

The Anorthite Crystal Structure at 410 and 830°C

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Abstract

The crystal structure of anorthite has been refined using data collected at 410°C and 830°C. Although at these temperatures the type 'c' reflections are nearly unobservable, the refinements yield results similar to those for primitive anorthite at room temperature. The structure on the unit cell level is therefore still primitive with 16 symmetrically nonequivalent Si and Al atoms. Calculation of 264 'c' reflection intensities using the position and thermal parameters of the structure at 25° (Wainwright and Starkey, 1971), 410°, and 830°C indicate that (1) both the Ca and the alumino-silicate framework atoms contribute to the diminution of 'c' reflection intensity with increasing temperature, and (2) the overall intensity decrease (calculated) due solely to the changes in atom position and thermal motion, while following the general trend of the observed decreases, is too small to account for the total decrease over the range 25–410°C. This suggests that within this temperature range another process, possibly a variation in domain texture, may also be taking place.

Introduction

The crystal structure of a primitive anorthite displaying sharp 'a', 'b', 'c', and 'd' type reflections was determined using film methods by Kempster *et al* (1962) and subsequently described by Megaw *et al* (1962). They found that the anorthite unit cell, space group $P\bar{1}$, was composed of four subcells related by three pseudosymmetry operations; body-centering, C-centering, and $c/2$ translation. The minor atomic coordinate differences between pseudosymmetrically related subcells give rise to the weak but sharp 'b', 'c', and 'd' subsidiary reflections, with the 'b' reflections having an additional contribution due to topochemical differences in the Si/Al distribution between the subcells related both by $c/2$ translation and C-face-centering. This crystal structure has recently been refined by Wainwright and Starkey (1971) using over 7000 counter-measured reflections.

The relative intensities and diffuseness of the 'c' reflections in primitive and transitional anorthite have been shown to be a function of both composi-

tion and temperature. Smith and Ribbe (1969) have comprehensively reviewed the experimental results and have summarized the interpretations. Therefore, only a brief resumé of the more significant relations will be given in this paper. In general, as the CaAl content of anorthite decreases, the intensities of the 'c' reflections decrease while they become increasingly diffuse. Fleet *et al* (1966) refined the structure of a "body-centered anorthite" of composition An_{80} which exhibited no observable 'c' or 'd' reflections. Appleman (1972) has refined the structure of a lunar plagioclase of composition An_{84} having 'c' reflections which were too weak and diffuse to measure, but lacking observable 'd' reflections. Both of these refinements were carried out using only 'a' and 'b' reflections and all show that each atom position is best approximated by a "split" atom pair, such that each "half atom" of the pair is related to the other by a body-centering translation, $(a + b + c)/2$. The general interpretation is that the crystal is composed of a mosaic of primitive anorthite domains related to each other by a body-centering translation across domain boundaries which parallel $(2\bar{3}1)$ (Ribbe and Colville, 1968). The electron microscope studies of Müller *et al* (1972) have shown

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that the diffuseness of the 'c' reflections at room temperature is a function of domain size; the more diffuse the 'c' reflections the smaller the domains.

The variation of 'c' reflections in anorthite as a function of temperature is more complex. Laves and Goldsmith (1954) demonstrated that the diffuseness of the 'c' reflections could be increased by quenching from high temperatures (950–1350°C) in much the same way that the diffuse 'c' reflections of a volcanic transitional anorthite are produced by natural quenching. The structure of a transitional anorthite was refined by Ribbe and Megaw (1962). Although weak and diffuse 'c' reflections were present, they were omitted from consideration since their intensities could not be accurately determined. Except for slight differences in temperature factors, the structure was indistinguishable from that of primitive anorthite. Brown *et al* (1963) and Bruno and Gazzoni (1967) using film techniques at high temperatures, observed a continuous and reversible change in the diffuseness of the 'c' reflections as a function of temperature, with the temperature of disappearance varying from 125 to 350°C depending upon the composition and thermal history of the sample. Foit and Peacor (1967b), using a single-crystal diffractometer technique, confirmed the previously observed changes in diffuseness and intensity and also showed that they occurred simultaneously with temperature change. However, these results were ambiguous as to whether the 'c' reflections were truly absent above 350°C or were merely too weak and diffuse to be observed. Czank *et al* (1970) found that the intensities of the 'c' reflections diminish rapidly between 25 and 230°C, but that for some reflections a very small residual intensity is observable to temperatures above 1500°C.

These observations at high temperatures, like those made with varying composition, have been interpreted using a domain model. An essential aspect of this model is the increase in the number of domains related by the body-centering vector (corresponding to a decrease in domain size) as an equilibrium function of temperature (Czank *et al*, 1970; Laves *et al*, 1970). However, recent electron microscope studies of anorthite conducted at high temperatures (Nord, personal communication; Wenk, personal communication) revealed no change in the number or the position of the domain boundaries as a function of temperature. The domain boundaries which were imaged using the diffuse 'c' reflections merely "faded" away with increasing temperature

such that above ~400°C, they were no longer observable. Upon cooling to room temperature the domain boundaries reappeared in the same (pre-heating) position. While the "fading" of the domain boundaries is correlated with the marked increase in the diffuseness of the 'c' reflections, the reappearance of the original texture on cooling has been interpreted to indicate that the domain texture has undergone no actual change as a function of temperature at least up to 600°C (Nord, personal communication).

The interpretation of the nature of the change in the anorthite structure with increasing temperature is further complicated by the ²⁷Al nuclear quadrupole resonance (n.q.r.) data of Brinkman and Staehli (1968a,b). They observed spectra indicative of eight symmetrically non-equivalent Al sites at low temperatures, as consistent with the X-ray diffraction results for primitive anorthite. In the temperature range 250–350°C (temperature depending upon sample composition) there occurs a reversible transition to a more diffuse four-fold overlapping spectrum which they interpret as a change to a body-centered cell with only four non-equivalent Al sites. This temperature range is in accord with the X-ray results which show the near absence of the 'c' reflections, and thus the apparent presence of a body-centered cell. Smith and Ribbe (1969) gave an alternative explanation of the n.q.r. results based on a shifting of the Ca atom between body-centered related sites. They noted that if the electrostatic field gradients at the two pseudo-body-centered Al atoms is reversing more rapidly than 10⁻⁷ second (above 250°C) due to a possible "bouncing" of the Ca atoms within the framework cavities, then only four overlapping n.q.r. spectra would be observable. With reference to changes taking place in the structure as a whole they state that "increasing thermal vibration makes the Ca cation 'appear larger' thus promoting larger holes in the framework with a tendency towards the *I2/m* requirements of the celsian structure," and further that "Ultimately the vibrations become so large that the alumino-silicate framework begins to move to a body-centered configuration with displacements of the order of 0.1–0.3 Å." The ultimate result is alteration of the domain texture.

Therefore, there is doubt not only concerning the nature of the changes in the domain texture as an equilibrium function of temperature, but also concerning specific changes within a given domain on the unit cell level, especially with regard to the rela-

tive contributions of the Ca atoms and the aluminosilicate framework. The purpose of this study is to elucidate the general nature of the changes in the anorthite structure as a function of temperature and thereby resolve some of the ambiguities present in previous interpretations. The refinement at 410°C was undertaken to determine the structural changes taking place over the temperature range where the intensities of the 'c' reflections are subject to major change, while the refinement at 830°C was carried out both to reveal any additional changes and to provide a further basis for comparison of the structures at 25°C (Wainwright and Starkey, 1971) and at 410°C.

