Experimental Study on the Polymorphism of Enstatite[1]

JOSEPH R. SMYTH

Lunar Science Institute, 3303 Nasa Road 1, Houston, Texas 77058

Abstract

The polymorphism of enstatite has been studied under various heating and cooling rates using high temperature single-crystal X-ray techniques. Rapid quenches of protoenstatite produce twinned low clinoenstatite, while slower cooling rates produce mixtures of clinoenstatite and up to fifty percent orthoenstatite. Large strain energies appear to account for the martensitic nature of coherent transformations between enstatite polymorphs and the observation that different quench rates produce differing products. A modification of the transformation model of Sadanaga, Okamura, and Takeda (1969) and Coe (1970) better accounts for the observed nature of the transformations. No evidence of a stability field for high clinoenstatite above that of protoenstatite was observed when a crystal of protoenstatite underwent partial, incongruent melting to forsterite plus liquid.

Introduction

Since the first attempted synthesis of enstatite by Ebelman in 1851, the polymorphism of enstatite has been the subject of much study and the source of much confusion and controversy. An understanding of the relative stabilities of the various polymorphs of enstatite is of primary importance to the study of meteorites and of the few terrestrial rocks in which they occur. Although the polymorphs observed at room temperature, orthoenstatite and clinoenstatite, are essentially isomorphous with their iron-rich equivalents, hypersthene and pigeonite respectively, there are some important differences between iron-rich and iron-free low-calcium pyroxenes. The most important difference is the occurrence for the enstatite composition of a third major structure type, protoenstatite, which has not been observed for other pyroxene compositions. The existence of this polymorph greatly complicates the stability relations in the enstatite corner of the pyroxene quadrilateral.

At the composition of pure $MgSiO_3$, there exist three well-characterized structure-types which have distinct topologies: enstatite or orthoenstatite, orthorhombic, $a = 18.2$ Å; protoenstatite, orthorhombic, $a = 9.1$ Å; and clinoenstatite, monoclinic. Clinoenstatite has both low temperature (primitive) and high temperature (C-centered) modifications. Space groups and cell dimensions of these struc-

tures are presented in Table 1[2]. A critical review of studies on the polymorphism of enstatite by Smith (1969b) consolidated much of the work up to that time. However the relative stabilities of the polymorphs are still far from being well understood. Because proto and high clino are not quenchable, ambiguous and inconsistent results have been obtained from the study of quenched runs. Moreover, the products obtained appear to vary with different starting materials, different temperature maxima and duration of runs, and particularly with different heating and cooling rates and variations in the amount of shear present. A brief review of the relative stability relations and the mechanisms of transitions between polymorphs will serve here to outline some of the current controversies.

Proto appears to be the stable form of $MgSiO_3$ from about 1000°C to at least 1300°C and perhaps all the way to the incongruent melting point at about 1557°C as indicated by Kushiro (1972). It is unstable at room temperature and will invert spontaneously to a mixture of low clino and ortho upon quenching. The proto structure has a very small *M*2 site, and appears to be limited to the enstatite corner of the quadrilateral. Kushiro (1972), Nakamura (1971), and Yang (1973) indicate

---

[2] For the sake of brevity and clarity of prose style, I shall refer to protoenstatite, orthoenstatite, high clinoenstatite, and low clinoenstatite as proto, ortho, high clino and low clino respectively. If any other composition is intended, it will be so stated.

TABLE 1. Space Groups and Cell Parameters of Enstatite Polymorphs

Name	Space Group	a(Å)	b(Å)	c(Å)	β(°)	V(Å^3)	T(°C)
Low Clino*	P2$_1$/c	9.606(1)	8.815(1)	5.169(1)	108.33(1)	415.5(1)	20
High Clino**	C2/c	9.864(6)	8.954(4)	5.333(3)	110.03(4)	442.5(5)	1100
Ortho*	Pbca	18.225(1)	8.815(1)	5.175(1)	—	831.3(1)	20
Proto***	P2$_1$cn	9.304(4)	8.902(4)	5.351(3)	—	443.2(5)	1100

* Stephenson et al. (1966)   ** Smith (1969a)   *** Smyth (1971)

that the structure will accept no more than about two mole percent wollastonite, and it has never been observed with compositions more iron-rich than about Fs$_{13}$.

