

## The high–low albite relations revealed by reversal of degree of order at high pressures

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### Abstract

The equilibrium Al/Si order–disorder relations in albite have been clarified by reversal of the degree of order at high pressures ( $\sim 18$  kbar) in the absence of water to avoid melting, and for the most part in the presence of essentially anhydrous carbonates. At high pressures the Al/Si diffusive interchange proceeds orders of magnitude faster than observed at 1–2 kbar  $P(\text{H}_2\text{O})$ . At 18 kbar albite begins to disorder above 660°C, and the  $\Delta 2\theta(131)$  indicator of order goes from 1.10 at 660°C to 1.85 (high albite) at 790°C. The rate of change is  $9.1 \times 10^{-3}$   $\Delta/\text{K}$  in this region of stable intermediate albites. At temperatures from 790°C to 950°C disorder in high albite continues essentially linearly with temperature from  $\Delta = 1.85$  to  $\Delta \sim 2.0$ , but at an order of magnitude lower rate of  $9.2 \times 10^{-4}$   $\Delta/\text{K}$ . The pressure effect is calculated at 350 bars/K, and experimental data confirm this value; thus equilibrium order–disorder temperatures should be 45–50°C lower at 2 kbar than at 18 kbar.

Structural state modification is dominantly by the solid-state diffusion of Al and Si. Although both hydrothermal and carbonate-containing runs show some evidence of recrystallization, neither added water nor carbonate appear to be essential. For example, relatively rapid ordering or disordering takes place in the absence of fluxes at temperatures of 750–1000°C in albite dried at 1000°C for 24 hours prior to treatment and in albites treated without carbonate at pressures just below the albite  $\rightarrow$  jadeite + quartz transition. It is tentatively suggested that the observed great enhancement of diffusion at high pressures is the result of activation produced by transient higher coordination induced around Al atoms, with concomitant disruption of the linked Si–O units. This process may be aided by small amounts of water or hydrogen.

The low  $\rightleftharpoons$  high albite conversion takes place without change in symmetry ( $C\bar{1}$ ) over several hundred degrees, and if it can be called a phase transformation, it appears not to be first order in nature, at least up to the transition to the monoclinic modification, monalbite, at approximately 950°C.

### Introduction

The distinction between high albite and low albite was first made by Tuttle and Bowen (1950). A number of experimental investigations have been carried out since that time in the attempt to elucidate the polymorphic relations, but neither the order (type) of the transition nor its temperature or temperature range has been characterized. It has long been known, however, that Al/Si order–disorder relations are involved (Ferguson et al., 1958; and see Ribbe, 1983). Essentially all of the work to date has been carried out in cold-seal pressure vessels with the albite exposed to moderate pressures, for the most part at about 1 kbar, with or without “fluxes” such as sodium silicate or NaOH in

the hydrothermal fluid. Under these conditions reversal of the equilibrium has not been accomplished; the diffusive reaction involving the interchange of Al and Si atoms is extremely sluggish. The consensus in the literature is that the high albite–low albite inversion is a first-order transformation occurring at about 680°C (Raase, 1971; Senderov, 1980; Smith, 1983; summarized in Ribbe, 1983) although real evidence for the type of transition in  $\text{NaAlSi}_3\text{O}_8$  has been lacking.

In lieu of a rather lengthy historical summary of earlier work on the high–low albite relations, the following references are listed as those containing the bulk of the current data and thought. Smith (1974a, 1983) also summarizes some of this information: Tuttle and Bowen (1950), MacKenzie (1957), McConnell and McKie (1960), Stewart (1960), Eberhard (1967), Parsons (1968), Raase and Kern (1969), Martin (1969), Raase (1971), Trembath (1973), Senderov (1974), Senderov and Shchekina (1976), Mason

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(1979). Experimentalists before Mason (1979), perhaps because of wishful thinking, tended to avoid the issue of whether equilibrium or "quasiequilibrium" had really been attained or approached. Only Mason (1979) stated that, "... the phase relations of albite will remain obscure until true equilibrium can be demonstrated." Straightforward hydrothermal treatment of albites seems to have gone about as far as it can go, and it is apparent that a different approach is in order.

### Reversal of the degree of Al-Si order

Goldsmith, Clayton and Mayeda (unpublished data) have investigated direct oxygen exchange between albite and  $\text{CaCO}_3$  and anorthite and  $\text{CaCO}_3$  at high pressures in the absence of water. Equilibrium exchange of  $^{18}\text{O}$  and  $^{16}\text{O}$  between carbonate and feldspar at  $700^\circ$  and  $800^\circ\text{C}$  at pressures of about 15 kbar takes place in several days or less—a most surprising result. These observations prompted us to try carbonates at high pressures to promote the Al-Si order-disorder reaction in albite.

The experiments were done at pressures of 17–19 kbar, close to the breakdown of albite to jadeite and quartz. At these, and even at lower pressures,  $\text{H}_2\text{O}$  promotes extensive melting and severely limits attempts to alter the degree of order in albite.  $\text{CaCO}_3$  was the first carbonate to be used; results were good, but all subsequent runs were made with  $\text{Na}_2\text{CO}_3$  to avoid introducing a foreign cation. It should be pointed out, however, that no cation exchange was observed in runs made with  $\text{CaCO}_3$  and  $\text{NaAlSi}_3\text{O}_8$ —in an experiment at  $800^\circ\text{C}$  no significant amount of Ca was apparent in a microprobe analysis of the albite run-product. Equilibrium reversals of degree of order over the entire range of the transformation from low albite to high albite and vice versa were carried out.

### Experimental methods

#### *Apparatus and techniques*

Two types of apparatus were used for all of the experiments: piston-cylinder devices with NaCl pressure cells, and internally heated, argon-pressurized vessels (design after Holloway, 1971). Runs above 8 kbar were made in the solid-media devices and those at 8 kbar and lower in the gas vessels. However, a number of runs were made at 8 and 6 kbar with piston-cylinder devices to provide an overlapping check on the two types of apparatus. As the data will show, results are conformable. Two chromel-alumel thermocouples, calibrated at the melting points of Sn and NaCl were placed 6 mm apart in the gas vessels, with the sealed platinum or gold sample capsules between the two. The temperature difference between the two thermocouples did not exceed  $3^\circ\text{C}$ , and temperature control was maintained electronically to a fraction of a degree. Temperature accuracy is considered to be better than  $\pm 2^\circ\text{C}$ , even in runs of several weeks or more. Argon pressure was measured with a bourdon-type gauge and independently with a manganin cell, calibrated by the Harwood Engineering Co. Both the gauge and the manganin cell were further checked against a 100,000 psi Heise gauge, calibrated by the manufacturer. Pressure was read and controlled to a conservatively estimated  $\pm 50$  bars. Before heating, the NaCl assemblies were pressurized to a pre-determining value based on prior experience; the large thermal ex-

pansion of the salt during heating brought the run to the desired pressure, producing a "piston-out" condition. No pressure correction was used for the salt pressure medium in the  $P$ - $T$  range examined.

The hydrothermal experiments were carried out with 4–5 mg of albite and 2–3 mg of de-ionized water. Most of the direct order-disorder runs were carried out in the presence of anhydrous carbonates—"spar" calcite and for most of the runs, reagent grade  $\text{Na}_2\text{CO}_3$ . The analysis on the label of the  $\text{Na}_2\text{CO}_3$  indicated 1% moisture. No attempt to remove traces of moisture was made; it was felt that any additional help in fluxing that small amounts of moisture may provide was welcome. The samples usually, not always, were dark grey after a run, suggesting slight reduction of the carbonate, possibly from hydrogen produced externally to the capsule by decomposition of water. The albite and carbonate were mixed by mulling in a mortar and pestle under acetone, and used after air-drying; additional moisture might have been added by this procedure. The capsules of a typical run were sealed after loading with 4–5 mg albite and up to half as much carbonate. This amount of carbonate was used to insure complete "coverage" of all grains of albite, but, as will be seen, may not have been necessary at all, at least at high pressures. After the experiment carbonate was dissolved in a 1.2 M HCl solution and the sample washed and dried.

