

Long-Range-Short-Range Order in Calcic Plagioclases as a Continuous and Reversible Function of Temperature

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A continuous structural change in anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and contiguous plagioclases is described as a function of temperature and $\text{NaAlSi}_3\text{O}_8$ content. In pure anorthite, this transformation takes place over a temperature range of approximately 450°C ., and is complete or nearly complete at the melting point (1554°C .). The presence of $\text{NaAlSi}_3\text{O}_8$ in solid solution greatly extends this temperature range. The transformation is manifested in single-crystal X-ray photographs by the variation in diffuseness of certain X-ray reflections, as a continuous and reversible function of temperature. To interpret the observations it is suggested that two structurally equivalent $\text{Ca}(+\text{Na})$ atom positions permit the development of out-of-step domains; the size (and shape) of these $\text{Ca}(+\text{Na})$ atom domains is an equilibrium function of temperature. The time required for the establishment of domain equilibrium varies with temperature, from a matter of minutes in the upper temperature range, to several days at approximately 800°C . The transition is observable in plagioclase crystals of composition ranging from pure anorthite to approximately 27% $\text{NaAlSi}_3\text{O}_8$.

Introduction

A new example of a continuous phase transition was described by the authors in a series of abstracts (Laves & Goldsmith, 1951*a, b, c*; Goldsmith & Laves, 1951; see also Laves & Goldsmith, 1954). This transition is observed in calcic plagioclases by the change in the diffuseness of certain X-ray reflections as a function of temperature. The diffraction pattern was shown to consist of reflections subdivided in the following way:†

- (a) (hkl) with l even and $(h+k)$ even.
- (b) (hkl) with l odd and $(h+k)$ odd.
- (c) (hkl) with $(h+k+l)$ odd:
 - (1) $(h+k)$ even, l odd;
 - (2) $(h+k)$ odd, l even.

The type (a), or 'main reflections', are characteristic of all feldspars; the (b) reflections are dependent upon the Al-Si distribution; the (c) reflections are consequent upon the distribution of the calcium atoms. Additional evidence relating to these considerations will be presented at a later date.

Whereas the (a) reflections are always found to be sharp, the (b) and (c) reflections may be sharp or diffuse. The (c) reflections, in particular, show considerable variation in degree of diffuseness, both in natural calcic plagioclases and in synthetic anorthite, as a temperature-dependent function of heat treatment.

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† Using the standard orientation of calcic plagioclases where $a \sim 8 \text{ \AA}$, $b \sim 13 \text{ \AA}$, $c \sim 2 \times 7 \text{ \AA}$, $\alpha \sim 93^\circ$, $\beta \sim 116^\circ$, $\gamma \sim 91^\circ$. This cell contains 8 $\text{CaAl}_2\text{Si}_2\text{O}_8$ formula weights.

The effect of heat treatment on pure synthetic anorthite

Small single crystals of pure synthetic anorthite were prepared from the melt, by the crystallization of less than 1 g. of glass. After crystallization near the melting point (pure anorthite melts at 1554°C .) the small platinum crucible was removed from the furnace and cooled rapidly in air. Fig. 1 is an X-ray photograph of one of the crystals of pure synthetic anorthite; the different types of reflections are indicated. The single crystal of Fig. 1 was then subjected to the heat treatments shown in Table 1, X-ray photographs being taken after each heating. Fig. 1 corresponds to state (l) of Table 1.

Figs. 2-5 are X-ray precession photographs of this same crystal taken after heat treatment at 1150, 1300, 1400 and 1500°C .; the letter designation of each photograph corresponds to that of Table 1. The (c_1) spots, being rather strong, are particularly useful for observing the effect of heat treatment. Four of these reflections are indicated in Fig. 2. All degrees of diffuseness can be produced in the (c_1) spots, from sharp reflections at approximately 1100°C ., to those that virtually disappear at 1550°C ., just below the melting point.

It is quite apparent that an equilibrium is established in a rather short time, so that a particular 'degree of diffuseness' is produced in the (c_1) spots characteristic of a particular temperature above 1150°C . Table 1 also shows the reversibility of this process.

The 'degree of diffuseness' has been arbitrarily scaled between 0 and 10 on the basis of visual estimation. The (c_1) reflections when completely sharp are designated as having zero 'degree of diffuseness'; the

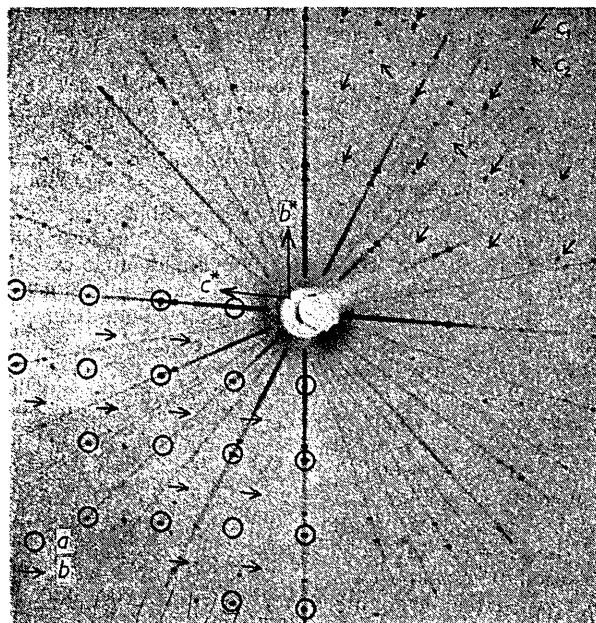


Fig. 1. Single-crystal a -axis precession picture of pure synthetic anorthite. The different types of reflections are indicated. Unfiltered Cu radiation used; β -reflections are unmarked, as are several additional spots due to contaminating Fe radiation.

