

The crystal structure of kalsilite, $KAlSiO_4$

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Summary. A full-matrix, three-dimensional refinement of kalsilite, $KAlSiO_4$ (hexagonal, a 5.16, c 8.69 Å, $P6_3$), shows that the silicon and aluminium atoms are ordered. The respective tetrahedral distances of 1.61 and 1.74 Å agree with values of 1.61 and 1.75 Å taken to be typical of framework structures. As in nepheline, an oxygen atom is statistically distributed over three sites displaced 0.25 Å from the ideal position on a triad axis. This decreases the bond angle from 180° to 163° in conformity with observations on some other crystal structures. The potassium-oxygen distances of 2.77, 2.93, and 2.99 Å are consistent with the wide range normally found for this weakly bonded atom.

THE crystal structure of kalsilite is of interest because the tetrahedral (T) atoms may be ordered, because the tetrahedral distances provide a test of the scheme proposed for silicates by Smith and Bailey (1963), and because the ideal tridymite structure requires an unusual T -O- T bond angle of 180° at the oxygen atom lying on the triad axis.

Five structures of composition near $KAlSiO_4$ were listed by Smith and Tuttle (1957), while the experimental data of Tuttle and Smith (1958) showed that kalsilite is the phase stable below 850° C. Claringbull and Bannister (1948) confirmed the conclusion of Wallmark and Westgren (1937) and of Nowacki (1942) that kalsilite and $BaAl_2O_4$ are related to tridymite by a rotation of the tetrahedron in the (0001) plane. Since the space group was given as $P6_322$, they probably thought that the tetrahedral atoms were disordered. They also suggested that the T -O- T bond angle along the triad axis was 180°. Smith and Sahama (1957) reported the occurrence of a natural kalsilite, in perthitic intergrowth with nepheline, which showed weak, diffuse reflections requiring an increase of the a dimension by $\sqrt{3}$ and a rotation of the a -axis by 30° about c . The diffuse reflections disappeared after the crystal was heated at 600° C for three days. They suggested that disordering of the tetrahedral atoms was the cause of this structural change.

Hahn and Buerger (1955) found three significantly different T -O distances in the structurally related nepheline. The first two, 1.64

and 1.78 Å, correspond to tetrahedra occupied principally by silicon and aluminium atoms, respectively, while the third distance, 1.68 Å, indicates random occupancy. The ordered tetrahedra are centred on the triad axis, but the linking oxygen atoms occupy a three-fold degenerate position off the triad axis giving a bond angle less than 180°. Sahama (1962) found that plutonic nephelines had different optical properties from volcanic nephelines, but assumed the properties of the latter after prolonged heating. By analogy with feldspars, he proposed a varying degree of order of the aluminium and silicon atoms. Careful X-ray and electron-diffraction studies of several nephelines by McConnell (1962) confirmed and extended the observation by Sahama (1958) of the occurrence of weak, subsidiary reflections irrationally disposed in pairs about positions corresponding to a unit cell $a' = a\sqrt{3}$ and $c' = c$. The sharpness of the reflections varied from specimen to specimen and decreased upon heating. McConnell suggested a statistical, antisymmetric array of structural faults and pointed to the degenerate oxygen atom and to the disordered tetrahedra of the Hahn-Buerger structure. He anticipated that the structural variations depended on Al-Si ordering because the diffuse maxima persisted after extended heating at 1000° C.

Hoppe and Schepers (1960) found from single-crystal and powder X-ray data that BaGa_2O_4 , also structurally related to tridymite, has a superstructure with $a' = 2a$ and suggested that BaAl_2O_4 may have a similar pattern. We have confirmed this suggestion and have also found a three-fold degeneracy of the oxygen atom similar to that in nepheline. Details of this study will be published upon completion of an analysis of the superstructure reflections.

Liebau (1961) has maintained that Si-O-Si bond angles of 180° do not normally occur in crystalline silicates, in conformity with the observations on nepheline, BaAl_2O_4 , and cristobalite (Nieuwenkamp, 1937), which also have degenerate oxygen atoms disposed about a triad axis. However, reasonably detailed studies of zunyite (Kamb, 1960), coesite (Zoltai and Buerger, 1959), and thortveitite (Cruikshank, Lynton, and Barclay, 1962) have yielded Si-O-Si angles of 180°.

