Acta Cryst. (1953). **6**, 647

The Structures of the Plagioclase Felspars. IV. Variations in the Anorthite Structure

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(*Received* 14 *March* 1953)

A structural interpretation is proposed for the variations, recently described, in the X-ray diffraction patterns obtained from plagioclases with composition between pure anorthite and $An_{70}Ab_{30}$.

It is suggested that the differences in the X-ray patterns are due to order–disorder transformations; although the precise nature of the transition has not finally been established, it is thought that the Si–Al arrangement is ordered over the whole composition range and that the slight structural changes are brought about by a rearrangement of the calcium (or sodium) ions.

On this view a low-temperature pure anorthite has a completely ordered structure with a primitive unit cell. The effect of either an elevated temperature or an increase in the sodium content is to leave intact the Si–Al ordered arrangement, whilst destroying the ordering of the calcium (or sodium) ions, so promoting a change to a body-centred unit cell.

1. Introduction

The extreme complexity of the plagioclase felspars has gradually been revealed in the course of a series of researches employing both X-ray and optical methods of examination. The early X-ray work (Taylor, Darbyshire & Strunz, 1934; Chao & Taylor, 1940) showed that while as a broad generalization it is true that all felspar structures are essentially similar, the plagioclase series includes no fewer than three distinct structure types. The simplest is that of (low-temperature) albite; the unit cell has axes $a \sim 8$ Å, $b \sim 13$ Å, $c \sim 7$ Å, interaxial angles $\alpha \sim 94°$, $\beta \sim 116\frac{1}{2}°$, $\gamma \sim 87\frac{1}{2}°$, and is base-centred on (001). In anorthite the corresponding cell is only a pseudo-cell, the true cell having a doubled c axis (~ 14 Å), and in addition there are small but significant differences in the axial lengths $a, b, c' = \frac{1}{2}c$ and in the interaxial angles α, β and γ. The structures of the intermediate plagioclases are most simply described as based on alternating layers of albite-type and anorthite-type structures; they vary in an exceedingly complex manner from one material to another.

More recently, in paper I of the present series, Cole, Sörum & Taylor (1951) showed that the cell with axial dimensions characteristic of the anorthite-type structure may be either primitive or body-centred, but their data did not enable these authors to decide under what conditions one or other of these variations of the structure is observed. In paper II of the series, Sörum (1953) described the structure of a body-centred anorthite. In paper III, Gay (1953) described an X-ray examination of a number of plagioclases, having the anorthite structure, with compositions in the range An_{100} to $An_{70}Ab_{30}$. On the basis of these data, Gay proposed a correlation between the nature of the X-ray diffraction pattern and the thermal history and composition of the felspar; the present paper is devoted to the structural interpretation of these data, particularly in relation to the problem of order–disorder changes.

In the meantime, largely as a result of the researches of Köhler and his co-workers, it had been shown that a consistent interpretation of the optical data for a large number of plagioclases could be given if the existence of both high-temperature and low-temperature series were assumed (see, for example, Köhler, 1949). The difference between the high-temperature form and the low-temperature form is easily demonstrated, either optically or by X-ray examination, for the albite structure (Tuttle & Bowen, 1950; Laves & Chaisson, 1950). For anorthite-rich materials, however, the optical methods fail to distinguish the high- and low-temperature forms (Reynolds, 1952) and Gay's X-ray examination of the anorthite structure is important in the first place because it provides a convenient means for doing this for plagioclases with this structure and lying in the composition range An_{100} to $An_{93}Ab_7$. For this purpose, no reference need be made to the structural interpretation which forms the subject matter of the present paper.

It should be made clear that we are, in this paper, concerned solely with the anorthite-type structure; we do not consider the intermediate plagioclase structures, nor the hexagonal and orthorhombic structures of $CaAl_2Si_2O_8$ (Goldsmith & Ehlers, 1952; Donnay, 1952).

2. Experimental data

In this section we summarize the new experimental data, described by Gay (1953), on which our interpretation of the variations in the anorthite structure is based; for details of the materials examined, and of the techniques used, reference should be made to the above paper.

It is convenient to group all possible X-ray reflexions from anorthite-type structures into four classes:

(*a*): $(h+k)$ even, l even;
(*b*): $(h+k)$ odd, l odd;
(*c*): $(h+k)$ even, l odd;
(*d*): $(h+k)$ odd, l even.