Experimental

The sample used in this study was a transitional anorthite from Miyake, Japan. A composition of $An_{9.8\pm 1}$ was obtained from refractive index measurements of anorthite glass. At room temperature the sample used in this study displayed sharp 'a' and 'b' and diffuse 'c' reflections. Although the 'c' reflections rapidly become weaker and more diffuse with increasing temperature (Fig. 1), their presence at temperatures in excess of 830°C requires that the space group be $P\bar{1}$ with $8 CaAl_2Si_2O_8$ formula units per cell.

A cleavage fragment of dimensions $0.49 \times 0.11 \times 0.24$ mm was mounted along the *a* axis in a silica capillary for use with a high temperature diffractometer furnace (Foit and Peacor, 1967a). The lattice constants at the two temperatures under study (410 and 830°C) were approximated using room-temperature least-squares refined parameters and the thermal expansion data for calcic labradorite given by Stewart *et al* (1966). The changes in three of the six lattice constants of Miyake transitional anorthite were observed over the temperature range 25–830°C and were found to be comparable to those for the calcic labradorite. In addition, the exact positioning of the diffraction peaks at the calculated values for all levels of data confirms the appropriateness of these lattice parameters. The lattice constants used for this anorthite at 410 and 830°C are listed in Table 1.

As a precaution, the crystal was allowed to equilibrate for a 24-hour period at both 410 and 830°C preceding the measurement of intensities, even though all previous temperature-induced changes were observed to be instantaneous. The intensities of five 'b'

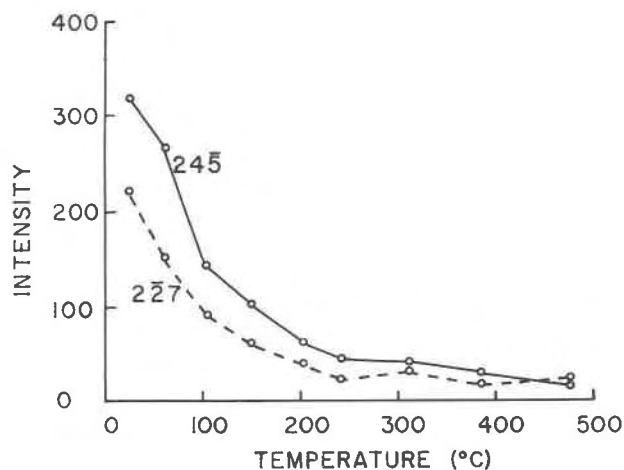


FIG. 1. A plot of integrated intensity (*I*) vs temperature (°C) for class 'c' reflections of Miyake anorthite.

reflections were monitored throughout the 6–10 day data collection periods to insure that any deterioration of the crystal or in the performance of the equipment would not go unnoticed. No significant change in the intensities of these 'b' reflections was observed during data collection. Also, a microscopic examination of the crystal at the termination of the experiments revealed no crystal-capillary reaction.

Approximately 2200 and 2400 non-equivalent 'a' and 'b' reflections were gathered at 410 and 830°C, respectively, using a single-crystal scintillation counter diffractometer employing Weissenberg flat-cone diffraction geometry and pulse-height-analyzed $MoK\alpha$ radiation. Due to a change in instrumentation between the two sets of data, the methods of data collection differed. The 410°C data were collected graphically using a chart recorder with the diffractometer in the manual mode. The reflections were integrated three times using a polar planimeter and

TABLE 1. Miyake Anorthite Lattice Parameters

	25°C*	410°C	830°C
<i>a</i>	8.179(2) Å	8.194(8) Å	8.223(4) Å
<i>b</i>	12.873(3) Å	12.897(8) Å	12.915(4) Å
<i>c</i>	14.172(3) Å	14.190(7) Å	14.204(7) Å
α	93.18(1)°	92.98(5)°	92.75(2)°
β	115.86(1)°	115.82(5)°	115.80(2)°
γ	91.23(1)°	91.15(5)°	91.02(2)°

*Values for primitive anorthite (An_{100}) from Val Pasma, Tyrol, Austria, *a* 8.173(1), *b* 12.869(1), *c* 14.165(1), α 93.113(6)°, β 115.913(6)°, and γ 91.261(6)°, Wainwright and Starkey (1971).

the values averaged. The 830°C data were collected using the diffractometer in the automatic mode (Supper-Pace System) and a flat graphite crystal monochromator. This system employs a background count on both sides of a peak scan. Temperature measurement was by means of a Pt/Pt-13 percent Rh thermocouple placed within one millimeter of the crystal. The estimated accuracy of the measurements is $\pm 10^\circ\text{C}$. The data were corrected for Lorentz-polarization factors and crystal absorption. No corrections were made for absorption by the silica capillary. The distribution of reflection intensities according to diffraction type is presented in Table 2.

Refinement

In their refinement of the structure of "body-centered anorthite" (An_{80}), Fleet *et al* (1966) found that the atom configuration was still primitive despite the body-centering symmetry indicated by the prominent 'a' and 'b' reflection pattern. It was suspected, therefore, that the anorthite structure (An_{98}) might still be primitive above 350°C. The starting parameters for the 410°C refinement were those of room temperature transitional anorthite (Ribbe, personal communication), while those for the 830°C refinement were the final parameters of the 410°C refinement. The use of the primitive atomic configuration of transitional anorthite (space group $P\bar{1}$) in conjunction with the high temperature 'a' and 'b' reflections resulted in an average structural model composed of "half-atom" pairs. In Figure 2 the atoms connected by solid lines represent two pseudo-body-centered T-O rings in the primitive anorthite structure projected on (010). The addition of body-centering symmetry, corresponding to refinement in space group $I\bar{1}$ ('a' and 'b' data), results in a superposition of subcells 1-4 and 2-3. Since the rings are not identical, "half atom" pairs are generated with the distance between them representing the deviation from body-centered symmetry. If the anorthite cell were truly body-centered above 350°C,

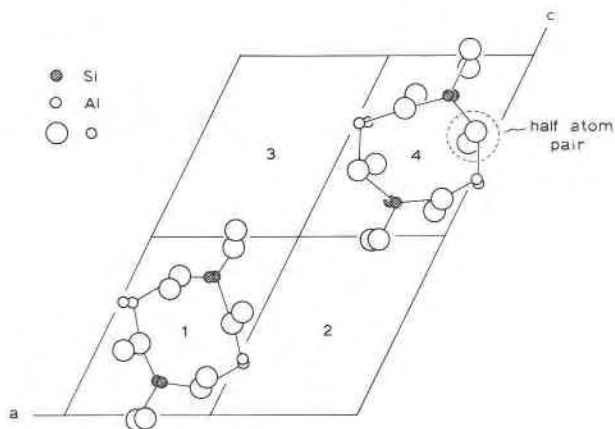


FIG. 2. Schematic representation of rings of silicon-aluminum tetrahedra in two subcells showing generation of "half-atom" pairs by the addition of a body-centering translation to a primitive ring configuration.

then during the course of the refinements the "half atom" pairs should coalesce to form single atoms and the atom arrangements in subcell pairs 1-4 and 2-3 (Fig. 2) should become equivalent.

