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The Crystal Structure of Spurrite, $Ca_5(SiO_4)_2CO_3$. II. Description of Structure*

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Spurrite contains 4 units of $Ca_5(SiO_4)_2CO_3$ in a monoclinic unit cell with

$$a = 10{\cdot}49,\quad b = 6{\cdot}705,\quad c = 14{\cdot}16\ \text{Å},\quad \beta = 101°\ 19',$$

space group $P2_1/a$. The atomic coordinates were determined from three-dimensional data by the direct probability method. The structure consists of isolated SiO_4 tetrahedra and CO_3 equilateral triangles linked together by Ca atoms, in an arrangement with pronounced pseudo-orthorhombic symmetry. The CO_3 groups lie perpendicular to the y-axis in conformity with y being the acute negative optical bisectrix. The SiO_4 groups bear no special relationship to the axes, but the Si, Ca and C atoms fall within 0·5 Å of a hexagonal grid. The polysynthetic (001) twin results from the pseudo-orthorhombic symmetry. The perfect (001) cleavage arises from planes of weakness where the density of Ca–O bonds is relatively low.

Introduction

Spurrite, $Ca_5(SiO_4)_2CO_3$, tilleyite, $Ca_5(Si_2O_7)(CO_3)_2$, and scawtite, $Ca_7Si_6O_{18}CO_3 . 2\,H_2O$, are the three known representatives of the calcium carbonate silicate group of minerals. All three are very rare, occurring as the product of thermal metamorphism in contact zones between hot basic magma and carbonate rocks. The crystal structure of tilleyite has been determined by Smith (1953) and the crystal structure of scawtite is at present under investigation by Dr Christine Kelsey in Cambridge, England. Crystal data for scawtite have been determined by McConnell (1955) and Murdoch (1955).

The structure determinations of tilleyite and spurrite were begun in 1948 by J. V. Smith at the University of Cambridge, England as part of a doctoral programme. The structure of tilleyite was solved in 1951 but that of spurrite was still undetermined when Smith obtained his Ph.D. and left for the Geophysical Laboratory, Washington D.C. While there he met the other three authors and offered his three-dimensional data on spurrite to them as a test of the probability method of phase determination. As described in the adjacent paper (Hauptman, Karle & Karle, 1960), this method proved to be completely successful, and we are now able to examine the rather unusual crystal chemical properties of this mineral.

Experimental data

The crystals used in this investigation were kindly supplied by Prof. C. E. Tilley from the well-known contact zone at Scawt Hill, North Ireland. Preliminary data on spurrite were given by Smith (1955). Spurrite contains 4 units of $Ca_5(SiO_4)_2CO_3$ in a monoclinic unit cell of symmetry $P2_1/a$ and dimensions $a = 10{\cdot}49$, $b = 6{\cdot}705$, $c = 14{\cdot}16$ Å (all plus or minus 0·05%), $\beta = 101°\ 19' \pm 5'$. These cell dimensions were measured from a powder pattern taken on a diffractometer using an internal standard of silicon mixed in a smear mount with the spurrite. The fully indexed powder pattern will appear elsewhere.

Two-dimensional intensity data for the three principal zones were obtained by eye-estimation of multiple films exposed in a Weissenberg camera. Patterson projections were computed from these data, but after several unsuccessful attempts to interpret the patterns, it was decided to collect three-dimensional data. Because of the excessive demand at that time for moving-film cameras, the three-dimensional data were collected from overlapping oscillation photographs. Multiple packs of film interleaved with copper foil were used to give a step-down factor from film to film of 3·2. To minimize indexing ambiguities the two longest principal axes, x and z, were used for the oscillations. A small crystal, almost cubical, was used to reduce the absorption error to insignificance. To cut down the labour, only reflections with spacings greater than 1 Å were measured. About 80% of the

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reflections occurred on both sets of oscillation photographs, providing an excellent check on the accuracy of the indexing and the intensity measurements. Correction for the factors that depend on zeta was made by correlating the two sets of data. Comparison of the two sets of data after correction for the zeta-factor indicates a probable error of about 8% in the mean observed structure amplitudes. At the time the data were collected, it was intended to use them only to compute the Patterson function, and to save time, an intensity range of only 100 was measured. The resulting range of observed structure amplitudes is only about 10, considerably less than normal.

