STRUCTURAL DISCONTINUITIES IN THE
PLAGIOCLASE FELDSPAR SERIES

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ABSTRACT

Optical and x-ray data measured on the same plagioclase grain have been plotted as functions of each other in order to avoid compositional scatter between grains. In the plot of the reciprocal angle $\gamma^*$ relative to the $\alpha$ refractive index the experimental points for plagioclases in the low structural state lie on nearly linear segments separated from one another by discontinuities near An$_{33}$, An$_{50}$, and An$_{98-99}$. These same discontinuities show up in the plots of the $\gamma^*$ angle and of the positions of non-Bragg subsidiary reflections as functions of individual grain compositions.

Along each of the linear segments it is proposed that Ca and Al substitute randomly for Na and Si over one or more, but not all, of the available sets of atomic positions. At compositions providing simple Na:Ca and Si:Al ratios, namely An$_{33}$ and An$_{98}$, reorganization takes place to provide ordering of Na and Ca and regular alternation of Si and Al over as many sets of tetrahedral positions as allowed by the composition and symmetry. An$_{98-99}$ appears to represent the boundary between transitional anorthite and primitive anorthite. The regions of structural reorganization can be correlated with changes at these compositions in a number of optical and physical properties of low plagioclases. These include refractive indices, birefringence, optic angle, orientation of optic plane and optic axes, orientation of rhombic section, wave length of infrared absorption bands, microhardness, types of non-Bragg subsidiary x-ray reflections, and x-ray powder pattern spacings.

INTRODUCTION

Prior to 1934 the plagioclase feldspar series was considered an ideal example of a continuous solid solution series. Taylor et al. (1934) provided the first x-ray evidence of structural discontinuity by demonstrating the presence of single subsidiary layer lines between the principal layer lines of Z axis rotation photographs of anorthite. This observation requires that the c repeat of the anorthite end member be twice as large as that of the albite end member. High, low, and intermediate structural forms, similar to those in the potassic feldspars and equated primarily with differences in crystallization and cooling rates, have been recognized since that time. Several additional complexities involving unmixing, non-Bragg subsidiary reflections, and symmetry changes have also been confirmed within the low series. Our present state of knowledge concerning the structural phases present within the low series is summarized in Fig. 1.

The present study reports new optical and x-ray measurements of low plagioclase. Discontinuities in unit cell geometry found within the series

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are interpreted in terms of the ordering patterns of Si, Al and Na, Ca that are possible at certain favorable compositions.

**EXPERIMENTAL**

Table 1 lists the 39 specimens employed in this study. Several crystals, 0.1 to 0.5 mm in each direction, were selected from each specimen on the basis of optical clarity, uniform thickness, and good cleavage. Grains containing visible imperfections or impurities were excluded. With the exception of specimens U and J at the anorthite end of the series, the samples were selected to represent the low structural state, so far as it is possible to judge from the rock types involved. We hope thereby to reduce to a minimum any variations that may occur as a consequence of a sample's position between the high-low states. A wide variety of rock types is represented in order to avoid undue bias from any one petrologic type. No compositions within the two-phase peristerite region An$_{3-14}$ were investigated.

The refractive indices of the grains were determined by the double variation method on a 5-axis universal stage. Directly measured refractive indices are considered more reliable than indices determined either by rotation from a prime ray or by calculation from the optic angle or the birefringence. For this reason an attempt was made to orient the grains manually so that the same refractive index could be read directly for all grains. The $\alpha$ refractive index was chosen for this purpose. Each grain was mounted on a spindle mount (Wilcox, 1959) in order to facilitate recovery for x-ray study of the same grain. X-ray oscillation and precession photographs were taken of most grains. The positions of the non-Bragg subsidiary type “e” reflections were measured on the oscillation photographs and the reciprocal angle $\gamma^*$ on the precession photographs.