Ortho is isostructural with bronzite, hypersthene, and eulite, but like proto, the structure does not occur with more than about three mole percent wollastonite. There is fairly general agreement that bronzite, hypersthene, and eulite are the stable low temperature forms of low-calcium pyroxene in their respective composition ranges; however, there is no such general agreement for enstatite. Because of its abundance relative to low clino, Smith (1969b) favors ortho as being the stable low temperature form. Grover (1972), however, has succeeded in crystallizing low clino below 566°C in the absence of shear using a MgCl$_2$ flux, and feels that ortho is stable only down as far as 566°C, and below that low clino is the stable form.

High clino (Perrotta and Stephenson, 1965, as reinterpreted by Smith, 1969a) is a non-quenchable high temperature modification of low clino occurring above 980°C. It is presumed isostructural with high clinohypersthene (Smyth and Burnham, 1972) and high pigeonite (Brown *et al,* 1972) which are apparently stable high temperature forms. At the enstatite composition, high clino may have a true field of stability occurring between that of proto and the incongruent melting point—as suggested by Kuno (1966)—or it may be everywhere metastable. However, due to experimental difficulties, there have been no single crystal studies reported above 1200°C. The work of Kushiro (1972) and Yang (1973) indicates a field of iron-free pigeonite, which is probably a high pigeonite, occurring at compositions from En$_{95}$ Wo$_5$ to En$_{90}$ Wo$_{10}$ above 1280°C. This field, however, does not extend to the Ca-free composition.

Low clino can be produced by several different methods, but it is possible that it, too, has no true field of stability in the absence of shear stresses. Low clino results from the quench of proto. If high clino has a stability field above 1200°C, low clino would be expected to result from the quench of high clino. Low clino is stabilized relative to ortho by the presence of shear (Coe, 1970), and can be produced in kink bands by shearing ortho. As suggested by Grover (1972), low clino may have its own field of stability in the absence of shear below 566°C. Because of the several possible means of forming low clino, its presence cannot be taken as being indicative of any particular cooling history.

Some of the difficulties in defining the stability relations between the polymorphs of enstatite are due to the coherent nature of transitions between them. The ortho, proto, and clino forms differ primarily in their a^* stacking sequence, but the structures are topologically distinct. Inversions must therefore be at least partially reconstructive, and large activation energies may be required though the free energy differences between structures are likely to be small. Unlike some other pyroxene compositions (En$_{43}$Fs$_{57}$ to En$_{22}$Fs$_{78}$, Smyth, 1969, 1970a, 1970b, and unpublished), all polymorphic transitions observed at the enstatite composition are coherent, that is the a^*, b, and c crystallographic directions are unchanged. Therefore Mg–O bonds but not necessarily Si–O bonds are broken during transitions. Differing cooling rates are known to affect these transitions (Brown and Smith, 1963), but a complete evaluation of these effects has never been attempted. As heating and cooling rates are particularly pertinent to the study of meteorites in which enstatites are common, it was decided to attempt such an evaluation. A second major cause of uncertainty in enstatite polymorphism is the lack of single crystal observations above 1200°C. It is not known whether there is a stability field of high clino above that of proto as suggested by Kuno (1966). A reconnaissance of polymorphism above 1200°C is needed to resolve this question.

Experimental Studies

The study consists of two parts; first, the observation of the effects of different heating and cooling rates on transitions to and from proto; and

second, a brief reconnaissance of transitions in the range 1200° to 1550°C. Because proto and high clino are not quenchable phases, crystals of enstatite were examined directly at temperature using recently improved high temperature single-crystal X-ray techniques on the precession camera. For the first part of the study, temperature control ±5°C for periods up to two days in the range 500° to 1050°C was required. This was achieved by the addition of a feedback controller device to the heater described by Smyth (1972). For the second part of the study, an electrolytic oxyhydrogen micro-torch was used. The geometry of the precession camera allowed both heat sources to be used simultaneously so that the crystal did not have to be cooled when changing from one to the other. All experiments were performed with the crystal mounted in air directly on the join of a Pt–Pt10%Rh thermocouple.