#### *Analytical techniques*

The degree of Al/Si order in albite has been determined in this study with the parameter  $2\theta(131)-2\theta(1\bar{3}1)$ , or simply  $\Delta 131$ , from powder X-ray diffraction scans, using  $\text{CuK}\alpha$  radiation. Kroll and Ribbe (1980) and Kroll (1983) have discussed the relative merits of several well-established X-ray techniques for determining the Al/Si order in plagioclases, particularly  $\Delta 131$ , measurement of  $\gamma$ , and of  $\alpha^*$  and  $\gamma^*$ . In working with plagioclases having a wide range of anorthite contents as well as significant amounts of orthoclase, a method of determining tetrahedral site occupancies involving  $\gamma$  is preferred over  $\Delta 131$  because the unit-cell angle  $\gamma$  has a smaller dependence on the orthoclase content than the  $\Delta 131$  parameter (Kroll and Ribbe, 1980). We, however, have dealt only with essentially pure  $\text{NaAlSi}_3\text{O}_8$ , eliminating ambiguity from both techniques. The  $\Delta 131$  method has been used here because it is readily measured and is considered by us as valid as any technique requiring a complete unit-cell refinement of each run product. Nevertheless, two experiments have been performed to directly compare the  $\Delta 131$  method to one involving  $\gamma$ .

An intermediate degree of disorder was induced in single crystals of natural low albite by imbedding a number of cleavage fragments in  $\text{Na}_2\text{CO}_3$  and heating at 18 kbar and  $760^\circ$  for 360 hours. Some of the crystals were crushed for an X-ray powder diffraction pattern, and a value of  $\Delta 131$  of  $1.35 \pm 0.03$  was obtained. This  $\Delta 131$  value corresponds to a tetrahedral site occupancy of  $t_{10} - \langle t_{1m} \rangle = 0.80 \pm 0.03$ . One of the remaining crystals was kindly examined with the precession X-ray technique by Paul Ribbe (Virginia Polytechnic Institute and State University) who, from  $\alpha^*$  and  $\gamma^*$  (Kroll and Ribbe, 1983) obtained a site occupancy of  $t_{10} - \langle t_{1m} \rangle = 0.81 \pm 0.03$ . Another set of single crystals of albite were partially disordered at  $750^\circ\text{C}$  and 18 kbar for 288 hours and when crushed produced a  $\Delta 131$  parameter of  $1.25 \pm 0.03$ . One of the remaining crystals was examined by Donald Swanson (SUNY, Stony Brook) and a complete unit-cell refinement was obtained. The value of  $\Delta 131$  calculated from the unit-cell refinement was 1.21. We feel that these single-crystal evaluations further the justification of our use of  $\Delta 131$  in this work.

All samples were examined by X-ray diffraction, and scanned at

least three times over the critical 131 and  $\bar{1}31$  region, 29–33°2 $\theta$ , Cu-radiation. In addition, a longer scan was taken (21–37°), so that at least four measurements of  $\Delta 131$  were made. The error in measuring  $\Delta 131$  is dependent on the quality of the diffraction pattern, which is largely a function of the crystalline quality and of the uniformity in degree of Al/Si order throughout the sample. It is generally of the order of  $\pm 0.02^\circ 2\theta$ , although some authors give  $\Delta$ -values to three decimal places. This degree of accuracy can readily be obtained by calculation from accurately determined lattice constants, but not, in our opinion, from direct measurements of 131 and  $\bar{1}31$  diffraction peaks. Although the high pressure experiments in the presence of carbonate generally had sharp X-ray diffraction peaks, in some runs, especially those producing albites in the low to intermediate  $\Delta$ -range, the 131 peak ( $\sim 31.3^\circ 2\theta$ ) was encroached upon by what is interpreted as an enhanced 132 peak ( $\sim 131.6^\circ 2\theta$ ), producing a doublet-like configuration. In all cases where a "doublet" was observed, the 131 peak was assumed to have the smaller  $2\theta$ . The powder diffraction patterns obtained from the two experiments with single crystals both showed this enhanced peak at  $\sim 31.5^\circ 2\theta$ , yet produced values of  $\Delta 131$  consistent with the single crystal data. We do not know the reason for the intensity-enhancement of 131, although it could be the result of preferred orientation.

Some runs with carbonate were examined under the petrographic microscope, and a JEOL JSM-35 scanning electron microscope was used to examine selected run products. Several run products were scanned on a computerized X-ray diffractometer with step-scanning at an interval of about 150 seconds and monochromatized Cu-radiation, but this technique was not deemed necessary for determination of  $\Delta 131$ .

#### Starting materials

The low albite used for most of the work was from an unusual albite-jadeitic pyroxene-glaucophane schist from a single (four feet in diameter) tectonic block from Valley Ford, California (Keith and Coleman, 1968, rock 4-CZ-60). Albite is intergrown with jadeitic pyroxene and glaucophane and also forms 1–2 mm veinlets. This was the first documented low albite from blueschists, and its chemical analysis (Keith and Coleman, 1968) and unit cell parameters are given in Table 1, where it is designated LoAb(a). Optical properties are also given by Keith and Coleman (1968). Our X-ray diffraction patterns show a suggestion of a split 131 peak and some additional peak broadening. The obliquity indicator on the average was  $\Delta 131 = 1.10$ , although values up to 1.12 were observed. This albite was selected because a purified grain fraction of  $\sim 1$  gram from rock 4-CZ-60 was made available to us by R. G. Coleman, and a homogeneous single sample this large was needed for this and the following study.

Two other low albites were used in a number of experiments. One is from Floras Creek, Oregon, with very sharp X-ray diffraction lines, and occurring in late fracture fillings in blueschist tectonic blocks (designated LoAb(b), chemical analyses and unit-cell parameters in Hemingway and Robie, 1977). The other albite also has a very sharp diffraction pattern and comes from a chlorite-albite vein cutting greenschists in the Froszitztal, Tauern Window, Austria (designated LoAb(c)). Electron microprobe analysis of all three low albites are also given in Table 1.

Three preparations of synthetic high albite were used. One was crystallized from  $\text{NaAlSi}_3\text{O}_8$  glass in a sealed gold tube with 10%  $\text{H}_2\text{O}$  at 850°C for five days at 1 kbar;  $\Delta 131 = 1.90$ –1.92. It is designated HiAb(a). The sample used for most of the order-disorder experiments with carbonate additives was crystallized in the same fashion for four days, with  $\Delta 131 = 1.92$ , and is designa-

Table 1. Analyses of natural albites.

Electron microprobe analyses of albites*			
	LoAb(a); 4-CZ-60	LoAb(b)	LoAb(c)
SiO <sub>2</sub>	68.5	68.5	68.5
Al <sub>2</sub> O <sub>3</sub>	19.0	19.0	19.3
Na <sub>2</sub> O	12.1	12.1	11.9
K <sub>2</sub> O	0.02 ± 0.02	0.04	0.09
CaO	0.0 ± 0.02	0.0	0.30
FeO	0.0 ± 0.02	0.0	0.0
TiO <sub>2</sub>	0.0 ± 0.02	0.0	0.0
	99.62	99.64	100.09

\* Na, Al, Si relative to albite glass.  
Ca relative to An<sub>10</sub> glass.  
K relative to microcline.

Chemical analysis of LoAb(a), from Keith and Coleman, 1968	
SiO <sub>2</sub>	68.1
Al <sub>2</sub> O <sub>3</sub>	19.9
Fe <sub>2</sub> O <sub>3</sub>	.08
FeO	.00
MgO	.00
CaO	.10
Na <sub>2</sub> O	11.6
K <sub>2</sub> O	.03
H <sub>2</sub> O <sup>+</sup>	.00
H <sub>2</sub> O <sup>-</sup>	.04
TiO <sub>2</sub>	.06
P <sub>2</sub> O <sub>5</sub>	<.01
MnO	.00
F	.00
	99.9

ted HiAb(b). A third, used for the higher temperature runs, was crystallized from glass at 1200° and 15 kbar,  $\Delta 131 = 2.02$ , and is designated HiAb(c). A number of the order-disorder experiments were made with intermediate albites produced in previous runs, in order to give the ordering or disordering process a "head start".