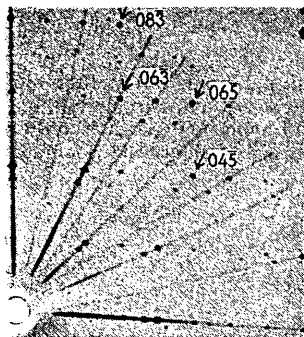


Fig. 2.

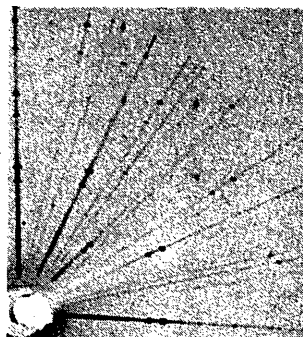


Fig. 3.

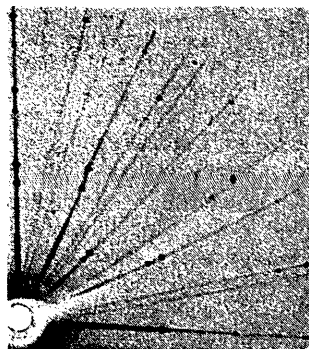


Fig. 4.

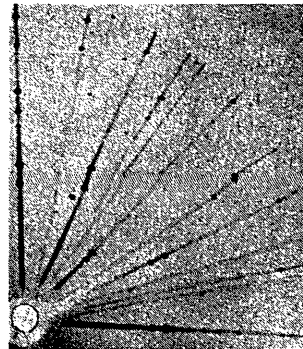


Fig. 5.

Figs. 2-5. Portions of single-crystal a -axis precession pictures of pure synthetic anorthite. Fig. 2 taken after heat treatment at 1150° C. Fig. 3 at 1300° C., Fig. 4 at 1400° C., and Fig. 5 at 1500° C. Four of the stronger (c_1) reflections are indicated (with indices) in Fig. 2. Unfiltered Cu radiation, 45 kV., 15 mA., exposure \sim 12 hr. The 'degrees of diffuseness' are respectively 0.2, 2-3, 6, and 9.

Table 1. *Thermal and X-ray data on pure synthetic anorthite**

Experiment	Temperature (°C.)	Time (hr.)	Condition of (c) reflections	Degree of diffuseness of (c ₁) reflections
<i>a</i>	As crystallized	—	Very diffuse	8
<i>b</i>	1400	48	Quite diffuse	6
<i>c</i>	1400	96	Quite diffuse	6
<i>d</i>	1300	48	Slightly diffuse	2
<i>e</i>	1150	96	Virtually sharp	0.2
<i>f</i>	1500	0.25	Very diffuse	9
<i>g</i>	1500	6	Very diffuse	9
<i>h</i>	1150	1	Virtually sharp	0.2
<i>i</i>	1150	168	Virtually sharp	0.2
<i>j</i>	1300	1	(Sample water-quenched) slightly diffuse	2-3
<i>k</i>	1300	1	(Sample cooled in ~ 15 sec.) no change	2-3
<i>l</i>	1300	1	(Sample water-quenched) no change	2-3
<i>m</i>	1400	1	(Sample water-quenched) quite diffuse	6
<i>n</i>	1400	1	(Sample cooled in ~ 15 sec.) no change	6

* Same crystal used in all above experiments.

value of 10 is assigned to (c₁) reflections that disappear by spreading into the background, even in heavily exposed X-ray photographs. On this basis, Figs. 2-5 represent degrees of diffuseness as shown:

Fig.	2	3	4	5
Diffuseness	0.2	2-3	6	9

This measure of diffuseness is, of course, qualitative, and certainly not accurate to more than approximately $\pm \frac{1}{2}$ of a unit.

The above heat treatments and X-ray photographs were all made with the same crystal (approximately 0.3 mm. in size). The same procedure was used in the work done on different specimens, to be described. The crystals were contained in tiny envelopes of platinum foil and heated in a platinum-wound quenching furnace. To determine what constitutes a 'quench', several cooling rates were tried. As indicated in Table 1, even moderately slow removal from the furnace into air is sufficiently fast; see runs (*j*) *v.* (*k*) and (*m*) *v.* (*n*). Runs (*k*) and (*n*) were withdrawn from the furnace rather slowly (samples pulled through the temperature gradient and into air in a period of approximately 15 sec.). This treatment produced results that could not be distinguished from an instantaneous water quench. All other runs on these and other samples were therefore quenched by rapid removal into the air and by immediately blowing the breath on the envelope.

