The structures of the plagioclase felspars.

V. The heat-treatment of lime-rich plagioclases.

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INTRODUCTION.

THIS work has been primarily concerned with plagioclase felspars within the composition range $Ab_{30}An_{70}$ to Ab_0An_{100}, i.e. felspars with the anorthite-type structure. Some results for less basic specimens will be quoted where appropriate; a fuller description of the effects of heat-treatments on intermediate plagioclase felspars will be published later.

It is convenient in describing the changes which occur in the diffraction patterns to classify the reflections in the following way:

Type (a) $(h+k)$ even, l even   (principal reflections)
,, (b) $(h+k)$ odd, l odd ⎫
,, (c) $(h+k)$ even, l odd ⎬ (subsidiary reflections)
,, (d) $(h+k)$ odd, l even ⎭

For all specimens, the principal reflections are sharp and are not appreciably changed by heat-treatment; the subsidiary reflections, however, do undergo substantial alterations. In the low-temperature series (Gay, 1953), for pure anorthite, which has a primitive unit cell with c-axis twice the length of that of albite, reflections of all these types are present and sharp. As the percentage of albite is increased, the (c) and (d) type reflections become diffuse and gradually disappear: the specimens examined of composition $Ab_{15-20}An_{85-80}$ show only types (a) and (b) reflections, i.e. they still possess the doubled c-axis of the anorthite-type structure but the unit cell, chosen as before, is now body-centred. This structure is observed until a composition of about $Ab_{30}An_{70}$ is reached.

At about this composition the regular periodicity of the structure giving rise to the 14 Å. c-axis is destroyed; reflections of type (b), which indicate the doubling of the c-axis, are replaced by pairs of reflections symmetrically disposed about the position of the odd layer-lines on c-axis photographs from bytownites and anorthites. Recent work by Cole, Sörum, and Taylor (1951) on these intermediate plagioclases suggested that the separation of these subsidiary reflections is a function of composition; they also correlated the separation of these subsidiary reflections on photographs taken about other principal axes with composition.

A number of specimens, some of which occur naturally, do not fit in with this sequence; it is thought that this is due to some special feature of their previous geological history. The difference between the high- and low-temperature forms of albite has been shown quite clearly (Tuttle and Bowen, 1950) and more recently (Laves and Goldsmith, 1951; Gay, 1953) it has become apparent that the structure of pure anorthite is temperature dependent. Very little has been published about the structural changes observed in plagioclases on heat-treatment. This seems surprising in view of the importance of the optical data of Köhler and his co-workers. In the present research, a number of lime-rich plagioclases have been subjected to various heat-treatments and examined by X-ray methods. No detailed optical measurements have been made, since at this end of the series it is known that the optical changes are small and their detection is difficult and uncertain; later, it is hoped to correlate the structural and optical changes. Similar investigations of other composition regions of the plagioclase series are also being undertaken. When these studies are complete, it is hoped that a 'structural phase diagram' can be built up, which will be explicable in terms of changes in the atomic structure of the felspars.

EXPERIMENTAL METHODS.

(a) *Selection and heat-treatment of specimens.*—So far as has been possible, single crystals have been isolated and used in this work. Some of the felspars from which the specimens were taken have been analysed; unzoned grains with extinction angles corresponding to the chemical composition of the bulk material were selected for use. For materials for which no analysis has yet been obtained, the composition was determined optically (no large errors in estimating composition by optical methods will arise at the lime-rich end of the series).

For temperatures up to 900° C. the specimens were heated in a nichrome-wound muffle furnace; a platinum-wound furnace was used for higher temperatures. There is some uncertainty about the exact temperature of heating owing to power input fluctuations.

The duration of heat-treatment was three days. In the present experiments no study of the rates of transformation has been made; it was desired only to find what structural modifications can exist. In transformations of the type found a particular structural state can be attained either by a relatively long treatment at a low temperature or by a relatively short treatment at a higher temperature. However, at the higher temperature, the structural state reached after the short treatment may not be the equilibrium state. In these experiments it was thought best to keep the time of heating constant and use different temperatures.

(b) *X-ray methods.*—As far as possible, each series of heat-treatment experiments was carried out on the same single crystal; i.e. each individual specimen was examined in the natural state and after each successive heat-treatment. At each stage oscillation and Weissenberg patterns about the principal axes were obtained; oscillation about other axes has been used sometimes for confirmatory purposes.

