The structures of the plagioclase felspars: III. An X-ray study of anorthites and bytownites.

By P. Gay, M.A., Ph.D.

Department of Mineralogy and Petrology; and Crystallographic Laboratory, Cavendish Laboratory, University of Cambridge.

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1. Introduction.

In a recent paper, Cole, Sörum, and Taylor[1] described X-ray measurements on a number of plagioclases with compositions ranging from pure albite to pure anorthite. As a result, they were able to make more precise, and extend, the structural interpretations proposed on the basis of earlier X-ray investigations of the three type-structures, albite, anorthite, and intermediate plagioclases (Taylor, Darbyshire, and Strunz;[2] Chao and Taylor[3]). At the same time, new complexities were revealed which called for more detailed examination, among them the fact that the anorthite-type structure, with *c*-axis ~14 Å., may have either a body-centred or a primitive unit cell. The body-centred cell was observed with a material containing 71·5% anorthite, the primitive cell with a nearly pure anorthite, but there was not sufficient evidence to show whether the difference was due entirely or largely to the difference in chemical composition, nor was a detailed investigation made of the effects of heat-treatments. The work now to be described was undertaken in the first place in order to clarify these aspects of the plagioclase problem.

It has however become clear, as the experimental data have accumulated, that, quite apart from any structural interpretation which may be proposed, the observed small differences in the X-ray single-crystal patterns may provide a direct method of supplying the petrographer with information, which could not easily be obtained otherwise, on the

[1] W. F. Cole, H. Sörum, and W. H. Taylor, Acta Cryst., 1951, vol. 4, p. 20. [M.A. **11**–427.]

[2] W. H. Taylor, J. A. Darbyshire, and H. Strunz, Zeits. Krist., 1934, vol. 87, p. 464. [M.A. **6**–177.]

[3] S. H. Chao and W. H. Taylor, Proc. Roy. Soc. London, Ser. A, 1940, vol. 176, p. 76. [M.A. **8**–13.]

geological thermal history of the samples. The present paper is concerned with this aspect of the research; its bearing on the problem of the atomic structure of anorthite will be discussed elsewhere.

The potential importance of the X-ray method becomes clear when the results of optical examination of the plagioclases are considered. Köhler's[1] interpretation of his optical data in terms of high-temperature and low-temperature series of plagioclases was followed by the researches of Tertsch,[2] van der Kaaden,[3] and others. In a critical review of the optical data Reynolds[4] concludes that while there is a marked difference between the high-temperature and low-temperature forms from Ab_{100} to $Ab_{65}An_{35}$, and a significant distinction may still be made in the range $Ab_{65}An_{35}$ to $Ab_{30}An_{70}$, from $Ab_{30}An_{70}$ to An_{100} no certain differentiation into two series can be established by optical measurements. The familiar and convenient methods which are so powerful for soda-rich plagioclases thus become increasingly ineffective for the lime-rich bytownites and anorthites.

2. Experimental data.

Twelve specimens have been examined in the range An_{100} to $An_{70}Ab_{30}$. The second and third columns of table I give the place of origin, and the nature of the rock where this is known; the fourth and fifth columns give the anorthite-content and the method used to obtain the composition. Except for the two cases noted in the table (nos. 6 and 9), where universal-stage methods were used, the 'optical methods' depend upon refractive-index and extinction-angle measurements. It should be noted that if it is accepted that for this region of the plagioclase system the optical properties for high-temperature and low-temperature materials are nearly identical no serious uncertainty arises in estimating composition from these measurements.

All plagioclases have similar structures. The most obvious and characteristic feature of the anorthite-type structure is that while the a and b axes, and the α, β, γ angles, of the unit cell remain approximately the same as those of albite (a 8 Å., b 13 Å., $\alpha \sim 90°$, $\beta \sim 116°$, $\gamma \sim 90°$), the true c-axis is approximately 14 Å. in anorthite, the albite c-axis of 7 Å. being only a pseudo-repeat distance in anorthite. Thus,

[1] A. Köhler, Journ. Geol., 1949, vol. 57, p. 592. [M.A. **11**–144.]
[2] H. Tertsch, Tschermaks, Min. Petr. Mitt., 1941, vol. 53, p. 50. [M.A. **8**–313.]
[3] G. van der Kaaden, Thesis, Univ. Utrecht, 1951. [M.A. **11**–282.]
[4] D. L. Reynolds, Geol. Mag., 1952, vol. 89, p. 233. [M.A. **12**–137.]

in general, X-ray reflections of anorthite with l odd are weak by comparison with reflections with l even.

TABLE I. Bytownite and anorthite specimens.

