Microstructures and high-temperature phase transitions in kalsilite

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ABSTRACT

A diversity of twinning and exsolution textures has been observed by transmission electron microscopy in natural kalsilite from volcanic and metamorphic rocks (Mount Nyiragongo, Zaire; Alban Hills, Italy; Kerala, southern India). The phase transitions responsible for these microstructures were examined by high-temperature powder and single-crystal X-ray diffraction. Pure kalsilite has P63mc symmetry at high temperatures but transforms to its P63 state through a two-phase field, between ~870 and ~920 °C. In this two-phase field, the low form coexists with a structure that has a sixfold repeat of its a unit-cell dimension. For ~Ks88, the high-temperature state is high tetrakalsilite with possible space group P63mc; a two-phase field between ~890 and ~930 °C involves the coexistence of this phase with P63, kalsilite. High tetrakalsilite with composition ~Ks74 reverts to low tetrakalsilite on quenching to room temperature from 950 °C. Lattice-parameter variations, and estimates of the Al-O-Si angles that can be derived from them, imply that the stability limit for the high structural states occurs when the angles for apical and basal O atoms converge. At lower temperatures, pure P63, kalsilite appears to have transformed during a metamorphic evolution in nature to an intergrowth of the P63 structure and a structure for which P31c symmetry is proposed. The latter can be thought of as a polytype of kalsilite, with (001) layers stacked in an eclipsed array rather than in the staggered array of normal low kalsilite. In this regard, KAlSiO3 seems to be remarkably similar to KLISO4. If ~3–12 mol% NaAlSiO3 is present in solid solution, a P63 structure with an a parameter √3 greater than normal low kalsilite develops. An anomaly in the lattice parameters of Ks88 suggests that the transition temperature below which this superstructure develops may be ~500 °C. Natural nepheline exsolved from kalsilite displays merohedral twinning, which can be accounted for by a P63mc → P63 transition during cooling. Transformation behavior in the Ne-Kss system may be explained, at least qualitatively, in terms of Na-K ordering between cavity sites, ordering of basal O atoms between two sites on either side of the mirror plane parallel to the c axis of P63mc structures, ordering of apical O atoms between three sites, and coupling between all these processes.

INTRODUCTION

Kalsilite (KAlSiO3) is a rock-forming feldspathoid that occurs mainly in K-rich silica-undersaturated lavas; it is also found in ejected blocks incorporated into pyroclastics and, rarely, in metamorphic rocks. It undergoes several phase transitions at high temperatures and displays a remarkable diversity of structures over a limited range of compositions at the K-rich end of the nepheline-kalsilite system. The first structure refinement, by Perrotta and Smith (1965), was of a volcanic crystal with Na:K ≈ 0.02:0.98 and space group P63 (low kalsilite). Perrotta and Smith explained the relatively large R value for their refinement as the result of disorder of the O atoms. In particular, apical O atoms linking successive (001) layers have mean positions on the threefold axes but appear actually to be randomly distributed among three sites displaced off these axes. The intersheet Al-O-Si bond angles are reduced from the improbable value of 180° as a consequence. Synthetic KAlSiO3 has P6,mc symmetry at 950 °C (high kalsilite; Kawahara et al. 1987), and a structural phase transition involving the symmetry change P6,mc → P63 has been proposed for the end-member composition (Andou and Kawahara 1982; Abbott 1984; Kawahara et al. 1987). The driving energy for this transition must arise predominantly from the ordering of displacements of O atoms linking the bases of the AlO4 and SiO4 tetrahedra. However, Capobianco and Carpenter (1989) found that the transition occurs by means of an intermediate phase, which coexists with low kalsilite between ~850 and ~920 °C and is characterized by weak superstructure reflections. New data presented in this paper suggest that the intermediate phase is hexagonal and not orthorhombic as originally suggested.

Four other room-temperature variants of the stuffed tridymite form of kalsilite have been reported in the composition range ~Ne30,Ks70=Ks100. Smith and Sahama (1957) observed diffuse reflections in diffraction patterns from crystals taken from a lava from Mount Nyiragongo, Zaire. The unit cell for this material is related to that of
pure kalsilite by a 30° rotation about the c axis and an increase of the \( a \) lattice dimension by a factor of \( \sqrt{3} \). These reflections disappeared after heating to 600 °C, but their origin has not been studied in any detail. Tetrakalsilite (proper mineral name: panunzite) and trikalsilite are also known from volcanic rocks, and tetrakalsilite has been synthesized (Sahama 1957, 1962; Sahama and Smith 1957; Smith and Tuttle 1957; Tuttle and Smith 1958; Merlino et al. 1985; Bonaccorsi et al. 1988; Hovis et al. 1992). Both typically contain \( \sim 30 \) mol% Ne in solid solution. Finally, kalsilite crystals produced from nepheline by ion exchange in molten KCl can give diffraction patterns with weak or absent \( hhl, l = \text{odd} \) reflections, which imply that the \( P6_3/mc \) structure might exist at room temperature. Dollase and Freeborn (1977) considered the high symmetry of these crystals to represent only the average structure of two \( P6_3 \), merohedral twins related by a mirror plane normal to the \( a \) axis and intergrown on a fine scale.

Kalsilite prepared by hydrothermal methods can have a similar domain structure according to Andou and Kawahara (1984), with the volume proportions of the domains varying from crystal to crystal.

The structures of kalsilite, tetrakalsilite, trikalsilite, and nepheline all have \( P6_3 \) symmetry at room temperature and are characterized by stacking of tridymite-like sheets of alternating \( \text{Al}_2\text{O}_3 \) and \( \text{Si}_2\text{O}_5 \) tetrahedra to give a repeat distance along the \( c \) axis of \( \sim 8.6 \) Å (referred to subsequently in this paper as \( C \)). The \( a \) lattice parameter is a multiple of the \( \sim 5.2 \) Å distance between the centers of sixfold rings in the ideal tridymite structure, referred to here as \( A \). The unit cells of kalsilite, nepheline, trikalsilite, and tetrakalsilite then have 1\( A \), 2\( A \), 3\( A \), and 4\( A \), respectively, as their \( a \) dimension. Details of the structures are subtly different, however (Merlino 1984). In the nepheline structure the six-membered rings are oval and nearly hexagonal in the proportion 3:1 (Buerger et al. 1954; Hahn and Buerger 1955; Dollase 1970; Foreman and Peacor 1970; Dollase and Peacor 1971), whereas in kalsilite they all have a ditrigonal shape (Perrotta and Smith 1965; Andou and Kawahara 1984). Trikalsilite and tetrakalsilite have three kinds of six-membered rings in their unit cells—hexagonal, ditrigonal, and oval—in the proportions 2:4:12 and 2:12:18, respectively (Merlino 1984). Another important difference between the structures is the stacking of the (001) layers, which are distorted relative to ideal expanded tridymite sheets. In the 2\( A \), 3\( A \), and 4\( A \) structures successive layers are stacked in an “eclipsed” conformation, with a marked \( P6_3/m \) pseudo-symmetry. In the 1\( A \), \( P6_3 \) structure they are stacked in a “staggered” conformation (Merlino 1984), which means that every layer is deformed in the same manner, but all the ditrigonal rings in one layer point in one direction and all the rings in the next layer point in the opposite direction. The 1\( A \), \( P6_3/mc \) structure at high temperatures has open hexagonal rings (Kawahara et al. 1987), with a mirror plane perpendicular to \( c \) violated only by the Al-Si ordering scheme. There were some early suggestions of incomplete Al-Si order in nepheline (Dollase and Peacor 1971), but NMR spectroscopic data indicate high degrees of order in natural and synthetic samples (Lippmaa et al. 1980; Stebbins et al. 1986; Hovis et al. 1992), and it now seems unlikely that any of these phases have substantial tetrahedral site disorder.

The highest temperature polymorph is \( 01\text{-KAlSiO}_4 \), which has a different framework topology than tridymite (Gregorkiewitz and Schäfer 1980; Merlino 1984). Other types of topologies are possible (Merlino 1984; Palmer 1994), but kaliophilite is the only phase with a kalsilite composition in this group that has so far been found in nature (Bannister and Hey 1931; Lukesh and Buerger 1942; Barbieri et al. 1970; Cellai et al. 1992). It has a unit cell that is a multiple of the low kalsilite cell, but its microstructure and thermal expansion behavior are not consistent with the enlarged cell simply being a kalsilite superstructure (Cellai et al. 1992). Both \( 01\text{-KAlSiO}_4 \) and natural kaliophilite undergo what appear to be displacive phase transitions at high temperatures (Lange et al. 1986; Capobianco and Carpenter 1989; Cellai et al. 1992).

Common to all these structures are (1) the influence of O-atom positional disorder in determining sequences of phase transitions and (2) the role of Na-K ordering in stabilizing particular framework distortions. The basic stuffed tridymite structure appears to be unable to accommodate changes in stoichiometry and temperature without also undergoing changes in symmetry. A primary objective of the in situ high-temperature X-ray diffraction study described in this paper, as opposed to previous anneal and quench experiments, was to define the relationships between the known variants of the kalsilite structure more explicitly. Close analogies with the behavior of compounds described in the literature, such as \((\text{Na},\text{K})\text{AlGeO}_4\), \((\text{Na},\text{K})\text{GaSiO}_4\), \(\text{SrAl}_2\text{O}_4\), and \(\text{KLiSO}_4\), provide new insights into the nature of the \( \sqrt{3}A \) superstructure of Smith and Sahama (1957) and have led to the discovery of a new kaliophilite structure with a suggested space group of \( P31c \). If there are so many possible phase transitions, the development of complex microstructures should be anticipated; natural and heat-treated samples have also been examined by transmission electron microscopy.

**EXPERIMENTAL DETAILS**

**Powder diffraction**

X-ray measurements were made with a multichannel CPS-120 diffractometer described in Salje et al. (1993), using CuKα1 radiation and a quartz monochromator. The sample was supported on a strip of platinum, which was used for resistance heating. Temperature was monitored using a Pt-13%Rh thermocouple welded to the underside of the strip and calibrated against the \( \beta = \alpha \) transition temperature (573 °C) of quartz mounted in the same configuration. The uncertainty of the temperature scale was estimated to be \( \pm 5 \) °C, but the stability was within 1 °C. All experiments were performed in air, and \( \text{AI}_2\text{O}_3 \) was used as an internal standard. Each powder diffraction
### Table 1. Lattice parameters of kalsilite obtained at high temperatures during heating cycles

<table>
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<tr>
<th>T (°C)</th>
<th>Homogenized Ks&lt;sub&gt;oo&lt;/sub&gt;</th>
<th>Metamorphic Ks&lt;sub&gt;oo&lt;/sub&gt;</th>
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<tr>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
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<tr>
<td>25</td>
<td>5.153(1)</td>
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<tr>
<td>25*</td>
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<td>147</td>
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<td>196</td>
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<td>966**</td>
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Note: Figures in parentheses indicate the uncertainty (± 1 σ) in the last digit. The data were collected using two batches of sample.
* Lattice parameters obtained from data collected at room temperature after quenching from high temperature at the end of the full heating cycle.
** Data collected using the second batch of sample.