EXPERIMENTAL RESULTS.

Table I contains a description of the specimens used and their mode of occurrence, together with a brief account of their diffraction patterns after each successive heat-treatment.

In the composition range of the anorthite-type structure, all four classes of reflections can occur. Type (a) reflections are apparently unchanged after any heat-treatment; however, it is probable that there are small changes in their relative intensities which would have become apparent in any detailed structural work. The other three reflection types can be appreciably changed by heat-treatment. Estimates of changes in the diffuseness and intensity of relatively weak spots are difficult to make. The photographs have been taken with identical exposure times, though this does not, unfortunately, ensure strictly comparable photographs. Nevertheless, in some cases it is quite clear that changes have taken place; in other cases it is possible that minor changes in the pattern have occurred but that they remain undetected.

The general trends of the changes are as expected from the earlier work. In the low-temperature series there exists the continuous change

(as the percentage of albite increases) from the primitive pattern to the body-centred pattern, i.e. $S \rightarrow D \rightarrow A$ patterns. For pure or almost pure anorthites, although heating at 1100° C. does not apparently lead to any change, heating at temperatures near 1300° C. produces a pattern approaching that from the synthetic material ($S \rightarrow D$): this has previously been noted by Laves and Goldsmith (1951). The heating of the least basic specimen showing a well-defined primitive pattern (anorthite, specimen G.C.) shows that the smearing out of the (c) (and (d)) type reflections can occur at a lower temperature ($\sim 1100°$ C.); at this temperature with the same period of heating pure anorthite is unchanged. This is to be expected if elevated temperatures and increased soda content act in the same way, as was suggested previously (Gay, 1953). Anorthite M.E. in the untreated state must be regarded as a partially inverted material; no change is observed when this specimen is heated at 1100° C. This may be due to the fact that any increase in diffuseness is relatively small and cannot be detected, or alternatively it is possible that 1100° C. is very close to the temperature from which this specimen was quenched under the conditions of natural occurrence. (This temperature is likely to be too high to sharpen the (c) reflections.)

The transitional material (which shows a D pattern in the low-temperature state) which has been most extensively examined is that from Rum. Here again heating at 1100° C. seems to have no appreciable effect on the pattern, but after treatment at a high temperature ($\sim 1350°$ C.) many of the original type (c) reflections have disappeared, leaving only the strongest barely visible and much more elongated (D–A pattern) than those from the pure synthetic anorthite which had effectively been quenched from 1500° C. At still higher temperatures ($\sim 1400°$ C.), type (c) reflections have finally disappeared, and type (b) reflections are very much reduced in intensity, although they do not become diffuse (A–bA pattern). It may be possible, with this material, to remove these reflections completely by more prolonged heating or by heating at a higher temperature; so far it has not been possible to carry out experiments of this kind. Bytownite S.2 in the natural condition shows a pattern very similar to that from the Rum specimen; on heating to 1300° C. no detectable change is observed. This seems surprising in view of the marked change in the pattern from the Rum material at a slightly higher temperature; it may be that at this composition the rate of change accelerates rapidly as the temperature is increased.

The Rum material was also heated at temperatures below 1100° C. to see whether the transition from $D \rightarrow S$ pattern which was found for the

TABLE I. List of specimens and origins with heat-treatments and types of diffraction patterns observed.

Specimen no.	Locality.	Origin.	Anorthite content (mol. %).	Method of determination.	Heat-treatments			Diffraction pattern type			
					1.	2.	3.	Untreated.	Heat-treatment 1.	Heat-treatment 2.	Heat-treatment 3.
Anorthite (S. 20)	—	Synthetic	100	—	3 days at 1100° C.	3 days at 1300° C.	—	D	S	D	—
Anorthite (F. 5)	Pasmeda Alp. Fassa Valley	Veins in limestone block	~100	Optically	3 days at 1100° C.	3 days at 1300° C.	3 days at 1100° C.	S	S	D	S
Anorthite (M.E.)	Miyake, Japan	Volcanic lava	~94	Optically	3 days at 1100° C.	—	—	D Type (c) reflections not so elongated and diffuse as S. 20 untreated.	D Same as untreated.	—	—
Anorthite (G.C.)	Grass Valley, California	Hornblende-norite	92·8	Chemical analysis	3 days at 1100° C.	—	—	S This pattern shows type (c) reflections which are effectively sharp though not so well defined as those from specimen F. 5.	D Type (c) reflections showing only slight diffuseness and elongation.	—	—
Bytownite-anorthite (B.A.)	Glen Harris, Rum	Allivalite	88–91	Optically (universal stage)	3 days at 1350° C.	3 days at 1400° C.	—	D	D–A Many type (c) reflections visible in S. 20 patterns have now disappeared, only the strongest are barely visible. Elongation and diffuseness trebled.	A–bA Type (c) reflections now disappeared completely. Type (b) reflections very weak.	—