The preliminary 2-dimensional Patterson projections had shown that most of the vector density lay on the planes (040) so five bounded Patterson projections were computed for the layers $y=-1/16$ to $+1/16$, 1/16 to 3/16, 3/16 to 5/16, 5/16 to 7/16 and 7/16 to 9/16. Interpretation of the projections had only just begun when Smith left for Washington and temporarily shelved the project. It is of some interest that the atomic coordinates found by the other three authors give vectors in excellent accord with the Patterson maps. The maps are available in a doctoral dissertation (Smith, 1951).

Table 1. *Atomic coordinates*

Atom	x	y	z
Ca_1	0·140	0·661	0·072
Ca_2	0·033	0·240	0·612
Ca_3	0·239	0·061	0·455
Ca_4	0·044	0·990	0·830
Ca_5	0·133	0·507	0·826
Si_1	0·135	0·221	0·056
Si_2	0·025	0·750	0·604
O_1	0·124	0·237	0·938
O_2	0·141	0·995	0·098
O_3	0·008	0·334	0·083
O_4	0·263	0·333	0·106
O_5	0·883	0·153	0·468
O_6	0·890	0·427	0·335
O_7	0·024	0·072	0·330
O_8	0·098	0·340	0·468
O_9	0·283	0·696	0·235
O_{10}	0·073	0·685	0·230
O_{11}	0·211	0·712	0·372
C	0·185	0·695	0·285

The atomic coordinates of spurrite were determined by Hauptman, Karle & Karle (1960) as described in the adjacent paper. The coordinates were subjected to a least-squares refinement using a programme made by Dr W. Busing of Oak Ridge, Tennessee in which each atom is assigned a different isotropic temperature factor. A copy of the final observed and calculated structure factors has been deposited at the Library of Congress (No. 6318). The final R factor is 18·9% for all reflections and 13·1% for observed reflections. The large difference results from the small range of structure amplitudes recorded on the photographic films.

Table 1 contains the atomic coordinates and Table 2 the more important of the interatomic distances. The random errors obtained from the least-squares programme together with the standard deviations in the interatomic distances (following Cruickshank, 1949) are shown in Table 3. Values for $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ for the different positions of the same chemical atom agreed within ten percent and only the average values are listed in Table 3.

Table 2. *Interatomic distances*

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
Si_1–O_1	1·656	Si_2–O_5	1·668	Ca_3–O_5	2·425
Si_1–O_2	1·625	Si_2–O_6	1·626	–O_5'	2·331*
Si_1–O_3	1·641	Si_2–O_7	1·658	–O_6	2·541
Si_1–O_4	1·580	Si_2–O_8	1·597	–O_7	2·580
Mean	1·626	Mean	1·637	–O_8	2·362
O_1–O_2	2·765	O_5–O_6	2·642	–O_8'	2·414
O_1–O_3	2·664	O_5–O_7	2·727	–O_{11}	2·607
O_1–O_4	2·615	O_5–O_8	2·580	–O_{11}'	2·609
O_2–O_3	2·654	O_6–O_7	2·772	Mean	2·484
O_2–O_4	2·595	O_6–O_8	2·652	Ca_4–O_1	2·298*
O_3–O_4	2·631	O_7–O_8	2·655	–O_2	2·363
Mean	2·654	Mean	2·671	–O_3	2·607
C–O_9	1·358	O_9–O_{10}	2·192	–O_4	2·303*
C–O_{10}	1·277	O_9–O_{11}	2·223	–O_7	2·277*
C–O_{11}	1·255	O_{10}–O_{11}	2·238	–O_9	2·589
Mean	1·283	Mean	2·218	–O_{10}	2·563
Ca_1–O_1	2·558	Ca_2–O_5	2·390	Mean	2·429
–O_2	2·269*	–O_6	2·442	Ca_5–O_1	2·420
–O_3	2·428	–O_7	2·367	–O_2	2·404
–O_3'	2·614	–O_8	2·371	–O_3	2·395
–O_4	2·547	–O_9	2·620	–O_4	2·546
–O_9	2·505	–O_{10}	2·733	–O_6	2·289*
–O_{10}	2·478	–O_{11}	2·632	–O_9	2·484
–O_1'	(2·830)	–O_{11}'	2·658	–O_{10}	2·506
Mean	2·484†	Mean	2·527	Mean	2·435

* Ca–O distances less than 2·35 Å.