(All indices refer to the true cell with $c \sim 14$ Å.) Reflexions of type (*a*) are common to all felspars and are in the main relatively strong and sharp. Type (*b*) are the relatively weak, but quite numerous, subsidiary reflexions characteristic of the doubled c axis seen in all anorthite-type structures; they may be slightly diffuse in comparison with type (*a*) reflexions. Types (*c*) and (*d*) comprise a relatively small number of weak additional reflexions which do not conform to the body-centring condition, $(h+k+l)$ even, satisfied by (*a*) and (*b*); (*c*) may be sharp, diffuse, or very diffuse; (*d*) are very few in number and it is uncertain whether they can exhibit the gross diffuseness sometimes seen in (*c*).

When Cole *et al.* (1951) first showed that the anorthite cell may be either body-centred (reflexions (*c*) and (*d*) absent), as in a specimen $An_{71.5}Ab_{28.5}$, or primitive (reflexions (*a*), (*b*), (*c*), (*d*) all present and sharp), as in a nearly pure anorthite, they pointed out that these two types of structure represent a progressive reduction in symmetry of the atomic arrangement from that of the albite structure with the small ($c \sim 7$ Å) base-centred cell. These authors did not obtain any definite information on the factors governing the occurrence of one type of structure or the other, nor on the nature of the transition from one to the other, though they directed attention to the possible influence of variation in the proportion of soda felspar present.

Gay (1953) examined materials with compositions in the range An_{100} to $An_{70}Ab_{30}$, and with different thermal histories known with varying accuracy from their mineral environment, and was able to present a systematic account of the conditions governing the occurrence of the two X-ray patterns already recognized by Cole *et al.* (1951) and of a third—now called the '*D*' pattern—not previously described.

The '*S*' pattern, in which reflexions of all classes (*a*), (*b*), (*c*), (*d*) are present and sharp, so that the cell is primitive, appears to be characteristic of pure or nearly pure anorthite (An_{100} to $An_{93}Ab_7$) formed at a low temperature or cooled very slowly from a higher temperature of formation. It is given by materials occurring in metamorphic or plutonic rocks.

In the '*D*' pattern, reflexions (*a*) and (*b*) are sharp, while (*c*) (and probably (*d*)) are diffuse. It is observed with materials cooled rapidly from a high temperature of formation, and for a range of composition from An_{100} (e.g. in a synthetic pure anorthite cooled rapidly from 1500° C.) to about $An_{90}Ab_{10}$.

The '*A*' pattern, in which reflexions (*a*) and (*b*) are sharp, while reflexions (*c*) and (*d*) are absent, so that the cell is body-centred, is formed when the proportion of soda felspar is relatively high ($An_{80}Ab_{20}$ and $An_{70}Ab_{30}$) in materials of low-temperature origin or cooled very slowly from a high temperature of formation.

The '*D*' pattern corresponds to an intermediate stage in a transition from the '*S*' pattern to the '*A*' pattern, and observed variations in diffuseness of the reflexions (*c*) (and probably (*d*)) correspond to different stages in this essentially continuous change from primitive to body-centred structure. Although Gay's experiments do not permit the fixing of accurate limits for the compositions and temperatures or cooling-rates appropriate to each type of pattern, it seems that the transition from the primitive structure characteristic of a low-temperature pure anorthite, to the body-centred structure, is favoured either by raising the temperature or by increasing the proportion of soda felspar.

A further observation, bearing on the nature of the transition between primitive and body-centred structures, is that in the '*D*'-type pattern, corresponding to an intermediate stage in transition, the diffuse reflexions are elongated in the b^* direction.

3. Structural interpretation

The experimental observations summarized in § 2 receive a simple and natural explanation if it is assumed that the '*S*' pattern corresponds to a perfectly-ordered structure, ideal formula $CaAl_2Si_2O_8$, based on the primitive cell, while the '*A*' pattern is that of a disordered structure, with the enhanced symmetry of the atomic arrangement in the body-centred cell. On this view, the '*D*' pattern corresponds to partial order, and the elongation of the diffuse reflexions along b^* indicates that the disorder must manifest itself as some kind of irregularity in that direction. The effects of a higher temperature of formation, followed by rapid cooling, and of the replacement of some of the lime-felspar by soda-felspar, in promoting disorder, correspond to the behaviour observed in other more familiar examples of the order–disorder transformation, as does the essentially continuous character of the transition.