### Experimental results

Table 2 contains the data on order-disorder relations as revealed by temperature-induced variations in  $\Delta 131$ . Most of the runs were made with high and low albites in association with  $\text{Na}_2\text{CO}_3$ , some with  $\text{CaCO}_3$ , some with no additives, and a few in the presence of water. The most revealing data from Table 2 are plotted in Figure 1.

#### The order-disorder data at 17–18 kbar

Definitions in the literature of "low" and "high" albite are somewhat arbitrary. MacKenzie (1957) defined high albite as having  $\Delta 131 > 2.00$  and low albite as material with  $\Delta 131 < 1.15$ . Rasse (1971) limited high albite to the range 1.70–2.00, pointing out that albites with  $\Delta$ -values from 2.00 to 2.03 become monoclinic on heating, and should be designated as analbite.

The arrows in Figure 1 represent reversals of the degree of order as measured by  $\Delta 131$ . The tail of each arrow emanates from the  $\Delta$ -value of the starting material, and the point of the arrowhead represents the value attained in the run. Run numbers are indicated at the tails.

At 680°C some disorder is apparent ( $\Delta 131 = 1.13$ ) in what, however, would still be considered low albite. It would be difficult to determine the lowest temperature at which observable disorder begins, but in run MAb-123 at 660°C (979 hours), no increase in disorder of the low albite was detected, and the comparison sample, a starting ma-

Table 2. Data on structural state,  $\Delta 131$ .

Run # MAB-	Starting material	T °C	P, kbar	Time, hrs.	Results*
P1-235	HiAb(c) + H <sub>2</sub> O	450	13	672	1.51 (original $\Delta = 2.02$ )
P1-244	HiAb(c) + Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O	450	13	77	1.25 ( " " " )
P1-238b	HiAb(c) + H <sub>2</sub> O	550	8	816	1.87 ( " " " )
P1-241a	LoAb(a) + H <sub>2</sub> O	550	14	958	1.09 (no change)
P1-241b	LoAb(b) + H <sub>2</sub> O	550	14	958	1.07 (no change)
P1-249	LoAb(b) + H <sub>2</sub> O	600	10	339	1.09 (no change)
P1-246a	LoAb(b) + H <sub>2</sub> O	650	13	816	1.10 (no significant change) some quench Hi Ab?
P1-246b	LoAb(a) + H <sub>2</sub> O	650	13	816	1.10 (no change) some quench Hi Ab?
123a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	660	17	979	1.10 (no change)
123b	MAB-116 + Na <sub>2</sub> CO <sub>3</sub>	660	17	979	1.11 (MAB-116 = 1.52)
P1-251a	LoAb(b) + H <sub>2</sub> O	685	8	768	1.11
P1-251b	LoAb(a) + H <sub>2</sub> O	685	8	768	1.15
67a	HiAb(b) + 0.2 mg H <sub>2</sub> O	700	15	190	some melt (undersaturated) 1.75
67b	HiAb(b) + CaCO <sub>3</sub>	700	15	190	1.67
71a	HiAb(b) + .28 mg H <sub>2</sub> O	700	15	576	some melt (undersaturated) 1.60
71b	HiAb(b) + CaCO <sub>3</sub>	700	15	576	1.65
76a	HiAb(b) + H <sub>2</sub> O	700	6	744	1.81
76b	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	700	6	744	1.77
109a	MAB-97 + Na <sub>2</sub> CO <sub>3</sub>	681	17	838	1.13 (MAB-97 = 1.50)
109b	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	681	17	838	1.13
89a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	700	17	667	1.16
89b	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	700	17	667	1.31
91a	MAB-84 + Na <sub>2</sub> CO <sub>3</sub>	700	17	695	1.24 (MAB-84 = 1.58)
91b	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	700	17	695	1.18
112a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	710	17	767	1.24
112b	MAB-97 + Na <sub>2</sub> CO <sub>3</sub>	710	17	767	1.29 (MAB-97 = 1.50)
85a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	720	18	432	1.28
85b	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	720	18	432	1.41
93a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	720	17	839	1.30
93b	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	720	17	839	1.40
131a	HiAb(b)	720	17½	215	1.55
131b	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	720	17½	215	1.63
131c	LoAb(b)	720	17½	215	1.25
124a	LoAb(b) + Na <sub>2</sub> CO <sub>3</sub>	720	7.00	962	1.15
124b	MAB-116 + Na <sub>2</sub> CO <sub>3</sub>	720	7.00	962	1.52 (MAB-116 = 1.52)
124c	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	720	7.00	962	1.75
86b	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	722	8.05	240	1.15
75b	HiAb(a) + Na <sub>2</sub> CO <sub>3</sub>	728	6.05	431	1.79
79	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	730	18	575	1.53
107a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	730	17½	647	1.32
107b	LoAb(c) + Na <sub>2</sub> CO <sub>3</sub>	730	17½	647	1.42
115a	MAB-78b + Na <sub>2</sub> CO <sub>3</sub>	730	17½	695	1.48 (MAB-78b = 1.67)
115b	LoAb(c) + Na <sub>2</sub> CO <sub>3</sub>	730	17½	695	1.45
84	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	740	18	460	1.58
97	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	740	17	571	1.50
116	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	740	18	553	1.52
117a	LoAb(b) + Na <sub>2</sub> CO <sub>3</sub>	740	18	844	1.42
117b	Ab glass + Na <sub>2</sub> CO <sub>3</sub>	740	18	844	1.49
120a	MAB-116 + Na <sub>2</sub> CO <sub>3</sub>	740	6.87	629	1.77 (MAB-116 = 1.52)
120b	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	740	6.87	629	1.82
81b	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	743	6.08	169	1.10, asymmetrical 131 and 131 peaks
81c	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	743	6.08	169	1.83
92b	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	749	6.00	166	1.24 (+ 1.62?)
92c	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	749	6.00	166	1.85
110	MAB-97 + Na <sub>2</sub> CO <sub>3</sub>	750	17½	550	1.62 (MAB-97 = 1.50)
128a	LoAb(a)	750	18	118	1.36
128b	HiAb(b)	750	18	118	1.69
128c	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	750	18	118	1.38
78a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	752	18½	648	1.55
78b	HiAb(b) + CaCO <sub>3</sub>	752	18½	648	1.67
88	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	760	18	235	1.65
90a	MAB-84 + Na <sub>2</sub> CO <sub>3</sub>	760	18	213	1.72 (MAB-84 = 1.58)
90b	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	760	18	213	1.73
87b	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	760	4.00	331	~ 1.65-1.85 (ambiguous)
87c	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	760	4.00	331	1.87
74c	LoAb(a) + CaCO <sub>3</sub>	761	3.60	354	LoAb, asymmetrical peaks toward HiAb
74d	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	761	3.60	354	HiAb + some residual LoAb 1.83
82c	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	768	4.02	184	HiAb + some residual LoAb 1.83
68a	LoAb(a) + CaCO <sub>3</sub>	775	19	330	1.55 oven dried
68b	LoAb(b) + Na <sub>2</sub> CO <sub>3</sub>	775	19	330	1.55 oven dried

Table 2. (cont.)

