American Mineralogist, Volume 70, pages 141–148, 1985

Structural aspects of phase transitions in Fe–Mg–Ca pyroxenes

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Abstract

For the Fe-rich silicate pyroxenes, the structural characteristics of the metastable high-temperature phase transitions vary with exact chemical composition and thermal history. X-ray diffraction studies of single Opx crystals show that the Opx–Cpx transitions of Fe-rich pyroxenes can be classified into three groups according to their differing thermal behavior and the orientational relationships between the two phases. Group I consists of the transition between orthoferrosilite and high clinoferrosilite, which is reversible, rapid, and topotactic. Group II is characterized by the transitions in Ca-free pyroxenes, which are topotactic, but non-reversible with fairly rapid transition rates when the Mg content is small, and with slower rates when it increases. Group III consists of Fe–Ca or Fe–Mg–Ca pyroxene transitions, which are neither topotactic nor reversible, but which have rapid rates of transition. A comparison of these three groups provides useful information for studying the mechanisms of these transitions.

Introduction

Natural pyroxenes with compositions in the pyroxene quadrilateral (Fe–Mg–Ca pyroxene diagram) belong to one of the following four classes of polymorph: *Pbca* orthopyroxene (Opx), $P2_1/c$ clinopyroxene, $C2/c$ clinopyroxene, and *Pbcn* protopyroxene (Ppx). All calcium-rich pyroxenes have $C2/c$ monoclinic symmetry, but calcium-poor (Mg, Fe) pyroxenes have *Pbca* or $P2_1/c$ symmetry at room temperature. $P2_1/c$ clinopyroxene (LCpx) transforms to $C2/c$ clinopyroxene (HCpx) at high temperature. The existence of $C2/c$ high-temperature clinopyroxene for Ca-poor compositions was predicted by Smith (1969) and confirmed experimentally by Smyth (1969) and Prewitt et al. (1970) as a non-quenchable, high-temperature form. The transition between $C2/c$ and $P2_1/c$ pyroxenes was found to be of a displacive type, and it has rapid, reversible, and topotactic characteristics. All the other transitions among the four low-calcium pyroxene polymorphs including protopyroxene are of a reconstructive type that involves the breaking and rearrangement of M cation–oxygen bonds.

The phase transitions among the four calcium–poor polymorphs have been studied by many workers using natural and synthetic pyroxenes under different temperature and pressure conditions, e.g., Smith (1969), Sadanaga et al. (1969). For the magnesium-endmember pyroxene (enstatite), Smyth (1974a) found that the transition between clinoenstatite and protoenstatite is rapid, reversible, and oriented. The transition from orthoenstatite to clinoenstatite was reported as a sluggish order–disorder type transition by Smyth (1974a), but Murakami et al. (1982) found that synthetic orthoenstatite crystals transformed instantaneously to protoenstatite at temperatures above 1100°C. Some investigators consider that the orthoenstatite–low clinoenstatite transformation takes place only under non-hydrostatic stress (Coe, 1970; Coe and Kirby, 1975), although Grover (1972) reported that it

0003–004X/85/0102–0141$02.00

could occur in the presence of a flux. Smyth (1969) and Smyth and Burnham (1972) were successful in transforming a natural Opx crystal to twinned HCpx by heating, but they observed neither crystallographic orientational relationships between these two phases nor the reverse of this transition under any annealing condition.

The iron-endmember pyroxene, ferrosilite, is stable only at high pressure and is found rarely as a mineral (Jaffe et al., 1978). Sueno and Prewitt (1983) studied the metastable high-temperature transitions among orthoferrosilite (Ofs), high clinoferrosilite (HCfs), and low clinoferrosilite (LCfs) using synthetic crystals and found that they were rapid, reversible, and topotactic, as was observed previously for the transition between protoenstatite and clinoenstatite.

It is clear that the varying behavior of pyroxene transitions depends partly on compositional differences. We have been interested in how solid solution in pyroxene structures affects transitional behavior, and have carried out high temperature X-ray experiments on several iron-rich Opx samples in order to examine how differences in composition affect the transitions among these pyroxenes with the object of understanding structural changes in the rest of the pyroxene system.

