An electron-microscope study of peristerite plagioclases

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Summary. Plagioclase feldspars in the peristerite range An_2–An_{17} have been investigated by transmission electron-microscopy and electron diffraction. All except the more anorthite-rich specimens were found to be unmixed into albite and oligoclase lamellae, between a few hundred and several thousand Å thick and approximately parallel to $(0\bar{8}1)$. A discussion is given of the part played by these lamellae when optical schiller is exhibited; and the effect of heat treatment on the lamellar structure and optical schiller is described.

THE plagioclase feldspars form a mineral series from albite (Ab), $NaAlSi_3O_8$, to anorthite (An), $CaAl_2Si_2O_8$. The liquidus and solidus of this system indicate that a classical solid-solution series exists at high temperatures (Bowen, 1913), but the subsolidus phase relations are exceedingly complex (see review by Gay, 1962). This paper is concerned with the peristerite range of the plagioclase subsolidus (cf. Brown, 1962; Ribbe, 1962).

Laves (1951, 1954) first recognized that peristerites occur in the composition range 5–17 wt. % An (An_5–An_{17}) and consist of two geometrically-distinct low-temperature plagioclases, which coexist in submicroscopic domains. By X-ray diffraction he identified these domains as albite and $An_{\sim 30}$. Gay and Smith (1955), using lattice parameters published by Smith (1956), gave these compositions more precisely as $An_{3\pm 2}$ and $An_{23\pm 2}$. Recent electron microprobe analyses by Ribbe and Smith of the specimens used by Smith (1956) indicate that the average compositions of the end members are more nearly An_2 and An_{22} with variations from grain to grain of An_{0-5} and An_{18-32} (cf. Brown, 1960, 1962; Ribbe, 1960, 1962).

A pale- to deep-blue schiller (iridescence) is often seen in peristerites. Bøggild (1924) determined that schiller can only be seen in a direction

normal to $(0\bar{8}1)$, and Brown (1960), who confirmed Bøggild's observation, investigated several schillered specimens with an optical microscope and saw lamellae parallel to $(0\bar{8}1)$. These lamellae were 1–3 μ thick and of very sporadic occurrence and separation: as such they did not suffice to explain the schiller phenomenon. With phase-contrast and dark-field microscopy, Ribbe and Van Cott (1962) observed submicron ellipsoidal blebs scattered throughout peristerite grains. Using indirect evidence, they reasoned that these blebs were domains of oligoclase ($An_{\sim 22}$) exsolved from the albite host. With the optical model of Raman, Jayaraman, and Srinivasan (1950) they explained the schiller in terms of diffuse reflection and scattering from these optically distinct, mutually oriented domains. Using an electron microscope, Saucier and Saplevitch (1962) observed submicron lamellae on a replica of the (001) face of a peristerite from Villeneuve, Quebec. They state that these lamellae are parallel to $(0\bar{8}1)$, but, inherently limited by the replica technique, they were unable to identify them.

In view of the recent electron-microscope investigation of a moonstone (Fleet and Ribbe, 1963), which to some extent discredits the optical model of Raman *et al.* (1950) for moonstone schiller and by extension that of Ribbe and Van Cott (1962) for peristerite schiller, the present authors decided to use transmission electron microscopy and electron diffraction methods to resolve the many uncertainties about peristerite unmixing and its relation to schiller. Are the exsolved domains lamellae or are they submicron blebs more or less randomly distributed throughout the host but mutually oriented one to another? In either case, what is their crystallographic orientation and how it is related to the plane of schiller $(0\bar{8}1)$? In what manner do the domains disorder when the peristerite is homogenized by heat treatment? Does their disappearance coincide with the disappearance of schiller?

To answer these questions a peristerite with unusually brilliant blue schiller was chosen for examination. The specimen comes from Froland, Norway, and was contributed by Mrs. B. Nilssen of the Mineralogisk-Geologisk Museum, Oslo. A chemical analysis by Mr. J. H. Scoon[1] gives the composition 9·9 wt. % An/(An+Ab), which is in good agreement with our electron-microprobe analyses (see table I).

