

Pyroxenes and Amphiboles: Crystal Chemistry  
and Phase Petrology

PART I

Crystal Chemistry and  
Intracrystalline Cation Distributions



## CRYSTAL STRUCTURE AND STABILITY OF THE $MgSiO_3$ POLYMORPHS; PHYSICAL PROPERTIES AND PHASE RELATIONS OF $Mg,Fe$ PYROXENES

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### ABSTRACT

The crystal structures proposed by Lindemann for clino- and proto-enstatite are discredited, and those proposed by Morimoto *et al.* and by Smith are reaffirmed.

Ortho- and clino-enstatite are not related exactly by "unit-cell twinning" as proposed by Ito.

The X-ray powder diffraction pattern of high clinoenstatite is reindexed on a monoclinic cell with a large cell volume and long *c* repeat. The rapid transition between the low and high forms is attributed to straightening of the silicate chains and associated high thermal motion of the  $Mg(2)$  atoms. Perhaps the space group changes from  $P2_1/c$  to  $C2/c$ . Pigeonite may also undergo a high-low transition.

The atomic nature of transformations between the polymorphs is discussed in terms of "autoepitaxy" with possible retention of some Mg-O bonds and all Si-O bonds. During transformation, the silicate chains may move cooperatively, perhaps analogous to the hump-backed motion of caterpillars.

The deformation angles observed during transformation from ortho- to clino-enstatite in kink bands might be explained by dislocation arrays formed by refitting of kinked continuous silicate chains.

The high pressure-low temperature transformation of ortho- into clino-enstatite is regarded as a nonequilibrium process. At lower temperatures, stress nucleation of clinoenstatite is believed to be rapid enough to overcome recrystallization back to the ortho form. *Kinetically*, clinoenstatite could be regarded as a "stress mineral."

For chemically pure  $MgSiO_3$ , protoenstatite is reaffirmed as the stable phase at low pressures from about 1000°C to at least 1380°C. Above 1380°C the evidence favors continued stability of protoenstatite. Substitution of Ca for Mg may favor high clinoenstatite.

After correction of cell dimensions for minor element effects, volcanic orthopyroxenes yielded larger cell volumes than plutonic and metamorphic ones in conformity with the greater Mg,Fe disorder revealed by the Mössbauer studies of Ghose and Hafner. Even for plutonic orthopyroxenes, estimate of chemical composition from cell dimensions is uncertain.

The assumption of a single *ideal* solid solution between En and Fs end members of the ortho series is unwarranted. For slowly annealed specimens with strong site preference, a better assumption is that there are two ideal solid solution series from  $En_{100}Fs_0$  to  $En_{50}Fs_{50}$  and from  $En_{50}Fs_{50}$  to  $En_0Fs_{100}$ .

### INTRODUCTION

In this paper I attempt to review and extend earlier interpretations of the crystal structures and phase transformations of enstatite, and to discuss the physical properties and phase relations of the enstatite-ferrosillite series. Since there are so many conflicting opinions and assertions in the scientific literature, I deliberately probe with a sharp scalpel. Various crucial experiments are proposed for resolving some of the problems.

The nomenclature of the different polymorphs poses problems because of (1) uncertainty in the structural properties and interrelationships of some of the polymorphs, and (2) assignment of different names to the same polymorph. Briefly enstatite is used as a general term for all the polymorphs of  $MgSiO_3$ . The prefixes ortho-, clino-, and proto- are used for the three principal polymorphs. The use of the prefix ortho- does not imply that this polymorph is the only one with orthorhombic symmetry. Often the unqualified term enstatite has been used for orthoenstatite: usually this practice was not confusing because of the context. Providing an appropriate nomenclature for the three recognized forms of disorder is particularly difficult, since there are no obvious prefixes which are simple, unambiguous and euphonious. Perhaps "cation-disordered" and "stacking-dis-

ordered" are suitable adjectives for pyroxenes showing, respectively, disorder of the *M* cations and stacking errors between the sheets of interlocked chains. Since the third type of disorder seems to be peculiar only to pigeonite and to  $Mg,Fe$  clinopyroxenes exsolved from augite, it will be discussed later. In this paper, the nomenclature of cation sites has been unified to accord with the practice of C. W. Burnham (1967) for the ferrosillite polymorphs.