Experimental

The synthetic Opx samples used in this study were kindly supplied by D. H. Lindsley of the State University of New York at Stony Brook. The methods of the synthesis are reported by Turnock et al. (1973). The chemical compositions of these samples, based on starting materials used in synthesis and confirmed by using electron microprobe analysis of several samples (Lindsley, personal communication), are shown in Table 1. Several crystals around 100 μm in diameter were selected from each pyroxene sample of different composition. Each crystal was mounted on a silica fiber using high-temperature cement and sealed in an evacuated silica-glass capillary to prevent oxidation. The high-temperature precession camera technique and the details of the heater used in this study were reported by Brown et al. (1973). The crystal samples were heated on a high-temperature precession camera with a rotating-anode X-ray source (Mo*K*α, 50 kV, 150 mA) while monitoring the structure change with *h0l* precession photographs (μ = 10°) using Kodak X-Omat or Fuji RXO fast film in contact with an intensifying fluorescent screen. This allowed us to obtain satisfactory photographs in 3–5 minute exposures for a crystal around 100 μm in size. In a typical experiment, the crystal temperature was increased from 24°C to 900°C in 20 minutes and then was increased slowly until a transition was detected. The temperatures quoted in this paper are thought to be accurate to ±10°C, but the relative errors are within ±2°C.

Table 1. The chemical compositions of orthopyroxenes and their observed transition temperatures

Starting materials (orthopyroxene, Pbca)	Transition temperatures
Fs	1020–1025° C
$Fs_{90}En_{10}$	1075° C
$Fs_{80}En_{20}$	1082° C
$Fs_{75}En_{25}$	1087° C
$Fs_{98}Wo_{2}$	1030° C
$Fs_{95}Wo_{5}$	1037–1045° C
$Fs_{72}En_{23}Wo_{5}$	1086° C

Ferrosilite transition

The detailed behavior of the transition between Ofs and HCfs ($FeSiO_3$) has been reported by Sueno and Prewitt (1983) as a rapid, reversible, and topotactic transition. The transition temperature is listed in Table 1.

Ca-free pyroxene transition

$Fs_{90}En_{10}$. An Opx crystal 100 μm in size was heated on the precession camera. When the crystal temperature reached 1075°C, the Opx to Cpx transition was detected in a monitoring photograph (three-minutes exposure time, Fig. 1b.). The newly-present clinopyroxene is (100)-twinned *C2/c* HCpx. The orientations between Opx and HCpx are crystallographically related as shown below:

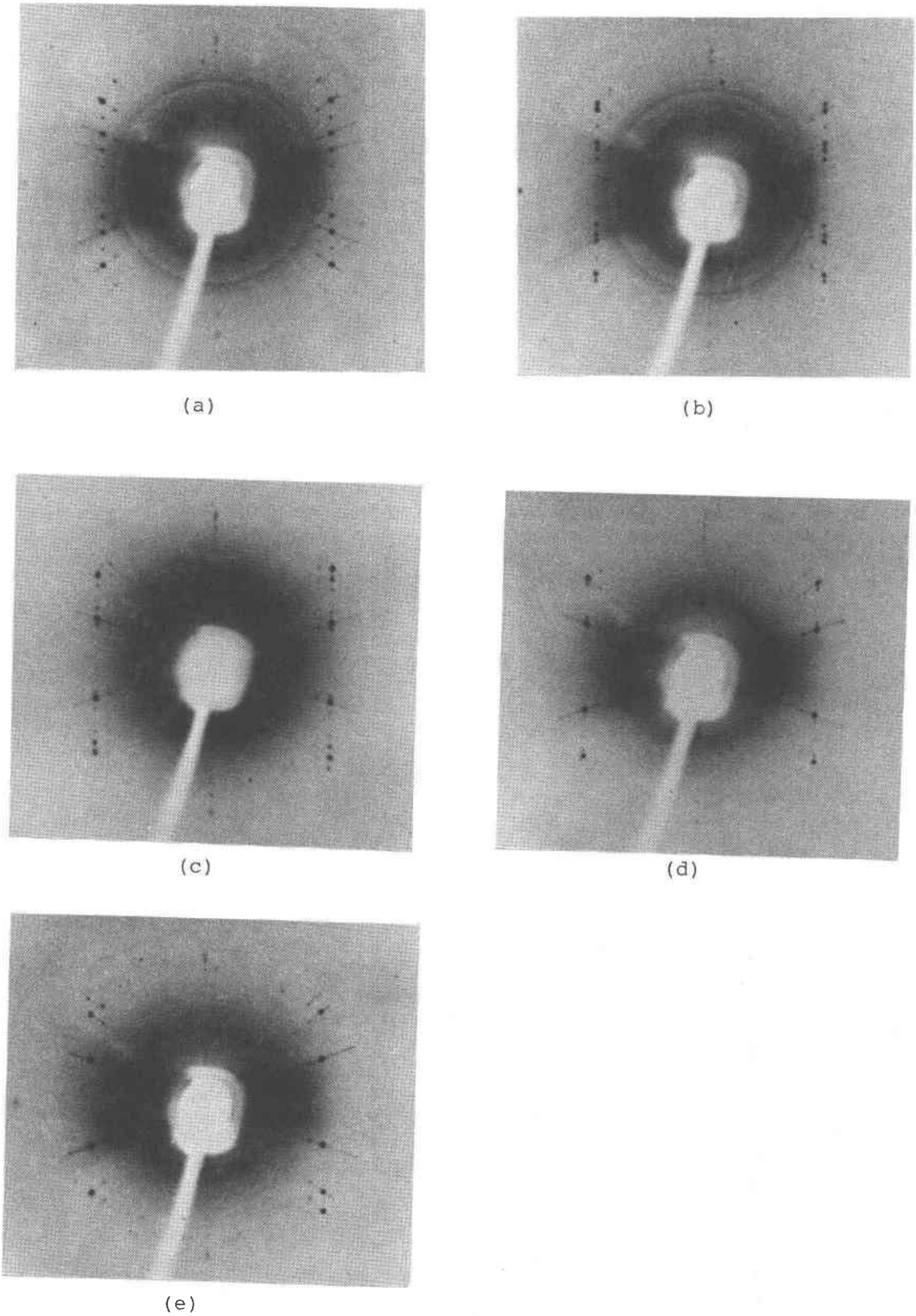
a (Opx) ‖ **a*** (HCpx)

b (Opx) ‖ **b** (HCpx)

c (Opx) ‖ **c** (HCpx)

From the observed diffraction intensities, it is apparent that each of the two components in the twinned HCpx are similar in volume. The crystal was quenched and another 10° photograph was taken using the same precession camera settings. In this photograph, diffraction spots of the clinopyroxene, which had $P2_1/c$ symmetry (LCpx) through the quenching interval, are much stronger than those of the Opx. The relative volumes between the LCpx and Opx are approximately 3:1 at this stage (Fig. 1c). The crystal was then heated again while taking 10° precession photographs. No significant change could be detected until 1075°C when the intensities of the Cpx diffraction spots increased once again (Fig. 1d). Upon cooling the crystal to 1020°C, a temperature low enough to stop the transition reaction, another photograph was taken (Fig. 1e). In this photograph, all the Opx diffraction spots had vanished and some faint, randomly-distributed, unidentified extra spots had appeared. All the HCpx diffraction spots were sharp and no diffuse streaks were observed, in contrast to diffraction patterns of transformed pure ferrosilite where the some Bragg reflections are always accompanied by diffuse streaks parallel to the **a*** direction. The crystal temperature was decreased at a fairly slow cooling rate to room temperature while taking 10° precession photographs, but the reverse transition from Cpx to Opx could not be observed. The HCpx to LCpx transition was observed at a temperature between 740 and 760°C. The total time for completion of the transition at 1075°C was within five minutes.