![Graph](image)

**Fig. 1.** Schematic representation of the structural types present in the plagioclase series for the low structural state.
### Table 1. General Description of Samples

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<th>Rock Type</th>
<th>Reported Mol % An</th>
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* References for Source of Data:
1. R. C. Emmons (1953).
The reciprocal \( \alpha^* \) and \( \beta^* \) angles were not measured because they do not change appreciably throughout the plagioclase series. The experimental data are recorded in Table 2.

The estimated probable error of the directly measured refractive indices is \( \pm 0.0005 \). In the regions near the structural discontinuities each listed \( \alpha \) index is the average of two separate determinations. The measurements of \( \delta_c \), the position of the non-Bragg subsidiary type "e" reflections on Z axis oscillation photographs, were made with a traveling cross hair and vernier attached to an engraved steel scale. These measurements are estimated to have an accuracy within \( \pm 3^\circ \) for compositions An_{38} to An_{40} and \( \pm 4^\circ \) to \( 10^\circ \) for more sodic compositions. All precession photographs were taken with unfiltered Mo radiation on carefully oriented grains. All angular measurements were repeated from two to six times. The estimated error of measurement of the reciprocal angle \( \gamma^* \) is less than \( 0^\circ 10' \).

**Results**

A plot of experimental data relative to bulk composition, as derived from chemical analysis, involves the possibility of compositional and structural variation from grain to grain within a sample. A resultant scatter of points, such as illustrated by Crump and Ketner (1953), Emmons et al. (1960), and Vogel (1964), is encountered frequently with plagioclases. The scatter is real and is present in both the optical and x-ray measurements of the present study (Table 2). In order to avoid the effect of compositional variation from grain to grain, the experimental data obtained from the same grain have been plotted with respect to one another rather than with respect to composition. This has the effect of smoothing out compositional scatter, provided the variable parameters are both functions of composition.

Of the measured variables the graph of the variation of \( \gamma^* \) as a function of the \( \alpha \) refractive index (Fig. 2) was found to be the most informative in delineating structural breaks in the low plagioclase series. The experimental points lie on linear or nearly linear segments separated by discontinuities at mol per cent values of An_{38-35}, An_{50-52}, and An_{90-95}. There is a slight overlap of the ends of adjacent segments at the first two breaks. The latter break near An_{90} is less well defined and could be interpreted as a flexure rather than a discontinuity. The maximum deviation of any point from the nearest linear segment is approximately equal to the estimated maximum error of measurement of \( \gamma^* \) and \( \alpha \).

The compositional markers were placed in Fig. 2 by cross reference with an average \( \alpha \) refractive index curve. For this purpose we have averaged our own measurements with those of Crump and Ketner.
Table 2. Summary of X-Ray and Optical Data

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* Rotated indices.
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(1953), Ribbe (1960), and Smith (1960) on the same samples. We assume in this procedure that enough grains have been measured with comparable precision in each sample for the averaged α index to be representative of the bulk composition. After drawing a smooth line of best fit through the plotted average values for the specimens used, the composi-

![Graph](image-url)

**Fig. 2.** Variation of reciprocal angle $\gamma^*$ with respect to the $\alpha$ refractive index measured on the same grain. Compositional markers were placed by cross reference with an average $\alpha$ index curve. Scatter within samples is mainly parallel to the linear segments.
tion corresponding to a given $\alpha$ index could be transferred to the graph of Fig. 2. The published index curves of Crump and Ketner were also used to check the accuracy of the positioning of the composition markers. The two methods agreed within less than one per cent An over most of the curve. A second check utilizing a curve of averaged $\gamma^*$ values relative to bulk composition also showed close correspondence with the composition markers as given in Fig. 2.

Special mention must be made of the composition in the vicinity of the discontinuities of Fig. 2. In order not to prejudge the presence or absence of corresponding breaks in the refractive index curves, we have intentionally drawn a smooth curve through the points of the average $\alpha$ index curve. In Fig. 2, therefore, a given $\alpha$ index can represent only one composition, even on opposite sides of a discontinuity. It could be argued that the presence of breaks implies that a compositional difference should exist between the ends of adjacent segments. Some evidence for this view can be found in small deviations of points from the average index curve near An$_{33}$ and An$_{66}$, but the samples are not spaced closely enough together for us to be certain of the exact trend of the curve. For these reasons the compositional markers as now given at the ends of each segment are subject to change.