TABLE I (cont.)

Bytownite-anorthite (R.E.)	Glen Harris, Rum	Allivalite	88–91	Optically (universal stage)	3 days at 1100° C.	—	—	D	D Same as untreated.	—	—
Bytownite-anorthite (R.G.)	,,	,,	,,	,,	3 days at 900° C.	—	—	D	D Same as untreated.	—	—
Bytownite-anorthite (R.I.)	,,	,,	,,	,,	3 days at 800° C.	—	—	D	D Same as untreated.	—	—
Bytownite (S.2)	Stillwater, Montana	Gabbro	86	Chemical analysis	3 days at 1300° C.	—	—	D	D Same as untreated.	—	—
Bytownite (L.1)	St. Louis Co., Minnesota (B.M. 1921,33)	Anorthosite	~80	Optically	3 days at 900° C.	3 days at 1250° C.	3 days at 1350° C.	A	A Same as untreated.	A–bA Type (b) reflections less intense relative to main reflections. They are still sharp.	bA Type (b) reflections almost completely disappeared. The strongest, barely visible, are still sharp.
Bytownite (C.B.2)	Crystal Bay, Minnesota	,,	70·1	Chemical analysis	3 days at 1350° C.	—	—	A	bA	—	—

S Pattern
Type (a), reflections present, sharp
Type (b), reflections present, sharp
Type (c), reflections present, sharp
Type (d), reflections present, sharp

D Pattern
Type (a), reflections present, sharp
Type (b), reflections present, sharp
Type (c), reflections present, diffuse
Type (d), reflections absent (?)

A Pattern
Type (a), reflections present, sharp
Type (b), reflections present, sharp
Type (c), reflections absent
Type (d), reflections absent

bA Pattern
Type (a), reflections present, sharp
Type (b), reflections absent
Type (c), reflections absent
Type (d), reflections absent

synthetic anorthite (S.20) and for the specimen (F.5) (see also Laves and Goldsmith, 1951) can take place. No change is found, which supports the suggestion that the S pattern can never be obtained from bytownites. It seems that the increasing albite content lowers the temperature below which the primitive anorthite st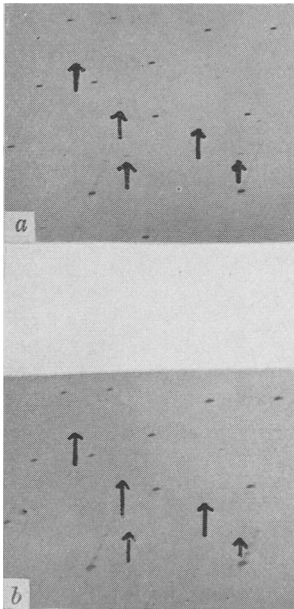ructure is stable, so that with more than about 10 % Ab the type (c) reflec-tions are always diffuse. The heating of the specimen G.C. suggests that the 'annealing temperature' for the produc-tion of sharp (c) reflections is lowered by the increased albite content. Even if this 'annealing temperature' for the Rum material is as high as 500–600° C. it is unlikely that a primitive structure can be formed, since any tran-sition at such low temperatures would proceed very slowly.

The specimen bytownite L.1 shows the A type pattern in the untreated condition. As the temperature is in-creased above 1100° C. type (b) reflec-tions begin to fade in intensity with respect to the principal reflections, until at 1350° C. hardly any type (b) reflections remain (fig. 1), i.e. there is a change A → bA. Specimen C.B.2 shows a similar change after being heated at 1350° C. when no type (b) reflections remain. The type (b) reflec-tions do not appear to smear out; even when they are only just visible they seem to be quite sharp. No changes in the intensities of type (b) reflec-tions have been obvious when pure or almost pure anorthites have been

Fig. 1 (a). Section of a zero-layer Weissenberg photograph of untreated bytownite L.1. Some type (b) reflec-tions marked. a-axis oscillation, Cu-Kα radiation.

