Linear compressibilities of low albite: high-pressure structural implications

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Abstract

Linear compressibilities of low albite have been determined at several pressures to 26 kbar (4.0% volume reduction). Axial compression ratios at 26 kbar are $\Delta a/a : \Delta b/b : \Delta c/c = 1.00 : 0.31 : 0.35$. Unit-cell angles α and β increase with increasing pressure, while γ remains constant. Changes of the unit cell during compression from 1 atm to 20 kbar are similar to the unit-cell changes on cooling from 1000° to 23°C. Therefore, continuous structural variations with changing pressure may be deduced from previously determined high-temperature structural data. The principal structural changes during compression are shortening of Na–O bonds and increasing triclinicity of the silicate framework. A possible transition to a less-symmetric albite phase analogous to primitive anorthite was not detected.

Introduction

Knowledge of the continuous changes of a mineral's unit cell and other structural parameters with temperature and pressure is of fundamental importance in characterizing these solid phases. Such changes provide the key to understanding the pressure–temperature variation of physical properties such as density, electrical conductivity, and indices of refraction. In some mineral groups (*e.g.* olivines and micas, Hazen, 1977) it may even be possible to predict limits of stability from these data.

In the past several years, high-temperature crystallographic studies on minerals have appeared in increasing numbers. However, there are few publications on the continuous variation of mineral structures with pressure, and no such published articles on monoclinic or triclinic phases. The present work defines the unit-cell variation with pressure of low albite, and suggests probable continuous structural changes which result in albite compression.

Experimental

Specimens of colorless low albite from Amelia Court House, Virginia, were kindly provided by Dr. Stewart Agrell, Department of Mineralogy and Petrology, University of Cambridge. An untwinned (100) cleavage plate approximately $150 \times 100 \times 30$ μm was selected and mounted in a miniature diamond pressure cell (Merrill and Bassett, 1974) using the metal-foil gasketing technique of Van Valkenburg (1970). Index-of-refraction oil was used as the hydrostatic pressure medium.

Unit-cell parameters of Amelia low albite were measured at room pressure using X-ray film techniques. Values of all triclinic parameters agree with previously determined data (Table 1). The pressure cell was tightened, and cell parameters were measured at 1, 11, 20, and 26 kbar; calibration of pressure was based on known volume compressibility of albite (Yoder and Weir, 1951; Fig. 1). Unit-cell parameters were remeasured at room pressure following the high-pressure experiments, and were found to agree, within estimated standard deviations, with the original values (Table 1).

One of the original reasons for performing this experiment was to explore the possibility that low albite might transform to a more ordered form analogous to primitive anorthite. A primitive anorthite unit cell contains four crystallographically unique Ca positions which degenerate into two distinct positions in body-centered anorthite at the transition temperature of 230°C (Czank *et al.*, 1975). However, the calcium atoms in these two sites appear as elongated peaks on electron density maps, indicating the presence of a spatial disorder. With the electron micro-

Table 1. Albite unit-cell parameters at high pressure

P(Kbar)[a]	V (Å³)	Δ V/V$_o$	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
1 atm[b]	664.0	0.0000	8.1385(9)[c]	12.7852(9)	7.1579(7)	94.277(6)	116.618(6)	87.697(4)
1 atm[d]	664.2	0.0000	8.138(6)	12.793(5)	7.158(5)	94.22(5)	116.66(5)	87.71(5)
1.0	663.1	0.0017	8.128(8)	12.781(8)	7.155(7)	94.29(10)	116.59(20)	87.77(10)
11.0	651.1	0.0197	8.046(8)	12.764(8)	7.136(7)	94.53(10)	116.78(20)	87.65(10)
20.0	643.3	0.0315	7.992(8)	12.707(8)	7.125(7)	94.61(10)	116.88(25)	87.83(10)
26.0	638.1	0.0390	7.962(8)	12.700(8)	7.104(7)	94.70(10)	116.98(25)	87.80(10)
1 atm[e]	664.2	0.000	8.135(6)	12.801(6)	7.151(6)	94.22(5)	116.59(5)	87.75(5)

a) Pressure calibration based on known volume compressibility of albite (Yoder and Weir, 1951).
b) Data of Sueno et al. (1973) at 1 atm and 24°C.
c) Parenthesized figures represent the esd in terms of least units cited.
d) Room pressure data, in pressure cell, before high-pressure.
e) Room pressure data, out of pressure cell, after high-pressure.