A general review of the crystal chemistry of pyroxenes by Zussman (1968) provided an excellent basis for this more critical review. I am indebted to many people, directly and indirectly, for information and discussion. D. E. Appleman, F. R. Boyd, Jr., G. M. Brown, W. G. Ernst and G. V. Gibbs presented a short course on chain silicates in 1966 under the auspices of the American Geological Institute. W. L. Brown, J. R. Goldsmith, S. Hafner, M. H. Hey, R. A. Howie, N. Morimoto, R. C. Newton, A. J. Perrotta, J. R. Smyth and D. A. Stephenson worked with me on various research problems concerned with pyroxenes, or kindly discussed them in detail.

### LITERATURE REVIEW

*Enstatite.* The phase relations between, and the crystal structures of, the enstatite polymorphs were discussed, respectively, by

Brown and Smith (1963) and by Brown, Morimoto and Smith (1961). Since then the following experimental data and discussions have appeared.

Lindemann (1961a) gave atomic coordinates for clinoenstatite grossly different from those given by Morimoto, Appleman and Evans (1960). No supporting evidence has appeared since then. Lindemann (1961b) listed revised atomic coordinates for orthoenstatite based on 2-D Fourier synthesis. Morimoto and Koto (priv. commun.) refined the crystal structure of orthoenstatite using 3-D least-squares methods obtaining positions accurate to about 0.01 Å, which differ by up to several tenths of an angstrom from those listed by Lindemann. Lindemann (1961c) stated that  $\gamma$ -MgSiO<sub>3</sub>, obtained by heating talc at 1250°C, is monoclinic with space group  $P2_1/n$ . He identified this phase with protoenstatite, and claimed that the orthorhombic crystal structure for the latter, proposed by Atlas (1952) and checked from powder X-ray data by Smith (1959) is wrong. The monoclinic cell dimensions of  $\gamma$ -MgSiO<sub>3</sub> cannot be obtained accurately by transformation of the orthorhombic cell of protoenstatite. Perhaps talc does not yield a pure MgSiO<sub>3</sub> phase, and Lindemann's  $\gamma$ -MgSiO<sub>3</sub> is not identical with protoenstatite obtained from pure synthetic MgSiO<sub>3</sub>. Von Gehlen (1962) measured the grain orientation of  $\gamma$ -MgSiO<sub>3</sub> obtained by heating a pressed block of talc. He stated that the results favor Lindemann's monoclinic structure, and criticized in detail the ideas of Brown, Morimoto and Smith on the structures and transformation mechanisms of the enstatite polymorphs. A detailed discussion will be given later, but in the meantime this review will be based on the assumption that there are three principal structure types of pure MgSiO<sub>3</sub>, namely ortho-, clino- and proto- enstatite as specified respectively by the structure determinations of Morimoto and Koto, of Morimoto *et al.*, and of Smith.

Perrotta and Stephenson (1965) reported X-ray powder diffraction data for a new form of MgSiO<sub>3</sub> solid solution obtained by heating clinoenstatite (itself a quench product from 1350°C) to 1000°C prior to inversion to protoenstatite. For the composition Di<sub>15</sub>En<sub>85</sub> (wt %), the new type of X-ray pattern occurred from about 1000°C to at least 1390°C. The new phase was thought to match the intermediate form encountered when Foster (1951) heated a natural Fe-bearing orthopyroxene. Because the inversion from clinoenstatite to the new form was rapid, and because the (310) X-ray reflection appeared to split reversibly and rapidly over an interval of 10°C, the transition was believed to be displacive. Hence the new phase was denoted *high clinoenstatite* thus requiring the traditional clinoenstatite to be called *low clinoenstatite*.

The indexing of the X-ray powder pattern on a triclinic unit cell was unconvincing since only few of the possible lines were observed, and especially since few of the stronger lines had indices common to those of the low form. Smith (1969) reindexed the powder pattern on a monoclinic cell with edges considerably greater than those of low clinoenstatite. The strong lines have indices common to those of clinoenstatite as would be required for a rapid displacive transition. Since all but one line could be ascribed to pyroxene with space group  $C2/c$ , contaminated with forsterite and cristobalite, Smith suggested that clinoenstatite inverts from  $P2_1/c$  to  $C2/c$ . Furthermore Morimoto and Tokonami (1969a) suggest that the diffuse ( $h+k$ ) odd reflections of some pigeonites at room temperature result from an inversion upon cooling from  $C2/c$ . Smith suggested that upon heating the silicate chains of clinoenstatite straighten out with concomitant vibration of the Mg atoms. He drew an analogy with the suggested "rattling" of Ca atoms in the cavities of the aluminosilicate framework of anorthite.