98a	MAb-84 + Na <sub>2</sub> CO <sub>3</sub>	775	18½	480	1.79 (MAb-84 = 1.58)
98b	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	775	18½	480	1.82
118a	LoAb(c) + Na <sub>2</sub> CO <sub>3</sub>	780	18	410	1.82
118b	LoAb(b) + Na <sub>2</sub> CO <sub>3</sub>	780	18	410	1.81
113a	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	790	17	314	1.85
113b	MAB-97 + Na <sub>2</sub> CO <sub>3</sub>	790	17	314	1.85 (MAb-97 = 1.50)
65	LoAb(a) + CaCO <sub>3</sub>	800	19	187	1.83
72	LoAb(a) + CaCO <sub>3</sub>	800	15½	162	1.85
94a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	800	18	216	1.85
94b	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	800	18	216	1.83
129a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	800	18	90	1.86
129b	LoAb(a)	800	18	90	1.78
114a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	822	19	259	1.87
114b	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	822	19	259	1.87-1.88
119a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	850	18	146	1.90
119b	LoAb(b) + Na <sub>2</sub> CO <sub>3</sub>	850	18	146	1.90
48	LoAb(a) + H <sub>2</sub> O	896	0.77	150	1.95
121a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	902	18	73	1.92
121b	HiAb(c) + Na <sub>2</sub> CO <sub>3</sub>	902	18	73	1.95
122a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	950	18	24	1.99
122b	HiAb(c) + Na <sub>2</sub> CO <sub>3</sub>	950	18	24	1.99
126a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	975	17	64.5	2.00
126b	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	975	17	64.5	x1s + glass (1.92)
126c	HiAb(c) + Na <sub>2</sub> CO <sub>3</sub>	975	17	64.5	x1s + glass (1.98)
125a	LoAb(a) + Na <sub>2</sub> CO <sub>3</sub>	1000	18	17	1.97
125b	LoAb(a)	1000	18	17	1.97
125c	HiAb(b) + Na <sub>2</sub> CO <sub>3</sub>	1000	18	64.5	1.97
127a	LoAb(a)	1000	18	17	1.92
127b	LoAb(a) heated to redness	1000	18	17	1.93
127c	HiAb(b)	1000	18	17	1.95
130	LoAb(a)	1000-1030	0.001	24	1.10
132a	LoAb(a) 1000-1030 <sup>∇</sup> , 24 hrs.	1000	18	23	1.96
132b	LoAb(b)	1000	18	23	1.96

§ In order of increasing temperature.  
 \* No = Δ131 value.  
 † Decimal values indicate gas vessel runs.  
 ∞ MAb- unless otherwise prefixed P1-.  
 †† See text for temperature uncertainties.  
 ∇ In air.

terial with  $\Delta 131 = 1.52$ , achieved a value of 1.11. The largest change in  $\Delta 131$  is between approximately 680° and 790°C, and the disorder relations between 700° and 770°C are fairly linear with temperature, and the most rapid rate of change is  $9.1 \times 10^{-3} \Delta/K$ . At 770–790°C at 17–18 kbar this rate changes, and from 790°C ( $\Delta 131 = 1.85$ ) to approximately 950°C ( $\Delta 131 = 2.0$ ), disorder increases relatively slowly and almost linearly with temperature. There is no indication of a discontinuity in the curve, at least in the temperature region in which NaAlSi<sub>3</sub>O<sub>8</sub> is presumed to be triclinic, from the lowest temperatures to over 950°C.

#### The effect of pressure on order-disorder relations

*Calculation of the pressure effect.* Orville (1967) calculated the effect of pressure on the low albite-high albite transition, assuming it to be a first order transition or that the major part of the ordering takes place over a limited range of temperature. He obtained, from his determination of unit-cell volume curves a  $\Delta V$  of  $3.8 \pm 51.1 \text{ \AA}^3$ , or  $0.51 \pm 0.17 \text{ cm}^3/\text{mole}$ . He calculated the entropy change of the transition as largely due to disordering the Al and three Si

cations over four tetrahedral sites, and determined from the Clausius-Clapyron equation

$$dP/dT(\text{low Ab} \rightarrow \text{high Ab}) = \Delta S/\Delta V = 83 \pm 25 \text{ bars/K,}$$

such that an increase of 1000 bars should raise the transition by 9 to 17°C.

More recent data on volumes and on the enthalpy of disordering are available for calculation of the  $dP/dT$  slope of the transition, and are given in Table 3. Using the average value of  $\Delta V = 0.39 \text{ cm}^3/\text{mole}$  and the theoretically complete  $\Delta S = 4.469 \text{ cal/K}$ ,  $dP/dT = 480 \pm 70 \text{ bars/K}$ . Using Holland's (1980) value derived from experimental data of  $\Delta S = 3.394 \text{ cal/K}$ ,  $dP/dT = 364 \pm 60 \text{ bars/K}$ . This smaller value is probably more realistic, as the value for complete disorder probably includes higher temperature disorder that involves the triclinic-monoclinic transition. Using the average enthalpy data (calorimetric data obtained at 700°C)  $dP/dT = \Delta H/T\Delta V = 337 \pm 30 \text{ bars/K}$ .

These calculations were made, as were Orville's (1967), without regard for the fact that the transition takes place continuously over a large temperature interval, whereas the

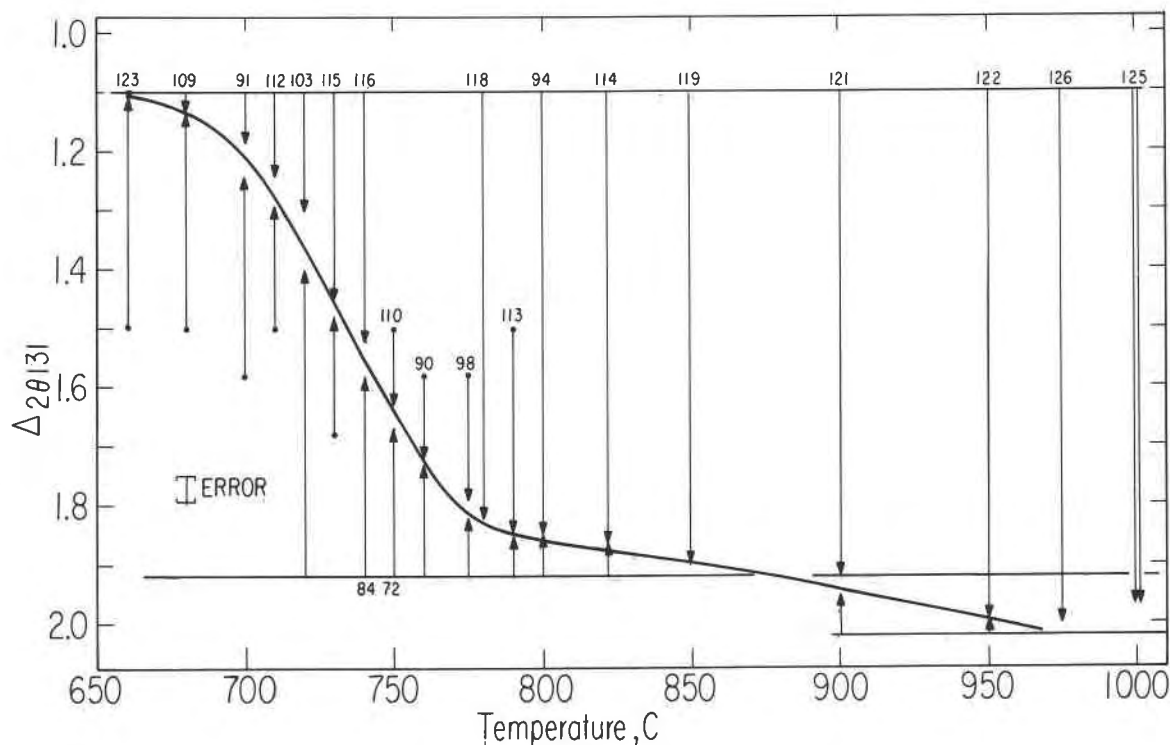


Fig. 1. The structural state of  $\text{NaAlSi}_3\text{O}_8$ , using  $\Delta 131$  as the indicator of degree of Al/Si order, as a function of temperature at 17–19 kbar. See text for pressure correction. The arrows indicate reaction direction, with the tails plotted as the  $\Delta$ -values of the starting materials, and the tips of the arrowheads represent the  $\Delta$ -values of the reacted albite. The equilibrium structural state is bracketed by the reversals. The numbers (prefixed by MAb-) refer to the runs listed in Table 2.