Fig. 1 (b). The same section of a zero-layer Weissenberg photograph of bytownite L.1. after three days at 1350° C. Type (b) reflections marked are barely visible. a-axis oscillation, Cu-Kα radiation.

heated, although the effect of prolonged heating at very high temper-atures is not known. The existence of type (b) reflections for syn-thetic anorthite suggests that their removal is not possible for pure anorthite. A schematic representation of these structural changes is given in fig. 2.
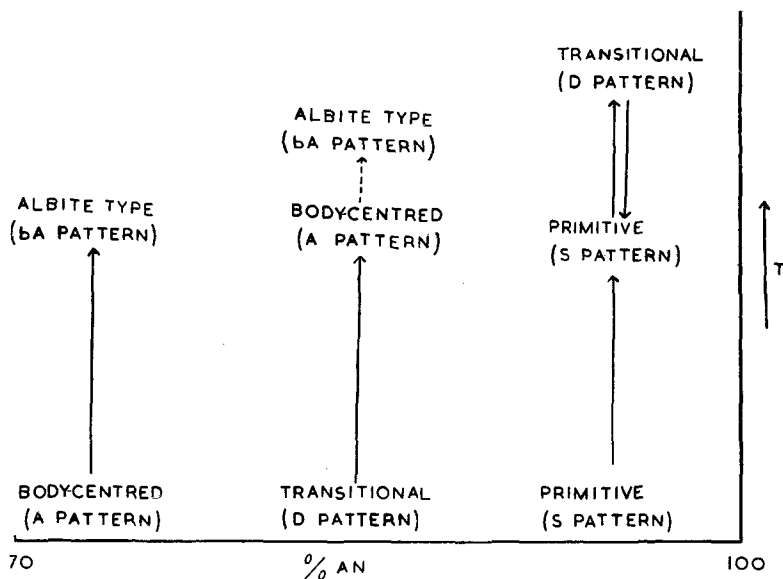
FIG. 2. Schematic representation of structural changes occurring for lime-rich plagioclase felspars.

DISCUSSION.

(a) *Thermal history and other observations.*—The pattern of the changes which occur when lime-rich felspars are heated is now quite clear, although no detailed information about the temperatures and rates of transformation is available. It has been suggested that the trans- formations between the high- and low-temperature forms in felspars are order-disorder effects (Buerger, 1948; Laves, 1952). This suggestion is in agreement with the general nature of the changes observed. With such changes, intermediate stages of transition can exist quite stably as has been shown here for several specimens. In natural materials, the final state of the felspar depends, not only on the temperature of the initial crystallization, but also on any subsequent thermal changes.

The significance of intermediate states of transition has not been fully appreciated in the past, particularly by optical workers, who have drawn up determinative optical curves for two series, one for the high- temperature forms and another for the low-temperature forms.[1] It must

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[1] The use of the terms 'high'- and 'low'-temperature forms which is common practice is unfortunate; it follows from the discussion above that they are not necessarily the most suitable for the description of the final state of the felspar, e.g.

be realized that these are only two limiting states, and that by the very nature of the inversion, felspars in intermediate states can exist which presumably have intermediate optical and other properties. While this would not be important for the determinative work for the lime-rich felspars considered here, there is little doubt that inversions of this kind exist over the whole of the plagioclase system; the determination of composition for less basic plagioclases by any method other than chemical analysis is complicated by the existence of these intermediate states. Probably the most satisfactory method of composition determination for small fragments such as those used in single-crystal work is by measurement of the refractive index of the fused specimen.

Reynolds (1952) in a critical examination of previous optical data states that 'in the range An_{70} to An_{100}, the question still remains whether two series do in fact exist'. From this work there is little doubt that structurally there is a difference between the high- and low-temperature felspars in this composition range, though the detection of this difference optically may be difficult.

