

Investigation of short-range Al,Si order in synthetic anorthite by ^{29}Si MAS NMR spectroscopy

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ABSTRACT

Spectroscopic data from ^{29}Si MAS NMR are presented for a series of synthetic anorthite samples crystallized from a glass of the same composition and annealed at 1400 °C for times of 1 min to 179 h. The NMR spectra resemble those of natural Al,Si ordered An-rich feldspars but contain peaks at more negative chemical shifts, indicating the presence of Al-O-Al linkages. We describe a simple method to determine the average number of Al-O-Al linkages per formula unit ($N_{\text{Al-Al}}$) based on the first moment of the ^{29}Si NMR spectrum. For the synthetic An_{100} samples, $N_{\text{Al-Al}}$ ranges from 0.40 after 1 min at 1400 °C to 0.19 after 179 h, corresponding to large degrees of short-range order, $\sigma = 0.80\text{--}0.91$. The short-range order parameter, σ , varies linearly with the square of the macroscopic order parameter determined by X-ray diffraction measurements on the same samples:

$$Q_{\text{od}}^2 = 2.66\sigma - 1.72, \quad r = 0.99.$$

The correlation of σ with Q_{od} implies that An_{100} with no long-range order ($C\bar{1}$) would still be about 65% short-range ordered. The values of $N_{\text{Al-Al}}$ also correlate well with the inverse of the spacing of type b and type e antiphase boundaries, indicating that much of the change in the number of Al-O-Al linkages with short annealing time is related to the reduction in total surface area of the antiphase domains.

Comparison with calorimetric data for similar synthetic anorthite samples yields an enthalpy of -39 ± 12 kJ per mole of Al-Si exchanges in the reaction



INTRODUCTION

A powerful tool for investigating Al,Si disorder in crystalline aluminosilicate phases (Engelhardt and Michel, 1987), ^{29}Si MAS NMR spectroscopy has proved to be a useful probe of the local structure of feldspars (Smith et al., 1984; Kirkpatrick et al., 1985, 1987; Sherriff and Hartman, 1985; Yang et al., 1986). Many questions remain, however, about the local arrangement of Al and Si, especially in the plagioclase feldspars. Recent work on the kinetics of Al,Si ordering in anorthite (Carpenter, 1991a, 1991b) has shown that immediately after crystallization the structure of An_{100} is incommensurately modulated. This observation has important implications for the phase relationships of plagioclase feldspars because it suggests that the incommensurate structure of the e plagioclases can arise as a consequence of Al,Si ordering alone. A detailed understanding of this Al,Si ordering process in

anorthite might shed some light on the complicated structural relationships of intermediate plagioclase feldspars.

This paper presents a ^{29}Si MAS NMR study of synthetic An_{100} ($\text{CaAl}_2\text{Si}_2\text{O}_8$) that was crystallized from An_{100} glass and annealed at 1400 °C for times from 1 min to 179 h. The purposes of this work were (1) to investigate the extent of Al,Si disorder in rapidly crystallized plagioclase without the complication of Ab,An solid solution, (2) to assign the observed NMR peaks to the eight crystallographic sites occupied by Si in fully ordered $P\bar{1}$ anorthite, and (3) to provide a basis for interpreting the ^{29}Si MAS NMR spectra of high-temperature, potentially disordered plagioclase feldspars of intermediate composition.

The results for anorthite show significant Al,Si disorder, the extent of which decreases with increasing annealing time. From the ^{29}Si NMR spectra, the number of Al-O-Al linkages and thus a short-range order parameter, σ , can be determined. Comparison of σ determined from NMR with the long-range order parameters determined from changes in lattice parameters (spontaneous strain)

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TABLE 1. Annealing time and temperature, approximate spacing of antiphase boundaries, scalar strain (ϵ_s), and long-range order parameter (Q_{od}), for the synthetic anorthite samples

Sample	Annealing time	Annealing <i>T</i> (°C)	Approximate spacing of APBs (Å)		ϵ_s	Q_{od}
			Type e	Type b		
ANC10	1 min	1374–1378	29 ± 2		0.0038	0.62
ANC11	4 min	1371–1395	~44		0.0045	0.68
ANC12	15 min	1373–1399	~61		0.0057	0.76
ANC8	2.5 h	1400 ± 2		~220	0.0060	0.78
ANC7	47 h	1400 ± 2		~600	0.0065	0.81
ANC9	179 h	1400 ± 10		1024 ± 130	0.0068	0.83

Note: The ϵ_s and Q_{od} were determined following the procedures described by Carpenter et al. (1990) and Carpenter (1991b); uncertainties propagated from 1σ for the refined lattice parameters are ± 0.0002 and ± 0.01 , respectively. For ANC10 and ANC9, electron microscopic observations were made on the same sample examined by NMR; for the remaining samples, domain sizes have been estimated by comparison with observations on samples given similar heat treatments (Carpenter, 1991b). The nominal annealing time excludes an initial 1–2 min while T increased rapidly after loading the sample into the furnace. The three longest experiments had a lead time of ~ 10 min before reaching 1400 °C.

indicates that the degree of short-range order is more extensive than previously believed. These data illustrate the difference between experimental methods whose coherence lengths are shorter (NMR) and longer (X-ray) than the correlation length of Al,Si ordering in anorthite.

EXPERIMENTAL

The synthetic anorthite samples used for the present study (Table 1) were crystallized from a glass of composition An_{100} by heating at 1400 °C for times from 1 min to 179 h (see Carpenter, 1991a, for details). These samples are part of a larger set that was examined by transmission electron microscopy (Carpenter, 1991a; see also a separate study by Kroll and Müller, 1980), X-ray diffraction, and solution calorimetry (Carpenter, 1991b). Optical examination of the samples used for this study revealed no residual glass.

Annealing anorthite glass for times of less than ~ 1 h at 1400 °C gives rise to crystals with an incommensurate structure, as indicated by the presence of *e* reflections in electron diffraction patterns. Samples annealed for longer times develop *b* reflections and type *b* antiphase domains (APDs), which then coarsen with increasing annealing time (Table 1). These observations indicate that the Al,Si ordering scheme present in the samples annealed for the shortest times is related to the ordering of the incommensurate intermediate plagioclase and that the Al,Si ordering scheme produced by longer annealing approaches that of $I\bar{1}$ anorthite. The presence of streaked *c* reflections in all the samples indicates that they have undergone the low-temperature displacive transition and, at least on a local scale, have $P\bar{1}$ distortions. All the crystalline samples also contain abundant submicroscopic lamellar twinning (albite twin law) and a small proportion ($< 1\%$) of an unidentified impurity phase believed to contain some MgO (Carpenter, 1991a).

Lattice parameters were determined from X-ray powder diffraction data for the synthetic samples used for NMR, following the procedures described by Carpenter (1991a). Values of the room-temperature spontaneous strain, ϵ_s , were then calculated and converted into values

of the macroscopic order parameter, Q_{od} , using the calibration of Carpenter et al. (1990): $Q_{od} = 10.1\sqrt{\epsilon_s}$. The results are given in Table 1.