Figure 2 does not require the use of analyzed specimens for its construction. Accordingly, data from the eleven unanalyzed samples listed at the end of Table 1 have been utilized to fill out those portions of the plot where data from the analyzed samples were scarce. Unfortunately, two of these samples, U and J, are anorthite phenocrysts from lava flows and may reasonably be interpreted as high structural forms. For this reason the small break or flexure at the anorthite end of the curve must be considered tentative until data can be obtained for true low-state anorthites in this region. The similarity in the refractive indices of the high and low forms at the anorthite end (Reynolds, 1952) and the break in the index curves of Smith (1960) around An$_{98}$, however, provide supporting evidence for the reality of the break as shown. An additional supporting fact is that the $\gamma^*$ value for the low anorthite whose structure was determined by Kempster, Megaw, and Radoslovich (1962) would fall on our graph at An$_{98}$. Although an $\alpha$ index is not given, Gay (1953) states that this material is nearly pure anorthite on the basis of refractive index and extinction angle measurements.

The data of J. V. Smith (1956), J. R. Smith (1958), Tomisaka (1959), and Brown (1960a) can be combined with measurements of our own on heated and volcanic plagioclases to show that the $\gamma^*$ angle—$\alpha$ index curve for the high structural state would be a nearly straight, horizontal line having a $\gamma^*$ angle of $88.0 \pm 0.2^\circ$ from An$_0$ to An$_{67}$. At An$_{67}$ the curves
for the low and high structural states join and remain nearly coincident to $\text{An}_{100}$. It is observed in the present study that the scatter of values between grains from the same specimen is predominantly parallel to the linear segments of Fig. 2 rather than normal to them. For compositions $\text{An}_6$ to $\text{An}_{15}$, at least, this scatter must be a result of compositional differences from grain to grain rather than of differences in degree of order. For most specimens the indicated scatter amounts to less than three per cent $\text{An}$ because more extreme compositions were eliminated by centrifugation during preparation of the sample for chemical analysis. The maximum compositional variation encountered between grains was 8.8 per cent $\text{An}$ for specimens 15 and Fd-26. Specimen 15 is also the only sample in which the compositions of the individual grains do not agree closely with the composition by chemical analysis, the difference amounting to approximately 10 per cent $\text{An}$. Glauser (1961) has also commented that compositions derived optically from thin sections of this specimen do not correspond with the chemical analysis.

In Fig. 3 the $\gamma^*$ angle is plotted as a function of the $\beta$ and $\gamma$ refractive indices. Over half of these indices are rotated values rather than direct measurements. Despite the resultant greater scatter and the smaller number of experimental points, the two curves are very similar to that in

![Graph](image)

**Fig. 3.** Variation of reciprocal angle $\gamma^*$ with respect to the $\beta$ and $\gamma$ refractive indices measured on the same grain. Lines through the points and compositional markers were placed by cross reference with Fig. 2. Different symbols are used to distinguish points lying on the different linear segments of Fig. 2.
Individual grain compositions determined by projecting the individual points normally onto the linear segments of Fig. 2 have been used to construct more precise curves of the variation of $\gamma^*$ and of the $\alpha$ refractive index as a function of mol per cent anorthite, illustrated in Figs. 4 and 5 respectively. The scatter of $\gamma^*$ values is reduced substantially in Figure 4 so that the discontinuities in unit cell geometry at An$_{33}$ and An$_{40}$ show up more clearly than in the preceding figures. The lines through the individual points represent the linear segments from Fig. 2 as transferred to this graph point by point. The maximum deviation of any point from its corresponding segment is 0.1°, whereas the difference in $\gamma^*$ between the ends of adjacent segments is 0.5°. The segment from An$_{50}$ to An$_{90}$ transfers as a slightly concavo-convex curve that could also be interpreted as two straight lines of different slopes joining at about An$_{87}$. No discontinuities are apparent in the $\alpha$ refractive index curve of Fig. 5, but it must be remembered that this curve is derived from Fig. 2 in which a
smooth variation of index with composition is assumed. The actual $\alpha$ index values in the regions near An$_{33}$, An$_{46}$, and An$_{67}$ are subject to change for this reason. The present work suggests that if any discontinuities in index do exist in these regions they will be small. It is also noted that the trend of points in Fig. 5 could be described equally well by a series of straight lines with changes of slope at An$_{33}$, An$_{46}$, and An$_{67}$.

