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Defects and Short-range Order in Nepheline Group Minerals: a Silicon-29 Nuclear Magnetic Resonance Study

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Abstract. ^{29}Si magic-angle spinning *nuclear magnetic resonance* (NMR) spectra are presented for seven crystalline phases of the nepheline group: natural nephelines from a plutonic environment (Bancroft, Ontario) and a volcanic deposit (Mt. Somma, Italy), kalsilite, synthetic pure Na nepheline, carnegieite, and two samples of orthorhombic $KAlSiO_4$. In all phases, nearly all of the Si sites have four Al neighbors, indicating nearly complete Al-Si ordering. Excess Si over the 1:1 stoichiometric *Si/Al* ratio appears to substitute randomly for Al on an ordered lattice, adding Si sites with 3 and 0 Al neighbors in a 3:1 ratio. Various types of structural disorder, including Al-Si disorder, that are reported from some x-ray diffraction studies are probably long range in nature and are due to the presence of ordered domains.

In naturally occurring nepheline, the relative abundance of T sites with three-fold local symmetry is maintained at the ideal stoichiometric value of 1/4, even when the $K/(K+Na)$ ratio is substantially lower. This is in agreement with conclusions reached about the average structure from x-ray data. The distinction between the two sites, at least in terms of the local structure that is reflected in ^{29}Si NMR chemical shifts, is lost in a pure Na nepheline sample.

Introduction

Minerals close in composition to the $NaAlSiO_4-KAlSiO_4$ binary (the nepheline group) are common in silica-undersaturated igneous rocks such as syenites and phonolites and their metamorphic equivalents. Their synthetic analogs have also long been of interest to ceramists and materials scientists. The phases are all tectosilicates, and are made up of open, three dimensional frameworks of SiO_4 and AlO_4 tetrahedra, with Na, K, and Ca as interstitial charge-balancing cations. As for pure crystalline SiO_2, the minor energy differences between structures with slightly different Si–O–(Al,Si) bond angles (Gibbs et al. 1981) and the great topological variety of networks of corner-shared tetrahedra lead to an intriguing number of polymorphs related by either reconstructive or displacive phase transitions. Because of the complexity of these transitions, and the difficulty of characterizing aluminum-silicon ordering by x-ray techniques on often finegrained, highly twinned materials, the detailed crystal structures of some of the low-temperature, low-symmetry forms are not known exactly. It is therefore often difficult to interpret and apply thermochemical data for these materials, or to understand precisely the relationships between observed structure and thermal history in both nature and the laboratory. In one example of concern to the present authors, Stebbins et al. (1984) presented systematic relationships between the entropies of fusion of minerals and the field strengths of the non-framework cations. One potentially interesting comparison is between nepheline and anorthite, both tectosilicates with the same *Al/Si* ratio but different charge balancing cations. The comparison was uncertain because of the unknown structural state of the latter: either the two entropies were approximately equal (if nepheline is disordered at melting), contrary to the pattern seen in many other minerals, or the entropy of fusion for anorthite was significantly larger, as expected with its more highly charged cation.

Nuclear magnetic resonance (NMR) spectroscopy has recently been used to help understand tectosilicate mineral structures, especially of zeolites and feldspars (e.g. Putnis and Angel (1985); Kirkpatrick et al. 1985; Fyfe et al. 1983; Vega 1983; Lippmaa et al. 1980 and 1981). The technique is a good complement to x-ray diffraction, as it is sensitive primarily to local electronic environments instead of long-range geometry. Direct structural information can therefore be obtained independently of the averaging effects of disorder and pseudosymmetry. Separate NMR spectra can also be measured for isotopes of many of the major constituents of silicates, such as ^{23}Na, ^{27}Al, ^{17}O, and ^{29}Si.

It is not yet possible, however, to rigorously calculate the NMR spectra of solids of known structure and composition. This results from the complex shielding effect of chemical bonding and electronic configurations on the local magnetic fields experienced by nuclear spins. Progress in the theoretical prediction of NMR chemical shifts is being made (Tossell 1984; Tossell and Lazzareti 1985; Englehardt and Radeglia 1984), but interpretation of spectra is still largely limited to (sometimes precise) empirical correlations and (generally qualitative) simple, general information about the influences of structure.

In spite of this problem, ^{29}Si NMR has been of great value in mineralogy. In particular, the technique of magic angle spinning (MAS) NMR has been used to obtained high-resolution spectra of solids: the broadening effect of the anisotropic part of the chemical shielding tensor is removed by rapid rotation at the "magic" angle (54.7°) with respect to the magnetic field (Andrew 1981). Because the spin-1/2 ^{29}Si nucleus is spherical, there are no complications caused by nuclear quadrupole coupling to electronic field gradients. The resulting spectra are relatively straightforward to interpret from empirical relationships. The isotropic ^{29}Si chemical shift δ (the relative shift in resonant frequency from that of a reference compound, typically tetramethylsilane) is very sensitive to the local chemical environment of the Si atom. The value of δ has been shown to depend on several interrelated structural variables, which include the average Si–O–(Al,Si) bond angle around an Si, the mean bond strength around the cation, the average distance to neighboring tetrahedral cations, the number of surrounding oxygens bound to other tetrahedral units (i.e. the extent of polymerization of the anionic structure), and the number of those tetrahedral neighbors that are AlO_4 instead of SiO_4 groups (Smith and Blackwell 1983; Ramdas and Klinowski 1984; Mägi et al. 1984; Smith et al. 1983; Grimmer and Radeglia 1984; Lippmaa 1980). The latter relationship has played a major role in the determination of the Si–Al ordering and site distribution in complex zeolite structures (e.g. Fyfe et al. 1982, 1983), information that could probably be obtained in no other way.

It must be emphasized that Al–Si distributions determined by ^{29}Si NMR are related to the local structure that affects individual Si sites. This may be quite different from the long range, average structure observed by x-ray diffraction. In particular, it is possible (and perhaps even common) for a crystal structure to be made up of small domains, each of which has a high degree of short-range order. If the ordering sequence of these domains varies through a crystal, however, the material may exhibit little or no long-range order. Short range order can have major effects on thermodynamic properties: McConnell (1985) has pointed out that the entropy changes of many order-disorder phase transitions are often only half that expected from complete disorder, because of short-range effects. In the case of a tectosilicate with $Si/Al=1$, for example, a crystal with an unconstrained random arrangement of Si and Al atoms will contain many Al–O–Al bonds, and may behave thermodynamically quite differently from a phase with ordered domains. Domain boundaries themselves may make an important contribution to the energetic differences between a phase with short range order only and one with long range order.

The nepheline family of minerals is well studied, and structures of some have been reviewed in detail by several authors, including Buerger (1954), Smith and Tuttle (1957), Merlino (1984), and Abbott (1984). They may be described most easily by comparing them to topologically similar structures of various polymorphs of SiO_2. Tridymite, for example, has an open framework consisting of layers of rings made up of six SiO_4 tetrahedra, with successive layers arranged to give at least topological hexagonal symmetry. Cristobalite is similar, except that successive layers are rotated 60°, giving overall cubic symmetry. "Stuffed" derivatives such as the nepheline minerals can be made by replacing silicons with aluminum atoms and adding charge balancing cations in the large interstitial sites in the framework. In the natural members in this group, the Si/Al ratio is generally close to 1, although some solid solution away from ideal stoichiometry occurs.

Most compositions have multiple polymorphs, related by two types of phase transitions. First order transitions, which involve T–O–T bond breaking and reconstruction of the framework, are slow, and the high temperature or high pressure phases can be quenched. Higher order transitions, which involve only bond bending and minor displacive shifts that lead to symmetry changes, are rapid, and high temperature phases are generally unquenchable. Many nepheline group minerals also undergo displacive transitions that during cooling produce low temperature structures with relatively low symmetry and complications such as multiple twinning. Unfortunately, the fine grain size of some of these materials makes single-crystal x-ray studies impossible. In these cases, heat capacity and phase transition data such as those reported by Lange et al. (1986) on the samples studied here can be a very important part of sample characterization.