† (excluding Ca_1–O_1')

Table 3. *Errors*

	$\sigma(x)$		σ (dist.)
Ca	$0{\cdot}00_7$ Å	Ca–O	$0{\cdot}02_2$ Å
Si	$0{\cdot}01_0$	Si–O	$0{\cdot}02_3$
O	$0{\cdot}02_1$	O–O	$0{\cdot}03_0$
C	$0{\cdot}03_2$	C–O	$0{\cdot}03_8$

Discussion

The crystal structure is shown in Fig. 1, which is a projection down b, the shortest axis. The arrangement of the SiO_4 tetrahedra, CO_3 equilateral triangle and Ca ions is quite complex but has elements of pseudo-symmetry which result in some simplification (Fig. 2). The elements of pseudo-symmetry arise because the planes $(40\bar{1})$ are almost exactly at right angles to the x-axis, and because the atoms are arranged about the $(40\bar{1})$ planes with a high degree of pseudo-symmetry. The true symmetry elements of $P2_1/a$ are centers of symmetry at the origin and related positions, screw diads at $x=\frac{1}{4}$, $z=0$ and related positions, and a glide planes at $y=\frac{1}{4}$ and $\frac{3}{4}$. Some of the elements of pseudo-symmetry are shown in Fig. 2. Pseudo-screw diads that operate on all the atoms occur at $y=0$ and $\frac{1}{2}$, $z=\frac{1}{2}$ but not $z=0$. Elements of pseudo-symmetry that operate on some of the atoms but not on others are as follows: c glide plane at $z=\frac{1}{2}$, planes of symmetry lying half-way between the (40$\bar{1}$) planes, rotation diads lying between the (40$\bar{1}$) planes at $y=\frac{1}{4}$ and $\frac{3}{4}$. The latter two types are especially interesting because the planes and diads alternate as shown in Fig. 2. Additional elements of pseudo-symmetry can be listed but the ones given above are sufficient for an understanding of the crystal structure. The deviation of atomic positions from those required by true symmetry is small, amounting to a maximum of 0·2 Å.

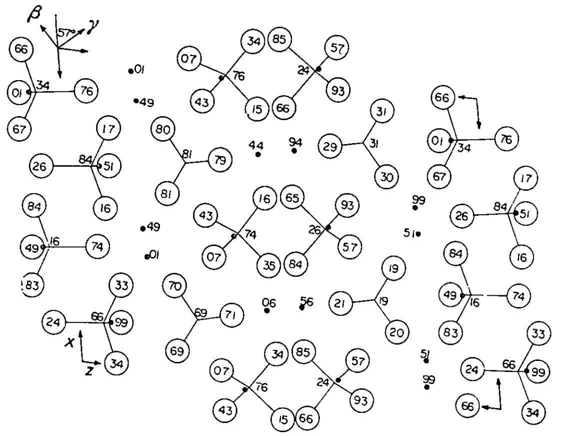

Fig. 1. The structure of spurrite. The oxygen atoms are shown by the large open circles and the calcium atoms by small filled circles. The Si and C atoms lie at the intersections of the lines drawn from the oxygen atoms. Heights of the O, Ca and C atoms are given in percentages of the b repeat unit. To avoid confusion, the heights of the Si atoms are omitted but may be readily found by comparison with Fig. 3. The positions of the principal optic axes Y and Z are shown in the upper left.

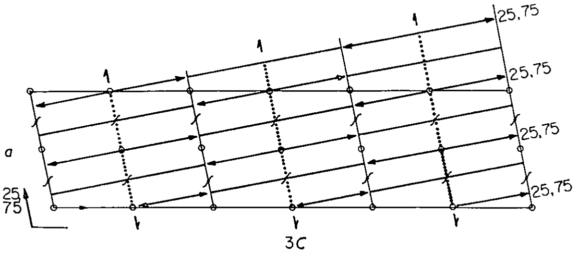

Fig. 2. The true and pseudo symmetry elements of spurrite. Three unit cells are shown projected down the b-axis. The true symmetry elements are the centres of symmetry, the screw diads lying in the planes $z=0$ and $\frac{1}{2}$, and the a glide planes at $y=\frac{1}{4}$ and $\frac{3}{4}$.

