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The Structure of Afwillite, $Ca_3(SiO_3OH)_2.2H_2O$

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The structural formula of afwillite (empirically $3CaO.2SiO_2.3H_2O$) may best be written $Ca_3(SiO_3OH)_2.2H_2O$. Silicon occurs in isolated tetrahedra, but with OH instead of O at some of the corners. The calcium coordination is 6 or 7, and the rather irregular calcium polyhedra share edges with each other and with silicon tetrahedra in the y direction. There are hydrogen bonds which fall into two groups of mean length 2·52 Å and 2·72 Å. The environment of one water molecule is approximately tetrahedral, of the other a plane triangle.

The structure was determined by three-dimensional Fourier methods, and distances are generally correct to less than 0·05 Å. The accuracy is discussed, with special attention to the rate of refinement of a non-centrosymmetric structure. Electron distribution at the centre of the atom is well represented by $A \exp [-pr^2]$, where p is close to 10 for Ca, 9 for Si, and 8 for O; the temperature factor is small.

1. Introduction

The mineral afwillite is of practical importance because of its occurrence in cement, and of intrinsic interest for the part played in its structure by the hydrogen. The formula is more usually written $3CaO.2SiO_2.3H_2O$, but Parry & Wright (1925), in their original description, suggested that it contained OH groups. No structure of any hydrated calcium silicate (without other cations) has hitherto been determined, so that from the structural view-point no guess could be made as to the probable arrangement of the hydrogens. The evidence on the role of hydrogen obtained from thermal decomposition curves is inconclusive, and was not used in the determination of the structure.

Since no *a priori* assumptions are made about the location of the hydrogens, and they are omitted in calculating structure factors, the term 'oxygen atom' throughout this paper will be used comprehensively to include O^{2-}, OH^- and H_2O, without distinguishing between them, except where the context makes the distinction obvious.

The structure determination proceeds in two steps. In the first, the arrangement of calcium, silicon and oxygen atoms is derived. The coordination of the oxygens and the requirements of Pauling's electrostatic valency rule then suggest a scheme for the arrangement of the hydrogens; refinement of the structure to obtain exact interatomic distances gives the positions of hydrogen bonds, from which the distribution of the hydrogen atoms is confirmed and developed in more detail.

The experimental work and determination of the cell size and space group are described in § 2. The determination of the structure by three-dimensional Fourier methods follows in §§ 3 and 4. In § 5 the accuracy is considered in some detail. A description of the structure is given in § 6, first (in outline) in terms of calcium, silicon and oxygen atoms only, and then with reference to the location of the hydrogen atoms. The final section, § 7, deals with certain physical and chemical properties in relation to the structure.

2. Experimental and descriptive

Description of material

The afwillite used consisted of clear colourless crystalline fragments from two localities, Scawt Hill (Northern Ireland) and Kimberley (S. Africa), kindly provided by Prof. C. E. Tilley. The symmetry is monoclinic, and the crystals are elongated and striated parallel to the b axis, with a perfect cleavage parallel to $(10\bar{1})$ and an imperfect one parallel to (100) (referred to the axes used throughout this paper, which differ from those of Parry & Wright's original description, as explained below). The crystals are strongly pyro- and piezoelectric. The Scawt Hill crystals (Tilley, 1930), of length 1 mm. or less, were used for most of the work; the larger Kimberley crystals had identical unit-cell dimensions.

Experimental work

Unit-cell dimensions were found from oscillation photographs with Cu $K\alpha$ radiation.

The intensities of over 1600 reflexions were found from Weissenberg photographs taken with Mo $K\alpha$ radiation, three films interleaved with thin nickel foil being loaded simultaneously in the camera. The reflexions recorded comprised the $hk0$ and $h0l$ zones, and the first five layer lines given by rotation about the y axis. Oscillation photographs taken with Mo $K\alpha$ and Cu $K\alpha$ radiation were used to supplement the Weissenberg photographs. Appropriate methods of calculation were used in treating these incomplete experimental data; the inclusion of more reflexions would have greatly increased the labour.

Intensities were estimated visually, and corrected by the usual methods; no correction was made for absorption, which was treated as negligible.

Reflexions of the zone *hk*0 appeared on more than one photograph, and these were used to determine the standard deviation $\sigma(|F|)$ of the modulus of the structure amplitude $|F|$. If there are N observations,

$$[\sigma(|F|)]^2 = \frac{1}{N}\Sigma\left\{|F|\cdot\frac{1}{2}\frac{\delta I}{I}\right\}^2,$$

where I is the measured intensity and δI the deviation of an individual observation from the mean. The value of $\sigma(|F|)$ so derived was 2·5 (where $|F|$ is on an absolute scale referring to the whole unit cell, not to the unique volume); this is used in subsequent work to estimate the accuracy of the results.

The absolute intensities of several 00*l* reflexions ($l = 2, 4, 6, 8$) were measured with an ionisation spectrometer, using a section cut from the South African material. The author is indebted to Dr W. A. Wooster for his kindness in carrying out this determination. This information was of value in the preliminary stages of the work; at a later stage, statistical comparison of calculated and observed $|F|$'s provided a more accurate value of the scaling constant, the change being of the order of 10%.

Cell size and space group

The dimensions of the unit cell are:

$$a=16{\cdot}27\pm0{\cdot}01,\quad b=5{\cdot}632\pm0{\cdot}004,\quad c=13{\cdot}23\pm0{\cdot}01\ \text{Å};$$
$$\beta=134^\circ\ 48'\pm2'\,.$$

(Cu $K\alpha$: $\lambda=1{\cdot}5405$ Å).

Space group *Cc*; number of formula units per cell 4. Calculated density, 2·643±0·005 g.cm.$^{-3}$; density recorded by Parry & Wright, 2·630 g.cm.$^{-3}$.

The axes of reference used here, and throughout this paper, are not those in the original description by Parry & Wright, which would have led to the space group *Ia*, an unconventional formulation and less convenient to handle mathematically. (The space group derived in the short note by Gottfried (1933) is quite incorrect.) The new axes are such that the y axis is unchanged, the old z axis is retained with a reversed sign, and the old x axis is the short diagonal of the (010) face of the new unit cell. The transformation matrix relating the old axes x', y', z' to the new axes x, y, z, is:

$$\begin{array}{cccc} & x & y & z \\ x' & 1 & 0 & 1 \\ y' & 0 & 1 & 0 \\ z' & 0 & 0 & \bar{1} \end{array}$$

The origin is chosen to lie in the *c*-glide plane.

3. Determination of approximate structure

Special absences

Besides the space group absences, *hkl* absent for $h+k$ odd, *h*0*l* absent for h or l odd, there are certain systematic weaknesses. It is noticeable that for small k most reflexions with l odd are weak or absent; there are a few exceptions for which h and l are also small. On the other hand, with $k = 5$ it is the reflexions with even l that are weak.

These special features can be interpreted quite simply. First, if all reflexions with l odd were zero, the c axis would be halved; this would result if, in the true cell with space group *Cc*, all the y parameters were zero. Since the intensities in fact increase with k, most of the atoms must have a small y parameter. Secondly, since for $k = 5$ the reflexions with even l are zero, it follows from the expression for the structure factor that $\cos 2\pi.5y = 0$, and hence that $y = 0{\cdot}05$. Thus a second approximation suggests that the heavier cations are displaced from the plane $y = 0$ by about 0·05.

The few strong reflexions with l odd and k small, since they all occur at fairly small θ, must be due to oxygen atoms. Hence, while the cations and probably some oxygen atoms lie very near to the planes $y = 0$ and $y = \frac{1}{2}$, some oxygen atoms lie between these planes.

In considering the contents of the following sections, it will be useful to bear in mind that, in projection on (010), the repeat unit has dimensions $\frac{1}{2}a$, $\frac{1}{2}c$. It is particularly important to emphasise the c halving, which is retained in three dimensions in the idealised structure, where the atoms either have y parameters 0 or $\frac{1}{2}$, or occur in pairs at $x, \pm\frac{1}{4}, z$.

Patterson syntheses

Patterson projections $P(u, w)$ and $P(u, v)$ were constructed. The latter showed an arrangement of vector peaks lying nearly but not quite on $v = 0$, together with weaker peaks near $v = \frac{1}{4}$ (see Fig. 1). This simple pattern is obviously derived from an arrangement of electron-density peaks which satisfies the same de-

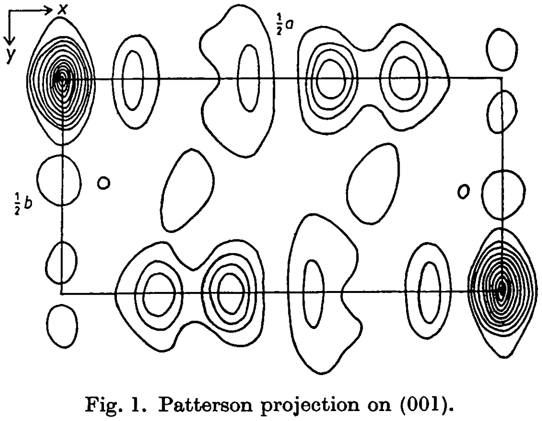


Fig. 1. Patterson projection on (001).

scription, and which is in fact identical with the atomic arrangement described in the last paragraph. The $P(u, w)$ projection showed discrete peaks, but attempts to solve it failed. It was therefore necessary to use three-dimensional data.