Various types of disorder occur in nepheline group minerals. In both kalsilite and nepheline, the oxygen atoms whose mean positions are on the trigonal axis (O_1) appear to actually be distributed among three sites slightly displaced from the axis (e.g. Hahn and Buerger 1955; Perotta and Smith 1965). The positions of at least some of the other atoms in the structure are probably coupled to that of O_1 as well, as the tetrahedra rotate more-or-less as units away from ideal symmetry (Simmons and Peacor 1972). Relatively large uncertainties in all atomic positions are therefore common in x-ray structure refinements. Occupancies of the three O_1 positions, and presumably the three sets of tetrahedral orientations, are randomly mixed on a small but unknown scale, even in untwinned single crystals.

McConnell (1962) and other workers have suggested that nepheline and related minerals are made up of domains with ordered O_1 atoms. A number of different types of boundaries between such domains are possible. If they are abundant enough, some of these should be directly detectable by ^{29}Si NMR.

Despite these complicated details, the overall structures of the nepheline family minerals are particularly simple, usually with small unit cells containing small numbers of symmetrically distinct atoms. Determination of some of the details of short range order and domain structure in these materials is thus more feasible than for more complex structures. Our goal in this study has therefore been to use ^{29}Si NMR to better characterize a number of both natural and synthetic nepheline family minerals, in particular to determine the number of Si sites that have distinct chemical shifts, the nature of the Si–Al order in the minerals, and the validity of the "aluminum avoidance" principle (Lowenstein 1954) in an important group of tectosilicates. In addition, we have attempted to derive as complete a picture as possible of the Al–Si distribution in the minerals, including the effects of defects and domain boundaries.

The compositions of the minerals studied are listed in Table 1. NMR spectra were recorded at room temperature for synthetic kalsilite (the low temperature, hexagonal form of $KAlSiO_4$), natural nephelines from plutonic and volcanic origins, carnegieite (the high temperature form of $NaAlSiO_4$), a synthetic nepheline of the same composition, and two different samples of $O_1-KAlSiO_4$ (the highest temperature form of this composition). Standard NMR nomenclature for speciation will be used throughout: $Q^n(kAl)$ refers to a tetrahedral ("quaternary", i.e., bound to four oxygens) silicon atom surrounded by n oxygens ($0 \leq n \leq 4$) shared by other tetrahedra, k of which are AlO_4 groups. ($n=4$ in all phases described here.) The displacive phase transitions of many of the materials described here were studied by calorimetry and are described by Lange et al. 1986).

Table 1. Electron microprobe analyses of nepheline group samples, in weight percent. Uncertainty in last digit(s) is shown in parentheses

	1 Carnegieite	2 Nepheline (plutonic)	3 Nepheline (volcanic)	4 Nepheline + carnegieite	5 Kalsilite	6 $O_1-KAlSiO_4$	7 $O_1-KAlSiO_4$
Na_2O	21.6 (3)	16.4 (3)	15.5 (2)	21.6 (2)	0.4 (1)	0.5 (1)	0.13 (1)
K_2O	0	6.5 (6)	4.9 (3)	0	28.5 (2)	26.0 (1.6)	28.5 (4)
CaO	0.03 (1)	0	2.1 (1)	0.02 (1)	0	0	0
Al_2O_3	36.1 (7)	33.9 (4)	34.1 (2)	36.5 (8)	31.6 (9)	32.1 (1.1)	32.0 (9)
SiO_2	42.1 (9)	42.9 (7)	42.9 (2)	41.6 (6)	39.3 (9)	40.6 (1.2)	38.8 (9)
Total	99.8	99.7	99.5	99.7	99.8	99.2	99.4
Si/Al (probe)	0.99 (3)	1.07 (2)	1.07 (1)	0.97 (3)	1.06 (4)	1.07 (4)	1.03 (4)
Si/Al (NMR)	1.00 (4)	1.11 (4)	1.09 (4)	1.02 (4)	1.06 (4)	1.07 (4)	1.02 (4)

Columns: 1. Synthetic, from glass; 2. Natural, Bancroft, Ontario; 3. Natural, Mt. Somma, Italy; 4. Synthetic, from same glass as (1); 5. Derived from (2) by ion exchange; 6. Derived from (5) by heat treatment; 7. Sintered oxides

Sample Preparation and Characterization

The volcanic nepheline studied here was separated from a rock containing primarily sanidine, alkali amphibole, and vesuvianite, in coarse, well formed crystals 0.2–0.8 cm in size (Smithsonian collection number NMNH R10014-1). The nepheline itself is colorless, clear, and in well-formed, occasionally euhedral crystals 0.1–0.3 mm across. The starting material for several samples was a natural nepheline from Bancroft, Ontario (University of California, Berkeley, Department of Geology and Geophysics, collection number 16616). Both natural samples were examined optically, by powder x-ray diffraction and electron microprobe. Neither was found to contain any other phases. Kalsilite was prepared from the Bancroft nepheline by ion exchange in molten KBr for 3 days at 1,033 K, followed by washing and drying at the same temperature for 4 hours. Powder x-ray diffraction (XRD) and electron microprobe analysis (Table 1) confirmed that the phase produced was the hexagonal, pure K end member described by Smith and Tuttle (1957). Microprobe data indicate that both the original nepheline and the kalsilite produced from it have a slight excess of Si over Al.

The "O_1" $KAlSiO_4$ phase (Smith and Tuttle 1957) was synthesized by repeatedly sintering and grinding SiO_2, Al_2O_3, and K_2CO_3 at 1,720 K for 4 days. The XRD pattern of the product is essentially identical to that reported by these authors, and to the high temperature orthorhombic phase reported by Cook et al. 1977. The material produced was slightly rich in SiO_2. Its heat capacity and phase transitions were described by Lange et al. 1986 (sample "O1" in that report). Two reversible, rapid, presumably displacive transitions were observed, at about 695 K and 817 K. A portion of the K-exchanged nepheline was heated for 48 hours at 1,770 K to produce another sample of the phase. Microprobe data show that the bulk of the sample (as shown in Table 1) retained the *Si/Al* ratio of the starting nepheline, but that a few grains of leucite (5%) were also formed. Its XRD pattern and microprobe analysis are similar to that of the sample synthesized from oxides, except that small extra reflections are present at d-spacings of 0.850, 0.603, 0.539, and 0.518 nm. (These do not seem to correspond to any known phase and may be related to some kind of superstructure).

Carnegieite was produced by crystallizing a glass of $NaAlSiO_4$ composition for 3 days at 1,670 K. Its XRD pattern was essentially identical to that published by Smith and Tuttle (1957). On heating in a differential scanning calorimeter (DSC), this material showed a sharp, endothermic, reversible, energetic (8 kJ/mol) phase transition with a heat capacity peak at 966 K. (See Lange et al. 1986; a shoulder is also present at 957 K, indicating a two-step transition.) This transition temperature and heat effect are in remarkably good agreement with those of the α-β transition at 963 K (9 kJ/mol) detected by differential thermal analysis by Bowen and Greig (1925).

Synthetic sodium nepheline was prepared by crystallizing the same glass for 5 days at 1,370 K, well below the nepheline-carnegieite phase transition reported by Tuttle and Smith (1958). This material was also investigated by DSC, and showed a small transition at about 950 K, indicating that about $25 \pm 5\%$ carnegieite was present (presumably metastably). An endothermic transition was also observed at 464 K, and a very small peak was seen at 398 K. This pattern of low-temperature phase changes is similar to that reported for "B-type", pure $NaAlSiO_4$ nephelines by Henderson and Thompson (1980). The XRD pattern is also similar to those of Henderson and Roux (1977) for "B-type" nepheline. As reported by these authors, extra peaks (relative to hexagonal nepheline) are present at 22.6, 28.2, and 30.2°2θ, and the 002, 210, and 300 peaks (21.28, 27.29, and 31.00°2θ) are split or broadened. The effects on at least the 002 and 300 peaks could well be due to the presence of carnegieite, however. Henderson and Thompson (1980) did suggest that nepheline-carnegieite "mixed phases" could occur that are analogous to the tridymite-cristobalite "mixed phases" observed by Thompson and Wennemer (1979).

