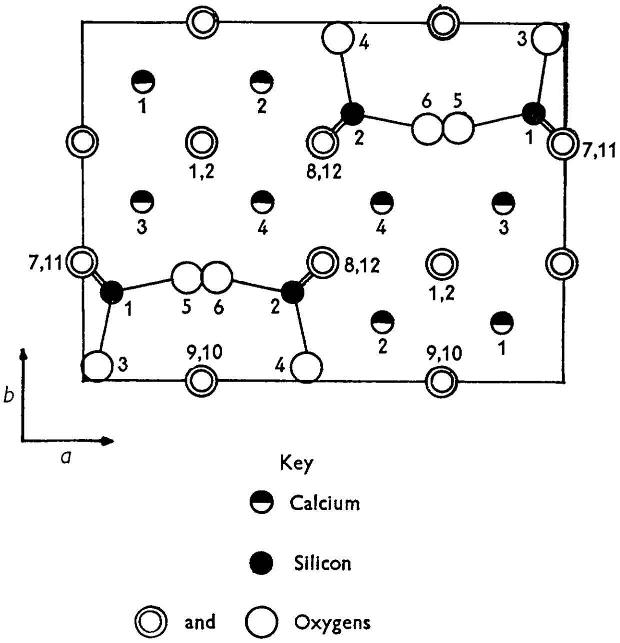

Fig. 4. Trial Structure II, which was derived from I by moving Si1_a along the $[\bar{3}40]$ direction away from Ca1 which is at the same height. All the cations and the anions 3, 4, 5, 6 are at heights $\frac{1}{4}$ and $\frac{3}{4}$; the remaining anions are at 0 and $\frac{1}{2}$.

It was still not possible at this stage to distinguish between oxygen or fluorine atoms, or to locate the hydrogens. Hence when calculating structure factors the contribution of the hydrogen atoms was ignored, and all the atoms were considered to be oxygens.

4. Refinement of trial structure II

Atomic scattering-factor curves were drawn from data of Berghuis *et al.* (1955) for Ca, Si^{4+} and O, Tomiie & Stam (1958) for Ca^{2+}, Si and Si^{4+}, and James &

Table 2. *Final co-ordinates and temperature factors for bultfonteinite*

Co-ordinates are expressed in fractions of cell edge, the temperature factors in units of cm.^{2}

	$hk0$			$h0l$			$0kl$		
	x	y	B	x	z	B	y	z	B
Ca_1	0·1331	0·7942	0·7	0·1331	0·7833	0·6	0·7934	0·7836	0·6
Ca_2	0·3692	0·7940	0·7	0·3699	0·2867	0·8	0·7945	0·2879	0·6
Ca_3	0·1197	0·4756	0·9	0·1208	0·2494	0·6	0·4763	0·2496	0·8
Ca_4	0·3829	0·4792	0·9	0·3829	0·7452	0·7	0·4791	0·7445	0·8
Si_1	0·4268	0·2403	0·6	0·4264	0·2142	0·4	0·2406	0·2150	0·5
Si_2	0·0698	0·2398	0·6	0·0705	0·7313	0·4	0·2396	0·7337	0·5
O_1	0·2512	0·6173	0·3	0·2513	0·0226	0·6	0·6199	0·0275	0·4
O_2	0·2489	0·6282	0·3	0·2468	0·5095	0·2	0·6224	0·5038	0·3
O_3	0·0444	0·0396	0·7	0·0401	0·6999	0·3	0·0367	0·7006	0·2
O_4	0·4575	0·0377	0·9	0·4584	0·1928	0·4	0·0360	0·1998	0·2
O_5	0·2779	0·2666	0·5	0·2815	0·1838	0·7	0·2691	0·1844	0·4
O_6	0·2203	0·2692	0·5	0·2182	0·7578	0·2	0·2724	0·7608	0·4
O_7	0·0172	0·3258	0·3	0·0153	0·4981	0·3	0·3302	0·4928	0·4
O_8	0·0012	0·3137	0·3	0·0024	0·9581	0·7	0·3168	0·9612	0·2
O_9	0·1928	0·9588	0·5	0·1963	0·1659	0·6	0·9540	0·1625	1·0
O_{10}	0·3111	0·9568	0·7	0·3077	0·6520	1·0	0·9590	0·6455	1·0
O_{11}	0·4945	0·6804	0·7	0·4925	0·9881	0·5	0·6856	0·9859	0·4
O_{12}	0·4795	0·3190	0·7	0·4796	0·4651	0·8	0·3191	0·4598	0·2