The ^{29}Si magic-angle spinning (MAS) NMR spectra were measured at 71.5 MHz using a spectrometer based on an 8.45T superconducting solenoid and a Nicolet 1280 automation system, as previously described by Smith et al. (1983). The samples were spun at ~ 4 kHz using a probe by Doty Scientific (Columbia, South Carolina). Pulse widths were 4 μs (approximately $\pi/4$ tip angle), and the recycle delay was 300 s (sufficient to ensure that relative peak areas are quantitatively correct). Between 200 and 300 transients were averaged to produce each spectrum. Chemical shifts are referenced to an internal standard of ^{29}Si -enriched forsterite, taken to be -61.8 ppm from tetramethylsilane.

The ^{29}Si NMR absorption envelopes were fitted to a sum of Gaussian curves using a computer program based on a Levenburg-Marquardt χ^2 minimization algorithm (Press et al., 1986). All parameters (intensity, position, and width for each component) were allowed to vary freely. The fitted parameters constitute a well-defined minimum, being independent of initial estimates to within 1σ . First moments of the spectra were calculated from the center bands, and uncertainties computed by propagating spectral noise. Base lines for these spectra are flat, and a linear correction applied to the spectra was computed from a least-squares fit to the flat noise regions 10 ppm above and below the center bands. Spinning sidebands are weak and symmetrical. They approximate the shape of the center bands and therefore were not included in the first-moment calculation.

RESULTS

The ^{29}Si NMR spectra of the synthetic An_{100} samples contain signals in the range -82 to -104 ppm (Fig. 1) and are similar to the spectrum of the natural Mikajima volcanic An_{97} (Fig. 2, spectrum C; Kirkpatrick et al., 1987; see Carpenter et al., 1985, for a detailed description of these and the other natural samples referenced). They are also broadly similar to, but less well resolved than, the

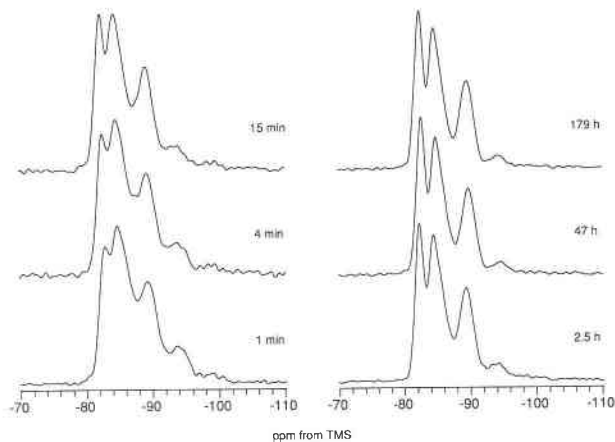


Fig. 1. Some ^{29}Si MAS NMR spectra of synthetic An_{100} plagioclase feldspars annealed at 1400°C used in this study. Times are nominal annealing times.

spectra of the natural and apparently more ordered Val Pasmada (An_{100}) and 115082a (An_{96}) samples (Fig. 2, spectra A and B, respectively).

The spectra of the synthetic samples contain three main peaks, at -82.5 , -85 , and -89 ppm, a less intense peak at -94 ppm, and a broad region of intensity centered at approximately -99 ppm (Fig. 1). Spectra of the samples annealed for shorter periods of time also contain a broad peak near -104 ppm. The positions of the three largest peaks correspond approximately to the positions of the three groups of peaks for the Val Pasmada sample and the most intense peaks for the Mikajima and 115082a samples. The less intense peaks at -94 and -99 ppm for the synthetic samples are also observed at approximately the same chemical shifts in the ^{29}Si NMR spectra of the Mikajima and 115082a samples.

The peaks that are present in the spectra of the synthetic An_{100} samples but not in the spectrum of the Val Pasmada sample must be due to Al,Si disorder in these synthetic samples. By analogy with the more ordered natural samples, the three most intense peaks in the spectra of the synthetic samples arise principally from Si atoms with four Al NNN [Si(4Al); NNN denotes next-nearest neighbor], and the intensity at more negative chemical shifts is due to Si with fewer than four Al NNN, as discussed by Kirkpatrick et al. (1987). The presence of Si-

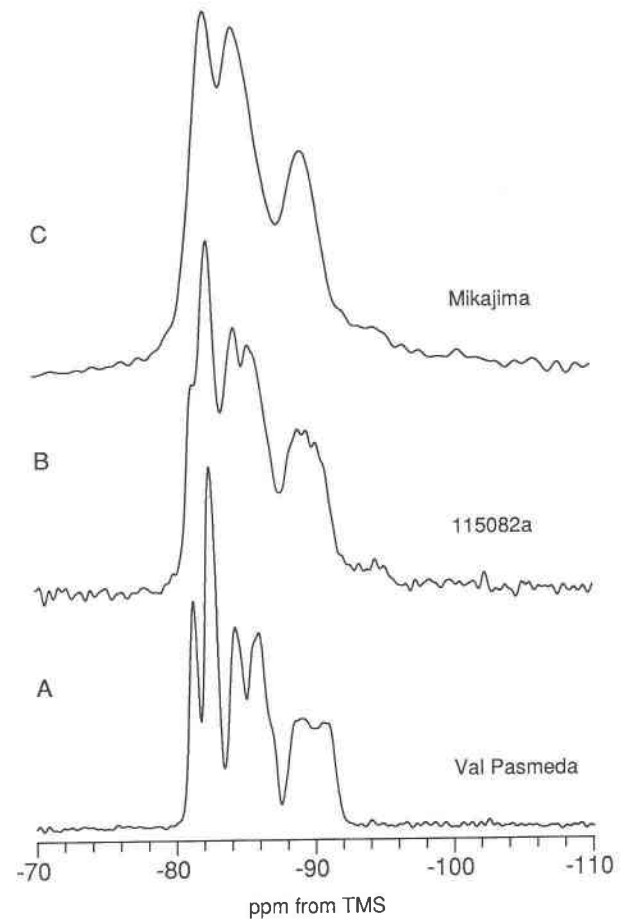


Fig. 2. Three ^{29}Si MAS NMR spectra of natural Ca-rich plagioclases. Spectrum A = Val Pasmada An_{100} , spectrum B = 115082a metamorphic An_{96} , spectrum C = Mikajima volcanic An_{97} . Peaks at -94 and -100 ppm in spectra B and C, but not present in spectrum A, are due to Si with fewer than 4 Al NNN. See Kirkpatrick et al. (1987) for further description of the spectra.

O-Si linkages inferred from the ^{29}Si NMR spectra is direct evidence of Al,Si disorder, because the number of Si-O-Si and Al-O-Al linkages in these synthetic samples must be equal ($\text{Si}/\text{Al} = 1$).