NMR Technique and Data Reduction

All NMR spectra were recorded with a "home-built" Fourier transform spectrometer with an 8.5 Tesla superconducting magnet. Powdered samples were packed in alumina rotors and spun at roughly 3 kHz in a magic-angle spinning probe manufactured by Doty Scientific. Spinning sidebands in the resulting spectra were small or non-existent, except for the Mt. Somma nepheline sample, where they could be clearly related to one of the main central peaks.

From 60 to 2,000 free induction decays were averaged together for each reported spectrum, using an rf pulse tip angle of roughly 45°. Delays of 20–90 seconds between successive pulses were chosen to minimize saturation effects resulting from incomplete spin-lattice (T_1) relaxation. A measurement of T_1 was attempted for the Bancroft nepheline sample only. Data could not be characterized by a single exponential, but the time required for the return of magnetization to 95 percent of its equilibrium value following a 90° pulse was approximately 3 seconds.

Silicon chemical shifts were measured relative to an external sample of tetramethylsilane (TMS). More negative values of δ correspond to greater shielding of the ^{29}S nucleus from the applied magnetic field.

Spectra were analysed using a modification of a Raman peak-fitting program (Mysen et al. 1982) based on the Argonne National Laboratory spectral deconvolution subroutine VA02A. No constraints were introduced in the fitting process: peak position, width, and height all were varied to minimize residuals. Gaussian lineshapes were chosen on the assumption that the relatively great breadth of the lines in these samples is the result of a statistical distribution of some structural variable that affects the chemical shift. The number of peaks for a given fit was selected as the number of obvious spectral features, such as clearly resolved peaks and shoulders. Mathematical stability was confirmed by experimenting with varying initial guess inputs to the fitting program. (For example, different initial values in a two peak fit of the carnegieite spectrum, Figure 4, produced relative peak areas that differed by 50 percent. Therefore we chose to describe the spectrum as a single peak, even though it is clearly non-Gaussian in shape.)

Results and Interpretation of NMR Spectra

General considerations and results for naturally occurring nepheline

Nepheline (*sensu stricto*) is a common mineral of both plutonic and volcanic igneous rocks which are silica undersaturated, and generally has a composition that is close to stoichiometric $Na_{.75}K_{.25}AlSiO_4$. The detailed structure was first described by Hahn and Buerger (1955). Na and K cations are ordered, producing a systematic distortion of the framework. Two types of tetrahedral sites can thus be distinguished: a "general" site with two Na and one K nearest neighbor ("T_G") and a "special" site (along a threefold axis, "T_S") with three Na neighbors. The trigonal rings of the high tridymite structure collapse to less symmetric rings around the sodium cations, but retain higher symmetry around the potassiums. Overall hexagonal symmetry ($P6_3$) is retained down to room temperature. No displacive phase transitions are observed.

The degree of Al–Si ordering in nepheline has been estimated in a number of studies, using typical differences between Al–O and Si–O bond lengths and observed average cation positions. Several authors have concluded that substantial disorder is possible, and that such disorder is greater in minerals formed at higher temperature (for example, Dollase and Peacor 1971). Sahama (1962) suggested that variations in Al–Si ordering could be the cause of an observed systematic relationship between optical properties, thermal expansions, and mode of occurrence (plutonic or volcanic) for nephelines. If local disorder occurs, then a substantial number of Al–O–Al bonds is implied. However, Gregorkiewitz (1984) reported that a nepheline synthesized at 1,270 K was as ordered as a highly ordered natural nepheline of low temperature origin. He concluded that earlier structure refinements could be subject to errors related to the uncertainty in the position of O_1 and that all nephelines are probably Si–Al ordered. This view was also adopted by Merlino (1984).

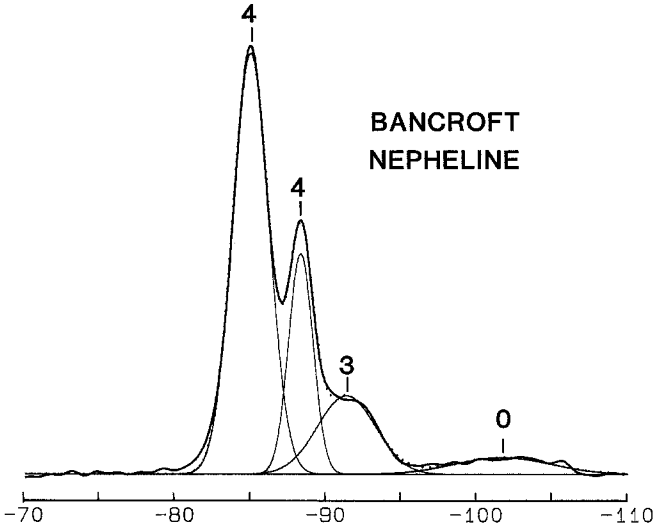

Fig. 1. ^{29}Si NMR spectrum for a natural plutonic nepheline from Bancroft, Ontario. Chemical shift is in ppm relative to TMS. The heavy solid line shows the experimental data, the dotted line is the simulated spectrum, and the thin solid lines are the individual Gaussian peaks used in the simulation. The numbers above the peaks refer to the number of nearest neighbor AlO_4 tetrahedra surrounding each silicon species

The nepheline from Bancroft, Ontario, is of relatively low temperature origin and thus should be well ordered. Its ^{29}Si spectrum is fairly simple, and, as shown in Figure 1 and Table 2, consists of four well defined peaks. By comparison with the spectrum of kalsilite derived from this sample by ion exchange (and thus presumably having the same framework ordering), we have assigned these to the two distinct framework sites with 4 Al neighbors, to a third type of site with 3 Al neighbors, and a fourth site which probably has no Al neighbors. The last assignment is less certain than the first three, but is most consistent with compositional data and models of excess Si substitution described below. These are slightly different interpretations from those of Murdoch et al. 1985 and of Lippmaa et al. 1980.

Fyfe et al. (1983) and others have shown that if no Al–O–Al bonds are present in an aluminosilicate framework structure, the *Si*/*Al* ratio (R) can be calculated exactly from the relative areas of the peaks in a ^{29}Si NMR spectrum. Applying their technique to our results for the Bancroft nepheline, we obtain $R = 1.11$, in good agreement with electron microprobe data (Table 1). This consistency suggests both that the assignments for the major peaks are correct, and that few, if any Al–O–Al linkages are present. Short range Al–Si order therefore predominates in the structure.

The Q^4(0Al) and Q^4(3Al) peaks are thus probably due to the presence of Si in excess of that for stoichiometric nepheline. One proposed location for the excess Si in the nepheline structure is along boundaries between domains

Table 2. Descriptions of NMR spectra of nepheline group minerals. Peak parameters, except those for carnegieite, are based on Gaussian deconvolutions. See text and Table 1 for detailed sample descriptions.

Material	Peak position, (ppm ± 0.2)	Relative area, (% ± 4)	FWHM, (ppm ± 0.5)	No. of Al neighbors
Carnegieite[a]	−82.2	100	2.9	4
Nepheline (plutonic)	−85.1	57	2.8	4
	−88.4	20	1.9	4
	−91.4	17	4.6	3
	−101.8	6	7.6	0 (?)
Nepheline (volcanic)	−85.1	66[b]	3.5	4
	−87.8	16	2.0	4
	−91.1	13	4.3	3
	−102.0	5	7.0	0 (?)
Nepheline plus carnegieite	−82.4[c]	28	3.2	4
	−86.0	63	4.6	4
	−90.1	9	5.8	3
Kalsilite[d]	−88.8	78	2.1	4
	−94.0	22	4.4	3
$O_1-KAlSiO_4$ (from kalsilite)	−85.6	54	4.2	4
	−88.8	26	2.7	4
	−92.0	15	4.1	3
	−97.0	5	4.9	2 (?)
$O_1-KAlSiO_4$ (sintered oxides)	−84.9	36	3.3	4
	−88.5	55	3.8	4
	−93.9	9	4.0	3

[a] Peak is obviously asymmetric towards less negative chemical shifts, and is therefore not completely fitted by the gaussian shown in Figure 1.