The material used for the study was enstatite from the Norton County, Kansas, enstatite achondrite. This material contains ortho and up to 40 percent low clino in a very fine-scale intergrowth. An {h0l} reciprocal lattice plane shows small intensity maxima at positions corresponding to low clino and diffuse streaks parallel to a^* in addition to the regular ortho reflections. Although disorder of this type is atypical of the enstatite achondrites, this material was chosen because it has been observed to invert readily to proto within 48 hours at 1200°C (Smyth, 1971) whereas well-ordered orthoenstatite tends to be a bit more sluggish (Brown and Smith, 1963; Sadanaga et al, 1969). By various heat treatments, nearly pure ortho or low clino can be obtained from this material. Reid and Cohen (1967) give the following chemical analysis of the Norton enstatite: MgO, 40.3; SiO_2, 59.0 weight percents; and in ppm: Ti, 30; Al, 230; Cr, 140; Fe, 100; Mn, 360; Ni, 50; and Ca, 2060.

A single crystal of the Norton County enstatite was mounted on the join of a Pt–Pt10%Rh thermocouple by natural adhesion to hot platinum. The output of this thermocouple was fed into the controller for the resistance furnace and was also continuously recorded. Using only the Pt40%Rh-wound resistance heater, temperatures up to 1150°C could be maintained ±10°C for several hours, and up to 1050°C ± 5°C indefinitely. For temperatures above 1150°C, an oxyhydrogen microtorch supplied from a Henes electrolytic gas generator was used. Without feedback control, this heater

maintained temperatures from 1100° to 1600°C ± 30°C for periods of up to several days. The heating history and polymorphs observed in the crystal are outlined in Table 2.

TABLE 2. Estimated Structural Composition of an Enstatite Single Crystal under Various Heating and Cooling Conditions

Film Number	Temp. °C	Minutes at Temp. Prior to Exposure	Exposure Time in Minutes	Heater*	Or	Cl	Pr	Fo**
100	20		1200		60	40	--	--
500	800	60	150	F	90	10	--	--
110	20	10	360		90	10	--	--
530	1230	20	15	T	50	--	50	--
531	1230	50	15	T	25	--	75	--
532	1230	90	15	T	15	--	85	--
533	1230	120	15	T	10	--	90	--
534	1230	140	120	T	5	--	95	--
535	1230	300	15	T	5	--	95	--
	650	5	0	F				
536	800	5	15	F	60	30	10	--
537	900	5	15	F	70	20	10	--
538	1000	5	15	F	30	--	70	--
539	950	3	15	F	30	--	70	--
540	900	3	15	F	30	--	70	--
541	850	3	15	F	30	--	70	--
542	800	3	15	F	30	--	70	--
543	750	3	15	F	60	20	20	--
130	20	10	120		60	40	--	--
544	925	10	15	F	80	20	--	--
545	950	2	15	F	80	20	--	--
546	975	2	15	F	80	20	--	--
547	975	30	15	F	80	10	10	--
548	985	2	15	F	70	10	20	--
549	1000	2	15	F	60	--	40	--
550	1000	30	15	F	60	--	40	--
551	1000	165	15	F	60	--	40	--
552	1180	10	15	F	20	--	80	--
553	1180	30	120	T	10	--	90	--
554	1180	1080	30	T	--	--	100	--

At this point, crystal was quenched in less than one second.

| 150 | 20 | 2 | 60 | — | | 100 | -- | -- |

At this point, temperature was increased at approximately 100°C/min.

460	1200	2	15	T	10	--	90	--
555	1200	40	15	T	--	--	100	--
556	925	2	15	F	--	--	100	--
557	850	2	15	F	--	--	100	--
558	800	2	15	F	--	--	100	--
559	775	2	15	F	--	--	100	--
560	750	2	15	F	--	--	100	--
561	725	2	15	F	--	--	100	--
562	700	2	15	F	--	--	100	--
563	675	2	15	F	40	30	30	--
564	675	30	15	F	40	30	30	--
565	675	60	480	F	40	30	30	--
566	675	660	15	F	40	30	30	--
567	650	2	15	F	40	40	20	--
568	625	2	15	F	50	40	10	--
569	600	2	15	F	50	45	5	--
160	20	2	15	F	50	50	--	--
570	1250	15	15	T	--	--	100	--
571	850	30	15	F	--	--	100	--
572	850	150	150	F	--	--	100	--
573	850	390	15	F	--	--	100	--
574	850	540	60	F	--	--	100	--
575	850	630	600	F	--	--	100	--
576	850	1440	80	F	--	--	100	--
577	900	15	120	F	--	--	100	--
578	900	150	60	F	--	--	100	--
580	1300	20	45	F	--	--	100	--
581	1400	20	30	T	--	--	90	10
582	1400	20	30	T	--	--	30	70
200	20	180	1400		--	30	--	70

*F indicates the Pt resistance furnace; T, the oxyhydrogen torch
**Abbreviations: Or, ortho; Pr, proto; Cl, low clino; Fo, forsterite.

