

## The Crystal Structure of Tilleyite

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The crystal structure of tilleyite has been determined. The crystals are monoclinic, space group  $P2_1/a$ , with four units of  $\text{Ca}_5\text{Si}_2\text{O}_7(\text{CO}_3)_2$  in a cell of dimensions  $a = 15.025 \pm 0.007$ ,  $b = 10.269 \pm 0.005$ ,  $c = 7.628 \pm 0.007$  Å,  $\beta = 105^\circ 50' \pm 10'$ . The approximate atomic coordinates were found from bounded Patterson projections and systematic comparison of structure amplitudes. These coordinates were refined by two-dimensional  $F_o$  and  $(F_o - F_c)$  syntheses. The shapes of the  $\text{Si}_2\text{O}_7$  and  $\text{CO}_3$  groups have been determined. The cleavages, twinning and optical properties have been explained in terms of the crystal structure.

### Introduction

Tilleyite,  $\text{Ca}_5\text{Si}_2\text{O}_7(\text{CO}_3)_2$ , is a mineral found in the metamorphic contact zones between siliceous matter and dolomitic limestone. It was first discovered and described by Larsen & Dunham (1933) in the contact zone at Crestmore, California, and was later described by Tilley (1947) and Nockolds (1947) from material obtained respectively from the Camas Mor and Carlingford contact zones. Two other calcium carbonate silicate minerals, spurrite (Wright, 1908) and scawtite (Tilley, 1930) have also been found in the contact zones.

The crystal structure of tilleyite is of interest in several ways. First, the crystal structure of a carbonate silicate mineral has not previously been determined; secondly, the dimensions of the  $\text{Si}_2\text{O}_7$  group have not previously been determined with precision; and thirdly, the coordination polyhedron of the calcium ion is of interest.

### Morphology and optical data

The crystals of tilleyite used in this investigation were kindly provided by the Department of Mineralogy and Petrology, Cambridge, by courtesy of Prof. Tilley, and were originally obtained from the Carlingford contact zone (Nockolds, 1947). In agreement with Nockold's observations, they were found to show four cleavages: perfect (201), poor (100) and (010), and very poor (001). Simple twinning occurred parallel to (100). The indices given by Nockolds differ from those given above but only because they have been transformed to the axes indicated by the X-ray work.

The optical measurements obtained by Tilley and Nockolds agreed with each other but differed to some extent from those obtained by Larsen & Dunham. Measurements made on the material used in this investigation confirm the measurements of Tilley and Nockolds. Nockolds found

$$\begin{aligned} \alpha &= 1.612, \beta = 1.632, \gamma = 1.653, \text{ all } \pm 0.003; \\ X \wedge c &= 24^\circ, Y = b, Z \wedge a = 38^\circ, \text{ all } \pm 1^\circ; \\ 2V &= 85-89^\circ, \text{ mean } 87^\circ; \text{ optically positive.} \end{aligned}$$

### X-ray measurements

The lattice parameters were obtained from single-crystal oscillation photographs using both the  $\theta$ -method (Weisz, Cochran & Cole, 1947), and the method of back-reflexion film mounting. They are:

$$\begin{aligned} a &= 15.025 \pm 0.007, b = 10.269 \pm 0.005, \\ c &= 7.628 \pm 0.007 \text{ \AA}, \beta = 105^\circ 50' \pm 10', \\ V &= 1132 \text{ \AA}^3. \end{aligned}$$

The calculated density for four units of  $\text{Ca}_5\text{Si}_2\text{O}_7 \cdot 2\text{CO}_3$  in the unit cell is  $2.88 \text{ g.cm.}^{-3}$ , whereas the value obtained experimentally by Nockolds is  $2.823 \text{ g.cm.}^{-3}$ . Examination of the systematic absences showed that the space group is  $P2_1/a$ .

The X-ray intensities of the ( $h0l$ ) and ( $hk0$ ) reflexions were obtained from Weissenberg zero-level photographs, using  $\text{Cu } K\alpha$  radiation. All ( $hkl$ ) reflexions which had a spacing greater than  $1.1 \text{ \AA}$  were recorded on single-crystal oscillation photographs taken about the  $x$  and  $z$  axes using  $\text{Mo } K\alpha$  radiation. Multiple packs of film interleaved with copper foils were used for the oscillation photographs giving a step-down factor from film to film of about 3.2. The intensities were measured visually by comparison with a calibrated intensity scale.

A small crystal was used in order to reduce the absorption and extinction effects; the crystal was cut and ground to a roughly spherical shape so that the absorption factor should be approximately a function of  $\sin \theta$ . A small correction was made for the intensities obtained with  $\text{Cu } K\alpha$  radiation so as to take account of the departure from a sphere. The correction for the intensities obtained with  $\text{Mo } K\alpha$  was negligible. The Lorentz and polarization factors were applied to the measured intensities by the method of Cochran (1948). The variation of intensity with  $\zeta$  on the oscillation

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photographs was corrected by the method of Clews & Cochran (1949) who showed that after these corrections have been made  $I_{hkl} = KF_{hkl}^2 f(\sin \theta)$ , where  $I_{hkl}$  is the corrected intensity,  $K$  is an unknown constant,  $F_{hkl}$  is the structure amplitude and  $f(\sin \theta)$  is an undetermined function of  $\sin \theta$ . The constant  $K$  and the function  $f(\sin \theta)$  were determined by comparison of the observed and calculated structure amplitudes after the approximate atomic coordinates had been found. For calculation of the structure amplitudes, the empirical atomic scattering curves of Bragg & West (1929) were adopted. Comparison of observed and calculated structure amplitudes, thus corrected, showed that the strongest reflexions obtained with  $\text{Cu } K\alpha$  radiation were affected by extinction, whereas all reflexions obtained with the more penetrating  $\text{Mo } K\alpha$  radiation were unaffected.

### Determination of the structure

As none of the atoms necessarily lay on special positions, 66 parameters had to be found in order to determine the positions of the 22 independent atoms. An attempt was made to find the arrangement of the  $\text{Si}_2\text{O}_7$  and  $\text{CO}_3$  groups from the cleavages and optical properties but the trial structure thus postulated proved to be incorrect. It was therefore necessary to examine the X-ray evidence without any preliminary knowledge of what to expect.

Rotation photographs about the  $z$  axis had alternate strong and weak layer lines with an intensity ratio of about 10 to 1, showing that the  $z$  axis was pseudo-halved. A very long-exposure rotation photograph did not show any more weak layer lines. The pseudo-halving implies that, to a close approximation, the atoms are arranged in pairs at  $x, y, z; x, y, \frac{1}{2}+z$ . Since the general position of the space group is fourfold and there are four formula units per true cell this means that the formula unit must be halved in the pseudo-cell. There is an odd calcium and an odd oxygen atom which do not fit into this approximation unless placed at centres of symmetry. This idealized approximation was used in the preliminary determination of the structure from the X-ray evidence. The unit cell of this idealized structure has  $c' = \frac{1}{2}c$ , which is true in three dimensions, introducing extra screw diads at  $0, y, \frac{1}{4}; \frac{1}{2}, y, \frac{1}{4}$  (referred to the old cell). The (010) projection of space group  $P2_1/a$  has  $a' = \frac{1}{2}a$ . Hence in this projection translations of  $\frac{1}{2}a$  or  $\frac{1}{2}c$  are identities. In the (001) projection the repeat distances are  $a$  and  $b$ , but the  $c$  halving remains.

Two-dimensional Patterson projections along  $z$  and  $y$ , the shorter axes of the crystal, were computed with the aid of Beevers-Lipson strips and are shown in Figs. 1 and 2.