[b] Peak area includes two spinning sidebands.

[c] Peak due to intergrown carnegieite.

[d] Some area (2–3% of total) in "tails" on both sides of main peak is not fitted by the 2 gaussians shown in Figure 5.

with different O_1 orientations or with opposite Si−Al ordering schemes (Stebbins et al. 1985). For example, Al−Si ordering could be reversed at a stacking fault perpendicular to the c-axis. If such a defect created Si−O−Si bonds, the silicons on both sides become Q^4(3Al) sites. When the boundary is in the opposite sense, with excess Si atoms included to eliminate Al−O−Al bonds, Q^4(1Al) sites are generated. Pairs of such boundaries produce the two site types in a 1:1 ratio, quite different from what is observed in the NMR spectrum. Substitution of Si along other types of boundaries (e.g., parallel or perpendicular to the a-axis) produces similar mismatches. We therefore conclude that ordered substitution of excess Si along domain boundaries is not important in this mineral.

Vega (1983) presented a model of the distribution of Al and Si in tectosilicates which fit ^{29}Si results for several zeolites very well. In this model, the distribution of cations is random except for the constraints of Lowenstein's rule (no Al−O−Al bonds) and Dempsey's rule (minimizing the number of Al−O−Si−O−Al linkages, Dempsey et al. 1969). However, this does not produce a good description of the nepheline spectrum (relative intensities of peaks for Si with 4, 3, 2, 1, and 0 Al neighbors in this model are roughly 0.80, 0.08, 0.08, 0.04, 0). A model with no constraints at all on Si−Al distribution gives the corresponding relative abundances of 0.51, 0.23, 0.37, 0.27 and 0.08, again grossly different from the observed spectrum. An excellent match is obtained, however, if the structure is modeled as a perfectly ordered framework in which a few Al atoms have been removed and replaced by Si atoms. A single, isolated replacement of this type produces a single Q^4(0Al) site surrounded by three Q^4(3Al) sites. Randomly arranged replacements (modeled on a 40 × 40 grid of initially ordered tetrahedral cations) sufficient in number to give $R = 1.1$ produce a distribution essentially identical to that observed, with relative abundances of Q^4(4Al) at 0.77, of Q^4(3Al) at 0.18, of Q^4(2Al) at 0.01, and Q^4(0Al) at 0.05. (Presumably, the small Q^4(2Al) signal is lost in the noise).

The two Q^4(4Al) peaks in the nepheline NMR spectrum are almost certainly correlated with the two crystallographic T sites in the mineral, corresponding to the T_G site (−85.1 ppm), and the T_S site (−88.4 ppm). The ratio $K/(K+Na)$ in our sample, 0.21, is well below the ideal stoichiometry of 0.25, as is commonly observed in natural samples. Several authors (e.g. Gregorkiewitz 1984) have reported that the nepheline structure is not greatly deformed by potassium deficiencies even larger than this, and thus that the low-symmetry T_G sites retain low symmetry even when some have three Na cations neighbors. The ratio $T_S/(T_G + T_S)$ of 0.26 determined from the NMR spectrum is very close to that for the ideal structure, confirming that these conclusions apply at the local level, as well as on the average. In our model of random substitution of Si for Al in an ordered structure, two peaks for the Q^4(3Al) and Q^4(0Al) species might also be expected, but are apparently not resolvable.

Several authors have published correlations between ^{29}Si NMR chemical shifts and various parameters describing local bonding arrangement (see introduction). The contribution of Ramdas and Klinowsky (1984) is the most complete compilation for tectosilicate minerals, and is based upon both the number of Al neighbors at an Si site, and the mean of the four distances from the adjacent tetrahedral cations to the Si. From structural data on a plutonic nepheline (similar to the sample studied here by NMR) of Dollase (1970), mean tetrahedral-tetrahedral distances around the Si sites can be calculated as 0.3177 nm for T_S and 0.3130 nm for T_G, assuming uncorrelated motion. The relationship presented by Ramdas and Klinowski (1984) predicts chemical shift values of −83.7 and −79.8 for the two sites. The relative positions are close to those observed, but a discrepancy of 5–6 ppm is present for the absolute values of δ for the two Q^4(4Al) sites. A discrepancy of the same size and direction as that for nepheline also exists between the chemical shift values predicted from the structure of anorthite (Wainwright and Starkey 1971) and those observed by Murdoch et al. (1985) and Kirkpatrick et al. (1985).

The chemical shift of the peak which we have assigned to Q^4(0Al) in nepheline is near the extreme deshielded (low absolute value) limit of values for such sites in compilations of data for tectosilicates such as that of Thomas et al. (1983). This could be due to unusually long Si−O−Si bonds around the defect site, which would result if the structure was unable to deform to completely compensate for Si−Al substitution. This apparent lack of response of the framework geometry to small variations in the Si/Al ratio might thus the analogous to the lack of deformation on substitution of K for Na.

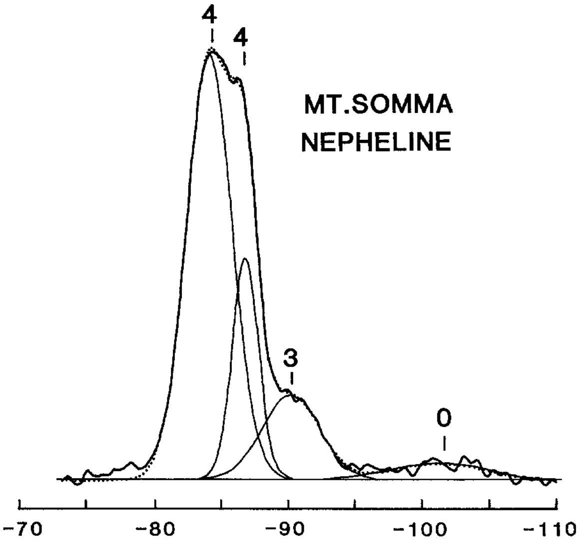

Fig. 2. ^{29}Si NMR spectrum for a natural volcanic nepheline from Mt. Somma, Italy

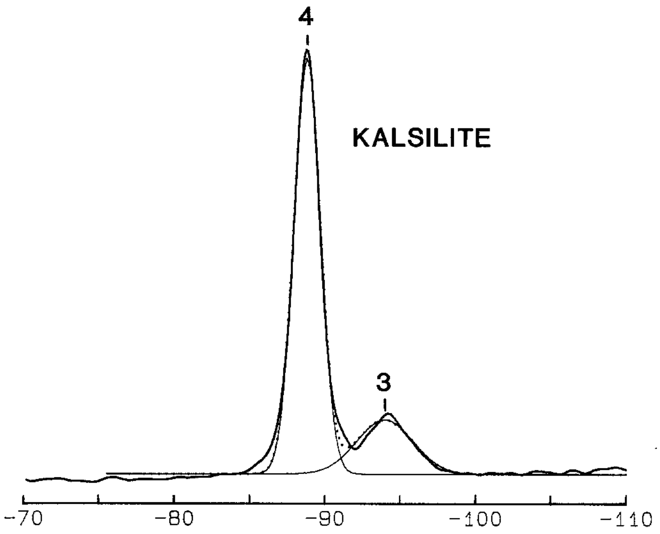

Fig. 3. ^{29}Si NMR spectrum for kalsilite produced by ion exchange of Bancroft nepheline

Volcanic Nepheline

The first detailed determination of the structure of nepheline was made on a sample from altered xenoliths found in the ejecta erupted from the Mt. Somma vent on Mt. Vesuvius (Hahn and Buerger 1955). The relatively high temperature origin of this material was used to explain the apparent Al—Si disorder observed in more recent single crystal x-ray diffraction studies (Dollase and Peacor 1971). The ^{29}Si spectrum of a sample from the same locality is shown in Figure 2. The two main Q^4(4Al) peaks are slightly closer together, and are thus less well resolved than those in the Bancroft nepheline, resulting in a less certain deconvolution and less well determined peak areas. (The difference may be due to slight compositional differences). Given these errors, however, the number of peaks observed, their positions, and their relative areas are very similar in the spectra of the two samples. Again, the Si/Al ratio calculated from the NMR spectrum is close to that from the microprobe data, and the distribution of silicon sites is well approximated by a completely ordered structure with occasional random replacement of Al by Si. We therefore conclude that the disorder seen in x-ray data is long-range only, and is the result of averaging over domains with short-range order. Boundaries between these domains are not directly detectable, however. This must be because either distortions of the framework along such boundaries are too small to perturb the NMR peak positions substantially (less than a few degrees in bond angles), or the density of such boundaries is too low for such effects to be seen (less than a few percent).