Clausius-Clapyron equation is normally applied to univariant reactions with coexisting phases. It is assumed that variation of volume with pressure is also a continuous function over the temperature range, and that the isopleths, or family of curves representing varying structural states through the transition band, can be calculated at any  $P$ - $T$  value by the Clausius-Clapyron equation, with differences in volume, entropy and enthalpy as linearly interpolated from Table 3.

The calculated pressure effect is large enough to produce a substantial difference in structural state at constant temperature in going from the experimentally determined values at 17–18 kbar to lower pressures. The 480 bars/K obtained from theoretically complete disorder may be too large, and the average of the two other values is 350 bars/K. This pressure effect is significantly less than that calculated by Orville (1967). Orville used the theoretically complete value of  $\Delta S$  (see Table 3), but calculated the disorder at only one of the four tetrahedral sites. His value is thus off by a factor of 4, and if corrected, closely approximates ours.

The value of 350 bars/K amounts to approximately 45°C if adjusted from 18 kbar to 2 kbar, and it is assumed that the entire curve of Figure 1 would be shifted down 45°C.

The value of  $\Delta 131 = 1.85$ , which most workers would call high albite (cf. Rasse, 1971), would be reached at approximately 745°C, and some observable disorder would be present at a temperature as low as approximately 635°C.

#### Experimental data on the pressure effect

Table 2 contains some information on the effect of pressure on the disorder-temperature relations. MAb-75b, high albite +  $\text{Na}_2\text{CO}_3$  at 728°, 6 kbar, for 431 hours went to  $\Delta 131 = 1.79$ . If this were considered to be an approximately equilibrated "half reversal", it lies at a point slightly less than 40°C below the ( $\Delta 131 = 1.79$ ) point in Figure 1. Runs MAb87b and c, a low-high albite pair at 760°, 4 kbar, 331 hours define a bracket of sorts, that can be interpreted as being at  $\sim 1.86$ , and if so, it lies approximately 40° below the curve, but in this region of Figure 1, the curve may be quite flat at 4 kbar, and the error may be large. Runs MAb74d (low albite +  $\text{Na}_2\text{CO}_3$ , 761°, 3.6 kbar, 354 hours) and MAb82c (low albite +  $\text{Na}_2\text{CO}_3$ , 768°, 4 kbar, 184 hours) have both attained a  $\Delta 131$  of 1.83. Although probably not equilibrated, and with no comparison high-albite samples to produce brackets, they have clearly gone beyond the 17–18 kbar value of 1.72. All of these runs have gone in the direction of greater disorder at lower

Table 3. Volume, entropy, and enthalpy data for low albite-high albite transition.

Volumes	
Low albite (Amelia Ab)	High albite
a) $99.98 \pm .03$ cm <sup>3</sup> /mole Carpenter et al. (1985)	a) $100.40 \pm .03$ cm <sup>3</sup> /mole Carpenter et al. (1985) Heat-treated Amelia Ab
b) $100.07 \pm 0.13$ cm <sup>3</sup> /mole Robie et al. (1978)	b) $100.43 \pm 0.09$ cm <sup>3</sup> /mole Robie et al. (1978)
c) $99.94$ cm <sup>3</sup> /mole Kroll and Ribbe (1983)	c) $100.33$ cm <sup>3</sup> /mole Kroll and Ribbe (1983)
<u><math>\Delta V</math> low albite-high albite</u>	
a) $0.42$ cm <sup>3</sup> /mole	} average = $0.39$ cm <sup>3</sup> /mole
b) $0.36$ cm <sup>3</sup> /mole	
c) $0.39$ cm <sup>3</sup> /mole	
<u><math>\Delta H</math> low albite-high albite</u>	
$3.08 \pm 0.30$ kcal/mole, Carpenter et al. (1985), solution calorimetry	
$3.4 \pm 0.25$ kcal/mole, Holm and Kleppa (1968), solution calorimetry	
$2.86 \pm 0.23$ kcal/mole, Newton et al. (1980), solution calorimetry	
$2.80 \pm 0.29$ kcal/mole, Blinova and Kiseleva (1982), solution calorimetry	
$3.09 \pm 0.8$ kcal/mole, Holland (1980), albite = jadeite + qtz reaction	
average = $3.05$	
<u><math>\Delta S</math> low albite-high albite</u>	
Theoretically complete = $-4R \left[ \frac{1}{4} \ln 4 + \frac{3}{4} \ln \frac{4}{3} \right] = 4.469$ cal/K	
From albite = jadeite + quartz reaction (Holland, 1980) = $3.394 \pm .57$ cal/K	

pressure, and the magnitude of the differences is compatible with the calculated value.

## Discussion

### Structural state equilibration

MacKenzie (1957) was the first to observe that at each temperature of crystallization from NaAlSi<sub>3</sub>O<sub>8</sub> glass the crystals formed after a few hours are similar to high albite in lattice parameters, but that in experiments of longer duration the lattice parameters change gradually and finally reach a steady value which is characteristic of the temperature of crystallization. This steady-value characteristic of temperature was also noted by Raase and Kern (1969), Martin (1969), Raase (1971), and Senderov and Shchekina (1976). MacKenzie (1957) interpreted the results as suggesting that for each temperature there is a stable form of NaAlSi<sub>3</sub>O<sub>8</sub> that is intermediate between high albite and low albite, high albite being stable only above about 1000°C and low albite only below about 450°C.

Most of the earlier work on albite was at 1–2 kbar. Hindsight shows that few of the studies came even close to equilibrium at temperatures below the upper limit of high albite in spite of a good deal of rationalization. Nevertheless, several workers correctly observed the direction of order or disorder with temperature (Tuttle and Bowen, 1950; Raase, 1971; Senderov and Shchekina, 1976; Mason, 1979) and with rather little to go on, placed fairly reasonable limits on the upper temperature stability of highly ordered albite.

The reversal data of Table 2 and Figure 1, determined at ~18 kbar in the presence of carbonates, show that equilibration can be achieved at elevated pressures, and that the approach to steady values of  $\Delta 131$  at different temper-

atures observed by earlier workers is a kinetic effect and not an equilibrium or quasi-equilibrium state. This fact is apparent in the hydrothermal experiments where a variety of fluxes produced a variety of "steady-values" of  $\Delta 131$ , not easily explained other than kinetically. This effect of temperature and flux is also shown in Table 2; note the first three runs in the table, Nos. Pl-234, 244, and 238b, all hydrothermal experiments.

MacKenzie (1957), Raase and Kern (1969) and Martin (1969) all show minimum  $\Delta$ -values at temperatures ranging from ~530 to ~300°C, depending upon the flux (or lack of it) and  $P(\text{H}_2\text{O})$ . This behavior is a good example of the relative effects of a large  $\Delta G$  as a thermodynamic driving force at low temperatures as opposed to greater thermal activation but a smaller  $\Delta G$  at higher temperatures. Inasmuch as albite should be highly ordered at temperatures below 600°C, it is apparent that the  $\Delta G$  effect dominates down to something like 300°C in fluxed hydrothermal systems at which point the ordering reaction is effectively arrested. The large driving force that expresses itself in the ordering process at temperatures well below that at which low albite begins to disorder has been confused with an equilibrium state.

### The structural modification process at elevated pressures

There are two obvious routes by which the Al/Si configuration may be altered: by diffusive Al-Si exchange within the crystalline framework, and by solution and recrystallization. The former requires extraction and rearrangement of the screened Si<sup>4+</sup> and Al<sup>3+</sup> ions from their tightly bonded 4-coordinated units, whereas the latter does not, although the tetrahedra must be "dissembled" and the structure reformed. Al-Si diffusion, even at very high temperatures, is extremely sluggish at low pressures in network silicates, and particularly in the alkali feldspars; the disordering of albite at one atmosphere requires temperatures not far below the melting point and is still slow, although enhanced by the presence of small amounts of water at pressures up to 10 kbar (Tuttle and Bowen, 1950; Yund and Tullis, 1980). The activation energy for diffusional exchange in albite is of the order of 50–60 kcal/mole, whereas for solution processes is approximately 15 kcal/mole (A. C. Lasaga, pers. comm.). It does not seem likely that Al/Si equilibration at temperatures below 700°C by a solid-state diffusional process would take place in laboratory times. On the other hand, hydrothermal crystallization at low or moderate pressures favors metastable formation of high albite except in the presence of fluxes at rather low temperatures (e.g., MacKenzie, 1957; Martin, 1969).

