The determination of composition and thermal history of plagioclase by the X-ray powder method.

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1. Introduction.

In a recent paper (hereafter referred to as GD) Goodyear and Duffin (1954) described X-ray powder data for a number of synthetic and chemically analysed plagioclases of composition An_0Ab_{100}–$An_{100}Ab_0$. Important aspects of this work were a correlation of the X-ray patterns with chemical composition, and a distinction between the pattern of a naturally occurring material of low-temperature origin and that of a synthetic of similar composition. The investigation showed quite clearly that the unit-cell dimensions of a synthetic plagioclase depend but little on composition from An_0Ab_{100} to $An_{70}Ab_{30}$, whilst they differ from those of the low-temperature modification greatly for albite, to a lessening degree as the composition approaches $An_{70}Ab_{30}$, and practically not at all in the range $An_{70}Ab_{30}$–$An_{100}Ab_0$.

These features were studied quantitatively by plotting the angular separations, $\Delta 2\theta°$, of certain selected reflections in the X-ray pattern against composition, both for the natural and the synthetic materials. The resulting curves provided a possible means of estimating plagioclase composition from X-ray data; but it was evident that, without a sufficient knowledge of a specimen's thermal history, this method of analysis would be severely restricted. For instance, it seemed quite possible that the X-ray pattern of a partially inverted material, of composition within the range An_0Ab_{100}–$An_{70}Ab_{30}$, might be indistinguishable from that of a low-temperature modification of higher anorthite content.

The present work, described in the next section, has been undertaken to determine to what extent possible states of partial inversion lead to complications in determining plagioclase composition from X-ray data, and to establish whether or not the X-ray patterns of synthetics are identical with those of naturally occurring materials when fully inverted. The work of Tuttle and Bowen (1950) has shown that Amelia albite

when heated for 10 days at 1050° C. gives a pattern the same as that of synthetic albite, but they have not given corresponding data over the whole composition range An_0Ab_{100}–$An_{100}Ab_0$.

2. Experimental results.

Eight natural plagioclases were selected for heat-treatment from those described in detail in GD: the specimen numbers used in that paper have been retained here for easy reference (see table II). Since there is no clear distinction between X-ray patterns of synthetic and low-temperature materials of composition about $An_{70}Ab_{30}$, only materials of composition An_0Ab_{100}–$An_{65}Ab_{35}$ and $An_{80}Ab_{20}$–$An_{100}Ab_0$ have been studied. Specimen 15 is of volcanic origin and is probably partially inverted (see GD), while the remainder are almost certainly low-temperature modifications.

Each sample was heated at a prescribed temperature (controlled to $\pm 10°$ C.) for a convenient length of time, after which it was cooled in air and examined by the X-ray powder method. All photographs were taken with filtered Co-$K\alpha$ radiation using a 20 cm.-diameter semi-focusing camera fitted with knife-edges for calibration purposes, the experimental arrangement being otherwise similar to that described in GD.

As preliminary experiments, samples of specimens 5 and 6 were heated for 2 days at 900° C. and 950° C. respectively and then at higher temperatures (for 2 days and at intervals of 50° C.) up to 1050° C., at which temperature significant changes were found to occur in the X-ray pattern. Both specimens were thereafter heated for varying lengths of time at still higher temperatures up to just below the melting point, the heating being continued at the final temperature until it was clear that the X-ray pattern was changing very little over a long period of time. With the changes occurring in specimens 5 and 6 as a guide, the specimens, 2, 4, and 7 were heat-treated similarly, commencing at 1050° C.

Specimen 14 was simply heated at 1400° C. for 2 days, and specimen 11 at 1350° C. for 3 days, while two separate samples of specimen 15 were taken, one being heated at 1400° C. for 2 days, and the other at 1100° C. for 4 days. This last treatment was an attempt to show that such 'annealing' leads to the production of a low-temperature form.

