An X-ray study of exsolution phenomena in the Skaergaard pyroxenes.

By M. G. Bown, M.A., Ph.D.
Dept. of Geology and Mineralogy, Oxford University,
and
P. Gay, M.A., Ph.D.
Dept. of Mineralogy and Petrology, Cambridge University.

[Taken as read 28 January 1960.]

Summary. The single crystal X-ray methods for the study of exsolution phenomena in pyroxenes previously described by the authors have been applied to the pyroxenes of the Skaergaard intrusion. The results for about fifty pyroxene crystals, selected from various levels between the chilled margin and a height of 2600 metres in the layered series, are presented and are correlated with previous optical descriptions. Whilst the correlation between the results of the optical and X-ray examinations is in general satisfactory, the present investigation shows that the X-ray techniques can in some cases extend our knowledge of the Skaergaard pyroxenes.

THE fine-scale textures of pyroxenes have nowadays achieved an importance and complexity rivalled only by the feldspars. The more important exsolution lamellae commonly occurring in both clino- and ortho-pyroxenes have been carefully studied under the microscope, particularly during the last 25 years, and the opinions as to their nature and significance as summed up by Poldervaart and Hess (1951) are now widely accepted. To some workers it has seemed that the identification of the lamellae (which can be exceedingly fine) as augite, pigeonite, or ortho-pyroxene on the basis of their orientation, supported by such of their optical properties as can be observed, was not always conclusive; however, it was not until recently that the methods of X-ray diffraction were used to make positive identification of lamellae (Morimoto, 1956; Gay and Bown, 1957). This first X-ray work confirmed that the (001) lamellae in several pigeonites did consist of augite, as had been suggested from the optical data. A routine X-ray method of identification of pyroxene intergrowths of several kinds has been suggested by Bown and Gay (1959), but no detailed correlation of the results of X-ray and optical examination of a suite of pyroxenes has yet been described.

The wide range of compositions and textures of the pyroxenes of the Skaergaard intrusion, originally described by Wager and Deer (1939), makes them particularly suitable for a comparison of the X-ray and microscopic methods, especially as a detailed study of the exsolution textures has recently been published by Brown (1957). In passing it is interesting to note that Wager and Deer (1939, p. 81) suggested that X-ray methods should be used to identify lamellae in their clinopyroxenes, but as far as we know this idea was not pursued until the present study twenty years later. About fifty pyroxene crystals, selected from various levels between the chilled margin and a height of 2600 metres in the layered series, have now been examined by X-ray techniques; the results of this study are presented here. As will be seen, in many cases the results of the optical work are confirmed, but some corrections are necessary and certain important additional information is obtained.

Experimental techniques.

It was found important to select for X-ray study crystals whose exsolution texture could be clearly seen with the microscope, and which corresponded as closely as possible to what could be seen of the same pyroxene in thin section. For this purpose well-shaped (100) or (110) flakes can be used, but (010) flakes are the best since they show clearly the traces of (001) and (100) lamellae; these (010) flakes occur more frequently in crushed pyroxene than is suggested in the literature. This comparison of the optics of the crystal and the thin section is necessary because of the variability of exsolution texture in a single rock, and for the same reason it was the practice to X-ray more than one crystal of each pyroxene. It must be emphasized that in work of this type in the pyroxenes, as in the feldspars, the combination of X-ray and optical studies is more valuable than either alone.

No attempt was made to determine unit cell parameters; the purpose was restricted for the present to the identification of the phases present and their relative orientations. For each crystal, *c*-axis oscillation photographs were taken in two 15° ranges as described in a previous paper (Bown and Gay, 1959). The photographs obtained mostly corresponded to one of the five combinations of pyroxene phases listed there, but two new arrangements were found and will be described.

The diffraction patterns to be expected from inverted pigeonite crystals were not discussed in the previous paper, and must now be considered. According to Poldervaart and Hess (1951) pigeonite on inver-

sion forms an ortho-pyroxene that nearly always retains the *b* and *c* axial directions of the pigeonite. On the other hand Brown (1957) found that the inverted pigeonites of the Skaergaard rocks do not often retain this orientation, but are usually randomly oriented compared

