

## AN X-RAY AND OPTICAL INVESTIGATION OF THE PERISTERITE PLAGIOCLASES

PAUL H. RIBBE,\* *University of Wisconsin, Madison, Wisconsin.*

### ABSTRACT

Low-temperature plagioclase feldspars in the peristerite range  $An_{5\pm 2}$  to  $An_{17\pm 2}$  unmix on a submicroscopic scale to relieve internal stresses created by substituting Al for Si in the tetrahedral framework. The unmixed components are  $An_{0-6}$  and  $An_{20-35}$ , averaging  $An_3$  and  $An_{25}$  respectively. Most peristerites exhibit a bluish schiller as a result of diffusion of light by the submicroscopic domains of different optical polarizabilities. The optical properties of the crystal are weighted averages of those of the domains. Heating at 1000° C. causes disordering of Na and Ca between domains, followed by disordering of Si and Al within domains, and final homogenization by disordering of Si and Al between domains. Schiller is retained until the final step of homogenization. Homogenization can not be studied by simple x-ray methods, owing to similarity in unit cell geometry of the high-temperature phases, but can be followed by optic angle measurements. An x-ray technique has been developed to determine the composition of individual unmixed grains, and has been applied to confirm the presence of a break or flexure in the plagioclase refractive index curves near  $An_5$ - $An_7$ , the lower limit of the peristerite region. The upper limit of the peristerite region has not been studied in detail, but deviations from the albite structure sufficient to incorporate the additional Al-content are inferred.

### INTRODUCTION

The plagioclase feldspars range in composition between the limits albite ( $NaAlSi_3O_8$ ) and anorthite ( $CaAl_2Si_2O_8$ ). Once believed to be a continuous solid solution series, the plagioclase series is now known to be structurally discontinuous. Information on the exact mechanism of the substitution of CaAl for NaSi in the series is important in explaining the nature of these discontinuities. This paper deals with a specific discontinuity within the series, located in the *peristerite* composition range.

As used herein, the term *peristerite* designates the low-temperature plagioclase feldspars from the albite-oligoclase range that are known to be submicroscopically unmixed into two coexisting plagioclase components and that may or may not exhibit schiller effects. The components have been found to correspond to  $An_{0-6}$  and  $An_{20-35}$  ( $An_3$  and  $An_{25}$  average) and to exist in varying proportions throughout the peristerite range,  $An_{5\pm 2}$  to  $An_{17\pm 2}$ . Unmixing occurs in this range when the 3:1 Si:Al ratio of the low albite composition is exceeded and is believed by this writer to be due to relief of stresses caused by successive replacement of Si by the larger Al, forming minute segregated domains of Si- and Al-rich plagioclase. The Na and Ca cooperate to balance electrostatic valence charges. The ratio of these Ab- and An-rich domains varies

\* Present address: Corning Glass Works, Corning, New York.

with total An content of the crystal. Since the two components are sub-microscopic in size, the optical properties of the crystal must be weighted averages of those of the components.

Historically, Böggild (1924) was the first to investigate the peristerites. He ascribed their light blue schiller to a reflection phenomenon caused by oriented "labradorizing lamellae" of unstated origin.

Cole, Sörum, and Taylor (1951) in their  $x$ -ray study of the plagioclase series mention no deviation from the known low-temperature albite structure, reporting solid solution for the entire range  $An_0$  to  $An_{30}$ . Laves (1951) was the first to note that the schiller of a peristerite was "due to exsolved plagioclase with a geometry slightly different from the geometry of the host." Laves (1954) expanded his study to show that the unmixing range was  $An_5$  to  $An_{17}$  and that the two peristerite phases had lattice geometries similar to low-albite and  $An_{30}$  respectively. Heated peristerites were homogenized to a high-albite form.

Emmons (1953, revised) in a thorough optical study of analyzed plagioclases gives evidence for a discontinuity in refractive index curves near  $An_{6-8}$ , the lower limit of the peristerites. An attempt is made herein to discover the nature of this break, which is anticipated from a structural viewpoint. Chayes (1952) shows no such break in his curves, reporting continuous variation of indices with increasing An content. J. R. Smith (1955 b) suggests a number of optical discontinuities, including  $An_{11}$  and  $An_{22}$ , but does not show the  $An_{11}$  break in subsequent curves (J. R. Smith, 1957).

J. V. Smith (1956) plotted the change of the reciprocal lattice angle  $\gamma^*$  with anorthite content, and Gay and Smith (1955) used the plot to determine that the peristerite phases were actually  $An_{3\pm 2}$  and  $An_{23\pm 2}$ . Most recently, Schneider (1957) investigated the change of lattice geometry of each of the peristerite phases with heat treatment, describing the process of homogenization.

The data on plagioclases used in this study are listed in Table 1.

#### OPTICAL PROPERTIES OF HEATED PERISTERITES

The optical properties of untwinned cleavage fragments selected from five chemically analyzed plagioclases in the range  $An_0$  to  $An_{20}$  were determined on the five-axis universal stage as described by Emmons (1943). The  $X^*Y^*$  precession photographs (see Fig. 1) showed four of the five specimens to be submicroscopically unmixed. Specimen 7a is structurally homogeneous ( $\gamma^* = 88^\circ 34'$ ,  $An_{18\pm 2}$  determined from Fig. 2). Following heating at  $1000^\circ$  C. for various lengths of time (Table 2), the same grains were  $x$ -rayed again and were found to have "homogeneous" structures

TABLE 1. SPECIMEN DATA

No.	Rock Type	Locality	Calculated Wt. %			Source of Analysis*	Comments
			An	Ab	Or		
0	pegmatite	Ramona, Calif.	0.25	98.7	1.1	CSR	0.11% impurities
1	—	Auburn, Maine	5.2	94.0	0.8	CDJ	many inclusions
2	—	Monteagle Tp., Ont.	5.7	90.3	4.0	VBM	
3	—	Villeneuve, Que.	7.6	90.6	1.7	VBM	
4	—	Haddam, Conn.	9.5	90.5	—	CDJ	
5	two-mica granite	Peekskill, N. Y.	11.4	87.0	1.6	RCE	0.10% impurities (chlorite)
6	—	Monteagle Valley, Ont.	13.3	82.8	3.9	VBM	
7	biotite granite	Parishville, N. Y.	16.1	81.1	2.8	RCE	0.17% liquid inclusions
8	granite	Llano County, Texas	16.6	81.5	1.9	RCE	0.10% liquid inclusions

\* References: RCE—R. C. Emmons (1953, reprinted 1956); CSR—C. S. Ross in Emmons (1953); CDJ—C. D. Jeffries (1936); VBM—V. B. Meen (1933). Specimens 2, 3, and 6 were contributed by the Royal Ontario Museum of Geology and Mineralogy. Specimens 0, 5, 7, and 8 were contributed by R. C. Emmons.