The crystal structure of the high clinoenstatite has not been determined, but qualitatively, it might be similar to diopside with the Mg atom simulating the larger Ca atom. The enlarged  $a$ ,  $b$ , and  $c$  repeats are consistent with silicate chains even more

extended than those in diopside, together with expansion of the Mg-polyhedra lying between the chains.

In view of the similarity of the X-ray patterns of the two structural forms of clinoenstatite solid solution, and because of the rapid reversibility of the transition between them, the assignment by Perrotta and Stephenson of prefixes *high* and *low* seems reasonable. However, there is a small possibility that the structural change is sufficiently great that the use of these prefixes is semantically misleading.

The discovery by Atlas (1952) and Brown and Smith (1963) of stacking-disordered varieties of enstatite obtained (1) by quenching synthetic protoenstatite and (2) directly from meteorites, was followed by comprehensive studies by Pollack and Ruble (1964) and Pollack (1966, 1968) of meteoritic and stressed natural pyroxenes. The disordered ortho variety was found in all but one of the enstatite achondrites, and in a eucrite and two chondrites. In most meteorites, grains of the disordered orthoenstatite were accompanied by grains of ordered orthoenstatite. In some meteorites, clinoenstatite was found (Pollack, 1968), sometimes twinned and sometimes untwinned. A preliminary report of a pyroxene with an  $a$ -axis repeat of 91 Å was discredited by Pollack (1966) who reinterpreted the X-ray photographs as deriving from twinned clinoenstatite. Previous reports of long  $a$ -repeats might also result from incorrect interpretation of twinned clinoenstatite.

Pollack (1966) found that disordered orthoenstatite occurred only in the brecciated type of enstatite achondrite, which suggested that the disordering occurred simultaneously with the brecciation. However he presented (1968) other evidence (twinning of clinoenstatite) which suggested that disorder in meteoritic pyroxene is caused mainly by rapid cooling from high temperature as well as by shock deformation.

The pioneering work by Turner, Heard and Griggs (1960) on experimental deformation in pyroxenite rock of orthoenstatite resulting in inversion to clinoenstatite was paralleled independently by Borg and Handin (1966). The results are mutually consistent, *viz.* clinoenstatite forms in kink bands under conditions of high stress by translation gliding along the direction [001] in the plane (100). Borg and Handin discovered further translation gliding in the clinoenstatite with "high certainty."

Optically the clinoenstatite was found to be untwinned by Turner *et al.* and by Borg and Handin. Trommsdorff and Wenk (1968) and Pollack (1968) confirmed the lack of twinning by single crystal methods. They also reported streaks on the X-ray photographs that indicate stacking faults similar to those described by Atlas (1952) and Brown and Smith (1963) for synthetic pyroxenes.

Brown, Morimoto and Smith (1961) discussed the atomic movements which might occur during the transformation of one polymorph into another. They predicted that the glide transformation of ortho- to clino-enstatite should lead to untwinned crystals. Starkey (1968) presented a simple model for the transformation of ortho- to clino-enstatite in kink bands, which did not consider detailed atomic movements, and utilized only the cell dimensions. The predicted orientation of the clinoenstatite conflicted with the optical and X-ray data listed earlier (Trommsdorff and Wenk, 1968).

The most surprising of the data obtained since 1960 on the phase relations was the discovery of the low temperature-high pressure conversion of ortho- to clino-enstatite by Sclar, Carrison and Schwartz (1964). Boyd and England (1965) confirmed the conversion but found the transformation curve to lie about 75° higher (Fig. 1). Sclar *et al.* claimed that the transformation pressure-temperature curve is reversible since (1) there is symmetrical zonation of phases controlled by thermal gradients in the "belt" and "girdle" apparatus, and (2) the transformation goes both ways at suitable pressures and temperatures. Stephenson, Sclar and Smith (1966) measured the cell volumes of syn-

thetic clino- and ortho-enstatite produced by Sclar *et al.*, finding that orthoenstatite is slightly less dense than clinoenstatite (at the 90% confidence level) in accordance with the low angle of slope of the transformation curves.

Lindsley (1965) found a similar reversible transformation of orthoferrosilite to clinoferrosilite below 800°C, essentially independent of pressure. Akimoto, Katsura, Syono, Fujisawa and Komada (1965), however, found a strong dependence of the transition PT curve for both  $FeSiO_3$  and  $CoSiO_3$ ; they gave the equation  $P(\text{kbar}) = -9 + 0.06T(°C)$  for the former composition.

