

*Orientation of the boundaries of out-of-step domains in  
anorthite*

By PAUL H. RIBBE

Department of Geological Sciences, Virginia Polytechnic Institute,  
Blacksburg, Virginia

and ALAN A. COLVILLE

Department of Geology, California State College at Los Angeles,  
Los Angeles, California

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*Summary.* The orientation of the boundaries of out-of-step domains in 'transitional' anorthite has been deduced from the direction of elongation of the diffuse X-ray reflections  $h+k+l = 2n+1$  in selected precession photographs. The reflections are elongated normal to  $(2\bar{3}1)$  which is in the zone  $[11\bar{1}]$  and contains the body-centring vector  $(\mathbf{a} + \mathbf{b} - \mathbf{c})/2$ . The structure is presumed to be perfect parallel to  $(2\bar{3}1)$ . Atoms in essentially identical, primitive anorthite-like domains are related across the out-of-step domain boundaries by body-centring vectors. Increasing diffuseness of the  $h+k+l = 2n+1$  reflections indicates progressively smaller domains (more frequent domain boundaries), and when these reflections disappear, the structure has become body-centred on the average.

**P**RIMITIVE anorthite is quasi-body-centred because the atoms related by body-centring vectors have slightly different atomic co-ordinates, although they are chemically identical. It is expected, therefore, that the  $c$ -type reflections  $h+k+l = 2n+1$  will be very sensitive to any changes in positional parameters of related atoms that make the anorthite structure more nearly body-centred on the average. Each of the following experimental observations indicates that the diffuseness of  $c$ -type reflections is not due to high-energy transformations such as Al/Si order-disorder (as Laves and Goldsmith (1951) clearly recognized), but must result from slight positional changes. The  $c$ -type reflections become increasingly diffuse with rapid quenching from increasingly higher temperatures above  $1100^\circ\text{C}$  (Laves and Goldsmith, 1951; 1954 *a, b*; Gay, 1954), with increased substitution of NaSi for CaAl (Laves and Goldsmith, 1954 *a, b*; Gay, 1953), or with heating in the range  $160^\circ$  to  $350^\circ\text{C}$  — above which the ' $c$ ' reflections disappear (Brown *et al.*, 1963).

Laves and Goldsmith (1951; 1954 *a, b*) attribute the increasing diffuseness of the *c*-type reflections to progressively smaller out-of-step domains within which perfect Al/Si order is essentially undisturbed. They postulate two types of domains based on Ca occupying one or the other of two slightly different sites, *A* and *B*. When Ca is completely ordered on either *A* or *B*, the *c*-type reflections are sharp and the space group is  $P\bar{1}$ ; when Ca is randomly distributed on *A* and *B*, the *c*-type reflections disappear and the space group becomes  $I\bar{1}$ . Intermediate or 'transitional' states exist in which ordered domains of *A*- or *B*-site occupancy predominate and the *c*-type reflections are diffuse.

Recent structural analyses of body-centred and transitional anorthites have shown that this out-of-step domain model is essentially correct and needed only to be modified to include the positional parameters of all atoms, not just the Ca atoms. Fleet *et al.* (1966) found that body-centred anorthite,  $An_{80}Ab_{20}$ , is really an average structure in which the atoms in small, identical domains of primitive anorthite are in effect related by body-centring vectors across domain boundaries. Because the domains are very small (or, alternately, the frequency of domain boundaries is high) the *c*-type reflections,  $h+k+l = 2n+1$ , do not appear in the X-ray photographs. A volcanic transitional anorthite,  $An_{98}Ab_2$  (Ribbe and Megaw, 1962), has a similar out-of-step domain texture; however, because the domains are substantially larger than those in body-centred anorthite (cf. Megaw, 1960, pp. 171-172), the *c*-type reflections are diffuse. They are also elongated, and it is the purpose of this study to determine the direction of elongation of these reflections in reciprocal space, thereby defining the orientation of the 'boundary' between these out-of-step domains.