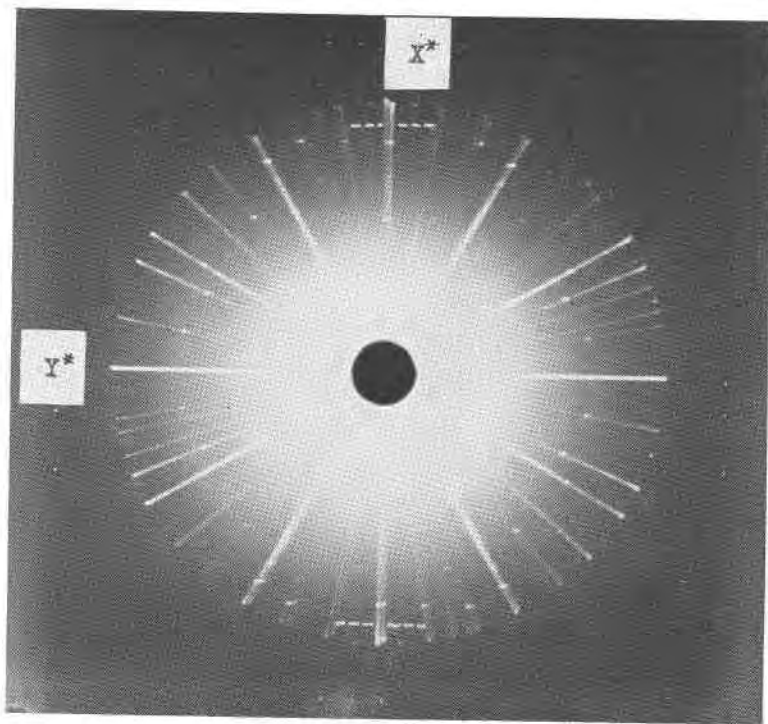


FIG. 1. A precession photograph of the zero-level  $X^*Y^*$  zone of the peristerite sample 3a. The two distinct  $X^*$  axes are evidence of the existence of two plagioclases in this specimen. The double  $Y^*$  and  $Z^*$  axes are not diagnostic in precession photographs because the reciprocal lattice angles  $\alpha^*$  and  $\beta^*$  vary only  $0.2^\circ$  and  $0.1^\circ$  respectively from  $An_{2+2}$  to  $An_{25+2}$ .  $\gamma^*$  varies by  $1.3^\circ$  in the same range. (J. V. Smith, 1956; Bown and Gay, 1958)

Dotted lines indicate the position of densitometer profiles.

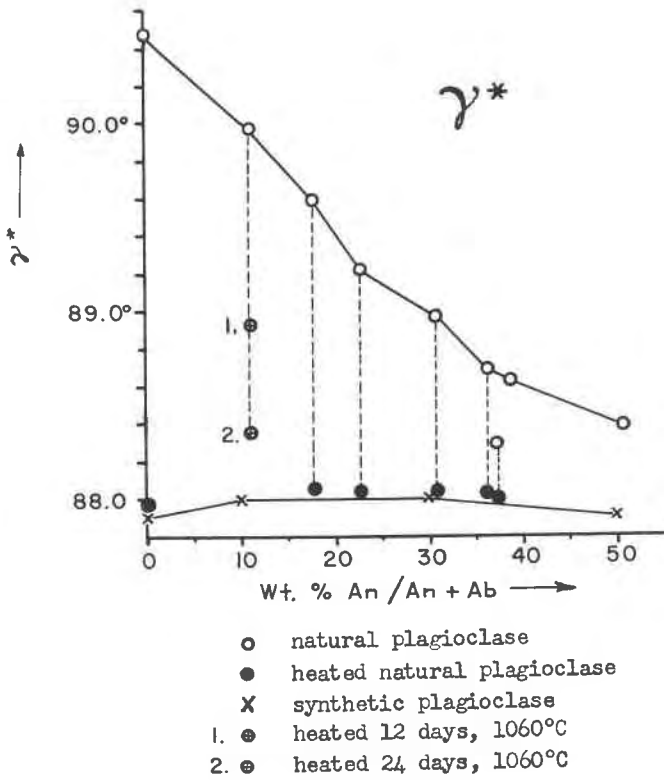


FIG. 2. Rate of change of  $\gamma^*$  with wt. % An/An+Ab for soda-rich plagioclases. After J. V. Smith (1956).

TABLE 2. DIFFERENCES IN REFRACTIVE INDEX AND BIREFRINGENCE BETWEEN HIGH- AND LOW-TEMPERATURE PLAGIOCLASES

No.	Time of heating	$\gamma^*$ ( $\pm 5'$ )	$2V_\alpha$	$\Delta$ index of refraction			$\Delta$ birefringence
				$\gamma$	$\beta$	$\alpha$	
0	260 hrs.	88°02'	N.D.	N.D.	N.D.	N.D.	N.D.
2b	112 hrs.	88°15'	58°	-.0020	+.0016	-.0002	-.0018
3a	240 hrs.	88°07'	51°	-.0017	+.0013	-.0008	-.0009
4a	260 hrs.	88°05'	76°	-.0008	+.0015	.0000	-.0008
6b	425 hrs.	88°01'	42°	-.0021	+.0006	-.0013	-.0016
7a	260 hrs.	88°07'	56°	-.0007	+.0021	-.0001	-.0006

similar to that of high-albite. With one exception (2*b*) these grains had attained the high-temperature geometry described by J. V. Smith (1956) for the range  $An_0$  to  $An_{50}$  (Fig. 2).