A bounded projection (Booth, 1945) was found the most helpful way of using the data. While bounded electron-density projections have been used by various authors, bounded Patterson projections are less common. Their meaning is not so easy to visualize, and hence it is desirable to consider the present example in some detail.

If the structure consists of point atoms with all y parameters 0 or $\frac{1}{2}$, it is obvious that the projection $P(u, w)$ is the sum of the two superimposed sections $P(u, 0, w)$ and $P(u, \frac{1}{2}, w)$. If the y parameters are small but not zero, a bounded projection $P_{-\frac{1}{4}}^{+\frac{1}{4}}(u, w)$ displays all the interatomic vectors in a single layer of the structure near $y = 0$. If no atom has a y parameter greater than 0·125, all the peaks will appear, and the unit cell will be halved in the c direction; but if some parameters are greater than this, certain peaks will be absent and the two halves of the cell will not be identical; to obtain the complete display of vectors we must superimpose the two halves. If the atoms are not point atoms but spheres whose effective radius is, say, 0·5 Å, (i.e. 0·1b) we have an intermediate case; even a moderately small difference of y parameters will exclude appreciable parts of the atoms from the vector region surveyed, and hence lower the height of the peak. Thus the unit cell shows only a pseudo-halving, the positions but not the heights of the peaks being the same in the two halves. For simplifying the interpretation of $x z$ parameters, we require the average of the two halves; this is achieved by synthesizing only the terms with even l (compare the 'hypothetical disorder' method of Harker (1948) for F syntheses). This gives

$$P(u,v,w)+P(u,v,\tfrac{1}{2}+w)$$
$$=\frac{2}{V}\sum_{h}\sum_{k}\sum_{l_{\text{even}}}|F|^2\cos 2\pi(hu+kv+lw)\,.$$

Since this is true for any section at height v it is true for the bounded projection.

Two bounded projections were constructed. The first had limits $v = \pm\frac{1}{4}$, and was summed only over the terms of even l; this was used for finding x and z parameters. The second had limits $v = \pm\frac{1}{12}$, and was summed over all l's; this was used for finding y parameters, the narrower limits of the slice emphasising the effect of different heights.

Fig. 2 shows the bounded projection,

$$\tfrac{1}{2}\{P_{-\frac{1}{4}}^{+\frac{1}{4}}(u, w)+P_{-\frac{1}{4}}^{+\frac{1}{4}}(u, \tfrac{1}{2}+w)\}\,.$$

It is noticeable that the strong peaks lie on the intersections of a grid formed by traces of the planes $80\bar{2}$, $8,0,\overline{12}$ (referred to the true cell). This provided the key to the solution. One layer of the pseudo-cell $(a, b, \frac{1}{2}c)$ contains one formula-unit, the second layer being identical with the first (though displaced laterally) and therefore making an identical contribution to the Patterson projection. Neglecting the oxygens, and taking calcium and silicon as equal, there are five cations to locate, giving ten vector peaks. There are forty grid intersections in the pseudo-cell, and we may choose, temporarily, a unit cell in which they are arranged in a one-dimensional repeat (see Fig. 3). If all the vector peaks lie on grid intersections, so do the cation peaks. Hence there are five cations to be distributed among forty equally spaced sites: it is the problem of five guests at a round table with forty chairs. It is not necessary to determine all possible arrangements, because certain of them are excluded; for example, since there are strong peaks on the 3rd and 12th intersections in Patterson space, there must be atoms separated by 3 and 12 steps in real space, and since the 4th intersection is empty, no two atoms can be separated by 4 steps.

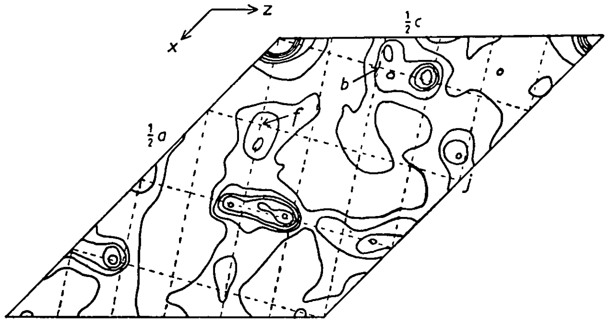


Fig. 2. Patterson bounded projection on (010), with limits $y = \pm\frac{1}{4}$, constructed from terms with l even.

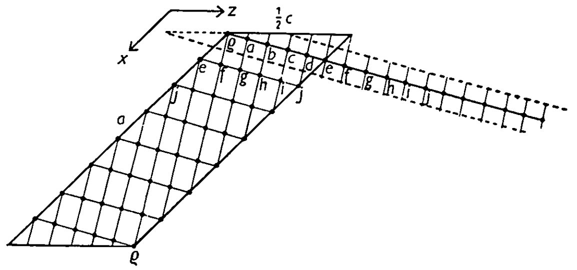


Fig. 3. Relation of (010) projection of pseudo-cell $a\times\frac{1}{2}c$ to 'one-dimensional' cell of grid carrying Patterson peaks.

There are enough clear-cut restrictions of this kind to leave only twelve possible arrangements. If we add the conditions that the peaks marked b and f in Fig. 2 cannot be cation–cation (both the heights of these peaks and also their vector distances are too small for such an interpretation to be plausible) we are left with only one possible cation arrangement. Small shifts of the atoms from the exact grid intersections improve the agreement with observed peak positions.

One of the ten peaks used, that at *j*, is rather surprisingly weak. If it is identified as Si–Si, the relative heights of all the other nine main vector peaks are in satisfactory agreement.

One rather unexpected feature of this arrangement is its pseudo-centre of symmetry, a feature which persists in the completed idealised structure with *y* parameters zero, as long as the hydrogen atoms are neglected. An examination of the final atomic parameters shows just how small are the departures from centrosymmetry ($C2/c$), especially for the cations.

It remains to place the oxygen atoms. The peaks *b* and *f*, at a distance 2·4 Å from the origin, suggested Ca–O vectors, and from this identification the rest followed unambiguously. When two oxygen atoms were placed as required by these vectors, they lay at a distance of about 1·6 Å from the silicon atoms and formed part of a tetrahedron round them, which could be completed by inserting two more oxygen atoms with $y = \pm\frac{1}{4}$. The two remaining oxygen atoms went into vacant spaces near a calcium atom. Fig. 4. shows the structure, with the atoms given their usual radii.

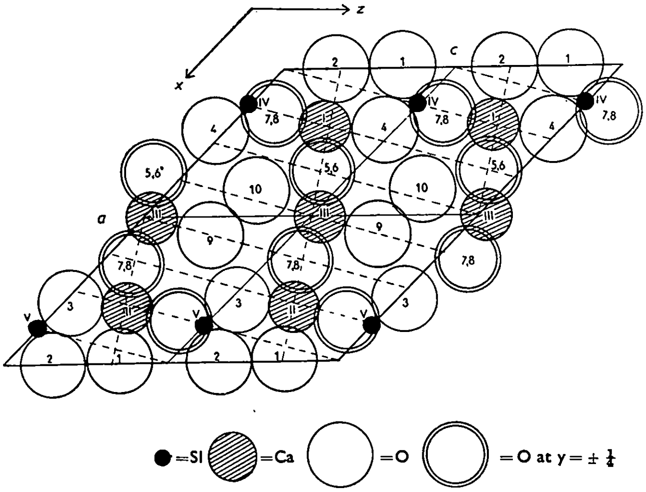


Fig. 4. Projection of idealised structure on (010), showing packing of atoms, with radii drawn to scale. All atoms are at $y = 0$, except those represented by double circles, which are at $y = \pm\frac{1}{4}$; atoms at $y = \frac{1}{2}$ are omitted for clarity. Broken lines show part of the same grid as in Fig. 3.

The correctness of the structure seemed obvious even at this stage, because of its self-consistency and the way in which it satisfied the rather exacting space and coordination requirements; and it was confirmed by the neat way in which the layers of atoms at $y = \frac{1}{2}$ and $y = \frac{3}{4}$ stacked above those at $y = 0$ and $y = \frac{1}{4}$. All the calcium atoms, in this approximation, have six oxygen neighbours. A fuller description of the structure, after subsequent refinement, comes later in the paper.

Coordinates of atoms

The *x*, *z* coordinates of the cations were estimated as closely as possible from the Patterson, and those of the oxygen atoms from consideration of interatomic distances and the (assumed) regularity of Si–O tetrahedra. Intensities of *h*00 and 00*l* reflexions calculated from these were at first disappointing, but very small displacements of the atoms gave much improved agreement with observation. Further refinement was made by varying the atomic coordinates within limits set by the closest reasonable approach of any two atoms, and comparing calculated and observed intensities of 25 important low-angle *h*0*l* reflexions.