$Fs_{80}En_{20}$. The Opx to HCpx transition at this composition was observed at 1082°C (three minute exposure time). The crystal was then quenched and a photograph



(a)

(b)

(c)

(d)

(e)

Fig. 1. Behavior of thermal transitions of $Fs_{90}En_{10}$ orthopyroxene. (a) Precession photograph (μ = 10°) before heating. (b) Photograph (*h*0*l* plane) taken at 1075°C (three minute exposure). (c) Photograph taken at 24°C after quenching from (b). (d) Reheating at 1075°C. (e) Taken at 1020°C after cooling from (d).

taken at room temperature. In this photograph, the relative intensities of the newly-present LCpx are much weaker than those observed in the photograph of $Fs_{90}En_{10}$ pyroxene taken after the three-minute heating at 1075°C. This suggests that the rate of transition is slower for the pyroxene with higher En content. We repeated the heating (three minutes at 1082°C) and cooling (to 1000°C) of the crystal, taking 10° precession photographs with a three minute exposure time for each thermal treatment until the diffraction pattern of the Opx disappeared. At this composition, the Opx to HCpx transition was completed within fifteen minutes (five photographs exposed at 1082°C). The HCpx had a topotactic relationship to the Opx with the same orientation as observed for Fs and $Fs_{90}En_{10}$. The reverse transition from HCpx to Opx could not be observed during the final cooling treatment despite the fairly slow cooling rate.

$Fs_{75}En_{25}$. The crystal size of this composition was much smaller than those of the other pyroxene samples (less than 50μm), and it required a ten-minute exposure time for a satisfactory precession photograph. At this composition, HCpx appeared at 1087°C with the same topotactic orientation as observed for the other Ca-free pyroxenes. The heating (10 minutes at 1087°C) and cooling (to 1000°C) treatments were repeated while monitoring the structure change with 10° *h0l* precession photographs every 10 minutes. The transition was completed after thirty minutes' total heating time at 1087°C (three photographs, each with a ten minute exposure time). The reverse transition was not observed during the cooling stage. The HCpx to LCpx transition was observed at 780°C.

Mg-free Fe-Ca pyroxene

$Fs_{98}Wo_2$. A crystal about 70 μm in size was heated on the precession camera while taking photographs with five-minute exposure times. When the crystal temperature approached 1030°C, many extra, but randomly-distributed and sharp, diffraction spots appeared in the photograph. Then the crystal was quenched and a photograph was taken at room temperature with the same precession camera settings. This photograph showed only randomly-distributed diffraction spots; the diffraction patterns for the original Opx and the expected topotactically-arrayed Cpx did not appear. After recording the precession camera settings, this new crystal was oriented and identified as a (100)-twinned LCpx with a unit cell compatible with the composition before the transition, based on the cell parameter-composition diagrams for Cpx (Turnock et al., 1973). However, no topotactic relationship between the original Opx and the transformed Cpx could be identified.

$Fs_{95}Wo_5$. A crystal was heated on the high-temperature precession camera while taking photographs every five minutes. When the crystal temperature reached 1037°C, many sharp reflections with random distribution appeared in an *h0l* precession photograph. The crystal was quenched and another photograph was taken. The Opx reflections had vanished and only the randomly-distributed spots remained. The new phase was oriented by adjusting the goniometer head on the precession camera and found again to be a (100)-twinned Cpx without any topotactic relation to the Opx. Then, five more single crystals of this composition were selected and the same heat treatment repeated. Four of the five crystals transformed rapidly within five minutes to twinned HCpx at a temperature around 1037–1045°C, each with a different random orientation. However, one crystal showed different behavior from the others. This crystal originally included a slight amount of topotactically-oriented and twinned LCpx within the Opx as shown in Figure 2a. When the crystal temperature reached 1060°C, randomly-distributed reflections appeared on a photograph taken at this temperature (Fig. 2b) and, at the same time, the diffraction intensities of the topotactically-oriented HCpx increased. The crystal was quenched and a photograph taken at room temperature (Fig. 2c). This photograph shows that the randomly-oriented reflections had become much stronger and the reflections from topotactically-arrayed LCpx had become much weaker, but no Opx diffraction spots were observed. The crystal was again heated for about two minutes at 1060°C and a photograph was taken after quenching (Fig. 2d): the topotactically-arrayed Cpx was found to have disappeared. The remaining randomly-distributed reflections were identified as originating from a (100)-twinned Cpx with irrational orientation.