In addition to the orthorhombic pseudo-symmetry of all the atoms, there is a further pseudo-hexagonal pattern for the Ca, Si and C atoms. From Fig. 3 it may be seen that the Si, C and some of the Ca atoms, lie within 0·2 Å of a hexagonal net based on the planes 20$\bar{5}$, 40$\bar{1}$ and 204 (actually for 40$\bar{1}$ and 204, the planes of the hexagonal net lie halfway between the 40$\bar{1}$ and 204 planes). The remainder of the Ca atoms lie somewhat further away, about 0·6 Å. In addition the Ca, Si and C atoms lie fairly close to the 040 planes. Upon examination of the atomic arrangement it is found that no simple pattern such as that in hexagonal or cubic close-packing of spheres occurs for the Ca, Si and C atoms of spurrite.

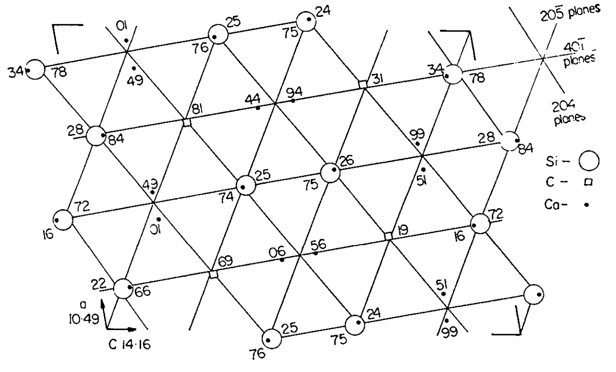

Fig. 3. The arrangement of Ca, Si and C atoms of spurrite shown in relation to the hexagonal grid formed by the planes 40$\bar{1}$, 20$\bar{5}$, 204. Heights of atoms are given as percentages of the b repeat unit.

The CO_3 groups are equilateral triangles lying perpendicular to the b-axis, thus explaining the optical property that the b-axis is parallel to the acute negative optical bisectrix. Each oxygen atom has four calcium atoms as near neighbours at distances of 2·5 to 2·7 Å, rather larger than the usual Ca–O distances of 2·4 Å. The arrangement of the Ca atoms around the CO_3 groups is quite different from either of those in calcite and aragonite as may be seen from Fig. 4. In calcite each oxygen atom has two near calcium neighbours, while aragonite has three.

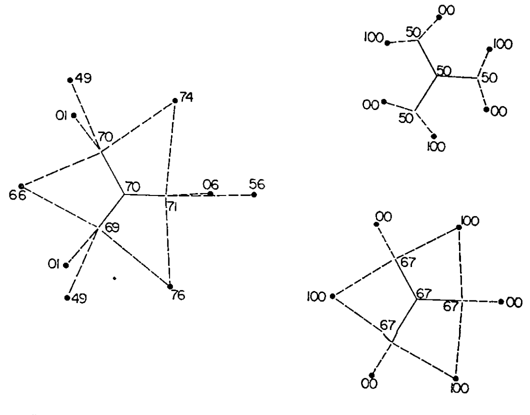

Fig. 4. The arrangement of Ca atoms and CO_3 groups in (left) spurrite, (upper right) calcite, and (lower right) aragonite. The relative heights of the atoms are shown by the numbers. The unit of vertical height is different for each structure.

The two unique silicon tetrahedra have different orientations, but the linkage between the tetrahedra and Ca atoms along the y-axis is similar (Fig. 5). Both tetrahedra have one edge nearly perpendicular to the *b*-axis. The tetrahedra alternate with Ca atoms that are bonded to the two oxygen atoms which form this edge and to a single oxygen atom from the next tetrahedron. The difference between the orientations of the tetrahedra can be seen from Figs. 4 and 1. The Si_2 tetrahedron has two opposite edges nearly perpendicular to the *b*-axis while the Si_1 tetrahedron has a face formed by the $O_2O_3O_4$ atoms nearly parallel to the (001) plane, with the O_3O_4 edge perpendicular to the *b*-axis.