Results

The unheated specimen of the Norton County enstatite contained 60 to 70 percent ortho and the rest low clino. Reactions which occur on heating can be summarized as follows: No reactions were observed below 650°C. In the range 650° to 975°C ortho grows slowly at the expense of clino. Above 975°C proto forms rapidly at the expense of clino, and above 1000°C proto forms more slowly at the expense of ortho. When the crystal was predominantly in the ortho form, more time was required to invert to proto (films 530–535) than when the crystal was more than fifty percent clino (films 150, 460). On cooling, proto showed no tendency to invert to either ortho or low clino in the range 1000° to 700°C (films 536 through 562) and was maintained metastably in this range for up to 24 hours. Below 700°, there is a rapid inversion to either ortho or low clino, depending upon the cooling rate. A quench accomplished in a second or less produced nearly pure twinned clino, while slower cooling through the range 700° to 600°C produced crystals containing as much as fifty percent ortho.

When the reactions were examined under conditions of precisely controlled step-wise heating and cooling, the rapid proto-to-clino and clino-to-proto transitions appeared martensitic in nature. Figure 1 shows a series of {h02} reciprocal lattice rows of a crystal of Norton County enstatite undergoing the clino-to-proto inversion. The first reflections of proto appear at 975°C. These appear in the first 15-minute exposure and do not increase in intensity when held at that temperature for 45 minutes; however, there is a noticeable increase in the intensity in the first 15-minute exposure taken at 985°C. Likewise, there was a large increase in the intensity of the proto reflections when the temperature was increased to 1000°C, but no additional change was observed when the crystal was held at that temperature for 2½ hours. Figure 2 shows a similar type of reaction occurring on the cooling of proto between 700° and 600°C. The amount of proto remaining does not appear to vary with time at constant temperature. The amount of proto remaining at 675° did not appear to change when held at that temperature for 12 hours, but an immediate change was apparent when the temperature was lowered to 650°C. These observations are consistent with a martensitic transition in which strain energies at the interface between two phases are large enough in comparison to the energy difference between phases to cause the transition to occur over a range of temperatures.

Using the oxyhydrogen flame as the heat source, precession X-ray photographs of the crystal were taken at temperatures up to the incongruent melting point of enstatite. These experiments gave no evidence of a field of high clino at temperatures greater than those of the proto field as indicated by the hypothetical phase diagram of calcium-free pyroxenes of Kuno (1966). In light of the rapid inversion rate of low clino to proto at 975°–1000°C, it is probable that if a high clino field existed at this
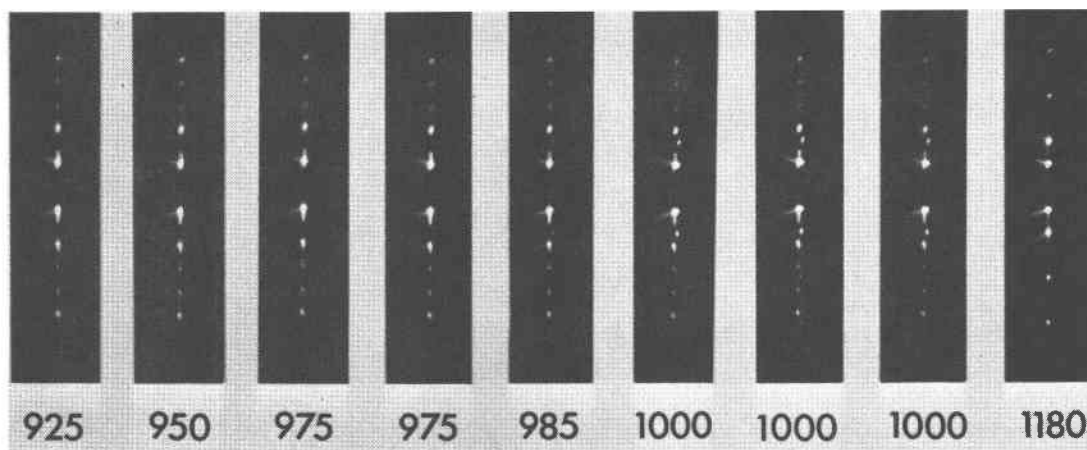