The two data sets were refined using a full-matrix least-squares method. The form factor tables were formulated assuming complete Si/Al ordering and half-ionization of all atoms, from data in Vol. III of the *International Tables for X-Ray Crystallography*. Isotropic approximations to atom thermal motion were used in all stages of both refinements. Only structure factors greater than zero were employed and these were weighted according to several trial schemes including ones proposed by Cruickshank (1965) and Hanson (1965). In the last analysis, unit weighting yielded the most reasonable bond distances. In general the refinements followed a pattern of cycles of coordinate and scale factor refinement alternating with isotropic temperature factor refinement. A problem encountered in the refinement of both data sets was the marked oscillation of approximately ten oxygen atoms about relatively fixed positions. During refinement of the 410°C data, there was a gradual damping with cessation at $R = 0.13$, while in the 830°C refinement the oscillation, though greatly diminished, continued to convergence. This is undoubtedly responsible for the relatively high standard errors in the positional parameters. The final cycles for both data sets were carried out varying coordinates, scale factor, and

TABLE 2. Distribution of Observed and Unobserved Data According to Diffraction Type for Miyake Anorthite

	410°C			830°C		
	'a'	'b'	'a'+ 'b'	'a'	'b'	'a'+ 'b'
Observed	980	452	1432	1013	627	1640
Unobserved	145	624	769	198	597	795
Totals	1125	1076	2201	1211	1224	2435

temperature factors simultaneously. The final residuals are:

	410°C	830°C
From observed reflections:	0.076	0.104
Observed <i>plus</i> unobserved:	0.099	0.137

The observed and calculated structure factors at 410°C and 830°C are given in Tables 3 and 4, respectively,² while the final structural parameters are listed in Table 5.

Figure 3 is a plot of the isotropic temperature

² A copy of Tables 3 and 4 listing the values of $F(o)$, $F(u)$, and $F(c)$ may be obtained by ordering NAPS Document Number 02122 from microfiche Publications, 305 East 46th Street, New York, N. Y. 10017. Please remit in advance \$1.50 for microfiche or \$6.50 for photocopies. Please check the most recent issue of this journal for the current address and prices. (40 pages).

TABLE 5. Atom Coordinates and Isotropic Temperature Factors for Miyake Anorthite at 410°C and 830°C

atom	410°C	830°C	atom	410°C	830°C
Ca(000)	x 0.2672(10) y 0.9878(5) z 0.0822(5) B 3.8(1)	0.2704(11) 0.9831(5) 0.0843(5) 4.4(1)	O _A (20i0)	x 0.0783(18) y 0.4874(8) z 0.6308(8) B 0.7(2)	0.0822(19) 0.4886(8) 0.6282(8) 1.2(2)
Ca(x00)	x 0.2740(7) y 0.0333(3) z 0.5452(3) B 1.65(7)	0.2756(9) 0.0325(4) 0.5468(4) 2.73(8)	O _A (2zi0)	x 0.0793(17) y 0.4905(8) z 0.1313(8) B 0.7(2)	0.0789(18) 0.4919(8) 0.1276(8) 1.0(2)
Ca(0i0)	x 0.7736(6) y 0.5326(3) z 0.5465(3) B 1.27(6)	0.7737(8) 0.5294(3) 0.5488(3) 2.68(8)	O _B (0000)	x 0.8103(32) y 0.1086(14) z 0.0865(14) B 1.9(3)	0.8046(32) 0.1144(13) 0.0866(15) 2.6(3)
Ca(z10)	x 0.7623(8) y 0.5099(4) z 0.0656(4) B 2.21(7)	0.7640(9) 0.5053(4) 0.0689(4) 2.73(8)	O _B (0z00)	x 0.8117(25) y 0.1013(13) z 0.6035(10) B 1.4(2)	0.8133(33) 0.1045(16) 0.6110(12) 2.8(3)
T ₁ (0000)	x 0.0132(16) y 0.1548(6) z 0.1069(8) B 1.0(1)	0.0144(14) 0.1556(6) 0.1087(6) 1.3(1)	O _B (0010)	x 0.3343(31) y 0.5947(14) z 0.5985(15) B 1.3(2)	0.3403(27) 0.5955(12) 0.5994(13) 2.0(2)
T ₁ (00i0)	x 0.5009(7) y 0.6644(7) z 0.6026(8) B 1.2(1)	0.5011(14) 0.6672(6) 0.6002(6) 1.4(1)	O _B (0z10)	x 0.2825(30) y 0.6068(16) z 0.0819(12) B 1.6(3)	0.2943(27) 0.6064(14) 0.0851(10) 1.8(3)
T ₁ (mz00)	x 0.9998(6) y 0.8116(5) z 0.6106(8) B 0.9(1)	0.9994(18) 0.8104(6) 0.6119(6) 1.7(1)	O _B (m000)	x 0.8226(36) y 0.8585(19) z 0.1374(14) B 2.6(3)	0.8008(38) 0.8460(14) 0.1255(20) 3.5(4)
T ₁ (mz10)	x 0.5066(17) y 0.3238(5) z 0.1129(8) B 1.1(1)	0.5063(15) 0.3234(5) 0.1105(7) 1.0(1)	O _B (mz00)	x 0.8129(31) y 0.8546(16) z 0.6066(11) B 1.6(3)	0.8142(23) 0.8556(11) 0.6015(9) 1.6(2)
T ₂ (0z00)	x 0.6723(20) y 0.1059(9) z 0.6625(8) B 1.4(1)	0.6742(16) 0.1087(6) 0.6658(6) 1.3(1)	O _B (m0i0)	x 0.2960(31) y 0.3546(16) z 0.6161(12) B 2.1(3)	0.3166(38) 0.3706(14) 0.6270(20) 3.6(3)
T ₂ (0z10)	x 0.1834(19) y 0.6063(8) z 0.1545(7) B 0.7(1)	0.1842(15) 0.6037(6) 0.1535(6) 1.2(1)	O _B (mzi0)	x 0.3403(37) y 0.3592(20) z 0.1262(15) B 3.2(4)	0.3402(33) 0.3569(17) 0.1319(13) 3.7(4)