The *y* coordinates were estimated from the bounded projection $P^{+\frac{1}{12}}_{-\frac{1}{12}}(u, w)$. Assuming that vector peaks belonging to like pairs of atoms differ in height only because of differing $y_1 - y_2$, and that for the cations $|y| \approx 0{\cdot}05$ (as estimated above), the sign of *y* for these was at once deducible; more detailed correlation of peak height with *y* difference, by trial-and-error methods, gave separate estimates of *y* for all the cations and some of the oxygens, those which remained indeterminate being left at $y = 0$.

At this point the main features of the structure were known, but the interatomic distances seemed to have random variations of up to 0·2 Å, which obscured the more interesting points of detail, and in particular prevented any deductions about the positions of the hydrogen atoms.

4. Accurate location of peaks

Preliminary F synthesis

Before embarking on a complete electron-density synthesis, an approximate synthesis was made as a check. Reflexions within a reciprocal sphere of radius 0·5 were used, and modified by a large artificial temperature factor. The *x*, *z* coordinates were found from multiple sections (Booth, 1945), the *y* coordinates from line syntheses through *x*, *z* peaks. The general atomic arrangement was confirmed, but there were still large diffraction effects. Interatomic distances calculated from the new parameters were reasonable, with the exception of those involving three oxygen atoms lying at some distance from the sections examined; the parameters of these were modified in accordance with radius requirements, and later work justified this. Even so, the approach of the parameters towards their final value brought about by this synthesis was not very marked.

One feature of the synthesis may be noted here. The crystallographically independent atoms may be grouped into two sets, close to the $y = 0$ and $y = \frac{1}{4}$ planes respectively. If they were exactly on these planes, we should have two independent syntheses, reflexions with even *l* contributing only to the section at 0, those with odd *l* only to the section at $\frac{1}{4}$. Since the atoms are slightly displaced from these planes, there will be some interaction, but improvements in the coordinates of one set will not lead to rapid convergence of the other, and moderate errors in one set will not seriously affect the accuracy of the other. The set at $y = \frac{1}{4}$ were less accurately located by trial-and-error methods in the first instance, and refined less rapidly, than those at $y = 0$.

Atomic scattering factor and natural temperature factor

The Hartree f values at absolute zero were used for calculating phase angles and structure amplitudes, F_z, corresponding to absolute zero. By comparison of F_o and F_z for reflexions near the limiting value of $(\sin\theta)/\lambda$ used for the synthesis, it was estimated that in the natural temperature factor B has the value 0·4 Å^2, assumed the same for all atoms. A statistical analysis of intensities by Wilson's method (1942) agreed with this, and showed that the difference between this room-temperature Hartree f value and the Bragg & West (1929) empirical f values lay within the limits of experimental error.

It is interesting to notice the low value of B, which was expected from the fact that fairly-high-angle reflexions with Mo $K\alpha$ had still appreciable intensity. For comparison, for rock salt at room temperature B is about 1·5 Å^2, for organic compounds about 2·5 Å^2.

Complete F synthesis

The complete F synthesis was made using all reciprocal-lattice points within a region bounded by the sphere of radius $s = 1{\cdot}25$ and the pair of planes $y^* = \pm 0{\cdot}75$ (with $\lambda = 0{\cdot}707$ Å). This gave about 1760 independent points, of which about 1300 were non-zero. Intensities of reflexions outside this region were appreciable, because of the small natural temperature factor; to reduce diffraction effects, an artificial temperature factor was applied with $B' = 1{\cdot}0$ Å^2. Subsequent work suggested that a larger value of B' might have been used with advantage.

Phase angles were calculated from the trial parameters and used with the $|F|$'s to give coefficients for the synthesis.

The synthesis was done by combining separate two-dimensional syntheses of each layer of reciprocal-lattice points, i.e. syntheses using all terms of the same k (Clews & Cochran, 1949). The zero layer and five others were available. The work was done on a Hollerith machine, by a punched-card modification of the Beevers–Lipson method (Hodgson, Clews & Cochran, 1949), using 6° intervals.

The final synthesis may be written

$$\varrho(x, y, z) = \frac{1}{V} \sum_{k=-\infty}^{k=+\infty} (J_{kxz} \cos 2\pi ky + j_{kxz} \sin 2\pi ky)\,,$$

where J_{kxz}, j_{kxz} are obtained from the two-dimensional syntheses, using terms of even and odd l respectively. The section at $y = 0$ is obtained by algebraic addition of the even terms:

$$\varrho(x, 0, z) = \frac{1}{V} \sum_{k=-\infty}^{k=+\infty} J_{kxz}\,.$$

This section is shown in Fig. 5. Line sections parallel to the y axis were calculated at several points near each peak.

The contours in the diagram were inserted by visual interpolation between the 6° points. They were sufficiently accurate to show that the displacements of the atoms were small, but not accurate enough to give the exact positions, and a better method of interpolation had to be devised.

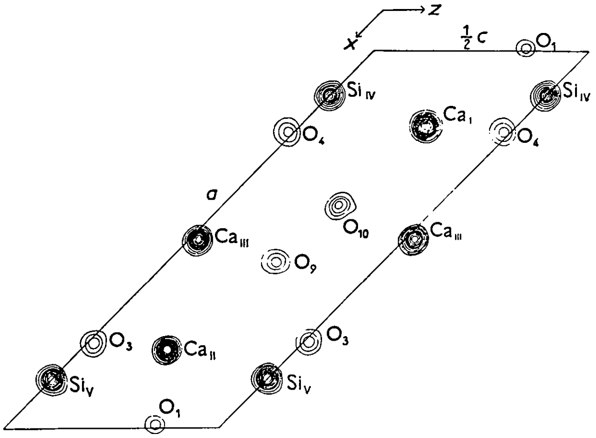


Fig. 5. Section parallel to (010), at $y = 0$, of the electron density distribution. Contours drawn at intervals of 5 e.Å^{-3}.

Interpolation method of locating peaks

It was assumed, following Booth (1946), that the electron density near the peak is represented by $A \exp[-pr^2]$, where A and p are constants. This was tested and found to hold for the central region of any atom, within the accuracy expected from a knowledge of the standard deviation $\sigma(|F|)$. The constant p had to be deduced empirically, and was found to be the same for atoms of the same kind in a given direction, but to differ according to whether the electron-density distribution was examined in or perpendicular to the plane (010). This is not surprising; for a Gaussian distribution, p is a measure of the half-breadth of the peak, which must depend not only on the amplitude of thermal vibration but also on the diffraction broadening brought about by series termination. Though p has thus no absolute significance, it is of interest to note its values, which are recorded in Table 3; the range of deviation in each case is about ±1. They may be compared with the values of about 5 recorded for organic compounds (Booth, 1946).

Using the relation in the form $\log_e \varrho = \text{const} - pr^2$, a graphical method of interpolation was devised which retained all the accuracy inherent in the synthesis. In each case the peak position was obtained as the mean of three independent intersections of pairs of lines.

The parameters obtained from this synthesis, corrected as explained in the next section, were used to

Table 1. *Atomic parameters*

Atom	Parameters derived from first full synthesis			Parameters derived from second full synthesis			Displacement by second full synthesis (before correction) (Å)		Final parameters, after Booth correction		
	x/a	y/b	z/c	x/a	y/b	z/c	In (010)	$\perp$ (010)	x/a	y/b	z/c
Ca_{I}	0·1968	0·0312	0·2892	0·1968	0·0352	0·2920	0·025	0·016	0·1968	0·0348	0·2920
Ca_{II}	0·7998	0·0478	0·2083	0·8012	0·0478	0·2093	0·040	0·004	0·8012	0·0485	0·2093
Ca_{III}	0·5022	0·0408	0·0287	0·5043	0·0357	0·0295	0·015	0·015	0·5037	0·0362	0·0288
Si_{IV}	0·1175	0·0628	0·9993	0·1185	0·0445	0·0013	0·020	0·003	0·1175	0·0442	0·0007
Si_{V}	0·8713	0·9742	0·0013	0·8698	0·9737	0·0005	0·010	0·002	0·8692	0·9753	0·9982
O_1	0·9923	0·9223	0·3450	0·9933	0·9178	0·3448	0·015	0·003	0·9918	0·9152	0·3410
O_2	0·0012	0·8872	0·1543	0·9985	0·9088	0·1540	0·025	0·081	0·9992	0·9045	0·1538
O_3	0·7842	0·9727	0·0232	0·7822	0·9683	0·0200	0·035	0·004	0·7837	0·9695	0·0207
O_4	0·2085	0·0487	0·9798	0·2185	0·0537	0·9902	0·090	0·015	0·2158	0·0545	0·9888
O_5	0·3363	0·7225	0·3918	0·3312	0·7325	0·3905	0·025	0·029	0·3312	0·7352	0·3905
O_6	0·3563	0·2800	0·4212	0·3620	0·2823	0·4332	0·055	0·008	0·3630	0·2820	0·4333
O_7	0·1562	0·2530	0·1025	0·1483	0·2613	0·0987	0·040	0·028	0·1473	0·2667	0·0983
O_8	0·1402	0·8340	0·0810	0·1335	0·8263	0·0775	0·090	0·001	0·1318	0·8125* (0·8257)	0·0778
O_9	0·5653	0·9998	0·2612	0·5645	0·9822	0·2598	0·005	0·051	0·5630	0·9795	0·2583
O_{10}	0·4102	0·9755	0·2683	0·4113	0·9675	0·2643	0·025	0·018	0·4120	0·9693	0·2647

* See text.

calculate a second refinement in exactly the same way. The final parameters, together with those at certain intermediate stages, are shown in Table 1.