Fig. 1. Series of {h02} reciprocal lattice rows taken of a crystal undergoing the clino-to-proto transition. (Film 544 through 552 inclusive; see Table 2). The temperature indicated below each film is in degrees Celsius. Each film is a 15-minute exposure on Polaroid Type 57 film taken with Zr-filtered Mo radiation.
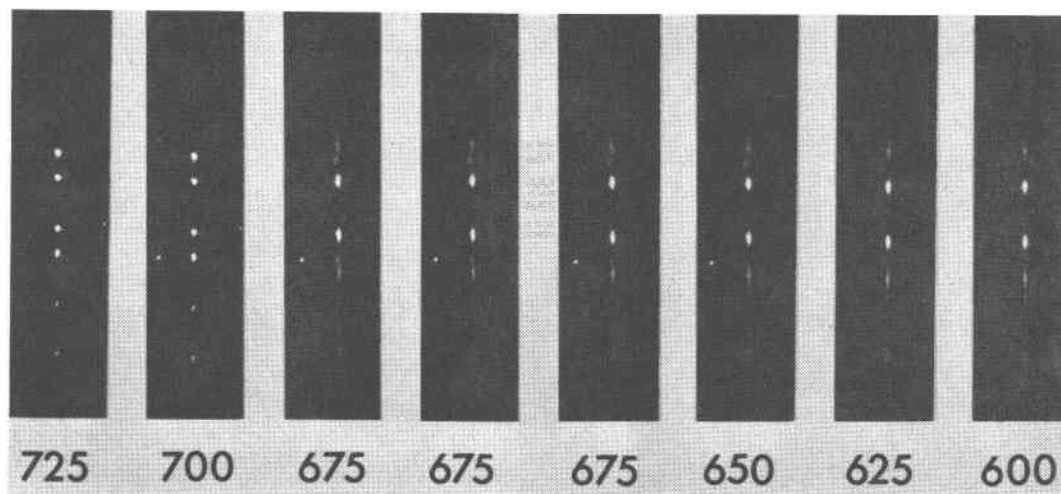
Fig. 2. Series of {h02} reciprocal lattice rows taken of a crystal undergoing the proto-to-clino transition (Films 561 through 569 inclusive; see Table 2). Each film is 15-minute exposure on Polaroid Type 57 film taken with Zr-filtered Mo radiation. The temperature is indicated below each film in degrees Celsius.

composition, it would have been observed in these experiments. At the incongruent melting point, several small crystals of forsterite formed which bore no epitaxial relationship to the enstatite. One such crystal was oriented and a *c*-axis zero-level precession photograph was taken. After termination of heating experiments, a 72-hour Gandolfi Camera exposure revealed no evidence of any crystalline phases other than enstatite and forsterite.

Discussion

Perhaps the most significant observation in these experiments is the difference between the ortho-to-proto, proto-to-ortho, and clino-to-ortho transitions on one hand, and the clino-to-proto and proto-to-clino transitions on the other. The ortho-to-proto transition appears from films 530 through 535 to be time-dependent, requiring up to several days for completion at a constant temperature of 1200°C. The amount of time required depends on the temperature and on the ratio of ortho to low clino in the original sample. This transition and its inverse require a coordinated motion of alternate *pairs* of octahedral layers. The inverse of this reaction could not be observed independently of a rapid proto-to-clino transition, and the proto-to-ortho transition may not take place without the clino phase as an intermediary. When low clino is heated in the range 650°–950°C, it undergoes a similar time-dependent inversion to ortho. This was observed in films 500 and 536–537. This

inversion behaves as a non-reversible, time-dependent ordering transition. The inverse of this reaction was not observed and has only been observed by other workers under conditions of externally-applied stresses.

In sharp contrast to the above reactions, the proto-to-clino inversion displays all the characteristics of a martensitic transition (Christian, 1964). The reaction is reversible, oriented, and diffusionless. It is a temperature-controlled and time-invariant reaction which takes place essentially instantaneously as the temperature is raised or lowered, but the amount of crystal inverted changes with temperature so that the inversion spreads over a temperature interval. In such transitions, large compensatory strain energies due to differences in cell dimensions cause a first-order transition in a single-component system to occur over a temperature interval. As can be seen in Figure 1, the difference in *c*-axis length between clino and proto at 985°C is about two percent and indicates a large amount of strain at the phase boundaries.

