161. X-Ray Study of the Phase Transformations of Enstatite

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Among seven polymorphs so far reported of enstatite, MgSiO$_3$, three major ones have been established: orthoenstatite (orthorhombic), clinoenstatite (monoclinic), and protoenstatite (orthorhombic). Warren and Modell (1930) and Ito (1935, 1950) studied the structure of orthoenstatite and revealed that the structure is built up of the unit cells of clinoenstatite repeatedly twinned. Ito (1950) also pointed out that the space group of clino should be $P2_1/c$ instead of $C2/c$, which is the space group of diopside, to produce the ortho structure of space group $Pbca$ upon twinning. Later, Morimoto (1956) and Bown and Gay (1957) experimentally verified this Ito's prediction. Recently, Burnahm (1964) refined the structures of the ortho and clino forms of FeSiO$_3$, Morimoto and Koto (1969) the structure of orthoenstatite, and they all demonstrated that Ito's theory of twinned space groups applies to these structures. The structure of protoenstatite stable above 985°C was proposed by Atlas (1952), and his proposal was endorsed by Smith (1959) by the powder diffraction technique. Brown et al. (1961) then discussed the structural relationship among these three polymorphs of MgSiO$_3$.

The phase relationship between these polymorphs, which had long been a point in dispute among research workers, seems to have since settled; clino-, ortho-, and proto-enstatite are the low-, intermediate-, and high-temperature forms respectively (Sclar et al., 1964), though some doubt is now being held about the thermodynamical behaviour of the clino phase (Munoz, 1966). The X-ray investigation of enstatite at high temperatures by the single-crystal method was first carried out by Brown and Smith (1963). They found that protoenstatite, when quenched from high temperatures, usually converts itself into clinoenstatite of low crystallinity, and upon slow cooling, into a disordered orthoenstatite. The present report deals with part of the work we have undertaken to unravel the structural change of one form of enstatite to another at elevated temperatures.

Natural crystals from three localities were employed in the present study: clinoenstatite, with an approximate composition of $(Mg_{0.9}Fe_{0.1})SiO_3$ in a volcanic rock from the Cape Vogel Area, Papua
(Dallwitz et al., 1966); orthoenstatite, (Mg$_{0.95}$Fe$_{0.05}$)SiO$_3$, in a plutonic rock from Kamogawa, Chiba, Japan; and orthoenstatite, (Mg$_{0.9}$Fe$_{0.1}$)SiO$_3$, in eclogite from Kimberley, Africa.

A crystal, apparently single, from Papua kindly supplied by Drs. Thompson and Dallwitz is of the dimensions, $3 \times 5 \times 10$ mm$^3$, and shows a perfect outer form. The morphological symmetry of the specimen was determined as orthorhombic with an axial ratio in good agreement with those of the proto phase derived from its X-ray data (Fig. 1 and Table I). Under the polarizing microscope, however, a thin section of the specimen cut parallel to (010) shows lamellae twinning on (100). Some fragments of the crystal were examined by X-ray methods, and were confirmed to be twinned clinoenstatite, producing sharp diffraction spots, though some of them being associated with sharp streaks of weak intensity. These discloses that the specimen is clino- after proto-enstatite.

Upon comparison of our precession pattern of a fragment, which happened to have twin individuals in an equal amount, with the Weissenberg photograph published by Byström (1943) as that of $\beta$-MgSiO$_3$ (orthorhombic with $a=36.4$, $b=8.79$, $c=5.20$ Å), a striking resemblance was noticed between the two. In fact, when we converted our precession pattern into a Weissenberg pattern having the same shape as Byström’s one, we found they were substantially identical. Therefore, $\beta$-MgSiO$_3$ is strongly suspected to be clinoenstatite polycrystally twinned with an equal amount of twin individuals.

The specimens of ortho from Kamogawa and Kimberley showed sharp orthorhombic patterns typical of the single crystal of this

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Table I. Axial ratios of protoenstatite

<table>
<thead>
<tr>
<th>Axial Ratio</th>
<th>Description</th>
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<tr>
<td>1.058 : 1 : 0.609</td>
<td>From the cell constants given by Smith (1959)</td>
</tr>
<tr>
<td>1.063 : 1 : 0.610</td>
<td>From the cell constants obtained by the authors at 1,100°C</td>
</tr>
<tr>
<td>1.065 : 1 : 0.617</td>
<td>From the morphological study of the Papua specimen</td>
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phase and were identical with each other.

Synthetic crystals were also prepared from the starting material with the composition of $3\text{SiO}_2 + 2\text{MgO} + 2\text{B}_2\text{O}_3$. This material, after pre-heated by a gas burner, was kept at $1,350^\circ\text{C}$ in a platinum crucible for two days, and then quenched. The products were confirmed to be disordered clino polysynthetically twinned and associated with some amount of disordered ortho, their (100) planes being parallel to each other.

Each of these specimens was mounted on the top of a thermocouple with the aid of alumina cement, and the thermocouple was set up on a goniometer head of a precession camera equipped with a small furnace. The temperature of the specimen was controlled by an electronic amplifier and a motor-driven transformer which changed the amount of power supply to the furnace according to the information fed back from the thermocouple.