Riecker and Rooney (1966) transformed orthoenstatite into clinoenstatite at temperatures up to about 900°C in the presence of shearing stress. Munoz (1968) found that application of shear to a piston-anvil apparatus caused orthoenstatite to transform completely in less than 5 minutes at 890°C. In less than 2 hours at 600°C, clinoenstatite formed slowly without rotation of the anvils, but Munoz explained this by inherent presence of shearing stress in opposed anvil equipment. Using a special "hydrostatic" cell containing molten AgCl as a medium for pressure transfer in single-stage equipment, no reaction to clinoenstatite was detected in 100 hrs. at 20 kbars and 600°C. Lindsley and Munoz (1969) reported similar results for ferrosilite polymorphs and concluded that at 20 kbar hydrostatic pressure orthoferrosilite appears to be the only stable polymorph of  $FeSiO_3$  below about 1100°C.

The significance of all the above results was unclear but it was obvious that there was increasing doubt concerning the existence of a stability field for clinoenstatite at low temperature and hydrostatic pressure. Shearing stress obviously aided, and perhaps even controlled, the transformations.

Additional papers on the stability of the enstatite polymorphs at atmospheric pressure have confirmed generally the conclusions of Brown and Smith (1963) based mostly on a review of

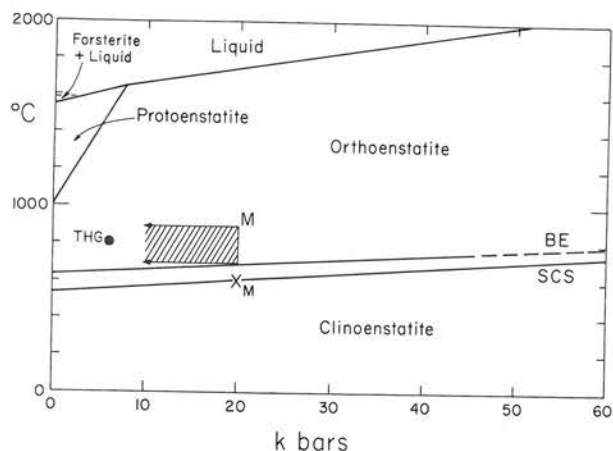


FIG. 1. High pressure-high temperature experiments on enstatite composition. The transition curves between orthoenstatite, protoenstatite, liquid, and forsterite plus liquid were given by Boyd and England (1965).

The two curves labelled SCS and BE were obtained respectively by Sclar, Carrison and Schwartz (1964) and Boyd and England for reversals obtained in piston-anvil equipment. The point THG shows the conditions used by Turner, Heard and Griggs (1960) to produce clinoenstatite by kink banding in a pyroxenite rock: the specimen was subjected to uniaxial compression. The shaded area M shows the region in which Munoz (1968) produced clinoenstatite in a shearing squeezer. The cross marked M shows a run in which orthoenstatite surrounded by AgCl did not invert to clinoenstatite even after 100 hours.

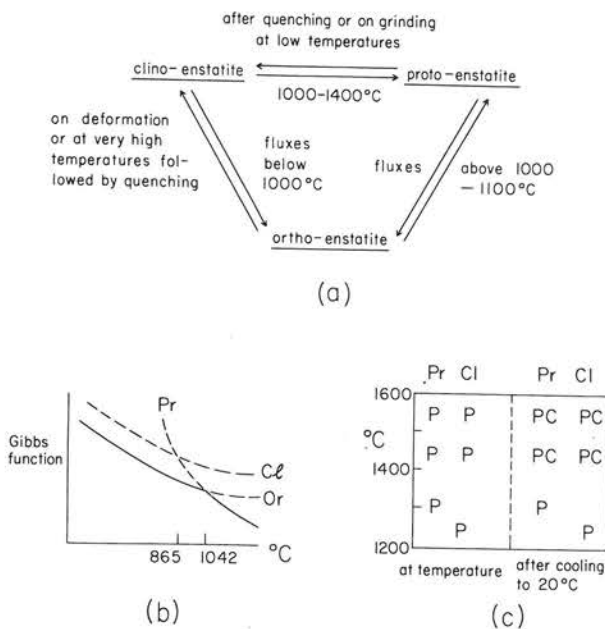


FIG. 2. Schematic diagrams of some results on the phase relations of  $MgSiO_3$ . (a) Summary of reactions observed by many workers as reviewed by Brown and Smith (1963). (b) Summary of results of Sarver and Hummel (1962), based on their Fig. 1 reexpressed in terms of the Gibbs function. (c) Summary of results obtained by Lange and Koltermann (1966). Pr, Cl; proto- and clino-enstatite starting materials; P, C; proto- and clino-enstatite products.

existing literature but partly on their own work. However there are indications of further complexities especially above 1380°C and near 1000°C. Briefly orthoenstatite is stable below about 1000°C and protoenstatite stable at high temperatures. Upon quenching protoenstatite usually transforms into a disordered form which resembles clinoenstatite more than orthoenstatite (Fig. 2).