This general explanation of the nature of the variations in the anorthite structure represents a development of one of the hypotheses tentatively advanced by Cole *et al.* (1951), and is similar to ideas put forward (independently) by Laves & Goldsmith (1951*a*, *b*, *c*) in papers of which, unfortunately, only abstracts have been published. It is therefore difficult to know how far the following more detailed discussion may overlap the results of the researches of Laves & Goldsmith, and all that can be done is to indicate where their briefly-reported findings appear to be relevant to the particular point under consideration.

(a) *The nature of the order–disorder change*

It is immediately obvious that the change from primitive to body-centred structure which occurs on disordering the anorthite-type structure is structurally distinct from the change seen on comparing the anorthite-type with the albite-type structure. For whereas the disordering process is revealed by increasing diffuseness of certain reflexions, with elongation in the b^* direction, it is the doubling of the c axis which differentiates all anorthites from albites. Moreover, the variations in structure which correspond to the extremes of the order–disorder process (as shown in the '*S*' and '*A*' anorthite patterns) have no obvious effect upon the large number of subsidiary reflexions of type (*b*) which demonstrate the doubling of the c axis in all anorthites.

A complete understanding of the nature of the order–disorder change, and of the relationship between anorthite and albite, awaits high-accuracy structure-analysis of minerals showing the different types of pattern. Sörum (1951*a*, *b*, 1953) has determined the atomic arrangement in a material ($An_{71\cdot5}Ab_{28\cdot5}$) described by Cole *et al.* (1951) as having the body-centred anorthite structure ('*A*' pattern, in the notation of this paper). He obtains fairly close agreement between observed and calculated intensities for the subsidiary reflexions (*b*) for a structure in which the doubling of the c axis is a consequence of the ordering of the Si and Al atoms into distinct sets of sites. An analysis of a nearly pure anorthite which gives the '*S*' pattern (primitive cell, perfectly ordered structure) is now in progress in this Laboratory. It may be expected to show similar Si–Al ordering to that found in Sörum's body-centred, disordered structure, and to reveal the nature of the disordering transition. In making the comparison of the two structures, it must not be forgotten that the ordered material is nearly pure $CaAl_2Si_2O_8$, while the disordered material contains nearly 30% (mol.) of $NaAlSi_3O_8$.

Almost simultaneously with the first publication of Sörum's analysis of body-centred anorthite there appeared abstracts by Laves & Goldsmith in which it was suggested that for anorthite the subsidiary reflexions are a consequence of order–disorder relations (1951*a*), 'with Al–Si ions controlling the (*b*) reflections, Ca ions the (*c*) reflections'* (1951*c*), supporting evidence being obtained from an examination of Ga- and Ge-substituted synthetic anorthites (1951*b*, *c*).

It thus seems extremely probable that the doubling of the c axis in all anorthites arises from ordering of Al and Si ions in the linked tetrahedral groups, but the nature of the disordering transition involving the Ca ions, which is responsible for the observed variations in the anorthite structure, remains obscure pending the completion of the accurate analysis of an ordered material.

(b) *Effects of heating anorthites*

In two experiments on the heating of anorthites, results were obtained which can be interpreted in terms of the assumed order–disorder transition.

First, a synthetic anorthite cooled rapidly from 1500° C., and giving the '*D*' pattern characteristic of partial disorder, was brought into the completely ordered state, indicated by the '*S*' pattern, by heating at 1100° C. for 72 hr.; this treatment is, in effect, a 'low-temperature anneal' which promotes the ordering process.

Again, the observation reported by Cole *et al.* (1951) that heating at 1100° C. for 30 hr. produced no change in the ('*S*') pattern of anorthite B.M. 49465 is in accordance with expectation, since this low-temperature nearly pure anorthite is already perfectly ordered. (It should be pointed out that Cole *et al.* (1951) mistakenly, by reason of its *place* of origin—Monte Somma, Vesuvius—regarded the material as of high-temperature origin. Its occurrence in an olivine-limestone block makes it clear that it is actually of low-temperature origin—see also Gay (1953).)

Similar observations have been mentioned by Laves & Goldsmith (1951*a*, *b*, *c*, 1952).

(c) *Variations in* Si–Al *ordering in anorthite-type structures*

In the range of composition An_{100} to approximately $An_{70}Ab_{30}$, in which the anorthite-type structure is observed, the subsidiary reflexions (*b*) which occur in '*S*', '*D*' and '*A*' patterns are never very diffuse, though they may be slightly diffuse in comparison with principal reflexions (*a*). Moreover, Laves & Goldsmith (1951*b*) have stated that reflexions (*b*) may be sharpened by heat treatment (by implication, near 1100° C.) but are not rendered diffuse at 'high temperatures' (? perhaps near 1500° C.): their observations appear to refer to pure or nearly pure $CaAl_2Si_2O_8$. These facts may be interpreted as meaning that in all these cases (i.e. when the (*b*) reflexions are sharp or fairly sharp) the Si–Al ordering responsible for the doubled c axis is perfect or nearly perfect.