Fe–Mg–Ca pyroxene

$Fs_{72}En_{23}Wo_5$. A crystal of about 100 μm in size was heated on the precession camera while taking 10° photographs, each with five minutes' exposure time. New diffraction spots in random distribution were observed in a photograph taken at 1087°C. In contrast to the Ca–Fe pyroxenes, the Opx was still present even after quenching from 1086°C. Then the crystal was heated again for five minutes at 987°C and quenched. In a room-temperature photograph, all Opx reflections had vanished. After reorientation, the new "crystal" was identified as mainly a (100)-twinned Cpx accompanied by several other irrationaly-oriented fine Cpx subcrystals as shown in Figure 3. None of these Cpx subcrystals showed topotactical relations to the original Opx. The heat treatment was repeated for another crystal of this composition and the results were similar. The results of heating experiments on the pyroxenes are summarized in Table 2.

Discussion

The Opx–Cpx transitions of iron-rich pyroxenes can be classified into three groups according to their differing thermal behavior and the orientational relationships between the two phases. The transition of pure ferrosilite is unique and constitutes Group I because of its reversible, rapid, and topotactic characteristics described by Sueno

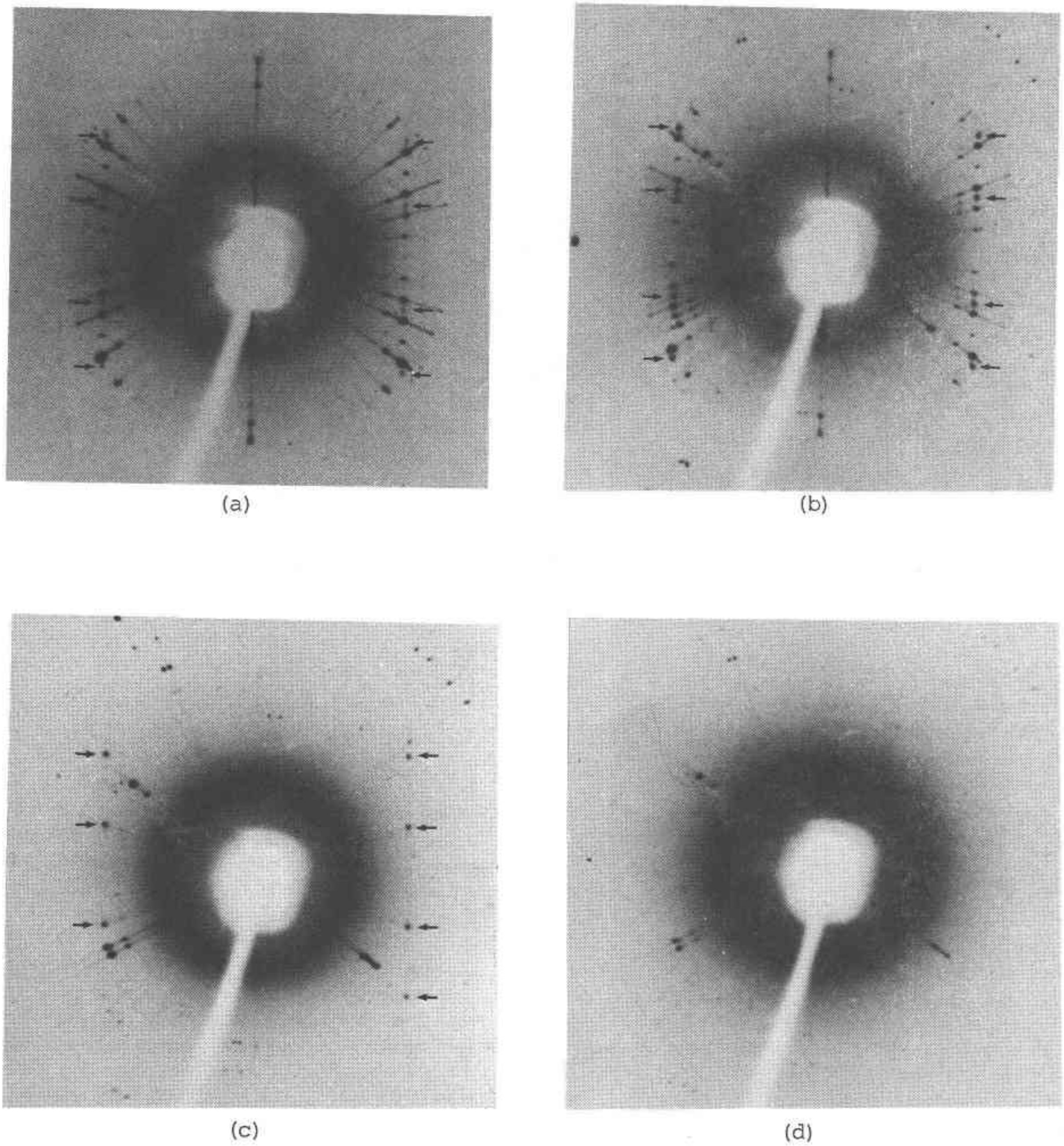

(a) (b) (c) (d)

