The crystal structure of kilchoanite, $Ca_6(SiO_4)(Si_3O_{10})$, with some comments on related phases

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SUMMARY. The crystal structure of kilchoanite, $Ca_6(SiO_4)(Si_3O_{10})$, has been determined from three-dimensional X-ray methods ($r = 0.089$ on 348 independent reflections). It is closely related to that of γ-Ca_2SiO_4, which is olivine-like. In kilchoanite, slabs of γ-Ca_2SiO_4 structure alternate with ones composed of Ca ions and finite chains of three tetrahedra; these have the composition $Si_3O_{10}^{8-}$ and have rarely been observed previously. A related, synthetic phase, $8CaO.5SiO_2$, probably has a similar structure but with a higher proportion of γ-Ca_2SiO_4 regions, and should thus be formulated as $Ca_8(SiO_4)_2(Si_3O_{10})$. Disordered synthetic phases also occur that appear to have similar structures with still higher proportions of γ-Ca_2SiO_4 regions. These phases collectively form an interesting contrast to the chondrodite minerals.

KILCHOANITE, a polymorph of $Ca_3Si_2O_7$, has been reported as a natural mineral by Agrell and Gay (1961), Agrell (1965), and Black (1969). Before its discovery in nature, it had been synthesized by Roy (1958a and b), who called it 'Phase Z' and considered it to have the composition $9CaO.6SiO_2.H_2O$. Roy, Gard, Nicol, and Taylor (1960) later showed that preparations made hydrothermally at 715 °C were essentially anhydrous, but Speakman, Taylor, Bennett, and Gard (1967) obtained evidence supporting Roy's view that those made at lower temperatures contained combined water. Equilibrium relations (reviewed by Taylor, 1969) and crystal data (Roy, Gard, Nicol, and Taylor, 1960; Agrell and Gay, 1961) have been reported. Ovramenko, Govorov, and Lantukh (1969) concluded from infra-red evidence that kilchoanite contains isolated SiO_4^{4-} groups and $Si_3O_9^{6-}$ rings, but no $Si_2O_7^{6-}$ groups. No study of the crystal structure has previously been made.

The unit cell of kilchoanite is related to that of γ-Ca_2SiO_4, which has a slightly expanded olivine structure (O'Daniel and Tscheischwili, 1942; Smith, Majumdar, and Ordway, 1965). Speakman, Taylor, Bennett, and Gard (1967) prepared a compound of composition $8CaO.5SiO_2$, which from cell parameters and other evidence appeared to have a structure composed of alternating blocks of kilchoanite and γ-Ca_2SiO_4. They also showed that the supposed compound, γ-dicalcium silicate hydrate or dicalcium silicate hydrate (C), was a mixture consisting chiefly of calcio-chondrodite $(Ca_5(SiO_4)_2(OH)_2$; Buckle and Taylor, 1958) and a disordered phase resembling $8CaO.5SiO_2$, but probably having an increased proportion of blocks of γ-Ca_2SiO_4 in its structure.

The object of the present work was to determine the crystal structure of kilchoanite, and to clarify the relationship between kilchoanite and these synthetic phases.

Experimental. The work was done using a specimen from the type locality. A roughly equi-dimensional crystal, about 0·3 mm in its longest dimension, was used. X-ray photographs yielded crystal data compatible with those reported by previous workers: orthorhombic, a 11·42, b 5·09, c 21·95 Å, $Z=8$. There were systematic absences of all reflections with $(h+k+l)$ odd, and of $h0l$ reflections with h and l odd. These results are compatible with either of two space groups, each of which could be in either of two orientations; *Imam* or *Imcm* (centrosymmetric) and *Ima2* or *I2cm* (non-centrosymmetric).