scope, Czank *et al.* also observed antiphase domains in $P\bar{1}$ anorthite which disappeared at the 230°C transition. Electron density maps of room-temperature low albite show a similar elongated peak in the Na position (Ribbe *et al.,* 1969) and this peak may represent a twofold degeneracy which would be removed at low temperature or at high pressure. An indication of such a transition could be given by a change in symmetry in which the *C*-centering of the triclinic albite cell would be destroyed, resulting in a primitive cell with two different Na sites but no major change in cell parameters. Alternatively, Na could select one of the two geometries consistent with $C\bar{1}$ symmetry. For the latter possibility there would be no change in symmetry or formation of a superstructure. Of the two kinds of transitions, the first is the only one that is theoretically possible, assuming that the transition is of second order. According to Landau's theory of phase transformations (Landau and Lifschitz, 1962), all second-order transformations must involve a lowering of symmetry with temperature, thus ruling out the second possibility.

In an attempt to examine whether low albite undergoes a transformation at low temperatures, we first tried electron microscopy using an AEI EM6G microscope fitted with a liquid-nitrogen cooling stage. No superstructure or diffuse reflections were observed in any of the diffraction patterns. This is consistent with the X-ray results of Williams and Megaw (1964) at liquid-nitrogen temperature. The next obvious step would have been to perform liquid-helium temperature experiments. However, it occurred to us that a high-pressure experiment could produce a greater reduction in cell volume than that possible at low temperature. A check of albite compressibility data (Yoder and Weir, 1951) showed that a pressure

of 25 kbar would result in a cell volume change of -25 Å³ (3.8%), which is more than would be expected for a crystal cooled to liquid-helium temperature. Although the $P-T$ phase diagram of albite (Bell and Roseboom, 1965) suggests that albite becomes unstable with respect to jadeite and quartz at about 5 kbar and 23°C, we assumed that albite would persist metastably to very high pressures in the diamond cell at room temperature.

Results

Unit-cell parameters and volumes for Amelia low albite at several pressures to 26 kbar are listed in Table 1. The variation of albite unit-cell volume with pressure (Yoder and Weir, 1951) and temperature (Sueno *et al.,* 1973) is illustrated in Figure 1; the
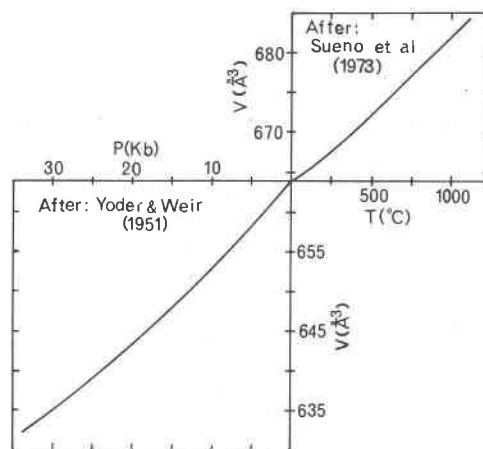