Fig. 2. Behavior of the Opx to Cpx phase transition of a crystal ($Fs_{95}Wo_5$) that originally included a slight amount of topotactically-oriented twinned Cpx (shown by small arrows). (a) An *h0l* precession photograph (μ = 10°) before heating. (b) Photograph taken at 1060° (10 minute exposure time). The appearance of randomly-distributed reflections and a relative increase of the intensities of the topotactically-oriented Cpx can be observed. (c) Photograph taken at room temperature after quenching from 1060°C. In this photograph the Opx reflections have disappeared and are replaced by stronger randomly-oriented reflections and weakened topotactically-arrayed Cpx reflections. (d) Photograph taken at room temperature after heating for two minutes at 1060°C The topotactically-oriented Cpx reflections have completely disappeared.

and Prewitt (1983). Smyth (1974a) studied the transition of enstatite using the single-crystal high-temperature X-ray technique, and confirmed rapid, reversible, and topotactic behavior for the transition between protoenstatite and (100)-twinned clinoenstatite. Smyth called this a martensitic transition based on the temperature-controlling behavior; therefore, if this designation is correct, the transition in ferrosilite is also martensitic, even though

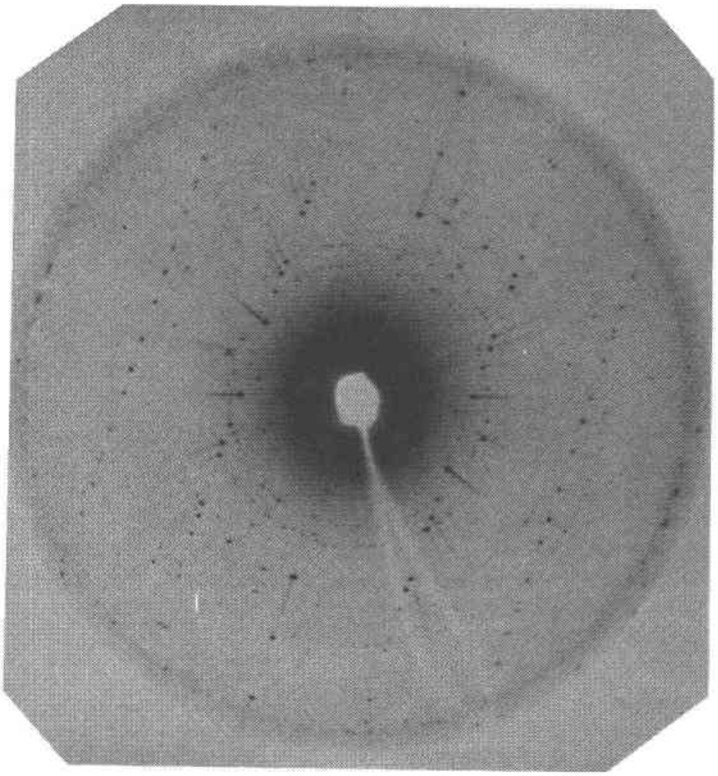


Fig. 3. Precession photograph of Cpx transformed at 1086°C from Opx ($Fs_{72}En_{23}Wo_5$). The "crystal" was reoriented to the largest Cpx subcrystal for taking this photograph, but reflections for several other irrational Cpx orientations can be observed.

the transition involves the breaking of some of the Fe–O bonds.