In this connection, observations reported by Cole *et al.* (1951) on certain 'anomalous' plagioclases are of considerable interest, and can now be interpreted in terms of variations in degree of Si–Al order.

(i) A labradorite of composition 5% orthoclase, 33% albite, 62% anorthite, which would be expected to have a structure of the 'intermediate plagioclase' type, actually showed 'abnormally weak and unusually diffuse' subsidiary reflexions in an anorthite-type pattern. The rock environment of this material, as described by Hutchinson & Smith (1912), clearly indicates that it has been cooled suddenly, but it is impossible to estimate the temperature before this quenching. Granted that special circumstances have prevented this material from forming the intermediate-type structure, it is interesting as an example of an

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* '(*c*) reflections' of Laves & Goldsmith include reflexions of classes (*c*) and (*d*) in our notation.

anorthite in which the Si–Al ordering must be far from complete, since the subsidiary reflexions indicating the doubled *c* axis are so ill-defined. Since high temperature does not appear to produce disorder in the Si–Al distribution in pure $CaAl_2Si_2O_8$, its occurrence in this material may be due either to the considerable inequality in the numbers of Al and Si atoms (2 Al to every 3 Si), or—perhaps less likely—to the influence of the small number of K atoms present, or to the replacement of Ca by Na atoms (the material contains 1 Na to 2 Ca).

(ii) A labradorite occurring as phenocrysts in a lava at Clear Lake, Utah, showed no subsidiary reflexions. The composition quoted by Cole *et al.* for their sample (obtained from Dr E. Spencer) was approximately $An_{55}Ab_{45}$. Another similar sample from the same locality, with composition $An_{64}Ab_{36}$, kindly supplied by the Geophysical Laboratory, Washington, also showed no subsidiary reflexions.* In this material, therefore, which is presumably quenched from a high temperature, there is a complete absence of Si–Al ordering and the cell is comparable with that of albite.

Thus it seems that the fully-developed Si–Al ordering, which is hardly affected (if at all) by high-temperature treatment of nearly pure anorthite, may be reduced or destroyed by suitable thermal treatment when more than approximately 30% albite is present. This situation is reminiscent of the influence of an increase in soda-felspar content in changing the anorthite-type pattern from '*S*' to '*D*' to '*A*', i.e. in facilitating the changes in the direction of disorder, which would be expected to follow the raising of the temperature.

Further heating experiments now in hand with these 'anomalous' plagioclases may clarify their relationships with anorthite and normal intermediate plagioclases.

4. Discussion

The new data summarized in § 2 have led to a considerable clarification of the anorthite problem, and to the understanding of a number of observations on plagioclases, the significance of which was previously obscure. Nevertheless, it is necessary to await the completion of detailed structure analysis now in progress before an accurate picture can be presented. To make this clear, it is sufficient to remark that although there is powerful evidence that the variations in the anorthite structure correspond to order–disorder changes, very little positive information has been obtained on the precise nature of these changes. It seems that they are in some way closely associated with the calcium ions (and sodium ions, if the proportion of soda felspar is considerable); but, as Goldsmith (1952) has shown, diffusion even of the calcium and sodium ions seems unlikely to take place rapidly in plagioclases and it is difficult to predict the probable inter-relationship of the distribution of these ions with the ordered Si–Al distribution.

In spite of these outstanding difficulties, one important generalization seems to be justified, in relating the variations in the anorthite structure to variations in the potash felspar structure. For in the potash felspars there is general agreement that the large differences in the optical properties of high-temperature and low-temperature forms are to be associated with order–disorder changes in the Si–Al distribution. Since the observed variations in the anorthite structure in materials in the range An_{100} to $An_{70}Ab_{30}$ are apparently not associated with Si–Al ordering effects, it naturally follows that there should be little variation in optical properties as between high-temperature and low-temperature forms; this is in fact in accordance with observation.

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* For these observations we are indebted to Mr S. W. Bailey (now at Department of Geology, Madison, Wisconsin, U.S.A.) who also examined, for comparison purposes, a natural low-temperature plagioclase (An_{64}) from the Stillwater Complex: this latter material showed a pattern of the normal 'intermediate plagioclase' type.