

High-resolution ^{29}Si , ^{27}Al , and ^{23}Na NMR spectroscopic study of Al-Si disordering in annealed albite and oligoclase

WANG-HONG YANG, R. JAMES KIRKPATRICK, DONALD M. HENDERSON

Department of Geology, University of Illinois, 1301 West Green Street, 245 Natural History Building, Urbana, Illinois 61801

ABSTRACT

^{29}Si , ^{27}Al , and ^{23}Na MASS NMR spectra are reported for Amelia (Virginia, USA) albite and Bancroft (Ontario, Canada) oligoclase that have been annealed in air at 1073°C ($\pm 3^\circ$) and 924°C ($\pm 3^\circ$) for various times up to 100 and 140 d, respectively. These spectra provide relatively direct evidence about Al-Si disordering and about the structural environment of individual types of Si, Al, and Na sites in heated sodic plagioclases.

The observed ^{29}Si spectra of albite heated for 30 d or more at 1073°C can be simulated with nine broad peaks corresponding to nine chemically nonequivalent Si sites. The results of the simulation indicate that the Al-Si distribution in even the longest-heated albite at 1073°C is not completely disordered. The ^{29}Si spectrum of the longest-heated oligoclase at 1073°C is very similar to that of the longest-heated albite at the same temperature except that the peaks at -93 and -87 ppm have higher intensity, reflecting the larger number of T(3Al) and T(4Al) Si sites in oligoclase.

For both materials, the ^{27}Al spectra consist of single peaks, for which the full width at half-height increases with increasing annealing time. This change probably is due to an increasingly random distribution of Al atoms as the second tetrahedral neighbors to Al during disordering, causing an increase in the number of chemically nonequivalent Al sites. The sites are sufficiently similar to one another, however, that their peaks cannot be resolved because of quadrupole-induced peak-broadening. The ^{27}Al chemical shifts at maximum intensity for both albite and oligoclase become more positive with increasing annealing time. This variation may be due to a progressively less shielded average chemical environment for Al sites or/and to progressively smaller average electric quadrupole coupling constants for ^{27}Al in the heated samples.

The ^{23}Na peak for albite changes from a doublet for low albite to a single peak with a smaller peak breadth for the heated samples. This type of variation implies that the Na sites become more symmetric with heating, in contrast to results by X-ray diffraction. The combination of our NMR and previous X-ray diffraction data suggests that the apparently large thermal anisotropy of Na in high albite and analbite indicated by X-ray diffraction arises from the averaging of several sites having relatively low anisotropy. The absence of a doublet in the ^{23}Na spectrum of low oligoclase correlates well with the Al-Si disorder indicated by the ^{29}Si spectra. The ^{23}Na data for heated oligoclases show that these Na sites also become less anisotropic with annealing.

As expected for thermally activated processes, the rates of variation in spectral shape for all three nuclides are much slower at 924°C than at 1073°C.

INTRODUCTION

In the last five years, high-resolution solid-state nuclear magnetic resonance spectroscopy (NMR) has become a powerful tool for investigating certain structural features of aluminosilicates. Since 1979, for example, there have been many determinations of the Al-Si distribution over the tetrahedral sites in zeolites using high-resolution solid-state ^{29}Si and ^{27}Al magic-angle sample-spinning (MASS) NMR (Engelhardt et al., 1981a, 1981b; Lippmaa et al., 1980, 1981; Bursill et al., 1981; Thomas et al., 1981a, 1981b, 1983; Ramdas et al., 1981; Klinowski et al., 1981a, 1981b; Fyfe et al., 1982; Melchior et al., 1982). ^{29}Si , ^{27}Al ,

and ^{23}Na MASS NMR spectra also contain a great deal of information about the Al-Si distribution; chemical bonding at the Si, Al, and Na sites; and distortion of these sites in feldspars (Kirkpatrick et al., 1985).

The major purpose of this study is to explore the use of ^{29}Si , ^{27}Al , and ^{23}Na MASS NMR spectroscopy in examining the Si, Al, and Na sites in a series of heat-treated albite and oligoclase specimens. In particular, we examine with respect to time and temperature (1) Al-Si disordering and (2) changes in structural environments of individual types of Si, Al, and Na sites in sodic plagioclase.

Two natural plagioclases, an albite from Amelia, Vir-

ginia, and an oligoclase from Bancroft, Ontario, were annealed in air at 924°C ($\pm 3^\circ$) and 1073°C ($\pm 3^\circ$) for various lengths of time up to 140 d. We present here (1) the ^{29}Si , ^{27}Al , and ^{23}Na MASS NMR spectra of the unheated and the annealed samples, (2) structural interpretations, and (3) correlations between NMR spectral parameters (including spectral shape, full width at half-height, and chemical shift) and annealing time and temperature. Our approach should be applicable to other feldspars and to other minerals.

The basic concepts of NMR are given by Davis (1965) and more advanced discussions by Abragam (1961), Farrar and Becker (1971), Becker (1980), and Akitt (1983). Summaries of the theory of solid-state MASS NMR are given by Lippmaa et al. (1980), Müller et al. (1981), K. A. Smith et al. (1983), and Kirkpatrick et al. (1985).

EXPERIMENTAL METHODS

Sample preparation, treatment, and characterization

Two natural plagioclases were used as starting materials for the annealing experiments: low albite ($\text{Ab}_{99.3}\text{An}_{0.1}\text{Or}_{0.6}$) (Harlow and Brown, 1980) from Amelia, Virginia, and oligoclase ($\text{Ab}_{72}\text{An}_{26.9}\text{Or}_{1.1}$) (by electron-microprobe analysis) from Bancroft, Ontario.

The samples were cleaned by abrasion in distilled water in a Spex vibratory ball mill and crushed to give pieces about $\frac{1}{2}$ cm across. More complicated cleaning methods were unnecessary because of the high purity of both samples. Each charge consisted of 3 g of sample wrapped in Pt foil.

Isothermal annealing experiments were carried out at 1073°C ($\pm 3^\circ$) and 924°C ($\pm 3^\circ$). At 1073°C, charges were annealed for various lengths of time from 1 to 100 d. At 924°C, charges were annealed for various lengths of time from 7 to 140 d. The measuring thermocouples were calibrated against the melting temperature of pure synthetic $\text{Na}_2\text{Si}_2\text{O}_7$ (874°C). After being annealed for a specific time, each charge was quenched in air and powdered for MASS NMR spectroscopy.

The indicated temperatures and times were chosen because high-temperature, single-crystal X-ray diffraction work by Winter et al. (1979) seems to demonstrate that heating Amelia albite to about 1070°C for 100 d should produce the high degree of Al-Si disorder required for the transformation to monalbite. (However, inversion to monalbite was not quite attained in a single-crystal study by Prewitt et al. (1976) on a synthetic (hydrothermal) intermediate albite annealed at 1060°C for 40 d.) On cooling, monalbite inverts to analbite, which should retain the complete or nearly complete Al-Si disorder of the monalbite. A temperature of 924°C should be just below that needed to produce the complete or nearly complete disorder required for monalbite, no matter what the length of time. The chosen range of annealing times at each temperature should provide a good series of disorderings ranging from the high degree of ordering in low albite to the high degrees of disordering in the high albite and analbite formed at high temperatures and long annealing times. Work such as that by McKie and McConnell (1963) indicates that the tetrahedral Al-Si distribution is correlated with annealing time as well as with temperature.

Cell refinements were made at room temperature for unheated albite and oligoclase and for several representative annealed specimens by powder X-ray diffractometry, using a Siemens Model D500 instrument, a graphite monochromator, and annealed CaF_2

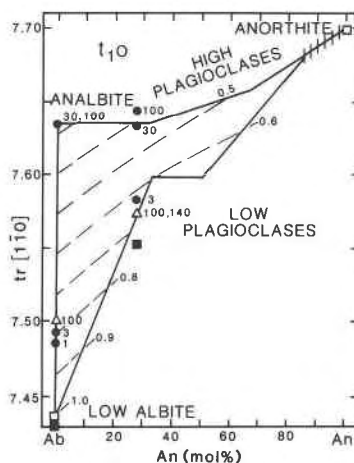


Fig. 1. $\text{Tr}[1\bar{1}0]$ versus An content for unheated and annealed Amelia albite (Ab_{99}) and Bancroft oligoclase (An_{27}). $\text{Tr}[1\bar{1}0] = \frac{1}{2}(a^2 + b^2 - 2ab \cos \gamma)^{1/2}$. Unheated albite and oligoclase are indicated by filled squares. Albite and oligoclase annealed at 1073°C are indicated by filled circles, and those at 924°C by open triangles. Adjacent numerals give annealing times in days. Approximate Al occupancies of T10 sites in plagioclase are contoured by inclined dashed lines (after Kroll, 1983).

as an internal standard. The computations for the refinements were done by the program of Appleman and Evans (1973).

NMR spectrometers

Two "home-built" Fourier-transform NMR spectrometers were used to obtain the spectra. One has an 8.45-T 3.5-in. bore superconducting solenoid ($T = \text{tesla}$; Oxford Instruments, Osney Mead, Oxford, England) and a variety of digital and radiofrequency electronics, including a Nicolet (Madison, Wisconsin) 1280 data system, 293B pulse programmer, NIC-2090 dual channel transient recorder, and a Diablo model 40 disc system for data storage (Diablo Systems, Inc., Haywood, California). The ^{29}Si spectra were obtained on this system at a resonance frequency of 71.5 MHz. The other spectrometer has an 11.7-T 2.0-in. bore solenoid, together with a Nicolet 1280 data system. The ^{27}Al and ^{23}Na spectra were obtained on this system. The 11.7-T corresponds to a ^{27}Al resonance frequency of 130.3 MHz and to a ^{23}Na resonance frequency of 132.3 MHz.

Andrew-Beams-type magic-angle sample-spinning rotor assemblies (Andrew, 1971) were used in both systems. The spinning rates were from 2.4 to 3.0 kHz at 8.45 T and from 3.0 to 4.2 kHz at 11.7 T. The magic angle was checked by the free induction decay and the intensity of the sidebands in the ^{79}Br spectrum of KBr packed with the samples.