Examination of the Froland peristerite

Optical study. A thin section of the rock cut parallel to (001) shows wide lamellae parallel to (010) in the orientation of the albite twin

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law.[1] The thickness of the twins varies from $\sim 0{\cdot}1$ mm downwards. The (010) thin sections exhibit finer lamellae ($< 0{\cdot}04$ mm) inclined at about 13° to the (001) cleavage. Extinction angles differ by $\sim 1°$ between adjacent lamellae consistent with their being in the pericline twin[2] orientation. There is no optical evidence of the fine ($0\bar{8}1$) lamellae seen by Brown (1960) or Saucier and Saplevitch (1962), or of the blebs reported by Ribbe and Van Cott (1962).

X-ray study. Zero-layer precession photographs of the a^* b^* plane of the Froland peristerite show that two phases are present. The reciprocal lattice angles γ^* were measured for the coexisting phases and were used with the curves γ^* *vs.* wt. % An/(An+Ab) (Smith, 1956) to determine the approximate compositions of the exsolved domains. One grain gave the values 1 % An for the Na-rich phase and 20 % An for the Ca-rich phase.

As optical methods do not reveal the domains, and the diffracted spots on X-ray photographs are sharp and clear, we may assume that the domains are smaller than the wavelength of light (~ 6000 Å) but somewhat larger than 200 Å in order to produce sharp X-ray reflections.

Electron-microscope study. Finely crushed grains of the peristerite were suspended in alcohol and dropped onto a carbon-covered grid for observation in the electron microscope. It was immediately evident that most grains were made up of fine lamellae. Fig. 1 is a dark-field electron micrograph of a typical grain. The lamellae are usually of very constant thickness along their length, but there is frequently a considerable variation in thickness from one lamella to another.[3]

In order to deduce the structural difference between adjacent lamellae, electron-diffraction patterns of grains were observed. Fig. 2 shows transmission photographs and diffraction patterns of three grains. The grain in fig. 2 (i) is lying with the prominent cleavage plane (001) approximately normal to the electron beam. The diffraction pattern contains the b^* axis and the axis defined by the origin and the point ($\bar{2}01$) in reciprocal space. It can be seen that the lamellae are very closely normal to b^*. Fig. 2 (ii) shows a grain whose orientation with respect to the electron beam is indicated in fig. 3 (i). The diffraction pattern contains the plane in reciprocal space defined by axes through the origin and

[1] Albite twins are formed by reflexion across (010).

[2] Pericline twins are formed by rotation about [010].

[3] Occasional grains with lamellae of very regular thickness (from about 200 to 300 Å) have electron diffraction peaks streaked out approximately parallel to b^*. Microscopic examination of the streaks reveals that they are made up of very closely spaced superlattice spots whose separation corresponds to the repeat distance between alternate lamellae.

reciprocal lattice points ($1\bar{3}0$) and ($\bar{3}\bar{1}1$). Lamellae are inclined 63° to the (000)–($\bar{1}30$) axis and are of quite constant thickness along their length. Fig. 2 (iii) shows a grain that has the reciprocal lattice section defined by the points (000), (130), and ($\bar{3}11$) normal to the electron beam. The orientation of the grain is shown in fig. 3 (ii). Lamellae for this third grain are inclined at 54° to the (000)–(130) axis.