Can a resolution-recrystallization mechanism take place in the high pressure runs in the presence of carbonate? SEM photographs of several starting materials and run products are shown in Figure 2. Figures 2a and 2b are LoAb(a) and HiAb(b) starting materials. LoAb(a) was prepared from cleavage fragments crushed in a mortar and pestle, producing a large range of particle sizes. The large

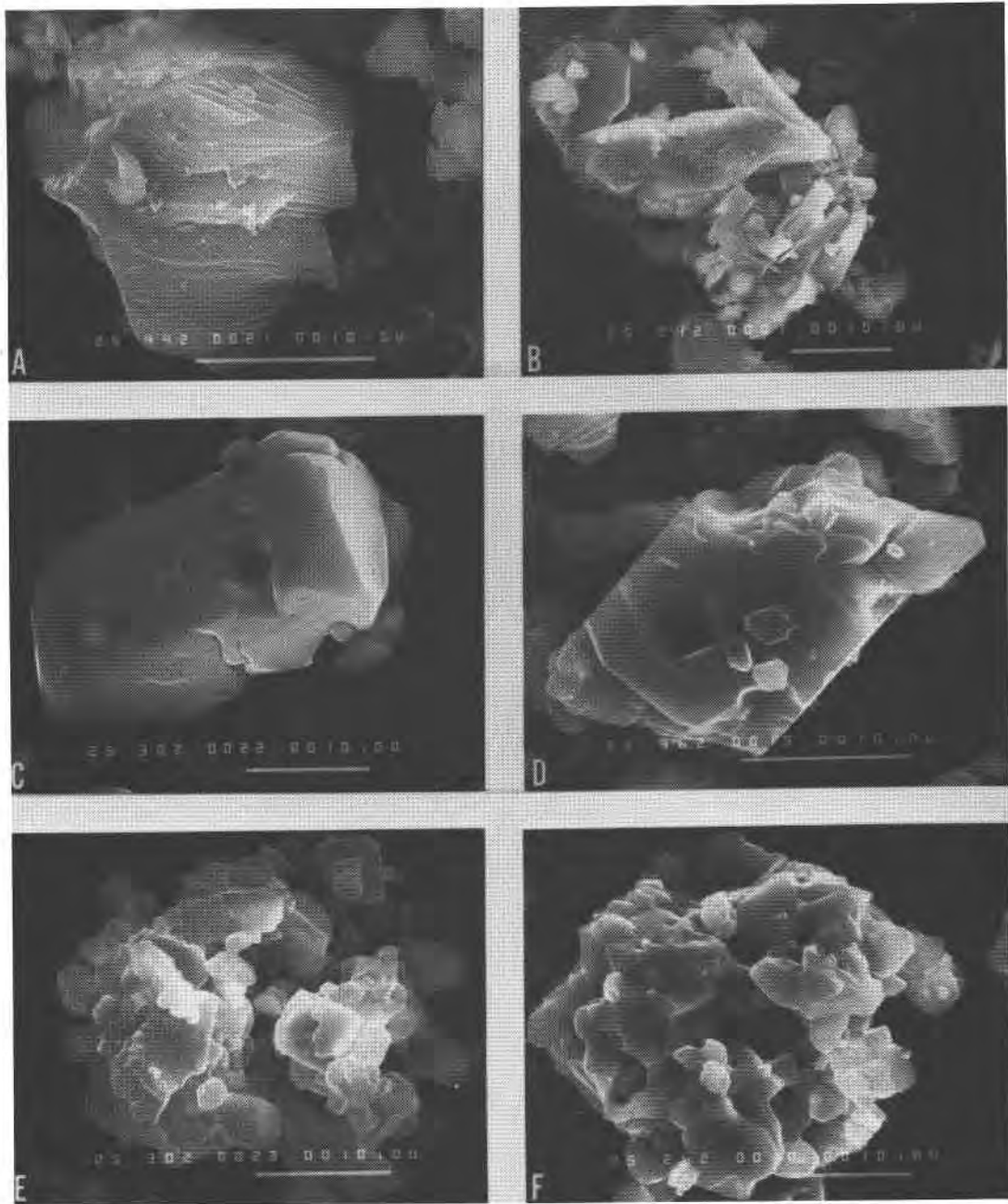


Fig. 2. SEM photographs of starting materials and some run products. A) LoAb(a) starting material. B) HiAb(b) starting material. C) MAb-48, LoAb(a) after 150 hours at 896° and 0.77 kbar  $P(H_2O)$ ,  $\Delta 131 = 1.95$ . D) MAb-74d, LoAb(a) plus  $Na_2CO_3$ , 761°C, 3.6 kbar, 354 hrs.,  $\Delta 131 = 1.83$ . E) MAb-79a, HiAb(b) plus  $Na_2CO_3$ , 730°C, 18 kbar, 575 hrs.,  $\Delta 131 = 1.53$ . F) MAb-78b, HiAb(b) plus  $CaCO_3$ , 752°, 19 kbar 648 hrs.,  $\Delta 131 = 1.68$ .

grain shows a typical terraced appearance, the result of two dominant cleavages. Many of the larger grains are observed to be more or less coated with fine fragments. HiAb(b) is typically seen as clusters of small crystals, many with well-formed crystal faces. Figure 2c is MAb-48,

LoAb(a) after 150 hours at 896° and 0.77 kbar  $P(H_2O)$ ,  $\Delta 131 = 1.95$  (Table 2). Extensive recrystallization in this hydrothermal run is apparent, and euhedrons with sharp edges are readily seen even in the optical microscope. Figure 2d is MAb-74d, LoAb(a) plus  $Na_2CO_3$ , 761°C, 3.6



kbar, for 354 hours,  $\Delta 131 = 1.83$ . The extensive disordering is accompanied by a "cleaning up" of most of the fine fragments as in 2c, the development of euhedrons with a range of sizes, and the loss of the terraced cleavages. In the larger crystal, there is what appears to be a well defined negative crystal, or the impression left by a smaller crystal, a not uncommon feature. Figure 2e is MAb-79a, HiAb(b)  $\text{Na}_2\text{CO}_3$ ,  $730^\circ$ , 18 kbar, 575 hours,  $\Delta 131 = 1.53$ . Although it is more difficult to be sure of recrystallization because the high albite starting material shows euhedral development, the crystal size appears to become more uniform, perhaps by solution of the smaller crystals. There appears to be signs of growth and coalescence. Figure 2f is MAb-78b, HiAb(b) plus  $\text{CaCO}_3$ ,  $752^\circ$ , 19 kbar, 648 hours,  $\Delta 131 = 1.68$ . Again, as with  $\text{Na}_2\text{CO}_3$ , growth and coalescence seem to have taken place. In all of the high pressure carbonate-containing runs at or near equilibrium, throughout the entire  $\Delta$ -range, the 131 and  $\bar{1}\bar{3}1$  X-ray reflection and others that are affected by structural state are sharp and well resolved. None of the patterns show smeared peaks that would be indicative of a range of structural states. Several runs, such as MAb-74d and MAb-82c (Table 3) that are not fully equilibrated, show both high albite and residual low albite with clearly defined peaks, indicating direct conversion without intermediate stages. Furthermore, if the change in degree of order took place by a common type of recrystallization known as "Ostwald ripening" (see, for example, Matthews et al., 1983a, b, c), in which large reactant grains become enlarged by overgrowths of  $\text{NaAlSi}_3\text{O}_8$  derived from dissolution of smaller grains, one would expect multiple or smeared peaks, for the cores of the armored grains would retain the original structural state until a diffusional mechanism took over. It appears that the carbonate-containing runs that develop significant changes in degree of order show solution and recrystallization effects.