The  $y$ -axis projection contains only four regions of high vector density, each of the regions having an elliptical shape and containing several peaks. It was found that there were only two ways of placing the

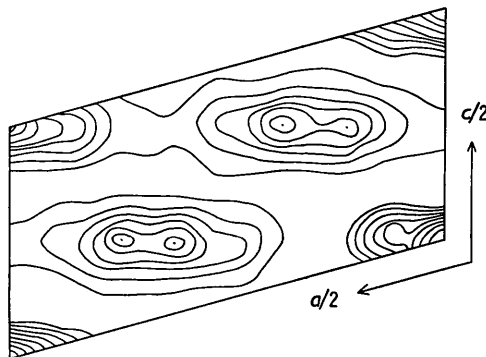


Fig. 1. The  $y$ -axis Patterson projection.

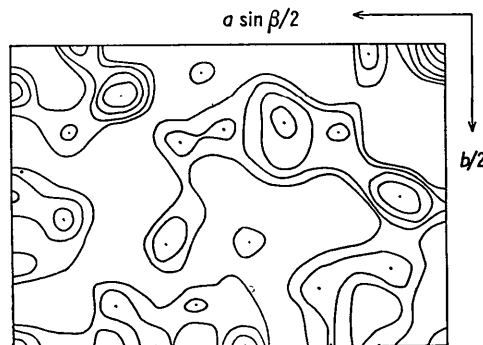


Fig. 2. The  $z$ -axis Patterson projection.

heavier concentrations of electron density in the projection. Both arrangements gave equally good agreement between the calculated vector map and the observed Patterson projection, and also between the calculated and observed structure amplitudes.  $F$ -syntheses computed from each arrangement of atoms gave further peaks which were plausible sites for other atoms. It was not possible to decide between the two arrangements nor to find the arrangement of calcium, silicon and oxygen atoms, within the concentrations of electron density. The interpretation of the  $z$ -axis Patterson projection was therefore begun. Using the possible sets of  $x$  coordinates obtained from the  $y$ -axis projection, the possible  $y$  coordinates were found. Several sets were found which gave some agreement between the calculated vector map and the Patterson projection. Two of these were much better than the others but, as in the  $y$ -axis projection, it was not easy to decide which was correct. Attempts to complete the structure determination from this two-dimensional evidence proved fruitless.

It was decided to compute a three-dimensional Patterson synthesis. In order to reduce labour, two bounded projections (Booth, 1945) were computed, each containing only one of the lines of peaks in the  $y$ -axis projection. The regions included in the bounded projections (labelled  $A$  and  $B$ ) are shown in Fig. 3.

The general expression for the vector density of a projection bounded by the planes  $z = z_1$  and  $z = z_2$  is given by

$$B_{z_1}^{z_2} = \frac{1}{V} \int_{z_1}^{z_2} \sum F^2(hkl) \cos 2\pi(hx/a + ky/b + lz/c) dz$$

$$= \frac{1}{V} \sum_h \sum_k \sum_l \frac{c}{2\pi l} F^2(hkl) [\sin 2\pi(hx/a + ky/b + lz_2/c) - \sin 2\pi(hx/a + ky/b + lz_1/c)].$$

In order to compute the bounded projections of tilleyite, the axes were transformed from  $x, y, z$  to  $x_1, y_1, z_1$ , where  $x_1 = [10\bar{2}]$ ,  $y_1 = y$ , and  $z_1 = z$ . Then the integration ranges were: for  $A$ ,  $z_1 = -0.125c$  to  $0.125c$ ; for  $B$ ,  $z_1 = 0.125c$  to  $0.375c$ . Figs. 4 and 5 show the two bounded projections.

It should be noted that at this stage in the structure analysis, the pseudo-spacing  $\frac{1}{2}c$  was still taken to be the true spacing. In addition, all the atoms were idealized on to the nearest  $(20\bar{4})$  plane, these being the central planes of the bounded projections. Interpretation of the bounded projections gave only one agreement of heavy atoms: this arrangement was the same as one of those deduced from the two-dimensional projections. The atoms thus located were later found to be the five calcium atoms.

The use of the 'vector convergence method' (Beevers & Robertson, 1950) led to the discovery of another two atomic peaks. The heights of the vector peaks suggested that these were medium heavy atoms, probably silicon atoms, and this was later found to be true. All vectors between calcium and silicon atoms are shown by crosses on Figs. 4 and 5.

The vector peaks near the origin were investigated to give information concerning the local arrangement of atoms. Two peaks were found at about  $1.5 \text{ \AA}$  from the origin on bounded projection  $A$  ( $p$  and  $q$ , Fig. 4) and these were identified as Si-O vector peaks. The approximate orientation of the  $\text{Si}_2\text{O}_7$  group was deduced from these positions. Two larger peaks at about  $2.4 \text{ \AA}$  from the origin in bounded projections  $A$  and  $B$  ( $r$  and  $s$ , Figs. 4 and 5) were identified as Ca-O vector peaks.

Since the sites of the heavy atoms were known, possible positions for oxygen atoms could be deduced from these vectors, and also from packing considerations. Twenty possible positions were found. All

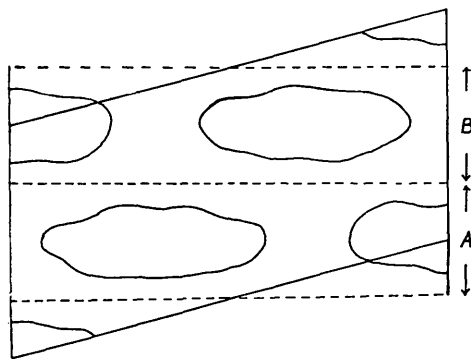


Fig. 3. Regions included in the bounded projections (cf. Fig. 1).

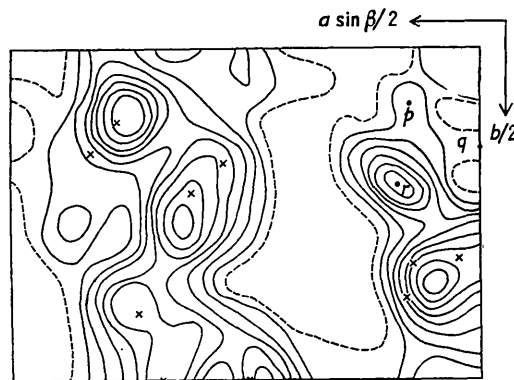


Fig. 4. Bounded projection A.

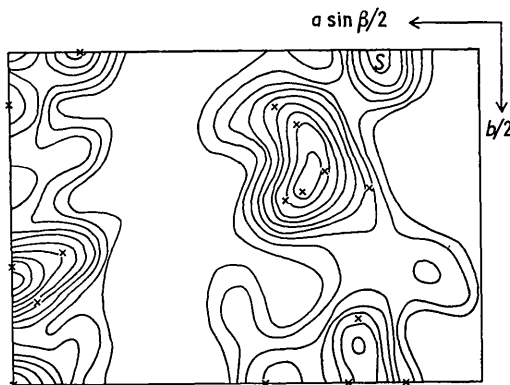


Fig. 5. Bounded projection B.

vectors between the heavy atoms and these possible oxygen atoms were calculated and compared with the Patterson bounded projections. Twelve of the twenty possible oxygen atoms were found to give better agreement than the rest. The shorter distances between the twelve positions were than calculated. Six of the oxygen atoms were found to form two parallel triangles separated by a distance  $\frac{1}{2}c = 3.8 \text{ \AA}$ , the sides of the triangles being of lengths  $2.7, 2.7, \text{ and } 3.1 \text{ \AA}$ . The two medium heavy atoms were found to lie approximately at the centres of the triangles at  $1.8, 1.7 \text{ and } 1.5 \text{ \AA}$  from the oxygen atoms. These atoms were identified as belonging to the  $\text{Si}_2\text{O}_7$  group. This conclusion was confirmed by the evidence of the short vectors which gave almost the same orientation for the  $\text{Si}_2\text{O}_7$  group. The five heavy atoms could then be definitely identified as calcium atoms. Using packing considerations, and four only of the six atoms, the two  $\text{CO}_3$  groups were located. The atoms still to be inserted were the central oxygen atom of the  $\text{Si}_2\text{O}_7$  group and the two carbon atoms. For each, there were two possibilities. These four arrangements differed (in the idealized structure which is still assumed) only in the  $z$  coordinates, and hence the refinement of the  $(x, y)$  parameters was possible without deciding between them.