Spinning sidebands were present in the spectrum even at the highest spinning rate obtainable, probably because of the presence of about 0.25% Fe_2O_3 component in this sample. The location of the sidebands, and their frequency separation in spectra taken at various spinning speeds clearly showed that they were related to the main T_G Q^4(4Al) peak and to this peak only. This suggests that the chemical shift anisotropy is greater for this site than for the more symmetrical T_S site, as expected from the geometry determined by x-ray diffraction.

Kalsilite

Kalsilite occurs in many potassium-rich, silica-poor lavas, but is unknown from plutonic rocks. In several ways, this polymorph of $KAlSiO_4$ has the simplest structure of the group of minerals described here. Our sample was derived from the Bancroft nepheline by ion exchange. Based on results of similar experiments on alkali feldspars (Waldbaum and Robie 1971), we assume that the distribution of framework cations is the same in both samples. The mineral, whose structure can be derived by the coupled substitution KAl = Si into the high tridymite framework, remains hexagonal even at room temperature (space group $P6_3$), with one potassium cation in each interstitial site at the ideal stoichiometry (Perotta and Smith 1965). Single crystal x-ray diffraction studies by these and other authors are consistent with complete long-range Al—Si order. Because of the high symmetry and simple structure, all Si sites are equivalent if $Al/Si = 1$ and defects are absent. No displacive transitions are observed between room temperature and at least 1,000 K (Lange et al. 1986), but a change from ditrigonal to hexagonal rings was observed at 1138 K by Andou and Kawahara (1982).

The NMR spectrum that we have obtained for synthetic kalsilite is entirely consistent with this description. As shown in Figure 3 and Table 2, only two peaks are obviously present. These can be assigned with little ambiguity to the predominant Si site type of Q^4(4Al) and a less abundant site for Q^4(3Al). As for the Bancroft nepheline sample, the presence of the latter peak is related to a silica content in excess of the ideal 1:1 Si/Al ratio. The ratio of the areas of the Q^4(3Al) and Q^4(4Al) peaks in the kalsilite is somewhat higher, probably because the peak shape chosen for the deconvolutions left substantial unfitted "wings" on both sides of the kalsilite Q^4(4Al) peak.

An important difference between the two spectra is the absence of significant signal in the kalsilite data that can be attributed to Q^4(0Al) or Q^4(1Al) sites. The lack of signal may be the result of a relaxation time for these sites in kalsilite that was much longer than the time between pulses during data acquisition. This has apparently not been a significant problem in sodium-bearing tectosilicates, but can cause severe difficulties in pure SiO_2 polymorphs (e.g. Murdoch et al. 1985). A similar effect has been observed in spectra for silicate glasses (Schneider et al. 1986), in which Q^4 relaxation appears to be much slower in a potassium containing glass than in one containing sodium. A relaxation mechanism involving interaction of Si with Na is implied. ^{39}K, like ^{23}Na, is an abundant quadrupole nucleus, but this type of coupling is proportional to the product of the gyromagnetic ratios (γ's) of the nuclei involved. γ for ^{23}Na is 5.67 times that for ^{39}K, so a much stronger coupling will occur between ^{29}Si and ^{23}Na than between ^{29}Si and ^{39}K.

As for nepheline, the correlations of Ramdas and Klinowski (1984) can be applied to kalsilite. Using the data of Dollase and Freeborn (1977), and assuming independent atomic motion, such T−T distances can be calculated for kalsilite. The separation between the two peaks of our observed spectrum of this mineral is again close to the average that is predicted (8 ppm). The predicted *absolute* positions of both peaks are too negative by about 5 ppm, however. The explanation of this discrepancy, and of those in the opposite direction described above for nepheline and anorthite, is not clear. They could be related to uncertainties in the x-ray structure determinations, or to a more complex relationship between structure, composition, and chemical shift than hypothesized. It is conceivable that some of the discrepancy could be related to the fact that the samples studied by NMR were not identical to those used in the structure refinements.

Despite this problem, predicted relative effects of bond angles on chemical shifts may be used to look for evidence of distortions of the framework along domain boundaries. Kirkpatrick et al. (1985), for example, attributed some features in the ^{29}Si NMR spectra of plagioclase feldspars to bond angle distortions. One simple effect of various types of twin planes in nepheline group minerals could be the increase of one T−O−T bond angle to as much as 180° for tetrahedra along the boundary. For kalsilite, this would change the mean bond angle from about 159° to 164°, leading to a chemical shift change of about -2 ppm. There is no obvious peak in such a position in our kalsilite spectrum, although a small amount of signal could be hidden under the main peak.

Carnegieite

On heating to about 1,520 K, the synthetic sodium endmember of nepheline ($NaAlSiO_4$, tridymite structure) undergoes a slow, quenchable, reconstructive transition to carnegieite (cristobalite structure), just as tridymite itself transforms to cristobalite (Greig and Barth 1938). Like cristobalite, carnegieite is cubic at high temperature, but transforms rapidly (and probably in at least two steps) to a lower symmetry form on cooling to room temperature (Barth and Posnjak 1932; Bowen and Greig 1925). A single crystal x-ray structure refinement of this finely twinned low-T polymorph has apparently not been made, but electron diffraction data indicate that it is triclinic (Klingenberg et al. 1981).

The ^{29}Si NMR spectrum of carnegieite is very simple, consisting of a single, somewhat asymmetric peak (Figure 4). All silicon sites must therefore have nearly the same mean T−O−T bond angle (within about ±2°) and mean Si−Al distance (within about ±0.005 nm), although variations from site to site of *individual* angles or distances perhaps could be present. The asymmetry of the peak could be the result of distinct Si sites in the crystal, with overlapping chemical shift ranges, or could be due to a continuous range of bond angles caused by some kind of displacive disorder. Within the signal to noise ratio of the NMR spectrum, all (>99%) silicon sites have 4 Al neighbors, precluding the possibility of a significant amount of excess Si (and in agreement with the microprobe analysis). Again, the distortions caused by domain boundaries are not observed.

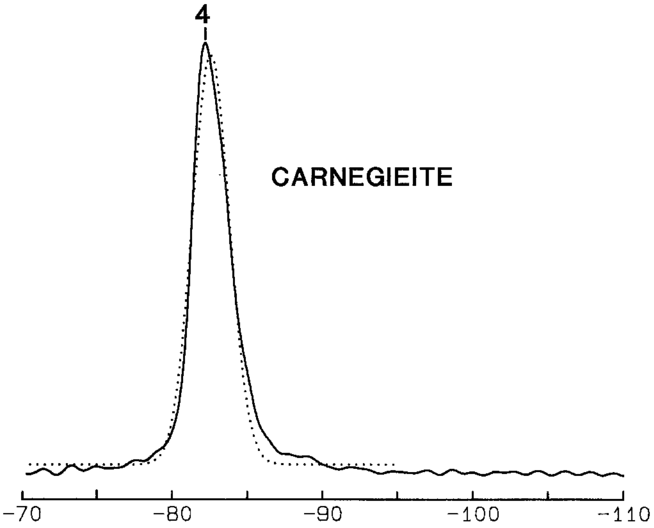

Fig. 4. ^{29}Si NMR spectrum for carnegieite

Clearly, there is no detectable Al−Si local disorder in carnegieite, since an randomization of the occupancy of the Si and Al sites in a phase with a 1:1 ratio will lead to Si sites with fewer than 4 Al neighbors. Peaks resulting from such sites are absent from the carnegieite spectrum.