Correction for incomplete refinement

Cruickshank (1950*a*) showed that in the final stages of refinement of a structure where all the *F*'s are complex the displacements of atomic positions resulting from the *F* synthesis should on the average be doubled to obtain a better approximation to the correct parameters. He suggested that this treatment would be legitimate if the average displacement, for structures of atoms with $p \approx 5$, was less than 0·1 Å; this limit (chosen somewhat arbitrarily as a guide) should increase with *p*. Luzzati (1951) has given an alternative derivation of the same result. Shoemaker, Donohue, Schomaker & Corey (1950) used the method independently for threonine, with a modified factor of 1·8 instead of 2 to correct for the fact that, as their point-group is 222, certain zones have real *F*'s.

Afwillite has the point group *m*, so that only 0*k*0 reflexions have real *F*'s, and they are negligible in number compared with the *hkl*'s. On these grounds Cruickshank's original factor of 2 should apply. Against this, the existence of a strongly marked pseudo-centre of symmetry suggests that the phase angles (at least of the low-order reflexions) are changing more slowly with change of parameter than would be the case in a completely random structure, and hence that 2 is an overestimate. Nevertheless it was taken as a reasonable approximation in deriving the second synthesis. A distinction was made, however, between the sets of atoms lying near $y = 0$ or $\frac{1}{2}$, and those lying near $y = \frac{1}{4}$ or $\frac{3}{4}$. The latter were not as accurately located as the former, for reasons explained above, and their parameters as given by the double shift were therefore slightly modified in accordance with steric considerations.

The results of the second synthesis can be used to examine the validity of this treatment and the numerical value of the factor. Shoemaker *et al.* (1950) emphasised the point that 'the double-shift is no substitute for repeated Fourier syntheses but ... an aid to more rapid convergence'. The present work illustrates this. If the rule were exact rather than statistical, and the factor correctly chosen, then the two sets of parameters derived by application of the rule to the first and second syntheses should be identical. Examination showed that no one factor was consistently best for all coordinates of all atoms. In Table 1 two such sets are shown, for which the factor is 1·8 (subsequently selected as best).

To find the best value of the factor, we may compare the difference between the two derived positions of one atom with the distance moved by the same atom as a result of the first synthesis, the same factor being used throughout. The results (evaluated for the root-mean-square displacements of atoms of the same kind) are shown in Table 2. A small value for the ratio of second displacement to initial displacement indicates that refinement is proceeding rapidly. Judged thus, it is clear from the table that a double shift is better than a single shift; there is little to choose between factors 2·0 and 1·8 from these figures, but consideration of the sign of individual parameter changes leads to a slight preference for 1·8. These conclusions are comparable to those reached by Shoemaker *et al.*

Table 2. *Root-mean-square displacements at different stages of refinement*

Col. 1. Initial displacement, in Å, brought about by first synthesis.
Col. 2. Second displacement: distance in Å between atomic positions derived from first and second synthesis.
Col. 3. Ratio of second displacement to initial displacement.

	Factor 2			Factor 1·8			Factor 1·5			Factor 1·0		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
Ca	0·098	0·046	0·47	0·089	0·036	0·41	0·074	0·037	0·50	0·053	0·053	1·00
Si	0·060	0·026	0·46	0·054	0·028	0·52	0·045	0·024	0·44	0·030	0·033	1·10
O near planes $y=0, \frac{1}{2}$	0·310	0·104	0·33	0·280	0·092	0·33	0·263	0·092	0·35	0·155	0·141	0·93
O near planes $y=\frac{1}{4}, \frac{3}{4}$	0·305	0·103	0·34	0·274	0·104	0·38	0·229	0·110	0·48	0·156	0·131	0·84

(1950), but apply to a structure at a much earlier stage of refinement. Examination of the intermediate and final parameters of O_{5-8} showed that on the whole a uniform application of the doubled shift would have given somewhat more rapid refinement than the attempt to use steric considerations.

Though the rule is not exact, it is the best available means of correcting for incomplete refinement.

Correction for diffraction

This was made by means of an F_c synthesis, as suggested by Booth (1946). An intermediate set of parameters was used rather than the final set, for the sake of practical convenience at the expense of some degree of accuracy; this point is referred to in § 5. The F_c's were multiplied by an exponential factor, $\exp\,[-(B+B')\,(\sin\theta)/\lambda]^2$, with $B' = 1{\cdot}0$ Å^2 as in the F_o synthesis, and $B = 0{\cdot}4$ Å^2 to correct for the natural temperature factor. The synthesis was carried out in the same way as the F_o synthesis.

Final parameters

The parameters, after correction for diffraction, and for incomplete refinement using a Cruickshank factor of 1·8, are listed in the last column of Table 1. For O_8, the y parameter thus derived is given in brackets, but the modified value standing first has been adopted, because it brings the atom to a position where its distances from its neighbours are more consistent. This atom belongs to the slow-refining set, and has suffered the largest displacement of any atom in the final synthesis. The modification requires only a 10% change in the magnitude of the displacement, together with a slight change of direction, and none of the conclusions drawn in what follows would have been altered if it had not been made.

5. Accuracy

It is usual to calculate as an index of reliability the quantity

$$R = \Sigma\big||F_o|-|F_c|\big| \div \Sigma|F_o|.$$

For the trial structure, R has the value of 0·33; for the parameters used in the final refinement, it is reduced to 0·245. It is rather doubtful, however, how far this index is really useful for assessing absolutely either the trustworthiness or degree of refinement of a structure. Fortunately there are other methods available for estimating the error.

The standard error in electron density, $\sigma(\varrho)$, may be estimated as suggested by Cruickshank (1949), taking $\sigma(|F|)$ to be the standard deviation in $|F_o|$. Assuming $\sigma(\varrho)$ to be entirely due to random errors in the $|F_o|$'s, we have

$$\sigma(\varrho) = \frac{4\sigma(|F|)}{V}\,\{\tfrac{1}{2}n\}^{\frac{1}{2}}\,,$$

where n is the number of reciprocal points in one quadrant of reciprocal space, the unique region examined. Substituting actual values,

$$\begin{aligned}\sigma(\varrho) &= 4\times 2{\cdot}5\times(880)^{\frac{1}{2}}/860\\ &= 0{\cdot}35\ \text{e.Å}^{-3}.\end{aligned}$$

For determining $\sigma(r)$, the standard error in the peak position, we are dependent on the estimates of p, made as described in § 4. Using these, there are three independent methods of estimating $\sigma(r)$.

(1) The first method assumes that the only sources of error are random errors in the $|F_o|$'s. Booth (1946, equation 5·18) gives an expression for $\sigma(r)$ for an orthorhombic centrosymmetric crystal for which all reciprocal points within a sphere of radius 2 have been included in the synthesis. In the present case the crystal is monoclinic, non-centrosymmetric, and the volume of reciprocal space contributing to the synthesis may be taken (to a reasonable approximation) as a cylinder of radius $s = 1{\cdot}25$, height $y^* = 0{\cdot}75$. The expressions for the error then become:
in the (010) plane,

$$\sigma(x) = \frac{2}{Np_1^{\frac{5}{2}}}\,\frac{\sigma(|F|)}{V^{\frac{1}{2}}}\sin\beta\,\frac{\pi^3}{\sqrt{2}}\,\frac{s^2y^{*\frac{1}{2}}}{\lambda^{\frac{5}{2}}} = \frac{8{\cdot}5}{Np_1^{\frac{5}{2}}}\,,$$

perpendicular to the (010) plane,

$$\sigma(y) = \frac{2}{Np_2^{\frac{5}{2}}}\,\frac{\sigma(|F|)}{V^{\frac{1}{2}}}\,\frac{2}{\sqrt{3}}\,\frac{\pi^3}{\sqrt{2}}\,\frac{sy^{*\frac{3}{2}}}{\lambda^{\frac{5}{2}}} = \frac{8{\cdot}3}{Np_2^{\frac{5}{2}}}\,,$$

the factor 2 in the numerator arising from the fact that the structure is non-centrosymmetric. The numerical values substituted here are: $\sigma(|F|) = 2{\cdot}5$, $V = 860$ Å^3, $\lambda = 0{\cdot}707$ Å. N may be considered as defined by the equation

Table 3. *Constants of atom, derived from synthesis, and errors of atomic coordinates*

Atom	Peak density (e.Å^{-3})	N	p_1 In (010)	p_2 $\perp$ (010)	Error from (1) (Å)			Error from (2) (Å)			Booth correction (Å)		
					$\sigma(x, z)$	$\sigma(y)$	$\sigma(r)$	$\sigma(x, z)$	$\sigma(y)$	$\sigma(r)$	$\varepsilon(x, z)$	$\varepsilon(y)$	$\varepsilon(r)$
Ca	69·6	17·5	9·7	5·2	0·002	0·008	0·009	0·008	0·011	0·014	0·004	0·003	0·005
Si	49·5	13·5	9·0	5·2	0·004	0·010	0·011	0·013	0·015	0·020	0·019	0·007	0·021
O*	19·9	6·2	8·2	4·9	0·010	0·025	0·027	0·034	0·041	0·053	0·022	0·015	0·026

* Excluding O_9 and O_{10} (see § 6).

$$\varrho_{\text{peak}} = Np_1\left(\frac{p_2}{\pi^3}\right)^{\frac{1}{2}}$$

(corresponding to Booth's expression $N(p/\pi)^{\frac{3}{2}}$ for a spherical atom). If the electron-density distribution in the atom is Gaussian at all points, and not merely near the peak, N gives the total number of electrons in the atom; this is discussed later. Table 3 gives the values of N and p derived from the synthesis, and the errors calculated from them. (Note that $\sigma(x, z)$ is the error of displacement in the (010) plane, and is $\sqrt{2}.\sigma(x)$; $\sigma(r)$ is the error of displacement in three dimensions.)