In all the diffraction patterns of fig. 2, diffraction peaks can be seen

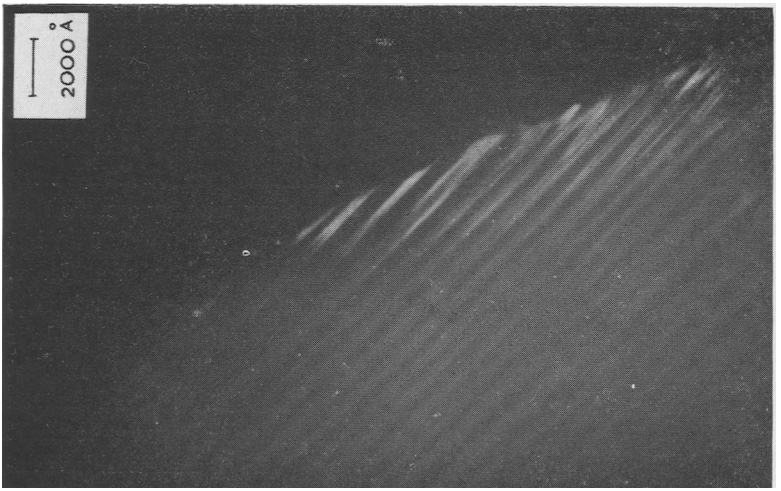

FIG. 1. Dark-field micrograph of a typical grain of Froland peristerite.

to be 'split' into pairs of adjacent maxima. Figs. 4 (i), (ii), and (iii) are sketches of superposed oligoclase and albite reciprocal lattice sections corresponding to the diffraction patterns of figs. 2 (i), (ii), and (iii). It is clear that the directions of 'splitting' of the maxima seen in the diffraction patterns correspond very well to a superposition of albite and oligoclase patterns (certainly to within the limits of error imposed by inaccuracies in the cell-dimensions of albite and oligoclase). The lamellae are therefore regions of unmixed albite and oligoclase: they are not twin lamellae. The identification of one or other set of lamellae can be established by dark-field methods using one or other of a pair of spots from the superposed diffraction patterns.

Several other grains were found to give identical diffraction patterns to those in figs. 2 (i), (ii), and (iii), and in each case the lamellae were inclined at the same angle (to within the accuracy of measurement, $\pm 1°$)