Another important feature revealed by these experiments is the existence in this region of the bA pattern at high temperatures; when the type (b) reflections fade and disappear (types (c) and (d) already having disappeared), the 14 Å. c-axis characteristic of the anorthite-type structure is halved, and the cell dimensions become similar to those of albite. The existence of a structure giving rise to the bA pattern at high temperatures has been demonstrated for specimens at least up to 80 % An and it seems probable that it persists up to about 90 % An. Some authors have noted that the weak pairs of subsidiary reflections appearing on photographs about the c-axis of the intermediate felspars ($\sim$ 30–70 % An) can be further reduced in intensity by heat-treatment (Sörum, 1951) and do not exist for some natural specimens (Cole, Sörum, and Taylor, 1951; Donnay, 1952). In the course of investigations on these materials to be described later, the author has found that all the intermediate plagioclase felspars examined can be homogenized by the appropriate heat-treatment to give a simple homogeneous structure with cell dimensions similar to those of albite. Further, once this homogenization has occurred, it seems very unlikely that any reverse transformation to the normal intermediate felspar structure can be carried out in the laboratory by simple annealing treatments for long periods; all such

a 'low-temperature' felspar may have been at a high temperature but have cooled relatively slowly. The final condition of a particular specimen depends, not only on the temperature which it has reached, but also on the rate of cooling relative to the rate of the high–low transformation.

treatments so far carried out have left the diffraction pattern from the homogenized specimen unchanged.

The existence of the albite structure for plagioclases containing up to 80–90 % An is some confirmation that a complete range of solid solution exists from albite to anorthite at high temperature as suggested by the early thermal work (Bowen, 1913). The discrepancy between previous X-ray work and the thermal work which has been noted by Buerger (1948) and Tuttle and Bowen (1950) arose because the X-ray work was carried out in the main on low-temperature minerals. Buerger suggested that albite and anorthite have a common, disordered, high-temperature form. Unfortunately the region of solid solution does not appear to extend quite as far as pure anorthite, for synthetic anorthite has a well-defined 14 Å. c-axis. It is possible that a non-quenchable inversion exists for the very basic plagioclases; this point is under examination.

Powder data obtained by Goodyear and Duffin (1954) for a series of synthetic plagioclases show a discontinuity in the region 70–80 % An; this may represent the limit of the region of solid solution, although the present single-crystal work suggests that the region of solid solution may be extended to more anorthite-rich specimens. The same authors, when plotting powder data for natural plagioclases, find two discontinuities, one at about 30 % An, and the other at about 70 % An, as expected from the earlier single crystal work.

(b) *Structural interpretation.*—Previous work (Laves and Goldsmith, 1951; Gay and Taylor, 1953) has suggested that the structural changes occurring when pure anorthite is heated are associated with the Ca ions; the Si–Al distribution remains fixed and it is an ordered arrangement. The effect of introducing albite is to promote the changes associated with the Ca ions only; the 14 Å. c-axis of the anorthite-type structure persists by virtue of the Si–Al ordered arrangement. The present experiments show that at least up to 80–90 % An, the Si–Al arrangement can be disordered by heat-treatment.

It seems likely that the changes associated with the Ca ions are reversible.[1] This is reasonable since the changes are small; they may only be associated with the movement of Ca ions within their interstices in the structure. The changes associated with the redistribution of Si and Al in the tetrahedral framework are necessarily more severe, and, as

[1] Certainly the transformation S → D is reversible. The transformation D → A has not yet been shown experimentally to be possible, although it seems likely; using material showing a D pattern initially, the correct heating conditions to complete the change to the A pattern without affecting the type (b) reflections have not yet been found.

might be expected, it has not been possible to reverse this process in laboratory times.

From the photographic evidence, it appears that the structural changes associated with the Si–Al distribution and the Ca ions are essentially of the same kind but differing in degree. Both are continuous in character, but whereas the suggested order–disorder relations of the Si–Al arrangement change the type (b) reflections without making them diffuse, the type (c) reflections which are thought to be governed by the Ca ions do become diffuse. Further, it also seems likely that the two structural changes are to some extent interdependent. There appear to be two definite stages in the transition of the anorthite-type structure to one which is akin to albite, for in experiments so far carried out type (b) reflections have shown no change, whilst types (c) and (d) reflections are still present, i.e. the process of change is: primitive anorthite (via transitional structure) $\rightarrow$ body-centred anorthite $\rightarrow$ albite-type structure. Thus the Si–Al disordering cannot take place until the changes associated with the cations are complete. The significance of this is not clear, and, together with other structural problems, must await the completion of the accurate structural analyses being carried out.

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