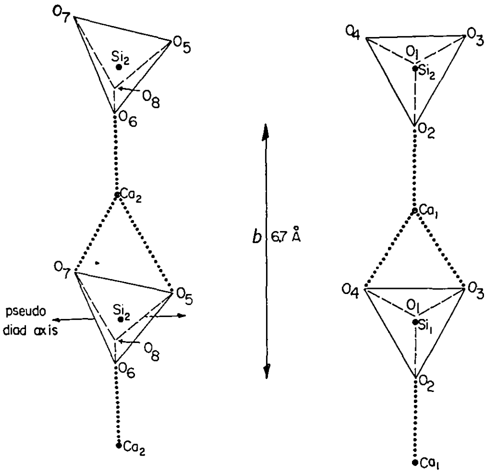

Fig. 5. Nature of the linkage of silicon tetrahedra by Ca atoms along the *y*-axis.

The linkage pattern of the CO_3 and SiO_4 groups by the Ca atoms is quite irregular and will not be described for it is thought that it has insufficient significance. The Ca–O distances are very variable ranging upwards from 2·27 Å. Deciding which oxygen atoms belong to the calcium polyhedra is somewhat arbitrary and a cut-off at 2·8 Å has been assumed. Three of the Ca atoms have seven neighbouring oxygen atoms and the other two eight neighbours. The irregularity of the Ca–O distances is paralleled by that in other calcium-bearing compounds. Only simple substances of high symmetry such as calcite have regular Ca polyhedra. In others such as afwillite, diopside, tilleyite and epidote, it seems that the more tightly bound polyhedra arrange themselves in the most convenient manner, and the calcium then fills in the holes between the oxygen atoms subject to a tolerance in the Ca–O distance of 0·25 Å and of three in the coordination number. In spurrite there are several Ca–O distances smaller than the sum of the ionic radii (approximately 2·4 Å). These distances, 2·27, 2·28, 2·30, and 2·33 differ from 2·4 Å by more than three times the standard deviation of 0·022 Å and hence have highly significant deviations. They have their counterparts in other structures such as afwillite (Megaw, 1952), tilleyite (Smith, 1955) and epidote (Ito, Morimoto & Sadanaga, 1954) where values as low as 2·2 Å have been recorded.

The mean Si–O distances in the tetrahedra, 1·626 and 1·637 Å, have an individual standard deviation of 0·011 Å and the mean value 1·63 is significantly greater than the value of 1·60 Å suggested by Smith (1954) after reviewing available measurements for a variety of silicates. He thought that the mean Si–O distance in a tetrahedron was uninfluenced by the linkage of the tetrahedron and suggested that precise values of the amount of substitution of Al in an Al, Si tetrahedron could be obtained from measurements of the size of the tetrahedron. The present measurement suggests that the Si–O distance may not be as constant as Smith suggested, and it is suggested that a programme of accurate structure determinations be carried out in a similar manner to those already completed for organic materials.

The C–O distances vary from 1·21 to 1·36 with a mean of 1·28 ± 0·02 Å which is in fair agreement with the other values: 1·294 Å, $\sigma = 0{\cdot}004$ Å, in calcite (Sass, Vidale & Donohue, 1957), 1·23 ± 0·01 Å and 1·26 ± 0·01 Å in sodium sesquicarbonate (Brown, Peiser & Turner-Jones, 1949), 1·27 Å in sodium bicarbonate (Zachariasen, 1933), 1·33 ± 0·04 Å in tilleyite (Smith, 1954).

