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# Crystal structure of synthetic yoshiokaite, a stuffed derivative of the tridymite structure

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## ABSTRACT

A Ca- and Al-rich silicate phase synthesized from glass and yoshiokaite, a Ca- and Al-rich silicate mineral found on the Moon, have compositions which can be described as $Ca_{8-0.5x}\square_{0.5x}Al_{16-x}Si_xO_{32}$ ($2.8 < x < 6.0$ for lunar samples). Powder diffraction patterns for these materials are very similar and suggest the same structure. Refinement ($R = 0.051$) of single-crystal intensity data for synthetic $Ca_{5.3}\square_{2.7}Al_{10.7}Si_{5.3}O_{32}$ ($P\bar{3}$, $a = 9.927$, $c = 8.220$ Å, $z = 1$, $D_{calc} = 2.74$ g/cm³) gives a structure which is a stuffed derivative of high tridymite with layers having the topology of nepheline. In contrast to nepheline, adjacent layers along *c* show opposite distortions. Ca occupies the Na site of nepheline, whereas the K site of nepheline is vacant. The observed space group is $P\bar{3}c1$, but this is an artifact of twinning; the true space group is $P\bar{3}$ (pseudo $P\bar{3}c1$) with intimate submicroscopic twinning (twin axis [110]) producing the higher average symmetry. No Si,Al ordering is present, based on the near-equal T-O average distances.

The structure is distinct from that of nepheline and kalsilite, and a complex structural series could exist in Na, K, Ca mixed compositions. The contrasting layer stacking in nepheline and yoshiokaite suggests a structural reason for the very limited substitution of Ca in nepheline. For compositions where sufficient Ca exists to require entry into the K site of nepheline, it is quite likely that the $CaAl_2O_4$ monoclinic structure is stabilized.

## INTRODUCTION

The tridymite framework forms the basis of a number of structures, generally termed stuffed derivatives of tridymite, in which some Si is replaced by Al and some framework cavities are occupied by (stuffed with) another cation such as Na or K. Common end-member stuffed tridymite structures include nepheline, $NaAlSiO_4$, and kalsilite, $KAlSiO_4$, both with an ideal Al/Si ratio of 1.0. Most natural samples have a ratio of less than 1.0, with the additional charge due to excess Si compensated for by vacancies in place of Na or K (Rossi et al., 1989). In natural samples only minor Ca has been reported. However, Ca-bearing nepheline has been synthesized (see Rossi et al., 1982 for summary). Goldsmith (1949) synthesized $Na_{3.4}Ca_{4.6}Al_{12.6}Si_{3.4}O_{32}$ where Al/Si = 3.7, and Donnay et al. (1959) showed that the phase with this composition, as well as other samples of synthetic high-Ca nepheline, has cell dimensions that can be extrapolated to the cell dimensions of end-member nepheline.

Vaniman et al. (1989) and Vaniman and Bish (1990) reported Ca- and Al-rich grains from a lunar highland sample that are chemically similar to a synthetic silica-poor phase with a nepheline-like structure reported by Sugiura and Yoshioka (1968) and Yoshioka (1970a). The compositions of the lunar grains show $SiO_2$ between 16 and 34 wt%, and the overall compositional range fits the formula $Ca_{8-0.5x}\square_{0.5x}Al_{16-x}Si_xO_{32}$ where □ represents vacancy. The lunar phase has been named yoshiokaite (Vaniman and Bish, 1990). The X-ray diffraction pattern and cell dimensions ($a = 9.923(5)$, $c = 8.226(6)$ Å) of the lunar material closely match those of the synthetic phase ($a = 9.9961$, $c = 8.2195$ Å; Table 1). A phase close to $CaAl_2SiO_6$ (termed H-CATS, after the compositional relation to Ca-Tschermaks molecule) was synthesized by Kirkpatrick (1972). X-ray properties ($a = 9.943$, $c = 8.228$ Å) and space group ($P\bar{3}c1$ or $P3c1$) were given in Kirkpatrick and Steele (1973). The X-ray diffraction patterns, cell parameters, and optical properties all suggest that the above synthetic materials have similar structures, which are based on the tridymite framework. A single-crystal X-ray refinement of the same material as that studied by Kirkpatrick and Steele (1973) is presented below; preliminary results were given in Steele and Pluth (1989). Yoshioka (1970b) described an additional phase close to $CaAl_2O_4$ that has a kalsilite-type structure with $a = 5.0$ and $c = 8.1$ Å and that occurs with the nepheline-like phase. Dialuminate, $CaAl_2O_4$, has also been shown to have a stuffed tridymite structure (Hörkner and Müller-Buschbaum, 1976) but is monoclinic ($P2_1/n$, $a = 8.700$, $b = 8.092$, $c = 15.191$ Å, $\beta = 90.1°$) with a cell related to that of nepheline by $a \approx a_{ne}\cos 30°$, $b \approx c_{ne}$, $c \approx 1.5\ a_{ne}$, $\beta \approx 90°$. The compositional relations of some of these materials are shown in Figure 1, and it is apparent that the Ca,Al-rich silicates noted lie between anorthite and $CaAl_2O_4$ and that $CaAl_2SiO_6$ lies within the range reported for yoshiokaite. The structure of the material synthe-