Group II is characterized by the transitions in Ca-free pyroxenes, which are topotactic, but non-reversible with fairly rapid transition rates when the Mg content is small, and with slower rates of transition when it increases. Group III consists of Fe–Ca or Fe–Mg–Ca pyroxene transitions, which show neither topotactic nor reversible features, but which have rapid rates of transition. It is worth noting that one of five Opx crystals ($Fs_{95}Wo_5$) that originally intergrew with a topotactically-oriented Cpx showed a topotactic Opx to Cpx transition at an early stage of heating. However, the topotactic Cpx quickly retransformed to Cpx with irrational orientation. This shows that for this composition, the topotactically-oriented Cpx does not persist, in contrast to those with irrational orientations. This suggests that these two kinds of Cpx have different atomic arrangements as well as different orientational relationships to the original Opx. Throughout the transitions of these three groups, the high-temperature form is commonly a (100)-twinned HCpx, except for the pyroxene with $Fs_{72}En_{23}Wo_5$ composition that transformed to an aggregation of several domains of (100)-twinned HCpx with different orientations. From the observations of diffraction intensities of individuals twinned on (100), it was concluded that the volumes of domains in the two twinned orientations are similar for all compositions.

Table 2. Characteristics of the ortho-clino phase transitions in Fe-rich pyroxenes

Composition	Reversibility upon cooling	Orientational relationship	Apparent time for transition
Fs	Yes	Topotactic	Rapid
$Fs_{90}En_{10}$	No	Topotactic	Less than 5 min.
$Fs_{80}En_{20}$	No	Topotactic	Less than 15 min.
$Fs_{75}En_{25}$	No	Topotactic	Less than 30 min.
$Fs_{98}Wo_2$	No	Irrational	Less than 5 min.
$Fs_{95}Wo_5$	No	Irrational	Less than 5 min.
$Fs_{72}En_{23}Wo_5$	No	Irrational	Less than 10 min.

The different thermal characteristics observed for the three pyroxene groups introduce several questions:

(1) Why is the Ofs to HCfs transition martensitic?

(2) Why do the Ca pyroxenes have non-topotactic transitions?

(3) Why do the Ca pyroxenes transform rapidly even when they have a high Mg content?

(4) Why do the Ca-free Fe–Mg pyroxenes have higher transition temperatures than do the other pyroxenes?

(5) Why does the Ca-free pyroxene with higher Mg content need a longer transition time?

(6) Why do the Fe–Mg–Ca pyroxenes not show a reverse transition?

It is not possible to give exact answers to all of these questions because not enough information is available. However, it is possible to give qualitative explanations for some questions based on our present knowledge of pyroxene crystal chemistry.

The Mg endmember pyroxene, enstatite, has at least four polymorphs and the thermal characteristics of these polymorphs are complicated (e.g., Smith, 1969; Sandanaga et al., 1969). In a study of the Pen–HCen transition, Smyth (1974a) proposed an unorthodox M-cation movement for the mechanism of pyroxene transition, i.e., a mechanism in which the M1 cation goes into the M2 site and becomes the M2 cation, while the M2 cation goes into the M1 site and becomes the new M1 cation. He suggested that if this exchange is required for a coherent (topotactic) transition in pyroxenes, it would explain why the martensitic transition was observed only for the pure Mg endmember that can allow the exchange of M cations without inducing a distortion in the pyroxene structure. The Fe endmember pyroxene, ferrosilite, could also undergo a similar transition because both the M1 and the M2 sites are occupied by Fe (Sueno and Prewitt, 1983), thus providing an answer for question (1), i.e., why the transitions in ferrosilite are martensitic.