Three successive refinements were made, the constant  $K$  and the function  $f(\sin \theta)$  being determined at this stage as described earlier. An artificial tem-

perature factor of  $\exp(-2.4 \sin^2 \theta/\lambda^2)$  was applied to the observed  $F$  values to reduce the diffraction ripples around the atoms. The termination-of-series error caused by the remaining diffraction ripples was corrected by the method of Booth (1946). The final  $R$  factor was 0.13.

The  $z$ -axis projection of the structure is shown in Fig. 6, together with the final  $F_o$  synthesis. The two

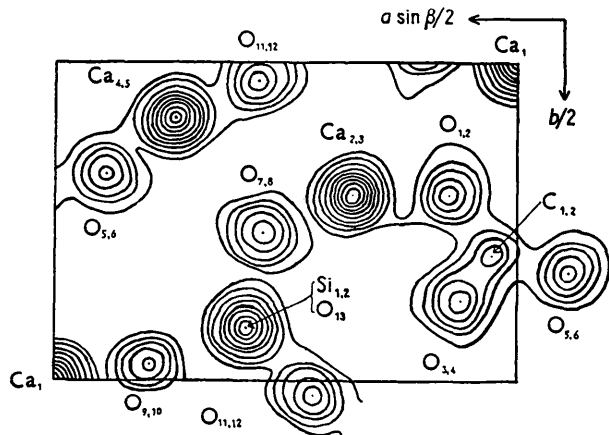


Fig. 6.  $F_o$  synthesis of the  $z$  axis projection. Contours at arbitrary levels.

halves of the cell are superimposed in this projection and it was not possible to resolve them (except, of course, by a bounded projection from  $z = 0$  to  $z = \frac{1}{2}c$ ). The coordinates derived from the  $F_o$  synthesis, therefore, are mean values of the coordinates of atoms related by the pseudo-halving of the  $z$  axis. This will be considered further in the section on the accuracy of the results.

To solve the structure, it was still necessary to find the  $z$  coordinates of one oxygen atom and the pair of carbon atoms, and to fix more exactly the  $z$  coordinates of the rest. In the idealized structure, two of the possible arrangements differ from the other two only in an interchange of the true symmetry axes and the pseudo-axes, affecting the relative positions of the central oxygen atoms of the  $\text{Si}_2\text{O}_7$  groups. From consideration of the known  $(x, y)$  coordinates and the expected interatomic distances, modifications were made in the  $z$  coordinates of the atoms of the  $\text{Si}_2\text{O}_7$  group. These modifications were departures from the idealized structure, and are shown in Fig. 7. For each of these two arrangements of  $\text{Si}_2\text{O}_7$  groups there are two different arrangements of the  $\text{CO}_3$  groups shown by the full-line and broken-line triangles. The positions of the oxygen atoms differ only slightly in the two arrangements, and they would not be resolved in the projection; the chief observable difference is likely to be in the position of the carbon atoms.

It was not possible to distinguish between the four arrangements by packing considerations. Arguments based on the known cleavages, however, indicated that one of the two arrangements of the  $\text{Si}_2\text{O}_7$  groups was

much more probable than the other. This, however, was not taken as conclusive and the correct position of the  $\text{Si}_2\text{O}_7$  groups was found independently from the X-ray measurements alone. Both methods agreed in giving the same position for the  $\text{Si}_2\text{O}_7$  group.

The differences in the two arrangements of the  $\text{Si}_2\text{O}_7$  groups consist entirely in their departure from the idealized structure, and hence chiefly affect the struc-

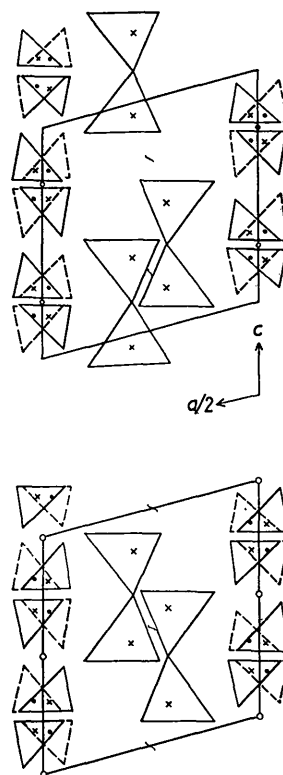


Fig. 7. The  $y$  axis projection showing four possible arrangements of the  $\text{Si}_2\text{O}_7$  and  $\text{CO}_3$  groups. Silicon and carbon atoms are shown by dots and crosses.

ture amplitudes that have  $l$  odd. These were calculated for the  $(h0l)$  zone and compared with the observed values. Neither gave good agreement, but one was definitely better than the other, and this arrangement was accepted; discrepancies were to be expected because the calcium atoms and  $\text{CO}_3$  groups could also show departures from the idealized structure, which were here ignored.

There were still two possible positions for the  $\text{CO}_3$  groups. The signs of the structure amplitudes were calculated for the two arrangements, and two  $F_o$  syntheses were evaluated. In both syntheses the peaks lay at the positions postulated for one of the two arrangements, and this arrangement, therefore, was chosen.

The approximate positions of all the atoms had then been found and the coordinates were refined by successive  $F_o$  syntheses of the  $y$ -axis projection. Refinement was very slow and after two  $F_o$  syntheses the

$R$  factor was still very high at 0.40. This slow refinement was probably caused by the overlapping of two or more atoms in most of the peaks, the termination-of-series error and the abnormal proportion of small structure amplitudes resulting from the pseudo-halving of the  $z$  axis.

The  $y$ -axis projection was finally refined by ( $F_o - F_c$ ) syntheses, (Cochran, 1951). The  $R$  factor successively fell from 0.40 to 0.26 to 0.19. The next synthesis gave no change in the  $R$  factor and contained only random peaks attributable to errors of measurement and calculation. Thus the refinement was judged to be complete.

The great advantage obtained by the use of the ( $F_o - F_c$ ) synthesis in this case is worth noting. Because of the overlapping of the atoms in the projection it would not have been possible to obtain accurate coordinates by means of the  $F_o$  synthesis.

tained from the synthesis were therefore the mean of the  $x$  and  $y$  coordinates of the contributing atoms; the separate  $x$  coordinates of all atoms could be found from the  $y$ -axis projection, but the  $y$  coordinates remained unresolved. Thus, in addition to the random errors, there are systematic errors due to the uncertainty of about 0.2 Å in the  $y$  coordinate of each atom. It has, however, been possible to overcome the resulting errors in the interatomic distances, not for individual distances but for pairs, by taking the mean. The atoms falling in each peak of the  $z$ -axis projection have similar environments. For example, consider the  $\text{Si}_2\text{O}_7$  group; in the  $z$ -axis projection (Fig. 6)  $\text{O}_7$  and  $\text{O}_8$ ,  $\text{O}_9$  and  $\text{O}_{10}$ ,  $\text{O}_{11}$  and  $\text{O}_{12}$  overlap to give three peaks. Although, for example, the distances ( $\text{O}_9 - \text{O}_7$ ) and ( $\text{O}_{10} - \text{O}_8$ ) may be individually in error by the random error plus the systematic error, the mean value should only be in error by the random error. Such means

Table 1. Atomic coordinates of tilleyite in fractions of the unit-cell parameters

Atom	$x$	$y$	$z$
$\text{Ca}_1$	0.0056	0.0000	0.7542
$\text{Ca}_2$	0.1810	0.2112	0.0978
$\text{Ca}_3$	0.1806	0.2112	0.6148
$\text{Ca}_4$	0.1280	0.5867	0.0520
$\text{Ca}_5$	0.1325	0.5867	0.5561
$\text{Si}_1$	0.2071	0.9153	0.1502
$\text{Si}_2$	0.2052	0.9153	0.5792
$\text{C}_1$	0.0297	0.2992	0.3470
$\text{C}_2$	0.0205	0.2992	0.8220
$\text{O}_1$	0.0770	0.2093	0.2860
$\text{O}_2$	0.0681	0.2093	0.7580
$\text{O}_3$	0.0713	0.3625	0.4790
$\text{O}_4$	0.0580	0.3625	0.9580
$\text{O}_5$	0.0622	0.6742	0.7724
$\text{O}_6$	0.0671	0.6742	0.3094
$\text{O}_7$	0.2295	0.7732	0.0700
$\text{O}_8$	0.2255	0.7732	0.6188
$\text{O}_9$	0.1050	0.9708	0.0575
$\text{O}_{10}$	0.1000	0.9708	0.5390
$\text{O}_{11}$	0.2176	0.5263	0.8800
$\text{O}_{12}$	0.2282	0.5263	0.3444
$\text{O}_{13}$	0.2206	0.9153	0.3679

A list of atomic coordinates is given in Table 1. A copy of the observed and calculated structure amplitudes may be obtained upon application to the author.