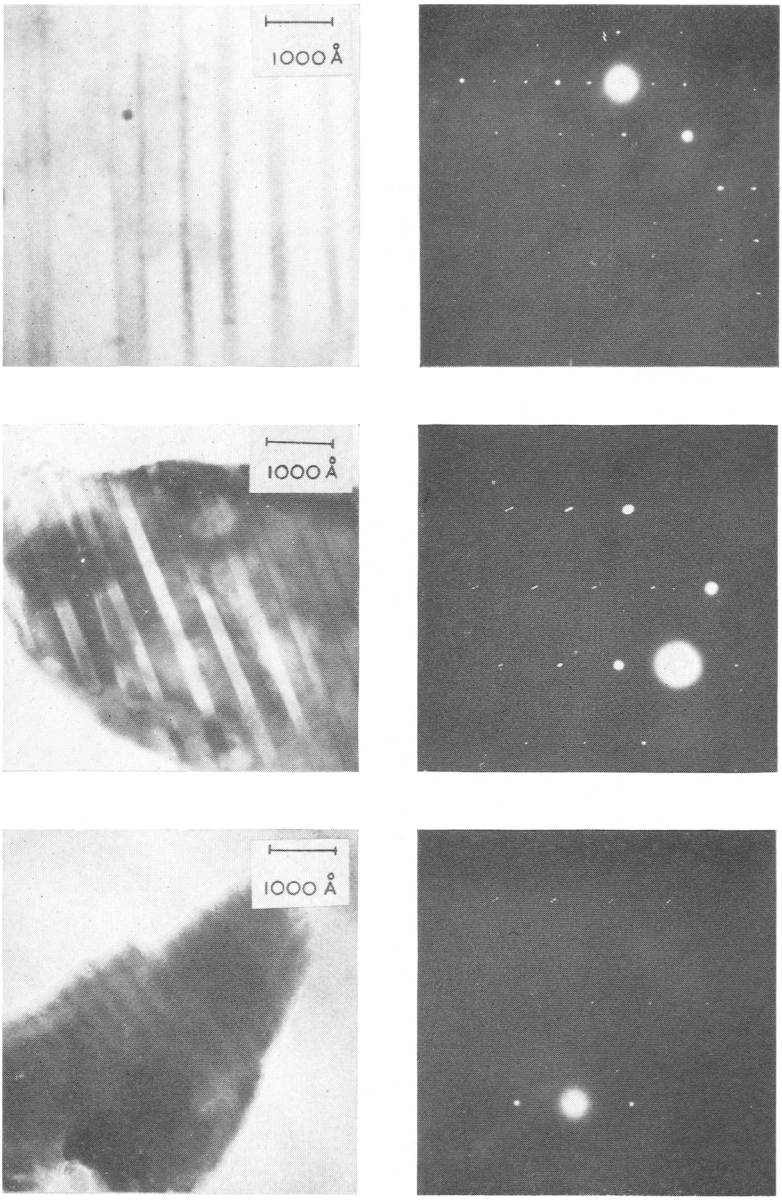

FIG. 2. Bright-field micrographs of Froland peristerite grains and the corresponding electron-diffraction patterns. See the text for a description of the orientation of the grains; (i) top, (ii) middle, (iii) bottom.

to the reciprocal axes. The lamellae are therefore always parallel to the same crystallographic direction in this peristerite.

Derivation of the plane of the lamellae. Measurement of angles between lamellae and directions in the crystal recognizable from diffraction patterns were used to work out the plane of the lamellae.

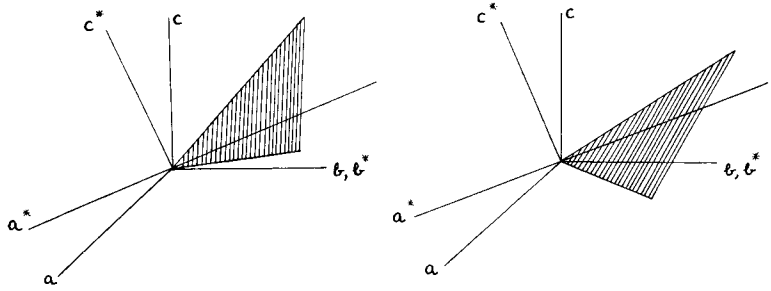

FIG. 3. Hatched regions show the planes of the grains photographed: (i), left, in fig. 2 (ii); (ii), right, in fig. 2 (iii).

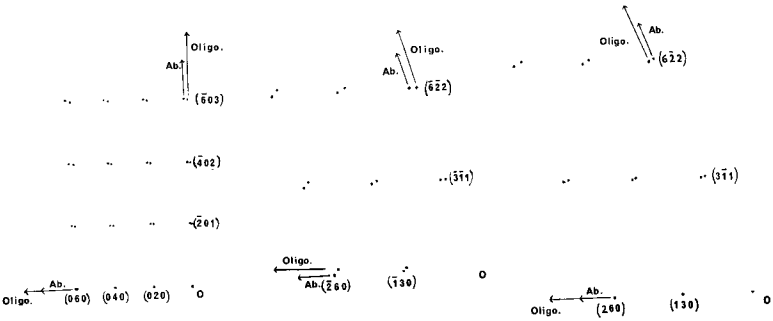

FIG. 4. Superposed oligoclase and albite reciprocal-lattice sections corresponding to the diffraction patterns of fig. 2 (i) (left), (ii) (middle), (iii) (right). Cell dimensions for oligoclase were taken from Waring (1961), and for albite from Ferguson, Traill, and Taylor (1958).

Grains like the one in fig. 2 (i), which lie with (001) approximately normal to the electron beam, always have lamellae normal to the b^* direction (directions referred to in this section are the average of the albite and oligoclase directions) and parallel to the a-axis. The lamellae are therefore planes of the type $(0kl)$. In order to find the values of k and l, the angles made by planes of different k/l with the direction defined by reciprocal lattice points (000) and $(\bar{1}30)$ in micrographs such as

fig. 2 (ii) were worked out. It was found that $k/l = \bar{8}$ gives the best fit (64° 52′) with the measured angle of 64° between lamellae and this direction. A similar calculation for micrographs such as fig. 2 (iii) showed that $k/l = \bar{8}$ also gave best fit (52° 32′) with the angle of 54° between lamellae and the direction specified by reciprocal lattice points (000) and (130). The plane of the lamellae is therefore very closely $(0\bar{8}1)$, confirming the observations of Brown (1960) and Saucier and Saplevitch (1962).