The main changes in the X-ray patterns due to heat-treatment are best described in terms of the angular separation of those reflections previously used (GD, table V); for convenience, descriptions of these

TABLE I. Descriptions of the reflections selected from the X-ray patterns.

Line.	Spacing (kX units).	Intensity.	Probable indices.
A	3·11–3·14	wm–ms	$2\bar{2}0$ or 220*
B	2·95–3·03	wm–ms	$1\bar{3}1$
C	2·63–2·65	wm–m	$\bar{1}32$
D	2·50–2·56	m–s	$24\bar{1}$
E	2·44–2·52	wm–s	$\bar{2}41$
F	1·825–1·833	m–ms	—
G	1·764–1·785	ms	—

* $2\bar{2}0$ for low-temperature albite.

TABLE II. Angular separations ($\Delta 2\theta°$ for Cu-$K\alpha$ radiation) of the A–B, C–D, C–E, and F–G reflections for heat-treated natural plagioclases.

Descriptions of specimens*								
Specimen No.	Composition wt. % An.	Heat-treatment.†				A–B.	C–D.	C–E.	F–G.
2	16·5	(i)	1050° C.	5	days	1·50	1·40	2·38	—
			+1100°	2	,,	1·43	1·52	2·35	—
		(f)	+1075°	21	,,	1·22	1·86	2·18	1·61
4	31·1	(i)	1050°	4	,,	1·26	1·67	2·18	—
		(f)	+1100°	7	,,	1·13	1·83	2·12	1·64
5	38·0	(i)	1050°	2	,,	1·23	1·70	2·14	—
			+1050°	2	,,	1·18	1·74	2·12	—
			+1075°	2	,,	1·15	1·83	2·09	—
		(f)	+1100°	7	,,	1·11	1·89	‡	1·70
6	51·6	(i)	1050°	2	,,	1·11	1·82	2·08	—
			+1050°	2	,,	1·09	1·83	2·07	—
			+1075°	2	,,	1·10	1·85	2·06	—
			+1100°	7	,,	1·08	1·87	‡	—
		(f)	+1150°	2	,,	1·07	1·91	‡	1·76
7	64·5	(i)	1050°	4	,,	1·05	1·87	‡	—
			+1100°	4	,,	1·07	1·90	‡	—
			+1150°	4	,,	1·07	1·92	‡	—
		(f)	+1200°	3	,,	1·07	1·91	‡	1·87
11	81·0		1350°	3	,,	—	—	—	1·98
14	93·0		1400°	2	,,	—	—	—	2·07
15	98·3		1400°	2	,,	—	—	—	2·09
	(volcanic)		1100°	4	,,	—	—	—	2·05

* Full descriptions of the specimens are given in GD, and the specimen numbers used in that paper are retained here.

† (i) and (f) indicate the initial and final stages of heat-treatment, values for which are plotted in Fig. 1. + indicates that the same sample was progressively heated.

‡ E reflection not sufficiently resolved from stronger D reflection for reliable measurement.

reflections are reproduced in table I. Table II gives the angular separations $\Delta 2\theta^\circ$ (calculated for Cu-$K\alpha$ radiation and accurate to within $\pm 0{\cdot}03^\circ$) of the A–B, C–D, and C–E reflections at those stages of the treatment where significant changes were obtained, and of the F–G reflections for the final stage. Where no entry is to be found for the C–E separation, the E reflection was no longer sufficiently resolved from the stronger D line for reliable measurements to be made. The column headed 'heat-treatment' gives temperatures and times of heating, a + sign indicating that the same sample was progressively heated.

3. Discussion.

It was clear from previous results (GD) that complications would arise in employing X-ray data for determining the composition of plagioclases with an anorthite content of 70–80 %. One of the features of the present work has been to examine the full potentialities of the X-ray method of analysis within the composition ranges An_0Ab_{100}–$An_{70}Ab_{30}$ and $An_{80}Ab_{20}$–$An_{100}Ab_0$, and consequently in discussing the new data in relation to the old it is desirable to consider each of these ranges separately.