The ^{29}Si chemical shifts are reported in parts per million relative to external tetramethylsilane (TMS), taken as +6.6 ppm upfield from hexamethyldisiloxane (in $\text{Cr}(\text{acac})_3$ -doped CH_2Cl_2) (HMDS). The ^{27}Al chemical shifts are reported in parts per million relative to 1 M AlCl_3 solution, and the ^{23}Na chemical shifts are relative to 1 M NaCl solution. More negative chemical shifts indicate greater shielding.

RESULTS

Powder X-ray diffraction

Before considering our NMR spectra, we present data obtained by powder X-ray diffractometry regarding the

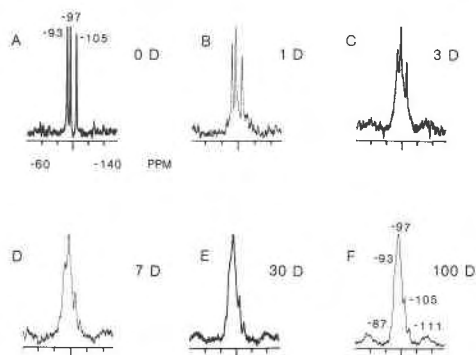


Fig. 2. ^{29}Si MASS NMR spectra of unheated Amelia low albite and of Amelia albite annealed at 1073°C for various times from 1 to 100 d. All spectra obtained with a 15-s recycle time, 50-kHz spectral width, $11.0\text{-}\mu\text{s}$ 90 degree pulse excitation and processed with 25-Hz line broadening due to exponential multiplication. (A) Unheated, 2.5-kHz spinning rate, and 3613 scans; (B) 1-d annealing, 2.9-kHz spinning rate, and 3613 scans; (C) 3-d annealing, 2.3-kHz spinning rate, and 3279 scans; (D) 7-d annealing, 2.8-kHz spinning rate, and 3613 scans; (E) 30-d annealing, 3.0-kHz spinning rate, and 3603 scans; (F) 100-d annealing, 2.7-kHz spinning rate, and 3585 scans.

structural states of representative samples. We compare the structural states of our samples by means of a part of the Kroll $[1\bar{1}0]$ method (summarized in Kroll, 1983) for estimating the structural states of plagioclases. For our purposes, it suffices to compare the approximate structural states of our albites with one another and of our oligoclases with one another by means of $\text{tr}[1\bar{1}0]$, the translational periodicity along $[1\bar{1}0]$. $\text{Tr}[1\bar{1}0]$ is obtained from the cell parameters of a feldspar via the expression (Kroll, 1983)

$$\text{tr}[1\bar{1}0] = \frac{1}{2}(a^2 + b^2 - 2ab \cos \gamma)^{1/2}.$$

Figure 1 shows a Kroll plot of $\text{tr}[1\bar{1}0]$ versus An content for most of our samples. Albite annealed at 1070°C for as little as a few days shows significant disordering of Al and Si atoms. Albite annealed at this temperature for 30 d apparently reaches the maximum disordered state. Heating for 100 d has little or no further effect on structural state. On the other hand, albite annealed at 924°C for 100 d only attains the structural state reached by albite after a few days at 1070°C . The situation for oligoclase is similar to that for albite.

In dealing with annealed specimens, several cases need to be distinguished. Therefore, we use the following terminology on an essentially operational basis. The phrase "the longest-annealed" feldspar refers to the specimen of the indicated composition that has been annealed for the longest time at the indicated temperature. The phrase "equilibrium"-annealed" feldspar refers to a feldspar annealed at an indicated temperature long enough that its state does not appear to change with longer heating; it is presumed to have reached its "equilibrium" state for that composition and temperature. The phrase "maximum-annealed" feldspar refers to a feldspar of the indicated composition that has been annealed long enough at a tem-

perature high enough to attain the highest possible structural state for that composition; the state does not appear to change with heating at a higher temperature or for a longer time. Inasmuch as our X-ray and NMR results were obtained at room temperature, it is to be understood that the above-mentioned "equilibrium" and maximum states refer to quenched annealed states. Other cases of annealing are referred to by stating the temperature and duration of the annealing.

Albite

Silicon-29. Figure 2 presents the ^{29}Si MASS NMR spectra of Amelia low albite and of Amelia albite annealed at 1073°C ($\pm 3^\circ$) for various lengths of time up to 100 d. These spectra show a systematic variation in shape from three narrow peaks for low albite to a complicated set of overlapping peaks for the longest-annealed albite. The number of peaks constituting each spectrum increases, the width of each peak broadens, and the relative intensity of each peak varies with annealing time. The total range of peak maxima changes from -93 to -105 ppm for low albite to -87 to -111 ppm for the longest-annealed albite. The range of chemical shifts from -87 to -111 ppm is almost equal to the total range of chemical shifts for T(0Al) to T(4Al) Si sites in framework aluminosilicates (Lippmaa et al., 1981; Thomas et al., 1983; K. A. Smith et al., 1983; Mägi et al., 1984). The symbol T(*n*Al) refers to the number (0 to 4) of Al tetrahedra that are linked to a given Si tetrahedron. T(3Al), for example, denotes those Si tetrahedra connected to three Al tetrahedra and one Si tetrahedron.

The spectrum of low albite (Fig. 2A) contains three narrow peaks and is essentially the same as that reported by Lippmaa et al. (1980) and Kirkpatrick et al. (1985). In this study, the peak assignment for this spectrum follows that proposed by K. A. Smith et al. (1983) and J. V. Smith et al. (1984). The peak at -93 ppm corresponds to T2m, which is T(2Al); and the peaks at -97 and -105 ppm correspond to T2o and T1m, respectively, which are T(1Al).

The spectrum of the longest-, and presumed equilibrium maximum-, annealed albite (Fig. 2F) contains five readily distinguished peaks or shoulders. Each peak or shoulder corresponds to one type of or a group of similar types of Si sites.

We use hereafter the phrases "crystallographically nonequivalent," "chemically nonequivalent," and "crystallochemically nonequivalent" (or "equivalent," as the case may be) in order to compare and contrast the X-ray and NMR behavior of various types of atomic sites. Crystallographically nonequivalent sites are sites belonging to different sets of equivalent positions in a structure. They lie on the equipoints of classical crystallography. The T1o, T1m, T2o, and T2m tetrahedral sites in low and high albite are familiar examples. The term chemically nonequivalent sites refers to sites producing distinguishable NMR chemical shifts. The earlier-mentioned T(*n*Al) sites are examples. Ordinarily, crystallographically nonequiv-

alent sites are also chemically nonequivalent. However, some crystallographically nonequivalent sites appear to be chemically equivalent because their shielding differs too little from that of other sites to produce a distinguishable peak or shoulder. Moreover, individual sites in a set of crystallographically equivalent ones may be chemically nonequivalent. An example of interest in this study is the occurrence of chemically nonequivalent sites in, for example, T1 crystallographically equivalent tetrahedral sites in monoclinic feldspars. Here, individual T1 sites can have differing $T(nAl)$ values, ranging from $T(0Al)$ to $T(4Al)$. According to classical space group theory, an ensemble of these differing T1 sites forms a statistically equivalent set; in diffraction records, for example, any differences in individual sites are averaged out. In NMR spectroscopy, however, each kind of site with a different shielding (e.g., different $T(nAl)$ value) produces a distinct signal if there are enough sites of that kind and the shielding differs enough from other sites, regardless of whether the sites are crystallographically equivalent or not. Consequently, we use the phrase crystallochemically nonequivalent sites when we wish to emphasize that certain resonances arise from both crystallographically and chemically nonequivalent sites. A simple example of this would be the 10 possible crystallochemically nonequivalent tetrahedral sites in monoclinic feldspar. These sets of sites arise from the 5 chemically nonequivalent $T(0Al)$, $T(1Al)$, $T(2Al)$, $T(3Al)$, and $T(4Al)$ sites in each of the T1 and T2 crystallographic types of sites. We use the symbols T1(0Al), T1(1Al), T2(0Al), etc., to designate the aforementioned 10 possible crystallochemically nonequivalent sites in monoclinic feldspars.

Deconvolution of the spectrum in Figure 2F obtained at a recycle time of 210 s into peaks for chemically nonequivalent sites is discussed below.

The peaks at -87 and -111 ppm first appear in the

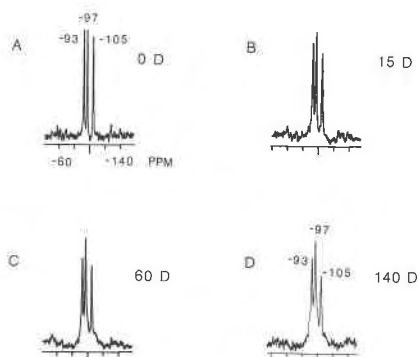


Fig. 3. ^{29}Si MASS NMR spectra of unheated Amelia low albite and of Amelia albite annealed at $924^{\circ}C$ for various times from 15 to 140 d. All spectra obtained with a 15-s recycle time, 50-kHz spectral width, $11\text{-}\mu s$ 90 degree pulse excitation and processed with 25-Hz line broadening due to exponential multiplication. (A) Unheated, 2.5-kHz spinning rate, and 3613 scans; (B) 15-d annealing, 2.4-kHz spinning rate, and 3613 scans, (C) 60-d annealing, 2.7-kHz spinning rate, and 3613 scans; (D) 140-d annealing, 2.6-kHz spinning rate, and 3400 scans.