TABLE 5, Continued

atom	410°C	830°C	atom	410°C	830°C
T ₂ (m000)	x 0.6742(18) y 0.8806(7) z 0.1864(6) B 1.2(1)	0.6763(16) 0.8820(6) 0.1864(6) 1.2(1)	O _C (0000)	x 0.0283(26) y 0.2754(13) z 0.1491(11) B 1.7(2)	0.0365(29) 0.2757(14) 0.1515(13) 3.0(3)
T ₂ (m0i0)	x 0.1805(17) y 0.3822(7) z 0.6753(6) B 0.9(1)	0.1814(16) 0.3815(7) 0.6735(6) 1.3(1)	O _C (0z00)	x 0.0384(24) y 0.2922(13) z 0.6471(13) B 1.6(3)	0.0108(32) 0.2952(16) 0.6342(11) 2.1(3)
T ₁ (0z00)	x 0.0059(19) y 0.1587(6) z 0.6111(9) B 1.1(1)	0.0053(16) 0.1586(5) 0.6099(8) 1.5(1)	O _C (00i0)	x 0.4994(23) y 0.7846(11) z 0.6253(9) B 1.1(2)	0.5017(22) 0.7873(11) 0.6226(10) 1.5(2)
T ₁ (0zi0)	x 0.4994(18) y 0.6704(6) z 0.1126(8) B 0.8(1)	0.5001(13) 0.6735(5) 0.1150(6) 0.8(1)	O _C (0zi0)	x 0.5002(24) y 0.7974(12) z 0.1511(13) B 1.3(2)	0.5210(33) 0.7967(15) 0.1572(12) 2.2(3)
T ₁ (m000)	x 0.9897(16) y 0.8110(8) z 0.1192(9) B 1.1(1)	0.9958(20) 0.8088(7) 0.1190(10) 1.6(1)	O _C (m000)	x 0.9987(33) y 0.6808(15) z 0.1152(14) B 1.3(2)	0.0021(31) 0.6780(13) 0.1187(13) 1.8(3)
T ₁ (m0i0)	x 0.5115(16) y 0.3187(7) z 0.6204(8) B 0.8(1)	0.5051(17) 0.3217(5) 0.6199(8) 1.0(1)	O _C (mz00)	x 0.0042(40) y 0.6888(17) z 0.6098(15) B 1.8(3)	0.0114(26) 0.6944(11) 0.6146(10) 1.3(2)
T ₂ (0000)	x 0.6896(28) y 0.1146(13) z 0.1565(9) B 1.6(2)	0.6940(20) 0.1173(9) 0.1543(7) 2.2(2)	O _C (m0i0)	x 0.5193(34) y 0.1812(15) z 0.6023(14) B 1.6(3)	0.5222(35) 0.1861(15) 0.6020(15) 2.4(3)
T ₂ (00i0)	x 0.1899(26) y 0.6126(12) z 0.6645(9) B 0.9(2)	0.1911(14) 0.6130(6) 0.6674(5) 0.7(1)	O _C (mzi0)	x 0.5114(39) y 0.1926(17) z 0.0946(15) B 1.5(3)	0.5060(31) 0.1881(14) 0.0918(12) 2.3(3)
T ₂ (mz00)	x 0.6835(20) y 0.8711(7) z 0.6727(8) B 1.1(1)	0.6881(20) 0.8725(8) 0.6726(7) 1.2(1)	O _D (0000)	x 0.1821(41) y 0.1131(17) z 0.1941(18) B 2.6(3)	0.1771(37) 0.1053(17) 0.1930(17) 2.5(3)
T ₂ (mz10)	x 0.1866(18) y 0.3799(7) z 0.1813(7) B 0.8(1)	0.1857(23) 0.3790(9) 0.1819(9) 1.8(2)	O _D (0z00)	x 0.2126(31) y 0.1087(13) z 0.6879(14) B 1.3(2)	0.2004(31) 0.1226(12) 0.6962(15) 2.9(3)
O _A (1000)	x 0.0156(39) y 0.1335(13) z 0.9943(19) B 1.7(3)	0.0102(21) 0.1413(7) 0.9929(9) 1.0(2)	O _D (00i0)	x 0.6984(32) y 0.6029(13) z 0.6822(13) B 1.1(2)	0.7009(34) 0.6093(15) 0.6812(14) 1.8(3)
O _A (1z00)	x 0.9785(22) y 0.1295(13) z 0.4869(13) B 1.2(3)	0.9678(24) 0.1276(14) 0.4843(14) 2.4(3)	O _D (0zi0)	x 0.6885(31) y 0.6001(14) z 0.1973(14) B 1.7(3)	0.6996(23) 0.5954(8) 0.1918(11) 1.2(2)
O _A (10i0)	x 0.4988(39) y 0.6191(14) z 0.4870(19) B 1.5(3)	0.4993(27) 0.6122(10) 0.4892(12) 1.8(2)	O _D (m000)	x 0.2043(29) y 0.8773(12) z 0.2136(13) B 1.7(2)	0.1981(28) 0.8832(12) 0.2076(13) 2.6(3)
O _A (1zi0)	x 0.5199(25) y 0.6262(15) z 0.9947(15) B 1.5(3)	0.5247(21) 0.6269(11) 0.9986(11) 1.2(2)	O _D (mz00)	x 0.1657(33) y 0.8592(15) z 0.7160(16) B 2.8(3)	0.1655(35) 0.8639(17) 0.7176(17) 3.9(4)
O _A (2000)	x 0.5826(20) y 0.9939(9) z 0.1516(9) B 1.3(2)	0.5817(21) 0.9948(9) 0.1556(9) 1.2(2)	O _D (m0i0)	x 0.6857(30) y 0.3597(12) z 0.7251(13) B 2.1(3)	0.6880(26) 0.3604(11) 0.7240(12) 2.1(2)
O _A (2z00)	x 0.5730(23) y 0.9931(10) z 0.6473(10) B 1.7(3)	0.5775(23) 0.9898(10) 0.6503(11) 1.8(3)	O _D (mzi0)	x 0.7024(25) y 0.3629(11) z 0.2041(12) B 1.3(2)	0.7034(26) 0.3621(11) 0.2023(11) 1.7(2)

factors for Ca, Si/Al, and O as a function of temperature. The data of Quareni and Taylor (1971) on albite are plotted for comparison. The temperature factors of all atoms extrapolate to zero in the vicinity of 0°K. The similarity of the Si/Al and O behavior for both albite and anorthite indicates that, for anorthite, the refinement using the "half atom"

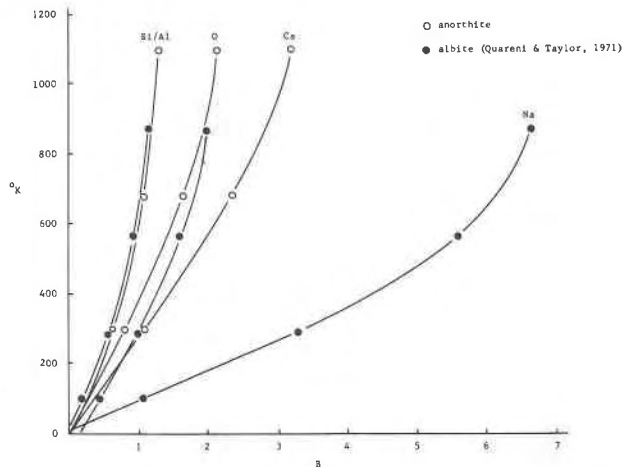


FIG. 3. A plot of isotropic temperature factors (B) vs temperature (K) for albite (Quaren and Taylor, 1971), for primitive anorthite at 25°C (Wainwright and Starkey, 1971), and for Miyake anorthite at 410 and 830°C.

model was realistic and accounts for all apparent positional disorder.

Description and Discussion of the Structure at Elevated Temperatures

In general, the average structure obtained using the 'a' and 'b' reflections measured at high temperatures is similar to the structures for primitive anorthite obtained by Kempster *et al* (1962), Megaw *et al* (1962), and Wainwright and Starkey (1971) (for structural details refer to the excellent diagrams in their papers). Therefore, as is indicated by the near absence of the 'c' and 'd' reflections, the anorthite unit cell does not become nearly body-centered above 350°C, but retains its primitive character at least to 830°C and probably to the melting point. It is of interest, therefore, to examine the ways in which the structure within the unit cell changes as a function of temperature. To accomplish this we made a comparison of the geometry of the coordination polyhedra and then analyzed the changes in pseudosymmetry of the atomic configuration in the anorthite unit cell.