Brindley (1931) for O^{2-}. Curves for the half-ionized atoms Ca^+, Si^{2+}, and O^- were drawn by interpolating from the above data, attaching greatest weight to those of Berghuis *et al.*, and least to those of James & Brindley. Half-ionized atoms probably represent more closely the atoms in a calcium silicate than the two extremes of un-ionized and fully-ionized atoms respectively.

Co-ordinates from trial structure II were used to calculate structure factors for the first 29 low-angle $hk0$ reflections with $(\sin\theta)/\lambda < 0{\cdot}33$ Å^{-1}; the agreement in predicting strong and weak intensities suggested that the co-ordinates were essentially correct. Packing considerations suggested that the calcium atoms should be displaced along [010] towards the silicon tetrahedra, to compensate for the movement of $O_{3,4}$ and $O_{5,6}$ away from them. Still retaining the monoclinic symmetry, the following co-ordinates were derived:

	x/a	y/b	z/c
$Ca_{1,2}$	0·12	0·79	0·75
$Ca_{3,4}$	0·12	0·47	0·25
$Si_{1,2}$	0·06	0·23	0·75
$O_{1,2}$	0·25	0·67	0·00
$O_{3,4}$	0·03	0·04	0·75
$O_{5,6}$	0·20	0·26	0·75
$O_{7,8}$	0·00	0·33	0·00
$O_{9,10}$	0·25	0·00	0·00
$O_{11,12}$	0·00	0·33	0·50

For the same 29 low-angle terms the R-factor, defined as $\Sigma|F_o-F_c|/\Sigma|F_o|$, the terms for which F_o was too weak to be observed being neglected, now became 0·33. With the same co-ordinates the complete set of $hk0$ reflections (out to $(\sin\theta/\lambda = 1{\cdot}3$ Å$^{-1}))$ gave an R-factor of 0·51, and the F_o synthesis gave peaks of reasonable height only where expected. On moving the atoms to the centres of the peaks the R-factor was reduced to 0·43, but the electron density projection now showed a small peak at the postulated position of O_9 and O_{10} (which are superimposed on this projection) as well as a pair near to it. All three were about the same height, roughly 2/3 that of a single oxygen. The pair of atoms $O_{9,10}$ was, therefore, placed one on each of the two new peaks. The R-factor fell to 0·30, the peak at the old site completely disappeared, and the two new peaks rose to the expected height for single oxygen atoms.

From this point onwards the [100] projection was refined without further difficulty by using difference Fourier syntheses. The monoclinic symmetry restriction was relaxed, though the centre of symmetry was retained, and the signs of the systematically weak reflections were found without ambiguity as the refinement proceeded. The departure from monoclinic symmetry was only very small, the differences between the co-ordinates of pseudo-symmetrically related atoms being less than 0·2 Å. All the atoms were given individual isotropic temperature factors, although the calciums in particular were noticeably anisotropic. Reflections thought to be affected by extinction were omitted when calculating difference syntheses, and their F_o's were set equal to their F_c's when calculating electron-density maps. The final R-factor, obtained using only a single scaling factor between the observed and calculated structure factors, was 0·114. The final co-ordinates and temperature factors are shown in Table 2.