The observation of a reconstructive transition taking place almost instantaneously requires that there be an exceedingly simple mechanism for the transition. Since polymorphs of enstatite differ from each other primarily in the stacking sequence along the a^* direction of the *b-c* layers of tetrahedral chains, and since all polymorph transitions in enstatite retain the orientation of the a^*, *b*, and *c* axes, the simplest mechanism for transitions be-

tween polymorphs is to slide layers of tetrahedral chains over one another, breaking Mg–O but not Si–O bonds. For all such transitions, the minimum
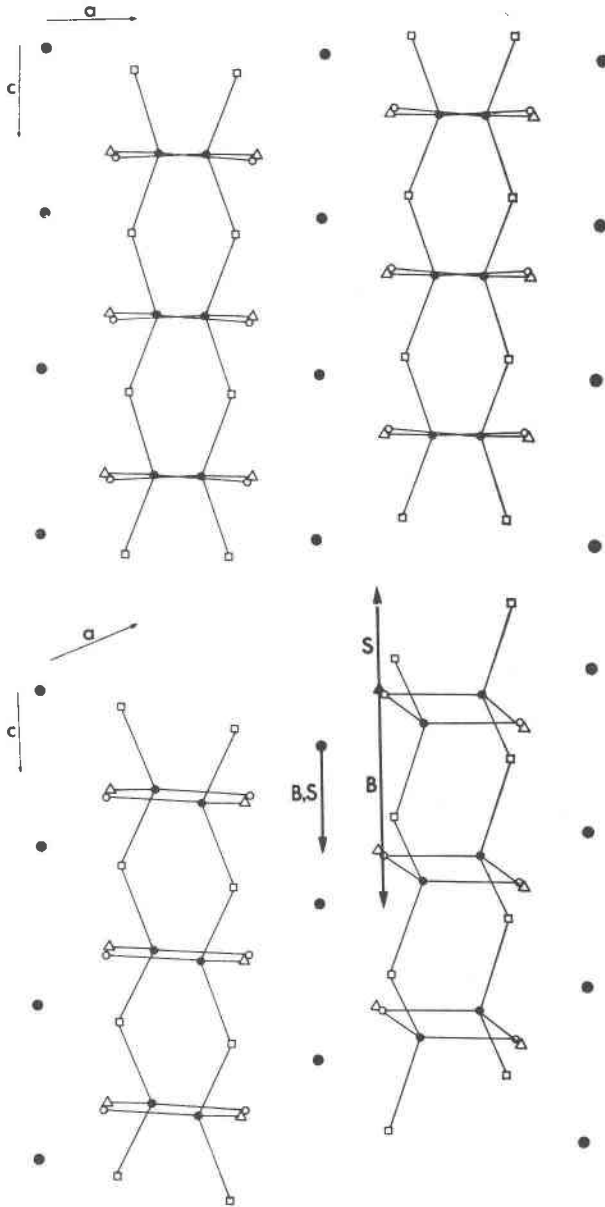
movement is required if the relative motion of chain layers is parallel to c, the chain axis. Since pyroxene structures contain no mirror symmetry, the directions of relative motion along c are not equivalent. The two mechanisms which have been proposed by previous workers, one by Brown, Morimoto, and Smith (1961) and the other by Sadanaga *et al* (1969) and independently by Coe (1970), differ primarily in the direction of relative motion of the tetrahedral chains along c.

Looking only at the amount of relative movements of the tetrahedral chain layers, the Brown *et al* model requires slightly more movement than the Sadanaga-Coe model (Fig. 1). However, both models apparently require an identical motion of the M-cations resulting in a movement of the M-cations in a direction opposite to that of the chain layers in the latter model, as illustrated in Figures 3 and 4. Coe and Müller (1973) confirmed that the relative movements of the chains of the latter model are consistent with the observed orientation of low
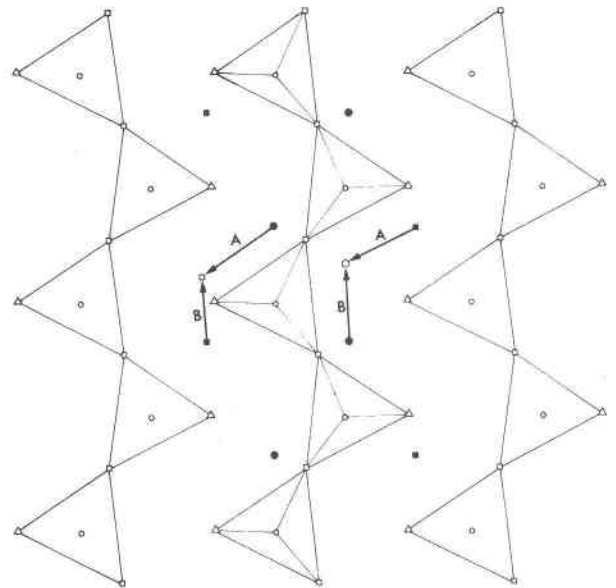