Fig. 1. Low albite unit-cell volume *vs.* temperature and pressure. The temperature and pressure axes have been scaled so that the slopes of the two portions of the graph appear similar. High-temperature data are from Sueno *et al.* (1973) and high-pressure data are from Yoder and Weir (1951).
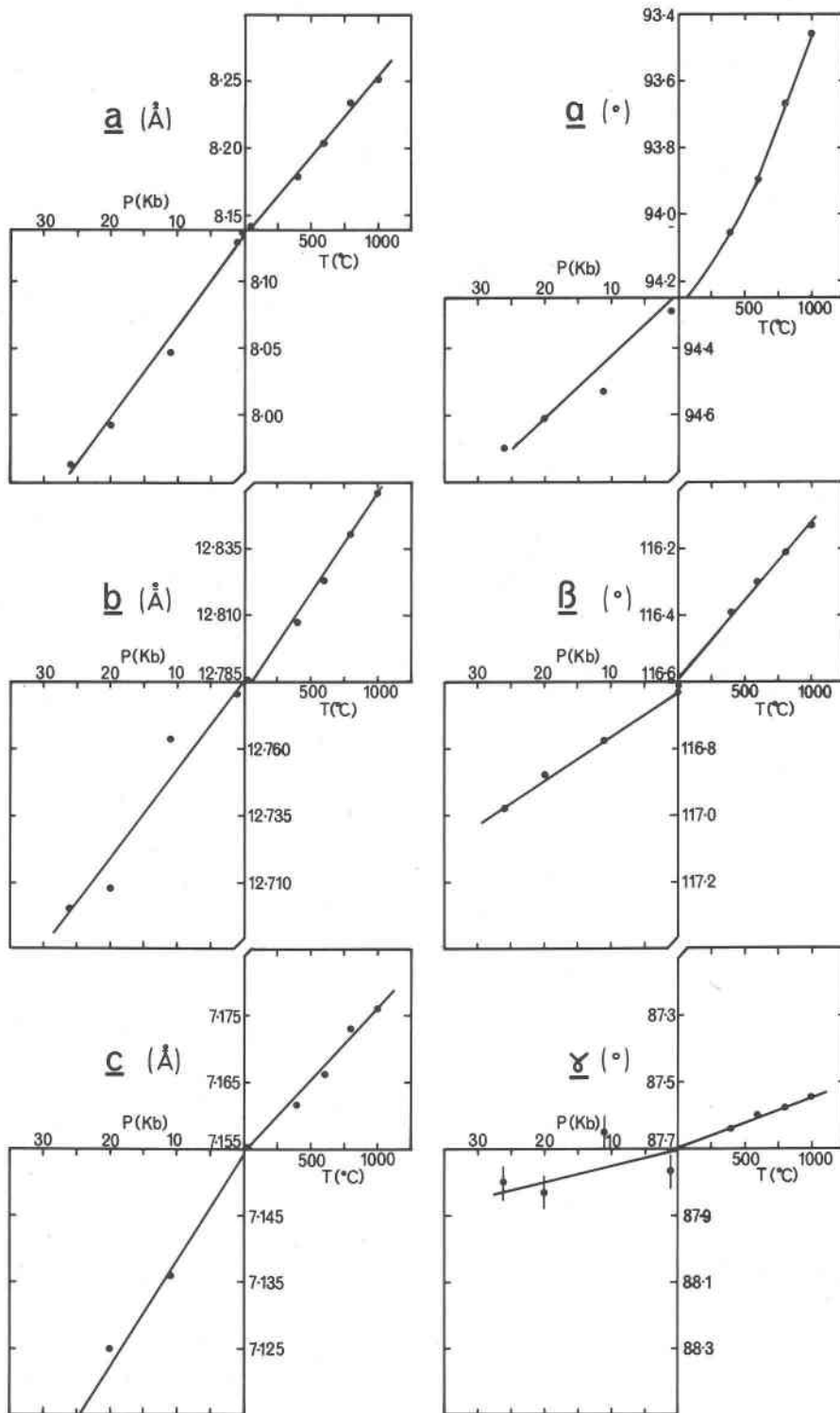
Fig. 2. Low albite unit-cell parameters *vs.* temperature and pressure. The temperature and pressure axes have been scaled in the same ratio as Fig. 1. Note the similarity in slopes of both sides of each plot: this implies that structural variations during compression are similar to those during cooling. High-temperature data are from Sueno *et al.* (1973).

pressure and temperature axes have been scaled so that the slopes are similar on both sides of this graph. In Figures 2a–f, plots with the same scaling of pressure and temperature axes are shown for the six triclinic unit-cell parameters. Since the slopes of the pressure and temperature portions of each plot are similar, compression of low albite's unit cell is approximately the inverse of its thermal expansion.