(2) Secondly, the error can be estimated from the expression

$$\sigma(x) = -2\sigma\left(\frac{\partial\varrho}{\partial x}\right)\Big/\left(\frac{\partial^2\varrho}{\partial x^2}\right)_{\text{peak}}.$$

The factor 2 is required in the numerator (Cruickshank, 1950*b*) to allow for the fact that in a non-centrosymmetric structure errors in the phase angles as well as direct errors in the $|F|$'s affect the final position of the atom. In the present case, the pseudo-symmetry may be allowed for by replacing 2 by 1·8, the factor found empirically for the refinement (§ 4). (This might also have been done in the expression for random errors, under (1), but the difference is small.) Cochran (1951) has shown that $\sigma(\partial\varrho/\partial x)$ may be evaluated by determining the slope of the background resulting from the synthesis, and this has the advantage of taking account of all sources of error, since they all give rise to background fluctuations: systematic errors in $|F_o|$, diffraction effects, and errors due to incomplete refinement, as well as the random errors considered in (1). The denominator, if the atom has a Gaussian distribution near the peak, simplifies to $-2p\varrho_{\text{peak}}$.

Surveys of the background remote from any atom gave

$$\sigma(\partial\varrho/\partial x) \approx \sigma(\partial\varrho/\partial y) \approx \sigma(\partial\varrho/\partial z) \approx 4{\cdot}4 \text{ e.Å}^{-4}$$

(as compared with 5·3 e.Å^{-4} from the first synthesis). This may be slightly over-estimated, since the regions most remote from all atoms were not conveniently available for survey, and thus the effect of diffraction ripples may be unduly large. However, it may be taken as yielding an upper limit for the error in peak position.

The values of $\sigma(x,y)$ and $\sigma(y)$ thus calculated are given in Table 3. It is seen that they are about double those obtained from (1), which takes account of experimental errors only. For comparison, the errors due to diffraction may be represented by the root-mean-square displacements required by the Booth correction, which are also given in the table. These also are roughly half the total errors derived from (2), except for silicon, where the high value of the Booth correction may be due to the more symmetrical environment of these atoms; there is approximately a mirror plane of symmetry through them parallel to (010) relating their four nearest neighbours, so that the diffraction effects of these, in the (010) plane, are not random. It is in this plane that the diffraction correction is large.

(3) The third line of evidence is empirical, and based on the graphical interpolation method described in § 4. It was found in using this that the position of the parabola $y = pr^2$ to fit the curve of $\log_e \varrho$ versus r for any line section could be determined to within $\pm 0{\cdot}01$ Å for the oxygens, and rather better for the cations, these limits being set by the random scatter of the values of $\log_e \varrho$. Since each peak position was the mean of three independent determinations in the (010) plane, the resultant value of $\sigma(x)$ is 0·006 Å, of $\sigma(r)$ 0·013 Å. This covers only random errors, and does not include diffraction errors or errors of incomplete refinement.

Errors due to incomplete refinement are included in (2), but they need further consideration. Another synthesis would ideally have been desirable, but the labour required was prohibitive. However, it is possible to estimate the limits of error of the present approximation by comparison of the displacements brought about by the two successive syntheses. The ratio of these is given in Table 2, column 3 (factor 1·8). For cations it is about 0·45, for oxygens about 0·33; the difference may perhaps be due to the relatively greater effect of other errors on the small displacement of the cations. Assuming that the same reduction would hold for a further synthesis, the average value of the expected displacements can be deduced from those brought about by the final synthesis, which are listed individually in Table 1; this gives a root-mean-square value for the cations of 0·02 Å, for the oxygens of 0·03 Å. (Though the table suggests that this holds true for oxygens of the slow-refining set O_{5-8} as well as the others, the use of steric considerations at an intermediate stage in placing these atoms means that the evidence for them is not so clear-cut.)

These remaining errors of incomplete refinement are of the same order of magnitude as the random errors at a single point, and it seems legitimate to abandon the distinction between them and to take them as measuring the total error of the resulting structure. The error estimated by (2) is an over-estimate, not relevant to the final result, because it represents the state of affairs before either the correction for incomplete refinement or the Booth diffraction correction had been made. The Booth correction is imperfect in that it was not made using the final parameters (as mentioned in § 4), but since its magnitude is in any case less than the errors due to incomplete refinement, the labour involved in a recalculation would not have been justified.

6. Description of the structure

The structure is built from isolated silicon tetrahedra, linked together through edges and corners by calcium polyhedra to form a fairly closely packed arrangement. It will be shown in the next section that some of the oxygens linked directly to silicon must be identified as OH's; for the time being, we do not attempt to distinguish.

The general arrangement is most easily visualised by considering an idealized structure with all y parameters $0, \frac{1}{2}, \frac{1}{4}$ or $\frac{3}{4}$. In this the calcium atoms are 6-coordinated, the neighbours of Ca_{III} being arranged at the corners of an octahedron, those of Ca_{I} and Ca_{II} at the corners of a trigonal prism. The silicon tetrahedra share edges parallel to y with the Ca_{I} and Ca_{II} polyhedra; each of these shares another vertical edge with a Ca_{III} polyhedron. There is thus a continuous line of shared edges parallel to the y axis; this is morphologically the fibre axis of the crystal.

In a single layer parallel to (010), the two silicon tetrahedra and the Ca_{I} and Ca_{II} polyhedra sharing vertical edges with them form a continuous belt running through the structure in the [001] direction. Two belts are linked by Ca_{III} polyhedra. Fig. 6 shows (with heavy lines) the projection of such a layer. The second layer, the lower half of the cell (thin lines in Fig. 6), shares the oxygen atoms at $\frac{1}{4}$, and the upper layer is superposed on it so that its Ca–Si belt lies above the inter-belt space of the lower layer. The Ca_{I} and Ca_{II} polyhedra share horizontal edges with Ca_{III} polyhedra of the adjacent layer.

The cleavage plane $(10\bar{1})$ cuts through no Si–O bonds or shared edges of polyhedra. It breaks only few relatively weak Ca–O bonds, never more than one per calcium atom, in addition to hydrogen bonds (discussed later). Its trace is shown by the dot-dash line in Fig. 6. The weak cleavage (100) (not shown) breaks slightly more Ca–O bonds, in pairs involving a common calcium atom.

The true structure is somewhat distorted from this ideal version. Qualitatively the chief effect is that the calcium coordination is raised to 7, but in an irregular way. The Ca–O distances are very variable, and so is

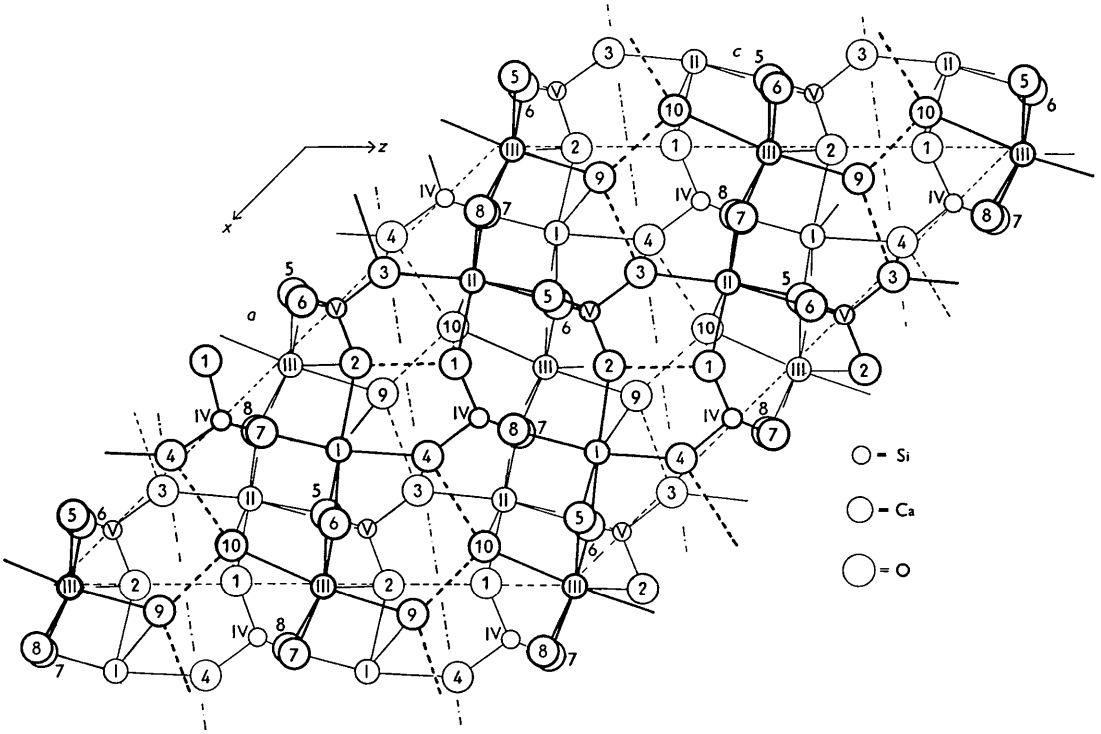


Fig. 6. Projection of structure on (010). Thick lines indicate atoms and bonds at approximate heights $y = \frac{1}{2}$ or $\frac{3}{4}$; thin lines indicate atoms and bonds at approximate heights $y = 0$ or $\frac{1}{4}$. Full lines, cation–anion bonds; broken lines, hydrogen bonds. Incomplete bonds join atoms shown in the diagram to others in next cell below. (There are corresponding bonds joining upper atoms to next cell above.) Dot-dash lines indicate position of cleavage planes.