It is clear that *the degree of diffuseness of the (c) reflections is a reversible function of the temperature, and equilibrium is attainable from either direction in a short time.*

Structural interpretation of the diffuseness

Publication of the full body of the writers' data on the plagioclases has been delayed in order to obtain more detailed information on the nature of the diffuse reflections in reciprocal space as a function of temperature, but certain information pertinent to the problem will be pointed out here. The fact that the (*a*)

reflections are sharp and unchanged at all temperatures up to the melting point indicates that a fundamental framework is maintained over the whole temperature range. Investigation of the reflection intensities produced by gallium- and germanium-containing synthetic anorthites as compared with normal (Al-Si) anorthite (Goldsmith & Laves, 1951) led the writers to the conclusion that the (*b*) reflections were a consequence of an ordered Al-Si distribution. This was also independently concluded by Sörum (1951, 1953) through the determination of the structure of a plagioclase (approximately 70% An).

The conclusion that the (*c*) reflections depend on the distribution of Ca atoms was drawn from two lines of evidence. First, the rapid equilibrium, obviously a low-energy phenomenon, cannot be ascribed to a rearrangement of the Al-Si-O framework. The extreme sluggishness of structural changes dependent upon Si-Al exchange has been discussed by Goldsmith (1952), Laves (1952*a*, *b*), and Goldsmith & Laves (1954). The second, and more direct line of evidence was afforded by a study of the gallium- and germanium-containing anorthites mentioned above.

Diffuse reflections associated with sharp reflections from the same crystal have been investigated by a number of workers (see, for example, Lipson, 1950). In all cases, this phenomenon is consequent upon disorder associated with some type of short-range order. If one interprets the critical temperature of disorder (T_c) as that temperature above which no long-range order is present, observations reported in the literature can be divided in two categories. Cowley (1950*a*, *b*) was able to show a temperature dependency of the size and shape of diffuse reflections above T_c in the alloy Cu₃Au. At temperatures below T_c , several attempts have been made to correlate diffuse reflections in alloys with the size and shape of 'domains' within the crystal (see treatment and further references in Edmunds & Hinde, 1952). No data are reported, however, indicating whether or not there is an equilibrium development of domains with temperature below T_c ; that is, whether or not any particular feature

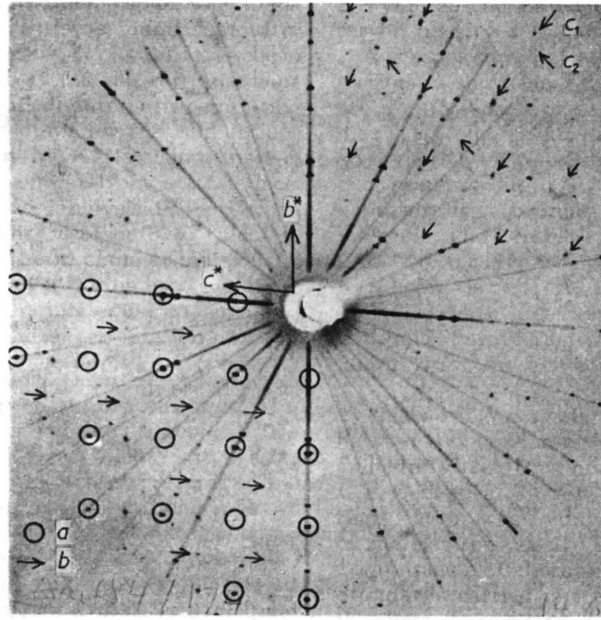


Fig. 1. Single-crystal a -axis precession picture of pure synthetic anorthite. The different types of reflections are indicated. Unfiltered Cu radiation used; β -reflections are unmarked, as are several additional spots due to contaminating Fe radiation.

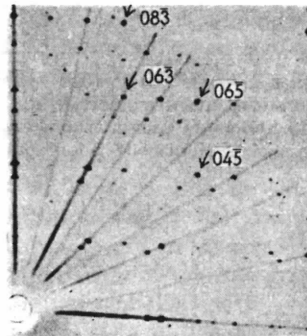


Fig. 2.

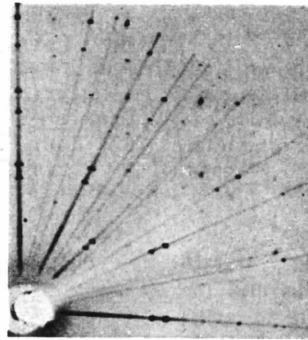


Fig. 3.

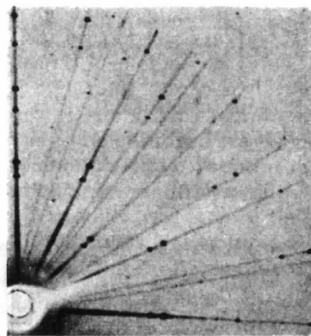


Fig. 4.