(*a*) An_0Ab_{100}–$An_{70}Ab_{30}$.

Figs. 1 (i) and 1 (ii) show the relations based on previous data (GD) between compositions, from An_0Ab_{100} to $An_{70}Ab_{30}$, and the angular separations of the A–B, C–D, and C–E reflections. These differ from those previously published (GD, figs. 4 and 5) only in that the curves for the natural materials are drawn to meet those of the synthetics at about $An_{70}Ab_{30}$. Included in the same figures are points corresponding to the initial and final stages of heat-treatment (table II) of specimens 2, 4, 5, 6, and 7.

It is clear that states of partial inversion are possible over the whole of this range, and it seems probable that the process of inversion is a continuous one, i.e. that any state between the low-temperature and high-temperature forms could be produced by appropriate heat-treatment. This greatly limits the assignment of a definite composition and thermal history to a plagioclase on the basis of its powder pattern, since the changes which take place as anorthite content increases are indeed found to be identical with those occurring on heat-treatment. An example of the ambiguity arising from this is afforded by specimen 2 (16·5 % anorthite), which after heating for 5 days at 1050° C. gives the same A–B, C–D, and C–E separations as a low-temperature oligoclase

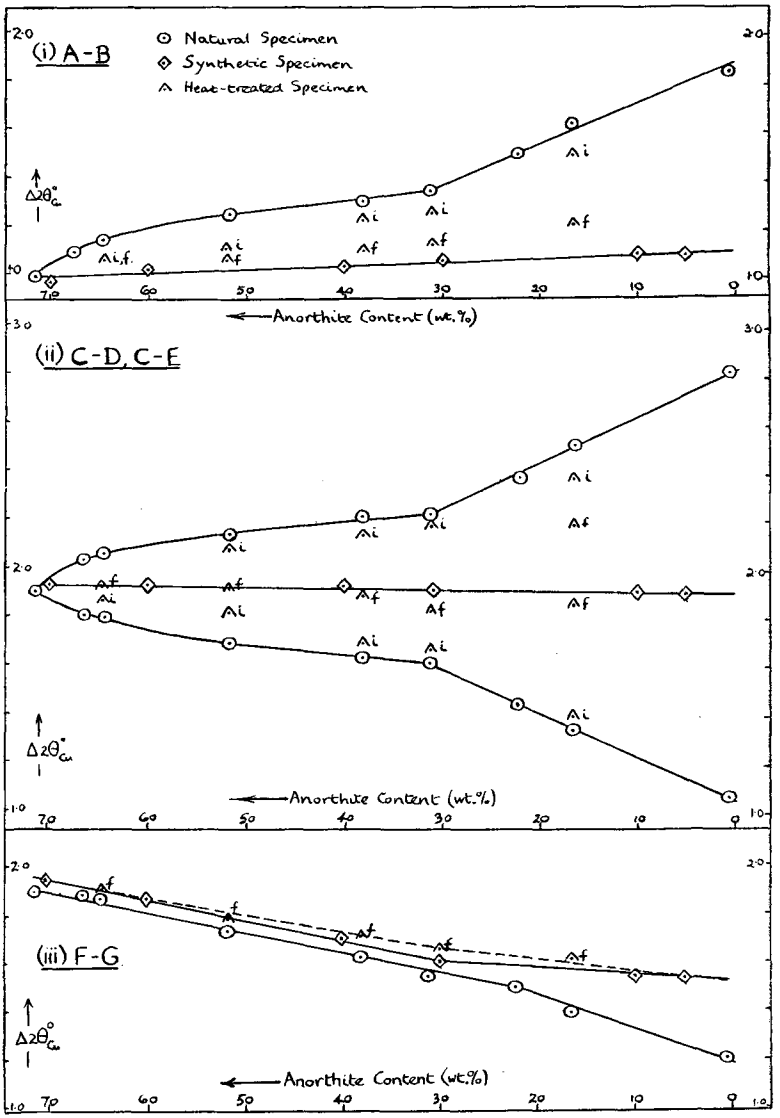

FIG. 1. Angular separation (calculated for Cu-$K\alpha$ radiation) of A–B, C–D, C–E, and F–G reflections plotted against plagioclase composition for the range An_0Ab_{100}–$An_{70}Ab_{30}$. i = value after initial heat-treatment. f = value after final heat-treatment.