Electron-microscope study of other peristerites

Table I gives details of the peristerites examined. Some grains of all except one of the specimens are unmixed into albite and oligoclase lamellae; diffraction patterns of grains showing lamellae indicate that they are closely parallel to $(0\bar{8}1)$.

In the Na-rich peristerites the lamellae are alternatively thick and thin (fig. 5), although there is considerable variation in the thickness of both types. That the thick lamellae are albite and the thin oligoclase is indicated by the relative intensities of the albite–oligoclase spot pairs in both electron and X-ray diffraction patterns. In the more Ca-rich peristerites there is no obvious indication of differences in the thickness of alternate lamellae. However, it is likely that any differences will be masked by the apparently random variations in thickness that occur in all specimens.

The Bakersville oligoclase (An_{17}) is the only specimen investigated whose composition lies near the upper limit of the accepted peristerite unmixing range (An_2–An_{17}). No distinct lamellae were observed; but of the many electron-diffraction patterns examined, six showed double spots characteristic of coexisting albite and oligoclase. Hundred-hour X-ray diffraction photographs, however, failed to indicate unmixing. The reciprocal lattice angle γ^*, measured from *c*-axis precession photographs, is 89° 34′±03′. This corresponds to 16 mol. % An (using the revised curves of γ^* *vs.* % An) and is in perfect agreement with the percentage of the anorthite molecule determined by electron-microprobe analysis. That exsolution has proceeded only with the greatest difficulty is evidenced by its rare and scattered occurrence and the absence of lamellae in the minute (1 μ) unmixed regions of this specimen. In any case, the Bakersville oligoclase falls on the flared portion of the peristerite 'solvus' proposed by Ribbe (1962), confirming the idea that only the slightest indication of unmixing is to be expected at or above An_{17}.

TABLE I. Particulars of the peristerites studied

No.	*Specimen locality*	*Composition (wt. %)** An	Or	*Nature of schiller†*	*Nature of unmixing*
1	Auburn, Maine	2·8*	0·4	Pale blue, medium to weak	Infrequent lamellae, alt. thick & thin
2	Hybla, Ontario	7·0	1·0	Yellow to blue, very strong	Infrequent lamellae, alt. thick & thin
3	Monteagle Township, Ontario	7·6	1·0	Pale blue, strong	Infrequent lamellae, alt. thick & thin
4	Bancroft, Ontario	8·3	0·5	Blue, strong	Infrequent lamellae, alt. thick & thin
5	Haddam, Connecticut	8·8	0·5	Pale blue, weak	Frequent lamellae
6	Villeneuve, Quebec	10·3	0·7	Pale blue, medium	Infrequent lamellae, alt. thick & thin
7	Froland, Norway	10·5	1·2	Blue to white, very strong	Frequent lamellae
8	Peekskill, New York	11·7	0·6	None visible (small grains)	Frequent lamellae
9	Monteagle Valley, Ontario	12·4	1·0	None visible	Infrequent lamellae
10	Bakersville, North Carolina	17·0	3·1	None visible	No lamellae

* Determined by electron microprobe X-ray analysis at the University of Chicago. An as a percentage of An+Ab, Or as a percentage of total feldspar. Anorthite content varies about $\pm$ 1 wt. % from grain to grain in all specimens except No. 1 where the variation is $\pm$ 2 % An. The maximum variation in orthoclase ($KAlSi_3O_8$) content is $\pm$ 0·5 wt. %. Compare chemical and X-ray analyses for specimens 1, 3, 5, 6, 8, and 9 in Ribbe (1960).