The change in refractive indices recorded for these specimens is in accord with the data of J. R. Smith (1957). It will be noticed that although  $\gamma^*$  indicates a high temperature state according to Fig. 2,  $2V_\alpha$  for four specimens is not at the minimum to be expected if the disordered distribution of Al-Si is complete for the entire grain. Schneider (1957) has plotted the change of  $\gamma^*$  against  $2V_\alpha$  with time of heating for a nearly pure albite. This curve, reproduced in Fig. 3, indicates that  $2V_\alpha$  is a more

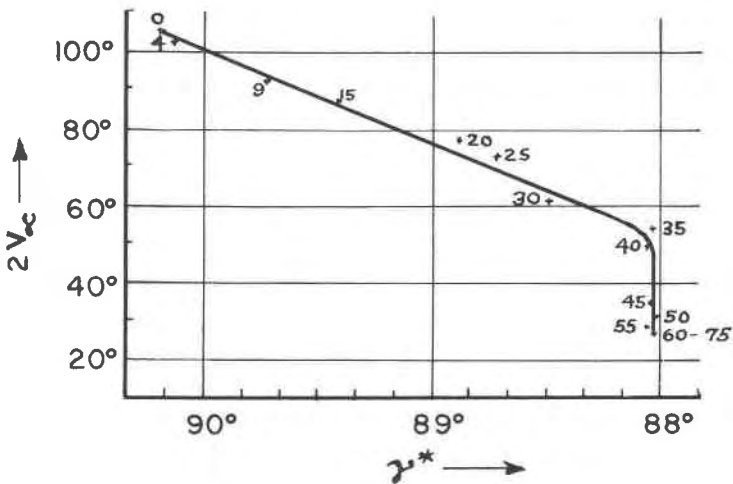


FIG. 3. A plot of  $2V_\alpha$  against  $\gamma^*$  for increased time of heating at 1000° C. of a nearly pure albite. After Schneider (1957). Small numbers along the curve represent days heated.

reliable indicator of disorder than is  $\gamma^*$ . The choice of  $2V_\alpha$  as an index to the degree of disorder is illustrated by specimen 6*b* (Table 2). It shows significantly larger decreases in the  $\alpha$  and  $\gamma$  refractive indices and less increase in  $\beta$  after heating than do the other specimens. One would thus expect 6*b* to be the most completely disordered. This is borne out by the fact that  $2V_\alpha$  for this grain is 42°, substantially lower than that for the others. On the other hand, it is impossible to distinguish relative degrees of order from their lattice geometry, for  $\gamma^*$  is very nearly equal for all the heated specimens.

In this paper, a detailed study of the change of lattice geometry with time of heating and an investigation of the optical effect known as schiller will lead to a reasonable explanation of the dynamics of the

“homogenizing” and disordering processes operative within the heated peristerite.

“HOMOGENIZATION” AND DISORDERING OF PERISTERITES

The phenomena of “homogenizing” the separate phases of a peristerite and disordering them were studied in detail by Schneider (1957). Schneider heated an oligoclase ( $An_{13}$ ) from Amelia Court House, Virginia, and observed the changes of  $\gamma^*$  with time of heating at temperatures of 950° C., 1000° C., and 1050° C. Two of his graphs are reproduced in Fig. 4.

The slopes of these curves are steepened by increasing temperature of heating, but a similarity of shape is maintained regardless of temperature. Of particular importance is the observation that the rate of change toward the high-temperature state is greater for the An-rich phase than for the Ab phase. Schneider suggests that the cause of this divergence is a slight degree of disorder that exists in the low-temperature form of the crystal because of its anorthite content. The possibility of slight disorder existing in one of the components is a promising idea in terms of peris-

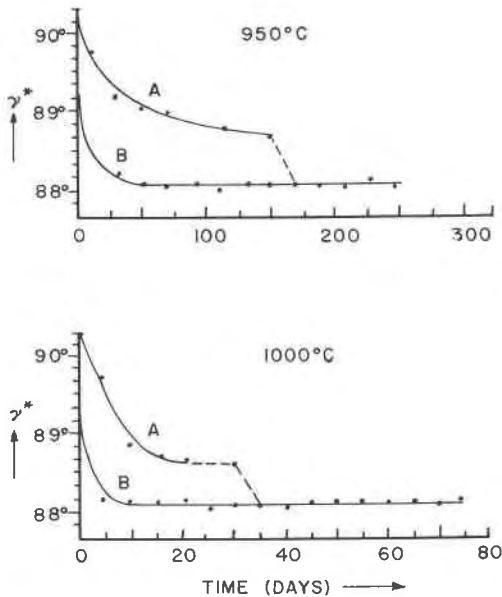


FIG. 4. Plots of the rate of change of the reciprocal lattice angle  $\gamma^*$  with heating time (days) at 950° C. and 1000° C. of an Amelia, Virginia, oligoclase. Modified after Schneider (1957). Dotted extensions of Schneider's curves are by this author. A=Ab-rich phase; B=An-rich phase.

terite dynamics. Since the An-rich phase reaches its geometrical high-temperature state in approximately one-third the time it takes for the Ab phase to do the same, it is not unreasonable to suppose that the An-rich phase was already partially disordered, even in the peristerite's low-temperature form.

The occurrence of domains of approximately 25% An in all peristerites (Table 6) is evidence that this structure is singularly stable, even though Schneider's findings suggest that it may not be completely ordered with respect to Al-Si. That structural stability is not necessarily synonymous with the classical concept of a completely ordered structure was suggested by Ferguson, Traill, and Taylor (1958), who found that a low-temperature albite they studied had but 72%\* of the Al in the  $Si_1(O)$  tetrahedral site. This albite was calculated to be electrostatically more stable than the classically ordered albite which theoretically has all the Al in this tetrahedral site.

If electrostatic balance exerts a more profound influence on plagioclase structure than has previously been known, it may be found that the low-temperature  $An_{25}$  unit cell does not have a totally regular Al-Si distribution taking into account its greater Al content as well as Schneider's discovery that the  $An_{25}$  component of an unmixed oligoclase attains a high-temperature configuration more readily than the albite phase. The foregoing statements are necessarily speculative, but it is hoped that the structure of  $An_{20}$ , presently being done at Cambridge University, may clarify this subject.

The dynamics of the "homogenization" of the two components of the peristerites are imperfectly known. Schneider (1957) does not show the details of the procedure on his curves of  $\gamma^*$  versus heating time. He reports that homogenization is completed in 170 days at 950° C. and in 35 days at 1000° C.  $\gamma^* = 88^\circ 05'$  for both homogenized specimens. This information is plotted as dotted extensions of his curves in Fig. 4.

Table 3 contains data on peristerites homogenized in the present study by heating at approximately 1000° C. The reciprocal lattice angle  $\gamma^*$  after heating varied from  $87^\circ 56'$  to  $88^\circ 07'$  and averaged  $88^\circ 02'$  for nine specimens. Specimens 5a and 6a failed to reach the "homogeneous" high-temperature lattice geometry after an initial  $7\frac{1}{2}$  day heating at 1000° C. Table 4 compares the unheated, intermediate, and "homogeneous" lattice angles with the two phases and gives a rough estimate of the relative percentage of the Ab phase as judged from the comparative intensities of the white radiation streaks of the  $X^*$  axes of the two phases.

In order to complete the picture of the disordering and homogenizing

\* This figure is subject to a possible error of 25%.