Intensity data over a hemisphere of reciprocal space were collected for about 1250 reflections (348 independent) using a Hilger and Watts automatic linear diffractometer. The crystal was mounted about the b-axis. Filtered molybdenum radiation was used, and each reflection was measured four times, with background corrections in each case. Absorption corrections appeared to be small, and none were applied. The intensities were averaged and converted to structure amplitudes using standard procedures; Wilson's method was used to obtain pre-liminary estimates of the scale and over-all temperature factors.

Initial processing of the data was done on an Elliott 803B computer, using North's (1964) program. All subsequent work was done on an ICL 4/50 computer, using programs written by Dr. F. R. Ahmed and collaborators, of the National Research Council of Canada. Atomic scattering factor curves for neutral Ca, Si, and O were taken from International Tables for X-ray Crystallography (1962).

Determination of the structure. The structure was solved by inspection of the three-dimensional Patterson function, considered in the light of the strong probable relationship to γ-Ca$_2$SiO$_4$. Further evidence for the closeness of this relationship was provided by a comparison of the observed structure amplitudes with those reported for γ-Ca$_2$SiO$_4$ (Smith, Majumdar, and Ordway, 1965), which indicated a close similarity in Fourier transforms. The a- and b-dimensions of the kilchoanite cell agree closely with the corresponding parameters for γ-Ca$_2$SiO$_4$, and the c-dimension of kilchoanite is just over three times that of γ-Ca$_2$SiO$_4$. Account was also taken of the need to explain the composition, cell, and space group of 8CaO.5SiO$_2$.

Packing considerations suggested that, of the four possibilities, the space group and orientation described by the symbol *I2cm* were the most likely, and this was adopted. The stronger Patterson peaks could all be assigned to Ca–Ca or Ca–Si vectors, and there were indications that the Ca was octahedrally co-ordinated, as in γ-Ca$_2$SiO$_4$. Various trial structures containing Si$_2$O$_7^{6-}$ groups were devised, but none was fully satisfactory on crystal-chemical grounds and none gave even moderate agreement between observed and calculated amplitudes. Eventually a structure was devised that contained both isolated SiO$_4^{4-}$ tetrahedra and isolated Si$_3$O$_{10}^{8-}$ groups, that is, chains of three tetrahedra; it was close to the final structure to be described shortly, but the Ca ions of one symmetry-related set were displaced by $y = \frac{1}{2}$ from their final positions. This structure gave $r = 0·41$ on all reflections. Several cycles of block-diagonal least-squares refinement lowered r only to 0·30. The Ca ions mentioned above were then shifted by $y = \frac{1}{2}$; r dropped immediately to 0·22. Further cycles of block-diagonal refinement, at first of atomic co-ordinates only, and later of co-ordinates and individual isotropic temperature factors, reduced r to 0·11.

At this point it was observed that there were two possible sites, differing by $y = \frac{1}{2}$, for the middle Si atom of the Si$_3$O$_{10}^{8-}$ groups. Both appeared possible on crystal chemical grounds, and the change from one to the other involved only relatively small consequential shifts in the positions of neighbouring atoms. A three-dimensional electron-density map was therefore computed; it gave no indication that this silicon should be moved to the alternative position,

or indeed, that the structure that had so far been assumed was incorrect in any material respect. As a further test, an attempt was made to refine the alternative structure; r could not be reduced below 0·22.

The observed structure amplitude data were now critically examined. A few intensities for which the background corrections were found to be in error were put right, and small corrections were made to individual layer scaling factors. Two further cycles of block-diagonal least-squares refinement produced convergence at $r = 0·089$ on all reflections; a few $h3l$ and $h4l$ reflections for which the experimental data were suspect were excluded from the refinement but included in computing the final r-factor. The weighting scheme used in the later stages of the refinement was $w = 1/[1 + \{(|F_0| - 70·0)/70·0\}^2]$; an analysis showed that this was

TABLE I. *Final atomic co-ordinates (fractional) and isotropic temperature factors (B, in $\overset{\circ}{A}$); estimated standard deviations on last digit in parentheses*