### Accuracy of results

The standard errors in the atomic parameters and the interatomic distances and angles have been evaluated by the statistical methods developed by Cruickshank (1949). The standard errors of the gradient of electron density which were needed for insertion in Cruickshank's formulae were obtained from the final  $F_o$  synthesis of the  $z$ -axis projection and from the final ( $F_o - F_c$ ) synthesis of the  $y$  axis projection.

Because of the pseudo-halving of the  $z$  axis, each peak of the  $F_o$  synthesis in the  $z$ -axis projection contains two atoms (or, in one case, three) which are completely unresolved. The  $x$  and  $y$  coordinates ob-

Table 2. Interatomic distances

$\text{Si}_1 - \text{O}_7$ , $\text{Si}_2 - \text{O}_8$	1.58 <sub>0</sub> Å
$\text{Si}_1 - \text{O}_9$ , $\text{Si}_2 - \text{O}_{10}$	1.62 <sub>0</sub>
$\text{Si}_1 - \text{O}_{11}$ *, $\text{Si}_2 - \text{O}_{12}$ *	1.59 <sub>5</sub>
$\text{Si}_1 - \text{O}_{13}$ , $\text{Si}_2 - \text{O}_{13}$	1.65 <sub>5</sub>
$\text{C}_1 - \text{O}_1$ , $\text{C}_2 - \text{O}_2$	1.33 <sub>0</sub>
$\text{C}_1 - \text{O}_3$ , $\text{C}_2 - \text{O}_4$	1.22 <sub>0</sub>
$\text{C}_1 - \text{O}_5$ *, $\text{C}_2 - \text{O}_6$ *	1.45 <sub>0</sub>
In ( $\text{Si}_2\text{O}_7$ )	
$\text{O}_{13} - \text{O}_7$ , $\text{O}_{13} - \text{O}_8$	2.58 <sub>0</sub>
$\text{O}_{13} - \text{O}_9$ , $\text{O}_{13} - \text{O}_{10}$	2.58 <sub>0</sub>
$\text{O}_{13} - \text{O}_{11}$ *, $\text{O}_{13} - \text{O}_{12}$ *	2.49 <sub>5</sub>
$\text{O}_7 - \text{O}_9$ , $\text{O}_8 - \text{O}_{10}$	2.71 <sub>5</sub>
$\text{O}_7 - \text{O}_{11}$ *, $\text{O}_8 - \text{O}_{12}$ *	2.72 <sub>0</sub>
$\text{O}_9 - \text{O}_{11}$ *, $\text{O}_{10} - \text{O}_{12}$ *	2.59 <sub>5</sub>
In ( $\text{CO}_3$ )	
$\text{O}_1 - \text{O}_3$ , $\text{O}_2 - \text{O}_4$	2.20 <sub>0</sub>
$\text{O}_1 - \text{O}_5$ *, $\text{O}_2 - \text{O}_6$ *	2.32 <sub>0</sub>
$\text{O}_3 - \text{O}_5$ *, $\text{O}_4 - \text{O}_6$ *	2.39 <sub>5</sub>
$\text{Ca}_1 - \text{O}_1$ , $\text{Ca}_1^* - \text{O}_2$	2.40 <sub>0</sub>
$\text{Ca}_1 - \text{O}_9$ , $\text{Ca}_1^* - \text{O}_{10}$	2.47 <sub>5</sub>
$\text{Ca}_1 - \text{O}_{10}$ , $\text{Ca}_1^* - \text{O}_9$	2.39 <sub>5</sub>
$\text{Ca}_2 - \text{O}_1$ , $\text{Ca}_3 - \text{O}_2$	2.32 <sub>0</sub>
$\text{Ca}_2 - \text{O}_2$ , $\text{Ca}_3 - \text{O}_1$	2.62 <sub>5</sub>
$\text{Ca}_2 - \text{O}_4$ , $\text{Ca}_3 - \text{O}_3$	2.36 <sub>0</sub>
$\text{Ca}_2 - \text{O}_5$ *, $\text{Ca}_3 - \text{O}_7$ *	2.41 <sub>0</sub>
$\text{Ca}_2 - \text{O}_7$ *, $\text{Ca}_3 - \text{O}_8$ *	2.41 <sub>0</sub>
$\text{Ca}_2 - \text{O}_{11}$ *, $\text{Ca}_3 - \text{O}_{12}$ *	2.36 <sub>0</sub>
$\text{Ca}_2 - \text{O}_9$ , $\text{Ca}_3 - \text{O}_{10}$	2.72 <sub>0</sub>
$\text{Ca}_4 - \text{O}_4$ , $\text{Ca}_5 - \text{O}_3$	2.52 <sub>0</sub>
$\text{Ca}_4 - \text{O}_5$ , $\text{Ca}_5 - \text{O}_6$	2.17 <sub>5</sub>
$\text{Ca}_4 - \text{O}_6$ , $\text{Ca}_5 - \text{O}_5$	2.45 <sub>5</sub>
$\text{Ca}_4 - \text{O}_7$ , $\text{Ca}_5 - \text{O}_8$	2.38 <sub>5</sub>
$\text{Ca}_4 - \text{O}_{11}$ , $\text{Ca}_5 - \text{O}_{12}$	2.36 <sub>0</sub>
$\text{Ca}_4 - \text{O}_{12}$ , $\text{Ca}_5 - \text{O}_{11}$	2.44 <sub>0</sub>
$\text{Ca}_4 - \text{O}_4$ *, $\text{Ca}_5 - \text{O}_3$ *	2.93 <sub>5</sub>
Long oxygen contacts	
$\text{O}_1 - \text{O}_4$ , $\text{O}_2 - \text{O}_3$	2.78 <sub>0</sub>
$\text{O}_1 - \text{O}_8$ *, $\text{O}_2 - \text{O}_7$ *	2.98 <sub>5</sub>
$\text{O}_3 - \text{O}_6$ *, $\text{O}_4 - \text{O}_5$ *	3.04 <sub>5</sub>
$\text{O}_5 - \text{O}_{11}$ , $\text{O}_6 - \text{O}_{12}$	2.76 <sub>5</sub>
$\text{O}_9 - \text{O}_9$ *, $\text{O}_{10} - \text{O}_{10}$ *	3.02 <sub>5</sub>

\* Atom whose coordinates are not given in Table 1.