Sarver and Hummel (1962) investigated the stability relations of the enstatite polymorphs using  $MgF_2$  and Li F mineralizers. The polycrystalline aggregates were studied by X-ray powder diffraction both at temperature and after quenching at various rates. Their results are shown schematically in Figure 2b. Enstatite, the stable low-temperature polymorph, inverted to protoenstatite, the stable high-temperature polymorph, at  $1042 \pm 3°C$  as determined by quenching and at  $1035°C$  as determined by high-temperature X-ray powder diffraction. Upon quenching the protoenstatite inverted to clinoenstatite at a rate which varied greatly with the amount of mineralizer, the firing temperature, the degree of compaction, the cooling rate and whether the sample was ground. Probably the transformation proceeds more rapidly for larger grains. In particular, samples heated above 1400°C inverted rapidly to clinoenstatite, as also observed by Kuzel (1963). Reheating of clinoenstatite caused inversion to protoenstatite at  $865 \pm 5°C$ . The protoenstatite in turn inverted rather rapidly to orthoenstatite above 865 but below 1042°C. The clinoenstatite did not invert directly to orthoenstatite. Sarver and Hummel did not report any evidence for the high-low inversion of clinoenstatite later reported by Perrotta and Stephenson. Krönert, Schwiete and Suckow (1964a,b) also found results indicating that protoenstatite is the stable high-temperature modification whereas clinoenstatite is unstable at all temperatures.

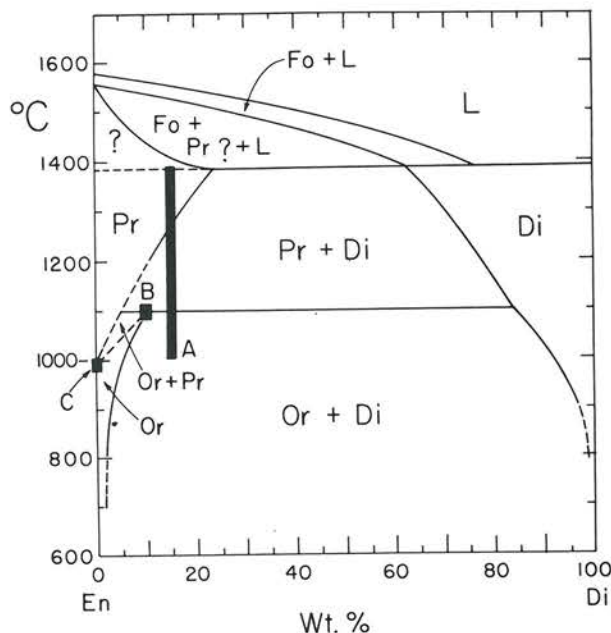


FIG. 3. Phase diagram at low hydrostatic pressure for the system  $\text{MgSiO}_3\text{-CaMgSi}_2\text{O}_6$  obtained by Boyd and Schairer (1964) from quenching experiments. Fo forsterite, L liquid, Di diopside, Or orthoenstatite, Pr protoenstatite.

Superimposed on the diagram are the results obtained by Perrotta and Stephenson (1965) for glasses held at  $1350^\circ\text{C}$  for 3 days and then examined at temperature in an X-ray diffractometer. The glass containing 15 wt.% Di component yielded low clinopyroxene below temperature A ( $995^\circ\text{C}$ ) and high clinopyroxene up to  $1390^\circ\text{C}$ , the limit of the apparatus. The X-ray pattern listed in their Table 1 was obtained at B, while for pure  $\text{MgSiO}_3$  glass the low clinoenstatite was stated to invert to high clinoenstatite at C just before inversion to protoenstatite.