By what means does this recrystallization take place, and is it essential to the change in structural state? The recrystallization textures may be produced by a small amount of liquid or carbonatite-like melt. As indicated, the  $\text{Na}_2\text{CO}_3$  contains approximately 1 percent moisture. This explanation may be somewhat less applicable to  $\text{CaCO}_3$ , which was crushed clear spar. Traces of water at high temperatures have been shown to be very effective in promoting the exsolution process in alkali feldspars, although the reaction does not involve Al/Si order-disorder (Goldsmith and Newton, 1974).

MAb-126a (Table 2), LoAb(a) plus  $\text{Na}_2\text{CO}_3$ ,  $975^\circ$ , 17 kbar, run for 645 hours, was converted to high albite,  $\Delta 131 = 2.00$ , yet under the optical microscope appears to consist of crystal fragments indistinguishable from the starting material, and presumably unrecrystallized. A number of runs were made in the absence of any carbonate or external water other than adsorbed moisture (see MAb-125b, 127a, b, and c, 128a, b, c, 129a and b, 130, 131a, b, c, and 132, Table 2), revealing that a significant degree of reaction could be obtained in relatively short runs and, presumably, without significant recrystallization.

At  $1000^\circ\text{C}$  the enormous effect of high pressures on the rate of the Al/Si order-disorder reaction is apparent in short runs. Low albite held 24 hours at  $1000\text{--}1030^\circ\text{C}$  at one atmosphere (MAb-130) showed no significant change in  $\Delta 131$ , although there may be a very slight general degradation of the X-ray diffraction pattern. This is in line with earlier data on heated albite (cf. Tuttle and Bowen, 1950). MAb-127a and b were low albite run at  $1000^\circ\text{C}$ , 18 kbar, for only 17 hours. Furthermore, MAb-127b was dried by heating the open loaded capsule with a torch to a red heat for a few minutes before sealing. Both went to high albite,  $\Delta 131 = 1.92$  and  $1.93$ , respectively. In MAb-132a and b, one of the samples of low albite was heated in air in the open capsule at  $1000\text{--}1030^\circ\text{C}$  for 24 hours before sealing, the other sealed with adsorbed water only. Both went to high albite in 23 hours at  $1000^\circ\text{C}$ , 18 kbar,  $\Delta 131 = 1.96$ . Hydrogen diffusion into the capsule is certainly possible, but the presence of significant amounts of water or hydroxyl is most unlikely. Disordering at 18 kbar is extraordinarily more rapid than at one atmosphere at  $1000^\circ\text{C}$ .

The presence of carbonate seems to be a secondary factor at best in the structural state equilibration of  $\text{NaAlSi}_3\text{O}_8$ . It would also appear that most of the apparent difference in effectiveness between the use of water and carbonate is a result of the increase in reaction rate at higher pressures. For example, MAb-76a and b (Table 2) with high albite at  $700^\circ\text{C}$  and 6 kbar for 744 hours give  $\Delta 131 = 1.81$  and  $1.77$ , with  $\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$  respectively. MAb-89b with high albite and  $\text{Na}_2\text{CO}_3$  also at  $700^\circ\text{C}$  but at 17 kbar for 667 hours, produced  $\Delta 131 = 1.31$ . The run at 17 kbar could not, of course, be done with water; at  $700^\circ\text{C}$  melting takes place. It is not yet certain that pressure is the whole story; carbonates may be somewhat more effective than water in modifying Al-Si order-disorder at the same pressure, particularly in the lower pressure range (see MAb-76a and b, and 129a and b, Table 2).

#### *A possible reaction mechanism at high pressures*

Although the activation energy for Al/Si diffusion in aluminosilicates is greater than processes involving solution-reprecipitation, it seems necessary to call upon solid-state Al/Si diffusional exchange in modifying the structural state in  $\text{NaAlSi}_3\text{O}_8$  under anhydrous conditions. Is there any way that high pressure per se can greatly increase the diffusion rate? Increase in pressure inhibits diffusion in normal substances, i.e. solids other than those with negative activation volumes (Lazarus and Nachtrieb, 1963). Large increases in diffusion rates would only be expected if activation could be induced by breaking of bonds. A change in coordination of  $\text{Al}^{3+}$  or  $\text{Si}^{4+}$  requires that the strong Al-O and Si-O bonds be broken. We propose that at elevated pressures, transient higher coordination is induced in Al-O complexes (see Purcell and Katz, 1977, for a discussion of 5-coordinated complexes, pp. 596-599). At the temperatures in which the order-disorder reaction takes place, the 17-19 kbar region of pressures used is not far below the albite = jadeite + quartz boundary, at which Al goes from 4-coordination in albite to 6-coordination in

jadeite. It seems quite reasonable that at these pressures some fraction of the Al atoms undergo transient coordination change.

In a network aluminosilicate in which all oxygens are shared, local change from 4- to 5- or 6-coordination of Al must necessarily affect the environment of the neighboring Si atoms, also inducing a transient modification of Si-O bonding and coordination. Severe local structural "damage" would take place, and diffusion would be activated. It is not necessary that a large percentage of the atoms be involved at any one time; a moderate number of local readjustments of Al and Si positions might produce an equilibrium array in a matter of days or weeks, depending on temperature. The higher coordination provides a negative activation volume. Thus, unlike normal diffusional processes, pressure and temperature can cooperatively and perhaps drastically increase the diffusion coefficient of Al and Si by this activating mechanism.

It is likely that more than a single mechanism is involved in the process of structural state equilibrium in  $\text{NaAlSi}_3\text{O}_8$ . Evidence for recrystallization has been noted, and recrystallization can of course promote Al/Si exchange. This effect may be more important in 4-coordinated Al compounds at lower pressures, and a diffusional mechanism may dominate at elevated pressures; similarly the relative effectiveness of the two processes may change with temperature. To date we have not evaluated the kinetic factor as a function of pressure and one might dispute the efficacy of a coordination-modifying mechanism at moderate pressures. Furthermore, it is very difficult to assess the role of even very small amounts of water or  $\text{OH}^-$  or hydrogen in the diffusional process. Elimination of all water from silicates may be next to impossible, and the bond-breaking potential of hydroxyl groups, particularly at high pressures, should not be underestimated. These factors, as well as the role of carbonates, remain to be evaluated.

### Structural transitions in albite

#### *Low albite-high albite*

The supposition in the literature (Raase, 1971; Senderov, 1980; Smith, 1983; also see Ribbe, 1983) that the transition from low albite to high albite is a first-order transformation that occurs discontinuously at approximately 680°C is incorrect in view of the results of this study. The data presented in Figure 1 show no evidence of a discontinuity in the degree of Al/Si order with temperature, at least over a temperature range of more than 200°C, short of the transition to the monoclinic monalbite. There is therefore no evidence for a first-order transformation in the course of the low-albite to high-albite change. In the absence of discontinuous thermochemical data, such as specific heat, this transition is perhaps better termed "non-first" order.

Using a completely different approach, Salje (1985) and Salje et al. (1985) have independently produced an Al/Si ordering curve very much like our experimental curve in Figure 1. Their approach involves modelling the thermodynamic properties of Na-rich feldspars with a Landau-type

free energy expression containing two parameters. One parameter describes the structural distortion during the displacive phase transition between monalbite and analbite, and the other parameter the Al/Si order. The structural phase transition  $C2/m \rightarrow C\bar{1}$  in the Na feldspar is due to both order parameters and is accompanied by what these authors call a continuous "crossover" from low to high Al/Si order. The term "crossover" might be better suited to the high-low albite behavior than the expression "phase transformation."