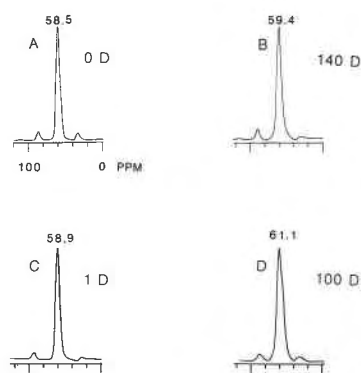


Fig. 4. ^{27}Al MASS NMR spectra of unheated Amelia low albite and of Amelia albite annealed at $924^{\circ}C$ and $1073^{\circ}C$ for various times from 1 to 140 d. All spectra obtained with a 5-s recycle time, 100-kHz spectral width, $4.2\text{-}\mu s$ 90 degree pulse excitation and processed with 100-Hz line broadening due to exponential multiplication. Spectra of other albite samples are very similar. (A) Unheated, 3.5-kHz spinning rate, and 1167 scans; (B) 140-d annealing at $924^{\circ}C$, 3.7-kHz spinning rate, and 225 scans; (C) 1-d annealing at $1073^{\circ}C$, 4.2-kHz spinning rate, and 452 scans; (D) 100-d annealing at $1073^{\circ}C$, 3.7-kHz spinning rate, and 924 scans.

spectrum of albite annealed 1 d (Fig. 2B). These new peaks become progressively more prominent with increasing annealing time (Figs. 2C–2F). There is almost no change in spectral shape between 30 and 100 d (Figs. 2E, 2F).

Figure 3 presents the spectra of low albite and of albites annealed at $924^{\circ}C$ for various lengths of time up to 140 d. As at $1073^{\circ}C$, there is a systematic variation in spectral

Table 1. Chemical shift at maximum intensity (CSMI) and full width at half-height (FWHH) of ^{27}Al MASS NMR spectra of unheated and annealed albites from Amelia County, Virginia

Annealing Time (Days)	^{27}Al Chemical Shift (PPM - 1 M $AlCl_3$)	Full Width At Half-Height (PPM)
Unheated		
0	58.5	6.5
$1073^{\circ}C$		
1	58.9	7.4
2	59.8	7.5
3	59.1	8.4
4	59.4	8.0
7	60.4	10.0
15	61.0	10.6
30	61.0	10.4
60	60.9	10.7
100	61.1	11.1
$924^{\circ}C$		
7	58.2	6.7
15	58.7	7.0
60	58.6	6.7
100	58.4	6.9
140	59.4	7.7

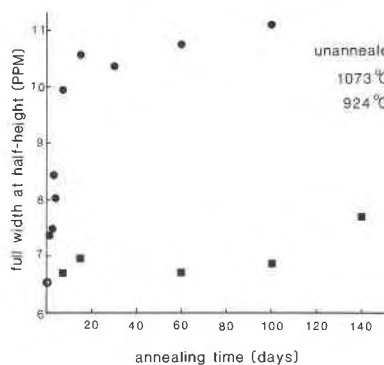


Fig. 5. ^{27}Al full width at half-height (ppm) for Amelia albite versus annealing time (days).

shape, but the rate of change is much lower. At 1073°C, changes in spectral shape are nearly complete after 7 d. At 924°C, changes still appear to be occurring after 140 d. The spectrum of the 140-d sample at 924°C is similar to that of the 1-d sample at 1073°C. At 924°C, the total range of peak maxima is the same as at 1073°C, -87 to -111 ppm, although for the 924°C samples, the peaks with high and low chemical shifts are less well defined.

The foregoing relations parallel the changes in structural state indicated by our powder X-ray diffraction results (Fig. 1).

Aluminum-27. Figure 4 presents the ^{27}Al MASS NMR spectra of albites at 1073 and 924°C along with that of low albite. Because ^{27}Al has spin $I = \frac{5}{2}$, these spectra suffer from second-order quadrupolar broadening (Kirkpatrick et al., 1985) so that MASS spectra with highly resolved peaks corresponding to individual Al sites are not to be expected. Each spectrum is composed of a single asymmetric, comparatively broad peak corresponding to tetrahedral Al only; there are no peaks in the region of 0 ppm corresponding to octahedral Al. The spectra of the heated albite samples not shown are very similar to those in Figure 4.

These ^{27}Al spectra show systematic variations in full

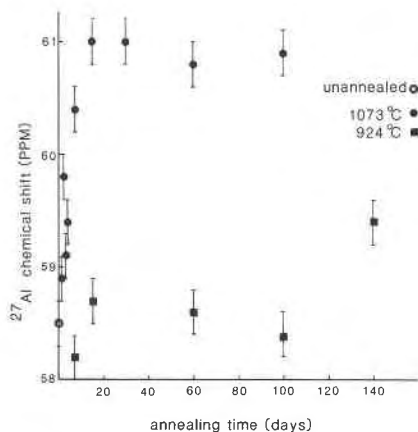


Fig. 6. ^{27}Al chemical shift at maximum intensity for Amelia albite versus annealing time (days).

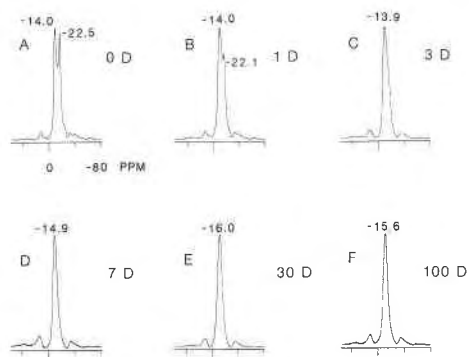


Fig. 7. ^{23}Na MASS NMR spectra of unheated Amelia low albite and of Amelia albite annealed at 1073°C for various times from 1 to 100 d. All spectra obtained with a 50-kHz spectral width, 3- μs 90 degree pulse excitation and processed with 10-Hz line broadening due to exponential multiplication. (A) Unheated, 3.4-kHz spinning rate, 981 scans, and 30-s recycle time; (B) 1-d annealing, 3.5-kHz spinning rate, 350 scans, and 20-s recycle time; (C) 3-d annealing, 3.4-kHz spinning rate, 704 scans, and 45-s recycle time; (D) 7-d annealing, 3.4-kHz spinning rate, 553 scans, and 45-s recycle time; (E) 30-d annealing, 3.4-kHz spinning rate, 1796 scans, and 25-s recycle time; (F) 100-d annealing, 3.4-kHz spinning rate, 400 scans, and 20-s recycle time.

width at half-height (FWHH) and in chemical shift at maximum intensity (CSMI) with increasing annealing time (Table 1; Figs. 5, 6). For the 1073°C samples, the FWHH changes asymptotically from 6.5 ppm for the low albite to about 11.0 ppm after 15 d (Fig. 5). For the 924°C samples, the FWHH increases much more slowly, to only 7.7 ppm after 140 d. For the 1073°C samples, the CSMI changes asymptotically from 58.5 ppm for the low albite to 61.1 ppm for the 100-d sample (Fig. 6), whereas for the 924°C samples, it changes to only 59.4 ppm after 140 d.

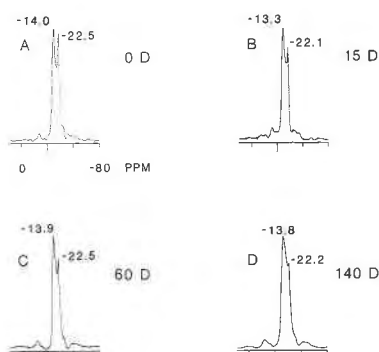


Fig. 8. ^{23}Na MASS NMR spectra of unheated Amelia low albite and of Amelia albite annealed at 924°C for various times from 15 to 140 d. All spectra obtained with a 50-kHz spectral width, 3- μs 90 degree pulse excitation and processed with 10-Hz line broadening due to exponential multiplication. (A) Unheated, 3.4-kHz spinning rate, 981 scans, and 30-s recycle time; (B) 15-d annealing, 3.0-kHz spinning rate, 271 scans, and 25-s recycle time; (C) 60-d annealing, 3.6-kHz spinning rate, 924 scans, and 40-s recycle time; (D) 140-d annealing, 3.7-kHz spinning rate, 1238 scans, and 20-s recycle time.

Table 2. Chemical shift of maximum intensity (CSMI) and full width at half-height (FWHH) of ^{23}Na MASS NMR spectra of unheated and annealed albites from Amelia County, Virginia

Annealing Time (Days)	^{23}Na Chemical Shift (PPM - 1 M NaCl)		Full Width At Half-Height (PPM)
<u>Unheated</u>			
0	-14.0	-22.5	14.2
<u>1073°C</u>			
1	-14.0	-22.1	14.1
2	-13.7	-20.3	12.9
3	-13.9		12.8
4	-14.8		13.6
7	-14.9		9.9
15	-15.0		9.1
30	-16.0		10.3
60	-16.0		10.2
100	-15.6		9.6
<u>924°C</u>			
7	-14.5	-23.3	14.6
15	-13.3	-22.1	14.7
60	-13.2	-21.9	14.2
100	-13.9	-22.5	14.2
140	-13.8	-22.2	14.0

The line broadening due to exponential multiplication used to process these spectra was 100 Hz, corresponding to about 0.8 ppm at half-height.

For the 1073°C samples, there is a significant reduction in the rate of variation of both FWHH and CSMI with increasing annealing time, and the variation is almost complete after 7 d. For the 924°C samples, changes appear to be still occurring at 140 d. Both these trends are similar

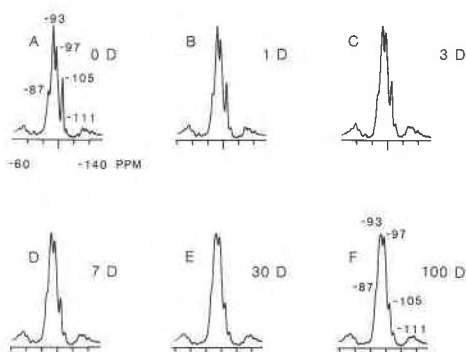


Fig. 9. ^{29}Si MASS NMR spectra of unheated Bancroft oligoclase and of Bancroft oligoclase annealed at 1073°C for various times from 1 to 100 d. All spectra obtained with a 10-s recycle time, 50-kHz spectral width, 5.0- μs 90 degree pulse excitation and processed with 25-Hz line broadening due to exponential multiplication. (A) Unheated, 2.7-kHz spinning rate, and 3589 scans; (B) 1-d annealing, 2.6-kHz spinning rate, and 3600 scans; (C) 3-d annealing, 2.4-kHz spinning rate, and 4744 scans; (D) 7-d annealing, 2.6-kHz spinning rate, and 3665 scans; (E) 30-d annealing, 2.8-kHz spinning rate, and 5000 scans; (F) 100-d annealing, 2.7-kHz spinning rate, and 3605 scans.