† Schiller characteristics of specimens 1, 3, 5, 6, and 9 were evaluated by S. W. Bailey of the University of Wisconsin.

Specimens 1 and 5 were contributed by S. W. Bailey (cf. Jeffries, 1936); specimen 2 by D. J. Fisher; specimens 3, 6, and 9 by the Royal Ontario Museum of Geology and Mineralogy (cf. Meen, 1933); specimen 4 by W. S. MacKenzie; specimen 7 by Mrs. B. Nilssen; specimens 8 and 10 by R. C. Emmons (cf. Emmons, 1953).

Peristerite schiller

The comments listed in table I show that there is an indisputable relationship between schiller and the nature of unmixing: reasonably extensive sequences of $(0\bar{8}1)$ compositional lamellae must exist in order to produce the schiller phenomenon. A series of optical experiments might make it possible to relate the average lamellar thickness and lamellar frequency to the colour and intensity of the schiller. Our data only suggest the relationships.

Thirty-two analysed specimens in the range An_2–An_{17} were available to the authors; 21 of the 24 peristerites containing less than 11 wt. % An exhibit schiller (cf. Brown, 1962, p. 356), but only one of the specimens above An_{11} shows the effect. The reason for this distribution may be related to the average thickness of albite and oligoclase lamellae in the peristerite. It has been observed from specimen to specimen that oligoclase lamellae are usually 250–500 Å thick. The albite lamellae, however, vary substantially and are generally much thicker than their oligoclase neighbours. The unmixing ratio of An_2 to An_{22} will be an important consideration in determining relative thicknesses of lamellae: it varies from 1:1 (the lowest ever observed) in the Ca-rich, no-schiller peristerites to as much as 50:1 (at $An_{\sim 2}$) in the Na-rich, schillered peristerites.

On the basis of an explanation of the schiller in terms of interference of light rays reflected at boundaries between albite and oligoclase lamellae, it is clear that the thicker lamellae found in the Na-rich specimens (cf. fig. 5) would provide boundaries separated by distances of the same order as the wavelength of light.[1] Therefore schiller would be more prevalent in these specimens. One specimen (Hybla; An_7) shows a yellow schiller; it has the thickest albite lamellae (1700 Å) observed in this study. Schiller in all other specimens is blue.

The optical model of Raman *et al.* (1950) for moonstones, which was extended by Ribbe and Van Cott (1962) to peristerites, must be modified: randomly scattered blebs will produce diffuse scattering, whilst most peristerite schiller is characterized by sharp reflections. That the blebs are not primarily responsible for schiller does not, however, necessarily imply that they were not exsolved oligoclase.

Most grains thin enough to be examined by transmission electron microscopy are $< 1\ \mu$ in size, and some of these small grains from all

[1] The role of lamellae whose thicknesses are less than one-tenth of the wavelength of light is uncertain. Experiments with short-wavelength radiation (e.g. ultra-violet light) would be useful.

peristerite specimens show neither lamellae nor the paired albite–oligoclase diffraction patterns. This suggests that there exist many non-planar 'grain-sized' volumes that are either albite or oligoclase. The majority are likely to be albite, since it is the dominant phase; but others may correspond to the submicron ellipsoidal blebs (oligoclase?) observed by Ribbe and Van Cott. However, since these authors were able to present only indirect evidence in their identification of the blebs, the possibility exists that the blebs are some other phase.

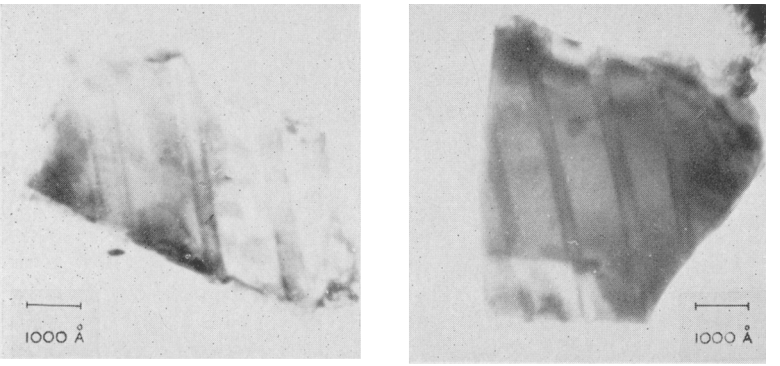

FIG. 5. Bright-field micrographs of typical grains of: (i), left, Hybla peristerite (7·0 % An); (ii), right, Monteagle Township peristerite (7·6 % An).