The "M-cation exchange" hypothesis also explains the non-topotactic transition of Ca pyroxenes (question (2)). If this exchange is necessary in a temperature-induced topotactic transition, Ca cations, which always prefer to stay in the larger M2 sites, are forced into the small M1 sites in the Cpx. This exchange would induce a large distortion in the structure and the resulting Ca-exchanged Cpx structure would be energetically very unstable. This may be a reason why the topotactically-transformed Cpx observed for one of the $Fs_{95}Wo_5$ crystals is retransformed rapidly to the pyroxene with the other orientation. The non-topotactic transitions observed for Ca pyroxenes probably take place through a nucleation and growth mechanism, that is, the structure of the low temperature form may become unstable at the transition temperature and, once a nucleus of the high-temperature form appears somewhere in a crystal, it introduces a rapid crystal growth of (100)-twinned Cpx through the complete rearrangement of atoms at a higher growth rate, as observed in dendritic crystal growth. The irrational orientation of the Cpx suggests that the nucleation of the Cpx is facilitated by crystal imperfections (heterogeneous nucleation) with the nucleus oriented in a direction to reduce the strain energy of the nucleation site. This could also explain why the rates of transition of Ca pyroxenes were similar to those of the pyroxenes with different Mg contents (question(3)), because the transition goes through the crystal growth process with complete atomic rearrangement, and the small difference of Mg content in Ca pyroxenes may not have an influence over the growth rate of new Cpx phase.

In the structure of irrationally-transformed Cpx, Ca ions probably occupy the M2 site. For Ca-free pyroxenes, exchange of M1 and M2 atoms during the transition is acceptable because of the similarities in ionic radii between Mg^{2+} and Fe^{2+} ions. However, M-cation exchange may require a higher transition temperature and longer transition time than for the pure ferrosilite composition because of the higher energy barrier for the movement of the larger Fe^{2+} ion to the small M1 site. This may be an answer for questions (4) and (5). Question (6) should be considered separately for Ca-bearing and Ca-free (Fe,Mg) pyroxenes, because the Ca ion, even in small quantities, has a significant effect on the M2–O distance (Smyth, 1973) and on the properties of the pyroxene. For Ca pyroxenes, monoclinic pigeonite can accommodate more Ca than can orthopyroxene. This explains why Cpx with Ca^{2+} in the structure did not show the reverse transition to Opx upon simple cooling. The reason for non-reversibility of Ca-free Fe–Mg pyroxenes, despite the similar ionic radii of Mg and Fe ions, is not so easy to understand, and the possible explanation of the non-reversibility must await the results of more detailed experiments.

In the above discussions, Smyth's M-cation exchange movement was assumed to be valid, but this movement is not yet confirmed experimentally. Structure and site occupancy refinements of $Fs_{90}E_{10}$ Opx and topotactically-transformed Cpx would help to solve this problem. Smyth and Burnham (1972) succeeded in transforming a natural metamorphic orthohypersthene of the composition $En_{31.5}Fs_{66.3}Wo_{1.5}$ into a (100)-twinned clinohypersthene by heating at 990°C for three days in an evacuated silica-glass capsule although they did not report the actual time for transition. This pyroxene is a natural one and the chemical composition is different from the pyroxenes used in this study, but their experiment proved that even the natural crystal, presumably different in complex microtextures and minor elements, containing 0.002 Ti and 0.005 Al to cations per six oxygens (Smyth, 1974b), can transform within an experimentally-possible period.

The present study confirmed that the different thermal transition phenomena of orthopyroxenes are profoundly influenced by differences in chemical composition. However, as evident from the review of ortho-clinoenstatite transformation by Buseck et al. (1980), the different phenomena will also be related to microstructures such as crystal defects, fine inclusions, twinning, order–disorder of atoms, environmental differences such as heating and cooling rates of the crystals, the existence of shear stress, and other factors.

Acknowledgments

We thank Dr. D. H. Lindsley for providing synthetic Opx crystals, and Mr. K. Kakefuda for his help with our high temperature experiments. This study was supported by Grant No. EAR81-20950 from the National Science Foundation and a Research Fellowship to C.T.P. from the Japan Society for the Promotion of Science.

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Manuscript received, July 5, 1983;
accepted for publication, September 4, 1984.