TABLE 3. DATA ON HOMOGENIZED SPECIMENS

No.	Wt. % An	Heating time (days)	$\gamma^*$ ( $\pm 05'$ )
3 <i>b</i>	7.6	4½	88°01'
4 <i>b</i>	9.5	4½	88°05'
6 <i>b</i>	13.3	4½	88°01'
1 <i>a</i>	5.2	7½	87°56'
3 <i>a</i>	7.6	10	88°07'
7 <i>b</i>	16.1	10½	88°06'
4 <i>a</i>	9.5	10½	88°05'
0	0.25	10½	88°02'
5 <i>a</i>	11.4	18	87°56'
6 <i>a</i>	13.3	18	88°01'

process, the optical effect known as schiller must be considered in detail.

Peristerites often exhibit a light to brilliant blue schiller. That schiller is a result of unmixing, at least in the peristerite range for plagioclases and certainly in the perthitic alkali feldspars, has long been assumed. An absence of schiller in unmixed feldspars may indicate that the domains are either too small or too large to cause diffusion of light. A number of investigators have found that under certain conditions some perthites and peristerites retained this schiller after heat treatment (Dittler and Köhler, 1925; Spencer, 1930; Heald, 1950). In this study, specimens 4*b* and 2*a* were observed to retain their schiller after 4½ days heating at

TABLE 4. INTERMEDIATE STATE PERISTERITES

	Unheated	Heated 7½ days	"Homogenized" (18 days)
Spec. 5 <i>a</i> Ab-phase $\gamma^*$	90°17'	89°45'	87°56'
An-rich $\gamma^*$	89°28'	88°12'	87°56'
Rel. % Ab-phase	65%	50%	0%
Spec. 6 <i>a</i> Ab-phase $\gamma^*$	90°26'	89°27'	88°01'
An-rich $\gamma^*$	89°17'	88°15'	88°01'
Rel. % Ab-phase	55%	2%	0%

(Compare to Schneider's curves in Fig. 4.)



1000° C. *X*-ray photographs, however, indicated that these same grains had reached a homogeneous high-temperature state.

The explanation for this enigmatic behavior after heating is dependent on analogy with the cause of schiller in moonstones as set forth by Raman, Jayaraman, and Srinivasan (1950). The following is a paraphrase of their significant article:

The blue color seen in moonstones is too rich a blue to be explained as an interference color due to the reflection of light by thin films, but matches the color exhibited in the diffusion of light by particles small in size compared with the wave length of light. The observed facts give no support to the hypothesis of a lamellar structure as the cause of schiller [contrary to Bögild, 1924]. Diffusion is substantiated by the color and the fact that schiller "reflections" are visible through a wide angle (14 to 18°).

Fluctuations of the refractive index consequent on the local fluctuations in chemical composition (and resultant structural adjustments) would give rise to a strong diffusion of light, its intensity increasing in proportion to the number of clusters, multiplied by the square of the volume of each cluster [of Na as segregated from K in the continuous tetrahedral framework of the feldspar]. This is possible provided that these clusters or "crystallites" are of sufficiently small dimensions and are not co-planar. These crystallites must be mutually oriented.

Since the diffusion of light in its passage through the crystal is a consequence of optical heterogeneity, its intensity depends on the magnitude of the differences in optical polarizabilities of the separate domains. Because birefringences are different for different directions in the crystal, the schiller effect varies.

With the exception of the degree of symmetry change between domains, the peristerites can be shown to fit the moonstone picture ideally. Table 5 shows that the differences in refractive indices for Or-Ab (moonstones) and for Ab-An<sub>25</sub> (peristerites) are of the same order of magnitude. This in itself appears to be sufficient explanation for the existence of schiller in low-temperature peristerites, which are known to be unmixed on a submicroscopic scale and segregated into domains of Ab- and An-rich plagioclases.

The retention of schiller in heated and supposedly homogenized peristerites can be explained in the same manner, for the high-temperature Ab and An<sub>25</sub> phases have differences in refractive indices comparable to those of the low-temperature phases (Table 5). Homogenization has been assumed from the X\*Y\* *x*-ray precession photographs where only one X\* axis—not two as in unmixed grains (Fig. 1)—is seen making an angle  $\gamma^* = 88^\circ 02' \pm 06'$  with the single Y\* axis. Because schiller persists in these "homogenized" grains, it is now suggested, following Laves (1952) and Hewlett (1959), that the domains actually still exist in the heated specimen, causing optical heterogeneity that in turn gives rise to diffusion of light or "schiller."

Inspection of the X\*Y\* zone of heated but not yet "homogenized" grains 5*a* and 6*a* (Table 4) shows that the reciprocal lattice parameter *a*\*

TABLE 5. DIFFERENCES BETWEEN REFRACTIVE INDICES OF DOMAINS IN MOONSTONES AND IN LOW- AND HIGH-TEMPERATURE PERISTERITES

Domain composition	Refractive index ( $N_D$ )			Source
	$\gamma$	$\beta$	$\alpha$	
Low-temp. Or	1.5245	1.5228	1.5192	Raman, <i>et al.</i> (1950)
Ab	1.5392	1.5328	1.5292	
Difference:	.0147	.0100	.0100	
Low-temp. Ab	1.5379	1.5314	1.5274	Chayes (1952)
An <sub>25</sub>	1.5486	1.5447	1.5408	
Difference:	.0107	.0133	.0134	
High-temp. Ab	1.535 <sub>6</sub>	1.534 <sub>2</sub>	1.527 <sub>3</sub>	J. R. Smith (1957)
An <sub>25</sub>	1.548 <sub>5</sub>	1.545 <sub>8</sub>	1.541 <sub>1</sub>	
Difference:	.012 <sub>9</sub>	.011 <sub>6</sub>	.013 <sub>8</sub>	

has become equal or very nearly so for the two partially disordered components. This may indicate that Na and Ca are randomly distributed throughout the crystal at this stage of heating, although two phases differing in Si-Al ratio still exist (Laves, 1952, p. 567). With further heating, the two X\* axes come together and coalesce as described by Schneider (1957), apparently indicating homogenization to a single phase crystal. It is proposed, however, that there are remnant domains that retain a high degree of their original Al-Si content and are disordered with respect to Al-Si, within themselves. Because they contain differing amounts of Al-Si, they still have different refractive indices and, therefore, still cause schiller. Heating has caused disordering of Si-Al within, but not between, domains at this stage.

It is important to note that both the Ab and the An<sub>25</sub> domains, now in the high-temperature state, have nearly identical lattice parameters (J. V. Smith, 1956). This geometrical similarity means that these phases are not distinguishable by simple x-ray techniques and thus give the erroneous impression of homogeneity. Optical heterogeneity persists, for the differences in refractive indices for high-temperature forms of Ab and An<sub>25</sub> are of the same order of magnitude as those causing moonstone schiller.