The reflections became diffuse with increasing temperature; a least-squares fit was performed using a Gaussian diffraction profile to determine the peak width.

### Transmission electron microscopy

TEM samples were prepared by ion-beam thinning of crystals removed from petrographic thin sections, using copper discs for support. Observations were all made using a JEOL JEM 100CX instrument operating at 100 kV. Kalsilite and nepheline are sensitive to beam damage but survive long enough to yield reasonable bright-field images, dark-field images, and diffraction patterns. Grains from mineral separates used in the heating experiments were also examined. They were mounted in epoxy resin, prepared as thin sections, and then ion-beam thinned, with titanium grids used for support. Preparation for the TEM experiments in this way involved heating the samples to ~130 °C for ~15 min to ~1 h to harden the epoxy and melt the thin-section mounting medium.

### IR spectroscopy

In this study, IR spectra were collected only to make the simplest of "fingerprinting" comparisons between different structure types. Samples were ground into a powder for about 5 min by hand in a mortar and pestle, and...
absorption experiments were performed using the standard pellet technique. The powders were diluted with KBr in the ratio 1:300 for the far infrared region (250–700 cm⁻¹) and 1:400 for the middle infrared region (500–1450 cm⁻¹). Spectra were collected under vacuum using a Fourier-transformation infrared spectrometer (Bruker IFS 113v). A liquid-nitrogen-cooled MCT detector was used for middle infrared and a room-temperature DTGS detector for the far infrared. The spectral resolution was set to 2 cm⁻¹ for middle infrared and to 4 cm⁻¹ for far infrared. The zero filling factor for the Fourier-transform algorithm was 4 because final spectral resolutions of 0.5 and 1 cm⁻¹, respectively, were obtained. For each sample the spectra in the far and middle region were normalized with respect to the maximum point of the 690 cm⁻¹ mode and to the minimum point between 500 and 600 cm⁻¹.

**SAMPLE DESCRIPTION**

**Starting materials**

Metamorphic kalsilite was separated from two samples of a granulite facies gneiss from the Punalur district in Kerala, southern India. The first was that used by Capobianco and Carpenter (1989), which was kindly provided by M. Sandiford (University of Adelaide, Australia), and the second was kindly provided by M. Santosh (Centre for Earth Science Studies, Akkalum, Trivandrum, India). This kalsilite is essentially end-member KAISiO₄, with only ~0.002 Na⁺ ions per K⁺ ion and an equivalent proportion of Fe substituted for Al (Capobianco and Carpenter 1989; Sandiford and Santosh 1991). Peak metamorphic conditions for the Punalur assemblages (kalsilite, leucite, hibonite, spinel, corundum, sphene, perovskite, Ti-bearing phlogopite, and potassium feldspar) have been estimated to be 700–800 °C and 3.5–6.5 kbar (Sandiford and Santosh 1991).

Volcanic kalsilite was separated from an ejected block of the “welded scoriae” formation of Colle Cimino (Marino), Alban Hills, Italy, which was kindly provided by A. Cundari (University of Melbourne, Australia). A description of these blocks, and the nepheline-kalsilite microperthites within them, was given by Federico (1976) and Aurisicchio and Federico (1985). Both kalsilite and kaliophilite have been found in the ejecta but not in coexistence. This suggests different crystallization histories for the two phases, perhaps because of variations in chemistry, temperature, or pressure in their respective environments of formation. In thin section the rock from which the kalsilite was separated consisted mainly of diopside and kalsilite; the latter contained ~10% nepheline lamellae exsolved on an optical scale. Powder X-ray diffraction of the kalsilite separate, using a Huber 621 Guinier camera with CuKα₁ radiation, confirmed that kalsilite was the predominant phase, with only a few weak reflections from nepheline. A typical composition of the

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**Table 2. Representative chemical analyses of kalsilite, nepheline, and tetrakalsilite**

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<td>0.02</td>
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<td>012</td>
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<td>0.89</td>
<td>0.97</td>
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<td>2.99</td>
<td>3.00</td>
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</tr>
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</table>

**Note:** 1 = Kalsilite matrix of Ks-Ne intergrowth; Alban Hills. 2 = Kalsilite; Alban Hills, after homogenization by annealing for 1 d at 950 °C. 3 = Kalsilite (90049). 4 = Nepheline in patches within kalsilite (90049). 5 = Kalsilite (75422). 6 = Nepheline lamellae in kalsilite (75422). 7 = Nepheline overgrowth on a kalsilite phenocryst (75422). 8 = Tetrakalsilite obtained after annealing crystals with Ks-Ne intergrowths from sample 75422 for 1 d at 950 °C. 9 = Nepheline in fine lamellae within the tetrakalsilite of sample 8. Data collected with a Cameca SX50 electron microprobe using a wavelength-dispersive system for Na and an energy-dispersive system for Si, Al, Cr, Fe, Ti, Mg, K, and Ca (20 kV, 10 nA). Only Si, Al, Fe, Na, and K were detected at levels >1σ of counting statistics. All Fe was assumed to be Fe²⁺. Oxide values in weight percent.
host kalsilite was determined by electron microprobe analysis to be Ne₇K₉₃ (Table 2, Fig. 1). No significant compositional variations within individual grains or between grains were detected.

Nepheline-kalsilite phenocrysts were selected from porphyritic lavas of the Virunga volcanic field in North Kivu, Mount Nyiragongo, Zaire (sample nos. 75422 and 90049, Harker collection, University of Cambridge). Similar material has been described in detail by Sahama (1957, 1960, 1962). As illustrated in Figure 2, these phenocrysts display a variety of intergrowth textures; some consist of perthitic kalsilite with nepheline lamellae, whereas in others the nepheline occurs as patches in the kalsilite (see Sahama 1960, 1962). The intergrown regions are surrounded by a homogeneous nepheline rim, which has a higher K content than the nepheline lamellae. Compositional data for these samples are given in Table 2 and Figure 1. Sahama (1957) and Smith and Sahama (1957) reported the presence of trikalasilite in the nepheline-kalsilite perthites, but this phase was not found during the course of the present study.

**Figure 2.** SEM images (backscattered electrons) showing phenocrysts of intergrown kalsilite (ks) and nepheline (ne) from Mount Nyiragongo (a–c). (d) Tetrakalsilite (tetrak) intergrown with fine lamellae of nepheline (ne) after annealing crystals from the same sample as shown in a–c at 950 °C for 1 d and quenching in water.

**Annealed samples**

Annealing experiments were performed on the Alban Hills and Mount Nyiragongo samples in an attempt to produce homogeneous crystals. The separated powders were wrapped in platinum foil and supported in conventional vertical resistance furnaces. Kalsilite samples with fine nepheline lamellae from the Alban Hills were annealed for 1 d at 950 °C and then quenched in water. The annealed product consisted only of kalsilite, as shown by the disappearance of the nepheline reflections in powder diffraction patterns. The change in lattice parameters is also consistent with homogenization ($a = 5.160$ and $c = 8.683$ Å before annealing, $a = 5.151$ and $c = 8.655$ Å after annealing). (The $c$ parameter, in particular, is sensitive to composition, e.g., Fig. 3 of Hovis et al. 1992). The average composition of homogenized crystals, from probe analyses, is $\sim$ Ne₇₃K₉₃ (Table 2, Fig. 1).

Crystals from Mount Nyiragongo (sample no. 75422) were annealed for 1 d at 950 °C and then quenched in water. The product crystals still contained some lamellar
patches of nepheline (Fig. 2d), but powder X-ray diffraction revealed that the dominant phase had transformed to tetrakalsilite, as found by Sahama (1957). The same products were obtained after annealing for 13 d using a different grain size for the starting material. Probe analysis gave compositions of \(~\text{Ne}_{26}\text{Ks}_{74}\) for the tetrakalsilite and \(~\text{Ne}_{48}\text{Ks}_{52}\) for the nepheline lamellae (Table 2, Fig. 1).

Small quantities of the \(\text{Ks}_{100}\) metamorphic kalsilite were annealed in platinum envelopes at 500 (1 h, 4 d) and 950 °C (1 d) and quenched in air. A small amount of Ne-Ks separated from sample no. 90049 was also annealed for 1 d at 950 °C for TEM observations.

**RESULTS**

**Powder X-ray diffraction**

Refined lattice parameters for the metamorphic kalsilite \((\sim\text{Ks}_{100})\) and homogenized Alban Hills kalsilite \((\sim\text{Ne}_{12}\text{Ks}_{88})\) are shown as a function of temperature in Figure 3. The data for \(\text{Ks}_{100}\) were collected using two batches of the sample used by Capobianco and Carpenter (1989). The first experiment was from room temperature to \(\sim 850 °C\), and the second from \(\sim 850\) to \(\sim 1000 °C\). Data for \(\text{Ks}_{88}\) were also collected in two batches, the first from room temperature to \(\sim 900 °C\), and the second from room temperature to \(\sim 1060 °C\). Published data for two synthetic kalsilite samples (Henderson and Taylor 1988; Kawahara et al. 1987) and natural nepheline (Sahama 1962) are included for comparison. The \(a\) parameter of the \(\text{Ks}_{100}\) and \(\text{Ks}_{88}\) samples increased approximately linearly up to \(\sim 900 °C\), where a discontinuity and an abrupt change in slope occur (Fig. 3a). The \(c\) parameter of \(\text{Ks}_{100}\) decreased approximately linearly, with a break in slope at about the same temperature as for the \(a\) parameter. In \(\text{Ks}_{88}\), the \(c\) parameter at first increased but then decreased with increasing temperature (Fig. 3b). The volume expansion (Fig. 3c) is dominated by the contribution from the variation in \(a\) for both samples. There also appears to be a change in the trends of \(a, c,\) and \(V\) at \(\sim 500 °C\), which is most evident in the variation of \(c\) for \(\text{Ks}_{88}\) and of \(V\) for \(\text{Ks}_{100}\). The synthetic kalsilite of Henderson and Taylor (1988) is almost indistinguishable from natural \(\text{Ks}_{100}\) in its thermal evolution, whereas the synthetic sample of Kawahara et al. (1987) behaved more like \(\text{Ks}_{88}\).