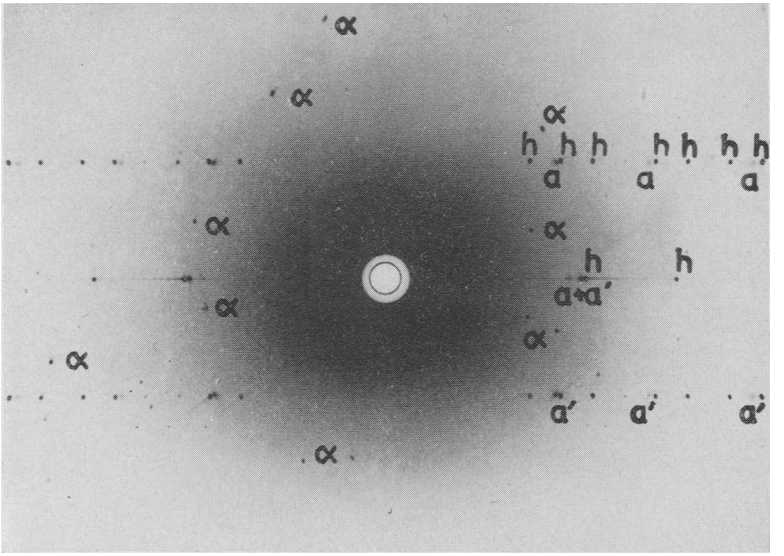

FIG. 1. Central portion of 15° *c*-axis oscillation photograph of inverted pigeonite from 1849 (perpendicular feldspar rock), taken with filtered Fe radiation. The X-ray beam was parallel to the *b*-axis in the centre of the oscillation range. Ortho-pyroxene spots (*h*) and slightly diffuse spots from post-inversion exsolution of augite (*a*, *a'*) are related by the symmetry elements, whereas spots (α) from augite formed before or at inversion are not. (Camera radius 3 cm., photograph enlarged ×1·25 approx.)

with the pigeonite axes. Therefore, in the crystals examined, the augite that exsolved on the (001) plane from the original pigeonite should normally have a random orientation with respect to the ortho-pyroxene. This augite would thus produce apparently randomly occurring diffraction spots, not related by the ortho-pyroxene symmetry elements, on the single-crystal photographs of the inverted pigeonite. Such random spots are characteristic of photographs of Skaergaard inverted pigeonites (fig. 1). The complexity of the powder pattern of augite makes it almost impossible to prove conclusively that these random diffraction spots are produced by augite, but the fact that such spots only occur in strength on photographs of inverted pigeonites makes the explanation

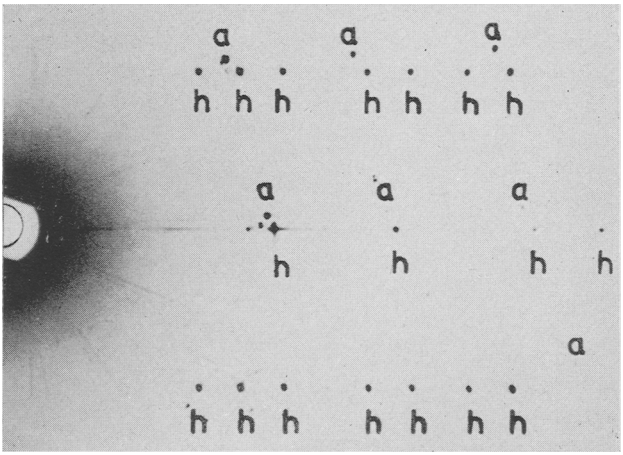

FIG. 2. Part of oscillation photograph of inverted pigeonite from 4087 (0 m.) showing ortho-pyroxene (*h*) and related augite (*a*) spots due to retention of orientation at inversion. Photograph taken under same conditions as fig. 1, but enlargement ×1·75 approx.

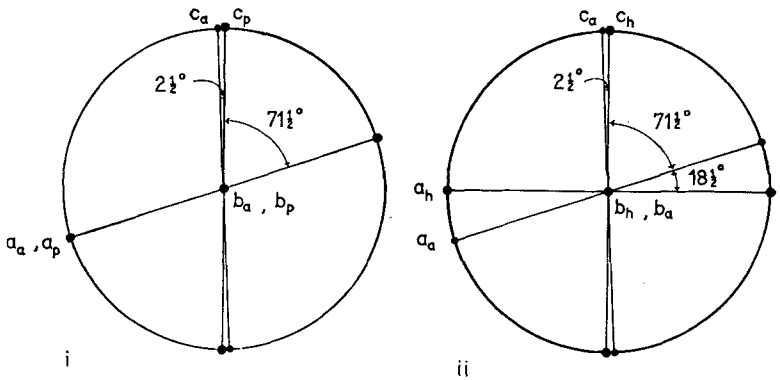

FIG. 3. (i) Orientation of augite and pigeonite axes before inversion of pigeonite. (ii) Orientation of augite and ortho-pyroxene axes after inversion, assuming orientation retained. Subscripts: *a* = augite, *p* = pigeonite, *h* = ortho-pyroxene.

most plausible. Augite exsolved after inversion would, of course, share the (100) plane with the ortho-pyroxene in the normal way, as shown in fig. 1.