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**TABLE 1.** X-ray diffraction patterns for synthetic and natural yoshiokaite

| Synthetic Yoshioka (1970a) | | Lunar Vaniman et al. (1989) | | Synthetic Kirkpatrick and Steele (1973) | |
|---|---|---|---|---|---|
| *d* (Å) | $I/I_0$ | *d* (Å) | $I/I_0$ | *d* (Å) | $I/I_0$ |
| 8.68 | 31 | 8.54 | 50 | 8.60 | 17 |
| 5.00 | 36 | 4.94 | 26 | 4.98 | 18 |
| 4.31 | 2 | 4.29 | 9 | 4.31 | 3 |
| 4.11 | 22 | 4.105 | 12 | 4.12 | 11 |
| 3.71 | 9 | 3.709 | 15 | 3.720 | 6 |
| 3.28 | 28 | 3.251 | 14 | 3.258 | 18 |
| 3.175 | 11 | 3.168 | 13 | 3.173 | 4 |
| 3.041 | 55 | 3.019 | 24 | 3.033 | 32 |
| 2.980 | 100 | 2.972 | 100 | 2.979 | 100 |
| 2.886 | 39 | 2.862 | 20 | 2.874 | 28 |
| 2.560 | 5 | — | | 2.552 | 2 |
| 2.499 | 6 | — | | 2.487 | 6 |
| 2.402 | 8 | — | | 2.402 | 3 |
| 2.362 | 3 | — | | 2.350 | 3 |
| 2.306 | 35 | 2.297 | 54 | 2.292 | 22 |
| 2.165 | 4 | — | | 2.151 | 1 |
| 2.101 | 15 | 2.093 | 4 | 2.097 | 11 |
| 2.074 | 26 | 2.061 | 20 | 2.065 | 18 |
| 2.000 | 11 | 2.000 | 4 | 1.999 | 11 |
| — | | — | | 1.974 | 2 |
| — | | — | | 1.921 | 5 |
| — | | — | | 1.880 | 4 |
| 1.856 | 18 | 1.857 | 8 | 1.856 | 12 |
| 1.841 | 11 | 1.830 | 8 | 1.831 | 12 |

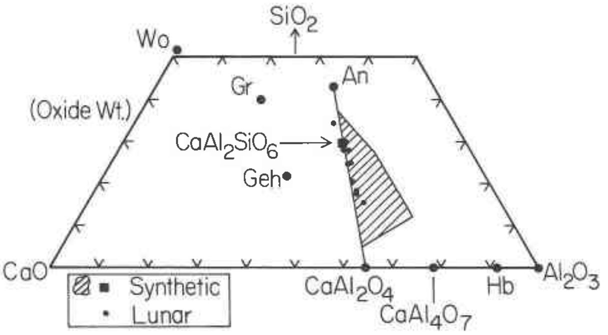

Fig. 1. Compositional relations among some Ca- and Al-rich silicates. Small solid circles represent analyses of Vaniman et al. (1989) for yoshiokaite, shaded region is approximate range of material synthesized by Yoshioka (1970a), point labeled $CaAl_2SiO_6$ is composition synthesized by Kirkpatrick (1972). Other compositions: An = anorthite, Gr = grossular, Hb = hibonite, Wo = wollastonite, Geh = gehlenite.

sized by Kirkpatrick (1972) is shown to be an additional type of stuffed tridymite with some structural features found in nepheline.