Koltermann (1964, 1965) studied the stability relations without mineralizers of  $\text{MgSiO}_3$  polymorphs made from oxides and from magnesium silicate hydroxides (e.g. talc). Lange and Koltermann (1966) described high-temperature X-ray diffractometer studies of the transformations between the enstatite polymorphs, and briefly reviewed earlier results. Protoenstatite (plus cristobalite) produced by firing talc at  $1200^\circ\text{C}$  did not invert to clinoenstatite at 200, 400, 600, 800, 1000, 1200, 1300, 1450,  $1530^\circ\text{C}$  for heating times of 1 hour. Upon cooling to room temperature from temperatures up to  $1350^\circ\text{C}$  over a period of one hour, only protoenstatite was formed. Heating above  $1400^\circ\text{C}$  followed by cooling led to clinoenstatite. Clinoenstatite made from  $\text{MgO}$  and  $\text{SiO}_2$  did not transform to protoenstatite after 10 hours at  $1100^\circ\text{C}$  but at 1250, 1450 and  $1530^\circ\text{C}$  only protoenstatite was observed. Upon cooling to room temperature the same results were obtained as for the sample produced from talc. Transformation to orthoenstatite was not observed in cooled specimens. From these results (Fig. 2c) Lange and Koltermann concluded that protoenstatite is the phase stable at high temperatures, and that the heating temperature merely changes the nature of the transformation to clinoenstatite upon cooling.

Boyd and Schairer (1964) published detailed data on the synthetic system  $\text{MgSiO}_3\text{-CaMgSi}_2\text{O}_6$  (Fig. 3). Their X-ray powder data on samples quenched to room temperature from temperatures up to about  $1380^\circ\text{C}$  are not inconsistent with the

scheme that orthoenstatite is stable up to about  $1000^\circ\text{C}$  in pure  $\text{MgSiO}_3$  where it inverts to protoenstatite, which itself reverts readily to clinoenstatite upon quenching. The results obtained by quenching of Ca-bearing specimens from temperatures above  $1385^\circ\text{C}$  were very confusing since the quench products gave complex X-ray patterns which varied erratically from one run to the next. The patterns were interpreted as arising from either clinoenstatite with anomalous cell dimensions, or from orthoenstatite of normal cell dimensions. From these data Boyd and Schairer suggested that a hitherto unrecognized form of Mg-rich pyroxene, stable above  $1385^\circ\text{C}$ , inverts in the quench to a clinoenstatite of anomalous cell size or occasionally to orthoenstatite. The X-ray data obtained by Lange and Koltermann for pure  $\text{MgSiO}_3$  indicated that protoenstatite is stable up to  $1530^\circ\text{C}$  thus arguing against the existence of a new form of enstatite. However, the difference in the results of quenching from above and below  $1380^\circ\text{C}$  do require an explanation. Kuno (1966) stated incorrectly that Boyd and Schairer synthesized a clinopyroxene above  $1385^\circ\text{C}$ , and went on to suggest that it may be analogous to the ferrosilite III phase of Lindsley, Davis and MacGregor (1964). This ferrosilite III phase was interpreted by Burnham (1966) as a complex pyroxenoid, and it is unlikely that it would produce a pyroxene upon rapid quenching. Boyd and Schairer were unable to reverse the ortho-proto inversion of pure  $\text{MgSiO}_3$  at low pressure and utilized the reversal at  $985^\circ\text{C}$  obtained by Atlas (1953) with a LiF flux.

As mentioned earlier, Perrotta and Stephenson claimed that high clinoenstatite was formed in pure enstatite from clinoenstatite at about  $1000^\circ\text{C}$ . close to the inversion temperature to protoenstatite (Fig. 3). This evidence is not compelling since the powder pattern might be interpreted to derive from a mixture of (low) clinoenstatite and protoenstatite. R. C. Newton (priv. comm.) pointed out that if Smith's interpretation of the powder pattern is correct, contamination by forsterite and cristobalite implies that the Perrotta-Stephenson clinoenstatite is more Ca-rich than the Ca-bearing bulk compositions. Probably this effect only moves the composition a few percent of diopside molecule, but a greater shift must be considered possible.