Among all the inverted pigeonite crystals examined, only one was found that had retained orientation; its diffraction pattern is reproduced in fig. 2. The corresponding axial orientation is shown in fig. 3,

compared with the orientation before inversion. The scheme is exactly as described by Poldervaart and Hess. Subsequent exsolution of augite would share (100) with the ortho-pyroxene, and so would have a slightly different orientation from the earlier augite.

Presentation of results.

No general account of the Skaergaard intrusion is necessary as the original work of Wager and Deer (1939) is well known, neither is the detailed study of the pyroxene phases and their relation to the crystallization history of the intrusion, which was given by Brown (1957), recapitulated here. Such microscopic description as is relevant will be given in each case; these descriptions have either been taken from Brown (1957) or were contributed personally by Dr. G. M. Brown or Dr. I. D. Muir. The pyroxenes will be considered in order of crystallization, from the chilled margin rocks, through the border group and upwards through the layered series. Only the pyroxene constituents of the crystals will be described although other phases, notably magnetite, ilmenite, and clino-amphibole were often detected by the X-ray method.

The specimen numbers, which should strictly be prefaced by E.G., refer to rocks from the East Greenland geological collection at Oxford.

Chilled margin. The rock examined was 1825, which contains both clino- and ortho-pyroxene. The augite has fine lamellae parallel to (001), and the two crystals examined by X-rays proved that these consisted of pigeonite. One of the crystals showed in addition a trace of ortho-pyroxene, sharing the (100) plane with the augite, though no (100) lamellae could be detected optically.

Texturally the ortho-pyroxene is an inverted pigeonite containing exsolved blebs of augite. Two crystals were examined, both showing strong unsymmetrically placed diffraction spots due to disoriented material. As has been explained above, this is consistent with the formation of ortho-pyroxene by pigeonite inversion with non-retention of the axes. One of the crystals also showed weak oriented augite spots, presumably due to post-inversion exsolution. No sign of (100) lamellae was detected optically.

Gabbro-picrite. In rock 4526 A, the texture indicates that a diopsidic augite crystallized early, while poikilitic plates of ortho-pyroxene formed later from the interprecipitate liquid. No lamellae were observed microscopically in the augite, but all four crystals examined by X-ray diffraction gave spots indicative of two orientations of pigeonite in addition to the augite (fig. 4). In one orientation it seems that the

pigeonite shares the (001) plane with augite as usual, but in the second orientation the *c*-axis of the pigeonite is almost (but conclusively and reproducibly not quite) parallel to that of the augite. This unusual intergrowth is discussed later.

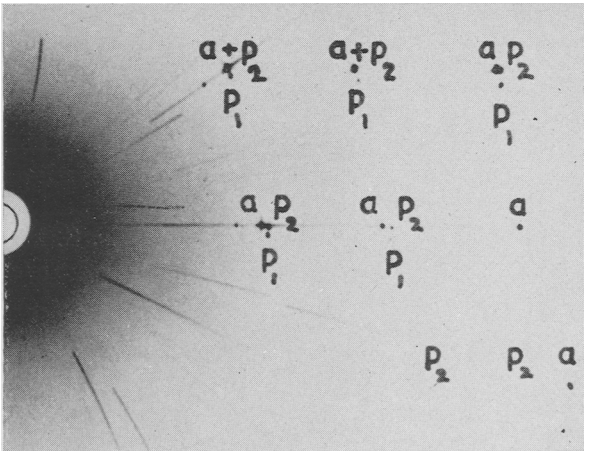

FIG. 4. Part of oscillation photograph of augite from 4526 (gabbro-picrite), showing reflections from the host augite (*a*) together with two orientations of pigeonite (p_1, p_2). Same conditions as fig. 1, enlargement $\times 1{\cdot}75$ approx.

The ortho-pyroxene shows lamellae parallel to (100), identified as augite microscopically; this is confirmed by the X-ray examination of three crystals.

Perpendicular feldspar rock. The rock 1851 described by Brown (1957) differs slightly from 1849, which was used for the X-ray work. For example, the augite of 1849 has many fine and closely-spaced (001) lamellae as well as the broad, widely-spaced (100) lamellae of ortho-pyroxene, whereas in 1851 there are very few of the fine lamellae. The two crystals of 1849 augite chosen for X-ray examination were not representative of the augite texture, for they contain virtually none of the broad lamellae. The photographs show augite and pigeonite sharing the (001) plane, and a small amount of ortho-pyroxene. This is interpreted as showing that the fine (001) lamellae consist of uninverted pigeonite, while the broad (100) lamellae are of ortho-pyroxene.