FIG. 3. A *b*-axis projection of the structures of low clino (below) and proto (above). Symbols used are: small solid circle, Si; open circle, O1; triangle, O2; square, O3; large solid circle— $M1$ and $M2$ (coincident in this projection). The arrows indicate the motion required of the M cations and silicate chains of clino to achieve the topology of proto according to the two proposed transition models. The arrows labeled **B** indicate the motion required by the model of Brown *et al* (1961) and those labeled **S** by the model of Sadanaga *et al* (1969) and Coe (1970). Note that the motion of the M cations is the same for both models.

FIG. 4. An *a*-axis projection of a hypothetical pyroxene layer indicating the motion of M-cations during a transition. The symbols used are the same as those in Figure 3 except that the solid circles indicate $M1$, the solid squares $M2$, and the large open square and circle indicate the alternate position of $M1$ and $M2$ after transition. The arrows labeled **B** represents the motion required by the models of Brown *et al* (1961), Sadanaga *et al* (1969), and Coe (1970) and corresponds to the arrow labeled **B, S** in Figure 3. The arrows labeled **A** represent an alternative motion suggested here (see text).

clino formed in kink bands in ortho (natural Bamle enstatite).

I would like to propose here a slight modification or clarification of the mechanism of Sadanaga *et al* (1969) and Coe (1970) which simplifies the atomic movements and allows the motion of the M cations to be in the same direction as the tetrahedral layers. If $M1$ is allowed to become $M2$, and $M2$ to become $M1$ by a motion corresponding to the arrows labeled A in Figure 4, their total movement can be minimized and the c-axis projection of their paths will be in the same direction as the movement of the layer of tetrahedral chains. If this type of exchange is required by coherent transformation in pyroxenes, it would explain why transformations are coherent in enstatite in which both M-sites are occupied by Mg, whereas the ortho to high clino transformations in Fs_{57} and Fs_{70} are completely reconstructive (Smyth, 1969, and unpublished).

Conclusions

These experiments have clearly demonstrated the differing natures of the proto-to-ortho and ortho-to-proto transitions on one hand and the proto-to-clino and clino-to-proto transitions on the other. The former are relatively slower, order-disorder type transitions while the latter are rapid martensitic transitions. These differences have been discussed in terms of the relative structural differences between polymorphs, and a structural model proposed by previous workers has been modified slightly to account for the observed difference in the nature of the transitions.

Although these experiments have yielded some valuable insight into the relative stabilities of the enstatite polymorphs and the nature of transitions between them, there are still some unanswered questions concerning stability relations, particularly below 600°C. As it now appears, proto is the stable phase from 1000°C up to 1557°C whereupon there is a non-epitaxial inversion to forsterite plus liquid. Below about 1000°C, ortho is the stable form down to at least 600°C and perhaps all the way down to room temperature. If proto is quenched in a few seconds or less, twinned clino will result, while slower cooling rates will allow the slower ordering process to form significant amounts of ortho. If experimental results are extrapolated to the very slow cooling rates hypothesized for some meteorites, the cooling of proto should result in a well-ordered ortho. That is, the experiment indicates that the proto-to-ortho (or the proto-to-clino-to-ortho) inversion is rapid enough to produce a crystal which is predominantly ortho if the cooling rate is slower than a few degrees per hour. This means that the disordered enstatites observed in meteorites must have been produced by rapid cooling or mechanical shock. Rapid cooling should produce an evenly distributed disorder in the enstatite, whereas the effects of shock are not expected to be evenly distributed. Below 600°C it is possible that low clino is the stable form; however, it is doubtful that any reaction would take place spontaneously in the absence of shear below 600°C even over geologic time. It should be pointed out that the relations observed here are for nearly Ca-free enstatite.