The changes in the ^{29}Si NMR spectra of the synthetic An_{100} samples with increasing annealing time are consis-

TABLE 2. Relative intensities of the peaks observed in the ^{29}Si NMR spectra of the synthetic anorthite samples

Sample number	Annealing time	Approximate peak position (ppm)					
		-82.5	-85.0	-89.2	-94.0	-99.0	-104.5
ANC10	1 min	0.21	0.36	0.29	0.10	0.03	0.005
ANC11	4 min	0.22	0.37	0.29	0.09	0.03	0.008
ANC12	15 min	0.23	0.41	0.25	0.08	0.02	0.007
ANC8	2.5 h	0.26	0.40	0.25	0.06	0.02	0.003
ANC7	47 h	0.31	0.39	0.26	0.04	0.01	—
ANC9	179 h	0.30	0.40	0.26	0.04	—	—

Note: Intensities are integrals of fitted Gaussian curves, and the intensity of the peak near -85 ppm is the sum of the integrals of two peaks fitted to that region. Dash = not detected.

tent with an increase in the degree of Al,Si order. The principal changes with increasing annealing time are a monotonic decrease of intensity arising from Si with fewer than four Al NNN (i.e., the peaks at -94 , -99 , and -104 ppm) and an increase in the intensity of the peak near -82.5 ppm [Si(4Al)] from 0.21 after 1 min to 0.31 after 179 h (Table 2). These changes reflect a shift of the distribution of Si environments from those with fewer than four Al NNN to those with four Al NNN, as required for Al,Si order in this structure. In addition, the widths of the ^{29}Si NMR peaks decrease with increasing annealing time, indicating a progressive decrease in the range of Si environments present, which can be interpreted as a narrower range of mean Si-O-T angles (e.g., Dupree and Pettifer, 1984; Phillips et al., 1988). This decrease in the peak widths with increasing annealing time is continuous; there is no qualitative difference among samples that have the incommensurate e structure (annealing times of 1–15 min) and those which have $I\bar{1}$ order. This result supports the observation of Carpenter (1991b) that the change from the incommensurate to the commensurate structure appears to be continuous.

DISCUSSION

Peak assignments

Any microscopic model for the Al,Si distribution in disordered anorthite must ultimately rely on the assignment of the observed Si(4Al) ^{29}Si NMR peaks to the eight crystallographic Si sites in $P\bar{1}$ anorthite, and this has not been achieved (Kirkpatrick et al., 1985, 1987). However, using a new refinement of the structure of what appears to be the most ordered anorthite available, Val Pasmada An_{100} (Angel et al., 1990), the empirical relationship between the ^{29}Si NMR chemical shift (δ) and the mean Si-O-T bond angle per tetrahedron ($\langle\angle\text{Si-O-T}\rangle$; Smith and Blackwell, 1983; Ramdas and Klinowski, 1984) and the empirical chemical shift correlation of Sherriff and Grundy (1988), it appears to be possible to assign crystallographic sites to regions of ^{29}Si NMR intensity.

Previous attempts to assign the ^{29}Si NMR peaks (Kirkpatrick et al., 1987; and our unpublished work) were based on the nearly linear correlation between $\langle\angle\text{Si-O-T}\rangle$ and δ (Ramdas and Klinowski, 1984; Smith and Blackwell, 1983; Radeaglia and Engelhardt, 1985). For $P\bar{1}$ anorthite, the $\langle\angle\text{Si-O-Al}\rangle$'s occur in three groups with relative populations 4:2:2: $133\text{--}134^\circ$, $137\text{--}138^\circ$, and $142\text{--}143^\circ$ (Fig. 3). Thus, these correlations based on $\langle\angle\text{Si-O-Al}\rangle$ predict three groups of resonances with relative intensities 4:2:2 from least shielded to most shielded (left to right in the spectra). However, the observed spectra of the most ordered An_{100} plagioclase samples (Figs. 1, 2) contain three groups of resonances with relative intensities of approximately 3:3:2. In contrast, ^{29}Si δ calculated using Equations 3 and 4 of Sherriff and Grundy (1988) occur in two groups with a population ratio of 3:5 (Fig. 3).

Reasonable assignments can be obtained by plotting the δ calculated using the methods of Sherriff and Grundy (1988) against $\langle\angle\text{Si-O-Al}\rangle$ from the refinement of Angel

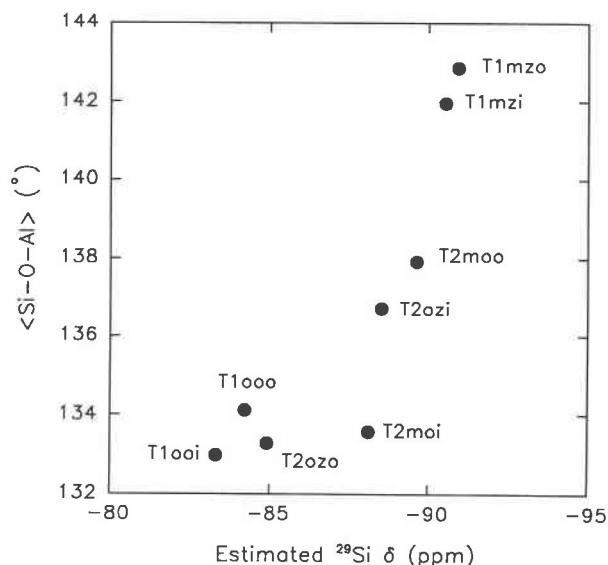


Fig. 3. Relationship between ^{29}Si chemical shifts (δ) for Si in An_{100} calculated from Equations 3 and 4 of Sherriff and Grundy (1988) and the mean Si-O-Al bond angle per tetrahedron ($\langle\angle\text{Si-O-Al}\rangle$), both based on an X-ray structure refinement of the Val Pasmada An_{100} (Angel et al., 1990). Note that the method of Sherriff and Grundy yields two groups that would have an intensity ratio of 3:5, and the bond angle method yields three groups with an intensity ratio of 4:2:2. Taken together, however, they appear to yield three groups with an intensity ratio of 3:3:2, as is observed.

et al. (1990) (Fig. 3). This plot arranges the Si sites into three groups with a population ratio of 3:3:2, as observed. The only major difference between the results using the two correlations is that Equations 3 and 4 of Sherriff and Grundy (1988) yield a value of δ ^{29}Si for T2moi about 4 ppm more shielded than expected on the basis of its $\langle\angle\text{Si-O-Al}\rangle$ alone. Otherwise, there is a positive, although not linear, correlation between the results of the two methods. Perhaps most importantly, both methods predict that Si on T1o sites has the least negative δ and Si on T1m sites the most negative δ , with Si on T2 sites between.

Thus, these two relationships, although totally empirical, appear to yield three groups of peaks with intensity ratios of 3:3:2 for the Val Pasmada An_{100} , as observed (Kirkpatrick et al., 1987). On this basis, we make the following tentative assignments for the Val Pasmada sample: -82 to -83 ppm—T1ooi + T1ooo + T2ozo; -85 to -87 ppm—T2ozi + T2moi + T2moo; -89 to -90 ppm—T1mzi + T1mzo. These peak assignments are also supported by our ^{29}Si NMR study of the $P\bar{1}$ - $I\bar{1}$ phase transition in anorthite (Phillips, 1990).