Table 3. *Interatomic angles*

(Values are given to nearest half degree)

Angle at carbon atom		
O <sub>1</sub> -C <sub>1</sub> -O <sub>3</sub> , O <sub>2</sub> -C <sub>2</sub> -O <sub>4</sub>		119°
O <sub>1</sub> -C <sub>1</sub> -O <sub>5</sub> *, O <sub>2</sub> -C <sub>2</sub> -O <sub>6</sub> *		113
O <sub>3</sub> -C <sub>1</sub> -O <sub>5</sub> *, O <sub>4</sub> -C <sub>2</sub> -O <sub>6</sub> *		127
Angle at silicon atom		
O <sub>7</sub> -Si <sub>1</sub> -O <sub>9</sub> , O <sub>8</sub> -Si <sub>2</sub> -O <sub>10</sub>		116½
O <sub>7</sub> -Si <sub>1</sub> -O <sub>11</sub> *, O <sub>8</sub> -Si <sub>2</sub> -O <sub>12</sub> *		119
O <sub>7</sub> -Si <sub>1</sub> -O <sub>13</sub> , O <sub>8</sub> -Si <sub>2</sub> -O <sub>3</sub>		106
O <sub>9</sub> -Si <sub>1</sub> -O <sub>11</sub> *, O <sub>10</sub> -Si <sub>2</sub> -O <sub>12</sub> *		108
O <sub>9</sub> -Si <sub>1</sub> -O <sub>13</sub> , O <sub>10</sub> -Si <sub>2</sub> -O <sub>13</sub>		104
O <sub>11</sub> *-Si <sub>1</sub> -O <sub>13</sub> , O <sub>12</sub> *-Si <sub>2</sub> -O <sub>13</sub>		100½
Angle at calcium atom		
O <sub>1</sub> -Ca <sub>1</sub> -O <sub>9</sub> , O <sub>2</sub> -Ca <sub>1</sub> *-O <sub>10</sub>		79
O <sub>1</sub> -Ca <sub>1</sub> -O <sub>10</sub> , O <sub>2</sub> -Ca <sub>1</sub> *-O <sub>9</sub>		83
O <sub>1</sub> -Ca <sub>1</sub> -O <sub>10</sub> *, O <sub>2</sub> -Ca <sub>1</sub> *-O <sub>9</sub>		101
O <sub>1</sub> -Ca <sub>1</sub> -O <sub>9</sub> *, O <sub>2</sub> -Ca <sub>1</sub> *-O <sub>10</sub> *		96½
O <sub>9</sub> -Ca <sub>1</sub> -O <sub>10</sub> , O <sub>10</sub> -Ca <sub>1</sub> *-O <sub>9</sub>		102½
O <sub>9</sub> -Ca <sub>1</sub> -O <sub>9</sub> *, O <sub>10</sub> -Ca <sub>1</sub> *-O <sub>10</sub> *		77½
O <sub>1</sub> -Ca <sub>2</sub> -O <sub>2</sub> , O <sub>1</sub> -Ca <sub>3</sub> -O <sub>3</sub>		100½
O <sub>1</sub> -Ca <sub>2</sub> -O <sub>4</sub> , O <sub>2</sub> -Ca <sub>3</sub> -O <sub>3</sub>		72½
O <sub>1</sub> -Ca <sub>2</sub> -O <sub>8</sub> *, O <sub>2</sub> -Ca <sub>3</sub> -O <sub>7</sub> *		86½
O <sub>1</sub> -Ca <sub>2</sub> -O <sub>9</sub> , O <sub>2</sub> -Ca <sub>3</sub> -O <sub>10</sub>		75
O <sub>1</sub> -Ca <sub>2</sub> -O <sub>11</sub> *, O <sub>2</sub> -Ca <sub>3</sub> -O <sub>12</sub> *		116
O <sub>2</sub> -Ca <sub>2</sub> -O <sub>4</sub> , O <sub>1</sub> -Ca <sub>3</sub> -O <sub>3</sub>		52
O <sub>2</sub> -Ca <sub>2</sub> -O <sub>7</sub> *, O <sub>1</sub> -Ca <sub>3</sub> -O <sub>8</sub> *		78
O <sub>2</sub> -Ca <sub>2</sub> -O <sub>9</sub> , O <sub>1</sub> -Ca <sub>3</sub> -O <sub>10</sub>		73
O <sub>2</sub> -Ca <sub>2</sub> -O <sub>11</sub> *, O <sub>1</sub> -Ca <sub>3</sub> -O <sub>12</sub> *		107
O <sub>4</sub> -Ca <sub>2</sub> -O <sub>7</sub> *, O <sub>3</sub> -Ca <sub>3</sub> -O <sub>8</sub> *		91
O <sub>4</sub> -Ca <sub>2</sub> -O <sub>8</sub> *, O <sub>3</sub> -Ca <sub>3</sub> -O <sub>7</sub> *		114
O <sub>7</sub> *-Ca <sub>2</sub> -O <sub>8</sub> *, O <sub>8</sub> *-Ca <sub>3</sub> -O <sub>7</sub> *		104
O <sub>7</sub> *-Ca <sub>2</sub> -O <sub>11</sub> *, O <sub>8</sub> *-Ca <sub>3</sub> -O <sub>12</sub> *		80
O <sub>8</sub> *-Ca <sub>2</sub> -O <sub>11</sub> *, O <sub>7</sub> *-Ca <sub>3</sub> -O <sub>12</sub> *		86½
O <sub>9</sub> -Ca <sub>2</sub> -O <sub>11</sub> *, O <sub>10</sub> -Ca <sub>3</sub> -O <sub>12</sub> *		60½
O <sub>4</sub> -Ca <sub>4</sub> -O <sub>4</sub> *, O <sub>3</sub> -Ca <sub>5</sub> -O <sub>3</sub> *		107
O <sub>4</sub> -Ca <sub>4</sub> -O <sub>5</sub> , O <sub>3</sub> -Ca <sub>5</sub> -O <sub>6</sub>		95
O <sub>4</sub> -Ca <sub>4</sub> -O <sub>6</sub> , O <sub>3</sub> -Ca <sub>5</sub> -O <sub>5</sub>		108½
O <sub>4</sub> -Ca <sub>4</sub> -O <sub>11</sub> , O <sub>3</sub> -Ca <sub>5</sub> -O <sub>12</sub>		81½
O <sub>4</sub> -Ca <sub>4</sub> -O <sub>12</sub> , O <sub>3</sub> -Ca <sub>5</sub> -O <sub>11</sub>		96
O <sub>4</sub> *-Ca <sub>4</sub> -O <sub>5</sub> , O <sub>3</sub> *-Ca <sub>5</sub> -O <sub>6</sub>		71
O <sub>4</sub> *-Ca <sub>4</sub> -O <sub>6</sub> , O <sub>3</sub> *-Ca <sub>5</sub> -O <sub>5</sub>		51½
O <sub>5</sub> -Ca <sub>4</sub> -O <sub>6</sub> , O <sub>6</sub> -Ca <sub>5</sub> -O <sub>5</sub>		110½
O <sub>5</sub> -Ca <sub>4</sub> -O <sub>7</sub> , O <sub>6</sub> -Ca <sub>5</sub> -O <sub>8</sub>		82½
O <sub>5</sub> -Ca <sub>4</sub> -O <sub>11</sub> , O <sub>6</sub> -Ca <sub>5</sub> -O <sub>12</sub>		74
O <sub>6</sub> -Ca <sub>4</sub> -O <sub>7</sub> , O <sub>5</sub> -Ca <sub>5</sub> -O <sub>8</sub>		88
O <sub>6</sub> -Ca <sub>4</sub> -O <sub>12</sub> , O <sub>5</sub> -Ca <sub>5</sub> -O <sub>11</sub>		63
O <sub>7</sub> -Ca <sub>4</sub> -O <sub>11</sub> , O <sub>8</sub> -Ca <sub>5</sub> -O <sub>12</sub>		81
O <sub>7</sub> -Ca <sub>4</sub> -O <sub>12</sub> , O <sub>8</sub> -Ca <sub>5</sub> -O <sub>11</sub>		85
O <sub>11</sub> -Ca <sub>4</sub> -O <sub>12</sub> , O <sub>12</sub> -Ca <sub>5</sub> -O <sub>11</sub>		105

\* Atom whose coordinates are not given in Table 1.