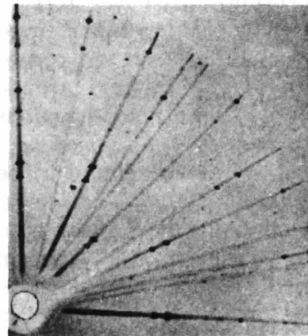


Fig. 5.

Figs. 2-5. Portions of single-crystal a -axis precession pictures of pure synthetic anorthite. Fig. 2 taken after heat treatment at 1150°C ., Fig. 3 at 1300°C ., Fig. 4 at 1400°C ., and Fig. 5 at 1500°C .. Four of the stronger (c_1) reflections are indicated (with indices) in Fig. 2. Unfiltered Cu radiation, 45 kV., 15 mA., exposure ~ 12 hr. The 'degrees of diffuseness' are respectively 0.2, 2-3, 6, and 9.

of the diffuse reflections can be identified as an equilibrium property of some particular temperature.

It was shown that the diffuseness of the (*c*) reflections in anorthite is a continuous and reversible function of temperature in the range from 1100° C. to the melting point. No discontinuity was observed. No analogous example is known to the writers. The X-ray effects appear to be best explained qualitatively by the following assumptions:

(1) There are two equivalent sets of lattice complexes that can be occupied by calcium ions; either arrangement produces an identical anorthite structure. These two sets can be called *A* and *B*.

(2) If all the calcium ions in an anorthite crystal were contained in either the *A*-sites or the *B*-sites, it would be fully ordered with respect to calcium, and the diffraction pattern would show sharp (*c*) reflections.

(3) If the calcium ions are distributed completely at random in the *A*-sites and the *B*-sites, the crystal is perfectly disordered with respect to calcium, and the (*c*) reflections would vanish into the background.

(4) If there are volumes within the crystal in which *A*-sites on the one hand, and *B*-sites on the other hand predominate,* these volumes can be called domains.

(5) The size and shape of such out-of-step domains will influence the intensity distribution of the (*c*) reflections. Qualitatively, the smaller the domains the more diffuse the reflections.

(6) The observations on the temperature dependency of the (*c*) reflections indicate that the domain size is a function of temperature, continuously ranging from exceedingly small domains at just below the melting point, to large domains that are effectively single

crystals (in terms of X-ray diffraction) at approximately 1100° C. in the case of pure anorthite.

(7) It is probable that the domain shapes are highly complex, and might not consist of finite volumes that are topologically equivalent to convex bodies. They might be as complex as two intertwined irregular networks. In this case, the 'domain size' might be represented by the two-dimensional area of a domain as revealed in a cross-section; or more properly, by the integrated 'interfacial' area dividing the *A* and *B* domains.

(8) The energy required to shift an individual calcium atom from an *A*-site to a *B*-site is very small, and as a consequence, the shifting of 'interfacial' areas involved in a change of domain size does not demand large energies. These energies are probably of the same order of magnitude as those necessary to move dislocations and shift twin boundaries in many substances.

Investigation of natural calcic plagioclases

In addition to the work on pure synthetic anorthite, twenty other crystals were examined. These specimens were from nine different occurrences, including one meteorite. All of these crystals were subjected to the same type of heat treatment as described in the case of synthetic anorthite. One of the samples was a single crystal produced in the laboratory from a melt of natural anorthite from Maikajima, Japan. All other specimens were fragments taken from larger natural crystals. Table 2 lists the crystals used, with composition indicated. (The compositions quoted were determined on the same tiny crystal fragment used for the thermal and X-ray work, or on an immediately adjacent fragment which was melted to a glass and a determination made based on the refractive index of the glass (see Foster, 1952).)

Tables 3-11 contain the thermal and X-ray data on the natural materials, presented in the same fashion

* Predominate in the sense that a greater number of *A* or *B* sites are occupied within a volume than would be by the development of local predominance expected within any small volume on the basis of statistical fluctuations.

Table 2. *Specimens examined*

Specimen No.	Locality	Anorthite content (Mol. %)
1	Synthetic	100
2	Corundum anorthosite, Salem, India	~ 100
3	Corundum anorthosite, Salem, India	~ 100
4	Corundum anorthosite, Salem, India	~ 100
5	Crystals in marble, Pasmada, Tyrol	~ 100
6	Eucrite, Wadaki, Japan	98-99
7	Eucrite, Wadaki, Japan	98-99
8	Granulite facies rock, W. Greenland	98
9	Crystal lapilli, Miakejima, Japan	97-98
10	Crystal lapilli, Miakejima, Japan	~ 97
11	Crystal lapilli, Miakejima, Japan	96-97
12	Crystallized from melt of Miakejima material	~ 97
13	Plagioclase-pyroxene rock, Grass Valley, Calif.	96
14	Plagioclase-pyroxene rock, Grass Valley, Calif.	96
15	Plagioclase-pyroxene rock, Grass Valley, Calif.	96
16	Achondritic meteorite (Juvinas)	~ 90
17	Troctolite, Merrill, Wisc. (Emmons, No. 166)	77-78
18	Anorthosite, India	75
19	Anorthosite, Split Rock Pt., Minn. (Emmons, No. 1A)	73
20	Anorthosite, Split Rock Pt., Minn. (Emmons, No. 1B)	73

as for the synthetic anorthite of Table 1. Discussion of the data follows.