The maximum rate of disorder with temperature is  $9.1 \times 10^{-3} \Delta/\text{K}$  over the intermediate albite range, and at temperatures above 790°C disorder in high albite continues essentially linearly with temperature, but at an order of magnitude lower rate of  $9.2 \times 10^{-4} \Delta/\text{K}$ . The reason for the rather sudden change in the rate of disorder is not obvious, but two possibly related factors might be involved: (1) increasing opportunity for Al-avoidance to become effective as disorder progresses, and (2) residual short-range order might be increasingly difficult to eliminate. Order-disorder phenomena are generally considered as cooperative phenomena, in which the rate of disorder increases rapidly as the "critical" temperature of disorder is approached (see, for example, Elcock, 1956), but such a treatment seems not to apply in the case of  $\text{NaAlSi}_3\text{O}_8$ . No catastrophic change in the order parameter close to a critical temperature is observed. If one selects values of  $\Delta_{131} = 1.10$  and 2.02 as the "limits" for highly ordered and essentially completely disordered albite, the value of  $\Delta_{131} = 1.85$  is reached at approximately 82% of "total" disorder. If the upper limit of  $\Delta$  is selected at 1.97, the value is approximately 86%. Thus, after about 80-85% of the Al/Si disorder has taken place, further disorder becomes significantly more difficult, and a great deal more thermal energy is required to carry out the disordering process. Holm and Kleppa (1968) observed the thermal disordering of albite to be a two-step process. The first step in dry-heated Amelia albite took place after three days at 1045°C ( $\sim 2.4$  kcal/mole), and the second step after three weeks at 1045°C ( $\sim 1$  kcal/mole). This nonequilibrium one-atmosphere process may, however, not be directly comparable with our results.

#### *The high albite-monalbite transition and the interpretation of $\Delta$ -values*

It has been noted that Raase (1971), in discussing the albite polymorphs, placed an upper limit on  $\Delta_{131}$  for high albite, designating albites with  $\Delta_{131} = 2.00$ -2.03 as analbite, which becomes monoclinic on heating. Analbite (see Kroll et al., 1980; MacKenzie, 1952; Laves, 1952) is a metastable disordered triclinic ( $C\bar{1}$ )  $\text{NaAlSi}_3\text{O}_8$  that is produced by a rapid displacive transformation from the monoclinic ( $C2/m$ ) disordered stable high-temperature modification (Schneider and Laves, 1957). High albite, when adequately disordered, transforms to monalbite. The high albite-monalbite transition is an equilibrium diffusive transformation, and the temperature is variously estimated from 965° to 983°C (Laves, 1960; Kroll and Bambauer,

1971; Thompson et al., 1974; Thompson and Hovis, 1978; Kroll et al., 1980). The temperature of the metastable displacive transformation monalbite = analbite is given as  $928 \pm 25^\circ\text{C}$  by Grundy and Brown (1969),  $903 \pm 35^\circ\text{C}$  by Okamura and Ghose (1975), and  $968 \pm 8^\circ\text{C}$  by Kroll et al. (1980). The transitions involving monalbite have been reviewed in detail by Smith (1974a, p. 292–305) and it appears that the conditions necessary to produce the high-albite to monalbite transition are not well known.

In this work no special effort has been made to observe the high albite–monalbite transition. The intersection of the high temperature portion of the disordering curve of Figure 1 with a  $\Delta 131$ -value representing that degree of disorder at which albite become monoclinic would represent the transition temperature at 18 kbar. Smith (1974a) called this state "maximum high albite", but the maximum degree of disorder in albite is not known, and the interpretation of  $\Delta 131$ -values in the  $950$ – $1000^\circ\text{C}$  temperature range relative to degree of disorder is not clear. In this work  $\Delta 131 = 2.0$  was the maximum value observed, at  $950^\circ$  and  $975^\circ\text{C}$ , exclusive of starting materials. In two sets of runs at  $1000^\circ\text{C}$  (MAB-125a, b, c, and MAB-127a, b, c) values in the range 1.92–1.96 were obtained, and the runs could not be bracketed. The erratic results at the higher temperatures can be rationalized by assuming that monalbite had been formed, and in going back through the monalbite  $\rightarrow$  analbite transition, metastable analbite of variable  $\Delta 131$ -values was produced. If this be the case, it would appear that monalbite is reached at  $\Delta 131 = 2.0$ , and at a temperature close to  $950^\circ\text{C}$ , even at 18 kbar. The attainment of  $\Delta 131$ -values in this laboratory and elsewhere  $> 2.0$  seem somewhat unpredictable and haphazard, and may be artifacts of inversion to a metastable phase.

In this as in prior work it has been assumed that  $\Delta 131$  is a linear function of Al/Si order–disorder. Prewitt et al. (1976) show, in agreement with data of Okamura and Ghose (1975) and with the view of Grundy et al. (1967), that lattice parameters at room temperature cannot define the precise state of high albite, as different crystals show different degrees of divergence of lattice angles with temperature, and that different crystals with very similar cell dimensions but different provenance exhibit different transition temperatures. Apparent transition temperatures to monalbite may differ by almost  $100^\circ\text{C}$ . We have not attempted to pursue these high-temperature phenomena, and it may well be that results obtained on crystals at room temperature are uncertain.

### Albite and peristerites

The relatively high temperature at which albite is highly ordered (over  $600^\circ\text{C}$  at 1 bar) makes it unlikely that "pure"  $\text{NaAlSi}_3\text{O}_8$  would exist or persist, as high albite in igneous or metamorphic rocks. There is generally enough calcium present in most environments to produce a plagioclase feldspar at moderately elevated temperatures, and one would therefore expect a "pure" albite to be formed only under the following conditions: (1) at low temperatures,

such as in the case of authigenic feldspars, (2) under the conditions of peristerite formation, in which (low) albite is in apparent equilibrium with an oligoclase, (3) at high pressure, where the calcium is strongly partitioned into a jadeitic pyroxene in association with albite. Under lower blueschist–greenschist conditions Ca is partitioned into lawsonite, pumpellyite, prehnite, or epidote (see also the description of rocks containing the albite [LoAb(a)] used in this work). Green (1968) has shown that there is a marked increase in albite content of the liquidus and near-liquidus plagioclase with increasing pressure. At high pressures in the presence of water, Ca will be sequestered by zoisite (Goldsmith, 1982).

The quantitative effect on order–disorder relations of small amounts of Ca and the concomitant increase  $> 1:3$  in the Al/Si ratio is unknown. Published phase diagrams of plagioclase feldspars, largely deduced from natural occurrences, generally depict first-order relations for high–low albite (see Smith, 1983), in part perhaps because diagrammatic representation of two-phase fields is straightforward as opposed to the complexity involved with a non-first order change. The latest diagram (Smith, 1984) attempts to illustrate the more complex relations, in part with spinodal representation. The compositions of interest here are those of the peristerite region.

The peristerite region is poorly understood, and the phase relations related to peristerite phenomena are highly speculative. Orville (1974) considered ordered (low) albite an essential phase in the formation of a peristerite assemblage of albite and disordered oligoclase, the assemblage having a lower free-energy than that of a single-phase disordered plagioclase. Now that the high–low albite relations are known, equilibration of compositions in the Na-rich region of the plagioclase system will be attempted. Work in this region has been hindered by the formation of zoisite at the expense of plagioclase in hydrothermal runs carried out at pressures high enough to promote equilibrium (Goldsmith, 1982).

### Note added in proof

The X-ray diffraction peak at  $31.6^\circ 2\theta$  which was interpreted as an intensity-enhanced  $\bar{1}\bar{3}2$  peak of albite in some of the abites equilibrated at the lower temperatures is now known to be the (unresolved)  $\bar{3}11$  and  $310$  peaks of jadeite at  $31.62^\circ$  and  $31.64^\circ 2\theta$ . The presence of minor jadeite in some of the run products has been confirmed by the observation that the  $31.6^\circ$  and other jadeite peaks increase in intensity with extended heat treatment of albite at approximately 18 kbar. The development of jadeite at pressure below the albite  $\rightleftharpoons$  jadeite + quartz boundary in some runs resulted from the presence of  $\text{Na}_2\text{CO}_3$  producing a silica undersaturated environment at the grain boundaries.

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