Powder patterns from \(\text{Ks}_{88}\) obtained at temperatures between \(\sim 480\) and \(\sim 770 °C\) contained nepheline reflections, showing that exsolution had occurred within the time scale of the data collection. Tuttle and Smith (1958) described similar in situ effects, with the onset of exsolution occurring at 450–500 °C on the nepheline side of the Ne-Ks solvs. In the present experiments the nepheline reflections disappeared above \(\sim 770 °C\), showing that the sample had rehomogenized. This unmixing might account for the nonlinearity in \(a\) and \(V\) over the same temperature interval (Figs. 3a and 3c) but cannot be responsible for the nonlinearity in \(c\) over the full temperature range.

Three types of structural changes are also indicated by the intensities of the \(hhl\), \(l =\) odd reflections in the powder.

**FIGURE 3.** (a–c) Thermal expansion behavior on heating of metamorphic kalsilite \(\text{Ks}_{100}\) (open circles) and homogenized \(\text{Ks}_{88}\) from Alban Hills (solid squares). A diamond represents \(\text{Ks}_{100}\) after cooling from high \(T\). The other data are from the literature for comparison: plus signs = synthetic kalsilite (Henderson and Taylor 1988); \(\text{Ks}\) = synthetic kalsilite (Kawahara et al. 1987); asterisks = natural nepheline from Nyiragongo (Sahama 1962), plotted as if it has the same unit cell as kalsilite. Vertical dashed lines indicate the limits of the two-phase intervals.
patterns. First, the intensities of these reflections were low in patterns from the metamorphic Ks_{100} sample at room temperature but increased irreversibly between \( \sim 250 \) and \( \sim 350 \) °C during heating (see also Capobianco and Carpenter 1989). Second, there was a transition regime, between \( \sim 870 \) and 920 °C in the present study, characterized by the appearance of superstructure reflections, decreasing intensity of \( hhl, l = \) odd lines and splitting of lines with large values of \( h \) and \( k \) relative to \( l \). The superstructure reflections faded above \( \sim 920 \) °C. Capobianco and Carpenter (1989) used a quite different experimental set up and obtained 860–920 °C for the transition interval. Andou and Kawahara (1982) and Kawahara et al. (1987) reported that the intensities of \( hhl, l = \) odd reflections diminished drastically at \( \sim 865 \) °C and were absent above \( \sim 875 \) °C, but they did not comment on the extra reflections that can be seen in their published powder patterns (see discussion in Capobianco and Carpenter 1989). Henderson and Taylor (1988) gave 890 °C for the onset temperature of structural changes, and Sandomisky and Urusov (1988) found what appears to be the same transition at 870 ± 20 °C. Third, on quenching the Ks_{100} sample back to room temperature from \( \sim 1000 \) °C, the \( c \) parameter consistently decreased from the starting value of 8.717(1) to 8.706(1) Å, with \( a \) unchanged. Capobianco and Carpenter associated this effect with possible volatilization of K, but no evidence of leucite formation, which would indicate alkali loss, was found in the present investigation.

No change in the intensity of \( hhl, l = \) odd reflections was found at low temperatures for the Ks_{88} sample, but a high-temperature transition region was again found. At \( \sim 890 \) °C a few weak superstructure reflections appeared and could be indexed on the basis of the tetrakalsilite structure, with \( a = 4 \) Å and \( c = 6 \) Å. The \( hhl, l = \) odd reflections weakened from \( \sim 890 \) °C until they disappeared between \( \sim 930 \) and 940 °C, suggesting a change of symmetry from \( P6_3 \) to \( P6_3mc \). For consistency with the description of kalsilite, this \( P6_3mc \) structure is referred to in the present study as high tetrakalsilite. The transition region is interpreted as the coexistence interval of low kalsilite and high tetrakalsilite. Reflections with large values of \( h \) and \( k \) relative to \( l \) were broad or showed clear splitting. For example, the 110 reflections of kalsilite decreased in intensity with increasing temperature in this range and were replaced by the 440 reflection of tetrakalsilite at lower 2\( \theta \). The cell parameters of the two phases remained distinct, and the proportion of high tetrakalsilite appeared to increase with increasing temperature. The powder patterns collected from \( \sim 940 \) to \( \sim 1060 \) °C could all be indexed as high tetrakalsilite. On quenching back to room temperature the \( a \) and \( c \) parameters could not be distinguished as consistently from their starting values as in the case of Ks_{100} (Table 1). For both Ks_{100} and Ks_{88} the transition range can be accounted for by a first-order transition, with high- and low-temperature phases coexisting isothermally. In each case the high-temperature phase, with presumed \( P6_3mc \) symmetry, reverted to a low-temperature \( P6_3 \) form on cooling.

**Figure 4.** (left) Integrated intensities of the 111 (open circles) and 112 (solid triangles) reflections during heating of Ks_{100}. (right) Integrated intensities of 111 on heating (open circles) and cooling (solid circles). The intensity of the superstructure reflection 650 (indexing for this reflection based on 660 of the superstructure = 110 of the 14 structure) was measured during a heating cycle (Xs) but only above \( \sim 945 \) °C. The intensity loss of 112 and gain of 111 on heating to \( \sim 350 \) °C was irreversible.

Lattice parameter data were not collected for Mount Nyiragongo kalsilite because fully homogeneous crystals were not obtained. Instead, the development of tetrakalsilite in crystals from sample no. 90049 was followed during in situ heating experiments. Diffraction patterns were collected in steps of \( \sim 100 \) °C from \( \sim 580 \) to \( \sim 870 \) °C. At \( \sim 870 \) °C the \( hhl, l = \) odd reflections of kalsilite became weak, indicating the onset of a transition from the low to the high structural state. After \( \sim 1 \) h at \( \sim 870 \) °C, tetrakalsilite reflections could be detected. The spectra still contained weak nepheline peaks, showing incomplete homogenization. After cooling to room temperature at \( 10^\circ \) min, the high-temperature pattern remained essentially unchanged except that \( hhl, l = \) odd reflections reappeared. The final product was therefore an intergrowth of nepheline and low tetrakalsilite. These in situ experiments match the results of the anneal and quench experiments on similar samples reported by Sahama (1957). He produced tetrakalsilite by annealing at temperatures above \( \sim 855 \) °C; annealing at 885–1000 °C, followed by quenching, produced mixtures of tetrakalsilite, nepheline, and kalsilite.

**Single-crystal diffraction**

The 111 and 112 reflections (and their symmetry equivalents) were selected for systematic study. If a symmetry change from \( P6_3 \) to \( P6_3mc \) occurs, all reflections with \( hhl, l = \) odd become extinct; therefore, 111 is a marker for the transition. The only influence of temperature on the 112 substructure reflection should be a steady decrease in intensity with increasing temperature because of normal thermal motions. Because 111 and 112 have similar \((\sin \theta)/\lambda\), the intensity variations of 112 (\( I_{112} \)) should provide a measure of the contribution of the Debye-Waller factor to the intensity variation of 111 (\( I_{111} \)). Superstructure reflections within the \( a^*b^* \) plane were examined to follow the development and evolution of 4A and 6A superstructures.
In Ks$_{100}$ (the second sample, provided by M. Santosh), the 111 reflection was weak at room temperature but became more intense on heating to $\sim$150 °C (Fig. 4). In the powdered samples the same change was observed at somewhat higher temperatures. The accompanying reduction in $I_{111}$ shows that significant structural changes must have occurred during this irreversible process. The peak profile of 111 illustrated in Figure 5 shows an initially weak and broad reflection, which became sharp at higher temperature and remained relatively intense but slightly broader on quenching from $\sim$1000 °C. Some of the intensity from the initial broad peak appears to have persisted through the heat treatment and is evident on the low 2θ side (Fig. 5).

$I_{111}$ dropped off precipitously between $\sim$850 and $\sim$950 °C (Fig. 4), corresponding closely to the transition range observed by powder diffraction. Only relatively minor variations in the peak width were observed, though there is an apparent step at the highest temperatures when $I_{111}$ becomes very small (Fig. 6). The intensity returned on cooling but with a hysteresis of $\sim$50 °C (Fig. 4). The only superstructure reflections found in the $a^*-b^*$ plane were those of the 6A superstructure. One such reflection, indexed as 650 for the superstructure (660, superstructure = 110, 1A structure), was followed above 945 °C in the heating cycle to find the upper stability limit of the superstructure. It tailed off at about the same temperature ($\sim$950–960 °C) that $I_{111}$ decreased to zero (Fig. 4), confirming that the high-temperature state ($T > \sim$950 °C) is indeed high kalsilite. These results are consistent with the single crystals having developed a two-phase assemblage, low kalsilite + high (P6$_3$mc) hexakalsilite, in the transition range, though they do not rule out P6$_3$ as the space group of hexakalsilite.

The evolution of $I_{111}$ and $I_{112}$ and the development of superstructure reflections in homogenized Ks$_{88}$ single crystals are illustrated in Figure 7. A steady state must have been achieved quickly at each temperature as no changes in intensity were detected as a function of time. The observed intensities were reproducible over two heating and cooling cycles. Up to $\sim$850 °C, the steady decline of $I_{111}$ and $I_{112}$ is entirely consistent with normal thermal vibrational effects. $I_{111}$ then decreased rapidly but continuously at the same time that $I_{12,10}$, from the 4A superstructure, increased. A hysteresis of $\sim$40 °C occurred on subsequent cooling. The 111 reflection was broad from the start and only broadened further at $\sim$900 °C (Fig. 8), when the reflection tailed off to its lowest intensity level. The data are entirely consistent with a
transition region of coexisting $P6_3$ kalsilite and $P6_3mc$ high tetrakalsilite. As temperature increased, the proportion of tetrakalsilite increased until no kalsilite remained.

**TEM observations**

Metamorphic $Ks_{100}$. New information on the analog phase KLiSO$_4$ (Bhakay-Tamhane et al. 1991; Rajagopal et al. 1991, and references therein) and the failure to find any significant peak splitting in X-ray diffraction patterns that might indicate orthorhombic distortions in pure kalsilite, prompted a thorough reexamination of the metamorphic $Ks_{100}$ sample. TEM observations were made on the second sample, provided by M. Santosh, which, as described by Capobianco and Carpenter (1989) for the sample used for powder diffraction, contained multiple lamellae parallel to (001) on a scale of a few hundred to a few thousand angstroms. Dark-field images using $hhl$, $l$ = odd reflections showed black and white contrast, with a proportion of the lamellae clearly not contributing to reflections that violate the $c$ glide of a $P6_3mc$ structure. The interpretation offered by Capobianco and Carpenter was that only one of the three possible sets of twins of a $Cmc2_1$ structure would have $hhl$, $l$ = odd absent in each $c^*-[110]^*$ section of the reciprocal lattice. An alternative hypothesis is that the lamellae represent an intergrowth of $P6_3$ and $P31c$ structures, sharing (001) and with the same unit cell. This would be consistent with the lack of splitting of $hk0$ reflections if the two phases have the same $a$ dimension and conforms almost exactly to the reported behavior of $P6_3$, KLiSO$_4$, on cooling below room temperature (Bhakay-Tamhane et al. 1991, and see discussion below).