The interatomic distances and angles were calculated using the function and error program ORFFE (Busing *et al*, 1964) along with the estimated errors in cell parameters and the correlation matrix of the least-squares refinements. An examination of the data in Tables 6, 7, and 8 reveals a greater variation in individual $T-O$ distances and $O-T-O$ angles within a given tetrahedron at high temperatures than at low, while for the Ca coordination polyhedra

TABLE 6. Tetrahedral Interatomic Distances for Primitive Anorthite (An_{100}) at 25°C and Miyake Anorthite at 410°C and 830°C

atoms	primitive anorthite*		Miyake anorthite	
	25°C	410°C	830°C	
$T_1(0000) - O_A(1000)$	$O_B(0000)$	1.645(2)	1.62(3)	1.63(2)
	$O_C(0000)$	1.619(2)	1.65(3)	1.69(3)
	$O_D(0000)$	1.582(2)	1.62(2)	1.62(2)
	$O_D(0000)$	1.616(2)	1.53(3)	1.54(2)
	Mean:	1.616	1.61	1.62
$T_1(0010) - O_A(1010)$	$O_B(0010)$	1.632(2)	1.71(3)	1.69(2)
	$O_C(0010)$	1.606(2)	1.60(3)	1.60(2)
	$O_D(0010)$	1.588(2)	1.57(2)	1.57(2)
	$O_D(0010)$	1.626(2)	1.75(2)	1.75(2)
	Mean:	1.613	1.66	1.65
$T_1(mz0c) - O_A(1z00)$	$O_B(mz0c)$	1.647(2)	1.69(2)	1.73(3)
	$O_C(mz0c)$	1.617(2)	1.62(3)	1.59(2)
	$O_D(mz0c)$	1.617(2)	1.58(2)	1.50(2)
	$O_D(mz0c)$	1.571(2)	1.60(2)	1.64(2)
	Mean:	1.613	1.62	1.62
$T_1(mzic) - O_A(1zi0)$	$O_B(mzic)$	1.644(2)	1.62(3)	1.62(2)
	$O_C(mzic)$	1.583(2)	1.53(3)	1.59(3)
	$O_D(mzic)$	1.599(2)	1.70(2)	1.76(2)
	$O_D(mzic)$	1.626(2)	1.61(2)	1.64(2)
	Mean:	1.613	1.62	1.65
$T_2(0z00) - O_A(2z00)$	$O_B(0z00)$	1.635(2)	1.61(2)	1.68(2)
	$O_C(m0i0)$	1.620(2)	1.69(3)	1.64(3)
	$O_D(m00c)$	1.606(2)	1.56(3)	1.59(2)
	$O_D(m00c)$	1.605(2)	1.60(2)	1.64(2)
	Mean:	1.617	1.62	1.64
$T_2(0z10) - O_A(2zi0)$	$O_B(0z10)$	1.617(2)	1.65(2)	1.61(1)
	$O_C(m000)$	1.628(2)	1.57(3)	1.59(3)
	$O_D(m01c)$	1.614(2)	1.70(3)	1.69(2)
	$O_D(m01c)$	1.574(2)	1.60(2)	1.63(2)
	Mean:	1.608	1.63	1.63
$T_2(m00c) - O_A(200c)$	$O_B(m00c)$	1.644(2)	1.66(2)	1.65(2)
	$O_C(0zic)$	1.581(2)	1.67(3)	1.66(4)
	$O_D(0z00)$	1.607(2)	1.64(2)	1.57(3)
	$O_D(0z00)$	1.629(2)	1.61(2)	1.53(2)
	Mean:	1.615	1.65	1.60
$T_2(m01c) - O_A(201c)$	$O_B(m01c)$	1.641(2)	1.62(2)	1.63(2)
	$O_C(0z00)$	1.618(2)	1.55(3)	1.53(4)
	$O_D(0z10)$	1.586(2)	1.54(2)	1.65(3)
	$O_D(0z10)$	1.616(2)	1.65(2)	1.74(2)
	Mean:	1.615	1.59	1.64
$T_1(0z00) - O_A(1z00)$	$O_B(0z00)$	1.760(2)	1.70(2)	1.70(2)
	$O_C(0z00)$	1.743(2)	1.70(2)	1.72(3)
	$O_D(0z00)$	1.709(2)	1.75(2)	1.78(2)
	$O_D(0z00)$	1.776(2)	1.73(2)	1.63(2)
	Mean:	1.747	1.72	1.71
$T_1(0z10) - O_A(1zi0)$	$O_B(0z10)$	1.772(2)	1.82(3)	1.83(2)
	$O_C(0z10)$	1.755(2)	1.80(3)	1.76(2)
	$O_D(0z10)$	1.727(2)	1.70(2)	1.65(2)
	$O_D(0z10)$	1.767(2)	1.79(2)	1.87(2)
	Mean:	1.755	1.78	1.78
$T_1(m00c) - O_A(1000)$	$O_B(m00c)$	1.777(2)	1.78(3)	1.73(2)
	$O_C(m00c)$	1.705(2)	1.63(3)	1.72(4)
	$O_D(m00c)$	1.738(2)	1.68(2)	1.69(2)
	$O_D(m00c)$	1.779(2)	1.84(2)	1.81(2)
	Mean:	1.750	1.73	1.74

* Wainwright and Starkey (1971)

TABLE 6, Continued

#ATOMS	primitive anorthite		Miyake anorthite	
	25°C	410°C	830°C	
T ₁ (m0ic) - O _A (10i0)	O _A (10i0)	1.777(2)	1.73(3)	1.79(2)
	O _B (m0ic)	1.747(2)	1.81(3)	1.73(4)
	O _C (m0ic)	1.752(2)	1.79(2)	1.77(2)
	O _D (m0ic)	1.702(2)	1.60(2)	1.63(2)
	Mean:	1.745	1.73	1.73
T ₂ (0000) - O _A (2000)	O _A (2000)	1.760(2)	1.75(2)	1.82(2)
	O _B (0000)	1.769(2)	1.68(4)	1.59(3)
	O _C (mz0)	1.740(2)	1.72(3)	1.72(2)
	O _D (mz0c)	1.698(2)	1.69(2)	1.68(2)
	Mean:	1.742	1.71	1.70
T ₂ (00i0) - O _A (20i0)	O _A (20i0)	1.769(2)	1.78(2)	1.77(1)
	O _B (00i0)	1.751(2)	1.81(4)	1.87(3)
	O _C (mz00)	1.754(2)	1.73(3)	1.74(2)
	O _D (mzic)	1.727(2)	1.69(2)	1.68(2)
	Mean:	1.750	1.75	1.77
T ₂ (mz0c) - O _A (2z0c)	O _A (2z0c)	1.755(2)	1.81(2)	1.75(2)
	O _B (mz0c)	1.748(2)	1.70(3)	1.74(3)
	O _C (00ic)	1.716(2)	1.72(2)	1.73(2)
	O _D (0000)	1.757(2)	1.72(2)	1.75(2)
	Mean:	1.744	1.74	1.74
T ₂ (mzic) - O _A (2zi0)	O _A (2zi0)	1.759(2)	1.71(1)	1.75(2)
	O _B (mzic)	1.713(2)	1.77(4)	1.73(4)
	O _C (000c)	1.735(2)	1.75(2)	1.70(3)
	O _D (00i0)	1.774(2)	1.75(2)	1.75(2)
	Mean:	1.745	1.75	1.73
Grand Mean	Si-O:	1.614	1.63	1.63
Grand Mean	Al-O:	1.747	1.74	1.74

these variations are not as marked. Two factors contribute greatly to these variations: (1) the greater error in the positional parameters of the high temperature refinements; (2) the distance between mean positions of the atoms may not be realistic in view of the increased anisotropy of atomic thermal motion at high temperatures. If, rather than comparing individual distances, we compare mean values, the effects of these factors are minimized. This is reflected in both the reasonable mean bond distances for individual polyhedra and also in the grand means for all coordination polyhedra of the same type. The following generalizations regarding changes in the anorthite structure with increasing temperature can be made on the basis of our data: (1) there is a significant increase in size of the Ca coordination polyhedra with no apparent change in the regularity (as deduced from the variations in Ca-O distances and O-Ca-O angles); (2) except for a possible increase in distortion, the mean dimensions of the Si and Al tetrahedra remain unchanged; (3) while the mean and grand mean *T-O-T* angles remain essentially unchanged, two of the four rings become more regular as reflected in a

large decrease in difference between the maximum and minimum angles (Table 9).