For the synthetic samples we use the same basis to assign the Si(4Al) intensity in the -83 ppm range to signals from T1ooi, T1ooo, T2ozo, the intensity in the -85 ppm range to T2moi, T2ozi, and T2moo, and intensity in the -90 ppm range T1mzi and T1mzo. We note, however, that because of the 2-ppm uncertainty in the calculation procedure of Sherriff and Grundy (1988), the

exact order of the assignment for the Val Paseda sample and the assignment of the synthetic samples is less certain than the assignment of the individual peaks to one of the three groups. The same assignments for the other well-ordered natural samples also seems reasonable.

Al-O-Al linkages

The presence of signals from Si atoms with fewer than four Al NNN indicates that these synthetic An_{100} samples contain Si-O-Si linkages, and therefore Al-O-Al linkages, because the Si/Al ratio of unity requires an equal number of Si-O-Si and Al-O-Al linkages. Combinations of Al-O-Al and Si-O-Si linkages are energetically unfavorable relative to Si-O-Al linkages and are rarely found in aluminosilicates formed at low temperatures (see Engelhardt and Michel, 1987, for a discussion of the Al avoidance principle, also known as Loewenstein's rule). Such linkages are, however, present in cordierite crystallized from glass (Putnis et al., 1987, and references therein) and in our synthetic anorthite samples.

In this section we develop a simple method for estimating the number of Al-O-Al linkages per formula unit or eight O atoms (N_{Al-Al}), which is based on the sensitivity of the ^{29}Si chemical shift to the number of Al NNN to the Si atoms. A result of the large change in the ^{29}Si chemical shift with a changing number of Al NNN is that the mean chemical shift of the ^{29}Si NMR spectrum ($\langle\delta\rangle =$ first moment) is, to a good approximation, a simple function of the number of Al-O-Al linkages present in the sample. Values of N_{Al-Al} obtained in this manner are independent of how one assigns the peaks in the spectrum.

We begin by considering the possible differences in the local structural environment of Si between ordered and disordered An_{100} and how these differences might affect the ^{29}Si chemical shift (δ). Such differences in δ can be related to two structural factors: the number of Si NNN and the mean Si-O-T angle ($\langle\angle\text{Si-O-T}\rangle$).

The presence of Si-O-Si linkages in Al,Si disordered samples can produce large changes in δ between ordered and disordered An_{100} . For framework aluminosilicates the δ for an Si atom on a particular site changes approximately -5 ppm for each Al atom replaced by Si in the second coordination sphere (i.e., Si-O-Al \rightarrow Si-O-Si; see Engelhardt and Michel, 1987, chapter 4). Furthermore, this shift is, to a good approximation, independent of the number of Si NNN. As a result, ^{29}Si NMR spectra of disordered framework aluminosilicates commonly contain up to five, approximately evenly spaced peaks corresponding to Si atoms having 0–4 Al NNN. Perfectly ordered An_{100} contains only Si(4Al) environments, and the Si(n Al, $n < 4$) environments that result from Al,Si disorder produce ^{29}Si NMR intensity at more negative values of δ .

Other possible differences in the local structural environments of the Si in ordered and disordered An_{100} include Si atoms on Al sites and strained regions of the crystal in which the bond lengths and angles differ from those of an ordered An_{100} . The effect of these structural

differences on δ can be described by the empirical relationship between $\langle\angle\text{Si-O-T}\rangle$ and δ mentioned in the previous section. For a given number of Al NNN, δ ^{29}Si correlates nearly linearly with $\langle\angle\text{Si-O-T}\rangle$: approximately -0.5 ppm per 1° increase in $\langle\angle\text{Si-O-T}\rangle$ (Smith and Blackwell, 1983; Ramdas and Klinowski, 1984; Radeaglia and Engelhardt, 1985; see also Fig. 3). Thus, occurrence of Si on an Al site that has a different $\langle\angle\text{Si-O-T}\rangle$ than the Si sites and strained T-O-T linkages may result in values of δ different from those of an Al,Si ordered An_{100} , with the difference proportional to the change in $\langle\angle\text{Si-O-T}\rangle$.

To describe the differences in the spectra obtained from An_{100} samples having various degrees of Al,Si order, we express the observed chemical shift of an individual Si atom (δ) as a sum of shifts due to these structural factors:

$$\delta = \delta_0 + \delta_{\text{Si-Si}}n_{\text{Si}} + \delta_{\text{site}} + \delta_i \quad (1)$$

where δ_0 is the chemical shift the Si atom would have if the sample were perfectly ordered. The second term describes the shift of δ due to Si NNN where $\delta_{\text{Si-Si}}$ is the change per Si for Al NNN substitution (ca. -5 ppm) and n_{Si} is the number of Si NNN. The third term, δ_{site} , is the difference in δ resulting if the Si atom is on an Al site having $\langle\angle\text{Si-O-T}\rangle$ different than the Si site it would occupy in an ordered An_{100} . The last term is the shift attributed to Si-O-T angles that are strained relative to those for the same crystallographic site of an ordered An_{100} .

An easily measured parameter from the ^{29}Si NMR spectra is the mean chemical shift ($\langle\delta\rangle =$ first moment), which can also be calculated by averaging Equation 1 over the N Si atoms in the sample:

$$\begin{aligned} \langle\delta\rangle &= \frac{1}{N} \sum_{i=1}^N \delta_i \\ &= \frac{1}{N} \sum_{i=1}^N [(\delta_0)_i + \delta_{\text{Si-Si}}(n_{\text{Si}})_i + (\delta_{\text{site}})_i + (\delta_i)_i]. \end{aligned} \quad (2)$$

Summing the terms in Equation 2 separately simplifies the first two terms:

$$\langle\delta\rangle = \langle\delta\rangle_0 + \delta_{\text{Si-Si}}\langle n_{\text{Si}}\rangle + \frac{1}{N} \sum_{i=1}^N (\delta_{\text{site}})_i + \frac{1}{N} \sum_{i=1}^N (\delta_i)_i \quad (3)$$

where $\langle\delta\rangle_0$ is the mean chemical shift of an Al,Si-ordered An_{100} and $\langle n_{\text{Si}}\rangle$ is the average number of Si NNN to the Si atoms.

Changes in $\langle\delta\rangle$ from sample to sample are likely to depend mostly on the second term. The $\delta_{\text{Si-Si}}$ is independent of the state of order, and $\langle n_{\text{Si}}\rangle > 0$ unless the sample is perfectly ordered, whereas each of the last two terms in Equation 3 may take both positive and negative values and thus nearly cancel upon summation. Small negative values for the last two terms in Equation 3, however, might occur for the following reasons. If unordered Si atoms occur on each of the crystallographic Al sites with equal probability, the average value of $\langle\angle\text{T-O-T}'\rangle$ for the Si atoms is the same as in an ordered sample. In this

case, δ_{site} averages to zero over the sample. It is conceivable, however, that the unordered Si atoms occur preferentially on the Al sites with larger $\langle \angle \text{T-O-T}' \rangle$ because theoretical studies have shown that the minimum energy $\langle \angle \text{Si-O-Si} \rangle$ for Si is slightly larger than $\langle \angle \text{Si-O-Al} \rangle$ (Geisinger et al., 1985). This effect would increase $\langle \angle \text{Si-O-T} \rangle$, shifting $\langle \delta \rangle$ to more negative values.