Thermal expansion and compression of albite may be represented by triaxial strain ellipsoids, calculated from the difference in unit-cell dimensions between room conditions and high temperature or high pressure. If expansion and compression are inversely related, then the orientations and axial ratios of the two strain ellipsoids should be similar. Magnitudes and orientations of these ellipsoids are given in Table 2a, and angles between the two ellipsoids axes are listed in Table 2b. Thermal expansion and compression strain ellipsoids are similar in axial ratios and orientations, thus confirming the inverse relationship between expansion and compression.

For both compression and thermal expansion *a* varies three times more than *b* or *c*, which show nearly equal expansion and compression. The interaxial angles α and β increase with pressure (decrease with temperature), while γ changes little with increasing pressure (decreases slightly with temperature). Note that α and β depart from 90° with increasing pressure, and approach 90° with increasing temperature. Thus, an increase in pressure increases the triclinicity of albite.

Careful examination of the precession photographs showed no evidence of superstructure reflections which would indicate a phase change. Because of the method used for pressure calibration, any discontinuity in cell volume resulting from a phase transformation would not be observed. Therefore, no evidence was found for a phase transformation in low albite at pressures up to 26 kbar.

Discussion

Little structural data on oxides and silicates at high pressure is available. For the few structures which have been studied both at high pressure and at high temperature, an inverse relationship appears to exist between structural response to temperature and pressure (Hazen and Prewitt, 1977). In general, polyhedra with cations of high coordination or small valence expand or compress more rapidly than those with cations of low coordination or large valence. In low albite an inverse relationship between compression and thermal expansion is observed in triclinic unit-cell dimensions. Thus continuous structure variations with increasing pressure are also inversely related to structural variations with increasing temperature.

Effects of temperature to 1000°C on low albite's crystal structure have been evaluated by Sueno *et al.* (1973). As the low albite structure expands with temperature its triclinicity decreases, but the crystals melt before a monoclinic symmetry can be achieved. Thermal expansion results from a "straightening" of the tetrahedral framework and expansion of the Na–O bonds, but with little expansion of the *T*–O bonds. Presumably the reverse happens as low albite is compressed. In compression, the cavity around Na should "collapse" and make Na favor one of its two equivalent sites.

It is intriguing to speculate on the general applicability of the inverse relationship between compressibility and thermal expansivity of minerals. It is not immediately obvious why the volume reduction of a compressed structure should occur in the same way as the volume reduction of a cooled structure. Certainly this behavior is related to bond strengths as defined by Pauling: weak bonds (*i.e.* bonds with large coordination or small valence such as Na–O in albite) will compress or expand more than strong bonds (such as Si–O in albite). However, the changes in bond lengths during thermal expansion are due to anharmonic vibration effects, which are not analogous to the forces which cause compression. Thus,

Table 2a. Albite thermal expansion (*T*) and compression (*P*) ellipsoid orientations and axial magnitudes

| | Strain Magnitude | Angles with respect to: | | |
		+X	+Y	+Z
R1(T)	0.021	29.28	64.36	76.82
R1(P)	−0.025	9.63	80.39	90.65
R2(T)	0.009	118.43	49.92	53.20
R2(P)	−0.010	96.60	43.55	47.21
R3(T)	−0.003	83.55	129.13	39.86
R3(P)	−0.003	83.01	131.95	42.80

Table 2b. Angles between albite expansion and compression ellipsoid axes. Note that for perfect alignment diagonal terms would be 0° while off-diagonal terms would be 90°

| Expansion Axis | Compression Axis | | |
	1	2	3
1	21.27	69.17	85.84
2	110.98	21.02	88.67
3	93.42	92.72	4.34

compression and cooling of a mineral are not expected to be structurally equivalent in all details. In any event, the similarity of the pressure and temperature response of oxides and silicates thus far studied provides valuable guidelines for the prediction of mineral structural variation within the solid earth.

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