Estimating the local charge balance by Pauling's second rule is subject to uncertainty because it is necessary to draw an arbitrary boundary in selecting the Ca–O linkages to be counted for the valence bonds. If all the distances below 2·8 Å are counted and given equal weight the charge contributions to the oxygen atoms vary from 1·75 to 2·4. The contributions to the three oxygen atoms of the CO_3 group are considerably larger than those to the oxygens of the SiO_4 tetrahedra. When the actual distances of the Ca–O bonds are examined it is found that the mean of the Ca–O distances to the CO_3 group, 2·58 Å, is considerably greater than the mean for the SiO_4 group, 2·44 Å, suggesting that the former bonds are weaker than the

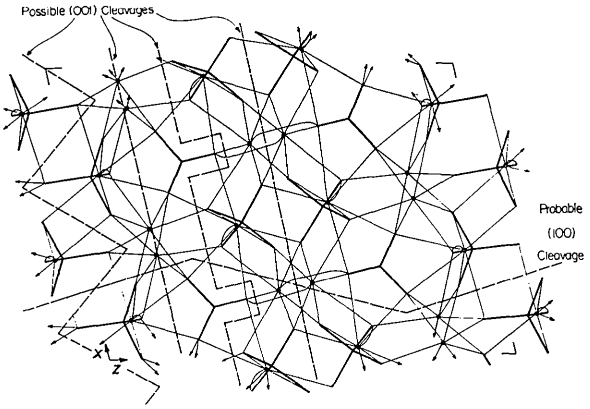

Fig. 6. The bonding and cleavages of spurrite. In this *y*-axis projection the Si–O and C–O bonds are shown by thick lines and the Ca–O bonds by thinner lines. Several of the Ca–O bonds have been bent into curves to avoid confusion. Four possible positions for the (001) cleavage and one for the (100) cleavage are shown by broken lines.

latter in an attempt to make a more uniform local charge distribution.

Spurrite has two cleavages, neither of which is particularly frequent. The better cleavage (001) described as a perfect cleavage, has four possible paths through the crystal structure (Fig. 6). If it is assumed that the ease of cleavage depends on the number of Ca–O bonds broken per unit cell then each of the four paths is equally likely for they all break 16 bonds per unit cell. However, other factors, whose significance cannot be assessed, will probably make one of the paths easier than the others. The poorer cleavage (100) probably passes through the path shown in Fig. 6. There are about 15% more Ca–O bonds lying across this cleavage plane than for the cleavage (001), in conformity with the observed ease of cleavage.

Spurrite has two twin laws. Polysynthetic twinning occurs on (001) and is readily explained in terms of orthorhombic pseudo-symmetry (Fig. 7). If the structure is rotated by a diad axis about the zone axis [104] and fitted together by a saw-tooth boundary a very good fit with atomic displacements of only about 0·2 Å is obtained.

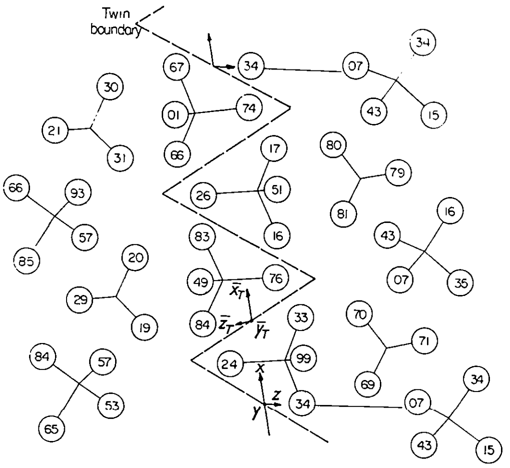

Fig. 7. Explanation of the polysynthetic (001) twin of spurrite. The subscript T stands for the twinned component. Other symbols have the same meaning as in Fig. 1.

According to Tilley (1929) the second twin is rare and occurs nearly parallel to the optic axial plane. The plane $(10\bar{1})$ is closely parallel to the optic axial plane (Fig. 1) but no obvious twin mechanism has been found.

Spurrite has been synthesized by Tuttle & Harker (1957). Two other synthetic compounds with the spurrite composition have been reported by Shepherd (1908) and Eitel (1923), the former produced by treating $CaCO_3$ and Ca_2SiO_4 with 10% NaCl solution at 350–400 °C. and the latter (called α-spurrite) from a melt at 120 atmospheres of CO_2. According to Eitel natural spurrite inverts to α-spurrite at 1200 °C. Both synthetic compounds were described as having orthorhombic optical properties. It is tempting to speculate that one of the synthetic spurrites made by Shepherd and Eitel may be merely ordinary spurrite polysynthetically twinned on a sub-optical scale thus giving orthorhombic optical symmetry.

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