Crump and Ketner (1953) and Ribbe (1960) have suggested a break in the refractive index curves near the sodic end of the two-phase peristerite region. Ribbe (1960) notes that this break at An$_{5-7}$ (wt %) does not correspond exactly with the sodic limit of unmixing at An$_{1-3}$, whereas in theory it should correspond. A similar situation exists near the calcic end of the peristerite region. Smith (1960) shows a break in his index curves at An$_{20}$ (mol %), whereas no unmixing is observed beyond about An$_{34}$. We have not attempted to verify either of these optical breaks in the present study. We do note on the basis of Fig. 5 that either a flexure or break would be needed to join An$_{9}$ with the trend of the curve beyond An$_{34}$, but that any deviation from continuity in these regions would have to be quite small, say 0.001 or less. Verification of these suggested breaks will require precise compositional control, perhaps by means of an electron microprobe, for the individual grains used for index determinations.

Brown (1960b) and Ribbe (1962) have pointed out another problem that exists at the calcic end of the peristerite zone. No unmixed specimen has ever been recognized in the composition region in which the calcic phase should be predominant, more calcic than An$_{16-2}$, where precession photographs show the two phases to be present in approximately equal

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**Fig. 5.** Plot of $\alpha$ refractive index with respect to individual grain composition. Line through points in an overlay of the average $\alpha$ index curve used to construct the compositional markers in Fig. 2.
DISCONTINUITIES IN PLAGIOCLASE SERIES

amounts (Fig. 1). Examples of unmixing on the calcic limb of the solvus appear to be missing. This is verified in our own study in which all specimens more calcic than An14 (mol %) were found to be homogeneous.

Figure 6 illustrates the variation in the positions of the non-Bragg subsidiary type “e” reflections as a function of individual grain composition. The discontinuities apparent at An33 and An60 represent differences of nearly 15° between the ends of adjacent segments whereas the estimated error of measurement is less than ±3° for An33–50. The position of the most sodic segment is uncertain because of the diffuseness of the subsidiary spots. Values of 180° near the calcic end probably represent Bragg difference reflections of the anorthite type structure rather than non-Bragg reflections. There is more scatter in the positions of the non-Bragg reflections for compositions between An60 and An80 than would be expected from the estimated error of measurement. The cause for this scatter is not known. A possible interpretation is that there is an additional flexure or discontinuity in the region An67–70.

Fig. 6. Plot of position of non-Bragg type “e” subsidiary reflections on Z axis oscillation photographs with respect to individual grain composition. Different symbols are used to distinguish points lying on the different linear segments of Figs. 2 and 3.
Intermediate compositions between NaAlSi$_3$O$_8$ and CaAl$_2$Si$_2$O$_8$ have non-integral values of the large cations, Na and Ca, and of the tetrahedral cations, Si and Al, within one formula unit. In an ideal substitutional solid solution these cations must be distributed at random over the corresponding structural positions of different unit cells so that these positions in the “average” unit cell would contain “half-breed” atoms (Na, Ca) and (Si, Al). The physical properties and average unit cell size and shape should vary smoothly with composition. Although there are compositional ranges in the low plagioclase series in which the unit cell shape, expressed by $\gamma^*$, does vary smoothly with composition, it is especially significant that these ranges are terminated abruptly at compositions with simple ratios of Na: Ca and Si: Al. At An$_{50}$ the ratio of Na to Ca and of Si to Al is 2 to 1. At An$_{50}$ the Na:Ca ratio is 1:1 and the Si:Al ratio is 5:3.