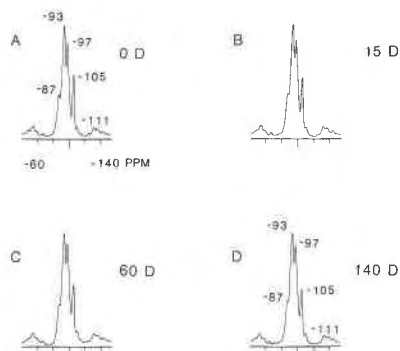


Fig. 10. ^{29}Si MASS NMR spectra of unheated Bancroft oligoclase and of Bancroft oligoclase annealed at 924°C for various times from 15 to 140 d. All spectra obtained with a 10-s recycle time, 50-kHz spectral width, 5.0- μs 90 degree pulse excitation and processed with 25-Hz line broadening due to exponential multiplication. (A) Unheated, 2.7-kHz spinning rate, and 3589 scans; (B) 15-d annealing, 2.8-kHz spinning rate, and 4101 scans; (C) 60-d annealing, 2.7-kHz spinning rate, and 3600 scans; (D) 140-d annealing, 2.8-kHz spinning rate, and 3600 scans.

to the variations in the ^{29}Si spectra (Figs. 2, 3) and our X-ray diffraction results.

Sodium-23. Figures 7 and 8 show ^{23}Na MASS NMR spectra of the same albite samples annealed at 1073 and 924°C. Because ^{23}Na has spin $I = 3/2$, its spectra also suffer from second-order quadrupolar peak broadening and sometimes splitting. The spectrum of low albite consists of a doublet with singularities at -14.0 and -22.5 ppm (Fig. 7A). This shape is due to second-order quadrupole effects, which are only partially eliminated by MASS, and not to the presence of two crystallographically nonequivalent Na sites (Kirkpatrick et al., 1985).

With annealing at 1073°C, the doublet gradually merges into a single peak, and the peak width becomes smaller with increasing annealing time (Table 2). As for ^{29}Si and ^{27}Al , change in the spectral shape is almost complete after 7 d. At 924°C, the rate of change is much slower, and the spectrum of the 140-d sample is very similar to that of the 1-d sample at 1073°C. These trends again parallel those of the ^{29}Si and ^{27}Al spectra and our X-ray diffraction data.

Oligoclase

Silicon-29. The ^{29}Si MASS NMR spectra of intermediate plagioclases are much more complex than those of endmember albite. Figure 9 presents the spectra of Bancroft low oligoclase and Bancroft oligoclase annealed at 1073°C for various lengths of time up to 100 d. These spectra also show systematic variation in spectral shape with annealing time. The spectrum of low oligoclase (Fig. 9A) consists of five readily distinguishable peaks at -87, -93, -97, -105, and -111 ppm. The peak widths in this spectrum are much broader than for low albite. With increasing annealing time, the peaks become even broader and are almost unresolvable for the longer runs. The relative intensity of each peak also varies with annealing

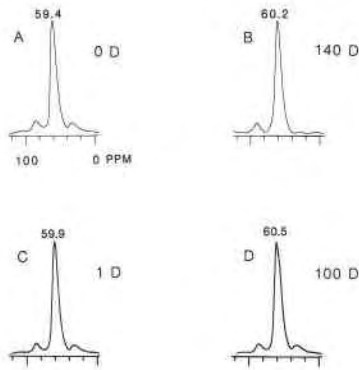


Fig. 11. ^{27}Al MASS NMR spectra of unheated Bancroft oligoclase and of Bancroft oligoclase annealed at 924°C and 1073°C for various times from 1 to 140 d. All spectra obtained with a 5-s recycle time, 100-kHz spectral width, 3.5- μs 90 degree pulse excitation and processed with 100-Hz line broadening due to exponential multiplication. Spectra of other oligoclase samples are very similar. (A) Unheated, 3.4-kHz spinning rate, and 4002 scans; (B) 140-d annealing at 924°C, 3.7-kHz spinning rate, and 225 scans; (C) 1-d annealing at 1073°C, 3.3-kHz spinning rate, and 3391 scans; (D) 100-d annealing at 1073°C, 3.3-kHz spinning rate, and 3234 scans.

time, although this is not as prominent as for albite. For oligoclase, the total range of chemical shifts covered by each spectrum ranges from -87 to -111 ppm and does not change with annealing time. Again, this range is almost equal to the total range of chemical shifts for T(OAl) to T(4Al) sites in framework aluminosilicates (Lippmaa et al., 1981; Thomas et al., 1983; K. A. Smith et al., 1983; Mägi et al., 1984).

Figure 10 presents the spectra of low oligoclase and of oligoclases annealed at 924°C for various times up to 140 d. There is some variation in spectral shape with increasing annealing time, but, as for albite, the rate of variation is much lower than at 1073°C. Changes in spectral shape are almost complete after 30 d at 1073°C but apparently are still occurring after 140 d at 924°C.

Aluminium-27. Figure 11 shows ^{27}Al MASS NMR spectra of the same oligoclases annealed at 1073 and 924°C.

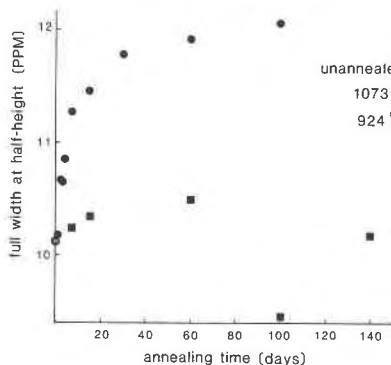


Fig. 12. ^{27}Al full width at half-height (ppm) for Bancroft oligoclase versus annealing time (days).

Table 3. Chemical shift at maximum intensity (CSMI) and full width at half-height (FWHH) of ^{27}Al MASS NMR spectra of unheated and annealed oligoclases from Bancroft, Ontario

Annealing Time (Days)	^{27}Al Chemical Shift (PPM - 1 M AlCl_3)	Full Width at Half-Height (PPM)
<u>Unheated</u>		
0	59.4	10.1
<u>1073°C</u>		
1	59.9	10.2
2	60.1	10.7
3	60.3	10.7
4	60.0	10.9
7	59.7	11.3
15	60.3	11.5
30	59.8	11.8
60	60.3	11.9
100	60.5	12.1
<u>924°C</u>		
7	59.6	10.2
15	60.0	10.4
60	59.9	10.5
100	60.4	9.5
140	60.2	10.2

As for albite, each spectrum of oligoclase consists of a single asymmetric peak corresponding to tetrahedral Al. The peak width of each spectrum of oligoclase is broader than for albite at the same annealing time and temperature. There is no peak in the region of 0 ppm corresponding to octahedral Al. The spectra of the heated oligoclase samples not shown are very similar to those in Figure 11.

The FWHH and CSMI also vary systematically with increasing annealing time (Table 3; Figs. 12, 13). For the 1073°C samples, the FWHH varies from 10.1 ppm for the unheated oligoclase to 12.1 ppm for the longest-annealed oligoclase, with the variation essentially complete at 30 d. For the 924°C samples, the FWHH increases to

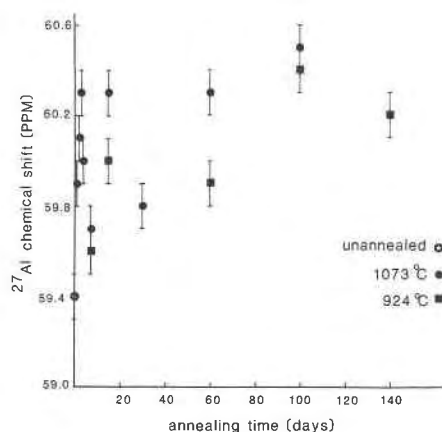


Fig. 13. ^{27}Al chemical shift at maximum intensity (ppm) for Bancroft oligoclase versus annealing time (days).

only about 10.5 ppm even after 60 d. The CSMI varies from 59.4 ppm for unheated oligoclase to 60.5 ppm for the longest-annealed oligoclase at 1073°C and to 60.2 ppm after 140 d at 924°C. The trends of these two parameters for oligoclase are not as clear as for albite, and the data points are more scattered than those for albite (Figs. 5, 6, 12, 13). This may be due to inhomogeneity (undetected by electron microprobe) or to a tiny amount of paramagnetic impurity in the oligoclase. These effects may also contribute to the peak broadening in the spectra of oligoclase.

For oligoclase annealed at 1073°C, the magnitude of variation in FWHH is about 2.0 ppm compared to 4.5 ppm for albite and that in CSMI is about 1.1 ppm compared to 2.6 ppm for albite. As for albite, both parameters show an initial rapid variation and a later slower variation, although for oligoclase the change in rate occurs at about 30 d instead of the 7 d for albite.

Sodium-23. Figure 14 shows the ^{23}Na MASS NMR spectra of some of the oligoclases. Each spectrum consists of a single, asymmetric peak. There is no doublet like that in the spectrum of low albite. The spectra of the heated oligoclase samples not shown are very similar to those in Figure 14. Table 5 lists the FWHH and the CSMI of these spectra. The FWHH of low oligoclase is narrower than that of low albite (Tables 2, 4). For the oligoclase, the FWHH decreases and the CSMI becomes more negative with increasing annealing time. For the 1073°C samples, variation in peak position is essentially complete after 1 d, and variation in FWHH is essentially complete after 2 d. For the 924°C samples, variation in both parameters continues up to 140 d.