Experimental

Single crystals of kalsilite intergrowth with nepheline were kindly supplied by Prof. Th. G. Sahama of the University of Helsinki out of sample S88 from Mt. Nyiragongo (Congo). Similar material has been described in detail by Sahama (1960) and was used by Sahama, Neuvonen,

and Hytönen (1956) to give a correlation between cell dimensions and composition for kalsilite. The dimensions derived by them (a 5.161 ± 0.004 ; c 8.693 ± 0.005 Å) were used to calculate the interatomic distances of Table II. A chemical analysis of the kalsilite recalculates to a cell content of $(K_{1.91} Na_{0.03} (H_2O)_{0.11}) (Al_{1.93} Si_{2.03} Fe_{0.05}) O_8$. However, microprobe analysis of the single crystal used for the collection of X-ray data gave a lower iron content (0.4% vs. 1.12% Fe_2O_3 in the chemical analysis). The role of the water in the chemical analysis is uncertain, and it has been included with the alkali atoms for convenience. Because of uncertainty in the composition, the atomic scattering factors were based on the ideal composition: as a result, the observed temperature factors may be systematically biased.

As described in the introduction, Smith and Sahama (1957) had observed weak diffuse reflections in kalsilite crystals. The present material was from the same locality, but we did not observe with certainty any diffuse reflections, though there were faint indications in two positions.

A crystal, approximately cylindrical, of diameter 0.32 mm and length 0.30 mm, was oriented about the c -axis. Weissenberg photographs showed good resolution between most reflections from the kalsilite and nepheline. The nepheline showed two weak sets of reflections about 1 to 3° out of alignment with each other and with the kalsilite reflections. Although the a and c axes were quasi-parallel for the three components, there was no obvious, rational relation between the axes. Intensities of the kalsilite reflections were collected using a stationary scintillation counter and a moving crystal in an equi-inclination Weissenberg goniometer. Tracings of the intensity profile were made to help detect any contribution from the nepheline satellites. 243 reflections were observed in the range down to 0.77 Å and were corrected for absorption, polarization, and Lorentz factors.

The systematic absences are consistent with either $P6_3$ or $P6_322$. Refinement of the atomic parameters in $P6_322$ proved to be unsatisfactory and final refinement was obtained in $P6_3$ using the programme ORFLS kindly supplied by Drs. Busing, Martin, and Levy. The atomic scattering factors of Berghuis *et al.* (1955), modified arbitrarily for half ionization, were used in the refinement. From the interatomic distances, it was possible to deduce that the silicon and aluminium atoms were ordered, thus permitting the use of separate atomic scattering factors. Four cycles of isotropic least-squares refinement gave a discrepancy index of 0.07, but the unusually high temperature factor of 3.6 for the

oxygen atom on the special position cast doubt on the validity of the refinement. Anisotropic refinement gave a negative value for the β_{33} coefficient of this oxygen atom, and to resolve the uncertainty a section was calculated through the difference Fourier synthesis. This showed the oxygen atom to be statistically distributed over three sites. A further isotropic refinement with one-third occupancy of oxygen in a general position resulted in a temperature factor of 0.9, indistinguishable from the value of 1.0 obtained for the other oxygen atom. Small displacements from ideal positions might be expected for the neighbours of the oxygen atom, but could not be detected in the refinement. The final atomic co-ordinates for refinements with the oxygen atom placed either on or off the triad axis are shown in table I, while the interatomic

TABLE I. Atomic co-ordinates, isotropic and anisotropic temperature factors

Case A. Oxygen on triad axis

	O ₁	O ₁ '	O ₂	Si	Al	K
x	0.3831 7	0.6169 7	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	0
y	0.9864 9	0.0136 9	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	0
z	0.4895 80	0.9895 80	0.2500	0.4300 70	0.0486 66	0.2435 68
B	0.97 5	0.97 5	3.58 31	0.37 4	0.52 7	1.18 3
$\beta_{1,1}$	0.0074 12	0.0074 12	0.0572 45	0.0044 5	0.0063 9	0.0148 5
$\beta_{2,2}$	0.0084 11	0.0084 11	0.0572	0.0044	0.0063	0.0148
$\beta_{3,3}$	0.0095 8	0.0095 8	-0.0005 43	0.0018 8	-0.0005 14	0.0034 7
$\beta_{1,2}$	0.0039 8	0.0039 8	0.0286	0.0022	0.0032	0.0074
$\beta_{1,3}$	-0.0020 17	-0.0020 17	0	0	0	0
$\beta_{2,3}$	-0.0016 11	-0.0016 11	0	0	0	0