$NaAlSiO_4$ nepheline

Smith and Tuttle (1957) showed that the unit cell parameters of pure sodium nepheline diverged slightly from the linear trend of more K-rich solid solutions, and varied slightly depending on synthesis technique. In a careful study of low-K nephelines by high temperature powder x-ray diffraction and differential scanning calorimetry, Henderson and Roux (1977) and Henderson and Thompson (1980) showed that all nephelines are hexagonal (with the Hahn and Buerger 1955, structure) between about 1,070 K and 470 K, but as the potassium content decreases, one or two reversible phase transitions take place on cooling to room temperature. An orthorhombic phase, or a mixture of two phases, results. These authors suggested that the phase transitions were the result of displacive structural collapse which can occur only if very few potassium cations are present (i.e., $K/(K+Na)<0.025$), in a way analogous to that which occurs in tridymite itself. The details of the low temperature, pure Na nepheline structures are not known: like carnegieite, it is generally finely and complexly twinned.

The ^{29}Si NMR spectrum of our sample of pure Na nepheline is best fit by two large and one small, overlapping, peaks (Figure 5, Table 2). The position, width, and relative area of the -82.4 ppm peak are very close those expected if the sample contains about 25% carnegieite, as was deter-

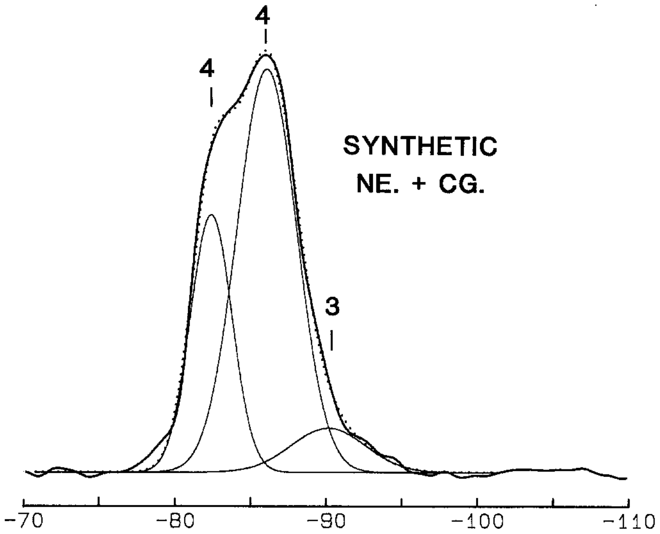

Fig. 5. ^{29}Si NMR spectrum for pure Na nepheline with approximately 25% intergrown carnegieite

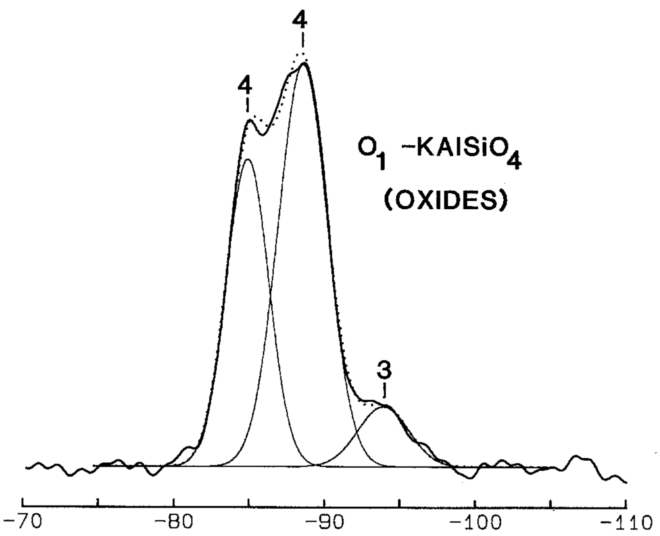

Fig. 6. ^{29}Si NMR spectrum of $O_1-KAlSiO_4$ grown by high temperature sintering of oxides

mined by calorimetry. Disregarding this peak, then, the nepheline spectrum consists of a single rather wide major peak and a minor shoulder. The separation into the T_G and T_S sites of the Hahn and Buerger (1955) structure is not apparent. As for carnegieite, most of the Si sites in Na nepheline must therefore be nearly equivalent in local bonding structure, although the large peak width indicates a range of perhaps ±3° in average $T-O-T$ bond angles. This suggests that despite the low overall crystallographic symmetry of the material, there is in a topological sense an *increase* in local symmetry from $(Na,K)AlSiO_4$ to $NaAlSiO_4$ as K is removed and the distinction between the nepheline site types is lost.

The small amount of signal attributable to Q^4(3Al) sites in this sample may result from a slight degree of Al−Si disorder, as the material is close to stoichiometric in composition.

The details of atomic positions, and thus the $T-O-T$ bond angles and distances, are not precisely known for either Na-nepheline or low carnegieite. However, the difference in chemical shift between the two phases (3.5 ppm) is of the same sign and approximately the same magnitude as the separation between the average chemical shift of tridymite and that for cristobalite (2.5 ppm, Smith and Blackwell 1983).

Orthorhombic $KAlSiO_4$

Kalsilite undergoes a slow, reconstructive transformation to a high temperature polymorph at about 1,170 K (Bowen 1917; Tuttle and Smith 1958). Above about 1,670 K, this phase changes slightly to one which gives a doubled unit cell and several extra x-ray reflections when quenched (Cook et al. 1977). When this highest temperature phase is cooled to room temperature, it undergoes two reversible, displacive transitions (Lange et al. 1986) which probably lower its symmetry to the observed orthorhombic form: as pointed out by Abbott (1984), it is unlikely that the stable high temperature phase has a lower symmetry than hexagonal kalsilite. For simplicity, we will refer to this quenched product of the high T phase as "$O_1-KAlSiO_4$", following Smith and Tuttle (1957). Several other polymorphs of $KAlSiO_4$ also exist, interrelated by other less well-known transitions (Abbott 1984; Tuttle and Smith 1958).

Based on powder x-ray diffraction, several different orthorhombic space groups for $O_1-KAlSiO_4$ have been published (Kunze 1954; Cook et al. 1977). Abbott (1984) pointed out that, on the basis of symmetry alone, these are incompatible with long-range Al−Si order. Gregorkiewitz and Schäffer (1980) reported a new structure for this phase, which has monoclinic real symmetry but orthorhombic pseudosymmetry. Unlike other proposals, this structure is *not* a simple derivative of any of the silica polymorphs, but is made up of six-membered rings with different up-down sequences of tetrahedral orientations. The structure refinement was made in a space group which does not allow Si−Al ordering on alternating T sites, and probably therefore represents an averaged structure.

Our ^{29}Si NMR spectra of two samples of $O_1-KAlSiO_4$ are similar, although not identical (Figs. 6 and 7). They both consist of two major peaks that almost certainly represent Q^4(4Al) sites, and one or two small peaks that are probably due to Q^4(3Al) or Q^4(2Al) species. *Si/Al* ratios calculated from the spectra again compare well with analytical data, indicating that few if any Al−O−Al bonds occur even in these very high temperature polymorphs. Once again, there is no obvious sign of short-range Al−Si disorder, implying that a domain structure creates a long-range average. Detailed interpretation of the distribution of the excess Si in these phases, however, is difficult because of the relatively poor separation of peaks and the likelihood that some signal for Q^4(0Al) sites is missing.