have been calculated and are given in Table 2. There is one exception to this caused by the triple overlap of Si<sub>1</sub>, Si<sub>2</sub> and O<sub>13</sub> (Fig. 6). In addition, there is no pseudo-related atom to O<sub>13</sub>. The possible error in the *y*-coordinate of O<sub>13</sub> is not always eliminated by taking mean values; however, the mean of all interatomic distances to O<sub>13</sub> is not subject to the unknown error. Mean values of the interatomic angles are given in Table 3. The standard errors of the atomic parameters and mean interatomic distances are given in Table 4. All distances have been rounded off to the nearest 0.005 Å. The statistical levels of significance suggested

Table 4(a). *Standard deviations of the random errors of the atomic parameters*

z-Axis projection		
Atom	$\sigma$ (x)	$\sigma$ (y)
Double Ca	0.00 <sub>6</sub>	0.00 <sub>6</sub>
Double Si and one O	0.00 <sub>7</sub>	0.00 <sub>7</sub>
Double O	0.02 <sub>5</sub>	0.02 <sub>5</sub>
Double C	0.03 <sub>0</sub>	0.03 <sub>0</sub>
y-Axis projection		
	$\sigma$ (x)	(z)
Single Ca	0.01 <sub>2</sub>	0.01 <sub>2</sub>
Single Si	0.01 <sub>7</sub>	0.01 <sub>7</sub>
Single O	0.05 <sub>0</sub>	0.05 <sub>0</sub>
Single C	0.06 <sub>2</sub>	0.06 <sub>2</sub>

Table 4(b). *Standard deviations of the random errors of the mean interatomic distances*

Atoms	$\sigma$ (Å)
O-O	0.05 <sub>3</sub>
C-O	0.06 <sub>8</sub>
Ca-O	0.03 <sub>8</sub>
Si-O	0.03 <sub>9</sub>
Ca-Ca	0.01 <sub>4</sub>

by Cruickshank (1949) have been used in the discussion of the interatomic distances. In the diagrams and tables, an asterisk is used to denote an atom which does not have the coordinates given in Table 1.

### Discussion of the structure

The structure is shown in Figs. 8-11. In the first two figures the arrangement of atoms in one unique unit is shown. In the last two figures the arrangement of the atoms over a larger region is shown.

The structure is not similar to any known structure type. There are no planes of close-packed oxygen atoms. It is best regarded as an arrangement of isolated Si<sub>2</sub>O<sub>7</sub> and CO<sub>3</sub> group linked together by calcium atoms and held apart by a few oxygen atoms of different groups. The outstanding feature of the structure is the pseudo-halving of the *z* axis. The next most important feature is that all the atoms lie near to the (204) planes, which are approximately normal to the *z* axis. Each calcium atom has approximately six near oxygen neighbours and all the Ca-O bonds are nearly parallel to one of three directions, one in the (204) plane and two others symmetrically inclined to this plane.

The mean Si-O distance is 1.61<sub>0</sub>±0.02<sub>0</sub> Å. This distance is to be compared with the value of about 1.62 which has usually been found in SiO<sub>4</sub> groups, though values from 1.5-1.8 Å are recorded in the literature. The deviations in the values of the four Si-O distances from the overall mean value of 1.61<sub>0</sub> are not significant. The average value of the O-O distances in the Si<sub>2</sub>O<sub>7</sub> group is 2.61<sub>5</sub>±0.02<sub>0</sub> Å; the deviations from the mean value are again not significant.

If there is any distortion in the  $\text{Si}_2\text{O}_7$  group it would be expected to show up in the distances and angles involving  $\text{O}_{13}$  because this central oxygen atom

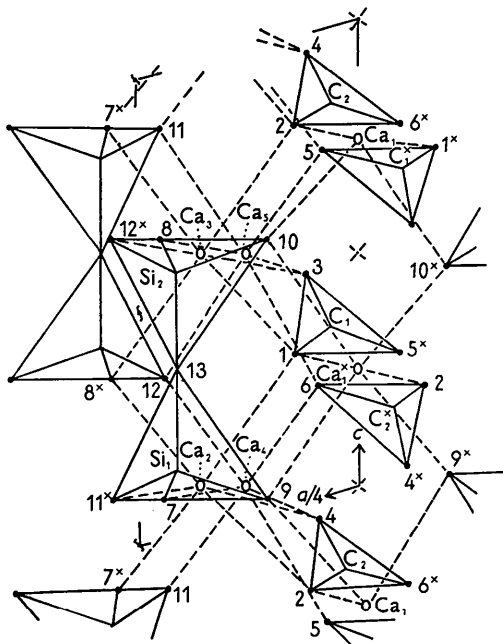


Fig. 8. The  $y$  axis projection of the structure. The adjacent  $\text{CO}_3$  groups have been moved apart to reduce confusion on the diagram. Atoms not in the unique unit are denoted by crosses. Other atoms have the coordinates given in Table I. Outlines of  $\text{CO}_3$  and  $\text{Si}_2\text{O}_7$  groups are shown by full lines and  $\text{Ca-O}$  bonds by broken lines.

is linked to two silicon atoms whereas all the other six are linked only to one. The mean of the two  $\text{Si-O}$  bonds to  $\text{O}_{13}$  is  $1.65_5 \text{ \AA}$  with a random error of  $0.04_0 \text{ \AA}$  and a possible systematic error which would increase the distance. The mean of all the other  $\text{Si-O}$  bonds is  $1.60_0 \pm 0.02_0 \text{ \AA}$  (random error only). The difference in the measured values is probably not significant, but it is in the direction expected from the Coulomb repulsion between the silicon cations and the two tetrahedra (Pauling, 1929). The mean of the  $\text{O-O}$  distances to the central oxygen atom,  $\text{O}_{13}$ , is  $2.55_0 \text{ \AA}$ , whereas the mean of the outer  $\text{O-O}$  distances is  $2.67_5 \pm 0.03_0 \text{ \AA}$ ; the difference is statistically significant. Comparing the means of the inner and outer  $\text{O-Si-O}$  angles, we have  $103^\circ 30'$  and  $114^\circ 20' \pm 3^\circ$ ; this difference is again significant. The distortion of the  $\text{O-O}$  distance is interesting; a possible explanation is that it is caused by Coulomb attraction between the outer oxygen atoms and the silicon atom in the adjoining tetrahedron. If the groups of inner and outer  $\text{O-O}$  distances are considered separately, the individual deviations from the mean for the group are not significant, except possibly for the distance involving  $\text{O}_9\text{-O}_{11}$  and  $\text{O}_{10}\text{-O}_{12}$ . This distance is smaller than the mean value, and the decrease may be caused by sharing of edges between silicon tetrahedra and the

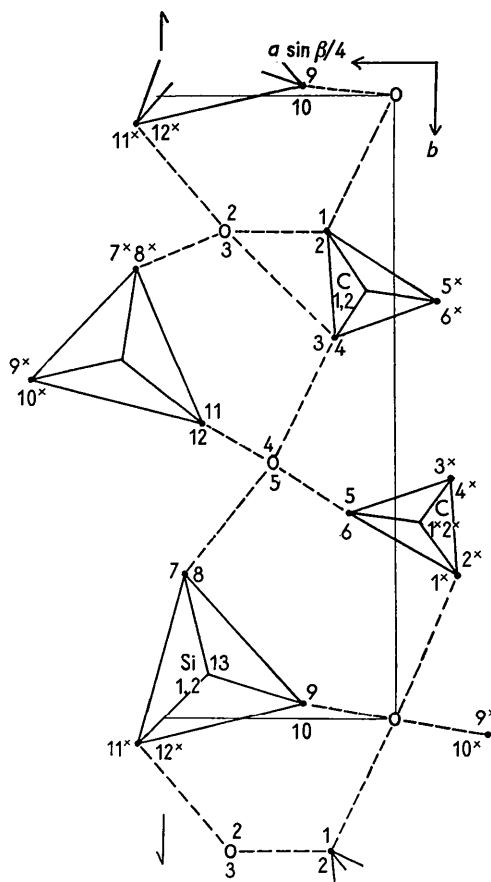


Fig. 9. The  $z$  axis projection of the structure. Atoms not in the unique unit are denoted by crosses. Other atoms have the coordinates given in Table I. Outlines of  $\text{CO}_3$  and  $\text{Si}_2\text{O}_7$  groups are shown by full lines and  $\text{Ca-O}$  bonds by broken lines.