Diffuseness of the (c_1) reflections as a continuous function of temperature

The reversibility and reproducibility with temperature of the degree of diffuseness of the (c_1) reflections

Table 3. *Anorthite, Salem, India, ~ 100% An**

Specimen No.	Heat treatment (°C.)	Degree of diffuseness of (c_1) reflections
2	None	0 (sharp)
2	1150, 168 hr.	0.5 (virtually sharp)
3	None	0
3	1548, $\frac{1}{2}$ hr.	10
4	None	0
4	1534, $\frac{1}{2}$ hr.	9-10
4	1000, 64 hr.	0

* Determined by chemical analysis, spectrographic analysis, and melting point.

Table 4. *Anorthite, Pasma, Tyrol, ~ 100% An**

Specimen No.	Heat treatment (°C.)	Degree of diffuseness of (c_1) reflections
5	None	0 (sharp)
5	1150, 3 hr.	0
5	1400, 1 hr.	6
5	1150, 3 hr.	0

* Determined by refractive indices.

Table 5. *Anorthite, Wadaki, Japan, 98-99% An**

Specimen No.	Heat treatment (°C.)	Degree of diffuseness of (c_1) reflections
6	None	0 (sharp)
6	1507, $5\frac{1}{2}$ hr.	9-10
6	1150, 168 hr.	2
7	None	0.5 (virtually sharp)
7	1150, 168 hr.	2
7	1000, 64 hr.	1
7	900, 168 hr.	0.5

* Determined by refractive index of glass produced by melting fragment of the crystal.

Table 6. *Anorthite, Greenland, 98% An**

Specimen No.	Heat treatment (°C.)	Degree of diffuseness of (c_1) reflections
8	None	0 (sharp)
8	1000, 24 hr.	0
8	1100, 24 hr.	0.2 (virtually sharp)
8	1200, 24 hr.	2
8	1300, 24 hr.	5
8	1400, 24 hr.	7
8	1500, 3 hr.	9
8	1150, 1 hr.	2

* Determined by refractive index of glass produced by melting fragment of the crystal.

Table 7. *Anorthite, Miakejima, Japan, ~ 97% An (variable)**

Specimen No.	Heat treatment (°C.)	Degree of diffuseness of (c_1) reflections
9	None	5
9	1150, 1 hr.	5-6
9	1150, 72 hr.	5-6
9	1500, 3 hr.	9
9	1150, 72 hr.	5-6
9	1000, 24 hr.	4-5
9	1150, 24 hr.	5-6
9	900, 168 hr.	3-4
10	1540, $\frac{1}{2}$ hr.	10
10	1150, 168 hr.	5
11	None	7
11	1400, 6 hr.	8
11	1510, 6 hr.	9
11	1510, 96 hr.	9
11	1150, 168 hr.	3

* Specimen No. 9 = 97-98% An, determined by refractive index of glass produced by melting fragment of the crystal.

Specimen No. 10, composition undetermined.

Specimen No. 11, 96-97% An, determined from refractive index of its glass.

Table 8. *Recrystallized anorthite, from melt of material from Miakejima, Japan, ~ 97% An**

Specimen No.	Heat treatment (°C.)	Degree of diffuseness of (c_1) reflections
12	a. Original, as crystallized	7
12	b. 1530, 5 hr.	10
12	c. 1400, 6 hr.	8
12	d. 1400, 21 hr.	8
12	e. 1530, $5\frac{1}{2}$ hr.†	10
12	f. 1400, $5\frac{1}{2}$ hr.	8
12	g. 1400, 48 hr.	8
12	h. 1300, 48 hr.	6
12	i. 1150, 48 hr.	3
12	j. 1150, 96 hr.	3
12	k. 1500, 0.2 hr.	10
12	l. 1500, 6 hr.	10
12	m. 1530, 0.25 hr.	10
12	n. 1530, 6 hr.	10
12	o. 1150, 170 hr.	3
12	p. 850, 170 hr.	1
12	q. 1150, 24 hr.	3

* Composition not determined directly, but material used for crystallization was 97% An.

† Slight melting noted in surface of crystal.

Table 9. *Anorthite, Grass Valley, California, 96% An**

Specimen No.	Heat treatment (°C.)	Degree of diffuseness of (c_1) reflections
13	None	1
13	1430, $1\frac{1}{2}$ hr.	8-9
13	1150, 24 hr.	6
13	1000, 64 hr.	5
14	None	1
14	1150, 24 hr.	6
14	900, 168 hr.	4
14	750, 114 hr.	3
15	None	1
15	750, 114 hr.	2

* Determined by refractive indices, and index of glass melted from fragment of crystal.

Table 10. *Anorthite from meteorite, Juvinas, ~90% An**

Specimen No.	Heat treatment (°C.)	Degree of diffuseness of (c_1) reflections
16	None	4-5
16	1150, 168 hr.	8
16	1000, 64 hr.	6-7
16	900, 168 hr.	6-7

* Determined by refractive indices.