DISCUSSION

Albite

Silicon-29. The ^{29}Si spectra of albite vary from three narrow peaks for low albite to a complicated set of multiple peaks and shoulders for the longest-annealed sample at 1073°C. The three equally intense, narrow peaks for low albite indicate a nearly completely ordered Al-Si distribution with essentially all the T1o sites occupied by Al and the others sites occupied by Si (J. V. Smith et al., 1984; Kirkpatrick et al., 1985). This distribution compares well with the tetrahedral Al occupancies found by Harlow and Brown (1980) for Amelia low albite by neutron diffraction: T1o, 0.97; T1m, 0.04; T2o, 0.0; and T2m, 0.0. The appearance of other peaks and the increased peak breadth for the heated samples clearly indicate progressively increasing Al-Si disorder with increasing annealing temperature and time, as expected from previous X-ray diffraction and TEM studies (McConnell and McKie, 1960; McKie and McConnell, 1963; Müller, 1969, 1970).

Five types of chemically nonequivalent Si sites arising from tetrahedral linkage are possible in framework aluminosilicates: T(0Al), T(1Al), T(2Al), T(3Al), and T(4Al). Completely ordered low albite contains only T(1Al) and T(2Al) sites. The peak at -93 ppm for low albite is T(2Al)

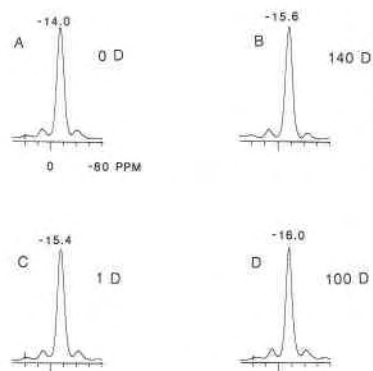


Fig. 14. ^{23}Na MASS NMR spectra of unheated Bancroft oligoclase and of Bancroft oligoclase annealed at 924°C and 1073°C for various times from 1 to 140 d. All spectra obtained with a 50-kHz spectral width, 3- μs 90 degree pulse excitation and processed with 10-Hz line broadening due to exponential multiplication. Spectra of other oligoclase samples are very similar. (A) Unheated, 3.4-kHz spinning rate, 271 scans, and 20-s recycle time; (B) 140-d annealing at 924°C, 3.7-kHz spinning rate, and 225 scans; (C) 1-d annealing at 1073°C, 3.4-kHz spinning rate, 400 scans, and 20-s recycle time; (D) 100-d annealing at 1073°C, 3.3-kHz spinning rate, 284 scans, and 25-s recycle time.

and the peaks at -97 and -105 ppm are T(1Al) (K. A. Smith et al., 1983; J. V. Smith et al., 1984). With even a slight degree of disordering, all five types of chemically nonequivalent Si sites from tetrahedral linkage could be present. The increase in the total range of chemical shifts of the peak maxima in even the shortest annealing run reflects the appearance of new chemically nonequivalent Si sites in addition to the original T(1Al) and T(2Al) sites. The total range from -87 to -111 ppm for these new sites in albite is almost equal to the total range of chemical shift for tetrahedral Si sites from T(0Al) to T(4Al) in framework aluminosilicates (Lippmaa et al., 1981; Thomas et al., 1983; K. A. Smith et al., 1983; Mägi et al., 1984).

There are four crystallographic kinds of tetrahedral sites in low and high albite, T1o, T1m, T2o, and T2m. When high albite inverts to monalbite on heating, these four crystallographic sites reduce to two, T1 and T2. Thus, a total of 10 crystallochemically nonequivalent Si sites is possible in monalbite, T1(0Al), T1(1Al), T1(2Al), T1(3Al), T1(4Al), T2(0Al), T2(1Al), T2(2Al), T2(3Al), and T2(4Al). When monalbite inverts to analbite on cooling, the two kinds of crystallographic sites change to four, so that a total of 20 crystallochemically nonequivalent Si sites is possible. However, despite the fact that analbite is triclinic and has four crystallographic sites (T1o, T1m, T2o, and T2m), departure of the aluminosilicate framework from monoclinic symmetry probably is so slight that the T1o and T1m sites are likely to be so similar to one another that they appear to be chemically equivalent by MASS NMR, and similarly for the sites T2o and T2m. (We label the pair of similar T1 sites T1o,m and the pair of similar T2 sites T2o,m.)

The complicated spectrum of maximum-annealed al-

Table 4. Chemical shift at maximum intensity (CSMI) and full width at half-height (FWHH) of ^{23}Na MASS NMR spectra of unheated and annealed oligoclases from Bancroft, Ontario

Annealing Time (Days)	^{23}Na Chemical Shift (PPM - 1 M NaCl)	Full Width At Half-Height (PPM)
<u>Unheated</u>		
0	-14.0	12.8
<u>1073°C</u>		
1	-15.4	12.6
2	-14.4	10.8
3	-15.5	11.4
4	-15.9	11.3
7	-15.8	11.0
15	-15.7	10.3
30	-15.9	10.6
60	-15.6	10.8
100	-16.0	10.6
<u>924°C</u>		
7	-14.7	12.4
15	-14.8	12.7
60	-15.2	13.0
100	-15.5	12.4
140	-15.6	12.7

bite, therefore, probably is due to up to 10 overlapping peaks corresponding up to 10 chemically nonequivalent Si sites arising from the five kinds of T(*n*Al) tetrahedral linkages for each of the crystallographic sites of type T1 and T2: that is, T1_{0,m}(0Al) to T1_{0,m}(4Al) and T2_{0,m}(0Al) to T2_{0,m}(4Al). The broadening of individual peaks is due to increasingly random substitution of Al atoms as the second tetrahedral neighbors to Si during Al-Si disordering.

Simulation of the ^{29}Si spectrum of albite annealed 100 d at 1073°C using the Nicolet peak-fitting program CAP indicates that it can be fitted by nine relatively broad peaks. The starting point for this simulation is the assignment of some of the resolved peaks (Fig. 2F). These assignments are based on the peak assignments for low albite (K. A. Smith et al., 1983; J. V. Smith et al., 1984; Kirkpatrick et al., 1985) and the ranges of ^{29}Si chemical shifts for the various T(*n*Al) sites in framework aluminosilicates (Lippmaa et al., 1981; K. A. Smith et al., 1983; Thomas et al., 1983; Mägi et al., 1984). An important feature of the spectrum of low albite is that T1_m(1Al) is about 8 ppm more shielded (more negative) than T2_m(1Al). We assume that a similar relationship holds here for each different type of T1_{0,m} and T2_{0,m} site. On the basis of this assumption, the peak at -111 ppm corresponds to T1_{0,m}(0Al), the peak at -105 ppm to T1_{0,m}(1Al), the peak at -97 ppm to T2_{0,m}(1Al), and the peak at -93 ppm to T2_{0,m}(2Al). The last three assignments are the same as in low albite. The positions of the peaks corresponding to other types of sites are determined by assuming that for both the T1_{0,m} and T2_{0,m} sites, substitution of an Al for a Si in the next-nearest-

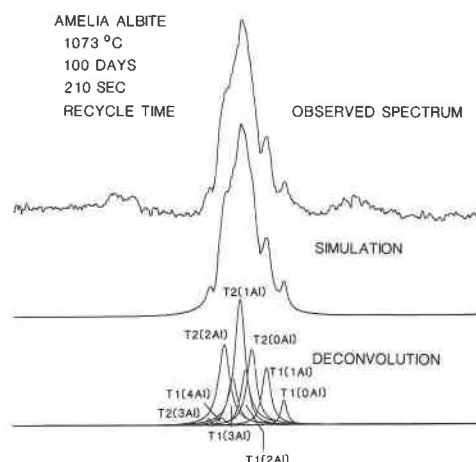


Fig. 15. Simulation of the ^{29}Si MASS NMR spectrum of Amelia albite annealed 100 d at 1073°C. Observed spectrum obtained with a 210-s recycle time is at the top; simulated spectrum in the middle (total RMS error = 5.4), and the nine individual peaks contributing to the simulated spectrum at the bottom. The nine broad deconvoluted peaks correspond to nine chemically nonequivalent sites. All individual peaks are 100% Lorentzian in shape. See text for further explanation.

tetrahedral-neighbor coordination shell to Si causes an approximately 5.5 ppm deshielding (shift to less negative value). This is the same sort of variation found for many zeolites with one crystallographic kind of Si site but several chemically nonequivalent sites (Lippmaa et al., 1981; Engelhardt et al., 1981b; Klinowski et al., 1982; Thomas et al., 1983). Figure 15 shows the result of this simulation. The lower spectrum shows nine individual peaks, and the middle spectrum shows the sum of the nine peaks. There are nine instead of ten broad peaks because the Si concentration in T2_{0,m}(4Al) appears to be too small to produce a recognizable peak or shoulder.

Because ^{29}Si has $I = 1/2$ and because a relatively long recycle time (210 s) was used, the area under each deconvoluted peak represents the relative population of Si in each type of site. The areas of the deconvoluted peaks are only slightly different than those in a spectrum collected with a recycle time of 15 s, indicating that all the sites are relaxing fully. Table 5 presents a comparison of these values with the values calculated using the method of Klinowski et al. (1982). The primary assumption of this calculation is that the aluminum avoidance principle (Loewenstein, 1954) is obeyed. Given this assumption—that is, that each Al tetrahedron is coordinated to four Si tetrahedra—the probability (P) of an Si-O-Al linkage is the Al/Si ratio, and the probability of an Si-O-Si linkage is $(1 - P)$. The average relative populations of Si in the five chemically nonequivalent tetrahedral sites can be calculated by the binomial formula as follows: P^4 for T(4Al), $4(1 - P)P^3$ for T(3Al), $6(1 - P)^2P^2$ for T(2Al), $4(1 - P)P$ for T(1Al), and $(1 - P)^4$ for T(0Al). The agreement between the simulated and calculated values is good.

Although the simulated distribution of the populations

Table 5. Comparison of the relative areas under deconvoluted peaks (simulated distribution) of the ^{29}Si MASS NMR spectrum of Amelia albite annealed 100 d at 1073°C in Figure 15 and the calculated relative populations of Si in the five chemically and crystallographically nonequivalent tetrahedral sites (calculated distribution) using the methods of Klinowski et al. (1982).