containing about 22 % anorthite; and quite clearly, in the absence of other information, the composition obtained by using figs. 1 (i) and 1 (ii) might have any value between 0 % and 22 % anorthite, depending on the state of inversion. It therefore seems that the use of these curves should be restricted as follows:

(i) A plagioclase known to be a low-temperature form from geological field data can be assigned a chemical composition as described previously (GD, section 5).

(ii) If the composition is known from chemical analysis, then the degree of inversion can be assessed from the values of the A–B, C–D, and C–E separations compared with the appropriate high- and low-temperature values (see 3 *c*, p. 655).

Further information might be obtained by using fig. 1 (iii) in which the angular separations of F–G reflections are plotted against composition from An_0Ab_{100} to $An_{70}Ab_{30}$. In this figure only the separations after the final stage of heat-treatment are added to the corresponding curves given in GD (fig. 6). Although the heat-treated specimens 2, 4, and 5 are not fully inverted according to their A–B and C–D separations, their F–G separations lie well above the synthetic curve. It has been mentioned previously (GD) that the synthetic materials of composition $An_{30}Ab_{70}$–$An_{60}Ab_{40}$ are poorly crystalline and give quite diffuse F reflections. Consequently values of their F–G separations might be in error more than the expected $\pm 0{\cdot}03°$ in $\Delta 2\theta$. Further, since the F reflections of the natural materials remain well defined on heat-treatment, it is probable that a more appropriate high-temperature curve is represented by the dotted line shown in fig. 1 (iii).

Between 30 % and 70 % anorthite content, the F–G curves show that a composition can be estimated to ± 8 % anorthite irrespective of thermal history, and this information may be of value in limiting the ambiguity arising when only figs. 1 (i) and 1 (ii) are used. It should also be noted that if a specimen is known to be a high-temperature modification, the F–G curve still provides the only means of obtaining a reasonable estimate of composition between 30 % and 70 % anorthite.

It is now evident that, unless a specimen's thermal history is known, X-ray data alone cannot provide an accurate estimate of composition in the range An_0Ab_{100}–$An_{70}Ab_{30}$. In these circumstances the X-ray method is inferior to those based on optical data, since a combination of refractive-index measurements and a study of the orientation of the optical indicatrix with respect to the crystallographic axes enables

composition to be determined to ± 3 % anorthite over the whole range An_0Ab_{100}–$An_{100}Ab_0$ (I. D. Muir, private communication, 1954).

(*b*) $An_{80}Ab_{20}$–$An_{100}Ab_0$.

In this range the D and E reflections are either unresolved or are very close, and changes in their separation from the C reflection brought about by heat-treatment are small. For this reason, only the A–B and F–G separations can be reliably used, and these are plotted against composition in figs. 2 (i) and 2 (ii) respectively, in which the appropriate parts of figs. 4 and 6 in GD are reproduced, with values for heat-treated specimens added to fig. 2 (ii).

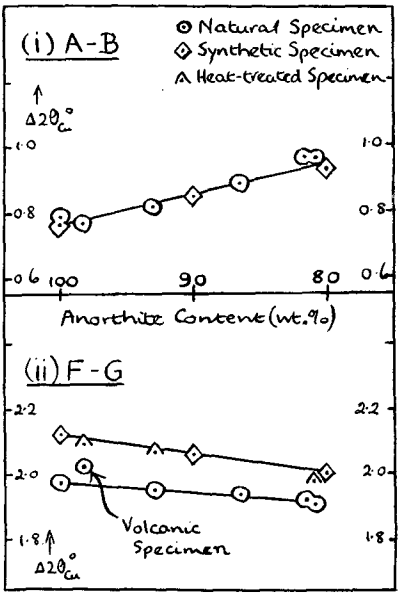

FIG. 2. Angular separation (calculated for Cu-$K\alpha$ radiation) of A–B and F–G reflections plotted against plagioclase composition for the range $An_{80}Ab_{20}$–$An_{100}Ab_0$.

