The structures of the plagioclase felspars: VII. The heat treatment of intermediate plagioclases.[1]

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Summary.—Previous work has established that natural 'low-temperature' intermediate plagioclases show single-crystal diffraction patterns in which the subsidiary reflections are split into two; the separation of these split reflections appears to be dependent on the composition of the felspar. Several of these specimens have been subjected to varying heat treatments and their diffraction patterns examined.

It is found that over the whole composition range the split subsidiary reflections have disappeared after treatment at high temperatures, and only the principal felspar reflections, which are characteristic of an albite-like structure, remain. Natural specimens initially showing anomalous patterns can also be homogenized in this way by suitable heat treatments. A careful study of the mode of disappearance shows that the separation of the subsidiary reflections is unchanged as long as they remain visible.

The structural and petrological implications of this work are discussed.

IN the preceding paper in this series (Gay, 1956), an X-ray investigation of forty natural plagioclase specimens in the composition range An_{20} to An_{70} was reported. The majority of these specimens gave 'normal' diffraction patterns in which the type (*b*) reflections were split into two, though often one member of a pair was absent or undetected (the nomenclature used here is that defined in previous publications in this series). Over the composition range changes in the quality and positions of the split type (*b*) subsidiary reflections were observed and a systematic scheme for the diffraction patterns of low-temperature intermediate structures was drawn up. A number of natural specimens, however, did not fit into this scheme. The single-crystal patterns for these specimens were distinguished from their normal counterparts in that the split (*b*) reflections were weak, very diffuse, or completely absent. In the present paper it will be shown that these irregularities are due to the existence of different thermal states of the felspar.

The existence of high- and low-temperature states of plagioclase

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felspars has been recognized by optical workers for some time, although their distinction requires a careful study of the optical properties. As pointed out by Muir (1955) there are few records of transitional optics in plagioclases, probably because of the difficulties of determination, which become greater the more basic the specimen. Very little work has been done in the intermediate composition range using X-ray methods to distinguish different thermal states. The effects of heat treatment on the single-crystal pattern of an intermediate plagioclase have been briefly mentioned by Cole, Sörum, and Taylor (1951); powder data on natural and synthetic specimens within the composition range have been given by Goodyear and Duffin (1954) and Smith (1956).

The work described in this paper is an exploratory, qualitative study of the diffraction patterns from intermediate plagioclases in various thermal states; no systematic study of the transformations or rates of transformation has been made.

Experimental results.

The specimens used were chosen from those described in paper VI of this series, in which details of origin, selection, and methods of examination may be found. A selection of those giving 'normal' diffraction patterns has been made covering the whole composition range; others have been included because their initial patterns showed abnormalities.

Single crystals have been given various heat treatments and their diffraction patterns obtained after each heating. The crystals were allowed to cool in air on removal from the furnace; since the transformations are sluggish they were effectively quenched. For each specimen the X-ray photographs were taken so that the same set of reflections was recorded each time, and the exposure times were similar except in the case of specimen 6. The heat treatments and resulting diffraction patterns are listed in table I.

Two principal features emerged from the experiments on the 'normal' group of specimens. Firstly, there is no perceptible change in the positions of the subsidiary (*b*) spots (or in the separation of a pair) due to the heat treatment. For each crystal the separations δ_a, δ_b, and δ_c remain constant at all temperatures to within the limits of experimental accuracy; these limits vary from about 1° to 3–4°, increasing as the number of measurable spots decreases at higher temperatures.

Secondly, as may be seen from table I (*a*), the effect of increasing the temperature above a certain lower limit is to reduce progressively the

TABLE I. Heat treatments and descriptions of diffraction patterns. The specimen numbers refer to the list of specimens given in Gay, 1956, table I. In the heat-treatment columns, which show successive treatments of the same crystal for each specimen, the temperatures are given in ° C.; the period of heating was 3 days unless otherwise stated.

The letter or letters following the temperature describe the character of the split type (*b*) reflections after heat treatment; they stand for: *u* unchanged, *sw* slightly weakened, *w* weakened, *vw* very weak, *sd* slightly diffuse, *vd* very diffuse, and *a* absent. These descriptions apply to photographs taken with similar exposure times for all crystals, except for specimen 6, for which longer exposure times were used.