In contrast to 1851, in which the calcium-poor phase is entirely original ortho-pyroxene, in 1849 there is also some inverted pigeonite, with a blebby texture of augite exsolution. X-ray diffraction from

two of these crystals gave patterns with strong unsymmetrically placed spots, typical of inverted pigeonite in which the axial orientation has not been preserved; slight exsolution of augite after the inversion is also indicated.

Layered series. The augites of the lowest members of the layered series, up to about 30 metres, contain both coarse (100) lamellae and fine (001) lamellae, as in the perpendicular feldspar rock 1849, but with the proportion of (100) lamellae becoming smaller with increasing height.[1] From about 30 metres up to about 1800 metres only (001) lamellae have been reported. The low birefringence of both sets of lamellae together with the fact that the calcium-poor pyroxene in the same rocks is inverted pigeonite led Brown (1957) to conclude that these lamellae are now probably all ortho-pyroxene, though the fine (001) lamellae were originally pigeonite and have inverted on cooling.

About twenty augite crystals from various levels up to 1800 metres were examined. The X-ray photographs of five crystals of 4087 (0 m.) augite showed the presence of both pigeonite and ortho-pyroxene in varying proportions, whereas crystals from 4084 (400 m.), 2307 (850 m.), 1691 (1100 m.), 2573 (1700 m.), and 1907 (1800 m.) all proved to contain pigeonite sharing the (001) plane with the host augite, but no ortho-pyroxene. It is concluded, therefore, that the pigeonite in the (001) lamellae has not inverted in any of these rocks, even when the same crystal has exsolved (100) ortho-pyroxene lamellae below the inversion temperature.

Above about 1800 metres in the layered series no lamellae have been seen in the augites, though in a crystal from 4144 (2300 m.) a little pigeonite was detected by the X-ray method. At about the level of the purple band (2350–2500 m.), the pyroxene occurs as interlocking disoriented grains of a green colour, often crowded with opaque granular inclusions; associated with some of the green pyroxenes, sometimes internal to them and sometimes bordering them, is a brown pyroxene usually in crystallographic continuity with the green. Both the green and brown varieties are ferro-augites, though the green pyroxene appears to have a slightly lower calcium-content and is thought to be inverted from an iron-rich β-wollastonite (Wager and Deer, 1939); no exsolution lamellae have been observed in either variety. X-ray examination of the brown ferro-augites of 4143 (2400 m.) and 1881 (2500 m.) shows only the simple

[1] There is now some evidence to suggest that rocks previously considered as the lowest members of the exposed layered series may in fact be more properly assigned to the border group (Prof. Wager, oral communication).

diffraction patterns of augite with no detectable exsolution; the green pyroxenes of 1974 (2375 m.) and 1881 are also single-phase augites. The green pyroxene of 4143 does show exsolution of an appreciable amount of a pigeonite, whose composition is likely to lie close to clinoferrosilite. The diffraction patterns from this specimen are notable also in that they show a streak joining the spots from the augite and pigeonite components; although this has been recorded for specimens from other localities (Bown and Gay, 1957), this feature of the diffraction patterns is unique to those of the green pyroxene 4143 from among all the rest of the Skaergaard specimens examined. In the specimen 4139 (2600 m.) from the unlaminated layered series that was examined, there is again a green pyroxene mantled by a brown variety. It proved very difficult to obtain single crystals suitable for X-ray study. Photographs from the one crystal of the green pyroxene that was found suggest that there is no exsolution; no suitable specimens could be obtained from the brown variety.

The calcium-poor pyroxene of the layered series is predominantly inverted pigeonite, with complex exsolution textures ranging from poorly developed (100), (010), and (001) plates low in the series to well-developed regular (001) lamellae higher up. These lamellae developed before inversion, and the indices refer to the original pigeonite axes. In all these inverted pigeonites there was post-inversion exsolution of augite parallel to (100) of the ortho-pyroxene. As few of the crystals have retained the pigeonite axes on inversion, in the majority of cases the pre-inversion lamellae are not crystallographically related to the ortho-pyroxene axes and so cannot be usefully investigated by the X-ray method. Most of the crystals examined from 4087 (0 m.), 4084 (400 m.), 4341 (1300 m.), and 4430 (1600 m.) were of this type, giving strong unsymmetrically placed diffraction maxima of augite, together with weak oriented spots indicating the post-inversion lamellae of augite parallel to (100). A description of the axial scheme and diffraction patterns from a crystal of 4087 that has retained orientation on inversion has been discussed in a previous section.