The A–B separation permits the composition to be obtained, any difference between the high- and low-temperature curves being so small that thermal history does not affect the estimate. The degree of inversion is then given by the F–G separation, and although even here the difference between high- and low-temperature curves is not large, this method of distinction could be used with advantage in conjunction with that of Gay (1953), which employs a single-crystal diffraction technique.

Although the volcanic specimen 15 (98·3 % anorthite) appears to invert readily to the high-temperature form on heating for 2 days at 1400° C., 'annealing' at 1100° C. for 4 days failed to convert it to a true low-temperature form. It is interesting to note that treatment of a synthetic anorthite at 1100° C. for 3 days (see GD) succeeded only in reducing the F–G separation to a value similar to that of specimen 15. According to the work of Laves and Goldsmith (1954) synthetic anorthite is completely converted to the low-temperature form when heated at 1100° C., but in the case of a plagioclase of 98 % anorthite content

complete conversion is possible only at a lower temperature, confirming the present results for specimen 15.

(c) *General.*

Although most of the heat-treatments described here did not lead to complete identity of powder patterns of the natural materials with those of synthetic materials of the same composition, there seems no reason

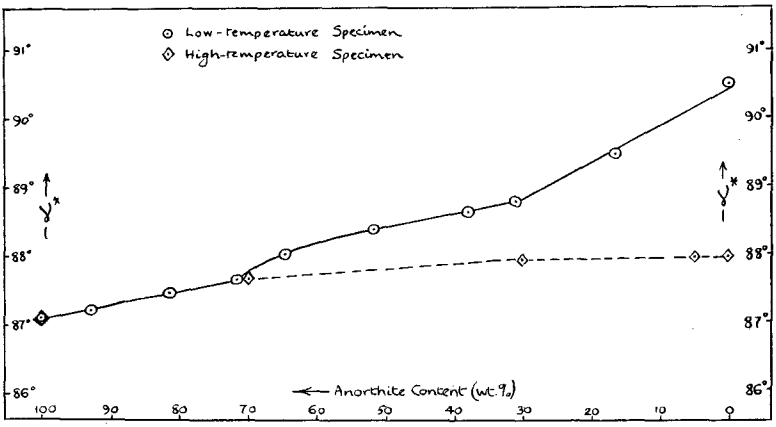

FIG. 3. The reciprocal-lattice parameter, γ^*, plotted against plagioclase composition.

to doubt that prolonged heating or, where possible, heating at temperatures rather higher than those employed in this work, would in fact produce this identity. Hence it may be safely assumed that the composition curves for the synthetics are those applicable for truly high-temperature modifications.

Calculations, based on previous X-ray powder data (GD, tables II and III), of reciprocal lattice parameters indicate that the changes which occur in the patterns of low-temperature plagioclases on increase of anorthite content, or on heat-treatment, are mainly due to a decrease in γ^* (see also Smith and Robbins, 1954). This is illustrated by the close similarity between the nature of the A–B, C–D, and C–E curves, and that of the variation of γ^* with composition shown in fig. 3, in which the values plotted are due to the authors, with the exception of those for synthetic albite (Donnay and Donnay, 1952) and natural anorthite (Cole, Sörum, and Taylor, 1951).

Although no distinction has been found between the parameters of

high- and low-temperature anorthites and bytownites, nevertheless it is clear that small differences must occur in view of the shifts of the higher order reflections (e.g. F and G) on heat-treatment. Corresponding movements of the lower-order reflections, which have been indexed (GD, tables II and III), are within the range of the experimental errors of the photographic technique used here, but they might very well be measurable using a high accuracy Geiger-counter spectrometer.

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