No.	% An.	Heat treatment and character of subsidiary reflections.					
(*a*) *Normal specimens.*							
		H.T. 1.	H.T. 2.	H.T. 3.	H.T. 4.	H.T. 5.	H.T. 6.
3	70	900: *u*	1200: *a*	700: *a*			
9	58	950: *sw*	1000: *w*	1050: *vw*	1150: *a*		
10	56	900: *u*	1200: *a*				
13	53	900: *u*	1200: *a*	800: *a* (38 days)	800: *a* (38 days)		
16	50	1000: *sw*	1050: *w*	1100: *vw*	1150: *a*		
21	45	800: *u* (28 days)	800: *u* (38 days)				
29	37	900: *u*	1000: *sw*	1100: *vw*	1200: *a*		
40	23	600: *u*	700: *u*	800: *u*	800: *u*	800: *u*	1200: *a*
6	64	950: *u*	1000: *sw*	1050: *w*	1100: *vw*	1150: *sd*	1200: *vd*
(*b*) '*Anomalous*' *specimens.*							
		Untreated	H.T. 1.	H.T. 2.	H.T. 3.	H.T. 4.	H.T. 5.
5	65	*vd*	950: *u*	800: *u* (15 days)	700: *u* (36 days)		
7	63	*vd*	950: *u*	1100: *w*	1250: *a*	800: *a* (15 days)	800: *a* (86 days)
22	43	*a*	1000: *a*	900: *a*			
28	41	*sw*	900: *w*	1200: *a*			
25	40	*sw*	1000: *w*	1150: *vw*	1200: *a*		

intensities of the split (*b*) spots, the intensities of the main (type (*a*)) reflections being apparently unchanged. The rate of weakening is different for different reflections, e.g. some strong reflections fade more rapidly than some weak ones. After treatment at sufficiently high temperatures the spots can no longer be seen unless longer exposure times are used, and it is reasonable to expect that they can be made to disappear completely. For specimen 6, instead of using the same exposure time after each treatment, as with the other specimens, the exposure was increased at each stage so as to keep the intensities of the subsidiary spots approximately constant. The necessary time after the fifth heat treatment was 72 hours, compared with 5 hours initially. At this stage the spots had the form of diffuse areas around sharp peaks.

After the sixth heat treatment only the diffuse areas remained and they were so large that spot pairs became apparently single. A long-exposure photograph of specimen 9 after the fourth heat treatment showed that the (*b*) spots were becoming diffuse.

The results obtained with those specimens that show anomalous patterns in the untreated state are included in table I (*b*). For specimens 25 and 28 the split (*b*) reflections of the untreated material are rather weaker than in the normal low-temperature pattern, for 5 and 7 they are weak and very diffuse, and for specimen 22 they could not be seen even after 36 hours' exposure. Each of these patterns could be produced by the appropriate heat treatment of a normal specimen, and this suggests that the so-called 'anomalous' specimens are in different intermediate temperature states. The results of heat treatment are in accordance with this interpretation since the reflections become weaker and eventually disappear.

Annealing experiments did not succeed either in making the subsidiary reflections reappear after vanishing or in increasing the intensities of weakened subsidiary reflections. See, for example, specimens 13, 5, and 7 in table I. It may be, however, that the annealing temperature required is quite critical, having to be sufficiently high to promote ionic movement within a reasonable time, and yet sufficiently low to allow the lower-temperature structure to be the equilibrium state. The present experiments have not exhausted all possibilities, though it seems probable that a high-to-low transformation cannot be made to occur by simple heat treatment within reasonable laboratory times; the difficulty is the same as that which, at present, prevents the synthesis of any low-temperature felspar.

The present experiments were not designed to give information about the rates of transformation. However, it is apparent that the transformation between the low- and high-temperature states is relatively rapid between about 900° C. and 1200° C., becoming faster at the higher temperatures. It is unlikely that equilibrium has been reached at the lower temperatures in these experiments. It may be found that the rates of transformation and the equilibrium states of the felspar at various temperatures are different for different compositions.

It is interesting to note that several crystals, originally apparently single, developed albite twinning on heating. Similar examples have been commented on by Muir (1955) and others. Two other crystals became opaque and gave powder patterns after being heated, although they retained their shapes.

Discussion.

The sequence of single-crystal patterns for low-temperature intermediate plagioclases of various compositions was established in the previous paper in this series. The present work shows that the high-temperature structural forms in this region have no subsidiary reflections. They show only the type (*a*) principal reflections, and are thus similar to high albite, a structure type which at high temperatures exists over almost the whole of the plagioclase series (Gay, 1954). Patterns in which the subsidiary reflections are present, but weak, represent intermediate stages in the structural transition. The patterns of specimens 5 and 7, which were not formerly understood, have now been shown to be characteristic of a structural state approaching very closely that of the true high felspar of this composition. There is supporting evidence for this interpretation of the anomalous patterns. Thus, specimen 7 occurs as phenocrysts in basalt, the matrix containing glassy material suggesting a rapid quench after a period of slower cooling. The thermo-chemical properties of plagioclase from the same locality as specimen 5 have been investigated by Kracek and Neuvonen (1952); their results show that this material has properties closely similar to those expected from the appropriate solid solution of albite and anorthite, i.e. it is very nearly in the high-temperature state. Powder diffractometer records also indicate that these specimens are in a transitional temperature state (Gay and J. V. Smith, unpublished).