True homogenization demands a random distribution of Al-Si *between* as well as within domains, thereby eliminating the domains. Specimens 2a and 4b and six schillered grains from sample 1 lost their schiller

only after 35 days heating at 1000° C. Two other grains from sample 1 required additional heating at 1050° C. to destroy the remnant domains. Duration of the heat treatment necessary to disorder completely and thus truly homogenize peristerites varies widely from sample to sample.

In the course of investigation of these chemically analyzed peristerites, the limits of unmixing ( $An_5$  and  $An_{17}$ ) suggested by Laves (1954) were confirmed. The lower boundary of the two-phase peristerites was established by chips from sample 1. These chips were selected from the same region of a 75 gm. schillerized single crystal ( $An_{5.2}Or_{0.8}$ ). Of the eight chips chosen, four were found to be structurally homogeneous and four were two-phase peristerites. Pertinent structural data are listed in Table 6. If the chemical analysis of this specimen is accurate, the boundary below which structural homogeneity exists can be fixed at  $An_{5\pm 2}$ .

Six grains from sample 7 ( $An_{16.1}Or_{2.8}$ ) were found to have homogeneous structures in their natural state. The composition of these grains determined by *x*-ray techniques described below is  $An_{18}$ . Laves (1954), however, claims to have observed unmixing in grains from this same sample (his #8). A single crystal from specimen 8 ( $An_{16.6}Or_{1.9}$ ) proved to be unmixed. Lattice measurements indicate that the two phases correspond to  $An_3$  and  $An_{26}$ . Since at least some grains from sample 7 are single phase and some from sample 8 (Laves' #9) are peristerites, the upper limit of structural inhomogeneity can be established at  $An_{17\pm 2}$ .

Specimen 8 is interesting also in that it could be determined that the  $An_3$  phase is either twinned by the Albite law or has two orientations within the crystal characteristic of this twin law, whereas the  $An_{26}$  phase is untwinned.

#### REFRACTIVE INDEX CURVES

Although there is agreement on the limits of the peristerite range, considerable differences exist in the published optic curves for this composition region. Consequently, a detailed study of this region demands *x*-ray, optical, and compositional data on *individual* grains.

For this purpose an *x*-ray method was devised to determine An content for individual unmixed grains, thereby permitting closer correlation of optics and composition than is possible with bulk chemical analysis. It is a moderately successful method, applicable only to low-temperature soda-rich plagioclases.

#### *Case I. Homogeneous low-temperature plagioclase*

The angle  $\gamma^*$  is measured from the  $X^*Y^*$  *x*-ray precession photograph and checked against J. V. Smith's (1956) plot of  $\gamma^*$  versus An content (Fig. 2). The accuracy of angular measurement is usually better than 05'

TABLE 6. OPTICAL AND X-RAY DATA FOR SELECTED PERISTERITES  
 Only directly determined indices of refraction and those whose rotated and  
 calculated (from 2V) values are equivalent are recorded

No.	Chem. analysis (wt. %)		Refractive indices (N <sub>D</sub> )			"Strong" phase		"Weak" phase		% An determined from refractive indices		X-ray
	An	Or	γ	β	α	γ <sub>1</sub> *	% An	γ <sub>2</sub> *	% An	Emmons Chayes		
0	0.25	1.1	n.d.	n.d.	n.d.	90°29'	0.0	—	—	—	—	0.0
1a	5.2	0.8	1.5417	1.5368*	1.5329	90°23'	2.0	89°00'	30.5	—	9.5	3.5
				1.5369†								
1b			1.5398	—	1.5300	90°16'	5.0	88°47'	35.0	—	5.0	6.7
1c			1.5400	—	1.5284	90°22'	2.5	—	—	—	3.5	2.5
1d			1.5393	1.5336	—	90°28'	0.5	—	—	—	3.5	0.5
1e			1.5406	1.5334*	1.5282	90°21'	3.0	88°57'	32.0	—	4.0	3.8
				1.5328†								
1f			1.5397	1.5337	1.5297	90°20'	3.0	—	—	—	4.0	3.0
1g			1.5392	—	1.5300	90°22'	2.5	89°02'	29.0	—	4.0	4.3
1h			1.5398	1.5337*	1.5293	90°12'	6.0	—	—	—	4.5	6.0
				1.5341†								
	Average:		1.5400	1.5342	1.5298							
2a	5.7	4.0	1.5423	1.5369	1.5330	90°22'	2.5	89°11'	24.0	6.5	1.50	—
2b			1.5426	—	1.5338	90°19'	4.0	89°03'	28.5	8.0	11.5	11.7
2c			n.d.	n.d.	n.d.	90°21'	3.0	89°15'	22.5	—	—	6.5
	Average:		1.5425	1.5369	1.5334							
3a	7.7	1.7	1.5428	—	1.5340	90°24'	2.0	89°09'	25.5	8.5	12.0	10.4
3b			1.5420	—	1.5337	90°18'	4.0	89°12'	23.0	—	11.0	8.7
3c			1.5421	—	1.5328	90°22'	2.5	89°09'	25.5	—	10.0	9.3
3d			1.5423	—	1.5327	90°23'	2.0	89°13'	23.0	—	10.0	9.7
3e			1.5420*	1.5365	1.5323	90°20'	3.0	89°19'	21.5	—	9.0	10.4
			1.5415†									
	Average:		1.5422	1.5365	1.5331							
4a	9.5	n.d.	1.5420	—	1.5330	90°18'	4.0	89°12'	23.0	—	10.0	—
4b			1.5422	—	1.5330	90°22'	2.5	89°21'	21.0	—	10.0	7.6
4c			1.5435*	1.5368	1.5320	90°19'	4.0	89°23'	20.5	—	10.5	9.1
			1.5435†									
	Average:		1.5426	1.5368	1.5327							
5a	11.4	1.6	1.5446	1.5391*	1.5355	90°26'	1.0	89°17'	22.0	13.5	15.0	—
				1.5390†								
5b			1.5440	—	1.5353	90°22'	2.0	89°07'	27.0	13.0	14.5	—
5c			1.5432	1.5384*	1.5351	90°19'	4.0	89°13'	23.0	11.0	13.5	10.9
				1.5387†								
5d			1.5422*	1.5379	1.5340	90°22'	2.0	89°12'	23.0	—	11.5	10.2
			1.5425†									
5e			1.5424	—	1.5337	90°17'	4.5	89°12'	23.0	—	11.0	11.1
5f			1.5430	1.5380*	1.5339	90°22'	2.0	89°16'	22.5	9.0	12.0	8.9
				1.5380†								
5g			1.5439	—	1.5350	90°25'	1.0	89°09'	26.0	12.0	14.0	—
5h			1.5441	1.5392*	1.5351	n.d.	—	n.d.	—	13.0	14.5	—
				1.5394†								
	Average:		1.5435	1.5385	1.5347							