The next step in the examination of the effects of temperature on the anorthite structure was to make a detailed analysis of the shifts in atomic coordinates with regard to the pseudosymmetry of the structure. The primitive anorthite structure is highly pseudosymmetric with the atomic configurations in the four subcells related to one another by three pseudosymmetry operations: body-centering, *C*-centering, and *c*/2 translational symmetry. If one of a pseudosymmetrically related pair of atoms is transformed by the corresponding true symmetry operation and the distance between the two is calculated, this distance (in Å) represents the deviation from true symmetry for that pair of atoms. If the value is zero, then the pair would be truly symmetry-related and not just pseudo-related. This analysis was carried

TABLE 7. Bond Angles at the Tetrahedral Sites for Primitive Anorthite (An₁₀₀) at 25°C and for Miyake Anorthite at 410°C and 830°C

	°C	O _A -O _B	O _A -O _C	O _A -O _D	O _B -O _C	O _B -O _D	O _C -O _D
T ₁ (0000)	25	100.90	118.07	101.40	111.73	113.80	110.44
	410	103.5	116.4	110.6	106.5	119.4	101.1
	830	103.0	112.8	112.4	106.2	118.7	103.8
T ₁ (00i0)	25	103.09	116.38	102.05	110.92	113.56	110.51
	410	99.0	119.1	95.1	117.1	106.4	116.7
	830	96.4	123.6	93.3	119.0	105.8	114.4
T ₁ (mz00)	25	100.78	113.70	108.85	111.38	113.45	108.61
	410	103.3	118.3	104.9	112.8	108.8	108.2
	830	101.9	119.1	100.7	116.1	109.0	108.7
T ₁ (mzi0)	25	106.15	112.27	102.08	113.14	112.06	110.54
	410	102.5	107.6	108.6	113.9	116.8	106.8
	830	105.6	107.8	109.8	111.1	114.6	107.7
T ₂ (0z00)	25	105.34	101.24	110.17	112.51	111.79	114.83
	410	109.0	106.2	104.2	107.5	107.8	121.7
	830	107.8	101.6	100.6	119.4	105.9	119.2
T ₂ (0zi0)	25	109.19	102.50	110.99	112.86	107.14	114.10
	410	105.4	99.0	116.1	114.2	113.3	108.1
	830	106.8	97.9	118.0	117.7	111.6	104.8
T ₂ (m000)	25	111.89	104.43	108.95	112.98	107.26	113.33
	410	110.1	104.6	106.3	117.8	107.0	110.6
	830	115.4	107.8	113.1	107.4	105.8	107.0
T ₂ (m0i0)	25	108.79	106.37	107.89	112.60	108.75	112.27
	410	108.0	109.1	110.2	106.1	110.3	113.0
	830	103.7	103.1	106.4	118.1	108.6	115.4
T ₁ (0z00)	25	99.75	117.51	98.98	112.77	115.60	111.25
	410	99.8	113.3	103.4	115.9	119.8	104.2
	830	101.0	111.1	113.2	109.1	117.8	104.7
T ₁ (0zi0)	25	97.25	121.03	97.16	113.20	116.44	110.66
	410	98.2	124.1	93.8	110.0	113.5	115.6
	830	105.8	124.4	86.8	117.6	105.5	114.4
T ₁ (m000)	25	107.57	112.19	99.12	114.34	111.15	111.40
	410	106.3	113.7	96.4	116.3	109.3	112.9
	830	105.9	113.9	94.9	108.9	114.6	117.6
T ₁ (m0i0)	25	99.28	113.08	108.52	113.59	113.26	108.83
	410	99.1	111.6	111.2	111.4	114.8	108.7
	830	100.0	106.3	108.5	120.7	110.5	105.8
T ₂ (0000)	25	108.87	104.11	107.84	112.63	108.08	115.02
	410	111.5	103.4	105.2	107.7	108.4	120.5
	830	115.4	98.8	99.8	108.4	110.5	123.5
T ₂ (00i0)	25	100.96	99.94	107.64	112.74	115.95	116.74
	410	97.8	99.8	111.2	118.9	116.0	110.8
	830	95.7	102.3	114.1	118.1	116.2	108.9
T ₂ (mz00)	25	108.59	105.69	103.15	110.45	111.95	116.30
	410	111.5	100.9	101.5	111.7	110.8	119.4
	830	112.6	99.2	98.1	110.0	112.9	122.3
T ₂ (mzi0)	25	110.32	105.24	107.35	111.99	108.71	113.09
	410	106.1	110.3	109.8	111.7	110.8	108.2
	830	105.9	112.1	113.0	110.7	109.2	105.9

TABLE 8. Calcium-Oxygen Interatomic Distances Less Than 3 Å for Primitive Anorthite (An₁₀₀) at 25°C and Miyake Anorthite at 410°C and 830°C

atoms	primitive anorthite			
	25°C	410°C	830°C	
Ca(000) - O _A (2000)	2.292(2)	2.33(2)	2.31(2)	
	2.378(2)	2.45(2)	2.50(2)	
	2.390(2)	2.52(3)	2.51(3)	
	2.515(2)	2.55(3)	2.57(2)	
	2.538(2)	2.62(2)	2.49(2)	
	2.608(2)	2.74(2)	2.90(1)	
	Mean:	2.454	2.54	2.55
Ca(z0c) - O _A (2z0c)	2.333(2)	2.33(2)	2.36(2)	
	2.372(2)	2.45(2)	2.68(3)	
	2.443(2)	2.50(2)	2.62(2)	
	2.494(2)	2.50(2)	2.46(1)	
	2.496(2)	2.56(2)	2.64(2)	
	2.559(2)	2.57(2)	2.64(2)	
	2.733(2)	2.79(2)	2.73(2)	
	Mean:	2.490	2.53	2.59
	Ca(0ic) - O _A (20ic)	2.336(2)	2.35(1)	2.37(2)
		2.426(2)	2.39(2)	2.41(2)
2.434(2)		2.41(2)	2.40(3)	
2.448(2)		2.36(3)	2.34(2)	
2.494(2)		2.65(2)	2.68(3)	
2.563(2)		2.57(3)	2.70(2)	
2.817(2)		2.80(3)	2.72(2)	
Mean:		2.503	2.50	2.52
Ca(z10) - O _A (2zi0)	2.300(2)	2.37(1)	2.36(2)	
	2.405(2)	2.40(2)	2.42(2)	
	2.440(2)	2.45(3)	2.31(2)	
	2.454(2)	2.40(2)	2.43(2)	
	2.616(2)	2.67(2)	2.68(2)	
	2.717(2)	2.98(2)	2.90(2)	
	2.834(2)	2.75(2)	2.79(2)	
	Mean:	2.525	2.57	2.56
	Grand Mean:	2.493	2.54	2.56

out for all atoms and all pseudo-operations for the structure at 25°C, 410°C, and 830°C. The results are presented in Table 10a and show that with an increase in temperature, the separation between atoms related by the pseudo-body-centering and the pseudo-C-centering increases. In contrast, no distinct trend is evident from coordinate shifts of the atoms related by the *c*/2 pseudo-translation.