Atom	x/a	y/b	z/c	B	Site symmetry and multiplicity	
Ca 1	−0·0134 (8)	0	0	1·7 (2)	2	4
Ca 2	0·2860 (8)	0·003 (2)	$\frac{1}{4}$	1·3 (2)	m	4
Ca 3	0·0107 (6)	0·005 (1)	0·1679 (3)	1·2 (1)	1	8
Ca 4	0·2177 (6)	0·501 (1)	0·1040 (2)	1·0 (1)	1	8
Si 1	0·097 (1)	0·426 (3)	$\frac{1}{4}$	1·3 (2)	m	4
Si 2	0·408 (1)	0·940 (2)	0·0997 (3)	1·0 (1)	1	8
Si 3	0·240 (1)	0	0	1·4 (2)	2	4
O 1	0·164 (2)	0·297 (4)	0·1919 (8)	1·2 (4)	1	8
O 2	−0·033 (3)	0·293 (7)	$\frac{1}{4}$	2·1 (6)	m	4
O 3	0·098 (2)	0·759 (6)	$\frac{1}{4}$	0·9 (5)	m	4
O 4	0·346 (2)	0·793 (4)	0·1584 (8)	1·2 (4)	1	8
O 5	0·035 (2)	0·707 (4)	0·0919 (7)	1·3 (4)	1	8
O 6	0·334 (2)	0·802 (5)	0·0402 (8)	2·1 (4)	1	8
O 7	0·404 (2)	0·255 (4)	0·0954 (7)	0·6 (3)	1	8
O 8	0·160 (2)	0·179 (4)	0·0412 (9)	1·9 (4)	1	8

satisfactory. As a further test of the correctness of the structure, a three-dimensional difference Fourier was computed; it showed no peaks exceeding $\pm 1·4$ e$\overset{\circ}{A}^{-2}$. Table I gives the final parameters, and table II the more important bond lengths and angles. A table of observed and calculated structure factors is available from the author on request.

Discussion. Kilchoanite contains isolated SiO_4^{4-} tetrahedra and isolated $Si_3O_{10}^{8-}$ groups, and its formula can be written as $Ca_6(SiO_4)(Si_3O_{10})$. This is one of the few silicates in which the $Si_3O_{10}^{8-}$ group, consisting of three tetrahedra linked into a short chain by sharing of corners, has been detected. Fig. 1a gives a general view of the structure, seen in projection along the shortest (b-) axis and fig. 2 shows part of the same projection in greater detail. The structure is closely related to that of γ-Ca_2SiO_4 (fig. 1c), and contains entire slabs of material in the ab-plane that are virtually identical with γ-Ca_2SiO_4. The analogy with the olivine–chondrodite relationship is obvious. In the chondrodite minerals, however, the slabs of material that alternate with those of the olivine structure contain hydroxyl or fluoride ions, whereas in kilchoanite they contain $Si_3O_{10}^{8-}$ groups, which run approximately parallel to [001].