TABLE 6 (Continued)

No.	Chem. analysis (wt. %)		Refractive indices (N <sub>D</sub> )			"Strong" phase		"Weak" phase		% An determined from refractive indices		x-ray
	An	Or	γ	β	α	γ <sub>1</sub> *	% An	γ <sub>2</sub> *	% An			
										Emmons	Chayes	
6a	13.3	3.9	1.5440	1.5393*	1.5352	90°17'	4.5	89°28'	20.0	12.5	14.5	—
6b			1.5446	—	1.5354	90°17'	4.5	89°25'	20.5	14.0	15.5	—
6c			1.5442	—	1.5343	90°20'	3.5	89°18'	22.0	12.0	14.0	10.7
	Average:		1.5443	1.5394	1.5350							
7a	16.1	2.8	1.5451	1.5406*	1.5368	89°34'	18.0	none	none	16.5	17.5	18.0
7b			1.5451	1.5406†	1.5361	89°33'	18.0	none	none	16.0	16.5	18.0
7c			1.5454	—	1.5359	89°35'	18.0	none	none	16.0	16.5	18.0
7d			n.d.	n.d.	n.d.	89°32'	18.5	none	none	—	—	18.5
	Average:		1.5452	1.5405	1.5362							
8	16.6	1.9	1.5448	1.5409	1.5368	twinned		untwinned		16.5	17.0	—

\* Indicates an index calculated from 2V using Wright's Diagram.

† Indicates a calculation from a prime ray.

of arc, and composition may be quoted to  $\pm 2\%$  An for the range An<sub>0</sub> to An<sub>23</sub>. This does not take into account errors in the graph itself. From An<sub>23</sub> to An<sub>40</sub>, precision is not better than  $\pm 3\%$  An.

#### Case II. Two-phase (unmixed) low-temperature peristerites

The angles  $\gamma^*$  are measured from the single Y\* axis to both X\* axes. It is important that the strong and the weak phases be designated. Using unfiltered x-radiation, care is taken to obtain maximum contrast of X\* streaks against the film. A fine grained film and the largest permissible precession angle are suggested. Finger prints or scratches along the profile to be measured for intensity are highly restricting and may render the film useless.

A densitometer is used to obtain an intensity profile across the X\* white-radiation streaks at a position of greatest resolution. The galvanometer deflection, directly proportional to the X\* axis intensity, is plotted against film movement as in Fig. 5. A convenient method of determining peristerite single crystal composition is given by the formula:

$$\frac{\text{Area}_A}{\text{Area}_{(A+B)}} \cdot (\text{wt. \% An}_A) + \frac{\text{Area}_B}{\text{Area}_{(A+B)}} \cdot (\text{wt. \% An}_B)$$

with reference to Fig. 5. Anorthite contents determined by this method are shown in Table 6 and Fig. 7.

The method for unmixed grains may well be questioned regarding its cumulative error. Contrasting it with An-contents determined by optics

and by chemical analysis, the deviations amount at most to  $\pm 2.5\%$  An. This is not a true test of accuracy, however, since deviations from the bulk chemical analysis may only reflect chemical variations within the sample, which may take any value. Existing optical curves are also based on bulk chemical analyses and depend for their validity on an adequate sampling and averaging technique. Considerable differences exist between published curves for this composition region. These factors affect accuracy of the  $x$ -ray method: (1) background darkening from scattered radiation, (2) degree of resolution of white radiation streaks, (3) error of measurement of  $\gamma^*$ , and (4) accuracy of Smith's (1956) curves, which also require an adequate sampling and averaging technique for their validity. There is an occasional chance that the  $+X^*$  axis intensity profile does not show exactly equivalent area ratios as the profile over the  $-X^*$  axis. Averaging will minimize an otherwise small error.

At this stage of development, this method cannot claim the desired  $\pm 2\%$  accuracy. It is suggested that this system be used with caution and due regard to the variables, and it is hoped that refinements that will both expedite and amend the procedure can be developed. The method fails for a peristerite in an intermediate thermal state, for  $\gamma^*$  changes with the degree of order-disorder and thus cannot be used as an index to composition. Since the high-temperature modifications of all soda-rich plagi-

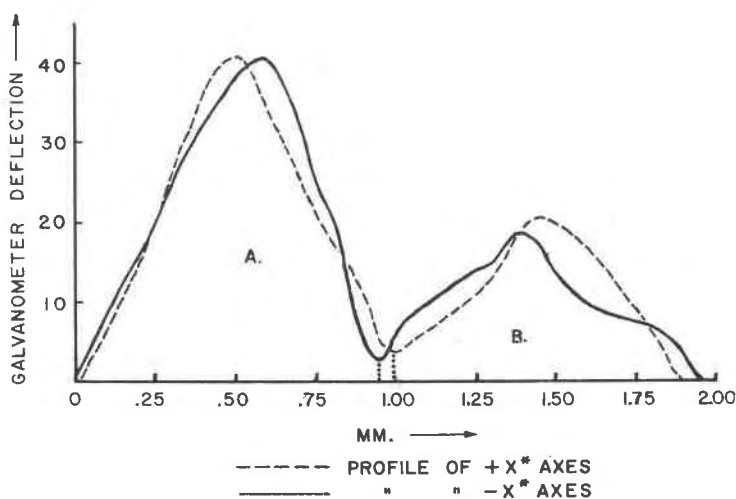


FIG. 5. Plot of the traverse in mm. of resolved  $X^*$  axes of peristerite 5f against the intensity of their white-radiation streaks in units of galvanometer scale deflection. The method of determining peristerite single crystal composition is given by the formula:

$$\frac{\text{Area}_A}{\text{Area}_{(A+B)}} \cdot (\text{wt. \% An}_A) + \frac{\text{Area}_B}{\text{Area}_{(A+B)}} \cdot (\text{wt. \% An}_B)$$

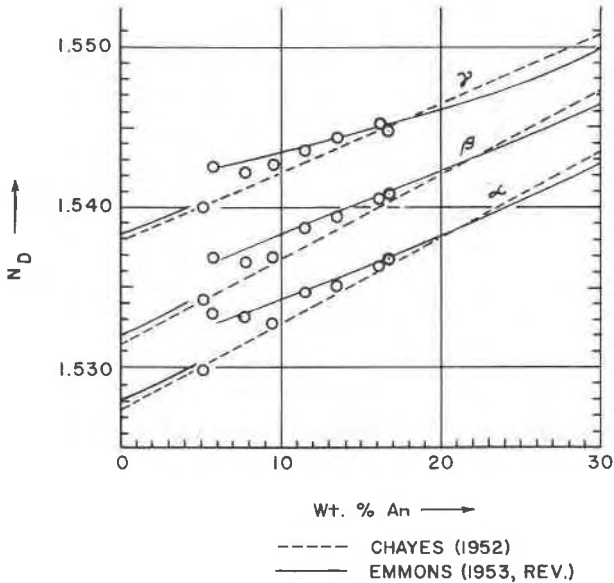


FIG. 6. Refractive index curves of low-temperature soda-rich plagioclase plotted against wt. % An by chemical analysis. Circles represent the author's average indices.

classes have very similar geometry, they are indistinguishable one from the other by ordinary  $x$ -ray techniques.