Values for δ_i may also be positive or negative as the framework flexes about T-O-T linkages to accommodate the Al,Si disorder. Strained T-O-T angles probably contribute a line broadening which is mostly symmetrical, causing the lower resolution observed for synthetic An_{100} samples relative to the more ordered natural samples (cf. Figs. 1, 2). Symmetrical line broadening does not affect $\langle \delta \rangle$. However, a small negative value for the last term in Equation 3 may be deduced from the negative volume of ordering in An_{100} . The most disordered synthetic An_{100} samples have unit-cell volumes that are about 0.4% larger than that of the Val Pasmada sample (Carpenter, 1991b; Angel et al., 1990). The larger volume of the disordered samples can be viewed as a slight opening of the structure about the T-O-T linkages, leading to a net increase of $\langle \angle \text{T-O-T} \rangle$ averaged over all the sites ($\langle \langle \angle \text{T-O-T} \rangle \rangle$). Comparison of the $\langle \angle \text{T-O-T} \rangle$ averaged over all of the sites of the Val Pasmada sample with that of more disordered An-rich plagioclase (Angel et al., 1990) shows that the increase in $\langle \langle \angle \text{T-O-T} \rangle \rangle$ is of the order of a few tenths of a degree, corresponding to a maximum change in $\langle \delta \rangle$ of -0.1 to -0.3 ppm for the most disordered samples. (The value of $\langle \langle \angle \text{Si-O-T} \rangle \rangle$ might be smaller than that of $\langle \langle \angle \text{T-O-T} \rangle \rangle$ determined from a structure refinement due to the contribution from Al-O-Al angles to the latter.)

The discussion above shows that the change in $\langle \delta \rangle$ with degree of Al,Si order due to changes in the number of Si NNN appears to be about an order of magnitude greater than that due to other structural factors. Ignoring the last two terms in Equation 3 leaves

$$\langle \delta \rangle = \langle \delta \rangle_0 + \delta_{\text{Si-Si}} \langle n_{\text{Si}} \rangle \quad (4)$$

as a first approximation.

To relate Equation 4 to the number of Al-O-Al linkages we note that each Si-O-Si linkage corresponds to two Si NNN per two Si atoms and that the number of Si-O-Si and Al-O-Al linkages are constrained to be equal. Thus, the number of Al-O-Al linkages per formula unit (two Si atoms) is equal to the average number of Si NNN to the Si atoms:

$$N_{\text{Al-Al}} = \langle n_{\text{Si}} \rangle. \quad (5)$$

Combining Equations 4 and 5 and rearranging gives an expression for the number of Al-O-Al linkages in terms of the average chemical shift:

$$N_{\text{Al-Al}} = \frac{1}{\delta_{\text{Si-Si}}} (\langle \delta \rangle - \langle \delta \rangle_0). \quad (6)$$

Values for $N_{\text{Al-Al}}$ were calculated from Equation 6 (Ta-

TABLE 3. Observed center of gravity ($\langle \delta \rangle$) of ^{29}Si MAS NMR spectra, shift of $\langle \delta \rangle$ from that of the Val Pasmada sample ($\langle \delta \rangle - \langle \delta \rangle_0$), the corresponding number of Al-O-Al linkages per formula unit ($N_{\text{Al-Al}}$) and short-range order parameter (σ)

Annealing time	$\langle \delta \rangle$ (ppm)	$\langle \delta \rangle - \langle \delta \rangle_0$ (ppm)	$N_{\text{Al-Al}}$	σ
1 min	-87.12(24)	1.98	0.40(6)	0.802
4 min	-86.99(28)	1.85	0.37(5)	0.815
15 min	-86.48(28)	1.34	0.27(4)	0.865
2.5 h	-86.28(20)	1.14	0.23(4)	0.886
47 h	-86.13(19)	0.99	0.20(3)	0.901
179 h	-86.09(13)	0.95	0.19(3)	0.905

Note: Uncertainties in the last digits are given in parentheses. Those for $\langle \delta \rangle$ are propagated from spectral noise, and changes caused by small variation of spectrum phasing fall within these values. Uncertainties for $N_{\text{Al-Al}}$ include assumption of 0.5-ppm uncertainty in the shift of the ^{29}Si resonance frequency per substitution of one Al for one Si NNN.

ble 3) using the first moment of the ^{29}Si NMR spectrum of the Val Pasmada anorthite (Fig. 2, $\langle \delta \rangle = 85.14 \pm 0.10$ ppm) as an estimate for $\langle \delta \rangle_0$ because it is the most ordered anorthite available (Carpenter et al., 1985; Angel et al., 1990), and -5 ± 0.5 ppm for $\delta_{\text{Si-Si}}$.

The value of -5 ppm for $\delta_{\text{Si-Si}}$ is based on three observations.

1. The ^{29}Si NMR spectrum of the Val Pasmada anorthite (Fig. 2, spectrum A) has a shoulder at -86.9 ppm that is likely to be the Si(3Al) peak due to the same Si sites that produce the Si(4Al) peak at either -81.2 ppm or -82.5 ppm, a shift of -4.4 or -5.7 ppm.

2. The T1(0Al) peak (-111.7 ppm) of Amelia albite annealed at 1073 °C is shifted -5.6 ppm from that due to T1(1Al) (-96.1 ppm; Yang et al., 1986).

3. Similar Si for Al substitutions cause a shift of δ ^{29}Si , which averages -5.3 ppm over 17 measurements from a wide variety of zeolites and other framework aluminosilicates (Ramdas and Klinowski, 1984).

Our use of the Val Pasmada sample to estimate $\langle \delta \rangle_0$ may introduce some systematic errors in the calculation $N_{\text{Al-Al}}$, but we believe these to be small and of the opposite sign to the systematic errors introduced by ignoring the last two terms in Equation 3. Because we have used $\langle \delta \rangle$ of the Val Pasmada sample for $\langle \delta \rangle_0$, the values of $N_{\text{Al-Al}}$ presented in Table 3 are actually the difference in the number of Si-O-Si linkages between the corresponding synthetic sample and the Val Pasmada sample and, thus, represent minimum values for $N_{\text{Al-Al}}$. By the method outlined in Appendix 1, we estimate the Val Pasmada sample to have between 0.023 and 0.064 Si-O-Si per formula unit. The maximum correction to the values of $N_{\text{Al-Al}}$ for the synthetic anorthite samples due to the presence of Si-O-Si linkages in the Val Pasmada sample ($+0.064$) is of the order of the uncertainty in the computed value of $N_{\text{Al-Al}}$ (Table 3) and is the same for each sample. This systematic error in $\langle \delta \rangle_0$ is also of the same order but of the opposite sign to the possible systematic errors from the last two terms of Equation 3 discussed above. For example, a value for the average of δ_i of -0.3 ppm (vide