First, in order to examine the transformation from clino- to ortho-forms. The specimen from Papua was employed, and the $h0l$ precession photographs were taken at $1,000^\circ\text{C}$. The diffraction pattern obtained was almost the same as the pattern at room temperature of the disordered clino-forms we synthesized, showed short diffuse streaks from some of the diffraction spots along the $a^*$ direction, and broad maxima of intensity were observed along the streaks and at the positions of the diffraction spots to be expected from an ortho crystal in such an orientation as for its (100) plane to be parallel to that of the clino, indicating the formation of disordered ortho in the clino specimen. As the lapse of time at this temperature, both the spots from clino and the broad maxima began transferring their intensities to the streaks connecting them, which suggested that the temperature was too high for the further growth of the ortho phase. Therefore, the temperature was slightly lowered ($960^\circ\text{C} \sim 995^\circ\text{C}$), and a new fragment of the Papua crystal was kept under this condition for three days. Though the short diffuse streaks mentioned above was observed in the X-ray photographs taken at the end of the treatment, no sign of formation of the ortho phase was detected. The transformation from clino to ortho-forms will no doubt be caused by the regularly repeated twinning on the unit cell scale of clinoenstatite as pointed out by Ito (1935, 1950). However, as to the rate of this progress, the experimental results described here reveal that though the twinning takes place at $1,000^\circ\text{C}$ promptly here and there in a clino crystal, that is, nuclei of ortho phase are easy to form, it seems almost hopeless to obtain experimentally a well-ordered crystal of it. It is considered that an exorbitantly lengthy period of annealing will be required to bring the twinning
into such regular repetition as realized in the single crystal of ortho phase. It is also to be noted that the ortho nuclei, once formed in clinoenstatite, can grow bigger after prolonged heating at temperatures between 800° and 1,000°C as already shown by Brown and Smith (1963), but it is difficult even to form the nuclei at these temperature in such well-ordered a clino crystal as the Papua enstatite.

Next, the formation of proto- from clino- and ortho-enstatite was examined. As pointed out by Smith (1959), a stretching of the SiO₃ chains is required for this transformation, and accordingly the mechanism of the transformation includes shifts of atoms inside the structural unit. The disordered clino crystal synthetically prepared was heated up to 1,000°C within 90 minutes and a photograph then taken indicated that the specimen was still in the course of transformation into photo form. So, the temperature was raised to 1,100°C, and the transformation, by retaining the orientation of (100), to a single crystal of proto enstatite was completed within a short period of time. The cell constants of the proto crystal thus derived were measured as: \( a=9.34, b=8.79, c=5.36 \) Å (±0.01 Å).

The clino specimen from Papua was treated in the same way as above, and it was found that it could complete the transformation into proto form after heated at 1,100°C for three hours, namely, for a period longer than that required with the synthetic disordered clino form. This fact is believed to be due to that the proto is brought about from clino-structure with the aid of ortho nuclei, which were contained in a sufficient amount in the synthetic disordered clino crystals from the beginning, but had to be newly produced in the Papua specimen in the course of heating above 1,000°C. Accordingly, the polysynthetic twinning, which gives rise to the ortho nuclei, may be looked upon as the one premonitory of the transformation from clino to proto.

On the other hand, when the ortho specimen from Kimberley was heated up to 1,000°C within one hour and kept at the temperature for five hours, no change of the X-ray pattern was observed. However, when heated at 1,150°C for longer than three hours, relative changes in intensity were noticed among some of the spots. It was confirmed in the next photograph taken under the same condition that the specimen had completely been converted into a single crystal of proto-form having the same axial directions as those of the original ortho crystal. This indicates, in combination with the above cases of clinoenstatites, synthetic and natural, that though the ortho nuclei play an important role in the transformation, the completed regular twinning as realized in the ortho structure gives little help, if not a strong resistance, to the transformation.
It should be pointed out here that 'high-clinoenstatite' reported to appear between 995° and 1,010°C (Perotta and Stephenson, 1965) could not be detected in the present investigation in spite of repeated experiments. Though this phase has lately been confirmed with a specimen containing, in some quantity, cations larger than Mg (Smith, 1969), it seems improbable for it to appear in the Mg-rich materials under consideration.

Finally, protoenstatite derived from the synthetic disordered clino crystals was cooled from 1,100°C at the rate of 100°C/hour, and photographs were taken at the intervals of 50°C for 30 minutes for each. The proto phase was observed to persist without any appreciable change down to 650°C, where the whole body of the specimen suddenly transformed itself, with an abrupt shortening of the c axis, into disordered clino polysynthetically twinned on (100) whose orientation was again retained as it had been in the proto crystal. As far as the temperature of this transformation is concerned, the present result is in good agreement with that obtained by Brown and Smith (1963) from their high-temperature powder diffraction study, but our study by the single-crystal method clearly indicated a sudden instead of gradual change reported by them.

Among the results of the present study, it is perhaps worthwhile to pay special attention to the one that to obtain a crystal of orohenstatite of an appreciable size through transformations from clino and proto is hardly possible. In contrast to this, all the specimens of terrestrial enstatite, perhaps with the only exception of the Papua enstatite, are of the ortho phase and most of them are crystals with a well-ordered structure at room temperature, suggesting that scarcely ever has ortho transformed itself into clino in nature. These facts seem to support the view that the clino phase can be produced, perhaps except under high pressure, only through quenching from the temperatures higher than the stability range of the ortho phase (Boyd and Schairer, 1964).

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References

Meeting, Amer. Geophys. Union, 121.