*Experimental procedure.* Single crystals of transitional anorthite from Miyaké, Japan (Gay, 1953, specimen no. 4) were mounted on a Buerger precession camera and four reciprocal lattice planes were photographed. The inclinations of the elongate, diffuse *c*-type reflections were measured in each case; pertinent data are:

Photo no.	1	2†	3‡	4
Plane of photo	$a^*c^*$	$b^*[10\bar{1}]^*$	$b^*c^*$	$b^*a^*$
Level	0	0	0	1
Inclination of diffuse streaks	$16^\circ$ to $+a^*$	$47^\circ$ to $-b^*$	$0^\circ$ to $-b^*$	$50^\circ$ to $-b^*$

† Fig. 1.

‡ Cf. fig. 2 of Goldsmith and Laves, 1955.

Because of the shape and diffuseness of the X-ray reflections and the influence of precession geometry on the orientation of the streaks

(cf. Wood, 1959), it is difficult to measure inclinations precisely. Measurements were made as near as possible to the origin. Estimated errors are  $\pm 5^\circ$  in photographs nos. 1 and 2 and  $\pm 10^\circ$  in photographs nos. 3 and 4.

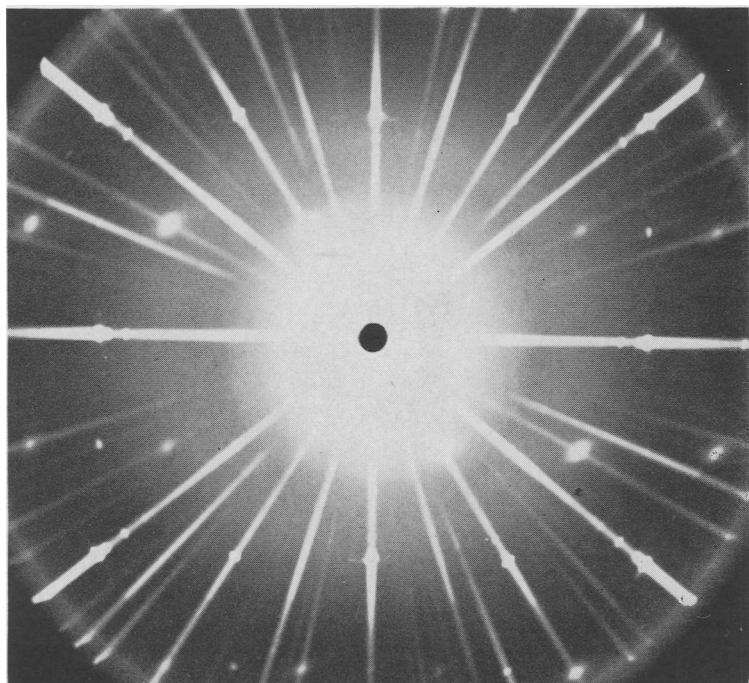


FIG. 1. A  $b^*[101]^*$  precession photograph taken with iron radiation.  $b^*$  is the horizontal axis;  $[101]^*$  is vertical. The diffuse  $c$ -type reflections are inclined  $47^\circ$  to  $-b^*$ .

Since the measured direction of elongation on each photograph is the projection of the true elongation onto the plane of that photograph, the true direction of elongation is the line of intersection of the numbered planes shown in the stereographic projection (fig. 2). These planes are drawn perpendicular to the planes of their respective precession photographs and contain the direction of elongation of the diffuse  $c$ -type reflections observed in that photograph. The intersection of the most well-defined planes,  $\perp 1$  and  $\perp 2$ , occurs at the projection of the pole to the plane  $(2\bar{3}\bar{1})$ ; the less well-defined planes, subject to larger errors, intersect at four points nearby. There are, of course, poles of other rational planes in the large spherical triangle outlined by the intersecting

planes. They are  $(3\bar{4}1)$  at the 'apex' and  $(3\bar{4}2)$  near the base; however,  $(2\bar{3}1)$  is most probably the correct plane not only because it lies at the intersection of the well-defined planes, but also because it alone is in the zone  $[11\bar{1}]$ , which is the direction of the body-centring vector  $(\mathbf{a}+\mathbf{b}-\mathbf{c})/2$  in transitional and body-centred anorthite.