The [010] and [100] projections were refined by starting with x and y co-ordinates from an intermediate stage in the refinement of the [001] projection when the R-factor was 0·15, and ideal z co-ordinates derived from trial structure II. For the $h0l$ reflections out to $(\sin\theta)/\lambda < 0{\cdot}7$ Å^{-1}, the R-factor was initially 0·57. Although all the peaks on the corresponding electron-density map were at the expected places, several were elongated along the z-axis, suggesting that these atoms were slightly displaced from

Table 3

Standard deviations of co-ordinates of bultfonteinite, in fractions of the cell edge

	*hk*0		*h*0*l*		0*kl*	
	$\sigma(x)$	$\sigma(y)$	$\sigma(x)$	$\sigma(z)$	$\sigma(y)$	$\sigma(z)$
Ca	0·0004	0·0004	0·0002	0·0003	0·0001	0·0002
Si	0·0005	0·0006	0·0003	0·0004	0·0002	0·0002
O	0·0017	0·0022	0·0007	0·0019	0·0005	0·0011

Standard deviations of bond lengths in Ångström units

	σ
Ca–O	0·02
Si–O	0·02
O–O	0·04

Bond lengths in Ångström units

A. Calcium co-ordination

Ca_1 to O_1	2·41	Ca_2 to O_1	2·37
O_2	2·39	O_2	2·36
O_3	2·31	O_4	2·31
O_7	2·42	O_9	2·45
O_8	2·32	O_{10}	2·47
O_9	2·53	O_{11}	2·34
O_{10}	2·52	O_{12}	2·38
Mean	2·41 ± 0·08	Mean	2·38 ± 0·05

Ca_3 to O_1	2·31	Ca_4 to O_1	2·40
O_2	2·30	O_2	2·37
O_5	2·46	O_6	2·49
O_7	2·24	O_{11}	2·40
O_7	2·58	O_{11}	2·47
O_8	2·40	O_{12}	2·28
O_8	2·52	O_{12}	2·59
Mean	2·40 ± 0·12	Mean	2·43 ± 0·09

Mean calcium to anion	2·41 ± 0·09
oxygen	2·41 ± 0·09
fluorine	2·36 ± 0·04
‘hydroxyl’	2·39 ± 0·08
water	2·49 ± 0·03

B. Silicon co-ordination

Si_1 to O_4	1·69	Si_2 to O_3	1·67
O_5	1·64	O_6	1·66
O_{11}	1·62	O_7	1·67
O_{12}	1·60	O_8	1·59
Mean	1·64 ± 0·03	Mean	1·62 ± 0·03

Mean silicon to oxygen	1·62 ± 0·03
‘hydroxyl’	1·67 ± 0·02

C. Oxygen co-ordination

Oxygen–oxygen contacts less than 2·8 Å

O_3–O_3	2·48	O_9–O_3	2·73
O_4–O_4	2·47	O_9–O_5	2·72
O_5–O_6	2·49	O_{10}–O_4	2·69
Mean	2·48 ± 0·01	O_{10}–O_6	2·78
		Mean	2·73 ± 0·03

their ideal positions in a way which did not conform exactly to the monoclinic symmetry. A consistent set of small displacements for these atoms was eventually derived, and the projection was then refined. For the *h*0*l* reflections the final *R*-factor was 0·095, and for the 0*kl* reflections 0·087. The final co-ordinates and temperature factors for these projections are listed in Table 2.

5. Accuracy

The standard deviations of the co-ordinates were evaluated from the final difference syntheses using the method described by Lipson & Cochran (1953). They showed that the standard deviation of the x-co-ordinate of the nth atom, $\sigma(x_n)$, is given by:

$$\sigma(x_n)=[\overline{(\partial D/\partial x)^2}]^{\frac{1}{2}}/C_n\,,$$

where $\overline{(\partial D/\partial x)^2}$ is the mean square value of the slope of the difference synthesis in the x direction, averaged over the whole area of the map, and C_n the curvature in the x direction of the F_o electron density map at the site of the nth atom. The results, expressed as fractional co-ordinates of the cell edge, are given in Table 3. Also tabulated, are the standard deviations of the various bond lengths expressed in Å-units.