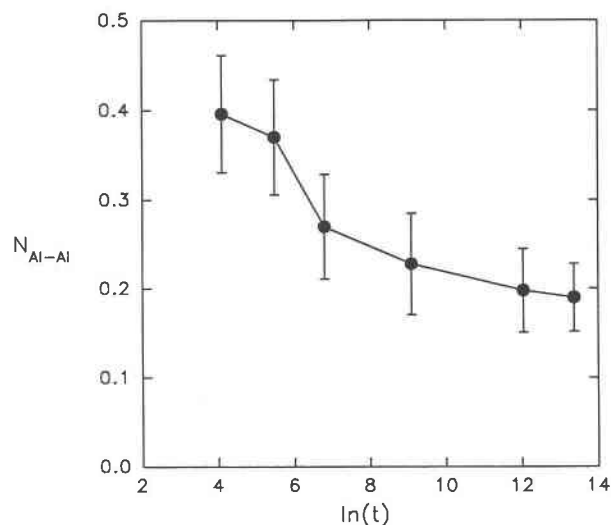


Fig. 4. Plot of the average number of Al-O-Al linkages per formula unit (N_{Al-Al}) against the natural logarithm of annealing time (t) for the synthetic anorthite samples. N_{Al-Al} was determined from Equation 6 in the text.

supra) gives an error in N_{Al-Al} from Equation 6 of -0.06 . For these reasons, we shall use the values of Table 3 as best estimates, assuming these systematic errors approximately cancel. Certainly, most of the change in $\langle\delta\rangle$ among the samples is due to changes in the number of Si NNN.

The method of Appendix 1, which is based on the intensities of the individual ^{29}Si NMR peaks, can provide an independent estimate of N_{Al-Al} for the most ordered synthetic samples, and these values agree well with those computed from Equation 6. Using the fitted intensities for the sample annealed for 179 h (Table 2), a procedure similar to that in Appendix 1 gives N_{Al-Al} between 0.17 and 0.19 (cf. 0.19 computed from Eq. 6). The good agreement between the values from these two different methods supports our assertion that the systematic errors in the application of Equation 6 approximately cancel. Unfortunately, it is not possible to apply this procedure to the more disordered samples because they contain a significant fraction of Si(2Al) environments, as indicated by the peak at -100 ppm.

A separate application of Equation 6 to a slightly sodic, but relatively Al,Si-ordered, anorthite is presented in Appendix 2 and gives additional support for the general procedure outlined above. For this sample the number of calculated Si-O-Si linkages is approximately equal to the number expected from its composition due to substitution of Si + Na for Al + Ca.

As expected from the qualitative changes in the ^{29}Si NMR spectra and the relative peak intensities noted above, N_{Al-Al} of the synthetic anorthite samples determined from $\langle\delta\rangle$ decreases monotonically with increasing annealing time, from 0.40 after 1 min to 0.19 after 179 h, and appears to approach asymptotically a value of about 0.18 at long annealing times (Fig. 4). As discussed below,

these values of N_{Al-Al} are smaller than would be predicted on the basis of the values of the long-range order parameter (Q_{od}) and indicate rather large degrees of short-range order.

N_{Al-Al} and size of the APDs

A linear dependence of N_{Al-Al} on $\ln(t)$ is the simplest form of the rate law for systems in which the degree of order is not homogeneous through the crystal (e.g., Carpenter and Salje, 1989). However, in contrast to the results of a similar NMR study of the kinetics of Al,Si ordering in cordierite (Putnis and Angel, 1985), N_{Al-Al} does not decrease linearly with the logarithm of the annealing time (t) in anorthite, but shows a distinct positive curvature (Fig. 4).

Some indications of how the Al,Si ordering varies within the crystals is provided by the nearly linear inverse correlation between N_{Al-Al} and the mean size of the type b antiphase domains (APDs) at longer t , and the wavelength of the incommensurate modulation at short t , as observed by electron microscopy (Fig. 5, Table 1). Because the transition from the incommensurate structure with type e APDs to an $I\bar{1}$ structure with type b APDs is apparently continuous (Carpenter, 1991a) and the domains are large compared to distances over which structural features can affect NMR chemical shifts, we take the difference between the two structures to be principally one of domain size for present purposes. The antiphase boundaries (APBs) separate domains which are Al,Si ordered and antiodered, and because the Al,Si order must reverse sign across an APB, the regions near APBs have low average degrees of order. The number of Al-O-Al linkages contained within the APBs is approximately proportional to the ratio of surface area to volume of the APDs, i.e., d^{-1} , where d is a linear measure of the domain size. The proportionality constant is a function of the density of framework atoms, a geometrical factor that depends on the shape of the domains, and of the average degree of order within the domain boundary layer, with a correction for the finite width of the domain boundaries.

The nearly linear decrease of N_{Al-Al} with d^{-1} (Fig. 5) suggests that much of the change in N_{Al-Al} with increasing t for these samples can be ascribed to coarsening of the APDs, i.e., to the change in the ratio of surface area to volume of the domains. At short annealing times, where the density of APBs is high, a significant fraction of the Al-O-Al linkages may be contained within the boundaries. In fact, the number of Al-O-Al linkages present at short annealing times (up to about 15 min) is of the same order as that calculated assuming zero-width APBs between perfectly ordered domains (i.e., a square modulation wave). A zero-width APB is a surface of Si-O-Si and Al-O-Al linkages, and the dashed line in Figure 5 shows values of N_{Al-Al} determined for equant domains with linear dimension d containing only Si(3Al) and Al(3Si) environments on the domain boundaries. Thus, at short

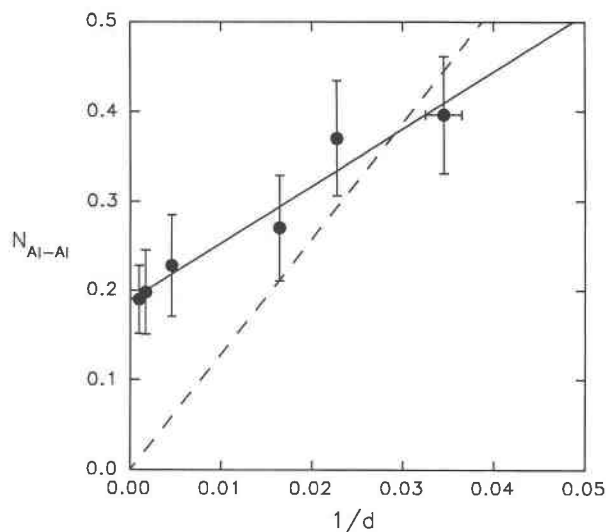


Fig. 5. Variation of $N_{\text{Al-Al}}$ with d^{-1} for synthetic An_{100} , where d is the approximate spacing of the type e and type b APBs (in Å); d^{-1} is proportional to the ratio of surface area to volume of the APDs. Dashed line corresponds to $N_{\text{Al-Al}}$ calculated for zero-width APBs (see text).

annealing times the density of APBs is great enough to contain a large fraction of the Al-O-Al linkages.