## EXPERIMENTAL DETAILS AND STRUCTURE DETERMINATION

Experimental details are summarized in Table 2 and the following provides additional details, particularly regarding the observed vs. true space group. From a gently crushed sample of 100% crystallized material, a crystal was selected that showed even extinction under crossed polars. Precession photographs showed diffraction symmetry $3m$ and systematic absences of $l$ = odd for $h0il$ diffractions, consistent with space group $P\bar{3}c1$ or $P3c1$ (Kirkpatrick and Steele, 1973). For the 4708 diffraction intensities measured, 351 were systematically extinct in space group $P\bar{3}c1$. Of these extinct diffractions, 57 had intensities greater than $3\sigma$ above background, suggesting violations of the $c$ glide (see later). No corrections were made for absorption because of the low linear absorption coefficient and the irregular shape of the grain. The cell parameters were obtained by least-squares refinement using 20 centered diffractions ($50 < 2\theta < 60$), each the average of automatic centering of eight equivalent diffractions. The distribution of diffraction intensities corresponded to that of a centric structure.

Initial atom positions were obtained by symbolic addition, and the relation to the tridymite framework became obvious; however, the nepheline structure is not compatible with $P\bar{3}c1$ symmetry in the neighborhood of the threefold axis because of the $c$ glides. For this reason, as well as the violations of the $P\bar{3}c1$ space group, refinement was continued in $P\bar{3}$, which is not inconsistent with the nepheline structure. Refinement of the tetrahedral framework gave an $R$ value below 0.20, and difference-Fourier maps showed the position of the Ca in the Na site of nepheline. Upon addition of the Ca, appropriate scattering factors, and anisotropic thermal parameters, the $R$ value dropped to below 0.06, with a difference-Fourier synthesis showing a complex distribution of electron density on the threefold axis. The T-O framework distances showed no obvious differences, and a disordered Si-Al T-site population was assumed. Efforts to fit the remaining electron density on the threefold axis required assigning Si and O sites with half occupancy on this axis and resulted in a final $R$ value of 0.051. Posi-

**TABLE 2.** Experimental details for synthetic yoshiokaite

| | |
|---|---|
| **(A) Crystal-cell data** | |
| *a* (Å) | 9.927(1) |
| *c* (Å) | 8.220(2) |
| *V* (Å³) | 701.5(2) |
| Space group (observed) | $P\bar{3}cl$, hexagonal |
| Space group (actual) | $P\bar{3}$, hexagonal |
| *Z* | 1 |
| Formula | $Ca_{5.3}\square_{2.7}Al_{10.7}Si_{5.3}O_{32}$ |
| $D_{calc}$ (g·cm$^{-3}$) | 2.74 |
| $\mu$ (cm$^{-1}$) | 18.9 |
| **(B) Intensity measurements** | |
| Crystal size | Irregular, 0.1 × 0.1 × 0.2 mm |
| Diffractometer | Picker, Krisel control |
| Monochromator | Graphite |
| Radiation | Mo$K\alpha_1$ |
| Scan type | $\theta$-$2\theta$ |
| $2\theta$ range | 3.0–80.0 |
| Diffractions measured | 4708 |
| Unique diffractions | 2890 |
| **(C) Refinement of the structure** | |
| *R* 0.051 | $R = \Sigma(\lVert F_o\rvert - \lvert F_c\rVert)/\Sigma F_o$ |
| $R_w$ 0.049 | $R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma wF_o^2]^{1/2}$,<br>$w = \sigma^{-2}(F)$ |
| Variable parameters | 96 |
| Goodness of fit (GOF) | 2.82 |