To test the suggestion of a two-phase intergrowth, systematic dark-field experiments were conducted on ion-beam-thinned specimens, and the observed intensity distributions were compared with X-ray structure factors, $F_{hkl}$, for the two structures. $F_{hkl}$ Values were calculated for $P6_3$ kalsilite using the refined atomic coordinates given by Andou and Kawahara (1984). A hypothetical $P31c$ kalsilite structure was created by analogy with KLiSO$_4$, in which the atomic positions are almost identical in the asymmetric units of both $P6_3$, and $P31c$ phases (Bhakay-Tamhane et al. 1991). The $P6_3$ coordinates of Andou and Kawahara (1984) were taken directly to represent the asymmetric unit in the structure-factor calculations for $P31c$ kalsilite. Two types of merohedral twinning can occur (Bhakay-Tamhane et al. 1991). $P6_3$ (Laue class 6/m) twins are related to each other by reflection across a plane parallel to the $c$ axis such that the diffraction pattern from an area of crystal containing both twins has the $hkl$ reflection from twin 1 superimposed on the $khl$ reflection from twin 2 (and $khl$ from twin 1 superimposed on $hkl$ from twin 2). Because structure factors $F_{hkl}$ and $F_{khl}$ are not identical under $P6_3$ symmetry, the dark-field image obtained using a superimposed $hkl$ (twin 1) and $khl$ (twin 2) reflection should show the twins in contrast. Equivalently for the $P31c$ structure (Laue class 3m), $F_{hkl}$ is not related by symmetry to $F_{khl}$, and the $hkl$ reflection from twin 1 is superimposed on the $khl$ reflection of twin 2 ($khl$ of twin 1 is likewise superimposed on $hkl$ of twin 2). Dark-field images using a reflection of this form should therefore show the $P31c$ twins in contrast. These critical structure-factor relationships are evident in the selected values given in Table 3.

Figure 9 contains a $c^*-[110]^*$ section imaged with 111 (Fig. 9a) and 112 (Fig. 9b) reflections. The contrast between the two images is reversed: The darkest lamellae in one image are the lightest in the other. This is at least consistent with the calculated X-ray structure factors because there should be no intensity contribution to 111 from $P31c$ lamellae, and $I_{112}$ is expected to be greater from $P31c$ than $P6_3$ structures (Table 3). Two areas of

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**Figure 7.** (left) Integrated intensities of the 111 (open circles) and 112 (solid triangles) reflections during heating of homogenized $Ks_{86}$. (right) Integrated intensities of 111 reflection on heating (open circles) and cooling (solid circles), and of the superstructure reflection 12.10 for a cell with $a = 4A$, $c = C$, on heating (plus signs) and cooling (Xs).

**Figure 8.** Peak width at half-maximum height for the 111 reflection of $Ks_{86}$. 
FIGURE 9. Dark-field electron micrographs of metamorphic KsIO (all at the same scale). (a) Section approximately parallel to c*-[110]*, g = 111. Dark lamellae parallel to (001) are interpreted as having P31c symmetry. (b) Same area as a, g = 112. Lamellae interpreted as having the P31c structure in a are lightest (largest intensity contribution to 112), as expected from calculated Fhkl values (Table 3). Very weak contrast from P6 twins (e.g., the twin labeled A) is assumed to be anomalous and due to the fact that ideal two-beam conditions were not obtained. A characteristic pattern of beam damage is the development of relatively ragged twin boundaries, as most clearly seen at the topmost boundary. (c) Section approximately parallel to c*-[210]*, g = 211. The (001) lamellae show three shades of contrast. (d) Same area as c, g = 211. The lamellae indicated by arrows now show reverse contrast with respect to c and must correspond to the two possible P31c twins. (e) Same area as c and d, g = 210. The lightest areas (greatest diffraction contribution to 210) have P31c symmetry on the basis of the calculated structure factors. (f) Same area as c, d, and e, g = 113. The light areas have P6 symmetry, and the dark areas have P31c symmetry. An X indicates the same position on the sample in each micrograph.

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Figure 10. Variability of (001) lamellar textures in K$3_{100}$. (a) Section approximately parallel to c*-[310]*, $g = 310$. The light lamellae are interpreted as having $P31c$ symmetry, and boundaries between $P6_3$ twins can also be seen (arrows). (b) $g = 111$. Predominantly $P6_3$, with (001) twin boundaries and thin $P31c$ lamellae. (c) $g = 113$. Larger proportion of $P31c$ than in b. The blocky texture could be interpreted as evidence for a ledge mechanism for growth of one phase from the other. (d) $g = 210$. ~80% $P31c$. (e) $g = 221$. A ragged interface crosses the (001) lamellae, separating regions of predominantly $P6_3$ material (light) from $P31c$ material (dark). (f) $g = 211$. Lamellar spacings are so fine as to resemble (001) stacking faults and could account for the broadening of the 111 reflection shown in Figure 5a.

Figure 10a contains lamellae imaged with the 310 reflection. $I_{310}$ calculations indicate that $I_{310}$ could be significantly greater for the $P31c$ structure than for the $P6_3$ structure. Accordingly, the more intensely diffracting lamellae were expected to be $P31c$ kalsilite and to show only one shade of contrast. The less intensely diffracting regions actually contain two sets of lamellae with approximately the same weak contrast, corresponding to the two $P6_3$ twins. Other dark-field images support the same explanation in every case examined in any detail, namely that the K$3_{100}$ sample contains lamellae of two $P6_3$ twins intergrown with two $P31c$ twins. The proportion of $P6_3$ and $P31c$ phases varied widely even within a single crystal, from being more than ~90% $P6_3$ (Fig. 10b) to ~50:50 (Fig. 10c) to ~80% $P31c$ (Fig. 10d) and more than ~90% $P31c$ (Fig. 10e). In some cases the spacing of the twin lamellae was so fine as to resemble (001) stacking disorder (Fig. 10f). Although the lamellae tended to have parallel boundaries, some showed a characteristic blocky texture (Fig. 10c), such as might arise by ledge growth of one twin from another. In rare instances this was on a coarser scale with a broad stepped interface at a steep angle to (001), illustrated in Figure 10c. One dark-field image from an a*-b* section showed twin boundaries parallel to {100}. These were presumably the twin bound-
Some diffuse intensity was observed in overexposed electron diffraction patterns. This was not fully characterized in three dimensions, but it consisted of curved bands passing through the Bragg reflections in $a^* - c^*$ sections (Fig. 11a). It bears some resemblance to the distribution of diffuse intensity in $c^* - [110]^*$ sections of rapidly cooled natural nepheline crystals described by McConnell (1962) (and see Fig. 11e). Rather similar diffuse scattering was also observed in $c^* - [110]^*$ sections and included a component parallel to $[110]^*$.

The microstructures in metamorphic K$_3$Si$_2$O$_7$ crystals annealed for 1 h at 500 °C consisted of (001) twins on a scale comparable with that of the starting material. Separating the twins were either sharp twin boundaries or narrow lamellae, which were out of contrast in dark-field images formed with $hhl$, $l =$ odd reflections. The latter showed contrast in other dark-field images consistent with their being relict $P3_1c$ lamellae. Their width was typically less than ~500 Å, though one lamella ~900 Å wide was observed. Crystals annealed for 4 d at 500 °C contained $P6_3$ twins with no detectable $P3_1c$ lamellae. A reduction in the proportion of the $P3_1c$ phase at 500 °C is consistent with the powder and single-crystal diffraction data, which showed a steep decrease in $I_{110}$ and a steep increase in $I_{111}$ at temperatures of ~150–350 °C. Crystals annealed for 1 d at 950 °C contained (001) boundaries separating $P6_3$ twins on a scale of several hundreds of angstroms.

Preparation of the crystals for TEM involved heating them to ~130 °C. Given that the single-crystal X-ray study implied that structural changes might occur at a temperature as low as ~150 °C, it is possible that this treatment caused some change to the original microstruc-
ture of the natural sample. The experimental data suggest that any changes, if they did occur, would involve some small reduction in the proportion of the P31c phase present.

Mount Nyiragongo. Host kalsilite in the Mount Nyiragongo samples (75422 and 90049) contained twin lamellae parallel to (001), but the average spacing between twin boundaries was at least 5–10 μm. A small number of narrower twins were found, and these invariably showed the expected dark-field characteristics of P6₃ twins. For example, a narrow twin imaged with the 311 reflection and the boundaries of a twin in a different crystal imaged with 113 are shown in Figures 12a and 12b. In some cases the twin boundaries contained 90° steps between straight segments. In the section oriented approximately parallel to c*[110]* shown in Figure 12c, some of these steps are narrow and sharp, whereas others are broad and contain fringes. The thin boundaries could be parallel to (110), whereas the broader steps are clearly inclined at a steep angle to the section and are not inconsistent with the {100} orientation apparently favored in the metamorphic K₅SO₄ sample.

Electron diffraction patterns were indexed as the $\sqrt{3}A₃$ kalsilite superstructure first reported by Smith and Sahama (1957). Reflections indicating tripling of the unit cell along [110]* were diffuse (Figs. 11b and 11c). Their intensity appeared to vary between different crystals, but they were strong enough, in one case at least, to give a dark-field image containing small antiphase domains (APDs) on a scale of ~100 Å and elongate parallel to $c$ (Fig. 12d). Diffuse intensity was evident both along [110]* and as curved bands emanating from, or passing through, some of the main Bragg peaks in overexposed diffraction patterns. The curved bands were similar to the diffuse bands in pure kalsilite (compare Figs. 11a and 11b).