Table 11. *Data on plagioclases in composition range 70-80% An*

Specimen No.	Mol. % An*	X-ray observations
17	77-78	(c_1) reflections very diffuse; degree of diffuseness near 10. (b) reflections sharp. (c_1) reflections still observable after 5 hr. at 1150° C.
18	75	(c_1) reflections considerably sharper than above; degree of diffuseness ~ 7. (b) reflections are split ($\delta_c = 167^\circ$),† but connected by diffuse lines $\sim \perp (01\bar{1})$; true cell
19	73	(c_1) reflections exceedingly diffuse, barely observable. In 60 hr. exposures, reflections become apparent. (b) reflections sharp
20	73	(c_1) reflections not observed, even after 60 hr. exposure. (b) reflections sharp

* Composition determined by refractive indices on (010) or (001) cleavage. Specimens 17, 19 and 20 described by Emmons (1953). Chemical analyses listed by Emmons in weight % show specimen 17 (Emmons, No. 166) to be 81.5% An, specimen 19 (Emmons, No. 1A) is 77.2% An, and specimen 20 (Emmons, No. 1B) is 76.8% An. Specimens 17, 19, and 20 come from the same samples from which Cole *et al.* (1951) took their samples Nos. 25, 1, and 2. Our determinations show 2-3% less An than Emmons', even after converting his data to mol. %. One must consider compositional variations within a sample, however, and must determine the composition of the particular tiny crystal used. This point is also mentioned by Cole *et al.* (1951).

† Notation of Cole *et al.* (1951). This value of 167° is larger than any observed by Cole *et al.*, but is present in a more calcic plagioclase than they had found to contain split (b) reflections. The value fits their extrapolated curve (Fig. 2, p. 26) exceedingly well, i.e. $\delta_c = 167^\circ$ should be found in plagioclase of 75% An. Another observation should be mentioned. Many of the main reflections show satellite reflections, an observation also noted briefly by the above authors. In this material, these satellites have an average intensity approximately 10 times that of the (b) reflections (and are also connected to the main reflections by diffuse streaks), those observed by Cole *et al.* were reported to have intensities 100 times less than the (b) reflections. The satellites here noted, along with the split (b) reflections, can be indexed on the basis of a superstructure ~ 200 Å in the c direction. These reflections appear in c -axis rotation photographs on the 2nd, 26th, 30th, 54th, and 58th layer lines (the main reflections appear on the 0th, 28th, and 56th layer lines); the (b) reflections appear on the 13th, 15th, 41st, 43rd, 69th, and 71st layer lines.

was observed in all of the specimens studied. As in the case of pure anorthite, a specific degree of diffuseness is characteristic of a particular temperature, although

variable between specimens. This is clearly shown in the tabulated data. For example, specimen No. 12 (Table 8) was subjected to a series of 16 heat treatments at temperatures of 850, 1150, 1300, 1400, 1500, and 1530° C., and a specific diffuseness was observed in the (c_1) reflections for each temperature, irrespective of the previous heat treatment. The diffuseness value was 3 at 1150° C., whether approached from temperatures above 1150° C., as in states (i) and (o), or from below 1150° C., as in state (g). In Table 5, it is seen that the diffuseness value of 2 is characteristic of the Wadaki anorthite at 1150° C., whether produced from the originally sharp state, as in sample No. 7, or from the very diffuse state first produced by heating at 1507° C., as in sample No. 6. As shown in the remaining tables, all of the specimens examined from this point of view exhibit this reversible behavior. It is quite clear that an equilibrium relating temperature and the degree of diffuseness of the (c_1) reflections is established in natural calcic plagioclases as it was in the case of pure synthetic anorthite. The specific values of diffuseness as a function of temperature are discussed below with relation to the sodium content of the samples. In addition, the continuous nature of this transition is illustrated in a plot of the data of Tables 1, 6, 7, 9 and 10, shown as Fig. 6.

Diffuseness of the (c_1) reflections as a function of NaAlSi₃O₈ content

In pure synthetic anorthite observable diffuseness of the (c_1) reflections does not set in until a temperature of approximately 1100-1150° C. is reached.* Tables 3 and 4 show that the same is true of pure or virtually pure natural anorthites. The effect of NaAlSi₃O₈ content on the relation between temperature and (c_1) reflection diffuseness is, however, quite striking. Fig. 6 illustrates this effect by data on six of the crystals. At 1150° C., equilibrium degrees of diffuseness of 0, 2, 3, 5-6, 6, and 8 are shown for these six samples. Thus a change from 100% to approximately 90% An produces a spread over the greater part of the diffuseness range at this temperature. The change produced by even a few per cent NaAlSi₃O₈ is very great indeed.

The general trend of the curves suggests that they reach a value of 10 (virtual disappearance of the (c_1) reflections) at or near the melting points of the respective specimens. Fig. 6 also suggests that plagioclase compositions, somewhat more sodic than 90% An, might have (c_1) reflections so diffuse, even at low temperatures, that these reflections might escape observation.†

It can also be seen from Fig. 6 that although pure anorthite develops sharp (c_1) reflections below 1150° C.,

* In this and succeeding discussions of temperature, reference is to the high-temperature equilibrium state as observed in quenched crystals.