6. Description and interpretation of the structure

Bond lengths were calculated from the mean values of the co-ordinates listed in Table 2 and are given in Table 3. Oxygen–oxygen contacts less than 2·8 Å and not occurring as edges of the silicon tetrahedra are also included, for these are shown below to be hydrogen bonds.

(*a*) *Hydrogen and fluorine positions*

Before the structure can be discussed in detail, it is necessary to locate the two fluorines and the six hydrogens. Since the formula is stoichiometric, with no evidence for disorder, it is reasonable to assume that the oxygens and fluorines are perfectly ordered in separate sites. The most probable sites for the fluorine atoms were derived by considering the co-ordination of the various anions. The anion co-ordination is summarized in Table 4, which also gives the electrostatic valence calculated on the assumption of 7-co-ordinated calcium, and 4-co-ordinated silicon.

Table 4. *Summary of anion co-ordination*

Name of site	Neighbours	Electrostatic valence from cations
$O_{1,2}$	4 Ca	1·1
$O_{3,4,5,6}$	1 Ca, 1 Si, 2 O	1·3
$O_{7,8,11,12}$	3 Ca, 1 Si	1·9
$O_{9,10}$	2 Ca, 2 O	0·6

If the two fluorines have similar environments (as seems most reasonable) they must be either $O_{1,2}$ or $O_{9,10}$; of these, the best choice is $O_{1,2}$ for these have the same environment as in fluorite, and the correct electrostatic valence requirements, while $O_{9,10}$, are later shown to be more probably water molecules.

In these positions, the fluorine atoms cannot be involved in any hydrogen bonding. The mean Ca–F bond length of 2·36 Å agrees exactly with that in fluorite.

Atoms $O_{7,8,11,12}$ have the environment and electrostatic valence expected for O^{2-}, and are identified as such.

In order to locate the hydrogen atoms it has been assumed that any O–O contact of less than 2·8 Å is probably a hydrogen bond, an assumption which has been considered valid by many other workers, *e.g.* Megaw (1952). In Fig. 5 the arrangement and lengths of these bonds in bultfonteinite are shown schematically. The number of hydrogens available, that is six, corresponds exactly with the number of proposed sites —a powerful indication of the validity of the argument. The bonds fall into two groups—short bonds of $2{\cdot}48 \pm 0{\cdot}01$ Å, and long bonds of $2{\cdot}73 \pm 0{\cdot}05$ Å. The difference between them of 0·25 Å is certainly significant, whereas differences within a group are barely significant.

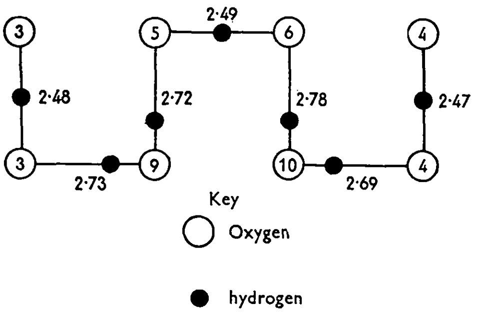

Fig. 5. The arrangement of hydrogen bonds in bultfonteinite.

From the work of Bacon & Curry (1956), who made a neutron-diffraction study of trona, $NaHCO_3 . Na_2CO_3 . 2H_2O$, and Bacon & Pease (1953, 1955), who made similar studies on KH_2PO_4, the long hydrogen bonds of 2·73 Å probably indicate that the hydrogen atom is about 0·98 Å from one or other of the oxygens—an asymmetric bond. On the other hand for the 2·48 Å bonds the hydrogen is probably equally shared by the two oxygens. We must distinguish in principle between short bonds passing through a symmetry centre or a special position, in which the hydrogen must either be at the centre or equally distributed between two symmetrically placed sites on either side of it, and short bonds not affected by symmetry, where it is possible for all the hydrogens to be in one off-centre site. Unfortunately the exact positions of the hydrogens cannot be found with the present experimental data, but for our purposes that is not necessary. In the symmetrical short bonds, each oxygen atom must be associated on the average with half of a hydrogen atom; this applies to bonds O_3–O_3, and O_4–O_4. In the unsymmetrical short bonds a similar situation seems to be the most reasonable; this applies to bond O_5–O_6. Therefore, O_3, O_4, O_5 and O_6 are all $OH_{\frac{1}{2}}$ groups. Both O_9 and O_{10} are involved in two long hydrogen bonds, and, as they do not have the environment expected of oxygens, it seems reasonable to suppose that they are water molecules. This arrangement of the hydrogens fits well with the electrostatic valences shown in Table 4.