Coarse nepheline patches in these crystals, presumably corresponding to the nepheline regions optically visible in thin sections, were readily distinguished from kalsilite in bright-field images by their significantly higher density of dislocations. They also contained twin textures, though with quite different characteristic properties, as illustrated in Figure 13. In a*-b* sections a distinctive microstructure consisted of criss-crossing twin boundaries parallel to {100}; that defined triangular or diamond-shaped twin domains (Fig. 13a). The twin boundaries were not invariably linear, however, and they also showed evidence of interaction with dislocations (Fig. 13b). In sections containing c*, the domain boundaries tended to be aligned approximately parallel to c*, consistent with the {100} orientation inferred from a*-b* sections (e.g., Fig. 13c). Only one example of a strongly preferred orientation consistent with {001} has been found so far (Fig. 13d). A systematic analysis of the imaging conditions for these domains was not attempted, but contrast was observed in dark-field images using reflections such as 210, 211, 212, 311, and 213. The domains were out of contrast in dark-field images using 300, 201, and 021 reflections (indexed with respect to the normal 2A, P6₃, nepheline unit cell). The list of X-ray structure factors given for nepheline by Foreman and Peacor (1970) suggests that these contrast conditions are consistent with P6₃, twins that might have developed at a $P6₃mc \rightarrow P6₃$ transition. Doubling of the $a$ repeat of nepheline from a parent 1A structure could also result in the development of APDs related by displacement vectors $\frac{1}{2}a$, $\frac{1}{2}b$, and $\frac{1}{2}(a + b)$. If they are present, the antiphase boundaries (APBs) should be imaged in dark-field images formed with any reflection having $h = odd$ or $k = odd$. The microstructure in Figure 13e, imaged with a 211 reflection, contains an irregular, curved boundary transecting two twin boundaries but not influencing the contrast of the domains themselves. A similar looking lineation was observed in another area using 300. These features appeared to be rare and could also be understood as stacking faults generated by the passage of partial dislocations, rather than as transformation-induced APBs.

Exsolution lamellae with widths on a scale of ~1 μm (Fig. 13c) characteristically had interfaces approximately parallel to {001}. There is a substantial volume difference between nepheline and kalsilite, but these lamellae in general showed little evidence of coherency strains; the
FIGURE 13. Microstructures in nepheline exsolved from Mount Nyiragongo kalsilite. The scale bar indicates 0.5 μm in a–e. (a) Diamond-shaped twin domains with characteristic boundary orientations approximately parallel to (100) (75422; dark field). (b) (100) twin boundaries together with wavy twin boundaries, some of which terminate at or pass through dislocations (90049; bright field). (c) Within a single nepheline exsolution lamella, which has ~{(001)} interfaces with kalsilite, there are twin boundaries approximately parallel to (100) (75422; dark field, g = 211Ne). (d) ~{c}*{[310]}* section showing one straight twin boundary parallel to (001) together with curved boundaries (75422; dark field, g = 311Ne). (e) Most boundaries observed in dark field clearly separate twin domains. In rare instances, a boundary with no twin contrast was found, such as indicated by an arrow (75422; dark field, g = 211Ne). Note that this boundary crosses from one twin domain to another. (f) En echelon lozenges of exsolved nepheline in kalsilite, with interfaces generally following a (001) trend. The same type of contrast within the nepheline was observed in bright field and in dark field and is interpreted as indicating strain arising from a more or less coherent interface (75422; g = 212Ne).

interfaces are presumed to be incoherent. In the finest scale generation of exsolution, however, small en echelon lozenges of nepheline showed substantial strain contrast, consistent with a more or less regular array of dislocations at the interfaces (Fig. 13f). The interfaces of these lozenges are approximately parallel to (001) but are distinctly curved. Splitting of an original thin lamella into small segments could yield this texture, perhaps in response to a change in orientation of the lowest energy interface between the host kalsilite and exsolved nepheline during cooling.

Nepheline diffraction patterns all conformed to the expected reciprocal lattice of the 2A, $P6_3$ structure. Over-exposed diffraction patterns showed curved diffuse branches of the type reported by McConnell (1962) for volcanic nephelines, illustrated in Figure 11e from the Alban Hills sample. This diffuse intensity is also remarkably similar to that found in the kalsilite patterns (compare Figs. 11a, 11b, 11e).

The tetrakalsilite product of annealing kalsilite-nepheline intergrowths from sample no. 90049 for 1 d at 950 °C gave sharp 4A superstructure reflections in electron diffraction patterns. It also contained a domain texture that closely resembled the merohedral twinning microstructure in nepheline from specimen 75422. Tetrakalsilite in the heat-treated sample 75422 had $P6,m_c$ symmetry at 950 °C and $P6$, symmetry at room temperature. As argued for nepheline in the Mount Nyiragongo crystals, therefore, twinning in the 4A superstructure might have originated at a $P6,mc \rightarrow P6$, transition during cooling.

Alban Hills. Twin boundaries were even less frequently observed in the Alban Hills kalsilite than in the Mount Nyiragongo kalsilite. Only one boundary was imaged in
FIGURE 14. Microstructures in Alban Hills nepheline and kalsilite. (a) Zigzag boundary in kalsilite; segments of the boundary are rotated by ~120° and are consistent in orientation with approximately (100) (dark field, g = 011). (b) Polygonized texture in exsolved nepheline. Some of the individual subgrains contain straight boundaries consistent with (100) twins (bright field). (c) The tip of a thinner lamella of nepheline, which has irregular interfaces with kalsilite and is one subgrain wide (bright field). (d) α*-c* diffraction pattern from kalsilite enclosing a thin nepheline precipitate similar to that shown in c. In spite of the Ne-Ks interface being inclined at an angle of ~20° to (001), the two reciprocal lattices share common principal axes.

Exsolved nepheline in the Alban Hills crystals gave diffraction patterns characteristic of the 2A, P63 structure, with the diffuse intensity in curved bands typical of volcanic crystals (Fig. 11e). Diffraction patterns from the host kalsilite were consistent with the \( \sqrt{3}A, P63 \) structure, having relatively weak and diffuse \( \sqrt{3}A \) superstructure reflections (Fig. 11f). Annealing these crystals for 1 d at 950 °C caused the disappearance of nepheline by rehomogenization but did not markedly alter the apparent structural state of the kalsilite, as discerned from electron diffraction patterns. Only a very small number of \( P63 \) twin boundaries, parallel to (001) and containing jogs approximately consistent with {100}, were found in the annealed crystals.

IR spectroscopy

The IR spectra of homogenized Ks88 crystals, natural Ks100, and Ks100 after annealing at 500 °C for 1 h and 4 d are shown in Figure 15. The three Ks100 samples have different proportions of \( P63 \) and \( P31c \) material. After 4 d at 500 °C only the \( P63 \) phase remained, but its spectrum is almost indistinguishable from the spectra of two-phase intergrowths. On the other hand, there are two additional peaks in the spectrum of Ks88, at ~920 and ~970 cm\(^{-1}\), which are absent from the Ks100 spectra. The intensity of the peak at ~380 cm\(^{-1}\) is also different. Additional vibrational modes in this sample could be associated with its enlarged unit cell (\( \sqrt{3}A \times \sqrt{3}A \times C \)).

DISCUSSION

Structural variants

The \( nA \) superstructures. The multiple superstructures make an interesting set, with the repeat distance in the \( a-b \) plane increasing with increasing K+ content. Natural nepheline (~Ne75Ks25) has a basic 2A repeat and might
be thought of in this context as "dikalsilite." It has a
distortion that permits complete ordering of Na⁺ onto
small sites and K⁺ onto large sites, and, as discussed by
Merlino (1984), the chemistry of trikalsilite and tetrakal-
silite can be understood in analogous terms. The 6₄ superstructure represents the potassic end-member of this
sequence, but it has a much more restricted occurrence.
Indeed, it may develop only as an intergrowth sharing
(001) with 1₄, P₆₃ kalsilite because there is no possibility
of stabilization by alkali ordering.

High tetrakalsilite, with hhl, l = odd reflections absent
 presumptively thought to be P₆₃mc), was identified for the first time
in this study. It exists, apparently as an equilibrium state,
above ~930 °C at K₉₈₆, and above ~870 °C at ~1K₉₈₆.
Whether "hexakalsilite" has space group P₆₃ or P₆₃mc is
not yet certain, but, given that the multiple A superstructures appear to develop during heating only when the P₆₃,
structure becomes unstable, P₆₃mc seems more likely.

The \sqrt{3}A structure. In marked contrast with the multi-
ple A superstructures, extra reflections from the \sqrt{3}A
superstructure are diffuse, indicating relatively short-range
correlations. The extra reflections are discs with a larger
dimension in the a*-b* plane than perpendicular to it.
Within each crystal, APDs of the superstructure must be
columnar in shape, with their long axes normal to the
triadymite sheets (Fig. 12d). Smith and Sahama (1957)
reported that annealing natural Nyiragongo specimens
with this structure at 600 °C for 3 d caused the extra
reflections to disappear. Alkalis are certainly mobile in
nepheline and kalsilite at this temperature, and the change
could be associated with varying composition as much as
with a simple structural relaxation. In the present study,
all crystals with compositions in the range ~K₉₈₆~9.₅ gave
electron diffraction patterns containing these reflections,
including K₉₈₆ crystals that had been annealed at 950 °C.
Variations in the intensities of these reflections were found
between crystals, but it seems likely that, although the
most diffuse reflections might be overlooked in single-
crystal X-ray diffraction patterns, all crystals of kalsilite
containing 3–12 mol% Ne in solid solution have the \sqrt{3}A
structure at room temperature. The compositional range
could be wider.

The \sqrt{3}A superstructure is also found in crystals from
the (Na,K)GaSiO₄ and (Na,K)AlGeO₄ solid solutions
(Barbier and Fleet 1988; Barbier et al. 1993). Rietveld
refinement of a member of the Ga solid solution by Bar-
bier et al. (1993) confirmed that it is isostructural with
BaMSiO₄ (P₆₃), where M is Co, Zn, or Mg (Liu and Bar-
bier 1993). Apart from the larger unit cell, the primary
difference between the \sqrt{3}A, P₆₃ structure (Fig. 16a) and
the 1₄, P₆₃ structure (Fig. 16b) is that in the former the
apical O atoms linking successive tetrahedral sheets are
displaced off the threefold rotation axes in a fully ordered
array. A basic requirement for the stability of this struc-

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**Figure 16**. Kalsilite structures viewed down [001]; one unit cell is indicated in each case. (a) The \sqrt{3}A, P₆₃ structure, after Barbier et al. (1993), showing that the ordering scheme for apical O atoms involves rotations about the 6₁ axes located at the corners of the unit cell (atomic coordinates taken from Ga = Al substituted form). (b) The 1₄, P₆₃ structure, after Andou and Kawahara (1984). If the same rotatory ordering scheme of the apical O atoms about one 6₁ axis occurred, it would be compatible only with ordering in the opposite sense around the adjacent 6₂ axis. The 6₁ axis adjacent to both of these could not then have the same ordering as either. The system is frustrated, and, on average, has a disordered distribution of apical O atoms around the triad axis. (c) Hypothetical P3₁c structure for kalsilite, derived by adopting atomic coordinates from the asymmetric unit of the P₆₃ structure. Apical O atoms are probably disordered off the triad axes. Successive (001) layers have an eclipsed conformation, as opposed to the staggered conformation of the 1₄, P₆₃ structure.
ture in (Na,K) solid solutions containing combinations of Ga, Ge, and Si as the tetrahedral cations seems to be that there is some Na substitution for K away from the potassic end-member. The KGa and KGe phases do not even have a tridymite framework topology (Barbier and Fleet 1988; Barbier et al. 1993). The implication is, again, that a degree of Na-K ordering between two symmetrically distinct alkali sites may be required to stabilize the $\sqrt{3}A$ kalsilite form.