Above 1300 metres a few grains of the pigeonite have resisted inversion, and these show (001) lamellae. X-ray examination of crystals from 4341 (1300 m.), 4430 (1600 m.), 1907 (1800 m.), and 4147 (2050 m.) confirmed that these lamellae are augite. Higher rocks contain no calcium-poor pyroxene as a separate phase. None of the pigeonite, whether host or lamellae, produced the diffuse diffraction spots with $(h+k)$ odd reported for other pigeonites by Bown and Gay (1957).

Discussion.

In general the correlation between the X-ray and optical identification may be considered most reassuring. The present investigation has, however, not merely confirmed but has also extended our knowledge of the Skaergaard pyroxenes in two respects. Firstly, of crystallographic interest rather than petrological, is the discovery that the (001) pigeonite lamellae in augite have not inverted to ortho-pyroxene, even though the same augite crystal may also contain (100) ortho-pyroxene lamellae, and though the associated calcium-poor pyroxene may be inverted pigeonite. The frequent non-retention of axes on inversion, and the presence in some of the rocks of small quantities of uninverted pigeonite may be regarded as evidence that pigeonite crystals experience difficulty in accomplishing the energetically desirable transformation to ortho-pyroxene on cooling. In the arrangement of silicon-oxygen chains pigeonite and augite are likely to be more closely related to one another than are augite and ortho-pyroxene. In the thin pigeonite lamellae it must be presumed that the structurally similar augite tends to stabilize the pigeonite structure, and to increase the general sluggishness of the transition to such a degree that, in the Skaergaard intrusion at least, no transformation has occurred. Whether the transformation has occurred in the augites of other plutonic masses is a matter for speculation and further experiment. Muir (1954) has proposed a similar explanation for the partial retention of pigeonite in a rock from the Beaver Bay diabase.

In addition, the present study has provided several instances of the detection of exsolution by the X-ray method where no lamellae have been described in the thin section work. Many of these are trivial, such as the discovery of pigeonite exsolution in 4144 (2300 m.) or the presence of ortho-pyroxene as well as pigeonite in the augite of 1825 (chilled margin). The appearance of pigeonite in two orientations in the augite of 4526 A (gabbro picrite) is a more remarkable instance, and is of some petrological significance. In the same rock the calcium-poor pyroxene is a bronzite (i.e. not an inverted pigeonite) that crystallized later than the augite from the interprecipitate liquid. As the trend of differentiation is from ortho-pyroxene to pigeonite it is certainly to be expected that any exsolution lamellae in the augite would be ortho-pyroxene. The perpendicular feldspar rock, thought to be of later formation, contains augite with broad ortho-pyroxene lamellae, which give place to pigeonite lamellae in still later rocks at the base of the exposed layered series. It is thus apparently anomalous that pigeonite should exsolve

from the augite of 4526 A. There remains also the problem of interpretation of the two orientations of pigeonite, so that this rock and others of the same horizon merit further investigation.

Conclusions.

The validity of the optical identification of lamellae as set out by Poldervaart and Hess (1951) has been largely confirmed, but the X-ray method has proved itself a valuable complementary tool to thin section work, particularly in the positive identification of very fine lamellae, and in cases where exsolution may be suspected but cannot be observed microscopically.

Acknowledgements. For the opportunity of working on pyroxenes from the Skaergaard intrusion the authors are deeply indebted to Prof. L. R. Wager, F.R.S., and Prof. W. A. Deer; from both Prof. Wager and Prof. C. E. Tilley, F.R.S., they have received much encouragement during the present investigation. They also wish to express their thanks to Dr. G. M. Brown and Dr. I. D. Muir for much helpful advice and many valuable discussions. Mr. K. O. Rickson took many of the X-ray photographs.

References.

BOWN (M. G.) and GAY (P.), 1957. Acta Cryst., vol. 10, p. 440.
——, 1959. Amer. Min., vol. 44, p. 592.
BROWN (G. M.), 1957. Min. Mag., vol. 31, p. 511.
MORIMOTO (N.), 1956. Proc. Japan. Acad., vol. 32, p. 750.
MUIR (I. D.), 1954. Min. Mag., vol. 30, p. 376.
POLDERVAART (A.) and HESS (H. H.), 1951. Journ. Geol., Chicago, vol. 59, p. 472 [M.A. **11**–290].
WAGER (L. R.) and DEER (W. A.), 1939. Medd. Grønland, vol. 105, no. 4, p. 1 [M.A. **11**–32].