Using these methods, compositions may be assigned to individual grains in the low-temperature state. The value of these devices becomes obvious when the refractive index curves plotted against analyzed bulk compositions are contrasted with those plotted against An content determined by  $x$ -ray techniques for individual grains (Figs. 6, 7).

Refractive indices of thirty-three grains from eight analyzed low-temperature plagioclases are recorded in Table 6 along with pertinent  $x$ -ray data. The average indices of these samples are plotted according to bulk chemical analyses in Fig. 6. Figure 6 also contrasts the plagioclase index curves of Emmons (1953, revised) and Chayes (1952). The experimental points fall between the two curves, although slightly closer to Emmons' curves and confirming a break or flexure in the 5% An region. This break is to be expected from a structural viewpoint at the lower boundary of the unmixed peristerite range, and further evidence for it appears in Fig. 7 where individual indices are plotted against wt. % An/An+Ab of individual grains determined by the  $x$ -ray methods described above. Of particular interest is sample 1. It contains both unmixed, two-phase grains and structurally homogeneous grains. Although chemical analysis

(Jeffries, 1936) indicates  $An_{5.2}Or_{0.8}$  to be the bulk composition, *x*-ray methods show a range from  $An_{0.5}$  to  $An_{6.7}$  for individual fragments. The homogeneous grains range from  $An_{0.5}$  to  $An_6$ ; unmixed grains range from  $An_{3.5}$  to  $An_{6.7}$ .

It was expected that all the unmixed grains would have higher refractive indices than the structurally homogeneous grains of the same composition, for unmixing can be considered an extreme case of ordering, representing a closer packing of ions, increased polarization, and higher refractive index. But this is not the case for sample 1. For example, grain *1b* is unmixed and its two components, approximately  $An_5$  and  $An_{35}$ , are pres-

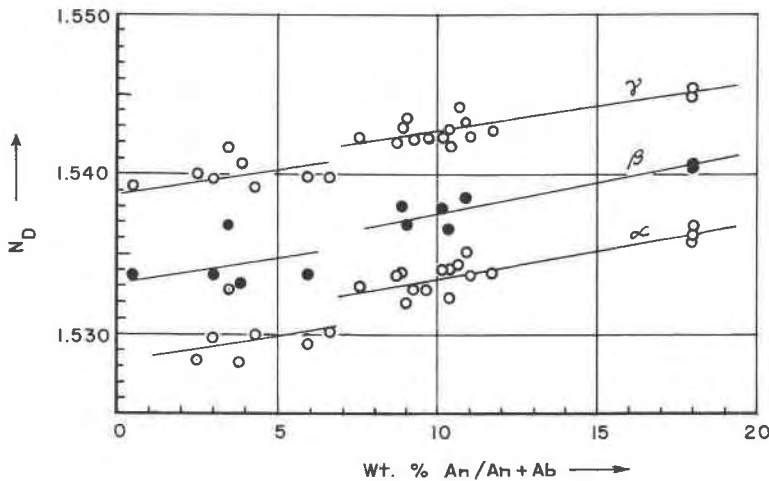


FIG. 7. Refractive indices of twenty-three grains from eight low-temperature soda-rich plagioclases plotted against wt. %  $An/(An+Ab)$  determined by *X*-ray methods. All specimens of less than 7%  $An$  are from sample 1. Lines of best fit are indicated.

ent in the ratio 94.4/5.6 (*x*-ray method) and give a total composition of  $An_{6.7}$ . This grain has the same indices as grain *1h*, which is homogeneous and contains approximately 6%  $An$  according to  $\gamma^*$  measurements. Further contrasted with *1h* is the homogeneous grain *1d* whose reciprocal lattice angle  $\gamma^*$  indicates a composition of only  $An_{0.5}$ . Yet the indices of *1b*, *1h* and *1d* are nearly identical within the limits of error of measurement ( $\pm .0004$ ).

Because  $\gamma^*$  varies so widely for these homogeneous grains and because both structurally homogeneous and unmixed grains exist in the same crystal, a significant variation in  $An$  content from grain to grain is unquestioned. The plot of the refractive indices of the grains from this crystal against composition as determined by the *x*-ray method (Fig. 7)



demonstrates that some sort of break or flexure in index curves is present in the  $An_5$  to  $An_{10}$  region. The break here falls at  $An_7$  whereas in Fig. 6, using average indices and bulk chemical analyses, the break falls at  $An_5$ . Emmons (1953, revised) indicated a break between  $An_6$  and  $An_8$  in his determinative chart of plagioclase optics. Neither Chayes (1952) nor J. R. Smith (1957) shows a change of slope here.

Alternate explanations of these unusual properties include nonequilibrium conditions and factors other than composition that affect the  $\gamma^*$  parameter. At present there is insufficient evidence to permit intelligent speculation on either of these possibilities.

The anomalous optical and structural situations in the 5% An region attest the necessity of a re-evaluation of this composition range. More analyzed specimens and an improved method of determining composition of individual grains are indispensable to a thorough understanding of the peristerite plagioclases. The possibility of another break of flexure in the optic curves at the other end of the peristerite range as suggested by J. R. Smith (1957) at  $An_{21}$ , was not examined in this study.

#### DISCUSSION

The cause of peristerite unmixing as a soda-rich plagioclase cools during crystallization is not certain, although in the case of the somewhat similar moonstones or crypto-perthites it is assumed to be due to stresses caused by the 35% discrepancy in ionic radii of K and Na. It is proposed here that the original homogeneous crystal of peristerite composition is caused to unmix during cooling by the large size difference between Al and Si in the feldspar tetrahedral framework. This size difference is 38% based on radii of 0.29 Å and 0.47 Å for Si and Al respectively. The radii are determined from the data on feldspar bond lengths as listed below. The O-O distance was obtained from the data of Bailey and Taylor by plotting their O-O bond lengths versus Al content for the individual tetrahedra and extrapolating to zero Al content. It is assumed that the oxygens are in contact at this composition.