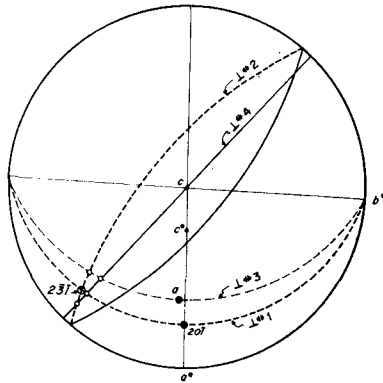


FIG. 2. A stereographic projection showing the orientation of the four planes that are defined by the direction of diffuse streaks on each of the four precession photographs (see table). The intersection of the well-defined planes,  $\perp 1$  and  $\perp 2$ , occurs at the pole of  $(2\bar{3}1)$ ; the other intersections are nearby.

*Discussion of results.* As mentioned in the introduction, it is easy to induce changes in positional parameters of the atoms in primitive anorthite that are approximately related by body-centring vectors. For example, heating above  $160^\circ\text{C}$  causes increasing positional disorder and the structure becomes more nearly body-centred on the average. The perfect Al/Si alternation is not disturbed —  $h+k+l = 2n$  reflections remain sharp; however, the  $h+k+l = 2n+1$  reflections become weaker, more elongate and more diffuse. The remaining problem is to interpret the  $[2\bar{3}1]^*$  direction of elongation of the diffuse streaks in transitional anorthite. An understanding of this phenomenon is best gained with reference to an optical analogue of this type of X-ray diffraction pattern in which elongated diffuse streaks exist side by side with sharp spots.

A type of structural disorder that produces such a diffraction pattern was illustrated by Willis (1958). Using optical masks carrying a displaced square net similar to that illustrated in fig. 3a, Willis obtained the optical diffraction pattern shown in fig. 3b. This simple pattern is

composed of rows of sharp spots and diffuse streaks; the latter are drawn out in a direction normal to the line in which a shift of a half unit cell has taken place. In addition, the diffuse spots have indices that violate the primitive net. The mineral wollastonite (Jeffrey, 1953) provides a good example of this same type of disorder. The diffuse reflections are streaked along  $a^*$ , indicating that the arrangement of atoms in planes parallel to (100) must be perfect. Similar atoms within

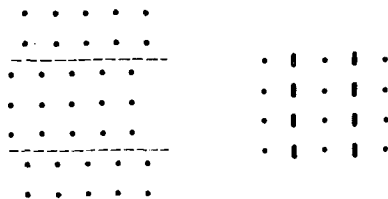


FIG. 3 *a* (left), diagram representing an idealized type of lattice faulting in which primitive areas are displaced by a shift of half the unit cell across parallel boundaries. *b* (right), the optical diffraction pattern corresponding to the mask of which fig. 3 *a* is a small part (modified from Willis, 1958).

domains of perfect structure are related by a translation vector  $\mathbf{a}$ , but across the (100) domain boundaries they are related by a vector  $\mathbf{a} \pm \frac{1}{2}\mathbf{b}$  (see fig. 3*a*). The diffraction evidence for this is that the diffuse reflections have indices  $hkl$  with  $k$  odd and the sharp reflections  $hkl$  with  $k$  even (see Wooster, 1962, for other examples).

Transitional and body-centred anorthites can be interpreted similarly if we expand the optical model (fig. 3) to three dimensions and consider that blocks of primitive anorthite structure *between* domain boundaries are related by body-centring vectors  $(\mathbf{a} + \mathbf{b} - \mathbf{c})/2$  *across* domain boundaries. With increasing frequency of domain boundaries (often misleadingly called 'stacking faults') the structure becomes statistically more body-centred and the reflections  $h+k+l = 2n+1$  become increasingly more diffuse, finally disappearing altogether above 350° C (Brown *et al.*, 1963).<sup>1</sup> In this case the diffuse streaks are parallel to  $[2\bar{3}\bar{1}]^*$  and thus the structure is primitive within any plane parallel to  $(2\bar{3}\bar{1})$ . This plane contains the body-centring vector  $[11\bar{1}]$  and is the boundary between small out-of-step domains of primitive anorthite,

<sup>1</sup> Fort and Peacor (priv. comm.) are undertaking a structure analysis of anorthite at 400° C. Their final results may provide the detailed structural data to document the phenomenon, which is merely deduced from this study of the orientation of the diffuse reflections.

which are the building blocks of transitional and body-centred anorthite (Ribbe and Megaw, 1962; Fleet *et al.*, 1966).

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