No high level of precision is claimed for the atomic parameters, especially the y-co-ordinates. Several points nevertheless deserve comment. Of the calcium ions, those of three sets (Ca 2, 3, and 4) are octahedrally co-ordinated, while the fourth (Ca 1) is eight-co-ordinated (table II and fig. 2). The electrostatic valency rule is not satisfied exactly; as appears not unusual in condensed silicates, the bridging oxygen
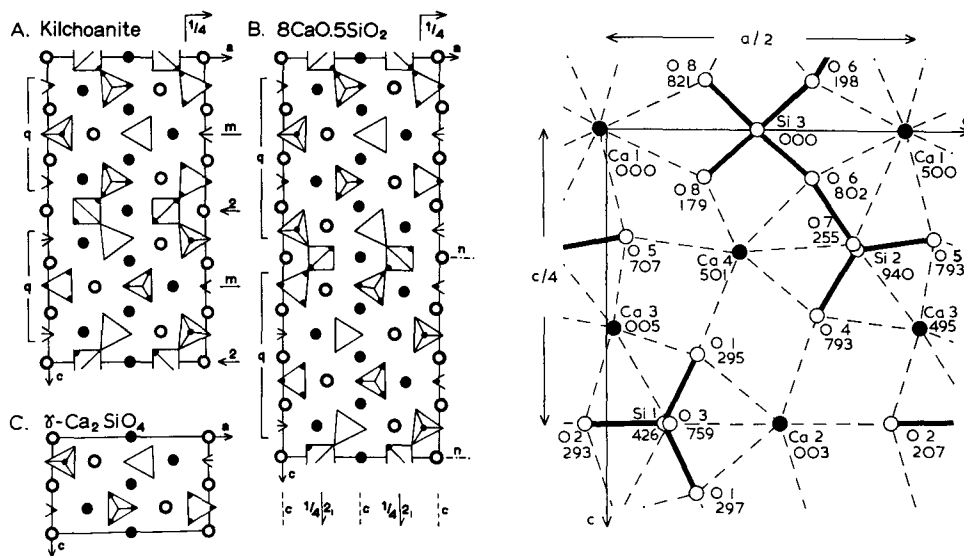
TABLE II. *Interatomic distances and angles (estimated standard deviations on final digit in parentheses)*

Distances		Distances		Angles	
Ca 1–O 5	2·57 (2) Å	Si 1–O 1	1·63 (2) Å	At Si 1: O 1–O 1	103 (1)°
O 6	2·49 (2)	O 2	1·64 (4)	O 1–O 2	105 (1)
O 7	2·62 (2)	O 3	1·70 (3)	O 1–O 3	114 (1)
O 8	2·36 (2)			O 2–O 3	115 (1)
Ca 2–O 1	2·41 (2)	Si 2–O 4	1·65 (2)	At Si 2: O 4–O 5	104 (1)
O 2	2·31 (4)	O 5	1·64 (2)	O 4–O 6	101 (1)
O 3	2·48 (3)	O 6	1·71 (2)	O 4–O 7	119 (1)
O 4	2·38 (2)	O 7	1·60 (2)	O 5–O 6	110 (1)
Ca 3–O 1	2·36 (2)	Si 3–O 6	1·71 (2)	O 5–O 7	119 (1)
O 2	2·38 (2)	O 8	1·57 (2)	O 6–O 7	111 (1)
O 3	2·41 (2)				
O 4	2·42 (2)	O–O (within tetrahedra)		At Si 3: O 6–O 6	103 (1)
O 5	2·27 (2)	Shortest:		O 6–O 8	114 (1)
O 7	2·35 (2)	O 1–O 1	2·55 (3)	O 8–O 8	109 (1)
		Longest:		At O 6: Si 2–Si 3	117 (1)
Ca 4–O 1	2·27 (2)	O 2–O 3	2·81 (4)		
O 4	2·41 (2)			Smallest in Ca–O polyhedra:	
O 5	2·35 (2)			At Ca 1: O 8–O 8	65·7 (7)°
O 6	2·47 (2)			At Ca 2: O 1–O 1	64·1 (7)
O 7	2·47 (2)	O–O (between tetrahedra)		At Ca 3: O 1–O 2	66·4 (8)
O 8	2·24 (2)	None < 2·9		At Ca 4: O 4–O 6	66·4 (7)

atoms (O 6) are also bonded to metal cations (Ca 1 and Ca 4), and are thus over-bonded, while some other oxygens, notably O 8, are under-bonded. This may be why the Si 3–O 8 bond is unusually short ($1·57 \pm 0·02$ Å) and the Si 3–O 6 and Si 2–O 6 bonds are unusually long (both $1·71 \pm 0·02$ Å), though it does not explain the fact that the Si 1–O 3 bond is probably also long ($1·70 \pm 0·03$ Å). The Si–O–Si angle at O 6 is relatively low ($117 \pm 1°$).