We interpret the linear segments and discontinuities evident in Figs. 2–4 in the following manner.

1) Along each linear segment random substitution of Al for Si and Ca for Na takes place over one or more sets of equivalent atomic positions. We do not attempt to specify which sets are involved because of the large number of possibilities. For example, in anorthite there are four sets of large cation positions and sixteen sets of tetrahedral positions. In albite and intermediate composition plagioclases the number of sets appears to be reduced to ½ that of anorthite because of higher symmetry and smaller cell volume (albite $CI$ with $c \approx 7$ Å and anorthite $PI$ with $c \approx 14$ Å). In the case of several different plagioclases, however, electron density maps based on an albite-size unit cell have shown distinct signs of atom-splitting. This effect can be interpreted as due to an average structure in which the contents of four slightly different albite-size subcells have been superimposed. Megaw (1962) suggests that the diffraction maxima characteristic of the true, larger cell have been smeared out by an antiphase domain structure.

2) At compositions that provide simple ratios of Si:Al and Na:Ca, structural reorganization takes place whereby the Si and Al are redistributed in a regular pattern over as many sets of tetrahedral positions as the bulk composition will allow. We assume that Na and Ca order at the same time. Especially at the calcic end of the series, the pattern of Si,Al ordering adopted would be expected to be the regular 1:1 alternation found in anorthite. Thus, for purposes of illustration, at An$_{50}$ the Si:Al ratio of 5:3 is correct for regular alternation of Si and Al over exactly three-fourths of the tetrahedral positions with the remaining positions occupied by Si alone. Although the exact details of the changes that take
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place at An$_{33}$ and An$_{50}$ cannot be specified, some major structural reorganization involving cation redistribution appears necessary to explain the large observed change in $\gamma^*$ of 0.5° between the ends of adjacent linear segments. A small change in refractive index might also be expected from such a reorganization.

3) The experimental data can be interpreted to have either a discontinuity or a flexure in the region An$_{96-98}$. This is about the boundary between primitive anorthite and transitional anorthite (Fig. 1). It is also about the dividing line between the more calcic specimens that retain a $c$ axis periodicity of 14 Å on quenching from temperatures just under the solidus and the more sodic specimens that have a 7 Å $c$ axis characteristic of the high structural state (Gay, 1962).

4) There are also discontinuities near An$_{33}$ and An$_{50}$ of the positions of the non-Bragg type “e” subsidiary reflections (Fig. 6). Megaw (1960) has explained the non-Bragg reflections as due to stacking faults that nucleate within an ideal intermediate plagioclase structure as a result of atomic misfit inherent in the substitution NaSi—CaAl. Her ideal structure consists of 18 subcells differing from one another in Si,Al pattern and in distortion of the framework structure. The postulated stacking faults would be spaced at intervals of several unit cells and should not directly affect the geometry of the individual subcells. Megaw suggested certain sequences of filling up the tetrahedral positions within the ideal structure, but did not suggest any reorganization of Si,Al distribution except at An$_{78}$, where the ideal structure was believed to first form. Our data do not show a break at An$_{78}$.

The observation of discontinuities in the $\delta_6$ values eliminates the possibility that some of the effects noted in the present study might be due to use of specimens in intermediate structural states. Gay and Bown (1956) have shown that the positions of the subsidiary reflections do not change on heat treatment. The geologic occurrences of the specimens, the adherence of the points from different specimens to linear segments, and the occurrence of the breaks at simple Na:Ca and Si:Al ratios all suggest that we are dealing with structural changes taking place entirely within the low structural series. Vogel (1964) has especially examined our specimens near An$_{78}$ and An$_{50}$ that would approach closest on a $\gamma^*$—$\alpha$ graph to the high structural series. He reports that the poles of recognizable late-stage deformation twins in these specimens fall on the migration curves for the low structural state.