**TABLE 3.** Positional, anisotropic displacement, and equivalent isotropic displacement parameters for yoshiokaite

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| T1 | 0.67620(5) | 0.75715(5) | −0.06751(6) | 0.0089(1) |
| T2 | 0.75703(5) | 0.67636(5) | 0.56732(6) | 0.0090(1) |
| T3 | 1/3 | 2/3 | 0.9618(3) | 0.0137(4) |
| T3′ | 1/3 | 2/3 | 0.0421(2) | 0.0059(3) |
| T4 | 1/3 | 2/3 | 0.5407(2) | 0.0058(3) |
| T4′ | 1/3 | 2/3 | 0.4606(3) | 0.0138(4) |
| O1 | 0.2816(1) | 0.0567(1) | 0.0762(1) | 0.0164(4) |
| O2 | 0.0556(1) | 0.2814(1) | 0.4241(1) | 0.0163(4) |
| O3 | 0.5134(1) | 0.3560(2) | 0.0028(2) | 0.0292(5) |
| O4 | 0.3556(2) | 0.5132(1) | 0.4957(2) | 0.0301(5) |
| O5 | 0.6827(1) | 0.0004(1) | 0.2508(2) | 0.0186(4) |
| O6 | 1/3 | 2/3 | 0.2501(7) | 0.035(2) |
| O6′ | 2/3 | 1/3 | 0.2573(7) | 0.038(2) |
| Ca | 0.44328(5) | 0.00004(6) | 0.25008(5) | 0.0230(2) |

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| T1 | 0.0079(2) | 0.0087(2) | 0.0108(2) | 0.0048(1) | 0.0002(1) | −0.0009(1) |
| T2 | 0.0086(2) | 0.0079(2) | 0.0111(2) | 0.0046(1) | 0.0010(1) | −0.0002(1) |
| T3 | 0.0072(4) | $U_{11}$ | 0.027(1) | $1/2U_{11}$ | 0 | 0 |
| T3′ | 0.0054(4) | $U_{11}$ | 0.0070(6) | $1/2U_{11}$ | 0 | 0 |
| T4 | 0.0046(3) | $U_{11}$ | 0.0083(6) | $1/2U_{11}$ | 0 | 0 |
| T4′ | 0.0085(4) | $U_{11}$ | 0.025(1) | $1/2U_{11}$ | 0 | 0 |
| O1 | 0.0189(5) | 0.0161(5) | 0.0147(5) | 0.0092(4) | 0.0014(4) | −0.0002(4) |
| O2 | 0.0164(5) | 0.0181(5) | 0.0150(5) | 0.0090(4) | −0.0015(4) | −0.0019(4) |
| O3 | 0.0129(5) | 0.0153(5) | 0.060(1) | 0.0075(4) | 0.0088(6) | 0.0099(6) |
| O4 | 0.0160(5) | 0.0129(5) | 0.062(1) | 0.0074(4) | −0.0111(6) | −0.0116(6) |
| O5 | 0.0193(5) | 0.0200(5) | 0.0174(5) | 0.0104(4) | −0.0003(4) | 0.0013(4) |
| O6 | 0.042(2) | $U_{11}$ | 0.020(2) | $1/2U_{11}$ | 0 | 0 |
| O6′ | 0.047(2) | $U_{11}$ | 0.021(2) | $1/2U_{11}$ | 0 | 0 |
| Ca | 0.0192(2) | 0.0425(3) | 0.0151(2) | 0.0214(2) | −0.0023(1) | −0.0043(1) |

*Note:* Ca occupancy set at 0.92, and occupancy of T3, T3′, T4, T4′, O6, and O6′ all set to 0.5; the inclusion of T3′, T4′, and O6′ in the table is only to satisfy the refinement and does not represent the actual structure (see text). Estimated standard errors refer to the last digit, and identities are noted.

tional and thermal parameters for this structure are given in Table 3, and bond distances from central cations in Table 4. A copy of the observed and calculated structure factors (Table 5) is available.[1]