Table 4. *Interatomic distances*

(All distances are in Ångström units.)

(*a*) Cation–oxygen.

	O_1	O_2	O_3	O_4	O_9	O_{10}	O_5	O_6	O_7	O_8
Ca_I	—	2·44	—	2·45	3·14	—	2·30	2·37	2·45	2·55
Ca_{II}	2·37	—	2·35	—	—	2·75	2·33	2·80	2·40	2·46
Ca_{III}	—	2·69	—	—	2·48	2·66	2·38	2·44	2·36	2·30
Si_{IV}	1·61	—	—	1·71	—	—	—	—	1·61	1·57
Si_V	—	1·65	1·61	—	—	—	1·60	1·58	—	—

(*b*) Oxygen–oxygen, coordinated round same cation.

Shared edges, Ca and Si polyhedra

Cations	O–O	Distance
I, IV	7–8	2·57
II, V	5–6	2·59
III, V	2–5	2·61

Shared edges, two Ca polyhedra

Cations	O–O	Distance
I, II	5–8	2·98
I, III	2–8	3·00
II, III	5–10	3·05
II, III	7–8	3·08
I, III	5–6	3·11
I, II	6–7	3·17

Unshared edges, Si tetrahedra

Cation	O–O	Distance
V	2–3	2·60
V	3–5	2·60
IV	1–7	2·63
IV	4–7	2·65
IV	1–4	2·66
V	3–6	2·66
IV	1–8	2·70
IV	4–8	2·72
V	2–6	2·73

Unshared edges, Ca polyhedra

Cation	O–O	Distance
III	2–9	2·59
II	1–3	3·05
II	1–6	3·17
I	2–4	3·18
I	4–5	3·17
II	3–7	3·24
II	1–10	3·29
III	6–10	3·35
I	2–9	3·39
III	6–9	3·39
II	8–10	3·45
III	7–9	3·45
III	6–7	3·47

All others greater than 3·50

(*c*) Oxygen–oxygen contacts, forming hydrogen bonds.

	Length	Mean		Standard deviation
O_3–O_4	2·49	2·523	±	0·025
O_9–O_{10}	2·52			
O_1–O_2	2·56			
O_4–O_{10}	2·70	2·716	±	0·011
O_1–O_{10}	2·71			
O_3–O_9	2·73			

the angular distribution of the oxygens (considered in more detail in a later section); however, the region in which each calcium atom lies is in fact enclosed by seven oxygen atoms, and hence for packing purposes the coordination is 7. For estimating the Pauling electrostatic valence, however, it is not legitimate to count all seven atoms. Some of the Ca–O distances (given in Table 4(*a*)) are much larger than the sum of the Goldschmidt radii, 2·40 Å. Though these radii are empirical, and the interatomic distances derived from them are dependent to some extent on coordination number, the variations are generally of the order of a few per cent only. Hence distances of more than 2·60 Å imply that there is not contact between the atoms in the Goldschmidt sense. The equilibrium distance is in these cases not determined by the mutual forces of the atoms but by their interaction with their other neighbours. The electrostatic attraction of the two must be smaller than that for true neighbours, and they cannot be counted as such in estimating electrostatic valence.

Interatomic distances

Interatomic distances are given in Table 4. It follows from the last paragraphs of § 5 that cation–oxygen distances have a standard error of 0·035 Å, O–O distances of 0·045 Å; but, for reasons explained in that section, distances involving O_{5-8} may well be somewhat less accurate than the rest. Further, since distances to O_8 have been used in deriving its parameters, they cannot be cited as independent evidence for any feature of the structure; fortunately this is not necessary.

Before any more detailed comment on the distances can be made, it is necessary to distinguish between O^{2-}, OH^- and H_2O groups.

Location of hydrogen atoms

The most interesting feature of the structure so far noted is the coordination of the oxygens (see Fig. 6, and Table 4(*a*)). The oxygens at $\pm\frac{1}{4}$, namely O_{5-8}, have each four cation neighbours—three calcium and one silicon—arranged tetrahedrally (though one Ca–O distance involved is too long for a strictly Goldschmidt contact). These may be identified as O^{2-}. The others, O_{1-4}, O_9, O_{10} have all a smaller number of cation neighbours, arranged one-sidedly (as shown in Figs. 4 and 6), with close contacts to other oxygens on the other side. It is on these that the hydrogens must be placed, and there must be a number of hydrogen (or hydroxyl) bonds.

It is worth pointing out at this stage that the very existence of discrete $Si–O_4$ groups implies a direct linkage of OH to silicon; there are only two remaining oxygens not so linked, O_9 and O_{10}, and unless each of these carries three hydrogens and becomes OH_3^+ (which seems improbable) some of the hydrogens must be placed elsewhere.

We have six hydrogens to allocate to six oxygens; if any H_2O groups are formed, there will be an equal number of O^{2-}, the remainder of the six being OH^-. There are three separate lines of argument.

(1) *Electrostatic valency.* It will be clear from what was said in the last section that this approach needs care, since the concept of electrostatic valency has no very welldefined meaning when the coordination is not regular. Nevertheless we may usefully examine it, making for simplicity the arbitrary assumption that all Ca–O distances less than 2·6 Å correspond to equal electrostatic forces, distances greater than that to zero force. The resultant electrostatic valencies at the oxygen atoms are shown in Table 5. It is obvious that these can best be satisfied by taking O_9 and O_{10} as H_2O, and O_5, O_6, O_7, O_8 as O^{2-}. Of the first four atoms in the table, it is not clear which are OH^- and which O^{2-}, though there is a slight hint that O_1 and O_3 are O^{2-}.

Table 5. *Electrostatic valencies*

Atom	Neighbours at distances less than 2·60 Å	Electrostatic valency
O_1	II, IV	1·40
O_2	I, V	1·33
O_3	II, V	1·40
O_4	I, IV	1·33
O_5	I, II, III, V	2·13
O_6	I, III, V	1·73
O_7	I, II, III, IV	2·13
O_8	I, II, III, IV	2·13
O_9	III	0·40
O_{10}	—	0

(2) *Interatomic distances.* Distances from a given cation are likely to be shortest for O^{2-}, intermediate for OH^-, and longest for H_2O. From Table 4(*a*) it can be seen that this criterion would identify O_9 and O_{10} as H_2O, O_2 and O_4 as OH^-, and the rest as O^{2-}. In Table 6 the same facts are arranged to make the distinction clear. Distances involving the 4-coordinated oxygens (O_5–O_8) are tabulated separately from those involving the two unsymmetrically coordinated oxygens (O_1, O_3) which are identified by this evidence as O^{2-}.

This argument holds good only if the differences in bond length are significant. That this is so can be shown from Table 6, where the mean of each set of distances is given, together with the standard deviation of an individual observation. Abnormally large distances (distinguished by square brackets) were excluded in calculating these, for they cannot be regarded as bond contacts between the atoms concerned; and so were distances involving O_8 (distinguished by round brackets), since they are not independently determined. The standard deviation of most sets is small. Only for $Ca–H_2O$ does it exceed the standard error deduced from the synthesis, and here its large value is an indication that the three bonds are not all of the same kind. For $Ca–O_{5-8}$ the range of values is wider than elsewhere, and though it is not greater than the limits of accuracy of the synthesis would allow another explanation must be considered, which may be put crudely as follows. The distance between two ions is determined primarily by the mutual attractive and

Table 6. *Interatomic distances, with mean values and standard deviations*

(All distances are in Ångström units. Distances involving O_8 (round brackets) and abnormally large distances (square brackets) are excluded from the means.)