Specimen no.	Locality.	Origin.	Anorthite content (Mol. %).	Method of determination.	Type (c) reflections.
1	Pasmeda Alp, Fassa Valley	Limestone block	~ 100	Optically	Present; sharp
2	Monte Somma, Vesuvius	Olivine-limestone block	~ 100	Optically	Present; sharp
3	—	Synthetic	100	—	Present; diffuse
4	Miyaké, Japan	Volcanic lava	99·1	Chemical analysis	Present; diffuse
5	Tarumaé, Japan	Volcanic lava (?)	95·5	Chemical analysis	Present; diffuse
6	Northern Province, Tanganyika	Zoisite-amphibolite	95–97	Optically (universal stage)	Present; sharp
7	Miyaké, Japan	Same as no. 4	~ 94	Optically	Present; diffuse
8	Grass Valley, California	Hornblende-norite	92·8	Chemical analysis	Present; sharp
9	Glen Harris, Rum	Allivalite	88–91	Optically (universal stage)	Present; diffuse
10	Juvenas, France	Eucrite (meteorite)	~ 88	Optically	Present; diffuse
11	St. Louis Co., Minnesota	Anorthosite	~ 80	Optically	Absent
12	Crystal Bay, Minnesota	Anorthosite	70·1	Chemical analysis	Absent

For the present purpose it is convenient to group all possible X-ray reflections into four classes (a), (b), (c), (d) in which for (a) $(h+k)$ is even, l even; for (b) $(h+k)$ is odd, l odd; for (c) $(h+k)$ is even, l odd; for (d) $(h+k)$ is odd, l even. Reflections of type (a) are common to all felspars and are, in the main, strong and sharp; (b) are relatively weak subsidiary reflections characteristic of the doubled c-axis of anorthite and given by all materials having the anorthite-type structure; types (c) and (d) are weak additional reflections the presence of which indicates that the true cell is primitive since (c) and (d) do not conform to the body-centring condition ($h+k+l$ even) satisfied by both (a) and (b). It is found that all reflections (b), (c), (d) may be diffuse by comparison with (a), though those of type (b) do not show the gross diffuseness which is sometimes observed in type (c); reflections of type (d) are very few in number and it is uncertain whether they can exhibit extreme diffuseness. It will be seen, below, that it is primarily with reflections of type (c) that this work has been concerned.

Diffuse reflections may be seen in oscillation photographs, but moving-film methods are more convenient for their study, and for most of the materials examined zero- and third-layer Weissenberg photographs taken about the a-axis, with Cu-$K\alpha$ radiation, have been used; confirmatory photographs, with oscillation about other prominent

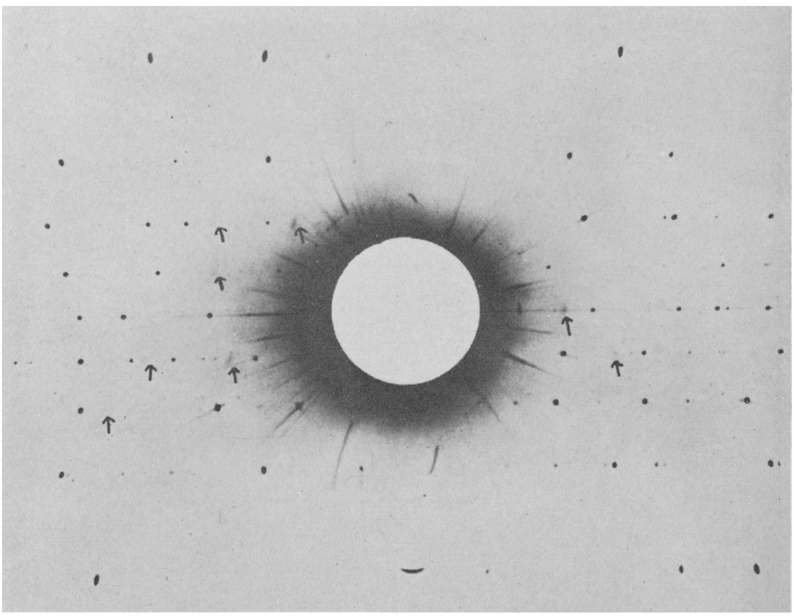

Fig. 1. Part of an oscillation photograph taken about the a-axis of a crystal of synthetic anorthite using Cu-$K\alpha$ radiation. The diffuse reflections present are marked with arrows.

crystallographic directions, have been obtained where necessary. Figs. 1 and 2 illustrate the appearance of reflections of the different types, in oscillation and Weissenberg photographs.

The last column of table I shows whether X-ray reflections indicating a primitive unit cell are seen, and if so, whether they are sharp or diffuse; these observations are discussed in detail below.