Si-O.....	1.60 Å (J. V. Smith, 1954)
Al-O.....	1.78 Å (J. V. Smith, 1954)
O-O in $SiO_4$ , tetrahedron.....	2.61 Å (Bailey & Taylor, 1955)

This 38% size difference contrasts with an 8% variance between Na and Ca in octahedral coordination ( $r_{Na} = 0.98 \text{ \AA}$ ;  $r_{Ca} = 1.06 \text{ \AA}$ ). The driving force for the unmixing can thus be reasonably associated with the Al-Si, the Ca-Na cooperating to balance the electrostatic valence charges.

The albite structure can tolerate only minor deviations from the composition  $NaAlSi_3O_8$ , for with increasing substitution of the larger Al for Si, strains are established in the crystal lattice that can be relieved only

by a different distribution of the misfit atoms—changing from a random distribution of the Al in excess of the geometrically stable 1:3 Al:Si ratio within the tetrahedral sites of the homogeneous crystal to a segregation into Al- and Si-rich regions. It is presumed that the framework is continuous throughout the two-phase peristerite, but distorts elastically within the individual domains to assume the geometry of the local composition, namely  $An_3$  or  $An_{25}$ . This view infers that the structure of  $An_{25}$  is enough different from that of pure albite to tolerate the additional Al content, perhaps by an ordered geometry different from that of albite. It is presumed that the unmixed components remain submicroscopic in size, in contrast to perthites, because of the difficulty of diffusion of Al and Si over any appreciable distance as a consequence of the strength of their bonds (Goldsmith, 1952).

## ACKNOWLEDGMENTS

This study was supported in part by a fellowship from the Wisconsin Alumni Research Foundation. S. W. Bailey suggested the problem and supervised the course of research. The author wishes to thank R. C. Emmons of the University of Wisconsin and V. B. Meen of the Royal Ontario Museum for furnishing some of the specimens used.

## REFERENCES

- BAILEY, S. W., AND TAYLOR, W. H. (1955), The structure of a triclinic potassium feldspar: *Acta Cryst.*, **8**, 621–632.
- BÖGGILD, O. B. (1924), On the labradorization of the feldspars: *Det Kgl. Danske Videnskabsbernes Selskab.*, **6**, 79 pp.
- BOWN, M. G., AND GAY, P. (1958), The reciprocal lattice geometry of the plagioclase structures: *Zeits. Krist.*, **111**, 1–14.
- CHAYES, F. (1950), On the relation between anorthite content and  $\gamma$ -index of natural plagioclase: *J. Geol.*, **58**, 593–595.
- (1952), Relation between composition and indices of refraction in natural plagioclase: *Amer. J. Sci., Bowen Vol.*, **1**, 85–106.
- (1954), A test for the revised determinative chart for plagioclase: *Amer. J. Sci.*, **252**, 172–180.
- COLE, W. F., SÖRUM, H., AND TAYLOR, W. H. (1951), The structures of the plagioclase feldspars, I: *Acta Cryst.*, **4**, 20–29.
- DITTLER, E., AND KÖHLER, A. (1925), Zur Frage der Entmischbarkeit der Kali-Natronfeldspäte und über das Verhalten des Mikroklin bei hohen Temperaturen: *Tschermaks. Min. u. Petr. Mitt.*, **38**, 229–261.
- EMMONS, R. C. (1943), The universal stage: *Geol. Soc. Amer. Mem.*, **8**.
- , ed. (1953, reprinted 1956), Selected petrogenic relationships of plagioclase: *Geol. Soc. Amer. Mem.*, **52**.
- FERGUSON, R. B., TRAILL, R. J., AND TAYLOR, W. H. (1958), The crystal structures of low-temperature and high-temperature albites: *Acta Cryst.*, **11**, 331–349.
- GAY, P., AND SMITH, J. V. (1955), Phase relations in the plagioclase feldspars, composition range  $An_0$  to  $An_{70}$ : *Acta Cryst.*, **8**, 64–65.

- GOLDSMITH, J. R. (1952), Diffusion in plagioclase feldspars: *J. Geol.*, **60**, 288-290.
- HEALD, M. T. (1950), Thermal study of potash-soda feldspars: *Am. Mineral.*, **35**, 77-89.
- HEWLETT, C. G. (1959), Optical properties of potassic feldspars: *Bull. Geol. Soc. Amer.*, **70**, 511-538.
- JEFFRIES, C. D. (1936), II. Optical studies of feldspars: Ph.D. Thesis, University of Wisconsin.
- LAVES, F. (1951), Relationships between exsolved plagioclase and its host: Abstract, Amer. Cryst. Assoc. Program of Winter Meeting.
- (1952), Phase relations of the alkali feldspars: I. Introductory remarks. II. The stable and pseudo-stable phase relations in the alkali feldspar system: *J. Geol.*, **60**, 436-450, 549-574.
- (1954), The coexistence of two plagioclases in the oligoclase compositional range: *J. Geol.*, **62**, 409-411.
- MEEN, V. B. (1933), A description of a few plagioclases: *Univ. of Toronto Stud., Geol. Ser.*, **35**, 37-45.
- RAMAN, C. V., JAYARAMAN, A., AND SRINIVASAN, T. K. (1950), The structure and optical behavior of the Ceylon moonstones: *Ind. Acad. Sci.*, **32A**, 123-140.
- SCHNEIDER, T. R. (1957), Röntgenographische und optische Untersuchung der Umwandlung Albit-Analbit-Monalbit: *Zeits. Krist.*, **109**, 245-271.
- SMITH, J. R. (1955a), Optical properties of plagioclase feldspars: *Ann. Rep. Dir. Geophys. Lab.*, 1954-1955, 119-120.
- (1955b), Optical properties of some low-temperature plagioclases: *Bull. Geol. Soc. Amer.*, **66**, 1618-19.
- (1957), Optical properties of heated plagioclases: *Ann. Rep. Dir. Geophys. Lab.*, 188-190.
- SMITH, J. V. (1954), A review of the Al-O and Si-O distances: *Acta Cryst.*, **7**, 479-481.
- (1956), The powder patterns and lattice parameters of plagioclase feldspars. I. The soda-rich plagioclases: *Miner. Mag.*, **31**, 47-68.
- SPENCER, E. (1930), A contribution to the study of moonstone from Ceylon and other areas and of the stability relations of the alkali feldspars: *Miner. Mag.*, **22**, 291-367.

*Manuscript received August 25, 1959.*