According to current views, the high–low transformations in felspars depend on the ordering or disordering of Si and Al atoms. The split (*b*) spots in the intermediate felspar patterns are probably caused by some ordering scheme of both Si–Al and Ca–Na ions, though details of the arrangement are unknown. The scheme must be such that the disordering produced by heat treatment leads to the reduction of the intensities of these spots without a change of position. The annealing experiments show that the change from the disordered high form to the ordered arrangement is sluggish. The split (*b*) reflections are diffuse for both high-temperature basic and low-temperature sodic members of the series, which may be due to a similar scheme of partial ordering in each case. Thus increased temperature and increased soda content both seem to promote a disordered arrangement in the intermediate plagioclases, as they do in the anorthite structural region (Gay, 1953).

It is of some petrological interest to discuss the possible use of intermediate plagioclases in geological thermometry. First, if the subsidiary

reflections are present and sharp on the diffraction patterns their separation can be used to determine the composition of the felspar (Gay, 1956); for if the (*b*) spots can be observed (no matter whether they are weak or not) their separation is independent of the thermal state of the felspar, but varies with its composition. The intensities of the subsidiary reflections can be used to find the thermal state of the felspar; this may be done by comparing the intensities for a particular specimen with those of the corresponding reflections for a specimen of similar composition known to be in the low-temperature state. In this way, the plagioclase under examination may be placed within a broad structural category, e.g. low, low-transitional, transitional, transitional-high, or high. A method of this kind was used to obtain confirmatory evidence for the optical examination described by Muir (1955); a similar combined X-ray and optical examination of the plagioclase of the Skaergaard intrusion, which will be described elsewhere, has been successfully carried out by Muir and Gay. It does, however, require some experience by the investigator in the examination of the single crystal patterns of intermediate plagioclases.

It should be emphasized that the various physical properties which have been used to deduce the so-called 'temperature state' of a plagioclase, viz. the intensities of subsidiary reflections, the magnitude and orientation of the principal refractive indices, and the unit-cell dimensions (or positions of powder lines), all depend directly on the detailed crystal structure of the felspar. With the sluggish transformations involved, there can be no unique correlation between the crystal structure of a particular specimen and its thermal history; quite different thermal treatments will produce the same structure. At present, therefore, measurements of these physical properties lead only to the 'structural state' of the felspar; this may for convenience be classified as high, high-transitional, &c., by reference to the temperature at which such a structure would be in equilibrium. As far as the determination of structural state is concerned, the X-ray method mentioned above is capable of much greater precision than the optical measurements, certainly for intermediate plagioclases more basic than An_{40} for which the subsidiary reflections are sharp. For more sodic specimens, the diffuseness of these reflections, even for low-temperature material, introduces some difficulty into the X-ray method.

In transitions of the kind envisaged the major structural rearrangement differentiating the high and low forms will take place over a limited temperature range, assuming equilibrium conditions (equilibrium

states have not in general been reached in the present experiments since the heat treatments were of relatively short duration). It seems unlikely that any drastic redistribution of ions could take place at temperatures below, say, 500° C., while it is probable that the transition would eventually be carried to completion at temperatures of the order of 1000° C. Thus the major changes in physical properties from which the structural state is deduced will occur over a limited temperature range. This point is important when considering attempts to deduce the structural state. Let us consider in some detail, for example, the migration curves commonly employed by optical workers, which ideally represent the variation with composition of the optical properties of felspars in equilibrium at normal temperatures and just below the melting-point. For any given composition the major part of the difference between the curves will be due to the structural rearrangement which takes place over a relatively small temperature interval. Therefore, if it were possible to follow for a given felspar in equilibrium the movement of a point from the low- to the high-temperature curve on heating, it would be expected that this movement for the first 500 degrees or so (associated probably with slight changes in cell dimensions only) would be quite small. Over the next 500 degrees the structural rearrangement takes place, and so the point would move almost over to the high curve; the remaining short path would then be traversed with further temperature increase to the melting-point. Considerable caution should therefore be exercised in the interpretation of any optical plot, particularly where the separation of the low and high curves is small. Only felspars in a transitional structural state will deviate appreciably from the low and high curves; if, as suggested, the temperature interval of the transition is narrow, it would be expected that felspars showing the transitional structure and optics would be rare in nature.

In attempting to use plagioclase as a 'geological thermometer' the structural state may as yet be interpreted only in the most general way, as there is little information about the thermal conditions required to produce a particular structural state. A study of the rates of transformations under various conditions is in hand; the intermediate plagioclases are particularly suitable for such a study since quantitative measurements of the fading of the split (*b*) spots may be made. It is hoped that these experiments will show how far it is possible to define the geological history of a particular plagioclase, and whether the use of these felspars as reliable temperature indicators for petrological interpretation is practicable.

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