It should perhaps be made clear that the diffuseness of some reflections cannot be due to variation in composition over the crystal specimen: for all the fragments used were examined optically and showed no signs of the 'zoning' which is frequently seen in plagioclases; the diffuseness is confined to reflections with indices of certain types only; and it is seen in synthetic pure anorthite.

3. Discussion of results.

All the materials so far examined give one or other of three diffraction patterns. In the first, (S), reflections (c) and (d) are present and sharp; in the second, (D), reflections (c) are present and diffuse, reflections (d) are absent or so weak as to be doubtful; in the third, (A), reflections (c) and (d) are absent.

Pattern S.—Specimen 1 gives a diffraction pattern of the first type. Reflections of all types (a), (b), (c), (d) are observed, and although reflections (b), (c), and (d) may be slightly diffuse by comparison with (a), the difference in sharpness—if any—is very slight. A large number of reflections (b) are observed, but there are relatively few reflections (c) and very few reflections (d).

The same diffraction pattern is given by specimen 2, an observation which confirms the work of Cole, Sörum, and Taylor, who reported this material as having a primitive unit cell. Fig. 2(*a*) shows part of a zero-layer *a*-axis Weissenberg photograph of specimen 2 in which reflections of types (a), (b), (c) are marked.

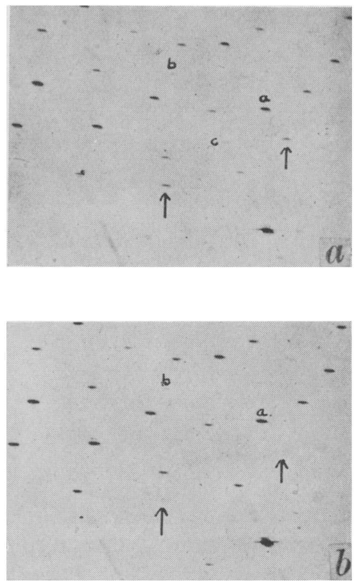

Fig. 2(*a*) Part of a zero-layer Weissenberg photograph taken about the *a*-axis of a crystal of an anorthite from *Monte Somma*, Vesuvius, using Cu-$K\alpha$ radiation. Typical reflections of types (a), (b), and (c) are marked.

Fig. 2(*b*) The corresponding part of a zero-layer Weissenberg photograph taken about the *a*-axis of a crystal of synthetic anorthite using Cu-$K\alpha$ radiation. It will be noted that the reflection marked (c) in fig. 2(*a*) is no longer present. Further, type (c) reflections denoted by arrows are diffuse; the corresponding reflections in fig. 2(*a*) are marked.

The patterns of specimens 6 and 8 are also similar, though some of the reflections (b), (c), (d) may be slightly more diffuse than for specimens 1 and 2.

Pattern D.—Specimen 3 (synthetic pure anorthite) gives a strikingly different pattern: no significant changes are seen in reflections (a) and (b), all reflections (d) have disappeared, and the few remaining (c) reflections are *very* diffuse—so diffuse that they might easily be overlooked, in which case the structure would be described as body-centred. The diffuse reflections observed (notably 007, 0015, $0\bar{6}3$, $0\bar{4}3$, $0\bar{6}5$, 025, $0\bar{2}7$, $0\bar{4}5$, $0\bar{2}15$, $3\bar{1}5$) are elongated along the b^* direction. Fig. 2(*b*) shows a part of a Weissenberg photograph of specimen 3, corresponding to figure 2(*a*) for specimen 2.

Specimens 4, 5, 7, 9, 10 give similar diffraction patterns. The degree of diffuseness of corresponding reflections may vary slightly for the different specimens, though this is difficult to decide; thus for specimen 9 (Glen Harris, Rum) reflections (c) while still being very diffuse are probably not quite so 'smeared out' as those from specimen 3 (synthetic).

Pattern A.—Specimens 11 and 12 give only reflections (a) and (b), reflections (c) and (d) being completely absent; the unit cell is thus truly body-centred.

Some tentative conclusions[1] of a general character may be drawn from these observations, though they can only be regarded as provisional on account of the absence of precise information about the geological thermal history of the mineral specimens.

(i) For pure or nearly pure anorthites, the occurrence of diffuse reflections (D pattern) indicates a high temperature of formation followed by rapid cooling, while the S pattern indicates either a low temperature of formation or very slow cooling from a high temperature. Specimens 3, crystallized from about 1500° C. overnight, and 1, certainly of low-temperature origin, may be taken as typical examples.