Although both domain coarsening and Al,Si ordering within the domains depend on the rate of exchange of Al and Si atoms, the NMR data indicate that, at least at short t , the process at the domain boundaries produces the greater decrease in $N_{\text{Al-Al}}$. As these domains coarsen, the total $N_{\text{Al-Al}}$ decreases, as does the fraction of $N_{\text{Al-Al}}$ that is present within the domain boundaries, producing large single domains with approximately 0.18 Al-O-Al per formula unit. The asymptotic variation of $N_{\text{Al-Al}}$ with $\ln(t)$ after long annealing times (Fig. 4) is consistent with calorimetric and X-ray diffraction results, which also suggests an asymptotic approach to an equilibrium degree of order.

Short-range Al,Si order in anorthite

The present study offers an opportunity to compare the degree of order measured at short (e.g., next-neighbor cations) and long distance scales. The values of $N_{\text{Al-Al}}$ determined from the ^{29}Si MAS NMR spectra of the synthetic An_{100} samples provide a quantitative measure of the average short-range Al,Si order in these samples. By "short-range order" we mean the number of Si-O-Al linkages relative to Si-O-Si plus Al-O-Al, i.e., the pair-wise probability that a Si atom has an Al NNN and vice versa. On the other hand, the macroscopic order parameter of these same samples determined from the spontaneous scalar strain, Q_{od} , provides a quantitative measure of the average tetrahedral site occupancies. Q_{od} is defined such that it varies between zero in crystals with $C\bar{T}$ symmetry and

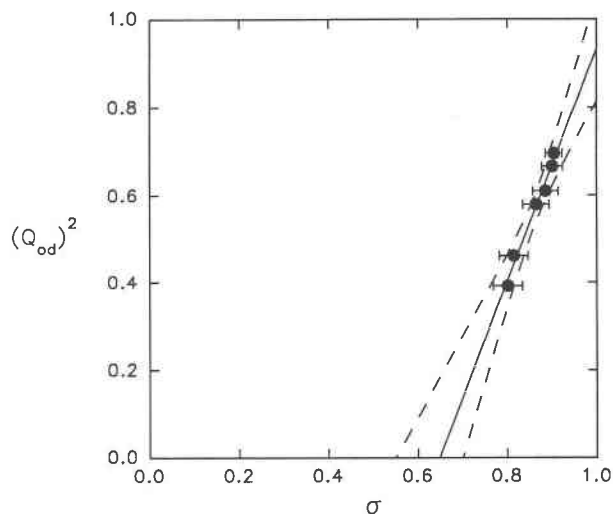


Fig. 6. Correlation of the short-range order parameter, σ , computed from $N_{\text{Al-Al}}$ (Eqs. 6, 8) with Q_{od}^2 determined from spontaneous strain (Carpenter, 1991b) for An_{100} . Best fit line (Eq. 10) has the intercept ($\sigma = 0.65, Q_{\text{od}} = 0$) and passes through the point ($\sigma = 1, Q_{\text{od}} = 0.97$), with $r = 0.99$. Dashed lines are 99% confidence limits.

unity in crystals with complete Al,Si order. More formally this is

$$Q_{\text{od}} = \langle \text{Al} \rangle_{\text{Al}} - \langle \text{Al} \rangle_{\text{Si}} \quad (7)$$

where $\langle \text{Al} \rangle_{\text{Al}}$ is the average occupancy by Al of crystallographic sites that in the fully ordered structure contain only Al, and $\langle \text{Al} \rangle_{\text{Si}}$ is the average occupancy by Al of sites that become preferentially filled by Si (Angel et al., 1990).

Fully ordered anorthite contains no Al-O-Al linkages, whereas completely disordered anorthite (random Al,Si distribution) contains two Al-O-Al linkages per formula unit. A short-range order parameter, σ , which depends on the probability of finding Al and Si on adjacent sites, can be defined to vary from 0 for complete disorder for 1 for complete order as

$$\sigma = 1 - \frac{1}{2}(N_{\text{Al-Al}}). \quad (8)$$

Values of σ computed from Equation 8 using values of $N_{\text{Al-Al}}$ determined from Equation 6 range from 0.80 after 1 min to 0.91 after 179 h (Table 3). Values of Q_{od} determined from spontaneous strain measurements for the same samples vary between 0.62 and 0.83 (Table 1). In the limit of homogeneous Al,Si order the average short-range order is equal to the square of the macroscopic order parameter (Carpenter, 1991b; after Becker, 1978):

$$\sigma = Q_{\text{od}}^2. \quad (9)$$

In synthetic anorthite prepared from glass, the incommensurate modulation present after short annealing times and the subsequent evolution to an antiphase domain structure indicate that large local gradients in Q_{od} (i.e.,

from $+Q$, through $Q_{od} = 0$, to $-Q$) exist on a scale that is smaller than the coherence length for X-ray diffraction. Thus, the crystals are clearly not homogeneous with respect to their degree of Al,Si order, and Equation 9 may not hold. A plot of σ calculated from Equation 8 and Q_{od} from the strain measurements, however, does show a nearly linear dependence of σ on the square of Q_{od} (Fig. 6):

$$Q_{od}^2 = 2.66\sigma - 1.72, \quad r = 0.99. \quad (10)$$

This empirical relationship between short-range order determined from NMR (σ) and the macroscopic order parameter (Q_{od}) is self-consistent for highly ordered states. For $\sigma = 1$, i.e., complete short-range order, Equation 10 gives $Q_{od} \approx 1$ (0.97), which is encouraging because a phase that is fully ordered in terms of site occupancies also necessarily has complete short-range order. At the other extreme, linear extrapolation of the best-fit line to $Q_{od} = 0$ (i.e., for the CT phase) gives $\sigma = 0.65$, which corresponds to $N_{Al-Al} = 0.70$ (or $\sigma = 0.68$ and $N_{Al-Al} = 0.64$ if the regression line is constrained to $\sigma = 1.0$ at $Q_{od} = 1.0$). This value for N_{Al-Al} differs appreciably from the value of 2.0 expected if the local arrangement of Al and Si is random and implies that a high degree of short-range order would be retained in the extrapolated CT structure. In other words, the loss of long-range order on the crystallographic sites does not preclude the existence of pairwise order, and Si-O-Al linkages are still favorable energetically over Si-O-Si + Al-O-Al.

Finally, the values of N_{Al-Al} presented here and the enthalpy measurements of Carpenter (1991b) allow the enthalpy (ΔH) of the following Al-Si exchange reaction in anorthite to be determined:



From the gradient of heats of solution against ϵ_s for many synthetic samples prepared in the same way, Carpenter (1991b) obtained an enthalpy change of -27 ± 8 kJ per mole for the structural change $Q_{od} = 0 \rightarrow Q_{od} = 1$. From the NMR measurements this would correspond to a reduction in N_{Al-Al} from 0.7 to 0, giving $\Delta H = -39 \pm 12$ kJ per mol of Al-Si exchanges. This value is comparable with or slightly greater than that determined for cordierite and albite, -34 and -25 kJ/mol, respectively (Putnis and Angel, 1985). It is significantly larger than the minimum value of -14 kJ/mol previously given for anorthite by Carpenter (1991b), which depended on the assumption that $N_{Al-Al} = 2.0$ at $Q_{od} = 0$.