Peak Position (PPM)	Simulated Distribution(%)		Calculated Distribution(%)		
-111.7	T1(OA1)	2.7	19.3	T(OA1)	19.3
-101.2	T2(OA1)	16.6			
-106.1	T1(1A1)	8.9	39.3	T(1A1)	39.2
-97.5	T2(1A1)	30.4			
-99.5	T1(2A1)	7.8	30.1	T(2A1)	30.0
-92.9	T2(2A1)	22.3			
-95.0	T1(3A1)	8.9	10.4	T(3A1)	10.2
-87.5	T2(3A1)	1.5			
-91.3	T1(4A1)	0.9	0.9	T(4A1)	1.3
--	T2(4A1)	0.0			
			100.0		100.0

T2/T1 = 2.4

$$T1 = T1(OA1) + T1(1A1) + T1(2A1) + T1(3A1) + T1(4A1)$$

$$T2 = T2(OA1) + T2(1A1) + T2(2A1) + T2(3A1) + T2(4A1)$$

of the different chemically nonequivalent Si sites is in good agreement with the theoretical values (Table 5), the relative populations of Si in T1_{o,m} and T2_{o,m} are not equal, as they should be in a fully disordered material. These values are the sums of the relative areas under all T1_{o,m} peaks and under all T2_{o,m} peaks. The population ratio T2_{o,m}/T1_{o,m} should be 1.0 if the Al-Si distribution is completely disordered whereas the ratio for the simulated peaks is 2.4. The latter ratio implies that the Al-Si distribution in the longest-annealed albite is still far from being completely disordered and that even at 1073°C the T1_{o,m} site still prefers Al relative to the T2_{o,m} site. Although our powder X-ray diffractometry results (Fig. 1) indicate no significant change in structural state after 30-d annealing at 1073°C, the method used probably is not a highly sensitive or accurate one. Grundy and Brown (1967) and Prewitt et al. (1976) have pointed out that it is impossible to determine the structural state of high albite (and analbite) accurately on the basis of room temperature X-ray data.

The ^{29}Si NMR data indicate that Al-Si disorder in our Amelia albite reaches a constant value after 30-d annealing at 1073°C and that it is not fully disordered. This in turn implies that this albite did not quite attain monoclinic symmetry, a result that is not consistent with the observation of monoclinic symmetry by Winter et al. (1979) for Amelia albite that had been annealed at tem-

peratures up to 1110°C for 133 d. On the other hand, Prewitt et al. (1976) observed that hydrothermally synthesized albite heated for 40 d at nearly 1100°C did not become truly monoclinic even at 1105°C, and Winter et al. (1979) found that Tiburon albite annealed at 1080°C for 60 d did not become truly monoclinic.

The inversion of high albite to monalbite clearly is not a simple matter and does not occur at a constant transition temperature independently of the thermal history of a specimen.

As expected for a thermally activated process, the rate of variation in spectral shape at 924°C is much slower than at 1073°C. Because of the relatively sluggish rate of Al-Si migration at 924°C, it would take an extremely long time to obtain an equilibrium Al-Si distribution at this temperature. The spectra of albites annealed at 924°C and shown in Figure 3 represent, therefore, nonequilibrium high albites with various states of Al-Si distribution. The ^{29}Si spectrum of an equilibrium albite annealed at 924°C probably would be different from that of an equilibrium albite annealed at 1073°C because of different equilibrium Al-Si distributions.

Aluminum-27. Despite the presence of only one resolvable peak in the ^{27}Al NMR spectra of our albites, these spectra can yield considerable information about variation in the albite structure during Al-Si disordering. We interpret the increase in FWHH with increasing annealing

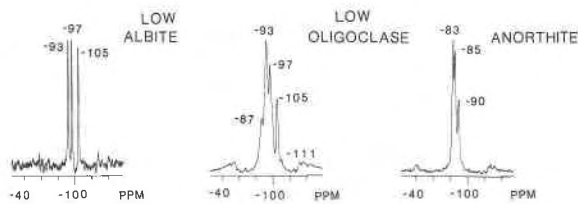


Fig. 16. ^{29}Si MASS NMR spectra of Amelia low albite, Bancroft low oligoclase (both obtained in this study), and synthetic anorthite (Kirkpatrick et al., 1985).

time to be due primarily to occupancy of sites other than T1o,m and to an increasingly random distribution of Al atoms in the second-tetrahedral-neighbor-to-Al sites during disordering. This variation in the second-tetrahedral-neighbor population causes an increase in the number of chemically nonequivalent Al sites. In addition, some departure from ideal aluminum avoidance is to be expected at these high temperatures.

In fully ordered low albite, Al occupies only T1o. The single ^{27}Al peak of unannealed low albite (Fig. 4A) can be simulated well by one peak (Kirkpatrick et al., 1985). If there is any Al-Si disorder, Al atoms can occupy all four kinds of crystallographically nonequivalent tetrahedral sites. For each of these crystallographically nonequivalent sites, there will be 11 chemically nonequivalent sites, corresponding to 0 to 10 Al atoms in the second nearest-neighbor tetrahedral sites. Unfortunately, because of peak broadening by second-order quadrupole interaction and the relatively small effect on the isotropic chemical shift, this increase in the number of chemically nonequivalent Al sites results only in an increased peak breadth and not in an increase in the number of peaks.

The progressive deshielding at Al sites with increasing annealing time is probably due to a less-shielded average electronic environment for the range of Al sites in the annealed samples. It could, however, also be due to a smaller average quadrupole coupling constant, which would reduce the displacement of the peak position from the isotropic value. The value of the quadrupole coupling constant for the annealed samples cannot be obtained because the observed peak is the sum of peaks from a large number of chemically nonequivalent sites.

Sodium-23. The variation in albite structure with annealing also affects the ^{23}Na spectra. The doublet in the spectrum of low albite (Fig. 7A) is the result of a large second-order quadrupole interaction that is only partially eliminated by MASS. Kirkpatrick et al. (1985) estimated an e^2qQ/h of 2.62 MHz for this site. This amount of quadrupolar splitting indicates an extremely anisotropic Na site with a large electric field gradient and is consistent with the X-ray diffraction data of Ferguson et al. (1958) and Ribbe et al. (1969). The doublet merges into a single peak, and the peak width decreases with increasing annealing time (Figs. 7, 8), because the extremely anisotropic Na site in low albite becomes less anisotropic on heating.

Apparently, Al-Si disordering reduces the electric field gradient at the Na nucleus, which decreases the ^{23}Na quadrupole coupling constant.

The ^{23}Na NMR data indicate that the greater anisotropy of the Na site in high albite (or analbite) shown by X-ray diffraction data (Prewitt et al., 1976; Winter et al., 1979) is due to spatial disorder of Na. The individual Na sites are actually less anisotropic than in ordered low albite. There must be a large number of chemically nonequivalent Na sites with different numbers of Al and Si nearest tetrahedral neighbors in annealed albite. Unfortunately, these chemically nonequivalent Na sites are not resolvable in our ^{23}Na MASS spectra because of second-order quadrupole effects and a small range of isotropic chemical shifts. As for ^{27}Al , e^2qQ/h and η for ^{23}Na cannot be calculated for the annealed samples because of the overlap of signal from different sites. The narrowing of the Na peak appears to be due to Al-Si disordering because at 1073°C the changes are complete in about 7 d, whereas at 924°C they are still occurring even after 140 d.

Oligoclase

Silicon-29. Interpretation of the more complicated spectra of oligoclase is based on the interpretation of the spectra of albite and anorthite and follows the interpretations of these spectra by Kirkpatrick et al. (1985). Figure 16 presents the ^{29}Si spectra of low albite and low oligoclase obtained in this study and that of synthetic anorthite reported by Kirkpatrick et al. (1985).

The spectrum of synthetic anorthite is composed of three poorly resolved peaks. Anorthite contains eight crystallographically nonequivalent T(4Al) Si sites (Megaw et al., 1962; Wainwright and Starkey, 1971; Staehli and Brinkmann, 1974a, 1974b). Kirkpatrick et al. (1985) have interpreted this spectrum and made peak assignments based on Si-O-Al bond angles. They pointed out that there are three groups of similar Si sites in anorthite, each group giving rise to one peak. All three peaks fall in the range of chemical shifts for T(4Al) Si sites in the framework aluminosilicates (Lippmaa et al., 1981; Thomas et al., 1983; K. A. Smith et al., 1983; Mägi et al., 1984).

The spectrum of low oligoclase is composed of five broad peaks with isotropic chemical shifts of -87, -93, -97, -105, and -111 ppm. These can be assigned to albite-like and anorthite-like Si sites such as would be expected for an *e*-plagioclase having both albite-like and anorthite-like domains. The bulk composition of this oligoclase is $\text{An}_{26.9}\text{Ab}_{72}\text{Or}_{1.1}$, which falls between the peristerite ($\text{An}_2\text{-An}_{16}$) and Bøggild ($\text{An}_{47}\text{-An}_{58}$) gaps. Most of the peak at -93 ppm and the peaks at -97 and -105 ppm correspond to the albite-like T2m, T2o, and T1m sites, respectively. The peak at -87 ppm and part of the peak at -93 ppm represent two groups of T(4Al) anorthite-like Si sites. The small peak at -111 ppm is from T(0Al) sites and probably indicates a small degree of Al-Si disorder in the albite-like domains.

This spectrum indicates clearly that the oligoclase is not

simply a mechanical mixture of low albite and anorthite, because the least-shielded anorthite peaks are not present and because the albite-like peaks are much broader and of different relative intensities than those in low albite. The *e*-plagioclase model of J. V. Smith and Ribbe (1969), which postulates alternating albite-like and anorthite-like domains separated by strained boundary regions, can account for the spectrum. The width of the albite-like and anorthite-like domains in *e*-plagioclase varies with bulk composition. In oligoclase the albite-like domains are relatively thick and the anorthite-like domains relatively thin, perhaps too thin to develop the complete anorthite structure. The anorthite-like domains are likely to be highly strained, with the Si–O bond lengths becoming shorter due to compression at the coherent phase boundary. On the other hand, the Si–O bond lengths in the strained portions of the albite-like domains become longer. Si sites in the strained portions of both components give rise to a broad signal in the range –90 to –100 ppm. Apparently, most of the sites in anorthite that normally give rise to the –83 ppm peak are sufficiently strained so as to cause more-shielded chemical shifts.

