ORTHOPYROXENE-HIGH-LOW CLINOPYROXENE INVERSIONS

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1. Introduction

High temperature single crystal X-ray studies of a natural iron-rich orthopyroxene (Mg0.30Fe0.70)SiO3 indicated two structural changes. Upon heating at 1050º ± 25º C for 60 hr, a crystal slowly inverted from an orthorhombic pyroxene of space group \( \text{P}b\text{ca} \) to a twinned high clinopyroxene of space group \( C2/c \) with a reorientation of the crystallographic axes. Upon cooling below 700ºC, the high clinopyroxene inverted rapidly to a low clinopyroxene of space group \( P2_1/c \) with retention of the axes.

2. Observations

A prismatic cleavage fragment of Bl-9 orthopyroxene (Virgo and Hafner[1]) was sealed in an evacuated silica glass capillary. The crystal was heated to 1050º ± 25º C and extra reflections appeared in the first six-hour exposure. The new reflections completely replaced the orthorhombic pattern after 60 hr at that temperature. The new pattern, of apparently irrational orientation, was oriented at temperature and found to be that of a monoclinic pyroxene (space group \( C2/c \)) twinned on 100. The common \( c \)-axis of the monoclinic twins was inclined 30º to that of the orthorhombic phase. The relative orientation and slow growth of the new phase indicate that the inversion was reconstructive, involving the breaking of silicon-oxygen bonds. Weak, diffuse reflections not belonging to the pattern of high clinopyroxene may result from a clinopyroxene of a different orientation or a slight amount of oxidation product. Attempts to orient and identify them were unsuccessful.

Upon quenching, the high clinopyroxene inverted to a low clinopyroxene (space group \( P2_1/c \)) with strong reflections of the type \( h + k = 2n + 1 \) and a significant reduction in cell dimensions. Upon reheating, these reflections completely disappeared above 800ºC, but were again present in patterns taken at 700ºC. The cell dimensions of the three polymorphs are compared in Table 1.

A complete literature review is given by Smith [2]. Bowen and Schairer [3] first explored the enstatite-ferrosilite join and regarded a monoclinic form as the stable polymorph above about 1000ºC. Much doubt has been thrown on their work by the discovery of non-quenchable high temperature forms such as protoenstatite and by the production of clinopyroxenes at comparatively low temperatures in the presence of \( \text{car} \). Perrotta and Stephenson [4] introduced the \( \text{i} \) clinoenstatite for a phase considered to in,ef from \( \text{l} \) clinoenstatite above about 1000ºC. Morimoto and Tokonami [5] interpreted diffuse reflections of the type \( h + k = 2n + 1 \) from some natural clinoenstatites as the result of inversion from a liicci temperature phase of space group \( C2/c \). Smith [6] indexed Perrotta and Stephenson's powder pattern on the basis of a monoclinic cell of space croup \( C2/c \) and that all Fe clinopyroxenes may undergo a non-quenchable inversion to \( \text{il} \)-\( \text{ll} \) clinoenstatite. The cell dimensions obtained by Smith are included in Table 1 for comparison.

3. Conclusions
The high-low clinopyroxene inversion predicted by Smith [6] is confirmed, and the inversion is indicated to be displacive, occurring rapidly on quenching. The inversion from orthopyroxene to twinned high clinopyroxene is reconstructive, requiring the breaking of silicon-oxygen bonds. A systematic study of the entire \((\text{Mg,Fe})\text{SiO}_3\) composition range is now underway to determine (a) the variation of the high-low clinopyroxene inversion with composition, (b) the nature of the atomic bonding in the high clino and proto forms, and (c) whether the ortho-clino inversion is crystallographically irrational over the entire composition range.

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References

2. J.V. Smith, Crystal structure and stability of the MgSiO\(_3\) polymorphs: physical properties and phase relations of Mg, Fe pyroxenes, M.S.A. Special Paper No. 2 (1969) in press.