A parent tridymite structure for the $\sqrt{3}A$ structure may be MX-1, which has the same unit cell (Hoffmann et al. 1983; Carpenter and Wennemer 1985). Although some MX-1 tridymite is incommensurate (Hoffmann et al. 1983; Löns and Hoffmann 1987; Ashworth 1989), a commensurate form is also found (Withers et al. 1994), and the metric difference between the two is small. The same basic distortion may also occur at low temperatures in natural nepheline, though tripling of the unit cell along $[110]^*$ (of the 2A structure) is accompanied by an irrational repeat parallel to $c^*$ (Sahama 1958; McConnell 1962, 1981; Parker and McConnell 1971; Parker 1972; Merlino 1984). In nepheline the framework distortion is believed to be stabilized by K-vacancy ordering in the large cavity sites but is still restricted to a low-temperature stability field (Parker and McConnell 1971; Parker 1972; McConnell 1981, 1991). Other synthetic nepheline samples may have analogous distortions (Brown et al. 1972; Henderson and Roux 1977). A relationship with the dynamical properties of tridymite is also highlighted by the diffuse diffraction intensity from its high-temperature forms (e.g., Fig. 3a of Withers et al. 1994), which is very similar to the curved diffuse bands visible in Figure 11.

The P31c structure. This newly proposed structure occurs in end-member kalsilite from metamorphic rocks. Although a structure refinement has not yet been attempted, several strands of evidence support the suggestion that it is isostructural with the P31c phase of KLiSiO$_4$ described by Bansal et al. (1980), Zhang et al. (1988), Rajagopal et al. (1991), and Bhakay-Tamhane et al. (1985, 1991). Individual layers of this structure are essentially the same as those of the 1A, P6$_3$ structure but are stacked in an eclipsed manner, as illustrated in Figure 16c. Apical O atoms still have their average positions on threefold symmetry axes.

Systematic absences and the pattern of dark-field images showing (001) twins observed by transmission electron microscopy are not consistent with the $Cmc2_1$ pseudohexagonal structure suggested by Capobianco and Carpenter (1989), but they are entirely consistent with an intergrowth of P31c and P6$_3$ phases sharing (001) interfaces. Coexistence of these two structure types is characteristic of crystals of KLiSiO$_4$ held below their P6$_3$ = P31c transition temperature (Bhakay-Tamhane et al. 1985, 1991; Bhakay-Tamhane and Sequeira 1986; Perpétuo et al. 1992), whereas Sorge and Hempel (1986) and Klapper et al. (1987) have described the common occurrence of (001) twin boundaries in P6$_3$ crystals. Dollase and Freeborn (1977) also argued that (001) should be a low-energy interface between P6$_3$ twins in kalsilite. The same orientation of interface between trigonal and hexagonal structures might be favored because the apical O atoms would either match up perfectly or could accommodate slight misfits by tilting of the SiO$_4$ tetrahedra.

According to Mukhopadhyay et al. (1986, and see Bhakay-Tamhane et al. 1991), the intensities of reflections of the type hkl should be sensitive to the structural change P6$_3$ → P31c. Those with $l = e$ even would be expected to increase in intensity, whereas those with $l = o$ should go to zero (and see calculated structure factors for kalsilite in Table 3). This explains the irreversible increase in $I_{111}$ and decrease in $I_{112}$ observed when the metamorphic kalsilite is converted to the P6$_3$ structure by annealing at temperatures greater than a few hundred degrees Celsius. Some intensity at the 111 peak positions in X-ray powder patterns from the starting material can be explained by the presence of P6$_3$ material intergrown with the P31c phase. The two structures of KLiSiO$_4$ have essentially the same IR spectra (Varma et al. 1990), which also accounts for the initially surprising observation that changing the proportion of P6$_3$ and P31c kalsilite by annealing at 500 °C gives no change in the spectra of K$_{5}$Si$_{100}$O$_{200}$ (Fig. 15).

Finally, the P31c structure of KLiSiO$_4$ has a slightly larger unit-cell volume and c dimension than the P6$_3$ structure (Tomaszewski and Lukaszewicz 1983; Rajagopal et al. 1991). Annealing metamorphic K$_{5}$Si$_{100}$ above a few hundred degrees produces a small irreversible change in the same parameters, measured at room temperature (Fig. 3), with the hypothetical P31c kalsilite also having slightly larger $V$ and $c$ parameters than P6$_3$, kalsilite. High-angle reflections in a Guinier X-ray powder diffraction pattern of the natural K$_{5}$Si$_{100}$ were examined for evidence of an intergrowth of phases with different $c$ parameters. The 006 (20 = 64°) and 108 (20 = 93°) reflections showed a slight asymmetry, consistent with a preponderance of material having $c = 8.72$ Å coexisting with a lesser component having $c = 8.71$ Å. The 220 reflection (20 = 73°) had a symmetrical intensity distribution. Heaney (personal communication, and see Moore and Reynolds 1989) pointed out that severe stacking disorder, such as occurs in turbostructurally disordered clays, might also contribute to this asymmetry.

Twinning. Structure refinements of the hexagonal and trigonal phases of KLiSiO$_4$ have had to consider the presence of merohedral twinning (Schulz et al. 1985; Zhang et al. 1988; Chen and Wu 1989; Bhakay-Tamhane et al. 1984, 1985, 1991). Pairs of twins in P6$_3$ structures are related by the former mirror plane parallel to the $c$ axis in P6$_3$mc, as are pairs of twins in the P31c structure. If the twin boundaries and interphase boundaries are all parallel to (001), then some simple structural relationships result. For each structure, the sequence of tetrahedral layers follows the tridymite sequence ABABAB. Within a single layer the distortions from hexagonal to trigonal rings require that the triangles outlined by the tetrahedra all point in either one direction or in the opposite direction. These two senses of deformation can be
Figure 17. Schematic stability limits for different superstructures at the Ks-rich end of the Ne-Ks system. The solvis is from Figure 3 of Ferry and Blencoe (1978) (their version calculated on the basis of polybaric Margules equations); compositions of a Ne-Ks intergrowth annealed at 950°C (Xs joined by a dashed line) are consistent with this solvis. I-shaped bars indicate the transition regimes of coexisting high- and low-temperature structures at KS88 and KS100°C. The dotted lines represent a self-consistent view of the effect of temperature and composition on the kalsilite structure; their positions are either poorly constrained or unconstrained, and no attempt was made to show them in a thermodynamically correct topology. At Ks-rich compositions, the stable high-temperature polymorph is O1 kalsilite (Tuttle and Smith 1958), but this is not shown.

Stability relations

The new observations allow some updating of the stability relations for the Ks-rich side of the Ne-Ks system, following the work of Sahama (1957), Tuttle and Smith (1958), Ferry and Blencoe (1978), and Abbott (1984). The solvis shown in Figure 17 is the version calculated from the “polybaric Margules equations” by Ferry and Blencoe, which are constrained by a considerable amount of experimental data. Nepheline and kalsilite compositions in the sample of 75422 that equilibrated at 950°C match this solvis closely. Stability limits for the different structure types are much less well defined and are shown only schematically in Figure 17. The ideal high-temperature structure with Al-Si disorder would have P6\textsubscript{3}/mmc symmetry (Abbott 1984; Kawahara et al. 1987) but is not included here because of the expectation that a high degree of Al-Si order is retained up to the melting points of all the phases in the system.

Most strikingly, the structural relationships do not conform to the simple symmetry hierarchy discussed by Abbott (1984). The known high-temperature phases (ignoring nontridymite structures, such as O1-KAlSiO\textsubscript{4}) are 1A, P6\textsubscript{3}mc high kalsilite and the multiple 4A superstructures derived from this, which are shown speculatively to vary in energy, the boundaries would tend to be wider than only two layers and could be expected to persist as metastable defects for prolonged annealing times on either side of the P6\textsubscript{3} = P31c equilibrium transition temperature.

One further observation is consistent with the suggestion that the excess energy associated with these defects might be small. Dollase and Freeborn (1977) deduced that kalsilite crystals produced by ion exchange of K\textsuperscript{+} for Na\textsuperscript{+} in nepheline contained abundant (001) twins. Formation of 1A, P6\textsubscript{3}mc, kalsilite in this way requires not only the compositional change but also a change from eclipsed to staggered layers. A coherent and persistent structure seems to result even if full reorganization of the stacking sequences is not achieved. It would not be surprising to find some P31c layers in such crystals.

Merohedral twins are not generally expected to show strongly preferred boundary orientations because, by definition, they are not associated with any ferroelastic strain, as reviewed by Nord (1992). Structural arguments can be made to explain why (001) might be a particularly low-energy orientation in kalsilite and thus tend to cause alignment of the twin boundaries. Why \{100\} should also be a relatively low-energy orientation is not so obvious, though Dollase and Freeborn (1977) predicted that it might permit a minimal disturbance of the polyhedral connectivity. The merohedral twinning in nepheline exsolved from the Mount Nyiragongo kalsilite is much less regular. Most of the twin boundaries have no preferred orientation, but a low-energy interface is again evident parallel to \{100\}. The (001) orientation is almost certainly unfavorable because the apical O atoms of 2A, P6\textsubscript{3}mc twins would not match up across this plane.

described by adding a + or − superscript to the A and B labels, giving A\textsuperscript{+}, A\textsuperscript{−}, B\textsuperscript{+}, and B\textsuperscript{−} as the possible layer conformations. One twin of the P6\textsubscript{3} structure is then characterized by the stacking sequence A\textsuperscript{B−}A\textsuperscript{B+}A\textsuperscript{+}, whereas the second has A\textsuperscript{B−}A\textsuperscript{B+}A\textsuperscript{−}. In the P31c structure the ditrigonal prisms of every layer point in the same direction, giving sequences parallel to c of A\textsuperscript{B−}A\textsuperscript{B+}A\textsuperscript{+} and A\textsuperscript{B−}A\textsuperscript{B+}A\textsuperscript{−} for the two twin components. A (001) twin boundary in P6\textsubscript{3} would thus be at the vertical line in A\textsuperscript{B−}A\textsuperscript{B+} | A\textsuperscript{−}A\textsuperscript{−}A\textsuperscript{+} (or, equivalently, reversing all the signs), and in the P31c structure it would be at the vertical line in A\textsuperscript{B−}A\textsuperscript{B+} | A\textsuperscript{−}A\textsuperscript{−}A\textsuperscript{+}. On this schematic basis, the twin boundary in P6\textsubscript{3} is a unit of P31c structure, and the twin boundary in P31c is a unit of P6\textsubscript{3} structure. If the P31c and P6\textsubscript{3} structures have only slightly different free
with composition from nepheline (2A) to hexakalsilite (6A). Capobianco and Carpenter (1989) found coexisting 4A and 6A superstructure reflections in the single-crystal X-ray diffraction pattern of a crystal with composition ~Ks$_{95}$ held at a high temperature, suggesting that the stability range for the 6A structure is restricted to compositions with Ks > 95 mol%. The nepheline structure could provide a more extensive high-$T$ solid solution (Sahama 1957), but the 1A, $P6_{3}mc$ structure seems an equally likely candidate. Birefringence and thermal anomalies found by Sahama (1957) at ~1000 °C for a composition in the vicinity of Ks$_{95}$ perhaps indicate the lower temperature limit for this solid solution. In situ observations above 1000 °C are clearly needed.