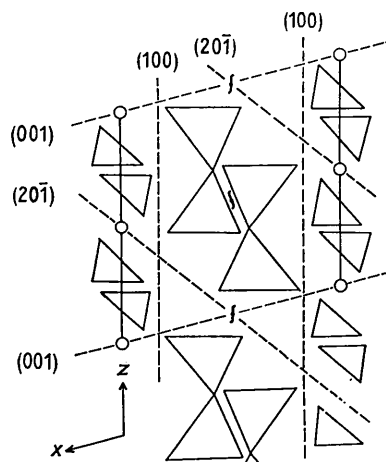


Fig. 10. The  $y$  axis projection, showing cleavages (100), (001) and  $(20\bar{1})$ . Outlines of the  $\text{CO}_3$  and  $\text{Si}_2\text{O}_7$  groups are shown by full lines, cleavages by broken lines.

polyhedra of  $\text{Ca}_2$  and  $\text{Ca}_3$ ; it would be expected (Pauling, 1929) that these edges would be shortened. In the literature, reports have been given of the

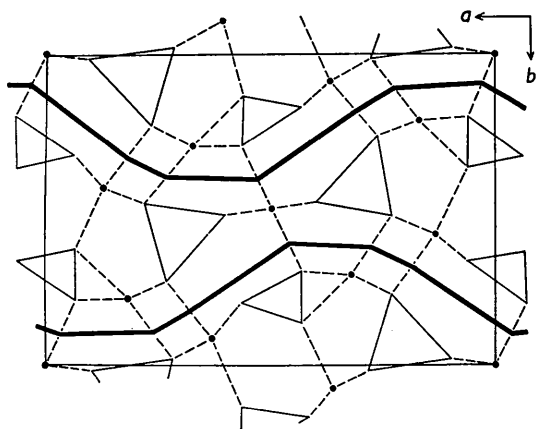


Fig. 11. The  $z$  axis projection, showing (010) cleavages. Outlines of  $\text{CO}_3$  and  $\text{Si}_2\text{O}_7$  groups are shown by full lines, cleavages by heavy full lines, Ca-O bonds by broken lines. Large triangles:  $\text{Si}_2\text{O}_7$ ; small triangles:  $\text{CO}_3$ .

structure determinations of five other minerals containing  $\text{Si}_2\text{O}_7$  groups: melilite (Warren, 1930), thortveitite (Zachariasen, 1930), hemimorphite, (Ito & West, 1932), idocrase, also called vesuvianite (Warren & Modell, 1931) and lawsonite (Wickman, 1947). For none of these structure has an assessment been made of the errors in the interatomic distances. It is not possible, therefore, to make an accurate comparison of the interatomic distances and the shapes of the  $\text{Si}_2\text{O}_7$  groups. The position of the  $\text{Si}_2\text{O}_7$  group in idocrase is uncertain and it is not described here. In all the four other minerals, the two tetrahedra are related by planes of symmetry. The  $\text{Si}_2\text{O}_7$  group of tilleyite has a pseudo-plane of symmetry relating the two tetrahedra and the displacement of the atoms from truly symmetric positions is only about 0.2 Å. There is, therefore, a close resemblance between the general shapes of the  $\text{Si}_2\text{O}_7$  groups in these minerals.

In considering the  $\text{CO}_3$  groups, the best data to use are again the means of corresponding distances in the two non-equivalent groups. The overall mean C-O distance is  $1.33_5 \pm 0.04_0$  Å and the overall mean O-O distance is  $2.30_5 \pm 0.03_0$  Å. This C-O distance is rather longer than those found in previous structures: 1.313 Å in calcite, (Elliott, 1937),  $1.23 \pm 0.01$  and  $1.26 \pm 0.01$  Å in sodium sesquicarbonate (Brown, Peiser & Turner-Jones, 1949), 1.27 Å in sodium bicarbonate (Zachariasen, 1933) and 1.22 and 1.25 Å in sodium bicarbonate monohydrate (Harper, 1936). The displacement of the carbon atom from the centroid of the  $\text{CO}_3$  group is not statistically significant; its value is 0.13<sub>5</sub> Å, but the error in the location of the carbon atom is greater than that of other atoms (as can be seen from Table 4). One edge of the  $\text{CO}_3$  group is significantly shorter than the other. This edge (mean of  $\text{O}_1-\text{O}_3$ ,  $\text{O}_2-\text{O}_4$ ) is shared with a calcium polyhedra and would be expected to be shorter (Pauling, 1929).

The surroundings of the calcium atoms are also of

interest. The Ca-O distances vary from  $2.17_5$  to  $2.62_5 \pm 0.04_0$  Å (with two larger ones of  $2.72_0$  and  $2.93_5$  Å), the mean value being  $2.40_5 \pm 0.01_0$  Å. Only the values of  $2.17_5$ ,  $2.62_5$ ,  $2.72_0$  and  $2.93_5$  differ from the mean by more than about twice the standard error. The distance of  $2.17_5$  Å is very short and appears very improbable. However, in the recent determination of tourmaline by Donnay & Buerger (1950) values of 2.22 and 2.28 Å were found for (Ca, Na) atoms. Many determinations by various workers have recorded values considerably greater than 2.40 Å, which may be compared with the three large distances found here.

The environments of the calcium atoms in tilleyite (see Fig. 12) are fairly similar but there are some differences worth noting.  $\text{Ca}_1$  has a slightly distorted octahedron with a range in O-Ca-O angles from  $77\frac{1}{2}^\circ$  to  $102\frac{1}{2}^\circ$ , and all distances nearly equal.  $\text{Ca}_2$  and  $\text{Ca}_3$  have five oxygen atoms at about 2.4 Å with angles from  $72\frac{1}{2}^\circ$  to  $116^\circ$  and instead of a sixth atom there are two at longer distances ( $\text{O}_2$  at 2.62 and  $\text{O}_9$  at 2.72 Å) and smaller angles. The steric coordination is seven but electrostatically the coordination is five.  $\text{Ca}_4$  and  $\text{Ca}_5$  have six oxygen atoms in a distorted octahedron with distances varying 2.17<sub>5</sub> to 2.52 Å, but there is an extra oxygen atom,  $\text{O}_7^*$ , at 2.93 Å and at smaller angles. Because of this large distance,  $\text{Ca}_4$  and  $\text{Ca}_5$  can almost be regarded as being six-coordinated, both electrostatically and sterically. This type of irregularity is typical of calcium polyhedra and numbers of oxygen neighbours varying from six to nine have been recorded in different structures. Relatively few of the structures have been studied with sufficient accuracy to make detailed discussion worth while. Two recent accurate determinations of calcium-containing minerals are those of awillite

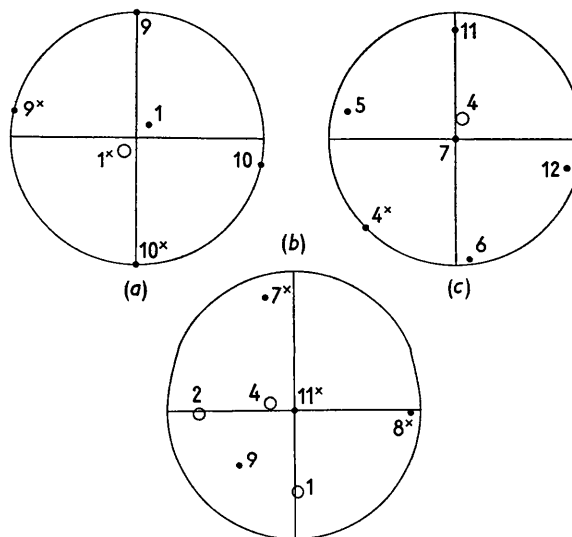


Fig. 12. Stereograms showing mean environments of pairs of calcium atoms. (a)  $\text{Ca}_1^*$ ,  $\text{Ca}_1$ . (b)  $\text{Ca}_2$ ,  $\text{Ca}_3$ . (c)  $\text{Ca}_4$ ,  $\text{Ca}_5$ . The diagram is actually drawn for the first-mentioned atom of each pair.