Figures 9 and 10 show that the ^{29}Si spectra of oligoclases change shape systematically with increasing annealing time. These changes reflect the variation in Al-Si order and in the periodic superstructure of oligoclase during annealing. The Al-Si disordering in the low oligoclase allows all five types of chemically nonequivalent tetrahedral Si sites to exist. This explains why the total range of peak positions in the ^{29}Si spectra (–87 to –111 ppm) does not change with increasing annealing time. The increase of peak width with increasing annealing time can, then, be ascribed to an increasingly random distribution of Al and Si. The variation in intensity of each peak reflects the redistribution of Si among the various tetrahedral sites.

McConnell (1974) found that the superstructure for An_{37} and An_{53} is eliminated and homogenized to a $\text{C}\bar{1}$ Al-Si disordered array analogous to high albite at 600°C and 800°C, respectively. Thus, if the annealing time is long enough, the superstructure of the *e*-plagioclase in maximum-annealed oligoclase should be eliminated at both 1073°C and 924°C because the critical temperature for eliminating the superstructure of oligoclase with a bulk composition of $\text{An}_{26.9}$ should be lower than 600°C. The similarity of the 30-d and 100-d spectra in Figure 9 shows that this has happened by 30 d at 1073°C. Figure 10 shows that it has not happened by 140 d at 924°C.

The spectrum of maximum-annealed oligoclase at 1073°C is very similar to that of maximum-annealed albite (Fig. 2F) except that the oligoclase has higher intensity in the –93 and –87 ppm peaks. This difference is due to the larger number of T(3Al) and T(4Al) Si sites in the oligoclase, reflecting its higher Al/(Al + Si) ratio. Some peak assignments for the five peaks and shoulders in the spectrum of maximum-annealed oligoclase can be based on the interpretation of maximum-annealed albite. These assignments are –111 ppm, T1(0Al); –105 ppm, T1(1Al); –97 ppm, T2(1Al); –93 ppm T2(2Al); –87 ppm, T2(3Al).

As for albite, the rate of Al-Si disordering in oligoclase is much lower at 924°C than at 1073°C.

Aluminum-27. The variation in the ^{27}Al spectra of annealed oligoclase is similar to but smaller than that of albite (Tables 1, 3). The spectrum of low oligoclase has a FWHH of 10.1 ppm, which is significantly broader than the 6.5 ppm FWHH of low albite. This increased peak breadth is consistent with the lack of complete Al-Si ordering in intermediate plagioclases and probably is caused by the Al signal from anorthite-like and albite-like domains and from the strained boundary regions between them.

As for albite, the increase in FWHH with increasing annealing time can be ascribed to an increased Al occupation of other than T1_{0,m} sites and to an increasingly random distribution of Al atoms as the second tetrahedral neighbors to Al. The magnitude of variation in the FWHH of oligoclase is significantly smaller than for albite. This is consistent with the idea that a completely disordered Al-Si distribution like that in analbite is not attainable in high plagioclases of intermediate bulk composition (Kroll, 1983). The smaller range of variation in FWHH indicates a smaller extent of Al-Si redistribution during disordering in oligoclase. The larger final value of FWHH for oligoclase may be due to the presence of a paramagnetic impurity. The variation in the CSMI is also similar to that for albite. The progressive deshielding at Al with increasing annealing time is probably due to a less-shielded average chemical shift for the range of Al sites in the annealed samples or to a decreased quadrupole coupling constant.

As for ^{29}Si , changes in the ^{27}Al spectra of oligoclase with annealing are complete after about 30 d at 1073°C but are still continuing after 140 d at 924°C. The FWHH and CSMI for the spectrum of maximum-annealed oligoclase at 1073°C may not be attainable at 924°C because the equilibrium distribution of Al and Si should be different at different temperatures.

Sodium-23. The ^{23}Na spectrum of low oligoclase is quite different from that of low albite. The absence of a doublet and the narrower peak width in the spectrum of low oligoclase implies a more isotropic Na site than in low albite. This suggests that for oligoclase the Al-Si disorder in the strained boundary regions and in the albite-like volumes indicated by the T(0Al) ^{29}Si peak at –111 ppm (Fig. 10A) reduces the electric field gradient at Na, thus reducing the quadrupole coupling constant. If this is true, ^{23}Na MASS NMR spectra are very sensitive to the existence of Al-Si disordering in plagioclase. The Ca in the oligoclase might also cause the same effect, although it is much farther from the Na than are Si and Al.

As for albite, the reduction in ^{23}Na peak width with increasing annealing time (Table 4) indicates that the Na site in oligoclase becomes more isotropic as the Al-Si distribution becomes more disordered. The increased shielding at Na with increasing annealing time could be due to a more shielded isotropic chemical shift or to a decreased e^2qQ/h . The ^{23}Na data indicate that the rate of

Al-Si disordering in oligoclase is significantly slower at 924°C than at 1073°C. This variation is fully consistent with the ^{29}Si and ^{27}Al data.

At 1073°C, the rate of variation indicated by the X-ray and NMR data is significantly faster for albite than for oligoclase (7 versus 30 d to attain maximum Al-Si disorder). This is likely to be a consequence of the exchange of Al and Si atoms over longer distances in oligoclase because of its modulated, *e*-plagioclase structure.

CONCLUSIONS

Al-Si disordering in plagioclase at high temperature is readily observable by ^{29}Si , ^{27}Al , and ^{23}Na MASS NMR. Of these, ^{29}Si is the most useful. The changes in spectral shape for all three nuclides are due to the combined effects of variation in number, width, and intensity of peaks caused mainly by increasing randomness in the Al-Si distribution.

The three narrow peaks with nearly the same intensity in the ^{29}Si NMR spectrum of low albite correspond to the three crystallographically nonequivalent Si sites T1m, T2o, and T2m and indicate a completely ordered Al-Si distribution. The range of chemical shifts covered by the spectrum expands from -93 to -105 ppm for low albite to -87 to -111 ppm for the maximum-annealed albite at 1073°C. This variation reflects the appearance of new chemically nonequivalent tetrahedral Si sites. The complicated spectrum of maximum-annealed albite can be simulated by nine broad peaks corresponding to nine of ten possible kinds of crystallochemically nonequivalent tetrahedral Si sites. Although a completely disordered Al-Si distribution in albite is theoretically attainable, the simulation indicates that the Al-Si distribution is not completely disordered, with Al still preferring T1o,m and Si preferring T2o,m.

The broader peaks and greater number of peaks and shoulders in the ^{29}Si spectrum of low oligoclase indicate a more disordered Al-Si distribution than for low albite. These peaks can be explained in terms of the *e*-plagioclase model for low oligoclase. The small amount of change with annealing in the chemical shift range covered by the spectra of oligoclase is additional evidence for the existence of Al-Si disorder in low oligoclase. Some of the five peaks in the spectrum of low oligoclase can be assigned to Si sites similar to those in albite and others to sites like those in anorthite.

The ^{29}Si spectra of maximum-annealed oligoclase and of maximum-annealed albite are quite similar. The higher intensity of the -93 and -87 ppm peaks for maximum-annealed oligoclase is due to the higher ratio of Al to Si, which causes a higher mean number of Al nearest-neighbor tetrahedra to Si. The five peaks in the ^{29}Si spectrum of maximum-annealed oligoclase can be assigned in the same manner as for the spectrum of maximum-annealed albite.

^{27}Al MASS NMR spectra also appear to be useful indicators of the state of Al-Si distribution. The increase in

FWHH with annealing is due mainly to an increasingly random distribution of Al atoms as the second tetrahedral neighbors to Al, which increases the number of chemically nonequivalent Al sites, and to Al occurring in both T1o,m and T2o,m sites. The progressive deshielding of the CSMI probably is due to (1) a less-shielded average chemical shift for the various Al sites in the annealed samples and/or (2) a decreased average quadrupole coupling constant.

The broader ^{27}Al peak for low oligoclase reflects a more disordered Al-Si distribution than in low albite. The smaller variations in FWHH and CSMI for oligoclase are consistent with there being no completely ordered low-intermediate plagioclase and no completely disordered high-intermediate plagioclase.

The ^{23}Na spectrum of low albite has a doublet caused by second-order quadrupolar interaction, indicating highly anisotropic Na sites. The merging of the doublet and decrease in peak width with increasing annealing time is due to the Na sites becoming less anisotropic as Al-Si disordering proceeds. The ^{23}Na spectrum provides, therefore, an indirect indicator of the degree of Al-Si disorder in albite. The greater anisotropy of the Na sites in high albite and analbite shown by X-ray diffraction data is caused by spatial disorder of the Na sites and thermal anisotropy. The Na sites within each domain in high albite and analbite are more isotropic than in low albite.

There is no quadrupole-induced doublet in the ^{23}Na spectrum of low oligoclase. This implies that the Al-Si disorder in this sample greatly reduces the anisotropy of the Na sites. The peak widths of the ^{23}Na spectra of oligoclase also decrease with increasing annealing time, but the magnitude of variation is smaller than for albite. This is related to the initially incompletely ordered Al-Si distribution in low oligoclase.

For both albite and oligoclase, the rate of change of spectral shape is much lower at 924°C than at 1073°C. In addition, at 1073°C the rate of change of spectral shape for all three nuclides decreases after 7 d for albite and 30 d for oligoclase. These systematic variations indicate that variations in the Al-Si distribution cause the changes in the spectra of all the nuclides.

ACKNOWLEDGMENTS

We wish to thank Eric Oldfield for his continuing interest in and help with this study and to Bernard Montez, Karen Ann Smith, and Gary Turner for their help in solving the frequently unexpected problems with NMR spectrometers. We thank also Youn Joong Kim for providing us with powder X-ray cell refinements for most of our samples, and John Higgins for a useful review of the manuscript.

This study was supported by NSF Grants EAR-8218741, EAR-8207260, and EAR-8408421 and has benefited from the use of the NSF-supported regional NMR facility at the University of Illinois at Urbana-Champaign.