## DESCRIPTION OF STRUCTURE

A polyhedral diagram is shown in Figure 2 that illustrates the relation between tridymite and a single nepheline layer (layer type A), which is the basis of the yoshiokaite structure. To generate the nepheline structure, two of the modified tridymite layers of Figure 2 are stacked along *c* so that they are almost completely superimposed, giving rise to the stacking sequence ··· AAAAA ···. In the case of yoshiokaite, a second layer (layer type B), with an opposite sense of rotation (Fig. 3), is stacked along *c* to give the stacking sequence ··· ABABABA ···. Figure 4 illustrates a section of the structure parallel to *c*, including the two threefold axes. The tetrahedra sharing apical O4 atoms are carried over from the tridymite structure, but to satisfy the refinement, they are repeated to give a face-sharing geometry at $z = ½$. The occupancy of T2, T2′, and O4 are near 0.5, suggesting that this feature is generated by two crystal orientations of equal volume. The acceptable distance and angular relationships in the remaining portion of the structure require that these two orientations contain most features of the structure as a continuous unit. An important point to note is that all atoms except those located on the threefold axis obey $P\bar{3}c1$ symmetry and hence lead to the original space-group identification (Kirkpatrick and Steele, 1973). The atomic configuration along the threefold axis, including the half occupancy and the apparent face-sharing tetrahedra, is most easily explained by a [110] twin axis, which is in fact a symmetry element of the $P\bar{3}c1$ space group and

**TABLE 4.** Bond lengths for yoshiokaite

| | | | | | |
|---|---|---|---|---|---|
| T1-O1 | 1.680(2) | T2-O5 | 1.684(2) | T3-O3 | 1.671(2) |
| -O1 | 1.698(1) | -O2 | 1.687(1) | -O3 | 1.671(2) |
| -O5 | 1.692(1) | -O2 | 1.692(2) | -O3 | 1.671(2) |
| -O3 | 1.724(1) | -O4 | 1.719(1) | -O6′ | 1.802(6) |
| Mean | 1.699 | | 1.696 | | 1.704 |
| T3′-O3 | 1.686(2) | T4-O6′ | 1.661(6) | T4′-O4 | 1.671(2) |
| -O3 | 1.687(2) | -O4 | 1.687(2) | -O4 | 1.671(2) |
| -O3 | 1.687(2) | -O4 | 1.687(2) | -O4 | 1.671(2) |
| -O6 | 1.710(6) | -O4 | 1.687(2) | -O6 | 1.730(6) |
| Mean | 1.693 | | 1.680 | | 1.686 |
| Ca-O1 | 2.416(2) | -O4 | 2.492(2) | | |
| -O2 | 2.412(2) | -O4 | 2.718(2) | | |
| -O3 | 2.482(2) | -O5 | 2.375(2) | | |
| -O3 | 2.726(2) | -O6 | 2.921(1) | | |
| | | Mean | 2.568 | | |

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[1] A copy of Table 5 may be ordered as Document AM-90-438 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

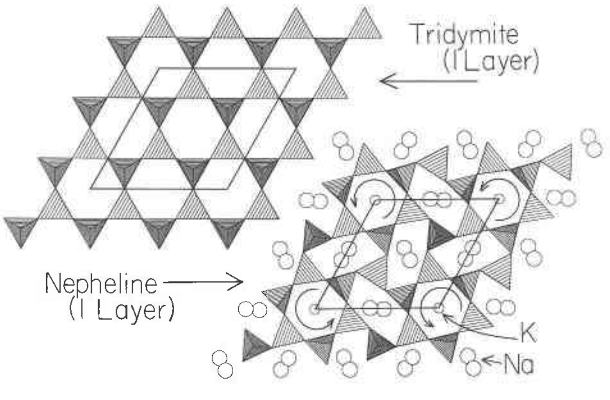

Fig. 2. Polyhedra projection parallel to *c* illustrating the relation between high tridymite and a single layer of nepheline. For nepheline, half the Si is replaced by Al with charge balance by Na and K. The resulting distortion within one layer is basically a 20° rotation of every other six-membered ring and a compression of the alternate six-membered rings to a near-rectangular shape. For the ideal composition, Na lies above and below the rectangular six-membered ring, and K above and below the hexagonal six-membered ring. This single nepheline layer (layer A) represents the basic unit of the yoshiokaite structure. The cell shown for tridymite has translation $2a_{\mathrm{trid}}$ to correspond to that of nepheline.

would effectively superpose the reciprocal lattice of the twin components. Because the structure has a symmetry so close to $P\bar{3}c1$, the twinned individuals form a continuous structure only differing by the tetrahedral orientations on the threefold axis. The violations of the *c* glide of $P\bar{3}c1$ result from the departure from $P\bar{3}c1$ for only those Si and O atoms located on the threefold axis.