The distinction is maintained from An_{100} to about $An_{93}Ab_7$, at least: for the D pattern is observed in specimens 4, 5, 7, which are from volcanic lavas, i.e. quenched from a high temperature, while the S pattern is given by specimens 6 (of low-temperature origin, most probably metamorphic or metasomatic) and 8 (plutonic, cooled slowly from a moderately high temperature).

[1] Some of these deductions are in accordance with results reported briefly by F. Laves and J. R. Goldsmith, in abstracts of papers to Amer. Cryst. Assoc. meeting, Chicago, 1951.

Specimen 2 is of special interest. In Cole, Sörum, and Taylor this material (B.M. 49465) is mistakenly (by reason of its place of origin—Monte Somma, Vesuvius, a classic locality for high-temperature sanidines) considered to be of high-temperature origin. Its occurrence in an olivine-limestone block makes it clear, however, that it is actually of low-temperature origin, probably being formed as a secondary product either by thermal metamorphism or metasomatism. In this connexion it is interesting to note that Monte Somma, Vesuvius, is also among the sources listed by Chaisson[1] for adularia, which is generally regarded as of low-temperature origin.

The X-ray pattern thus provides a direct means of distinguishing high-temperature and low-temperature types in the composition range An_{100} to $An_{93}Ab_7$.

(ii) As the proportion of soda-felspar increases, the distinction becomes less clear-cut. The change from the S pattern (in which sharp reflections (c) and (d) indicate a primitive cell) to the D pattern (in which the reflections are diffuse) represents a trend towards the A pattern in which these reflections have vanished, the cell being then body-centred. The occurrence of the A structure only, in specimens 11 and 12 and in a specimen $An_{71\cdot5}Ab_{28\cdot5}$ examined by Cole, Sörum, and Taylor (1951), suggests strongly that the presence of a considerable proportion of soda-felspar affects the symmetry, even of a low-temperature material, in the same way as raising the temperature of the nearly pure anorthite—i.e. in favouring the body-centred structure. For specimens 11 ($An_{80}Ab_{20}$) and 12 ($An_{70}Ab_{30}$), of plutonic origin, have cooled slowly from high temperatures and thus have thermal histories rather similar to that of specimen 8 ($An_{93}Ab_7$) which gives the S pattern. The specimen $An_{71\cdot5}Ab_{28\cdot5}$ is from Split Rock Point, Minnesota, and may have a similar thermal history, though definite information is, unfortunately, lacking.

It is thus suggested that diffuse reflections indicating an intermediate stage in the transition from a truly primitive to a truly body-centred anorthite-type cell may be observed *either* as a consequence of a high temperature of formation, followed by rapid cooling, *or* when a considerable proportion of soda-felspar is present, even if the material is of low-temperature origin or has been cooled very slowly from a higher temperature. It is also reasonable to assume, in the light of the observations recorded above, that the transition from primitive to body-centred structure is essentially continuous in character and does

[1] U. Chaisson, Journ. Geol., 1950, vol. 58, p. 537. [M.A. **11**–326.]

not occur suddenly at some particular composition or temperature—a point left undecided in the work of Cole, Sörum, and Taylor (1951).

It remains to consider specimens 9 and 10. Specimen 9, from a plutonic rock, has probably cooled slowly from a high temperature and so might be expected to give an S pattern such as is given by specimen 8. However, the presence of hornblende in association with felspar in that specimen probably indicates a lower initial temperature than for specimen 9, for which the initial temperature may be as high as those for the Japanese volcanic specimens 4, 5, and 7. In addition, it is possible that the appearance of the D pattern may, in part at least, be due to the influence of the soda-felspar; in view of the uncertainty as to the precise chemical composition it is difficult to decide whether this is an important factor for this specimen.

The thermal history of specimen 10 is probably similar to that of specimen 9, except that 10 has probably been reheated, to a low temperature, as is shown by the metamorphic clouding of the felspar. Here the considerable proportion of soda-felspar ($\sim$ 88% An) may well be an important influence in producing the structure to which the observed D pattern corresponds. Little weight can be given to the observations on the specimen, however, since P. M. Game (private communication, 1952) has shown that in this meteoritic material different grains have different optical properties.

4. Conclusions.

The experiments described in this paper establish a means of distinguishing high-temperature from low-temperature plagioclases when the soda-felspar content does not exceed about 7% (mol.). They also suggest that the transition from the primitive to the body-centred type of structure is continuous in character; the diffuse reflections observed with nearly pure anorthites of high-temperature origin indicate that in these materials the transition is incomplete; the truly body-centred structure is observed with plagioclases containing between 20% and 30% (mol.) of soda-felspar even after slow cooling.

In an investigation in which so little precise information on thermal history is available, all conclusions based on the examination of a rather limited number of specimens must be regarded as provisional. Further work is in hand.

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