REFERENCES

- Abragam, A. (1961) The principles of nuclear magnetism. Clarendon Press, Oxford.
- Akitt, J.W. (1983) NMR and chemistry: An introduction to the

- Fourier transform—multinuclear era (2nd edition). Chapman and Hall, London.
- Andrew, E.T. (1971) The narrowing of NMR spectra of solids by high-speed specimen rotation and the resolution of chemical shift and spin multiplet structures for solids. *Progress in NMR Spectroscopy*, 8, 1–39.
- Appleman, D.E., and Evans, H.T., Jr. (1973) Job 9214: Indexing and least-squares refinement of powder diffraction data. U.S. Geological Survey, Computer Contribution 20. U.S. National Technical Information Service, Document PB2-16188.
- Becker, H.D. (1980) High resolution NMR, theory and applications (2nd edition). Academic Press, New York.
- Bursill, L.A., Lodge, E.A., Thomas, J.M., and Cheetham, A.K. (1981) New light on the crystal structure of zeolite A. *Journal of Physical Chemistry*, 85, 2409–2421.
- Davis, J.C. (1985) *Advanced physical chemistry*. Ronald Press, New York.
- Engelhardt, G., Lohse, U., Lippmaa, M., and Mägi, M. (1981a) ²⁹Si-NMR-untersuchungen zur Verteilung der Silicium und Aluminiumatome im Aluminosilicatgitter von Zeolithen mit Faujasit-Struktur. *Zeitschrift für Anorganische und Allgemeine Chemie*, 482, 49–64.
- Engelhardt, G., Lippmaa, E., and Mägi, M. (1981b) Ordering of silicon and aluminum ions in the framework of NaX zeolites. A solid-state high-resolution ²⁹Si NMR study. *Journal of the Chemical Society, Chemical Communications*, 712–713.
- Farrar, T.C., and Becker, E.D. (1971) *Pulse and Fourier transform NMR: Introduction to theory and methods*. Academic Press, New York.
- Ferguson, R.B., Traill, R.J., and Taylor, W.H. (1958) The crystal structures of low-temperature and high-temperature albites. *Acta Crystallographica*, 11, 331–348.
- Fyfe, C.A., Gobbi, G.C., Hartman, J.S., Klinowski, J., and Thomas, J.M. (1982) Solid-state magic-angle spinning aluminum-27 nuclear magnetic resonance studies of zeolites using a 400-MHz high-resolution spectrometer. *Journal of Physical Chemistry*, 86, 1247–1250.
- Grundy, H.D., and Brown, W.L. (1967) Preliminary single-crystal study of the lattice angles of triclinic feldspars at temperatures up to 1200°C. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 47, 21–30.
- Harlow, G.E., and Brown, G.E., Jr. (1980) Low albite: An X-ray and neutron diffraction study. *American Mineralogist*, 65, 986–995.
- Kirkpatrick, R.J., Kinsey, R.A., Smith, K.A., Henderson, D.M., and Oldfield, E. (1985) High-resolution solid-state sodium-23, aluminum-27 and silicon-29 nuclear magnetic resonance spectroscopic reconnaissance of alkali and plagioclase feldspars. *American Mineralogist*, 70, 106–123.
- Klinowski, Jacek, Thomas, J.M., Fyfe, C.A., and Hartman, J.S. (1981a) Applications of magic-angle-spinning silicon-29 nuclear magnetic resonance. Evidence for two different kinds of silicon-aluminum ordering in zeolitic structures. *Journal of Physical Chemistry*, 85, 2590–2594.
- Klinowski, Jacek, Thomas, J.M., Audies, M., Vasudevan, S., Fyfe, C.A., and Hartman, J.S. (1981b) Solid-state ²⁹Si NMR and high-resolution electron microscopic studies of a silicate analogue of faujasite. *Journal of the Chemical Society, Chemical Communications*, 570–571.
- Klinowski, Jacek, Ramdas, S., Thomas, J.M., Fyfe, C.A., and Hartman, J.S. (1982) A re-examination of Si,Al ordering in zeolites NaX and NaY. *Journal of the Chemical Society, Faraday Transactions*, 2, 78, 1025–1050.
- Kroll, Herbert. (1983) Lattice parameters and determinative methods for plagioclase and ternary feldspars. In *Feldspar mineralogy* (2nd edition). Mineralogical Society of America Reviews in Mineralogy, 2, 57–98.
- Lippmaa, Endel, Mägi, M., Samoson, A., Engelhardt, G., and Grimmer, A.-R. (1980) Structural studies of silicates by solid-state high-resolution ²⁹Si NMR. *American Chemical Society Journal*, 102, 4889–4893.
- Lippmaa, Endel, Mägi, M., Samoson, A., Tarmak, M., and Engelhardt, G. (1981) Investigation of the structure of zeolites by solid-state high-resolution ²⁹Si NMR spectroscopy. *American Chemical Society Journal*, 103, 4992–4996.
- Loewenstein, Walter. (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates. *American Mineralogist*, 39, 92–96.
- Mägi, Mart, Lippmaa, E., Samoson, A., Engelhardt, G., and Grimmer, A.-R. (1984) Solid-state high-resolution silicon-29 chemical shifts in silicates. *Journal of Physical Chemistry*, 88, 1518–1522.
- McConnell, J.D.C. (1974) Analysis of the time-temperature-transformation behaviour of the plagioclase feldspars. In W.S. Mackenzie and J. Zussman, Eds. *The feldspars*, 460–477. Manchester University Press, Manchester.
- McConnell, J.D.C., and McKie, D. (1960) The kinetics of the ordering process in triclinic NaAlSi₃O₈. *Mineralogical Magazine*, 32, 436–454.
- McKie, D., and McConnell, J.D.C. (1963) The kinetics of the low → high transformation in albite. I. Amelia albite under dry conditions. *Mineralogical Magazine*, 33, 581–588.
- Megaw, H.D., Kempster, C.J.E., and Radoslovich, E.W. (1962) The structure of anorthite, CaAl₂Si₂O₈. II. Description and discussion. *Acta Crystallographica*, 15, 1017–1035.
- Melchior, M.T., Vaughn, D.E.W., and Jacobson, A.J. (1982) Characterization of the silicon-aluminum distribution in synthetic faujasites by high-resolution solid-state ²⁹Si NMR. *American Chemical Society Journal*, 104, 4859–4864.
- Müller, Dirk, Gessner, W., Behrens, H.J., and Scheler, G. (1981) Determination of the aluminum coordination in aluminum-oxygen compounds by solid-state high resolution ²⁷Al NMR. *Chemical Physics Letters*, 79, 59–62.
- Müller, G. (1969) Die Abhängigkeit der Gitterkonstanten und der Misch Kristallbildung der Na- und K-Feldspate vom Ordnungszustand. Ph.D. Dissertation, Technische Universität dem Karlsruhe.
- (1970) Der Ordnungs-unordnungsübergang in getemperten Mikroklinen und Albiten. *Zeitschrift für Kristallographie*, 132, 212–227.
- Prewitt, C.T., Sueno, S., and Papike, J.J. (1976) The crystal structures of high albite and monalbite at high temperatures. *American Mineralogist*, 61, 1213–1225.
- Ramdas, S., Thomas, J.M., Klinowski, J., Fyfe, C.A., and Hartman, J.S. (1981) Ordering of aluminum and silicon in synthetic faujasites. *Nature*, 292, 228–230.
- Ribbe, P.H., Megaw, H.D., and Taylor, W.H. (1969) The albite structures. *Acta Crystallographica*, B25, 1503–1518.
- Smith, J.V., and Ribbe, P.H. (1969) Atomic movements in plagioclase feldspars: Kinetic interpretation. *Contributions to Mineralogy and Petrology*, 21, 157–202.
- Smith, J.V., Blackwell, C.S., and Hovis, G.L. (1984) NMR of the albite-microcline series. *Nature*, 309, 140–142.
- Smith, K.A., Kirkpatrick, R.J., Oldfield, E., and Henderson, D.M. (1983) High-resolution silicon-29 nuclear magnetic resonance spectroscopic study of rock forming silicates. *American Mineralogist*, 68, 1206–1215.
- Staepli, J.L., and Brinkmann, D. (1974a) A nuclear magnetic resonance study of the phase transition in anorthite, CaAl₂Si₂O₈. *Zeitschrift für Kristallographie*, 140, 360–373.
- (1974b) Assignment and structural dependence of electric field gradients in anorthite and simple field gradient calculations in some aluminosilicates. *Zeitschrift für Kristallographie*, 140, 374–392.
- Thomas, J.M., Bursill, L.A., Lodge, E.A., Cheetham, A.K., and Fyfe C.A. (1981a) A reassessment of zeolite A: Evidence that the structure is rhombohedral with unexpected ordering in the aluminosilicate framework. *Journal of the Chemical Society, Chemical Communications*, 276–277.
- Thomas, J.M., Klinowski, J., Fyfe, C.A., Hartman, J.S., and Bursill, L.A. (1981b) Does the mode of preparation of an alu-

- minosilicate influence the short-range Si,Al ordering? *Journal of the Chemical Society, Chemical Communications*, 678-679.
- Thomas, J.M., Klinowski, J., Ramdas, S., Anderson, M.W., Fyfe, C.A., and Gobbi, G.C. (1983) New approaches to the structural characterization of zeolites: Magic-angle spinning NMR (MASNMR). G.D. Stuckey and F.G. Dwyer, Eds. *Intrazeolite chemistry*. American Chemical Society Symposium Series 218, 159-180.
- Wainwright, J.E., and Starkey, J. (1971) A refinement of the structure of anorthite. *Zeitschrift für Kristallographie*, 133, 75-84.
- Winter, J.K., Okamura, F.P., and Ghose, S. (1979) A high-temperature structural study of high albite, monalbite, and the analbite → monalbite phase transition. *American Mineralogist*, 64, 409-423.

MANUSCRIPT RECEIVED FEBRUARY 6, 1985

MANUSCRIPT ACCEPTED JANUARY 14, 1986