Schwab (1968) and Ernst and Schwab (1969), from an atmospheric pressure study of the system  $\text{MgSiO}_3\text{-MgNiSi}_2\text{O}_6$ , found that increasing contents of Ni favor the ortho polymorph resulting in a shift of the field for protoenstatite to higher temperatures (Fig. 4). Between the fields for ortho- and proto-

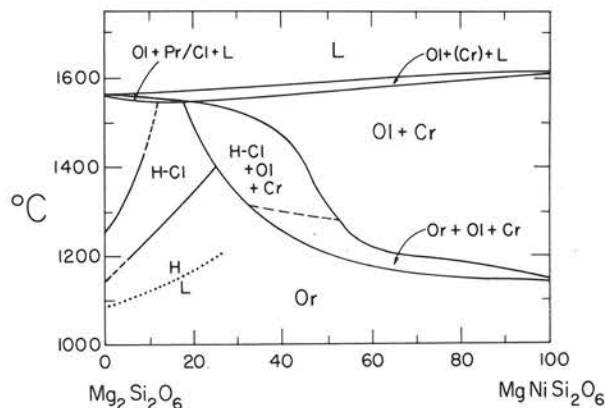


FIG. 4. The phase diagram for  $\text{Mg}_2\text{Si}_2\text{O}_6\text{-MgNiSi}_2\text{O}_6$  at one atmosphere pressure as given by Schwab (1968). Ol olivine; Pr protoenstatite; H-Cl high clinoenstatite; Cr cristobalite; Or orthoenstatite; L liquid. A metastable inversion from high to low clinoenstatite is shown by the dotted line in the stability field of orthoenstatite.

enstatite, a field for  $\beta$ -clinoenstatite was interposed. The  $\beta$ -clinoenstatite was assigned an inversion temperature to  $\alpha$ -clinoenstatite at 1080°C in pure  $MgSiO_3$  moving to higher temperatures with substitution of Ni. Schwab terminated the lower bound of the stability field of protoenstatite for  $MgSiO_3$  composition at 1260°C, a value which is much higher than those reported by other workers. Although study of quenched products was supplemented by high-temperature DTA measurements which revealed a small endothermic effect for the  $\alpha$ - $\beta$  transition in clinoenstatite, the phase relations remain obscure. The  $\alpha$  and  $\beta$  forms of clinoenstatite can be identified reasonably with the low and high forms of Perrotta and Stephenson, and the temperature for the high-low transition was apparently revealed by the endothermic effect. The temperature for pure  $MgSiO_3$ , 1080°C, is 80°C higher than the value of 1000°C given by Perrotta and Stephenson. Such a difference is not surprising since the inversion is probably affected strongly by small amounts of chemical substituents.

Boyd, England and Davis (1963) found that orthoenstatite was obtained at all temperatures up to the liquidus for pressures above 10 kbar (this was before the discovery of inversion of orthoenstatite to clinoenstatite at lower temperatures). Clinoenstatite found in runs made at high temperature and 5-6 kbar was interpreted as the inversion product of protoenstatite. Protoenstatite of  $MgSiO_3$  composition was found to be unstable at all pressures above 7 kbar. These results yielded the triangular field for protoenstatite shown in Figure 1.

Kushiro, Yoder and Nishikawa (1968) measured the effect of water on the melting of enstatite at pressures from 5 to 30 kbar. Preliminary experiments on the ortho-proto inversion indicated that the curve passes between 3.5 and 5 kbar at 1200°C and between 6 and 8 kbar at 1350°C, thus lying at higher pressures than that given by Boyd *et al.* (1964) on the basis of shorter runs. The X-ray powder patterns of the clinoenstatite (interpreted as a quench product of protoenstatite) formed at 1265 and 1275°C at 5 kbar were essentially like that of clinoenstatite but with intensities similar to the pattern of orthoenstatite. Probably the clinoenstatite has stacking disorder.

Kushiro (1964, 1969) studied the  $MgSiO_3$ - $CaSiO_3$  join at 20 kbar finding that, whereas for pure  $MgSiO_3$  orthoenstatite is stable up to the melting point, a small field of clinopyroxene appears from ~1450-1650°C for compositions near ( $Mg_{0.91}Ca_{0.09}$ )  $SiO_3$ . This clinopyroxene was described as an iron-free pigeonite because of its chemical composition and because its powder X-ray pattern resembles that of pigeonite. The presence of the 231 reflection indicates that the space group is not  $C2/c$ . Perhaps this phase has gone through a high-low inversion such that the stable phase at high temperatures is analogous to high clinoenstatite.

*Mg, Fe pyroxenes.* Since C. W. Burnham is describing the crystal structures of ortho- and clino-ferrosilite in a paper to be published shortly it is only necessary to state that there are merely minor differences between corresponding polymorphs of enstatite and ferrosilite arising principally from the slightly larger Fe ions, and probably from magnetic interactions.