The structure as proposed by Yoshioka (1970a) is closely related to the structure of nepheline, which in turn is based on the tridymite structure. Figure 2 shows the basic relationships among the three structures. Whereas the six-membered rings formed by six tetrahedra in tridymite superpose in projection parallel to *c*, the six-membered rings in yoshiokaite are alternatively rotated about 20° clockwise and then counterclockwise about the *c* axis. The surrounding six six-membered rings are consequently distorted from the ideal hexagonal geometry of tridy-

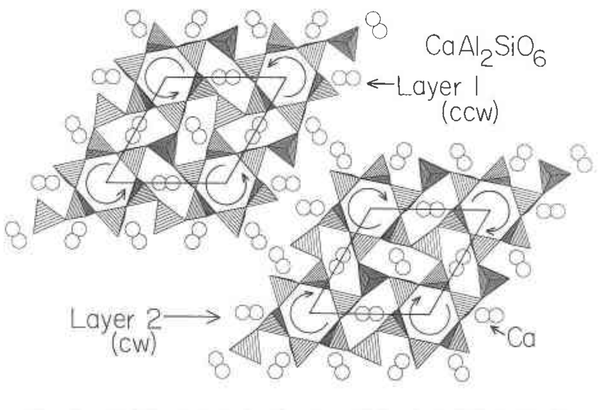

Fig. 3. Polyhedra projection parallel to *c* of the two layers composing yoshiokaite. Layer 1 (layer A) is similar except in detail to the nepheline layer of Figure 2. Layer 2 (layer B) is similar to the nepheline layer but with an opposite sense of rotation. Abbreviations: cw = clockwise; ccw = counter clockwise.

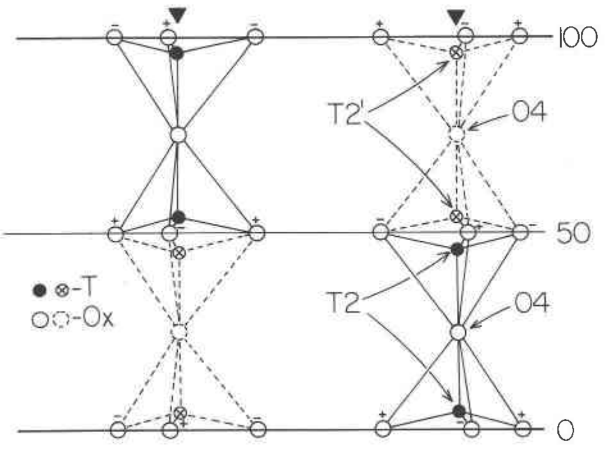

Figure 4. Section parallel to *c* of yoshiokaite and including the two threefold axes of $P\bar{3}$. The atoms lying on these axes and those forming coordination polyhedra with these atoms are included and the elevation above or below the plane indicated with + or −. The tetrahedral cations, T2 and T2′, as well as the apical oxygen O4, show an occupancy of 0.5. This refinement result requires that the tetrahedra share faces.

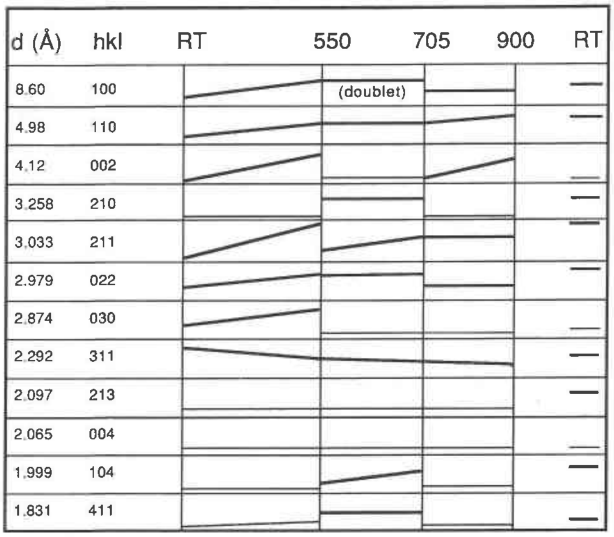

Fig. 5. Qualitative representation of intensity changes of X-ray diffractions as a function of temperature for $CaAl_2SiO_6$ from 23 °C to 900 °C and return to 23 °C (= RT). The ordinate within each box represents intensity increasing upward. A light line indicates a weak or diffuse line, whereas a heavy line with a positive slope indicates an intensity increasing with *T* and a solid line with negative slope an intensity decreasing with *T*. Discontinuities indicate phase changes at 550 and 705 °C, and the relative positions of lines for the two phases indicate the relative intensity at the phase change.