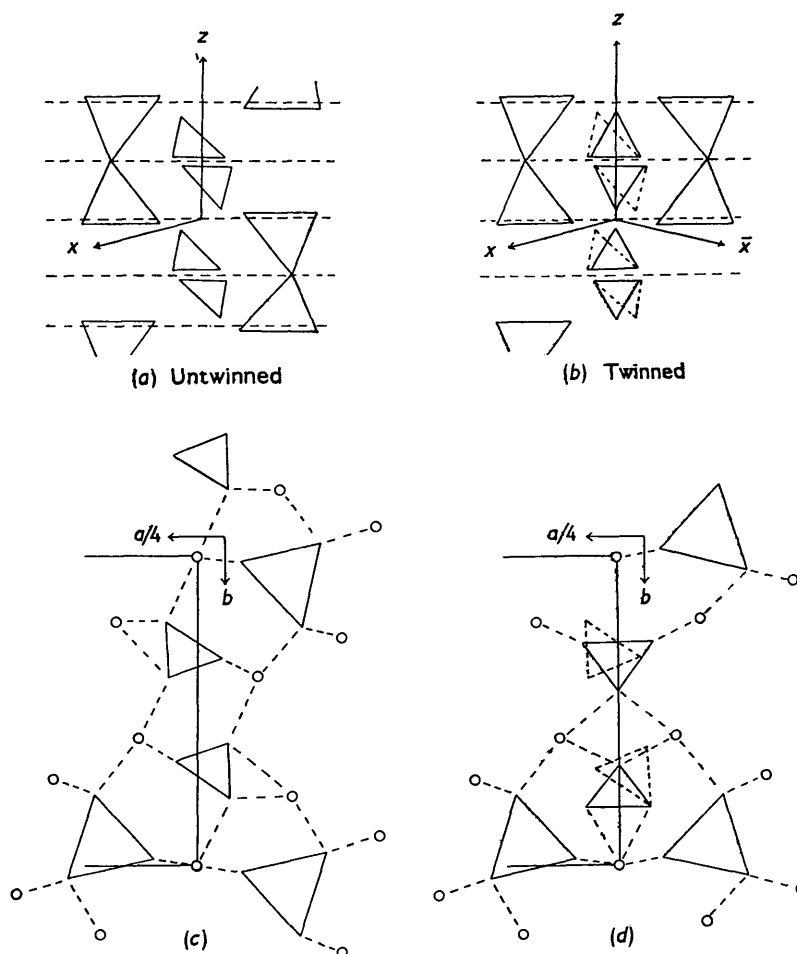


Fig. 13. The twinning of tilleyite.

(three-dimensional analysis, Megaw, 1952, and melilite, Smith, 1953). In afwillite, the environment of the calcium atoms is qualitatively very similar to that in tilleyite. In melilite, the calcium atom has four near and four distant neighbours and has a markedly different environment from those in afwillite and tilleyite. These differences are discussed further in the paper on melilite.

Because of the irregularity of the calcium polyhedra, Pauling's rule of electrostatic valence bonds (Pauling, 1929) cannot be expected to hold exactly as it applies only to approximately regular polyhedra. It is, however, satisfied for some of the oxygen atoms. If it is assumed for this purpose that each calcium has six oxygen neighbours, only  $O_1$ ,  $O_2$ ,  $O_9$  and  $O_{10}$  do not have the correct number of electrostatic valence bonds. The deviation from Pauling's rule is therefore small.

The closest approaches of oxygen atoms not in the same  $Si_2O_7$  or  $CO_3$  groups are at 2.76<sub>5</sub>, 2.78<sub>0</sub>, 2.98<sub>5</sub> and 3.04<sub>5</sub> Å. None of these distances is less than 2.7 Å, which is the smallest distance to be expected for van der Waals contacts.

#### Explanation of the physical properties

The predicted cleavages of tilleyite are shown in Figs. 10 and 11 and are the same as those found by Nockolds (1947). The three cleavages (100), (001) and  $(20\bar{1})$  are straight cleavages, whereas the (010) cleavage runs a zigzag course through the structure. The cleavages leave intact the tightly-bound  $Si_2O_7$  and  $CO_3$  groups and only break the weaker Ca-O and van der Waals bonds. Assuming that the number of Ca-O bonds per unit cross section of the cleavage plane gives a measure of the ease of cleavage, the  $(20\bar{1})$  cleavage should be the easiest. This prediction agrees with Nockolds's observations. All other ways of splitting the structure break a higher density of Ca-O bonds.

The explanation of the twinning of tilleyite is shown in Fig. 13. As shown by the measurement of the extinction angles, the composition-plane of the twins is (100). The effect of reflexion over this plane is shown in the Fig. 13(a) and (b). Because the atoms in the structure lie near to the  $(20\bar{4})$  planes and these planes are almost normal to the twin plane, the atoms

in the twinned portion also lie near the  $(20\bar{4})$  planes. At the contact of the twin, it seems likely that the  $\text{CO}_3$  groups move slightly from the usual position (broken line) to the symmetrical position (full line). In Fig. 13(c) and (d), the effect of the twinning in the  $z$ -axis projection is shown. In order that the oxygen atoms should not approach too near the calcium atoms, the  $\text{CO}_3$  groups move into the positions symmetrical to the twin plane. In the new positions, the oxygen atoms are then at the usual bonding distance from the calcium atoms. Each oxygen atom of the top  $\text{CO}_3$  group has two near calcium atoms, giving the ideal coordination. For the bottom  $\text{CO}_3$  group the coordination is not so good, since there are 2, 1 and 1 calcium atoms bonded respectively to the three oxygen atoms. The coordination of the calcium atom changes by only one oxygen atom, whereas the coordination of the  $\text{Si}_2\text{O}_7$  group is unchanged. This explanation of the twinning of tilleyite therefore indicates that there is only a small change in the structure, all the atoms being placed in reasonable positions.

An estimate of the refractive indices of tilleyite may be made from the structure on the lines suggested by the work of Born (1915), Bragg (1924) and Wooster (1931). We expect that each  $\text{CO}_3$  group in tilleyite will give a large contribution to the principal refractive indices in its plane and a small one to the principal refractive index normal to the plane. Comparison of the double refraction of carbonates and silicate-containing minerals suggests that the contribution from  $\text{CO}_3$  groups should be much larger than from  $\text{Si}_2\text{O}_7$  groups. To a first approximation, therefore, an attempt has been made to explain the double refraction solely from the  $\text{CO}_3$  groups.

There are only two orientations of the  $\text{CO}_3$  groups to be considered (if the pseudo-halving is taken as a true halving). These two orientations are related by a screw diad parallel to the  $y$  axis. The two  $\text{CO}_3$  groups both intersect the (010) plane at an angle of  $60^\circ$  to the  $z$  axis in the obtuse angle between the  $x$  and  $z$  axes. The planes of the two  $\text{CO}_3$  groups are symmetrically inclined at  $41^\circ$  to the  $y$  axis and are related by the axis of symmetry. Both  $\text{CO}_3$  groups should give a large contribution to the refractive index along the direction at  $60^\circ$  to the  $z$  axis. The refractive indices in other directions should be smaller since the contributions from each  $\text{CO}_3$  group do not both reach the maximum in the same direction. As the planes of the  $\text{CO}_3$  groups are inclined at  $41^\circ$  to the  $y$  axis and  $49^\circ$  to the normal to the  $y$  axis and the direction of the maximum contribution, the refractive index along the  $y$  axis should lie between the maximum and minimum values. Nockolds (1947) observed that the largest refractive index was along the direction at  $66^\circ$  to the  $z$  axis in

the obtuse angle between the  $x$  and  $z$  axes, and that the medium refractive index was along the  $y$  axis. The agreement is quite good.

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