Speakman, Taylor, Bennett, and Gard (1967) showed that the related phase $8CaO.5SiO_2$ was orthorhombic, with a 11·46, b 5·09, c 28·70 Å, $Z = 4$, and space group $Pcam$ or $Pca2_1$. X-ray powder evidence suggested that the Fourier transform closely resembled that of kilchoanite. Attempts to postulate a reasonable structure assuming either of these space groups were unsuccessful, but if the space group $Pcan$ is assumed, a structure can be suggested (fig. 1b) that satisfies all the other evidence. The space group determination mentioned above was based on electron-diffraction evidence, and the additional systematic absence required by the space group $Pcan$ could well

have been obscured by the effects of dynamic scattering. No crystals of $8CaO.5SiO_2$ of sufficient size for single-crystal X-ray work have been prepared, but preliminary calculations indicate that the structure shown in fig. 1b satisfactorily explains the intensities of the X-ray powder lines. It corresponds to the constitutional formula Ca_8 $(SiO_4)_2(Si_3O_{10})$.

FIGS. 1 and 2: Fig. 1 (left). Crystal structures of (a) kilchoanite, (b) (suggested) $8CaO.5SiO_2$, and (c) γ-Ca_2SiO_4. In each case a complete unit-cell is shown, projected along the shortest (5 Å) axis, which is taken as b. Open and full circles represent calcium ions at $y \approx \frac{1}{4}$o and $\approx \frac{1}{2}$ respectively. Corners of tetrahedra, where visible, are shaded if $y \approx \frac{3}{4}$ and unshaded if $y \approx \frac{1}{4}$. For kilchoanite and $8CaO.5SiO_2$, key symmetry elements are shown, and regions of γ-Ca_2SiO_4 structure are marked 'q'. In (b), the origin has been displaced from the centre of symmetry by c/4 to show more clearly the relation to kilchoanite. Fig. 2 (right). Crystal structure of kilchoanite, showing part of the unit cell projected along the b-axis. Broken lines denote Ca–O bonds, heavy full lines denote Si–O bonds, and heights are given as 1000 y/b.

From inspection of fig. 1, it is apparent that additional slabs of γ-Ca_2SiO_4 structure might readily be incorporated into the structure of $8CaO.5SiO_2$; this would increase the Ca:Si ratio, and, if it occurred in a random way, would give a 'crystal' of indefinite c-spacing. It is suggested that material of this nature is the main constituent of so-called 'γ-dicalcium silicate hydrate', which, as stated previously, also contains calcio-chondrodite. The possibility is not excluded that crystals occur in which slabs of kilchoanite, γ-Ca_2SiO_4, and calcio-chondrodite are all randomly intergrown with each other on a unit-cell scale.

No immediately obvious explanation can be offered for the observation that synthetic kilchoanite prepared at low temperatures contains water. There are no cavities in the structure in which water molecules could be placed. Speakman, Taylor, Bennett, and Gard (1967) suggested that this water might occur as hydroxyl groups present on

the surfaces of the very small crystals, or substituting for SiO_4^{4-} groups as a result of occasional hydrogarnet-type substitutions, and these are perhaps still the most likely explanations. Hydrogarnet-type substitution could be equivalent to incorporation of regions of calcio-chondrodite structure, which might be expected to form slabs parallel to (001). If such slabs are present, this could also explain the differing morphologies of kilchoanite crystals. The natural mineral, which is anhydrous, forms equant grains with no marked cleavage, but synthetic crystals of micrometre[1] size, especially when made at low temperatures, seem normally to crystallize as thin plates with (001) cleavage. The absence of a definite cleavage in the natural crystals is in accordance with the structure that has been described. The strong (001) cleavage of the synthetic crystals might be due to the presence of occasional slabs of calcio-chondodite structure, which could be planes of weakness.

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[1] S.I. name for the micron.