Our investigations as well as those of others indicate that variations in 'c' reflection intensity and in diffuseness with temperature are a function of at least one of the following parameters: (1) the small shifts in atomic coordinates and the marked changes in thermal motion observed in the high temperature refinements, and (2) an increase in domain boundary frequency with a concomitant increase in the relative volume of the structure represented by domain boundaries within which the structure must be very nearly body-centered (Czank *et al*, 1970; Laves *et al*, 1970). A comparison of these two factors may be obtained by computing 'c' reflection intensities for the anorthite structure as a function

TABLE 9. T-O-T Angles in the Four Rings of Primitive Anorthite (An₁₀₀) at 25°C and Miyake Anorthite at 410°C and 830°C

	primitive anorthite		
	25°C	410°C	830°C
O _B (0000)	129.41	134. (1)	134. (1)
O _D (0000)	136.45	142. (2)	136. (2)
O _B (mz00)	144.07	146. (1)	141. (1)
O _D (mz00)	165.21	162. (2)	158. (1)
Mean:	143.78	146.	142.
O _B (0z00)	138.79	141. (1)	146. (1)
O _D (0z00)	123.67	128. (2)	145. (2)
O _B (m000)	169.67	162. (2)	155. (2)
O _D (m000)	139.70	140. (2)	136. (1)
Mean:	143.03	143.	146.
O _B (m0i0)	145.76	149. (1)	154. (2)
O _D (m0i0)	165.08	162. (2)	158. (2)
O _B (0zi0)	126.88	126. (1)	128. (1)
O _D (0zi0)	135.01	131. (1)	120. (1)
Mean:	143.18	142.	140.
O _B (mzi0)	165.67	161. (2)	167. (1)
O _D (mzi0)	136.14	141. (2)	140. (2)
O _B (00i0)	137.61	131. (1)	131. (1)
O _D (00i0)	127.15	126. (1)	128. (2)
Mean:	141.64	140.	142.
Grand Mean:	142.90	143.	143.

of temperature (25, 410 and 830°C) and comparing these with the observed changes in the intensities of the 'c' reflections. In addition, this type of analysis allows separate assessment of the relative contributions of the Ca and the framework atoms to the variation in intensity of both individual 'c' reflections and the 'c' reflections as a whole.

A random sampling of 264 'c' reflections with

TABLE 10a. Deviation (in Å) from "True" Symmetry for Pseudo-Symmetrically Related Atom Pairs

pseudo-symmetry	25°C		
	Wainwright & Starkey (1971)	410°C	830°C
$\frac{a+b+c}{2}$	0.268	0.29	0.34
$\frac{a+b}{2}$	0.170	0.21	0.25
$\frac{c}{2}$	0.314	0.26	0.29

TABLE 10b. Deviation (in Å) from True Body-Centering for the Calcium, Silicon/Aluminum, and Oxygen Atoms

	25°C	410°C	830°C
Ca	0.770	0.63	0.66
Si/Al	0.152	0.17	0.20
O	0.263	0.30	0.37

$\sin \theta$ values within the range of the measured 'a' and 'b' reflections were chosen for computation. Structure factors were then calculated separately for the Ca atoms and for the Si, Al and O atoms using the positional and thermal parameters from each of the three refinements [25° (Wainwright and Starkey, 1971); and 410° and 830°C]. The separate contributions of the Ca atoms (F_{Ca}) and the Si, Al and O atoms (F_{frame}) for a number of the most intense 'c' reflections are listed in Table 11, with the averages for all 264 appearing at the bottom. These reflections are some for which (1) either the Ca atoms (025, 045, 065, 445, 447 and 625) or the framework atoms (221, 227, 267, 421, 623, and 663) have the greatest contribution, and (2) intensity has been previously monitored as a function of temperature (025 and 027; Foit and Peacor, 1967b), (227 and 245, Fig. 1), (045, Czank *et al.*, 1970) and (065, Laves *et al.*, 1970). The values presented in the third column ($I_{composite}$) are equal to $(F_{Ca} + F_{frame})^2$ which is proportional to the calculated intensity for a particular reflection. Since no corrections for Lorentz, polarization, or absorption effects have been made, $I_{composite}$ is only an approximate representation of the observed 'c' reflection intensity relationships. However, these corrections are not significant here since this analysis involves only comparison of intensity as a function of temperature.

The following generalizations can be made on the basis of the data in Table 11. First, the Ca atoms have a greater contribution to the total 'c' reflection intensity and its diminution with temperature than the framework atoms (refer to the mean values of F_{Ca} and F_{frame}). Secondly, the calculated (Table 11) as well as the observed intensity reductions (Fig. 1) were for the most part quantitatively similar regardless of the relative contributions of the Ca atoms and the framework atoms. This further emphasizes the "cooperative behavior" of the Ca and the framework atoms in bringing about an overall reduction in 'c' reflection intensity. Third, overall changes in atomic positions and thermal motion account for approximately 47 percent of the total intensity decrease for the 'c' reflection over the range 25-410°C and for approximately 2 percent over the range 410-830°C.

While these decreases conform to the observed general trend of the 'c' reflection intensity decreases with temperature (Fig. 1, Brown *et al.*, 1963; Foit and Peacor, 1967b; Czank *et al.*, 1970; and Laves *et al.*, 1970), the observed decreases in the range 25-410°C are greater than can be accounted for solely by the changes in atomic positions and thermal motion. Assuming that both the calculated and observed 'c' reflection intensities at elevated temperatures are accurate (*i.e.*, the reflections have

TABLE 11. Calculated Ca and Framework Contributions to Structure Factors and Resultant Intensities for 'c' Reflections

'c' reflection	25°C			410°C			830°C			Reference to high temperature observation
	F_{Ca}	F_{frame}	$I_{composite}$	F_{Ca}	F_{frame}	$I_{composite}$	F_{Ca}	F_{frame}	$I_{composite}$	
025	-11.5	-13.9	645	-6.1	-6.8	166	-6.1	-8.4	210	Foit, Peacor 1967b
025	-28.0	17.6	108	-21.2	5.7	240	-21.0	1.8	369	Foit, Peacor 1967b
027	-15.4	-11.8	740	-11.6	-10.3	479	-9.5	-13.7	538	
045	-30.2	-4.2	1183	-23.7	-1.3	625	-23.3	1.6	471	Czank <i>et al.</i> 1970
065	-27.7	-8.1	1282	-22.0	-5.6	762	-21.3	-5.1	697	Laves <i>et al.</i> 1970
221	-4.6	-20.1	610	-4.5	-17.2	471	-4.9	-10.5	237	This study
227	-0.5	-21.5	484	-2.1	-13.3	237	-1.3	-11.6	166	
227	7.5	32.8	1624	4.5	16.5	441	2.9	13.6	272	
245	30.7	7.9	1490	24.6	5.8	924	24.7	9.4	1162	This study
267	14.2	-31.7	306	11.0	-16.9	35	7.5	-16.0	72	
421	-0.5	17.2	279	-1.9	9.0	50	-1.0	1.3	0	This study
445	-24.6	1.1	552	-19.0	0.7	335	-18.7	3.6	228	
447	-25.1	1.5	557	-20.7	4.7	257	-18.6	1.5	292	This study
623	4.6	19.4	576	4.7	8.8	182	2.8	2.2	25	
625	18.2	1.6	393	13.2	0.5	188	11.7	-3.2	72	
663	-0.5	17.3	282	-1.3	12.2	119	-0.7	6.0	28	
mean for 264 reflections	8.8	6.4	205	6.7	4.5	109	6.0	4.7	105	

been fully integrated), it is difficult to escape the conclusion based on this data that reversible changes in the domain texture are taking place over the approximate temperature range 25-400°C, concomitant with the observed changes in atomic positions and thermal motion within the domains.

