172. The Existence of Monoclinic Pyroxenes with the Space Group $C_{2h}^{5} - P^{21}/c$

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All the X-ray studies of monoclinic pyroxenes, hitherto carried out, show, without exception, that they belong to the same space group $C_{2h}^{5} - C^{2}/c$.

T. Ito (1950) gave, however, an interesting suggestion about the space group of monoclinic pyroxenes. In his study of bronzite and hypersthene, he showed that the structure of the rhombic pyroxenes is to be regarded as a repeated twinning on (100) of a monoclinic pyroxene whose space group is not $C_{2h}^{6}$ (as in diopside) but is $C_{2h}^{5} - P^{21}/c$, owing to a slight change in Mg(Fe) positions. On the basis of this finding, he suspected the existence of a kind of monoclinic pyroxenes with the space group $C_{2h}^{5}$ instead of $C_{2h}^{6}$.

L. Atlas (1952) and H. Kuno and H. H. Hess (1953) observed some powder lines, in their studies of clinoenstatite and pigeonite, which could not be explained simply in terms of the space group $C_{2h}^{6}$. They attributed these lines as due to impurities. However, this might be indicating not only that these minerals are not of the space group $C_{2h}^{6}$, but also that monoclinic pyroxenes with the space group $C_{2h}^{5}$, as suggested by Ito, exist in nature.

In order to clarify this point, X-ray examinations were made of single crystals of pigeonite occurring as phenocrysts of augite-pigeonite-hypersthene andesite of Hakone Volcano described by Kuno (1936). The crystals, round in outline, are about 1 mm in length. In these crystals, pigeonite is always so intimately intergrown with a small amount of augite that it is very difficult to separate them from each other. The compositions of pigeonite and augite are Wo$_{16}$En$_{45}$Fs$_{39}$ and Wo$_{32}$En$_{37}$Es$_{31}$ respectively, as determined by Kuno from their optical properties, using the diagram by Hess (1949).

The Weissenberg photographs were taken about the $a$-, $b$-, and $c$-axes, and the [101]-, [101]-, and [011]-directions of pigeonite, up to the second or third layer in each case, using CuK$_\alpha$ radiation ($\lambda = 1.5418\ \text{Å}$). One of the Weissenberg photographs (rotation about [011], zero layer) is given in Fig. 1, where the X-ray reflections of both pigeonite and augite are observed (cf. Fig. 2).

As these two minerals have completely parallel orientation of the $b^*$- and $c^*$-axes, and their $a^*$-axes make an angle of about 2°,
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they must have the (001) plane in common.

The unit cell dimensions of pigeonite and augite determined are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Pigeonite</th>
<th>Augite</th>
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</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$9.709 \pm 0.005 ,\text{Å}$</td>
<td>$9.714 \pm 0.005 ,\text{Å}$</td>
</tr>
<tr>
<td>$b$</td>
<td>$8.940 \pm 0.005 ,\text{Å}$</td>
<td>$8.940 \pm 0.005 ,\text{Å}$</td>
</tr>
<tr>
<td>$c$</td>
<td>$5.240 \pm 0.005 ,\text{Å}$</td>
<td>$5.260 \pm 0.005 ,\text{Å}$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$71°30'\pm20'$</td>
<td>$73°48'\pm20'$</td>
</tr>
</tbody>
</table>

These values are in good agreement with those expected from Kuno and Hess's diagram of lattice constants of clinopyroxenes (1953) on the basis of the inferred compositions, except the length of the $b$-axis of augite which is same as that of pigeonite.

The extinction rules of the X-ray reflections of pigeonite are definitely not those of $C_{2h}^6$, but of $C_{2h}^5$, the reflections of $(hkl)$ being
present for any values of \( h, k, l \), those of \( (h0l) \) present only when \( l = 2n \), and those of \( (0k0) \) only when \( k = 2n \). Pigeonite, thus, has a primitive lattice whereas diopside a base-centred one.

The space group of augite, however, is \( C_{6h} \) as usual, the reflections of \( (hkl) \) being present only when \( h + k = 2n \), those of \( (h0l) \) only when \( h = 2n \) and \( l = 2n \), and those of \( (0k0) \) only when \( k = 2n \). Fig. 2 is the Weissenberg diagram corresponding to Fig. 1, and shows clearly the difference of the space groups of pigeonite and augite.

Atlas has shown, in his paper mentioned above, a 0-level \( b \)-axis precession photograph of clinoenstatite obtained by heating enstatite at 1400°C for 20 hours. An examination of this photograph shows that the same extinction rule holds as in pigeonite, the reflections of \( (h0l) \) being present only when \( l = 2n \) (for example, those of \( (702) \) and \( (304) \) are very strong). Clinoenstatite has, therefore, the space group \( C_{2h} \) as pigeonite.

The structure analysis of pigeonite is now in progress here.

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References


Postscript

After this paper had been submitted to the Japan Academy, the writer received a letter from Drs. P. G. Gay and M. G. Bown of the University of Cambridge, England, through which he knew that they obtained almost the same results independently.