† The effect of the sodium content on the diffuseness of the

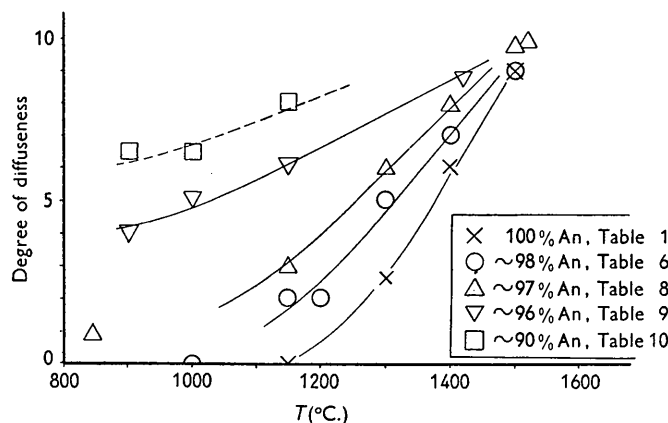


Fig. 6. Plot of 'degree of diffuseness' of the (c_1) reflections *v.* temperature for six calcic plagioclases in the composition range ~ 90 – 100% anorthite.

the presence of only moderate amounts of $\text{NaAlSi}_3\text{O}_8$ very markedly lowers the maximum temperature consistent with sharp reflections. For example, a crude (and admittedly uncertain) extrapolation of the diffuseness–temperature curve of the Grass Valley anorthite would indicate that sharp (c_1) spots could only be developed below roughly 400°C . Thus plagioclases containing somewhat more than approximately 5% $\text{NaAlSi}_3\text{O}_8$ might be expected to show (c_1) reflections that cannot be made sharp in any reasonable length of time, owing to the low rate of ionic movement at these low temperatures. Furthermore, it is not unlikely that plagioclases with approximately 10% or more $\text{NaAlSi}_3\text{O}_8$ cannot show sharp (c_1) reflections at all, as the 'sharpening temperature' may lie below normal earth-surface temperatures.

It is not certain that this effect on the temperature–diffuseness relation can be solely attributed to $\text{NaAlSi}_3\text{O}_8$ content. It is apparent that the (c_1) reflections are controlled by the Ca (+Na) atom distribution. The Na atoms may well act as any other impurity and thus strongly influence the domain–temperature relations. On the other hand, as Na enters the structures, the Al:Si ratio of the fundamental framework is also changed. The secondary effect of the change in the framework on the Ca-atom domains is not known.

Additional data on isomorphism in the range 70%–100% anorthite

Cole, Sörum & Taylor (1951) report that in a plagioclase with 72% An, the reflections that are here called

(c) reflections is also discussed by Gay & Taylor (1953) and by Gay (1953). Their observations, however, were limited to specimens that were not heat treated, and therefore conclusions could not be drawn as to the equilibrium states. The very diffuse nature of (c) reflections in plagioclases more sodic than $\sim 90\%$ An can account for the fact that Gay (1953) reported them absent in plagioclases with 20% or more $\text{NaAlSi}_3\text{O}_8$. These reflections have been observed by the present writers in compositions up to $\sim 27\%$ $\text{NaAlSi}_3\text{O}_8$, as will be discussed shortly.

the (c) reflections are absent. They state, 'We do not know whether the change from the body-centred to the primitive anorthite structure takes place discontinuously or by the gradual appearance of the additional reflections on passing from 72 to 100% anorthite'. The above authors thus have no evidence to show that the (c) reflections (indicative of a primitive cell) disappear at any particular composition between 100% and 72% An. Cole *et al.* propose two alternative models to explain their findings; the first proposal is that 'The region 100 – 85% anorthite is then one of true isomorphous substitution, in which random replacement of calcium and aluminium by sodium and silicon atoms raises the true symmetry from primitive to body-centered'. Their second alternative is, '... the whole range 100 – 72% anorthite corresponds to isomorphous substitution, with the associated symmetry change'. The first model is based on the extrapolation of a relationship between composition and the amount of 'splitting' of certain superstructure reflections (here called (b) reflections). No data are presented to support the second model. In the light of the data here presented it is now apparent that the change from the primitive anorthite structure to the body-centered structure is a gradual one. This view was independently arrived at by Gay (1953). However, it should be noted that this change is manifested by the gradual diffusing into the background of the (c) reflections, and not by the gradual diminution in total intensity of the reflections.