Megaw (1962) proposed that disorder of Si and Al provides the principal control over the formation of out-of-step domains in quenched specimens. Smith and Ribbe (1969) have reviewed the pertinent data and note that "If Megaw's idea is correct, the domain structure should be relatively unaffected by heating and cooling cycles below the temperatures at which the Si and Al atoms can diffuse. . . . If, however, the domain structure is controlled by uncorrelated vibrations of the alumino-silicate framework, such temperature cycling would drastically change the domain structure." The intensities and diffuseness of the 'c' reflections provide a measure of the nature of the domain structure. The crystal used for our intensity measurements has undergone a number of heating cycles. For example, intensity data have been collected at elevated temperatures on three occasions (410°C for 10 days, 830°C for 6 days, and again at 830°C for 6 days), the crystal being returned to room temperature after each set of measurements. The same crystal was also used to study the 'c' reflections as a function of temperature (up to a maximum of 1003°C for a brief period) both before and after measurement of these data sets, with the results of the first study being reported by Foit and Peacor (1967b). Figure 1 shows the variations in integrated intensity for some selected 'c' reflections as determined after the crystal had undergone the heating and cooling cycles. These results are qualitatively similar to those obtained with the first heating experiments, except that they were obtained using monochromated radiation, which permitted observation of residual intensity at high temperatures. In addition, electron microscope studies of anorthite have shown that the 'c' domain texture is altered only by heating to high temperatures. One sample of anorthite examined by G. Nord (personal communication) exhibited a change in domain texture only after heating to 975°C. These results are entirely consistent with Megaw's proposal that the domain texture of quenched samples as observed at room temperature may be altered only by heating to the very high temperatures required for Si-Al interchange.

The evidence regarding the possibility of changes

in domain texture in the temperature range 25-400°C is in part contradictory. The X-ray diffraction data suggests that the frequency of domain boundaries increases as a reversible, equilibrium function of temperature. On the other hand, electron diffraction data as earlier reviewed shows that the original textures are unaltered with heating, provided that temperatures on the order of 1000°C are not exceeded (Nord, personal communication). One explanation consistent with these data is that although the frequency of domain boundaries varies in the temperature range 25-400°C, the occurrence of specific boundaries is reversibly determined by the existing Al-Si distribution. We emphasize that this is highly speculative, and appears to be inconsistent with the electron diffraction data of Nord, who notes that the image of the domains simply "fades" with increasing temperature, as the 'c' reflections become increasingly diffuse. It is also interesting to note with regard to the "bouncing" Ca atom mechanism suggested by Smith and Ribbe (1969) that there is a significant increase in the pseudo-body-centeredness of the Ca atoms over the temperature range 25-410°C, while above this range there is little or no change (Table 10b). While our data does not by itself provide conclusive evidence of either the absence or the presence of domain texture changes in the temperature range 25-400°C, they do suggest that atomic position and thermal changes within the existing domain structure are not adequate to explain the observed changes in the 'c' reflection intensities.

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References

- APPLEMAN, D. E. (1972) Crystal structure of a lunar plagioclase of composition An_{84} . *Amer. Crystallgr. Ass. (abstr.) Amer. Mineral.* **57**, 324.
- BRINKMANN, D., AND J. L. STAEHLI (1968a) Magnetische Kernresonanz von ^{27}Al im Anorthit, $CaAl_2Si_2O_8$. *Helv. Phys. Acta*, **41**, 274-281.
- , AND ——— (1968b) Nuclear magnetic resonance of ^{27}Al in anorthite [$CaAl_2Si_2O_8$]. *Geol. Soc. Amer. Annu. Meet., Abstr. Programs*, 37-38.
- BROWN, W. L., W. HOFFMAN, AND F. LAVES (1963) Über kontinuierliche und reversible Transformationen des

- Anorthits ($\text{CaAl}_2\text{Si}_2\text{O}_8$) zwischen 25 und 350°C. *Naturwissenschaften*, **50**, 221.
- BRUNO, E., AND G. GAZZONI (1967) Ricerche roentgenografiche su plagioclasì bytownitico-anorthitici tra 15°C. e 1300°C. *Period. Mineral.* **36**, 683–698.
- BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1964) A Fortran crystallographic function and error program. *U.S. Nat. Tech. Inform. Serv.* **ORNL-TM-306**.
- CRUICKSHANK, D. W. J. (1965) Errors in least squares methods. In J. S. Rollet, Ed., *Computing Methods in Crystallography*. Pergamon Press, Oxford.
- CZANK, M., F. LAVES, AND H. SCHULZ (1970) On the domains of anorthite. *Naturwissenschaften*, **57**, 128.
- FLEET, S. G., S. CHANDRASEKHAR, AND H. D. MEGAW (1966) The structure of bytownite ("body-centered anorthite"). *Acta Crystallogr.* **21**, 782–801.
- FOIT, JR., F. F., AND D. R. PEACOR (1967a) A high temperature furnace for a single crystal X-ray diffractometer. *J. Sci. Instru.* **44**, 183–185.
- , AND ——— (1967b) High temperature diffraction data on selected reflections of an andesine and anorthite. *Z. Kristallogr.* **125**, 147–156.
- HANSON, A. W. (1965) The crystal structure of agulene, S-trinitrobenzene complex. *Acta Crystallogr.* **19**, 19–26.
- KEMPSTER, C. J. E., H. D. MEGAW, AND E. W. RADOSLOVICH (1962) The structure of anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$. I. Structure analysis. *Acta Crystallogr.* **15**, 1005–1017.
- LAVES, F., AND J. R. GOLDSMITH (1954) Long-range-short-range order in calcic plagioclases as a continuous and reversible function of temperature. *Acta Crystallogr.* **7**, 465–472.
- , M. CZANK, AND H. SCHULTZ (1970) The temperature dependence of the reflection intensities of anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ and the corresponding formation of domains. *Schweiz. Mineral. Petrogr. Mitt.* **50**, 519–525.
- MEGAW, H. D. (1962) Order and disorder in feldspars. *Norsk Geol. Tidsskr.* **42/2**, 104–137.
- , C. J. E. KEMPSTER, AND E. W. RADOSLOVICH (1962) The structure of anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$. II. Description and discussion. *Acta Crystallogr.* **15**, 1017–1035.
- MÜLLER, W. F., H. R. WENK, AND G. THOMAS (1972) Structural variations in anorthites. *Contrib. Mineral. Petrology*, **34**, 304–314.
- QUARENI, S., AND W. H. TAYLOR (1971) Anisotropy of the sodium atom in low albite. *Acta Crystallogr.* **27**, 281–285.
- RIBBE, P. H., AND A. A. COLVILLE (1968) Orientation of the boundaries of out of step domains in anorthite. *Mineral. Mag.* **36**, 814–819.
- , AND H. D. MEGAW (1962) The structure of transitional anorthite. *Norsk Geol. Tidsskr.* **42/2**, 158–167.
- SMITH, J. V., AND P. H. RIBBE (1969) Atomic movements in plagioclase feldspar: kinetic interpretation. *Contrib. Mineral. Petrology*, **31**, 157–202.
- STEWART, D. B., G. W. WALKER, T. L. WRIGHT, AND J. J. FAHEY (1966) Physical properties of calcic labradorite from Lake County, Oregon. *Amer. Mineral.* **51**, 177–197.
- WAINWRIGHT, J. E., AND J. STARKEY (1971) A refinement of the structure of anorthite. *Z. Kristallogr.* **133**, 75–84.

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