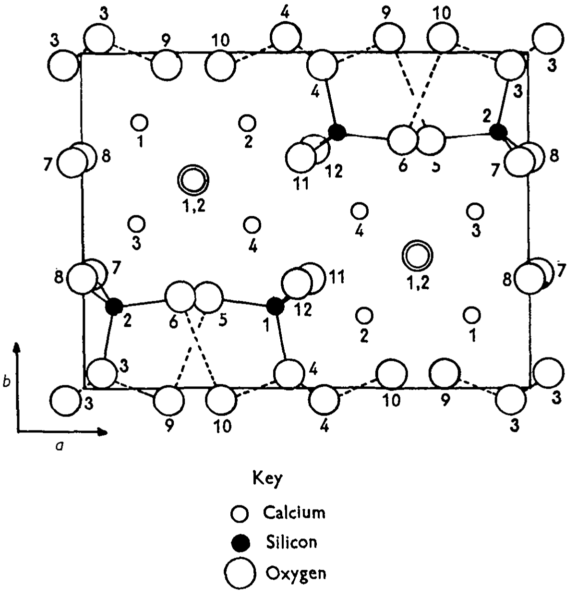

Fig. 6. The final structure of bultfonteinite. Si–O contacts are shown as full lines, hydrogen bonds by broken lines, and Ca–O contacts have been omitted.

The final structure is shown in projection down the *c*-axis in Fig. 6. Calcium–oxygen bonds have not been included; silicon–oxygen bonds are shown as full lines, and hydrogen bonds by broken lines.

(*b*) *Calcium co-ordination*

If only those calcium–anion contacts which are less than 3·0 Å are considered to be bonds, then in Table 3 it may be seen that all four independent calciums are 7-coordinated. The coordination polyhedra can best be described as being derived from trigonal prisms, with the seventh anion (in the case of $Ca_{3,4}$ an $OH_{\frac{1}{2}}$ group, and in the case of $Ca_{1,2}$ a water molecule) intruding on one of the square faces of the prism. The orientations of the prisms differ; for $Ca_{1,2}$ the triad axes lie along [100], and for $Ca_{3,4}$ along [001]. The mean calcium–anion bond distance of 2·41 Å is identical with the mean calcium–oxygen bond distance, and is only slightly greater than the mean calcium–fluorine and calcium–'hydroxyl' distances of 2·36 and 2·39 Å respectively. It appears, therefore, that the ionic radii of the oxygens, 'hydroxyls', and fluorines are almost identical. The mean calcium–water distance of 2·49 Å is, as would be expected, somewhat larger, and probably represents a significant difference.