Case B. Oxygen displaced off triad axis

x	0.3831 7	0.6169 7	0.3339 30	$\frac{1}{3}$	$\frac{1}{3}$	0
y	0.9875 8	0.0125 8	0.7155 25	$\frac{2}{3}$	$\frac{2}{3}$	0
z	0.4858 15	0.9858 15	0.2500	0.4281 10	0.0461 11	0.2411 38
B	1.01 5	1.01 5	0.94 25	0.35 4	0.51 7	1.18 3

Random experimental errors are listed under each parameter

TABLE II. Interatomic distances

A. Oxygen on three-fold axis		B. Oxygen displaced off three-fold axis	
Si-O ₁	(3) 1.623 Å	Si-O ₁	(3) 1.624 Å
Al-O ₁ '	(3) 1.729	Al-O ₁	(3) 1.729
Si-O ₂	(1) 1.564	Si-O ₂	(1) 1.570
Al-O ₂	(1) 1.751	Al-O ₂	(1) 1.787
K-O ₁	(3) 2.937	K-O ₁	(3) 2.929
K-O ₁ '	(3) 2.986	K-O ₁ '	(3) 2.992
K-O ₂	(6) 2.979	K-O ₂	(3)* 2.767
Mean Si-O	1.608	Mean Si-O	1.610
Mean Al-O	1.735	Mean Al-O	1.744

Number in brackets indicates multiplicity

* Depends on arrangement of oxygen atoms on the three possible sites

distances are given in table II. In space group $P6_3$, the z -co-ordinate of one atom may be arbitrarily fixed, and in the present refinement the oxygen on the triad axis was fixed at $z = 0.25$. Refinement was complicated by the strong interactions in the matrix, and it is likely that the true errors in the refinement are greater than the random errors listed in the tables. The final discrepancy index is 0.059. The observed and calculated structure amplitudes are listed in the Ph.D. thesis of Anthony J. Perrotta, available from the library of the University of Chicago.

Discussion

The crystal structure of kalsilite is shown in Fig. 1. The mean tetrahedral distances of 1.610 and 1.744 Å are indistinguishable from the values of 1.61 and 1.75 Å proposed by Smith and Bailey (1963) for silicon- and aluminium-centred oxygen tetrahedra in framework silicates. Thus kalsilite has an ordered pattern of aluminium and silicon atoms, which reduces the symmetry from $P6_322$ for a disordered structure to the actual $P6_3$. Because the uncertainty of the z -co-ordinate of O₂ is about 0.02 Å and that in the variable co-ordinates of O₁, Si, and Al is from 0.004 to 0.015 Å (table II), no significance should be ascribed to the difference between the two independent distances of each tetrahedron. The potassium atom is surrounded by twelve oxygen atoms, six of O₁, and six of O₂. The closest approach of an atom of type O₂ is 2.77 Å, while the average distance of all the oxygen atoms is 2.97 Å. These values are well within the range of distances tabulated in *International Tables for X-ray Crystallography*, Volume 3.

The displacement of O₂ by 0.25 Å from the triad axis changes the $T-O-T$ bond angle from 180° to 163°, thus lending support to Liebau's hypothesis described in the Introduction.

Through the courtesy of Prof. Th. G. Sahama, we were able to re-examine the weak superstructure reflections on photographs of a crystal of kalsilite described by Smith and Sahama (1957). Careful measurements confirmed the earlier conclusion that the weak reflections were

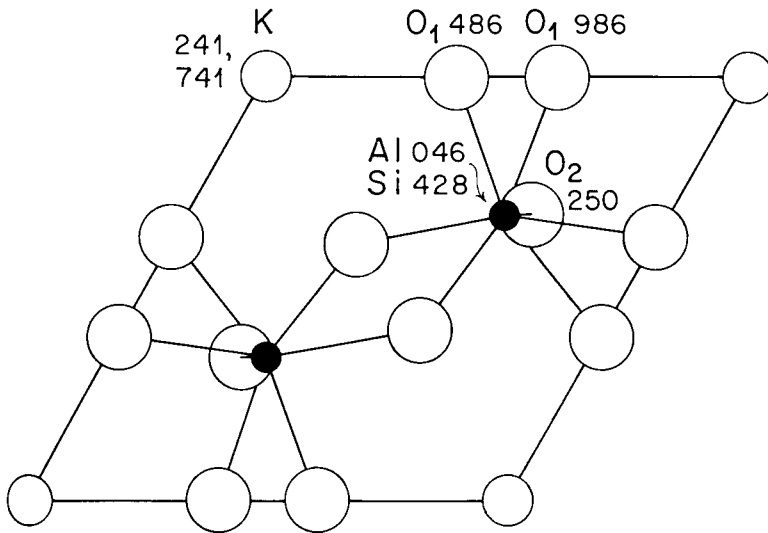


FIG. 1.