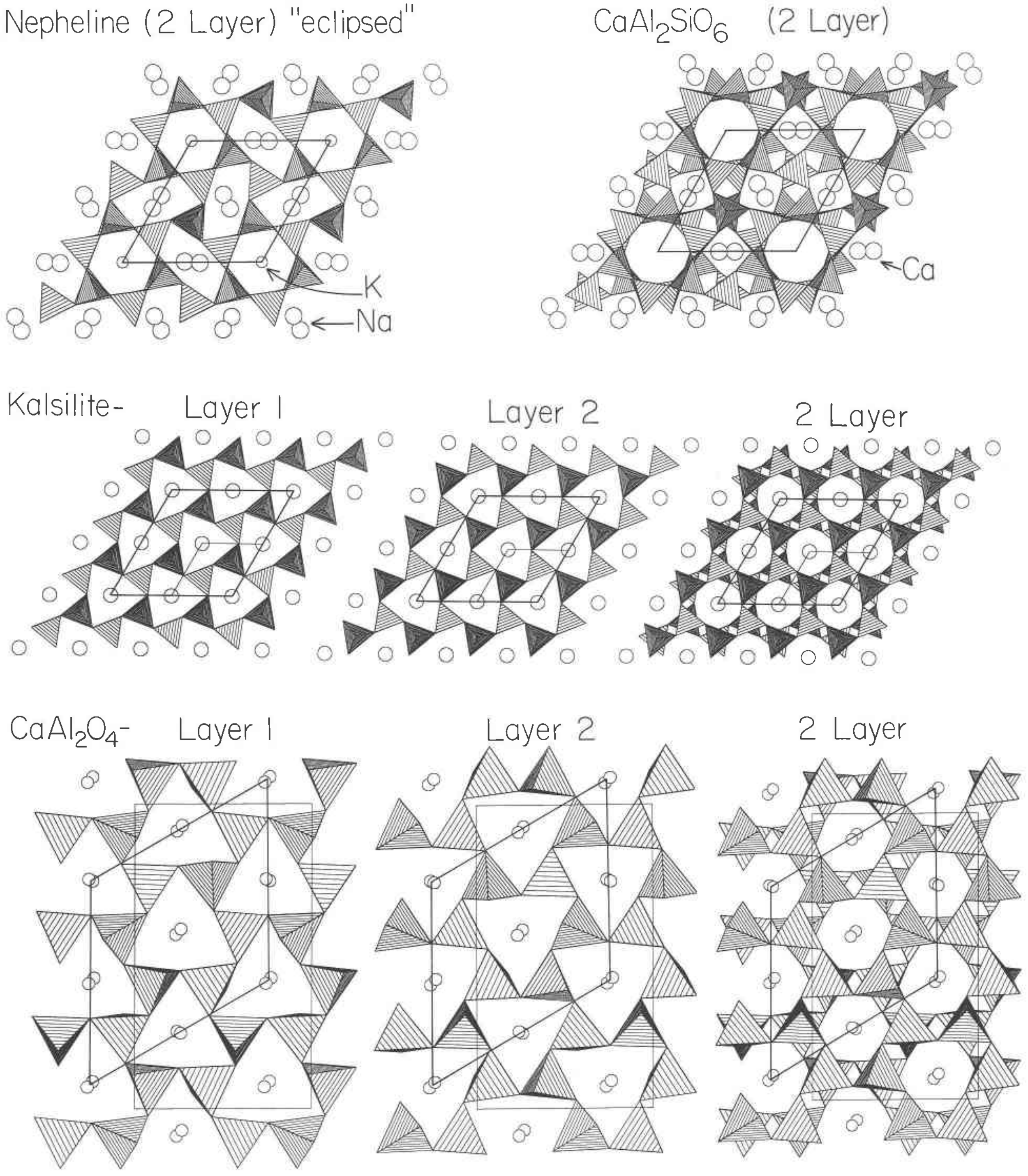

Fig. 6. Polyhedra projections of nepheline, yoshiokaite ($CaAl_2SiO_6$), kalsilite, and $CaAl_2O_4$ structures. **Top left:** nepheline composed of two layers similar to that shown in Figure 2; **Top right:** $CaAl_2SiO_6$ composed of the two layers shown in Figure 3; **Middle:** kalsilite layer units and resulting structure; **Bottom:** $CaAl_2O_4$ layer units projected parallel to *b* with *a* horizontal and *c* vertical, and resulting two-layer structure. For each projection, the cell edges corresponding to the cell $a = 10.0$ Å are indicated by heavy lines. For kalsilite, *a* is actually half this value, as shown by light lines, and for $CaAl_2O_4$ the monoclinic cell projected parallel to *b* is shown by light lines.

mite. Between these two distorted units are Ca sites, which in the present composition are partially (92%) occupied to compensate for the Al/Si ratio. The symmetry of the structure obeys pseudo-$P\bar{3}c1$ symmetry, as shown by the refinement in $P\bar{3}$, where the unconstrained positional parameters of all atoms maintained the apparent $P\bar{3}c1$ symmetry.

## TEMPERATURE VARIATION OF STRUCTURE

The material from which the above structure was deduced was mounted on a Guinier-Lenne camera, and the diffraction pattern was recorded in vacuum from room temperature to 900 °C with an additional pattern obtained after cooling to room temperature. The qualitative features of the diffraction patterns are illustrated in Figure 5. Two sharp phase transitions occur at 550 °C and 705 °C (each ±10 °C). The diffraction patterns in the three temperature regions are similar, suggesting no gross structural changes. However, the change at 550 °C is marked by splitting of the 100 diffraction and a weakening of the 002 diffraction, suggesting a lowering of symmetry, possibly to the orthorhombic $CaAl_2O_4$ structure. The change at 705 °C is marked by distinct changes in the intensity of nearly all diffractions and by the 100 diffraction reverting to a singlet and the reappearance of the 002 diffraction. The room-temperature pattern