The anisotropic thermal motion of the calcium

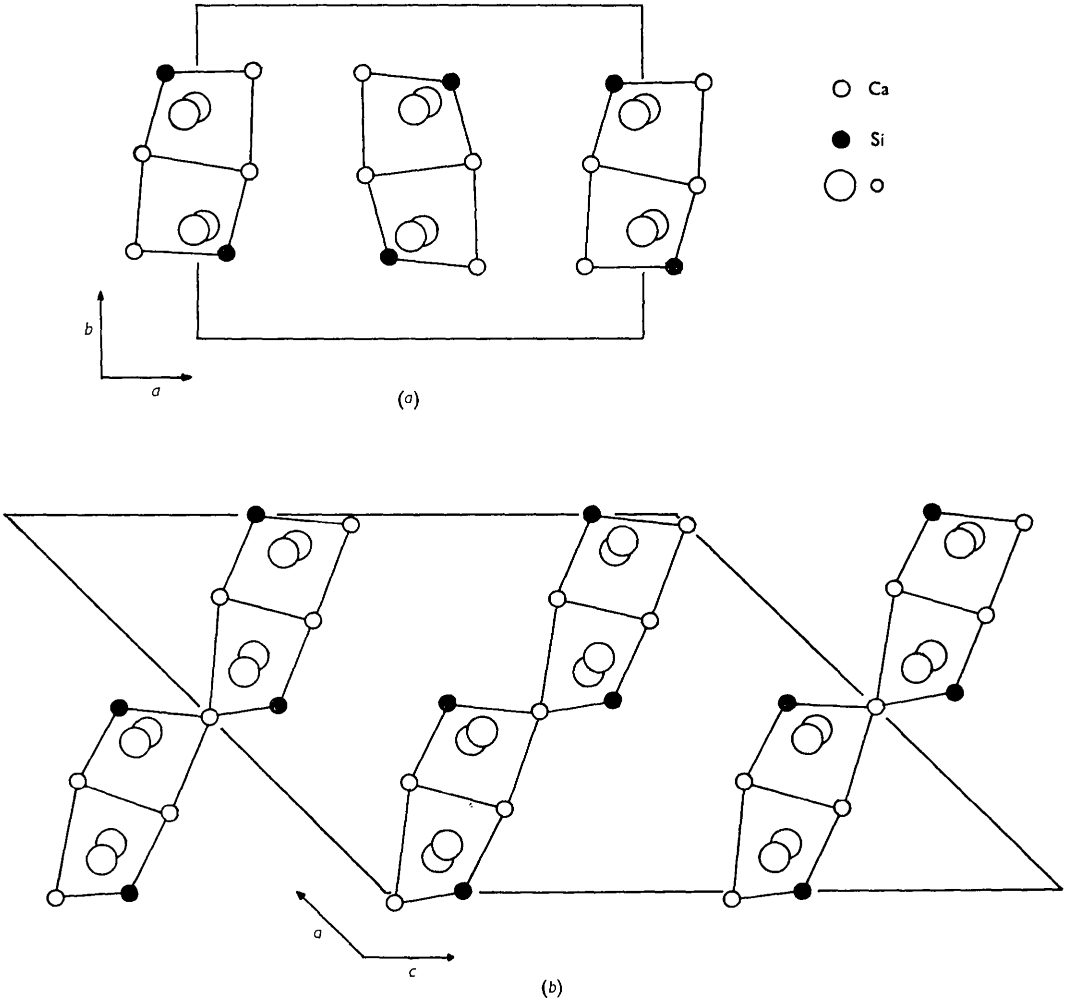

Fig. 7. (a) Arrangement of the $(Ca_4Si_2O_4)^{8+}$ strips in bultfonteinite. (b) Arrangement of the $(Ca_4Si_2O_4)^{8+}$ strips in afwillite. In this case they are joined together to form infinite sheets with composition $(Ca_3Si_2O_4)^{6+}$.

atoms is quite interesting, for although not taken into account when refining the structure, the final difference syntheses showed that these atoms were quite definitely anisotropic. The directions of maximum vibration are along [100] or [010] and in the (001) plane, but the vibrations of pseudo-symmetrically related pairs are not related by symmetry. Thus Ca_1, and Ca_4 vibrate along [010], while Ca_2 and Ca_3 vibrate along [100].

(c) *Silicon co-ordination*

Each silicon atom is bound to two oxygens and two 'hydroxyl' groups. The mean silicon–oxygen distance of 1·62 Å is slightly less than the mean silicon–'hydroxyl' distance of 1·67 Å, but the bond lengths are so scattered that it is questionable whether this difference is significant. The silicon atoms do not appear to have any anisotropic thermal motion, but the associated oxygens in 'hydroxyls' vibrate at right angles to their Si–O bonds in a way that suggests the tetrahedra are vibrating as a fixed unit about the silicon atoms, the axis of vibration being along [001].