References

ALLEN, E., F. E. WRIGHT, AND J. K. CLEMENT (1906) Minerals of the composition MgSiO₃: a case of tetramorphism. *Am. J. Sci.* **4,** v. 22, 385–438.

BROWN, W. L., N. MORIMOTO, AND J. V. SMITH (1961) A structural explanation of the polymorphism and transitions of MgSiO₃. *J. Geol.* **69,** 609–616.

BROWN, W. L., AND J. V. SMITH (1963) High temperature X-ray studies on the polymorphism of MgSiO₃. *Z. Kristallogr.* **118,** 186–212.

BROWN, G. E., C. T. PREWITT, J. J. PAPIKE, AND S. SUENO (1972) A comparison of the structures of high and low pigeonite. *J. Geophys. Res.* **77,** 5778–5789.

CHRISTIAN, J. W. (1964) *The Theory of Transformation in Metals and Alloys.* Pergamon, London, pp. 13–16.

COE, R. S. (1970) The thermodynamic effects of shear stress on the ortho-clino inversion in enstatite and other coherent phase transitions characterized by a finite simple shear. *Contrib. Mineral. Petrol.* **26,** 247–264.

———, AND W. F. MÜLLER (1973) Crystallographic orientation of clinoenstatite produced by deformation of orthoenstatite. *Science,* **180,** 64–66.

EBELMAN (1851) *Ann. Chim. Phys.* **3,** xxxiii, 58 (cited in Allen *et al,* 1906).

GROVER, J. E. (1972) The stability of low-clinoenstatite in the system Mg₂Si₂O₆-Ca Mg Si₂O₆ (abstr.). *Trans. Am. Geophys. Union,* **53,** 539.

KUNO, H. (1966) Review of pyroxene relations in terrestrial rocks in light of recent experimental work. *Mineral J.* **5,** 21–43.

KUSHIRO, I. (1972) Determination of the liquidus relations in synthetic silicate systems with electron probe analysis: The system forsterite-diopside-silica at 1 atmosphere. *Am. Mineral.* **57,** 1260–1271.

NAKAMURA, Y. (1971) Equilibrium relations in the Mg-rich part of the pyroxene quadrilateral. *Mineral. J.* **6,** 264–276.

PERROTTA, A. J., AND D. A. STEPHENSON (1965) Clinoenstatite, high-low inversion. *Science,* **148,** 1090–1091.

REID, A. M., AND A. J. COHEN (1967) Some characteristics of enstatite from enstatite achondrites. *Geochim. Cosmochim. Acta,* **31,** 661–672.

SADANAGA, R., F. P. OKAMURA, AND H. TAKEDA (1969) X-ray study of the phase transformations of enstatite. *Mineral. J.* **6,** 110–130.

SMITH, J. V. (1969a) Magnesium pyroxenes at high temperature: inversion in clinoenstatite. *Nature,* **222,** 256–257.

——— (1969b) Crystal structure and stability of the $MgSiO_3$ polymorphs: physical properties and phase relations of Mg, Fe pyroxenes. *Mineral. Soc. Am. Spec. Pap.* **2,** 3–29.

SMYTH, J. R. (1969) Orthopyroxene-high-low clinopyroxene inversions. *Earth Planet. Sci. Lett.* **6,** 406–407.

——— (1970a) High temperature single crystal X-ray studies of natural orthopyroxenes (abstr.). *Am. Mineral.* **55,** 312.

——— (1970b) *High Temperature Single-Crystal Studies on Low Calcium Pyroxenes.* Ph.D. Thesis, University of Chicago, Chicago, Illinois.

——— (1971) Protoenstatite: a crystal structure refinement at 1100° C. *Z. Kristallogr.* **134,** 262–274.

——— (1972) A simple heating stage for single crystal diffraction studies up to 1000°C. *Am. Mineral.* **57,** 1305–1309.

———, AND C. W. BURNHAM (1972) The crystal structures of high and low clinohypersthene. *Earth Planet. Sci. Lett.* **14,** 183–189.

YANG, H. V. (1973) Crystallization of iron-free pigeonite in the system anorthite-diopside silica at atmospheric pressure. *Am. J. Sci.* **273,** 488–497.