At lower temperatures, 1A, $P6_{3}$ kalsilite has the largest stability field according to the relations suggested in Figure 17. It gives way to $P31c$ kalsilite in the pure end-member phase at some temperature below ~200 °C if the upper stability limit implied by the single-crystal data in Figure 4 is accepted. Under equilibrium conditions, any $\sqrt{3}A$, $P6_{3}$ stability field would have to be rather narrow but could extend metastably into the solvus. Its upper temperature limit has not yet been investigated, though, as discussed below, the break in slope found in the $c$ parameter of Ks$_{95}$ at ~500 °C is a tempting point to place a 1A, $P6_{3}$ = $\sqrt{3}A$, $P6_{3}$ transition.

**Phase transitions**

A summary of isochemical phase transitions that might occur in kalsilite is shown in Figure 18. The lack of a consistent supergroup $\rightarrow$ subgroup hierarchy down the sequences requires that some of the transitions must be first order in character, even though the basic tridymite framework is common to all the phases. Transitions of the type $nA$, $P6_{3}mc$ $\rightarrow$ 1A, $P6_{3}$, where $n$ = 2, 3, 4, 6, would involve a reduction in unit-cell size with falling temperature, for example, whereas the symmetry change $P6_{3}$ $\rightarrow$ $P31c$ involves space groups that are subgroups of equal order with respect to the supergroup $P6_{3}mc$. They are designated as type I in Figure 18 and must occur by means of nucleation and growth mechanisms. They appear to be characterized by substantial hysteresis effects, with large temperature intervals of two coexisting phases. Single crystals of kalsilite develop two-phase intergrowths at the high-temperature transitions (this study), while the same behavior is displayed at the $P6_{3}$ $\rightarrow$ $P31c$ transition in single crystals of KLiSO$_{4}$ (Bhakay-Tamhane et al. 1991; Perpétuo et al. 1992). Henderson and Taylor (1982) explained the coexistence of two isochemical phases over a significant temperature interval in the analogous systems BaAl$_{2}$O$_{4}$ and Sr$_{2}$AlO$_{4}$ by making a comparison with martenstic transitions. The apparent violation of the phase rule can be accounted for if strain acts as an additional degree of freedom.

A second set of transitions has supergroup $\rightarrow$ subgroup relationships, but each transition is required to be first order in character because of the existence of third-order invariants of the order parameter in their excess free energies. From the symmetry properties listed in the tables of Stokes and Hatch (1988) these include the 1A, $P6_{3}mc$ $\rightarrow$ $nA$, $P6_{3}mc$ and 1A, $P6_{3}$ $\rightarrow$ $\sqrt{3}A$, $P6_{3}$ transitions labeled type II in Fig. 18. Only the $nA$, $P6_{3}mc$ $\rightarrow$ $nA$, $P6_{3}$ transitions, where $n$ has the same value above and below the transition point, are not excluded by symmetry from being thermodynamically continuous (type III in Fig. 18). An example of the latter has not yet been observed but must occur in tetrakalsilite somewhere between ~950 °C, where it probably has $P6_{3}mc$ symmetry (this study), and room temperature, where it has $P6_{3}$ symmetry (Merlino et al. 1985). If the 1A, $P6_{3}mc$ $\rightarrow$ 1A, $P6_{3}$ transition in pure kalsilite, the “high” $\rightarrow$ “low” transition of Andou and Kawahara (1982) and Kawahara et al. (1987), occurred without the appearance of the intermediate 6A structure, it too could be thermodynamically continuous according to symmetry arguments alone.

With regard to the thermodynamic driving forces behind all these transitions, four processes have been considered: Al-Si ordering, Na-K ordering, displacements of basal O atoms, and displacements of the apical O atoms. All the available evidence (reviewed by Palmer 1994) is consistent with a high degree of Al-Si order being maintained up to the solvus of the Ne-Ks system. Other framework structures with 1:1 ratios of Al-Si tend to have high transition temperatures; in anorthite the extrapolated transition temperature is ~2000 °C, for example (Car-
Large ordering energies equate with high transition temperatures, and Al-Si disordering can probably be ruled out as having any significant influence on the thermal evolution of natural kalsilite.

The second possible driving mechanism is Na-K ordering. The trend of increasing values of \( n \) with increasing Ks content in the \( nA, P6_3/mc \) superstructures discussed earlier is presumably dictated by the need of the framework to accommodate cations that differ in ionic radius by \( \sim 30\% \). Transitions from \( 1A, P6_3/mc \) to \( nA, P6_3/mc \) structures could therefore be driven by Na-K ordering, but their transition temperatures are as yet unknown and might fall above the liquidus.

Transitions from \( P6_3/mc \) structures to \( P6_3 \) structures are driven primarily by ordering of basal O atoms between two sites in each (001) layer, which are displaced off the mirror planes parallel to c of the ideal \( 1A, P6_3/mc \) structure (Dollase and Freeborn 1977; Andou and Kawahara 1982; Kawahara et al. 1987). Different patterns of such displacements can largely account for the differences between low kalsilite, low trikalsilite, and low tetrakalsilite, for example. The fact that the \( 1A, P6_3 \) structure, which has only one distinct alkali site, becomes stable with respect to \( nA \) structures below \( \sim 900 \)°C, between \( K_{500} \) and \( K_{70} \), implies that the energy of the local O-atom ordering scheme in this structure outweighs the energy of Na-K ordering. Alkali ordering also cannot be responsible for driving the \( P6_3 = P31c \) transition in pure KAlSiO\(_4\). These staggered and eclipsed forms differ only in their basal O-atom ordering schemes, and some small energetic difference between the two ordered configurations could account for the transition. A valid analogy is almost certainly that of polytypic systems because they have such a strongly preferred interfacial orientation.

Ordering of the apical O atoms appears to occur at the low-temperature limits of the sequences in Figure 18. In a discussion of KLiSO\(_4\), Pimenta et al. (1989) pointed out that the O atoms that form the bases of tetrahedra in stuffed trihydrate phases lie within a densely packed plane, whereas those at the apices linking successive sheets are much less restricted. librational motions of the tetrahedra about axes parallel to c, which would give displacements of the basal O atoms between the ordering positions, should therefore be subject to larger restoring forces than motions about axes perpendicular to c, which would cause the apical O-atom displacements. Accordingly, the energies of the latter are expected to be relatively low, consistent with the low ordering temperatures. The \( 1A, P6_3 \) structure has apical O-atom disorder (Perrotta and Smith 1965; Dollase and Freeborn 1977; Andou and Kawahara 1984; KLiSO\(_4\): Karppinen et al. 1983; Bhakay-Tamhane et al. 1984, 1991; Schulz et al. 1985), but the \( \sqrt{3}A, P6_3 \) structure has complete order (Fig. 16a) (Babier et al. 1993; Liu and Babier 1993). The preferred ordering scheme involves the tilting of tetrahedra in a rotational fashion around the \( 6_3 \) axes (Fig. 16a). An equivalent scheme in the \( 1A, P6_3 \) structure is impossible because of a frustration effect: Rotatory ordering about one \( 6_3 \) axis requires rotatory ordering in exactly the opposite sense about the adjacent \( 6_3 \) axis. The \( 6_3 \) axis adjacent to both of the first two cannot then adopt the same scheme in either sense (Fig. 16b). Some additional process is required to break the translational symmetry, and a small proportion of Na substitution for K appears to allow this to occur. Triggering of the \( 1A, P6_3 = \sqrt{3}A, P6_3 \) transition thus seems to involve coupling of the apical O-atom displacements with some Na-K ordering.

In KLiSO\(_4\), the apical O-atom ordering causes a symmetry reduction from \( P6_3 \) to a monoclinic (pseudoorthorhombic) \( Cc \) structure (Bhakay-Tamhane and Sequeira 1986; Dantas et al. 1991; Rajagopal et al. 1991; Bhakay-Tamhane et al. 1991; Perpétuo et al. 1992). The ordering scheme has all apical O atoms within the same (001) plane displaced in a single direction rather than in a rotatory manner (Bhakay-Tamhane et al. 1991). The existence of an equivalent \( P31c = Cc \) transition might reasonably be predicted for pure kalsilite below room temperature. It must be first order because of the existence of third-order invariants, and it would be expected to show hysteresis and two-phase coexistences just as has been observed in KLiSO\(_4\) by Bhakay-Tamhane and Sequeira (1986), Bhakay-Tamhane et al. (1991), Rajagopal et al. (1991), and Perpétuo et al. (1992). An analogous transition in structures with staggered rather than eclipsed sequences of layers is the \( P6_3 = P2_1 \) transition observed in SrAl\(_2\)O\(_4\), which displays similar first-order behavior (Henderson and Taylor 1982). In the \( P2_1 \) structure, the apical O atoms in a single (001) plane are displaced in a zigzag manner about the b axis (Schulze and Müller-Buschbaum 1981).