Specimens 17–20 (Table 2) were examined for the purpose of extending the composition limits to the point where the (c) reflections might not be observable. Table 11 presents the data on these crystals. Sample 19 shows that (c_1) reflections, although exceedingly diffuse, can be present in a plagioclase of 73% An. This indicates that the first of the two alternative models proposed by Cole *et al.* can be discarded, and that the gradual change in the structure extends at least to 73% An. On the other hand, it should be noted that specimen 18 (75% An, Table 11) has (b)

reflections that are split, which is unexpected in the light of the data of Cole *et al.*, who state that the splitting was not observed in plagioclases more calcic than 71.5% An. The following tentative suggestions are made:

(1) The (*b*) and (*c*) reflections are not directly related to each other; the splitting of the (*b*) reflections, and the presence and degree of diffuseness of the (*c*) reflections are not completely interdependent. This is likely in the light of the order-disorder relations mentioned in the introductory statements.

(2) Variations in the correlation between (*b*) and (*c*) reflections might be a function of the thermal history of the specimen. The (*c*) reflections can be relatively easily changed, whereas the (*b*) reflections cannot, inasmuch as they are controlled by the strongly bonded Al and Si atoms.

(3) It is thus possible that the 'first model' proposed by Cole *et al.* is correct for low-temperature plagioclases in the range considered (70–100% An).

(4) This model, however, is incorrect for what may be considered high temperature plagioclases, as it is here shown that the structural change is continuous between approximately 70% and 100% An.

Time required for equilibration

Several experiments were carried out to obtain some information on the rate at which equilibrium is established. For example, Tables 1 and 7 show that times of 15 min. and $\frac{1}{2}$ hr. were sufficient for equilibrium at temperatures of 1500–1540° C.; it is quite probable that several minutes would have been ample. At 1150° C., 1 hr. was found to be sufficient, as evidenced from Tables 1 and 6. No experiments of shorter duration were carried out. Experiments at 900° C. were done on a crystal of the Salem, India, anorthite (data not included in Table 3). This crystal, originally with sharp (*c*₁) reflections, was heated 30 min. at 1530° C., producing a diffuseness value of 9–10. It was then held 1 hr. at 900° C. Sharp (*c*₁) reflections appeared, although a diffuse area remained around the sharp spots. It can be concluded that equilibrium was not quite reached in 1 hr., and that some of the residual short-range order was superimposed on the long-range order (stable in this material below approximately 1150° C.). An additional heating period of 24 hr. at 900° C. obliterated the weak diffuseness; equilibrium is thus established in a period of less than 24 hr. at 900° C., and probably in several hours. Equilibrium was attempted at only one temperature below 900° C. Two crystals of the Grass Valley anorthite (Table 9) were held for 114 hr. at 750° C. One

(specimen 15) had not previously been heated and showed a diffuseness value of 1. The other (specimen 14) had previously been equilibrated at 900° C., with a diffuseness value of 4. Specimen 14 developed a diffuseness value of 3 during this treatment, whereas specimen 15 was raised to a value of 2. Thus at 750° C., in 114 hr., this material approaches, but apparently does not quite reach, equilibrium. It might be expected that at lower temperatures equilibrium times would become increasingly long, and its attainment would require times beyond those feasible in the laboratory.

There is no evidence that the amount of NaAlSi₃O₈ in solid solution has a very considerable effect on the rate at which equilibrium is established.

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References

- COLE, W. F., SÖRUM, H. & TAYLOR, W. H. (1951). *Acta Cryst.* **4**, 20.
 COWLEY, J. M. (1950a). *J. Appl. Phys.* **21**, 24.
 COWLEY, J. M. (1950b). *Phys. Rev.* **77**, 669.
 EDMUNDS, I. G. & HINDE, R. M. (1952). *Proc. Phys. Soc. B*, **65**, 716.
 EMMONS, R. C. (1953). Geological Society of America, Memoir 52.
 FOSTER, W. R. (1952). *Amer. Min.* **37**, 758.
 GAY, P. (1953). *Miner. Mag.* **30**, 169.
 GAY, P. & TAYLOR, W. H. (1953). *Acta Cryst.* **6**, 647.
 GOLDSMITH, J. R. (1952). *J. Geol.* **60**, 288.
 GOLDSMITH, J. R. & LAVES, F. (1951). A. C. A. Meeting, Chicago, October 1951. (Abstract, p. 11.)
 GOLDSMITH, J. R. & LAVES, F. (1954). *Geochim. et cosmoch. Acta*, **5**, 1.
 LAVES, F. (1952a). *J. Geol.* **60**, 436.
 LAVES, F. (1952b). *J. Geol.* **60**, 549.
 LAVES, F. & GOLDSMITH, J. R. (1951a). International Congress of Crystallography, Stockholm, June 1951. (Abstract.)
 LAVES, F. & GOLDSMITH, J. R. (1951b). A. C. A. Meeting, Chicago, October 1951. (Abstract, p. 10.)
 LAVES, F. & GOLDSMITH, J. R. (1951c). Mineralogical Society of America Meeting, Detroit, November 1951. (Abstract; also *Amer. Min.* (1952), **37**, 295.)
 LAVES, F. & GOLDSMITH, J. R. (1954). *Acta Cryst.* **7**, 131.
 LIPSON, H. (1950). *Progress in Metal Physics*, **2**, 1.
 SÖRUM, H. (1951). *K. norske vidensk. Selsk. Skr.* No. 3.
 SÖRUM, H. (1953). *Acta Cryst.* **6**, 413.