	Ca–O		Ca–OH	$Ca–H_2O$	Si–O		Si–OH
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
	O_1, O_3	O_{5-8}	O_2, O_4	O_9, O_{10}	O_1, O_3	O_{5-8}	O_2, O_4
	2·35	(2·30)	2·44	2·48	1·61	(1·57)	1·65
	2·37	2·30	2·45	2·66	1·61	1·58	1·71
		2·33	[2·69]	2·75		1·60	
		2·36		[3·14]		1·61	
		2·37					
		2·38					
		2·40					
		2·44					
		2·45					
		(2·46)					
		(2·55)					
		[2·80]					
Mean	2·36	2·38	2·44$_5$	2·63	1·61	1·60	1·68
S.D.	±0·01$_0$	±0·04$_5$	±0·00$_5$	±0·11	±0·00	±0·01	±0·03

repulsive forces—the latter, because of its rapid variation with distance, setting a sharp lower limit—but it is also affected by the forces between each ion and all its other neighbours, which may act to increase it. Here such an effect would be expected for the 4-coordinated oxygens, but, because their environment is irregular, the effect may vary in magnitude. It is analogous to the well-known increase in ionic radii with increasing cation coordination number in a simple structure. The Si–O distance, corresponding to the strongest bond, is not likely to be affected appreciably, but the Ca–O distances well may be. In the extreme case, the ions cease to be in contact; an example is the large distance of 2·80 Å, excluded in calculating the mean.

The difference between the mean values of Ca–O and Ca–OH, from columns 1 and 3, is 0·085 Å; the corresponding difference between Si–O and Si–OH is 0·070 Å. In each case the difference is at least twice the standard error derived from the synthesis, and a greater multiple of the standard deviation derived from the set of bond-lengths themselves. This is a significant difference. If the Ca–O and Si–O distances of columns 2 and 6 are included (though because of the different oxygen coordination number this does not seem justifiable for the Ca–O) the difference is still there, though more doubtfully significant.

(3) *Bond formation.* Of the O–O contacts where the oxygens are not coordinated round the same cation, six give short distances of less than 2·80 Å (see Table 4(*c*)). The rest are all greater than 3·10 Å and must be classed as van der Waals contacts. The short distances are shown formally in Fig. 7(*a*). They fall into two well-marked groups, with mean values 2·52 and 2·72 Å, which are to be identified as short and long hydrogen bonds. The standard deviations of the two groups are about 0·02 Å; the standard error derived from the synthesis is 0·035 Å. The difference between the two groups is thus highly significant, the differences within a group not significant.

We must expect to find a hydrogen located on or near each bond. If the identification of the atoms arrived at in the previous paragraph is valid, there is one arrangement of hydrogens which satisfies it, shown in Fig. 7(*b*); this may be taken as a first approximation to the correct structure.

For a second approximation we must distinguish between the long and short bonds. In the long hydrogen bonds the attraction is primarily electrostatic, and the hydrogen is associated closely with only one of its oxygen neighbours. In the short hydrogen bond, even if the hydrogen atom belongs originally to one oxygen, it is nevertheless in some way shared by the oxygen at the other end of the bond. Whether this is a consequence of strong electrostatic attraction arising from its close approach or of some kind of sharing of its electron system with the second oxygen is immaterial to the present argument; it is sharing of a kind, or to a degree, that does not occur with the long hydrogen bond.

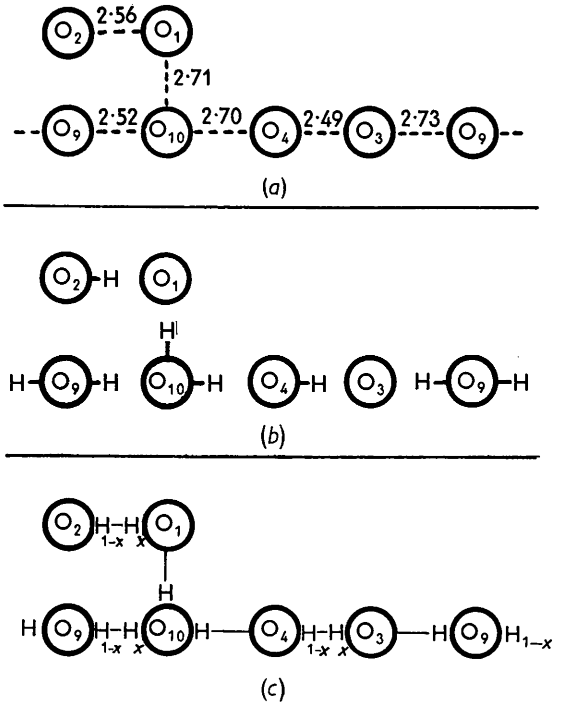


Fig. 7. Schematic diagram of system of hydrogen bonds: (*a*) bond lengths, (*b*) location of hydrogens, first approximation, (*c*) second approximation.

Suppose the fraction of electrostatic valence (less than ½) associated with the second atom in each of the short bonds is x. The system may then be represented as in Fig. 7(*c*). Thus O_{10} has something of the character of an oxonium ion OH_3^+, while O_9 is modified from H_2O in the direction of OH^-; O_2, O_4, O_1 and O_3 are

Table 7. *Distribution of* H's

	H content	Ca–O distance	Si–O distance	Electrostatic valency
O_1	x	2·37	1·61	1·40
O_3	x	2·35	1·61	1·40
O_4	$1-x$	2·45	1·65	1·33
O_2	$1-x$	2·44	1·71	1·33
O_9	$2-x$	2·48	—	0·40
O_{10}	$2+x$	2·66, 2·75	—	0

all intermediate between OH^- and O^{2-}, the former pair approximating more closely to OH^-, the latter to O^{2-}. Table 7 shows the oxygens arranged in this way, which agrees with the order suggested by the cation–oxygen distances and the electrostatic valencies.

It is not possible to carry the argument about the location of the hydrogens any further on structural evidence, and they cannot be found directly from the synthesis, since the experimental data do not allow sufficient accuracy. The evidence is, however, entirely self-consistent; it gives as the best approximation to the structural formula (avoiding fractional subscripts) the expression $Ca_3(SiO_3OH)_2.2H_2O$.

Peak heights and numbers of electrons per atom

The mean values of these are given in Table 3, N being derived on the assumption of a Gaussian density distribution, as explained in § 5. It would have been preferable to calculate N by direct integration, but this was not practicable.

Peak heights for atoms of the same kind did not differ significantly from their mean, except that the value for Ca_{III} was lower than that for the other two calciums by an amount which was possibly significant. The number of electrons per atom was the same for all three, within the limits of error; hence the interpretation of this effect, if real, is that Ca_{III} is more spread out than the other two atoms, presumably because of larger amplitude of thermal vibration. There was a slight difference of peak height between OH^- and the O^{2-} in the same plane, very doubtfully significant, the former being lower; this again did not affect the relative values of N.

The two water molecules, O_9 and O_{10}, were excluded from Table 3. The latter is not very different from the other oxygens; its peak height is 17·3 e.Å^{-3}, its value for N is 5·3, the differences being possibly significant; its p values lie within the range of the others. The other molecule, O_9, is strikingly different. Its peak height is 13·0 e.Å^{-3}, its value for N is 4·9, and its p_1 value is 6·5. This implies that the atom is very much more spread out in the (010) plane than the others are. Its departure from spherical symmetry at distances of 0·3–0·4 Å from the peak was quite conspicuous on the synthesis. These deviations are outside the limits of error quoted in § 5, and cannot be explained by any individually large diffraction ripples. It seems clear that the assumption of a spherical distribution of electron density is not legitimate in treating this water molecule.

Because of the method of deriving N, it can give information only about the central region of the atom, within about 0·3 Å radius of the centre, over which the Gaussian distribution is shown to hold. Then N is the hypothetical number of electrons which would be found by extrapolating this distribution to the outskirts of the atom. For calcium, the experimental value of about 18 is that appropriate for a Ca^{2+} ion. For silicon, the experimental 13·5 is appropriate for a neutral silicon atom, whose electrons are not involved in electrostatic bonds. For O^{2-} and OH^-, the experimental 6·2 suggests a loss of electrons below the values 8 and 9 respectively appropriate for an unionized group; but the loss need only be from the central region of the atom to that beyond the reach of the Gaussian approximation. Hence no conclusions can be drawn about their state of ionization. For H_2O the still lower values of 5·3 and 4·9 only imply a more marked departure from the Gaussian distribution in the same direction.