Peristerite homogenization

Dry heating near the melting-point of a peristerite produces changes in cell geometries of the coexisting phases (see, for example, Schneider, 1957). Because lattice parameters of the high-temperature (disordered) forms of albite and oligoclase are so nearly alike as to be indistinguishable by X-rays (Smith, 1956), it has been tempting to assume that extended heating of a peristerite produces a truly homogeneous crystal (Laves, 1954; Schneider, 1957). But Ribbe (1960) suggested that persistence of schiller in these heated specimens is evidence that only the geometries converged: the phases (now high albite and high oligoclase) remain distinct, and optical heterogeneity responsible for schiller persists. Dry heating produces disorder *within* the lamellae, but not *between* them.

The diffusion of Al and Si over the hundreds of Ångströms between the centres of adjacent peristerite lamellae is difficult, at best, because of the strength of the tetrahedral bonds (Goldsmith, 1952). However, the

presence of water under pressure at high temperatures permits the formation of occasional (OH) bonds at the tetrahedral vertices, thereby allowing the exchange of Al and Si from one tetrahedral site to another (Donnay *et al.*, 1959). The mobility of Na and Ca is also enhanced in the presence of water (Orville, 1962; Wyart and Sabatier, 1962).

Thus our initial attempt to homogenize the Froland peristerite was made at 2 kilobars water pressure and 800° C. After twelve days an electron-microscope investigation revealed that homogenization had

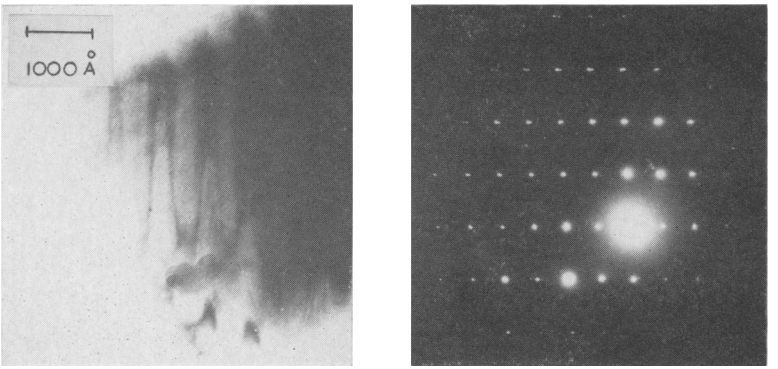

FIG. 6. Bright-field micrograph and the corresponding electron-diffraction pattern of a grain of Froland peristerite after heating at 800° C.

only begun. The lamellae were still distinguishable and were only slightly less distinct than before. The diffraction patterns (cf. fig. 6) showed a diffuse streaking[1] between the pairs of albite and oligoclase spots, indicating the partial inversion of the phases to their respective (and nearly coincident) high-temperature geometries. The heated specimen continued to exhibit schiller without any obvious change in brilliance.

Another specimen of Froland peristerite was heated for 30 days at 900° C under 1·5 kilobars water pressure. This time true homogenization was obtained. No lamellae were observed in any grains and the diffraction patterns had unsplit spots consistent with a homogeneous high-temperature phase. None of the heated grains exhibited schiller, clearly indicating the dependence of the phenomenon on the coexistence of the $(0\bar{8}1)$ albite and oligoclase lamellae.

[1] This is in contrast to the superlattice spots which were only occasionally observed in certain unheated grains (see above).

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