Using the correlation of Ramdas and Klinowski (1984), an NMR spectrum can be predicted for the new structure proposed by Gregorkiewitz and Schäffer (1980). If the phase does have short-range Al−Si order, then one of two sets of three peaks should be present, all with equal areas: either −80.4, −81.7, and −88.8 ppm, or −83.3, −84.5, and −88.2 ppm. These would probably be observed as two overlapping peaks, one with an area twice that of the other. The latter set is a reasonably close match to the Q^4(4Al)

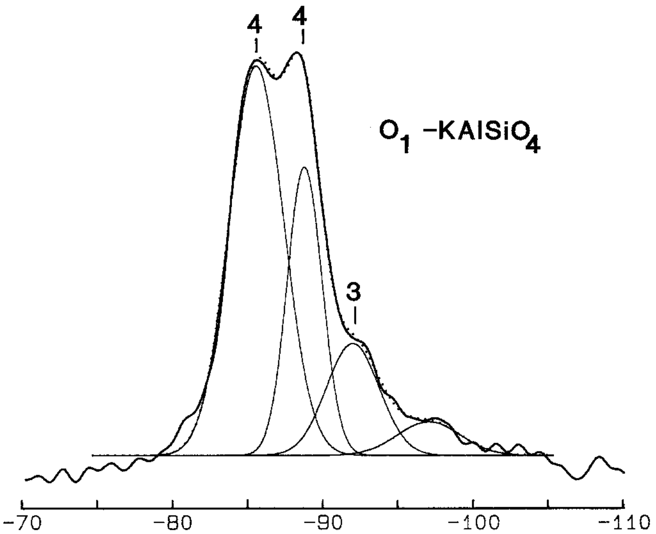

Fig. 7. ^{29}Si NMR spectrum of $O_1-KAlSiO_4$ produced by heating kalsilite

peaks in the spectrum for the sample synthesized by heating of kalsilite, but neither is close to the spectrum for the sample synthesized from oxides.

In detail, the relative intensities of the two major peaks in the observed NMR spectra are quite different for the two samples. This suggests that they may not represent sites inherent in the fixed structure of a single phase, but may result from a varying mixture of two separate phases, each with a single main $Q^4(4Al)$ site. In this way our samples of this material may be analogous to our mixed-phase nepheline-carnegieite sample: one can even speculate that in $KAlSiO_4$, a cristobalite derivative structure may exist at very high temperatures. The two phase transitions observed calorimetrically (Lange et al. 1986) could also, of course, be due to the presence of a mixture of two phases.

Summary and Conclusions

In the structurally simple minerals of the nepheline group, ^{29}Si NMR spectroscopy can provide important new information on details of local Si—Al distribution, ordering, and domain structure that complement x-ray diffraction data. Perhaps most importantly for thermochemistry, spectra for natural nephelines from plutonic and volcanic environments, synthetic kalsilite, pure $NaAlSiO_4$ nepheline, carnegieite, and $O_1-KAlSiO_4$ show little or no evidence of short-range aluminum-silicon disorder. The last two are the highest temperature end members phases in the $NaAlSiO_4$-$KAlSiO_4$ system, and might be expected to show such disorder if it could occur. Single-crystal x-ray diffraction data has indicated a substantial degree of Al—Si disorder, of uncertain scale, in a similar volcanic nepheline (e.g. Dollase and Peacor 1971). Our results suggest that this x-ray disorder in this and other phases in the system is long-range only, and results from the mixing of small, but ordered, domains.

Domain models have often been proposed to account for Al—Si and other types of structural disorder in tectosilicates, but characterization of the size of domains and the structure of their boundaries remains difficult. Much information may be obtainable about domain boundary orientation and density from those phases which are stable in the beam of a transmission electron microscope (Abbott 1984), but the details of changes in Al—Si distribution and bond angles at boundaries can not generally be determined by this technique. Several types of boundaries can be ruled out in these minerals by the details of the ^{29}Si NMR spectra. First of all, it is unlikely that excess Si is concentrated on domain boundaries, producing tridymite-like interlayers or analogous structures parallel to the c-axis. Secondly, any boundary that distorts single T—O—T bond angles by more than about 5–10° should be detectable if present in an appreciable amount. The absence of clear indications of such distortions, even in very simple, high quality spectra such as those of kalsilite and carnegieite, suggests either that low distortion boundaries dominate, or that boundaries are few enough in number to remain unobserved. If the latter is true, it simply means that the average domain size is greater than a few tens of nm, with less than perhaps two per cent of the Si sites on boundaries.

The spectra which we have presented also provide new data on several aspects of the overall crystal structure of some of the less well-known phases. In both carnegieite and "B-type" pure soda nepheline (Henderson and Roux 1977), all Si sites are nearly equivalent, at least in mean T—T distances and T—O—T bond angles. This may result from the lack of the distinction between sites created in most nephelines by the presence of both Na and K cations. The difference in ^{29}Si chemical shift between the two phases is similar to that between the mean value observed for tridymite and that for cristobalite, indicating that differences in bonds angles are comparable.

Both calorimetry and NMR spectroscopy show that mixtures of carnegieite and nepheline can be produced even at temperatures well below the supposed equilibrium phase transition. The NMR spectrum and the DSC data for $O_1-KAlSiO_4$ are similar in many ways to those of this nepheline-carnegieite mixed phase. This allows the speculation that mixtures of tridymite and cristobalite structures may exist for the potassium end-member as well.

Finally, these data have several thermochemical implications. Excess SiO_2 in kalsilite and nepheline seems to be randomly substituted for Al on a highly ordered lattice, indicating that at least the entropy component of the free energy of mixing should be ideal. The overall highly ordered structure means that the (metastable) entropy of fusion of nepheline (4.0 J g-atom^{-1}K^{-1}) can be directly compared with that for anorthite (5.7 J g—atom^{-1}K^{-1}, Stebbins, Carmichael, and Moret 1985; Richet and Bottinga 1984). As expected from comparisons of data for olivines, pyroxenes, sheet silicates, and the alkali feldspars, the entropy change on melting is indeed higher for the material with the smaller or more highly charged cation.

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References

Abbott RN (1984) $KAlSiO_4$ stuffed derivatives of tridymite: phase relationships. Am Mineral 69:449–457

Andou Y, Kawahara A (1982) The existence of high-low inversion point of kalsilite. Mineralog J 11:72–77

Andrew ER (1981) Magic angle spinning in solid state n.m.r. spectroscopy. Phil Trans Roy Soc London A:505–520

Barth TFW, Posnjak E (1932) Silicate structures of the cristobalite type: I. the crystal structure of α carnegieite ($NaAlSiO_4$) Zeit Kristallogr 81:135–141

Bowen NL (1917) The sodium-potassium nephelites. Am J Sci 38:115–132

Bowen NL, Greig JW (1925) The crystalline modifications of $NaAlSiO_4$. Am J Sci ser 5, 10:204–212

Buerger MJ (1954) The stuffed derivatives of the silica structures. Am Mineral 39:600–614

Cook LP, Roth RS, Parker HS, Negas T (1977) The system $K_2O-Al_2O_3-SiO_2$. part I. Phases on the $KAlSiO_4-KAlO_2$ join. Am Mineral 62:1180–1190

Dempsey E, Kuhl GH, Olsen DH (1969) Variation of the lattice parameter with aluminum content in synthetic sodium faujasites. Evidence for ordering of the framework cations. J Chem Phys 73:387–390

Dollase WA (1970) Least-square refinement of the structure of a plutonic nepheline. Zeit Kristallogr 132:27–44

Dollase WA, Freeborn WP (1977) The structure of $KAlSiO_4$ with $P6_3mc$ symmetric. Am Mineral 62:336–340

Dollase WA, Peacor DR (1971) Si–Al ordering in nephelines. Contrib Mineral Petrol 30:129–134

Dollase WA, Thomas WM (1978) The crystal chemistry of silica-rich, alkali-deficient nepheline. Contrib Mineral Petrol 66:311–318

Engelhardt G, Radeglia R (1984) A semi-empirical quantum-chemical rationalization of the correlation between SiOSi angles and ^{29}Si NMR chemical shifts of silica polymorphs and framework aluminosilicates (zeolites). Chem Phys Lett 108:271–274

Foreman N, Peacor D (1970) Refinement of the nepheline structure at several temperatures. Zeit Kristallogr 132:45–70

Fyfe CA, Gobbi GC, Klinowski J, Thomas JM, Ramdas S (1982) Resolving crystallographically distinct tetrahedral sites in silicalite and ZSM-5 by solid-state NMR. Nature 296:530–536

Fyfe CA, Thomas JM, Klinowski J, and Gobbi GC (1983) Magic-angle-spinning NMR (MAS-NMR) spectroscopy and the structure of zeolites. Angew Chem Int Ed Engl 22:259–275