Environment of the cations

Stereograms showing the environments of the cations are given in Fig. 8 (for bond lengths, see Table 4(*a*)). Ca_I has six neighbours, two OH^- and four O^{2-}, arranged at the corners of a trigonal prism,

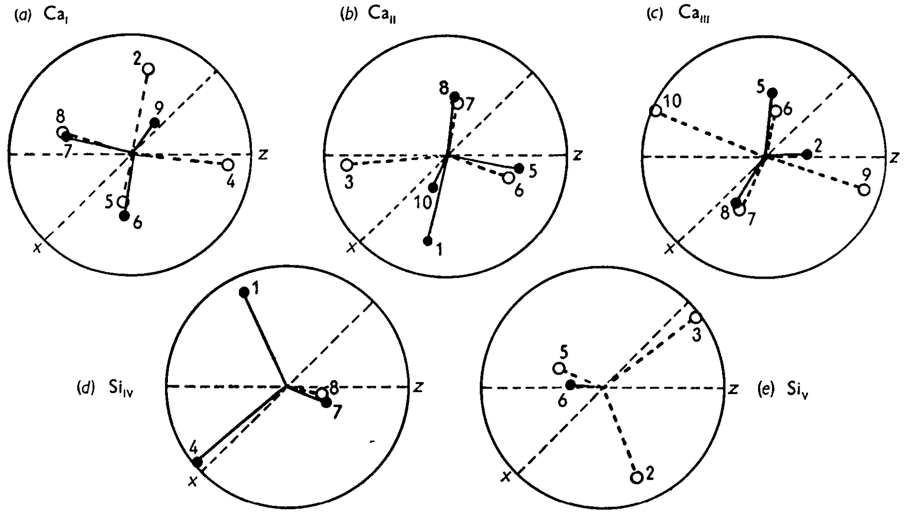


Fig. 8. Stereographic projection of environment of cations.

at distances ranging from 2·30 to 2·55 Å. A seventh neighbour, the water molecule O_9, comes opposite the middle of one face, at a distance (3·14 Å) so great that it must be counted a van der Waals contact. Ca_{II}, related to Ca_I by the pseudo-centre of symmetry, has six O^{2-} neighbours in a trigonal prism, but one of them, O_6, is at the abnormal distance of 2·80 Å. The seventh neighbour, the water molecule O_{10}, is at 2·75 Å. If we include O_{10} and omit O_6, the six atoms form an octahedral arrangement. Ca_{III} has six neighbours, four OH^- and two H_2O, in an octahedral arrangement, the longest distance being 2·66 Å; and a seventh, O_2 (which is OH^-) at 2·69 Å. The seven neighbours of Ca_{II} and Ca_{III} form groupings very similar to each other, though differently derived from the idealized structure.

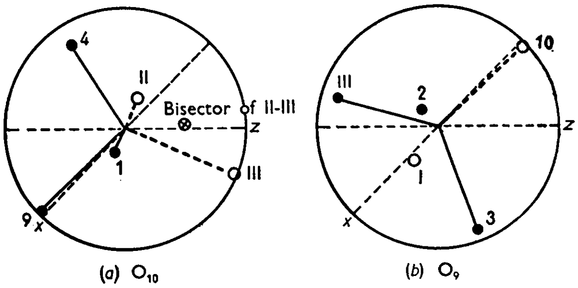
Each silicon atom has three O^{2-} neighbours and one OH^-, arranged at the corners of a nearly regular tetrahedron. This substance is the first in which the structure determination shows unambiguously that there is a direct linkage of OH to silicon (Megaw, 1949). The possibility of such an arrangement had been suggested on other grounds for various hydrated silicates, notably clays; the demonstration of its existence in a well crystallized material is therefore of interest.

The mean value of 1·60 Å found for the Si–O distance should be compared with that of 1·642 Å in the felspars (Cole, Sörum & Kennard, 1949), where the silicon atoms are partly replaced by aluminium; with 1·57 Å in tourmaline (Donnay & Buerger, 1950), where, however, the structure may not have been completely refined; and with 1·615 Å in tilleyite (Smith, 1951) which contains Si_2O_7 groups.

The bond angles at the silicon atoms have values ranging from 106° to 116°, with a standard deviation of about 3°; there does not seem to be any significant difference between those involving OH^- groups and the rest. The range is not very different from that observed by Cole *et al.* (1949).

Environment of the water molecules

The difference between the environments of the two water molecules, O_9 and O_{10}, is rather striking. The latter has two calcium neighbours at a mean distance of 2·70 Å (standard deviation 0·05 Å), and three anion or water neighbours, with which it forms two long hydrogen bonds (using its own hydrogen atoms) and one short hydrogen bond (directed towards it by the hydrogen atom of O_9) (Fig. 9(*a*)). If the three hydrogen bonds are considered together with the bisector of the angle between the two Ca–O bonds, they are directed towards the corners of an irregular tetrahedron. The other water molecule, O_9, has one calcium neighbour at the significantly shorter distance of 2·48 Å, and two anion or water neighbours, with which it forms one short and one long hydrogen bond (using its own hydrogen atoms for both) (Fig. 9(*b*)). The three bonds are almost coplanar. The short Ca–O distance may indicate appreciable homopolar character in this bond. The environment of O_9 is unusual in two other respects: the long distance of 3·14 Å to the second adjacent cation, showing a van der Waals contact where one would have expected an ionic bond; and the short distance of 2·59 Å to O_2, which is the shortest unshared edge of a calcium polyhedron in the whole structure. One could explain these by saying that distortion of the O_9 bond system from a planar configuration requires large energy, more than could be provided by the combined effect of Ca_I–O_9 electrostatic attraction and O_2–O_9 repulsion. Alternatively, the redistribution of electron energy brought about by the bond system may mean that it is less extensive perpendicular to the plane, which would allow a closer approach of the anion O_2 while reducing the electrostatic attraction between Ca_I and O_9. An explanation along these lines would receive support from the abnormality of the electron-density distribution discussed in the previous section. Perhaps the two explanations are merely different ways of expressing the same fact in pictorial terms.



(*a*) O_{10} (*b*) O_9

Fig. 9. Stereographic projection of environment of water molecules.

The environment of O_9 is reminiscent of the arrangement in oxalic acid dihydrate (Dunitz & Robertson, 1947), where the water molecule is linked to its neighbours by three nearly coplanar hydrogen bonds, one short and two long. On the other hand, the environment of O_{10} resembles the tetrahedral arrangement commonly found in hydrates with long hydrogen bonds. The OH^- and O^{2-} ions, O_{1-4}, all have tetrahedral environments too, though very irregular. It is of interest to notice that in the mineral trona $Na_2CO_3.NaHCO_3.2H_2O$ (Brown, Peiser & Turner-Jones, 1949), where both long and short hydrogen bonds are formed, the long bonds link the water to its neighbours, which are tetrahedrally arranged, while the short bond is found, as in $NaHCO_3$, between the oxygens of the carbonate groups.

Pseudo-symmetry

To a first approximation, while the hydrogen atoms are ignored, the structure possesses a centre of pseudosymmetry, relating the atoms in pairs, except for Ca_{III} which lies nearly on it. This relationship was very useful in deriving the structure. It now appears that the hydrogen atoms are not placed to satisfy the pseudo-symmetry. The pairs O_1 and O_2, O_3 and O_4, related by the pseudo-centre, each comprise one OH^- and one O^{2-}; and the bond systems of the two water molecules O_9 and O_{10} are completely unlike. The small departures of the parameters from centrosymmetry are thus to be associated with the energy differences involved between O^{2-}, OH^-, and H_2O.

It is of interest to notice that though the geometrical departure from centrosymmetry is small the crystal shows well-marked pyro- and piezo-electricity.

7. Physical and chemical relationships

Dielectric constant

The existence in the structure of continuous chains of hydrogen bonds, including long and short bonds, is reminiscent of Rochelle salt (Beevers & Hughes, 1941). Measurements were therefore made of the dielectric constant, in directions parallel to [010] and perpendicular to the cleavage plane $(10\bar{1})$. The author wishes to thank Mr R. G. Chambers for carrying out these measurements. At room temperature the values were small, about 7 ± 2 in both directions (i.e. of the same order of magnitude as the alkali halides); no more detailed work was therefore undertaken.

Infra-red absorption

Measurements of the infra-red absorption of the powdered material have been made by Dr N. Shepherd and Mr D. E. Bethell (private communication). They find a sharp band between 3300 and 3400 $cm.^{-1}$, of the kind characteristic of the long hydrogen bond in other substances; and a broad band in the 2500–3000 $cm.^{-1}$ region, which they associate with the short hydrogen bond. It is hoped to make more detailed measurements on oriented crystal sections.

Loss of water on heating

Parry & Wright (1925) state that 'the bulk of the water escapes at about 300° C. with no evidence of different dissociation points', and deduce that the water 'is all of the same kind and is water of constitution', i.e. non-zeolitic. In connection with the present work, a differential thermal analysis was carried out in the Department of Mineralogy by Dr R. J. McLaughlin, to whom the author wishes to express thanks. This shows at least three distinct transition temperatures within the range 250–450° C. corresponding to endothermic reactions, and hence indicates that the hydrogen atoms are not all in chemically equivalent situations, in agreement with the structural result.

It has been shown by Moody (1952*a*, *b*), by powder methods, that the products formed when water is lost by afwillite in this temperature range are γ-Ca_2SiO_4 (olivine structure), CaO and SiO_2 (quartz). It seems probable that Ca_{III} is involved in the oxide formation, while Ca_I and Ca_{II} remain linked to a SiO_4 tetrahedron, but the details of the transition to the olivine structure need further consideration.

I wish to express my thanks to Dr P. de Vos, who took the photographs used for the intensity measurements and determined the size of the unit cell, and to the many people who have helped me with the very lengthy calculations. I am grateful to Prof. C. E. Tilley for providing the material, and for helpful discussion of the mineralogical aspects; and to Dr R. J. McLaughlin for carrying out the differential thermal analysis. It is also a pleasure to acknowledge my indebtedness to Prof. Sir Lawrence Bragg and to Dr W. H. Taylor for their continued interest and encouragement, and to Prof. J. D. Bernal, whose interest in the cement-forming minerals suggested the problem to me in the first instance.

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