after heating shows a sharpening of most diffractions, subtle intensity changes relative to the starting material, suggesting that some tetrahedral ordering may have occurred during the approximately 3 d of heating, and the appearance of several lines (210 and 104) that were weak in the original sample. These qualitative observations indicate that yoshiokaite shows a series of structural inversions like other feldspathoids (Henderson, 1983).

## COMPARISON WITH OTHER STUFFED TRIDYMITE STRUCTURES

Yoshiokaite represents variation of the stuffed tridymite structures in addition to the nepheline, kalsilite, and $CaAl_2O_4$ structures. In summary, the essential features of each are shown in Figure 6, where the composite structures for nepheline and yoshiokaite ($CaAl_2SiO_6$) are shown as (001) polyhedral projections of the combined individual layers illustrated in Figures 2 and 3, respectively. For comparison, the individual layers and combined structure for kalsilite are included in Figure 6. The complex structural features in the nepheline-kalsilite solid solution series result from the two types of distortions, Si-Al ordering, exsolution, and microscopic twinning, thus providing a wealth of complexity for the structural mineralogist. Although not common in nature except for the rare lunar material, the third chemical variant, which includes Ca and its associated structure, potentially introduces even more complexity, possibly rivaling that of the common sodium, potassium, and calcium feldspars.

The addition of sufficient Ca to permit entry into the K site of nepheline may result in a departure from hexagonal symmetry to monoclinic, as represented by the $CaAl_2O_4$ structure (Hörkner and Müller-Buschbaum, 1976) and also shown in Figure 6, bottom. The very different structural distortions of yoshiokaite compared to nepheline would provide one reason why Ca does not readily enter natural nepheline, although the rarity of such Ca-, Al-rich natural systems may simply preclude formation of yoshiokaite.

## ACKNOWLEDGMENTS

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