5) The random substitution of Al for Si and of Ca for Na postulated along the linear segments differs from that in the high structural series in that the randomness does not involve as many of the available sets of positions for these elements. However, the high structural series is not
necessarily completely disordered. The similarity of the $\gamma^*$ curves from An$_{100}$ to An$_{67}$ suggests that the Si,Al distributions may be quite similar over this range for the low and high structural states, but become increasingly different for more sodic compositions. This implies that An$_{67}$ may represent another unique composition with respect to Si,Al distribution. The Na:Ca ratio is 1:2 and the Si:Al ratio is 7:5. Although there is no apparent discontinuity at An$_{67}$ in any of our figures for the low plagioclases, mention has been made in the text of possible small changes of slope at this composition in Figs. 4–6.

The discontinuities observed in the present study can be correlated with changes at these same compositions in a number of optical and physical properties of low plagioclases recorded in the literature. The possible breaks in the refractive index curves near the boundaries of the peristerite region have already been mentioned. Smith (1960) shows a break at An$_{90\pm3}$ in refractive index, birefringence, and optic angle curves and a reversal of slope in the optic angle curve at An$_{92}$. Van der Kaaden (1951) shows the optic angle reversal closer to An$_{66}$. Duparc and Reinhard (1924) show prominent changes in slope near An$_{35}$ and An$_{65}$ in curves of the angle between the optic plane and (001) for sections normal to optic axis B and in stereographic projections of the optic axes onto planes normal to the crystallographic axes. The curves of the variation of microhardness with composition (Mookherjee and Sahu, 1960) show a change in slope near An$_{52}$ for loads not exceeding 100 grams. The samples are not spaced closely enough together to define accurately a second change of slope that occurs somewhere between An$_{25}$ and An$_{40}$. Thompson and Wadsworth (1957) have found a marked flexure (bathochromic shift) between An$_{44}$ and An$_{58}$ in the wave length of the infrared absorption band in the 15.4–16.2 micron region. The non-Bragg type "e" reflections become diffuse at compositions more sodic than An$_{35}$ and the type "f" reflections are found only for compositions more calcic than An$_{50\sim55}$ (Bown and Gay, 1958).

The differences between the spacings of adjacent reflections on x-ray powder photographs have been used extensively to determine composition and structural state for the plagioclase feldspars (Goodyear and Duffin, 1954; Smith and Yoder, 1956; Smith and Gay, 1958). Changes in the relative spacings of the particular reflections used are primarily dependent on the variation of the $\gamma^*$ angle with composition and structural state. For this reason the spacing graphs for the low plagioclases show a general similarity to the $\gamma^*$ graphs in this paper with steep slopes at the two ends of the series and flattening out in the region An$_{35}$ to An$_{50}$. J. V. Smith (1958) has also pointed out that the position of the rhombic section varies in a similar manner because of its dependence on the value
of the crystallographic angle $\gamma$. The present study suggests that the existing x-ray spacing graphs must be modified in the region An$_{32}$ to An$_{50}$ to show the observed discontinuities. The overlapping of $\gamma^*$ values near An$_{33}$ and An$_{50}$ will make the interpretation of the observed spacings additionally ambiguous in these regions in terms of trying to separate the effect of composition as opposed to structural state. For a given composition the high and low structural states differ primarily in their $\gamma^*$ values. Our data now indicate that plagioclases of very similar compositions can have differences in $\gamma^*$ of 0.4° to 0.5° in the immediate vicinity of the discontinuities and still belong entirely within the low structural state.

ACKNOWLEDGMENTS

This study was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation. The authors wish to express their appreciation to R. C. Emmons, H. S. Yoder, Jr., H. H. Hess, R. E. Wilcox, G. A. Desborough, and T. A. Vogel for furnishing the specimens used and to P. H. Ribbe and T. A. Vogel for measuring optical and x-ray data on four specimens.

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Manuscript received, August 4, 1964; accepted for publication, April 1, 1965.