rationally related to the principal kalsilite reflections and not aligned with the reflections from the intergrown nepheline. The earlier suggestion of Al, Si order to explain the occurrence of kalsilites with or without the superstructure reflections can be refuted by the new results, which show that the tetrahedral atoms are ordered in a kalsilite that does not show the extra reflections. In addition, it is likely in view of heating studies on feldspars (e.g. McKie and McConnell, 1963) that disordering of the Al, Si atoms could not occur in the short heating time at 600° C previously mentioned.

Three alternative explanations may be postulated: ordering of the displacements of the oxygen atom O_2 from the triad axis, ordering of substituting atoms or molecules such as Na and H_2O in the alkali site to produce a larger unit cell such as occurs in nepheline, tri-kalsilite, and tetra-kalsilite, or occurrence of an alteration product, possibly hydrous, in parallel intergrowth with the kalsilite.

To test the first idea, intensities of the superstructure reflections were

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Table III. Kalsilite superstructure; calculated structure amplitudes

Observed by Sahama and Smith				Not observed by Sahama and Smith			
<i>hkl</i>	$F_{(calc)}$	<i>hkl</i>	$F_{(calc)}$	<i>hkl</i>	$F_{(calc)}$	<i>hkl</i>	$F_{(calc)}$
120	4.16	210	5.72	010	4.27	131	3.66
130	8.03	310	4.06	020	7.78	151	9.14
240	0.93	420	5.54	040	7.54	161	4.63
150	3.69	510	7.13	050	9.12	241	6.63
231	0.62	321	7.10	160	5.05	261	0.56
122	3.65	212	5.34	230	11.86	341	8.97
				260	8.88	022	6.72
				340	5.57	052	8.45
				350	3.60	132	7.21
				021	3.35	152	3.47
				041	6.53	162	4.77
				071	5.68	212	5.34
				121	9.56		

Note. Not known whether Smith and Sahama observed (*hkl*) or (*klh*) permutation.

calculated for the simplest ordered arrangement in $P6_3$ ($a' = \sqrt{3}$) of O_2 atoms arranged with the co-ordinates found in table I, Case B. Displacements of neighbouring atoms were ignored in the calculation and the values of table III were obtained. There is no correlation between the calculated values and the qualitative estimates of intensity for the subsidiary reflections. However, neglect of the possible shifts of neighbouring atoms may be the cause of the misfit. The activation energy for movement of oxygen atoms from one potential minimum to another should be low enough to permit disordering at 600° C under short heating times. To test the suggestion of ordered substitution of the alkali atoms it would be necessary to make a chemical analysis of the original crystal. This would be very difficult because of the presence of the intergrown nepheline. However, this suggestion is capable in theory of explaining the thermal and X-ray results, for alkali atoms diffuse quite rapidly at 600° C, and the superstructure reflections in tri-kalsilite and tetra-kalsilite are readily detectable. It is not possible to evaluate the third idea, but it is unlikely that an alteration product would have a lattice with a completely rational relationship to the host lattice. Much additional study will be required to resolve the origin of these subsidiary reflections. In the meantime, the prefixes *o*- and *d*- to describe the two types of kalsilite should be abandoned.

In conclusion it is interesting to speculate on the polymorphism of nepheline using the observations and suggestions of McConnell (1962) as a basis. The occurrence of an oxygen atom statistically displaced from a triad axis permits the possibility of an ordered pattern. The interatomic distances suggest disorder of Al and Si in two of the tetra-

hedral sites while the other two sites are ordered. Consequently order-disorder of the atoms in the first two sites would permit polymorphism. The heating experiments of McConnell showed increasing diffuseness in quenched nephelines heated to temperatures as low as 200° C, but the reflections persisted in samples heated as high as 950° for one day. This behaviour is more easily explained by movement of oxygen atoms across a low energy barrier than by movement of tightly bonded tetrahedral atoms. Persistence of reflections in material quenched from high temperature might result from ordering occurring during quenching from a disordered state rather than from partial ordering existing at the heating temperature. Another possibility is that both oxygen and the tetrahedral atoms contribute to the extra reflections. The occurrence of Si atoms over the stoichiometric ratio (8.4 vs. 8.0) might result in concentrations of Si atoms in boundaries between antisymmetric arrays of ordered Al and Si atoms.

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