CONCLUSIONS

The results of this study highlight the importance of combining experimental methods that are sensitive to short-range structure (NMR) and long-range structure (electron microscopy and X-ray diffraction). In general, considerable short-range order may be present in phases that are disordered over the correlation length of X-ray diffraction. Neglect of this short-range order would lead to estimates of configurational entropy, in thermodynam-

ic models for example, that might be seriously in error. As we have found for anorthite, this effect can be especially important in phases that are locally inhomogeneous due to the presence of antiphase boundaries.

The simple method used here to determine the number of Al-O-Al linkages by comparing the first moment of the ^{29}Si NMR spectrum with that of an Al,Si ordered anorthite can be extended easily to anorthite samples annealed at different temperatures, from which kinetic information regarding the short-range ordering process can be obtained. Similar methods involving moments of complicated spectra should be considered as an alternative to models involving curve fitting when the shapes (and number) of the peaks and their assignment are uncertain.

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- lographic site that has its Si(4Al) peak at -81.2 ppm (most likely, T100i).
- To estimate the number of Si-O-Si linkages present, it is sufficient to know the fraction of Si atoms having 4 Al NNN ($f_{4\text{Al}}$). The peaks at -81.2 and -82.5 ppm contain 0.360 ± 0.005 of the observed intensity compared to 0.375 of the crystallographic sites (three of eight). Assuming that this ratio of observed intensity to that of a fully ordered anorthite is the same for all the sites, then $f_{4\text{Al}} = 0.960 \pm 0.010$. However, there is no intensity in the region near -95 ppm, where 3Al intensity from sites whose 4Al peaks are near -90 ppm should occur. Therefore, a more reasonable model is for the peaks at -89 to -91 ppm to contain all of the intensity from two crystallographic sites (4Al) plus Si(3Al) intensity from the peaks at -85 to -87 ppm, the region from -85 to -87 ppm to contain the 4Al intensity from three of the crystallographic sites plus the 3Al intensity missing from the peaks at -81.2 and -82.5 ppm, and that these last two peaks contain the 4Al intensity from the three remaining crystallographic sites. This model gives a slightly higher value of $f_{4\text{Al}} = 0.977 \pm 0.005$.
- Isolated substitution, whereby the observed non-4Al Si environments result from substitution of excess Si on Al sites or a swap of Si and Al atoms, gives the maximum number of Si-O-Si linkages for a given value of $f_{4\text{Al}}$. Each isolated substitution creates one Si(0Al) and four Si(3Al) environments, giving 0.037 ± 0.008 Si-O-Si per formula unit (eight atoms) for $f_{4\text{Al}} = 0.977$, and 0.064 ± 0.015 for $f_{4\text{Al}} = 0.960$.
- A random distribution of unordered Si and Al atoms produces the minimum number of Si-O-Si linkages. In the random model the observed value of $f_{4\text{Al}}$ is the fourth power of the fractional Al occupancy of the Al-rich sites, giving 0.023 ± 0.005 Si-O-Si per formula unit for $f_{4\text{Al}} = 0.977$, and 0.041 ± 0.010 for $f_{4\text{Al}} = 0.960$.
- Based on these models, the number of Si-O-Si linkages in the Val Pasmada sample is probably between 0.023 and 0.064 per eight atoms. Unfortunately, it is not possible to determine the fraction of these Si-O-Si linkages due to Al,Si disorder vs. albite substitution. It seems likely that some of them are due to albite substitution because, although the Na content of this sample is near the detection limit of the electron microprobe, we have observed a ^{23}Na NMR signal from it (B.L. Phillips, unpublished data). If all the inferred Si-O-Si linkages are due to albite substitution, this range of Si-O-Si linkages would correspond to approximately 1 mol% albite.

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APPENDIX 1. ESTIMATION OF THE NUMBER OF Si-O-Si LINKAGES IN VAL PASMEDA ANORTHITE

For the present study, we wish to use the ^{29}Si NMR spectrum of Val Pasmada anorthite to approximate the ^{29}Si NMR spectrum of an Al,Si ordered anorthite. Previous studies indicate that the Val Pasmada anorthite is the most ordered and closest in composition to An_{100} known (see Angel et al., 1990, and references therein), and our investigation of numerous natural anorthite samples confirms this (Kirkpatrick et al., 1987; B.L. Phillips, unpublished data).

We can estimate the number of Si-O-Si linkages present in this sample by comparing the relative intensities of the individual peaks in the ^{29}Si NMR spectrum (obtained by fitting the spectrum with Gaussian curves) to those expected for a fully ordered anorthite. For example, the peak at -81.2 ppm contains about 0.115 of the intensity, whereas a value of 0.125 would correspond to one of the eight crystallographic sites. The intensity “missing” from the peak at -81.2 ppm occurs in the group of peaks from -84 to -87 ppm. And, in fact, satisfactory simulations require a small ($\sim 1\%$) narrow peak at -86.9 ppm to reproduce the small shoulder present in this chemical shift range. A reasonable interpretation of the shoulder at -87 ppm is that it is due to Si(3Al) environments from Si atoms on the crystal-

APPENDIX 2. COMPOSITION OF ORDERED Ca-RICH FELDSPAR FROM (δ)

Equation 6 in the text gives the number of Si-O-Si linkages present in a plagioclase feldspar, regardless of whether such linkages result from Al,Si disorder or albite substitution. For well-ordered but slightly sodic anorthite such as the 115082a sample (Carpenter et al., 1985; see Fig. 2, spectrum B), calculation of the number of Si-O-Si linkages can be used to determine the composition and thus provides a test of the model.

Assume the composition is that of slightly sodic anorthite:



where X_{An} is the mole fraction anorthite. If there are no Al-O-Al linkages, the average number of Al NNN to each Si is:

$$\frac{n_{\text{Al}}}{n_{\text{Si}}} = \frac{4 \times (1 + X_{\text{An}})}{3 - X_{\text{An}}}$$

Because each Si atom has 4 NNN,

$$\overline{n_{Al}} + \overline{n_{Si}} = 4.$$

Rearranging gives

$$X_{An} = \frac{8 - 3 \times \overline{n_{Si}}}{8 - \overline{n_{Si}}}.$$

For anorthite 110582a, $\langle n_{Si} \rangle = 0.14$, calculated from Equation 6 in the text. This value gives $X_{An} = 0.965$, which agrees well with the value 0.96 obtained from an average of ten electron microprobe analyses of this sample (Carpenter et al., 1985). Therefore, we conclude that the first-moment analysis gives an accurate figure for the number of Si-O-Si linkages present, as well as the number of Al-O-Al if Si/Al = 1.