(d) *The* 5·67 Å *repeat*

Along the *c*-axis run columns made of calcium and silicon coordination polyhedra sharing edges, and having composition $[Ca_3SiO_2]^{6+}$. These columns are joined in pairs to form strips of composition $[Ca_4Si_2O_4]^{8+}$, which are all parallel to (100) and placed in rows along [100] (Fig. 7(*a*)). Ideally the strips would be related by a *c*-glide plane, but the departure from ideal is only small. Exactly similar strips run along the 5·63 Å *b*-axis of afwillite, but they are joined together by sharing edges to give sheets of composition $[Ca_3Si_2O_4]^{6+}$ (Fig. 7(*b*)). These sheets are of infinite width and are parallel to the $(10\bar{1})$ planes. In afwillite the sheets are linked together almost entirely by Si–O–Ca bonds, with additional assistance from some of the hydrogen bonds. In bultfonteinite the strips are similarly linked together, but in addition the calcium atoms are linked by the fluorine atoms and water molecules. The role of the water molecules thus constitutes an important difference from afwillite; in afwillite they link calcium atoms in the same band, but in bultfonteinite they link calciums in neighbouring strips.

7. Discussion of the structure

Apart from the possible disorder of the hydrogens within a bond, this is a perfect structure. The 7-coordination of the calciums is quite usual. The oxygens and fluorines are each coordinated by four cations. None of the fluorines is directly linked to the silicon atoms, nor do they take part in F–H–O, or F–H–F bonds. Two of the neighbours of the silicons are $OH_{\frac{1}{2}}$ and the other two O^{2-}. The structural formula at our present state of knowledge, therefore, should be written as $Ca_4[SiO_2(OH_{\frac{1}{2}})_2]_2.F_2.2H_2O$. The water molecules are, however, combined in the structure in a way such that they cannot be removed without considerable re-arrangement of the rest. One feature of the structure is rather rare, namely, the existence of a short hydrogen bond which is not across a centre of symmetry.

It has been emphasized that the symmetry closely approaches monoclinic, and it is of interest to examine the factors which may influence the lowering of symmetry. All the pseudo-symmetrically related atoms have been found to have approximately the same co-ordination, with the exception of O_5 and O_6; these oxygens are linked across the pseudo *c*-glide plane by a short hydrogen bond. If the high symmetry were in operation then the hydrogen atom should be either translated by the *c*-glide to link the silicon tetrahedra in a continuous column along the *c*-axis, or removed completely to isolate the tetrahedra. But if the tetrahedra were linked in a continuous column, even by long bonds of 2·9 Å, the repeat distance in this direction could be no more than 5·4 Å. However, it has been shown that the repeat distance in this direction is defined by the columns of silicon and calcium co-ordination polyhedra, and so, from packing considerations, it is not possible to join the silicon tetrahedra by hydrogen bonds. If, on the other hand, the hydrogens were removed, then to preserve electrical neutrality an oxygen would have to be replaced by a fluorine or a hydroxyl, distributed at random between available sites. Since in fact the symmetry is lowered this is another line of evidence to support the view expressed earlier that the fluorine atoms are not distributed at random. In conclusion, it would seem that although the overall structure is determined by the arrangement of the $[Ca_3SiO_2]^{6+}$ units, the fine details are critically dependent on the role played by the hydrogen bonds.

I am indebted to Prof. N. F. Mott and Dr W. H. Taylor for provision of facilities, to Dr M. V. Wilkes for permission to use Edsac II, and to Dr H. D. Megaw for many helpful discussions during the development of this work, and for suggesting the problem initially. Finally I wish to express my thanks to the Department of Scientific and Industrial Research for financial support.

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