Gibbs GV, Meagher EP, Newton MD, Swanson DK (1981) A comparison of experimental and theoretical bond length and angle variations for minerals, inorganic solids, and molecules. In: O'Keefe M, Navrotsky A, eds., *Structure and Bonding in Crystals* NY, Academic Press, pp 195–226

Greig JW, Barth TFW (1938) The system $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ (nephelite, carnegieite) – $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$. Am J Sci 35A: 93–112

Gregorkiewitz M (1984) Crystal structure and Al/Si-ordering of a synthetic nepheline. Bull Minéral 107:499–507

Gregorkiewitz M, Schäffer H (1980) The structure of $KAlSiO_4$-kaliophilite-O_1: Application of the subgroup-supergroup relations to the quantitative space group determination of pseudosymmetric crystals. Sixth European Crystallographic Meeting, Barcelona, Italy. Text of oral presentation

Grimmer AR, Radeglia R (1984) Correlation between the isotropic ^{29}Si chemical shifts and the mean silicon-oxygen bond lengths in silicates. Chem Phys Lett 106:262–265

Hahn T, Buerger MJ (1955) The detailed structure of nepheline, $KNa_3Al_4Si_4O_{16}$. Zeit Kirstallogr 106:308–338

Henderson CMB, Roux J (1977) Inversions in sub-potassic nephelines. Contrib Mineral Petrol 61:279–298

Henderson CMB, Thompson AB (1980) The low-temperature inversion in sub-potassic nephelines. Am Mineral 65:970–980

Kirkpatrick RJ, Kinsey RA, Smith KA, Henderson DM, Oldfield E (1985) High resolution solid-state ^{23}Na, ^{27}Al, and ^{29}Si nuclear magnetic resonance spectrographic reconaissance of alkali and plagioclase feldspars. Am Mineral 70:106–123

Klingenberg R, Felsche J, Miehe G (1981) Crystal data for the low-temperature form of carnegieite $NaAlSiO_4$. J Appl Cryst 14:66–68

Kunze G (1954) Über die rhombische Modification von $KAlSiO_4$ in Anlehnung an der Kalsilite. Heid Beit Mineral Petrol 4:99–129

Lange R, Carmichael ISE, Stebbins JF (1986) Phase transitions in leucite ($KAlSi_2O_6$), orthorhombic $KAlSiO_4$ and their iron analogs ($KFeSi_2O_6$, $KFeSiO_4$). Am Mineral, in press

Lippmaa E, Mägi M, Samosen A, Englehardt G, Grimmer AR (1980) Structural studies of silicates by solid state high-resolution ^{29}Si NMR. J Am Chem Soc 102:4889–4893

Lippmaa E, Mägi M, Samosen A, Tarmak M, and Englehardt G (1981) Investigation of the structure of zeolites by solid-state high-resolution ^{29}Si NMR spectroscopy. J Am Chem Soc 103:4992–4996

Loewenstein W (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates. Am Mineral 39:92–96

Mägi M, Lippmaa E, Samosen A, Englehardt G, Grimmer AR (1984) Solid-state high-resolution ^{29}Si chemical shifts in silicates. J Phys Chem 88:1518–1522

McConnell JD (1962) Electron-diffraction study of subsidiary maxima of scattered intensity in nepheline. Mineral Mag 33:114–122

McConnell JD (1981) Time-temperature study of the intensity of satellite reflections in nepheline. Am Mineral 66:990–996

McConnell JD (1985) Symmetry aspects of order-disorder and the application of Landau theory. In: Kieffer SW, Navrotsky A, eds., *Microscopic to Macroscopic* (Reviews in Mineralogy V14), Mineral Soc Am, pp 165–186

Merlino S (1984) Feldspathoids: their average and real structure. In: Brown WL, ed, *Feldspars and Feldspathoids.* (NATO Advanced Study Institute) NY, Reidel Publishing Co, pp 435–470

Murdoch JB, Stebbins JF, Carmichael ISE (1984) Silicon-29 MAS nuclear magnetic resonance study of the structure of feldspathoid minerals. Geol Soc Am Abst w Prog 16, 6:604

Murdoch JB, Stebbins JF, Carmichael ISE (1985) High-resolution ^{29}Si NMR study of silicate and aluminosilicate glasses: the effect of network-modifying cations. Am Mineral 70:332–343

Mysen BO, Finger LW, Virgo D, and Seifert FA (1982) Curve-fitting of Raman spectra of silicate glasses. Am Mineral 67:686–695

Perrotta AJ, Smith JV (1965) The crystal structure of kalsilite, $KAlSiO_4$. Mineral Mag 35:588–595

Phillips MW, Ribbe PH, Gibbs GV (1973) Tetrahedral bond length variations in anorthite. Am Mineral 58:495–499

Putnis A, Angel RJ (1985) Al, Si ordering in cordierite using "magic angle spinning" NMR. II: Models of Al, Si ordering from NMR data. Phys Chem Minerals 12:217–222

Ramdas S, Klinowski J (1984) A simple correlation between isotropic ^{29}Si-NMR chemical shifts and T–O–T angles in zeolite frameworks. Nature 308:521–523

Richet P, Bottinga Y (1984) Glass transitions and thermodynamic properties of amorphous SiO_2, $NaAlSi_nO_{2n+2}$, and $KAlSi_3O_8$. Geochim Cosmochim Acta 48:453–470

Sahama TG (1962) Order-disorder in natural nepheline solid solutions. J Petrol 3:65–81

Schneider E, Stebbins JF, Murdoch JB, Wong J, Thomas JM (1986) Multinuclear NMR of silicate glasses. 27th Experimental NMR Conference

Simmons WB, Peacor DR (1972) Refinement of the crystal structure of a volcanic nepheline. Am Mineral 57:1711–1719

Smith JV, Tuttle OF (1957) The nepheline-kalsilite system: I. X-ray data for the crystalline phases. Am J Sci 255:282–305

Smith JV, Blackwell CS (1983) Nuclear magnetic resonance of silica polymorphs. Nature 303:223–225

Smith KA, Kirkpatrick RJ, Oldfield E, and Henderson DM (1983) High-resolution silicon-29 nuclear magnetic resonance spectroscopic study of rock-forming silicates. Am Mineral 68:1206–1215

Stebbins JF, Carmichael ISE, Moret LK (1984) Heat capacities and entropies of silicate liquids and glasses. Contrib Mineral Petrol 86:131–148

Stebbins JF, Murdoch JB, Carmichael ISE (1985) Defects and short-range order in nepheline group minerals: a Si-29 NMR study. Trans Am Geophys Union 66:1116

Thomas JM, Klinowsky J, Ramdas S, Anderson MW, Fyfe CA, Gobbi GC (1983) New approaches to the structural characterization of zeolites: magic-angle spinning NMR (MASNMR). In: Stucky GD, Dwyer FG, eds, *Intrazeolite Chemistry*. Am Chem Soc, Washington DC

Thompson AB, Wennemer M (1979) Heat capacities and inversions in tridymite, cristobalite, and tridymite-cristobalite mixed phases. Am Mineral 64:1018–1026

Tossell JA (1984) Correlation of ^{29}Si nuclear magnetic resonance chemical shifts in silicates with orbital energy differences obtained from x-ray spectra. Phys Chem Minerals 10:137–141

Tossell JA, Lazzeretti P (1984) Ab initio calculations of ^{29}Si NMR chemical shifts for Si oxides and fluorides. Trans Am Geophys Union 66:394

Tuttle OF, Smith JV (1958) The nepheline-kalsilite system, II. Phase relations. Am J Sci 256:571–589

Vega AJ (1983) A statistical approach to the interpretation of silicon-29 NMR of zeolites. In: Stuckey GD, Dwyer FG, eds. *Intrazeolite Chemistry*. Washington DC, Am Chem Soc

Wainwright JE, Starkey J (1971) A refinement of the structure of anorthite. Zeit Kristallogr 133:75–84

Waldbaum DR, Robie RA (1971) Calorimetric investigation of Na-K mixing and polymorphism in the alkali feldspars. Zeit Kristallogr 184:381–420

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