The rigid-unit modes of ideal high-temperature trihydrate were recently calculated by Dove et al. (1996). They found lines of rigid-unit modes along \( a^* \) and along [110]*, including the special points \( 0,0,0 \), \( 1/3,1/3,0 \), and \( 1/3,0,0 \), and curved surfaces elsewhere in reciprocal space. Some of the kalsilite transitions could therefore conform to a rigid-unit-mode type of displacive mechanism. The close relationships with MX-1 trihydrate, Ge and Ga derivatives of Ne and Ks, and among patterns of diffuse scattering in trihydrate, nepheline, and kalsilite certainly point to a strong control by the underlying framework. However, purely displacive mechanisms ought to give more regular supergroup-subgroup symmetry hierarchies. Jumping from one structure type to another in a seemingly erratic manner is more characteristic of thermodynamic control by order-disorder phenomena. Competition between ordering processes could result in diverse structures stable only over restricted temperature and compositional intervals if the most favorable configuration for each of the separate Na-K, basal O-atom, and apical O-atom distributions is not entirely compatible with the most favorable configurations of the others. In other words, there are several possible couplings between individual displacive and order-disorder processes that lead
to different structures with only marginally different energies.

Al-O-Si bond angles

The source of driving energies for O-atom positional ordering can be understood in terms of Al-O-Si bond angles in stuffed tridymite framework topologies. In ideal, fully expanded tridymite, all T-O-T bond angles are 180°, where T is the tetrahedral cation. Within (001) sheets every pair of tetrahedra is in the trans configuration, and all pairs linking sheets are in the cis configuration (as reviewed most recently by Heaney 1994, for example). Numerous studies have demonstrated that framework structures with any degree of flexibility are unlikely ever to match this limiting case (e.g., Gibbs et al. 1981; Geislinger et al. 1983; Navrotsky et al. 1985; Liebau 1985; Lasaga and Gibbs 1987). Apparent 180° angles can only be due to averaging over different O-atom positions, but determination of the true atomic distributions is not straightforward. Some insights into how the average T-O-T angles vary with temperature are, however, provided by variations in the lattice parameters. Capobianco and Carpenter (1989) derived approximate geometrical dependencies for the Al-O-Si angle of tetrahedra linked within a sheet on the a lattice parameter, φa, and for the angle of tetrahedra forming the linkage between sheets on c, φc, with the mean Si-O and Al-O bond lengths specified as dSi and dAl. For 1A structures these are

$$\cos \phi_a = -\left[\frac{\frac{a^2}{3} + \frac{1}{9}(d_{Al} + d_{Si})^2 - d_{Al}^2 - d_{Si}^2}{2d_{Al}d_{Si}}\right]$$

$$\cos \phi_c = -\left[\frac{\frac{c^2}{4} - \frac{16}{9}(d_{Al}^2 + d_{Si}^2)}{\frac{32}{9}d_{Al}d_{Si}}\right]$$

[Note that the equation for φc given by Capobianco and Carpenter (1989) contains two typographical errors.] Values of φa and φc were calculated using the lattice-parameter data in Table 1 and values of dAl = 1.74, dSi = 1.61 Å from Perrotta and Smith (1965). The latter are also close to the average values for trikalsilite (Bonaccorsi et al. 1988) and tetrakalsilite (Merlino et al. 1985), but the precise choice of tetrahedral bond lengths does not influence the overall pattern of results displayed in Figures 19 and 20. At room temperature the a and c parameters of P63, Ks100 give φa = 143.5°, φc = 154.1° and an average Al-O-Si bond angle for the complete structure of 1/4(φc + 3φa) = 146.2°. This compares with 147°, estimated on the basis of the chemical shift for 27Al NMR spectra from crystals containing ~94% Ks and its correlation with Al-O-Si angle given by Hovis et al. (1992; their Figs. 6 and 8). The structure refinement of a natural kalsilite (also not with pure end-member composition) by Perrotta and Smith (1965) gave φa = 140, φc = 163° and an average of 146° (from Liebau 1985).

The results in Figure 19 show that the high-temperature P63mc structures have φa > φc (though the equations are strictly valid only for the 1A structure). A geometrical degeneracy, φa = φc, appears to coincide with the stability
limit with respect to the $1\perp A, P6_3$ phase. A second, much smaller anomaly occurs in the bond-angle data at $\sim 500^\circ$C for both $K_{S_{88}}$ and $K_{S_{100}}$. In $K_{S_{100}}$ it coincides with a change in the slope of $V$ as a function of temperature (Fig. 3c) and, perhaps, in the width of the 111 reflection (Fig. 6). A break in slope of the lattice parameters at $\sim 600^\circ$C was also found by Kawahara et al. (1987) for a synthetic kalsilite, whereas the data of Henderson and Taylor (1988) show a change in slope of $V$ at $\sim 450^\circ$C for a different synthetic sample. There is no evidence for a change in macroscopic symmetry at this point, however, and some local short-range effects, which remain to be identified, may be implicated. The anomaly at $\sim 500^\circ$C for $K_{S_{88}}$ is more distinct (Fig. 19) and is even more evident if $\phi_v$ is plotted against $\phi_a$ (Fig. 20). With falling temperature the intersheeting angle, $\phi_v$, increases antipathetically with the intrasheath angle, $\phi_a$, in an almost identical manner for both $K_{S_{88}}$ and $K_{S_{100}}$ down to $\sim 500^\circ$C. The data for $K_{S_{88}}$ then diverge markedly from this trend, and it is tempting to invoke the onset of the $1\perp A, P6_3 \rightarrow P31c$ transition. An additional degree of freedom due to the loss of translational symmetry perhaps permits not only the apical O-atom ordering but also a more coherent deformation mechanism for the framework, with both $\phi_a$ and $\phi_v$ decreasing with falling temperature.

Microstructural evolution

End-member kalsilite has only been found in metamorphic rocks. A crystallization temperature of $\sim 700$–$800^\circ$C for the Indian sample (Sandiford and Santosh 1991) would be below the $6A, P6_3mc$ (or $P6_3? = 1\perp A, P6_3$) transition temperature. Twins related by the mirror plane parallel to the $c$ axis in $P6_3mc$ would be incorporated only as growth defects, therefore, but if they did occur they would presumably adopt twin boundaries parallel to (001). During slow cooling, the transition $P6_3 \rightarrow P31c$ would have been initiated at some temperature below $\sim 200^\circ$C by a nucleation and growth mechanism. Any (001) twin boundaries already present should provide prime nucleation sites given their local resemblance to the $P31c$ structure. Growth fronts from these or from nuclei at grain boundaries might be expected to advance most easily in directions perpendicular to the $c$ axis, giving a polytypic layer-by-layer change from $P6_3$ to $P31c$. The sluggishness of this process appears to be such that, even on a metamorphic time scale, the transition did not go to completion, and the proposed $P6_3 \rightarrow P31c$ intergrowth was preserved as a kinetically stranded state. The absence of an equivalent microstructure in $K_{S_{88}}$ from sample 90049 is due either to the stability of the alternative $\sqrt{3}A, P6_3$ structure when a small amount of Na is present or to the relatively fast rate of cooling of this volcanic sample.

For crystals with compositions of $\sim K_{S_{88}}$, such as in the Alban Hills sample, crystallization between $\sim 930^\circ$C and at least $1060^\circ$C would cause the initial growth of high tetrakalsilite. The $4A, P6_3mc$ structure would then transform by nucleation and growth to $1\perp A, P6_3$ kalsilite on cooling below $\sim 890–930^\circ$C. $P6_3$ twins would be expected to develop at this stage, but there is no evidence that their boundaries could be stabilized by effects associated with a potential $P31c$ phase, as in $K_{S_{100}}$. The twins might coarsen rapidly, therefore, and twin boundaries are certainly rare in the final product. The onset of nepheline exsolution would be expected at $\sim 750–800^\circ$C (Fig. 17); the scale of exsolution in natural samples is too coarse to yield evidence of the initial mechanism [spinodal decomposition, homogeneous nucleation, etc., as discussed by Yund et al. (1972)]. Stress fields set up by the $\sim 5\%$ volume difference between nepheline as a component in solid solution and as a separate phase probably generated many dislocations. Whether recovery of these dislocations, or stresses associated with some change in the preferred orientation of Ne-Ks interfaces as a function of temperature, could yield the polygonized texture remains to be determined. At some early stage in the exsolution process, the nepheline lamellae would also have had to undergo a transition from $1\perp A, P6_3$ to $2A, P6_3$. The occasional linear defects imaged in dark field may be antiphase boundaries that developed at this stage, but they could also be stacking faults resulting from the passage of partial dislocations. Finally, the $K_{S}$-rich phase would have transformed from $1\perp A, P6_3$ to $\sqrt{3}A, P6_3$, perhaps near $\sim 500^\circ$C. The dimensions of individual domains of the new superstructure remained restricted.

Exsolution in bulk compositions nearer to $\sim K_{S_{88}}$ leaves a rather different microstructure. The onset of exsolution would have been at $\sim 975^\circ$C, within or above the twophase field of $1\perp A, P6_3 + 4A, P6_3mc$ phases (Fig. 17). There would still have been a significant volume change to accommodate, but the stresses could have been dispersed more evenly at the higher temperatures, such that the nepheline lamellae did not become polygonized. Stability relations for $2A, 3A$, and $4A$ superstructures at the top of the solvus have not yet been investigated, but it is possible that the first nepheline to equilibrate at high temperatures also had a $P6_3mc$ structure. On cooling the Ne limb of the solvus, this would have transformed, perhaps by means of a $2A, P6_3mc \rightarrow 2A, P6_3$ transition, to the normal nepheline structure. This transition would be expected to generate merohedral twins in much the same manner as discussed by Abbott (1984) for a hypothetical $1\perp A, P6_3mc \rightarrow 1\perp A, P6_3$ transition in kalsilite. The twinning observed in nepheline from sample numbers 75422 and 90049 is at least consistent with this interpretation, especially as similar twinning was observed in tetrakalsilite, which must have undergone a $4A, P6_3mc \rightarrow 4A, P6_3$ transition during cooling from $950^\circ$C.

In pyroxenes and feldspars a diversity of microstructures is related to the constraints of kinetics and cooling rates. In nepheline and kalsilite, Na = K diffusion is sufficiently rapid that optical-scale exsolution occurs even in volcanic samples, but variable microstructures can still be generated because so many different transition sequences are possible. In principle the microstructures should also provide information relating to the thermal
history of the host rock. Observations on samples from a greater diversity of compositions and geological environments should be revealing, both of the effects of thermal history and of other possible structural sequences or transition mechanisms.

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REFERENCES CITED

 Ferry, J.M., and Blencoe, J.G. (1978) Subsolidus phase relations in the nepheline-kalsilite system at 0.5, 2.0, and 5.0 kbar. American Mineralogist, 63, 1225–1240.
structure of high temperature form of kalsilite (KAlSiO₄) at 950 °C. Mineralogical Journal, 13, 260–270.