Ghose (1965) showed from X-ray structure analysis that an intermediate orthopyroxene of composition  $Mg_{0.93}Fe_{0.07}Si_2O_6$  had strong site preference of Mg for the  $M1$  site and of Fe for  $M2$ . Such preference has been confirmed by other techniques, particularly Mössbauer resonance studies of  $^{57}Fe$  nuclei. Since then Mössbauer resonance studies by Virgo and Hafner (1969) showed that the site preference is changed by heating natural orthopyroxenes to temperatures around 500-1500°C for times of the order of hours to days, and that some unheated volcanic specimens show smaller site preferences than metamorphic and plutonic specimens.

Morimoto, Appleman and Evans (1960) from 2-D X-ray

analysis found that the crystal structure of a pigeonite  $Ca_{0.10}Mg_{0.34}(Fe, etc.)_{0.56}SiO_3$  was intermediate between that of clinoenstatite and diopside. Morimoto and Güven (1968) made a detailed 3-D X-ray analysis of a pigeonite of composition  $(Ca_{0.08}Mg_{0.41}Fe_{0.51})SiO_3$  showing diffuseness of the  $h+k=2n+1$  reflections. They estimated that the  $M2$  site is mostly occupied by Fe and Ca atoms, while the Mg atoms mostly if not completely occupy  $M1$ .

The reflections of type  $h+k=2n+1$  arise because there are two types of silicate chains twisted in different ways, with associated minor displacements of the  $M1$  and  $M2$  cations. In diopside there is only one kind of chain causing the space group to be  $C2/c$  instead of  $P2_1/c$ . Ito (1950) correctly predicted the spacegroup of clino Mg,Fe pyroxenes by postulating that orthopyroxenes are formed by completely regular twinning of clinopyroxene such that a  $b$ -glide plane is inserted along every (100) face of the unit cell of the clinopyroxene. Morimoto and Koto (priv. commun.) recently compared their refined structure of orthoenstatite with the less accurate data for clinoenstatite (Morimoto, Appleman and Evans, 1960) and concluded that Ito's hypothesis was obeyed exactly.

Morimoto (1956) and Bown and Gay (1957) found that pigeonites contain weak extra reflections of type  $(h+k)$  odd showing that the space group is  $P2_1/c$  in contrast to the space group  $C2/c$  of augite. Bown and Gay found that the subsidiary reflections were slightly diffuse, but did not find any obvious correlation between the extent of diffuseness and the chemical composition or petrologic environment of the pigeonite. Morimoto and Güven (1968) suggested that a domain structure was responsible, and Morimoto and Tokonami (1969a) proposed that the domain structure is produced by rapid growth of a number of nuclei in a high-temperature phase with monoclinic symmetry. Morimoto and Tokonami pointed out that for space group  $C2/c$  there is only one kind of silicate chain whereas in space group  $P2_1/c$  there are two kinds which should alternate regularly. If there are mistakes in the alternation, and the mistakes are correlated so that domains of perfect alternation are separated by boundaries, the  $(h+k)$  odd reflections will appear diffuse. Since the boundary regions can be similar to the diopside structure when silicate chains of the SiB type are adjacent, Morimoto and Tokonami suggested that Ca atoms tend to populate the boundaries in preference to Mg and Fe atoms.

Morimoto and Tokonami finally made the important suggestion that at high temperature pigeonite has the symmetry  $C2/c$  as a result of the loss of distant order in the alternation of the silicate chains. They believed that the two types of chains did not become strictly identical in geometry since this would produce voids too large to be occupied by Mg and Fe atoms. This suggestion is contrary to that of Smith (1969) who proposed that at high temperature the high thermal agitation permits Mg(2) to simulate Ca thus permitting the silicate chains to obey  $C2/c$ .

Knowledge of the phase relations of Mg, Fe pyroxenes is still rather primitive because modern synthesis and identification techniques have been hampered by technical problems, especially oxidation of iron. Present knowledge is based principally on (1) qualitative extrapolation of relations found synthetically for the end members (2) the classic but obsolete investigation by Bowen and Schairer (1935) of the En-Fs join using dry heating methods and optical identification of quenched material (3) high-temperature syntheses in the pyroxene quadrilateral by Yoder, Tilley and Schairer (1963, 1964) in which the pyroxene was described as Opx without distinction between orthopyroxene and protopyroxene (4) inversion studies of pigeonite by Brown (1968) (5) qualitative use of the occurrence in rocks of pyroxenes, often containing considerable Ca, Al and other minor elements.

Kuno (1966) reviewed the occurrence of Mg,Fe pyroxenes

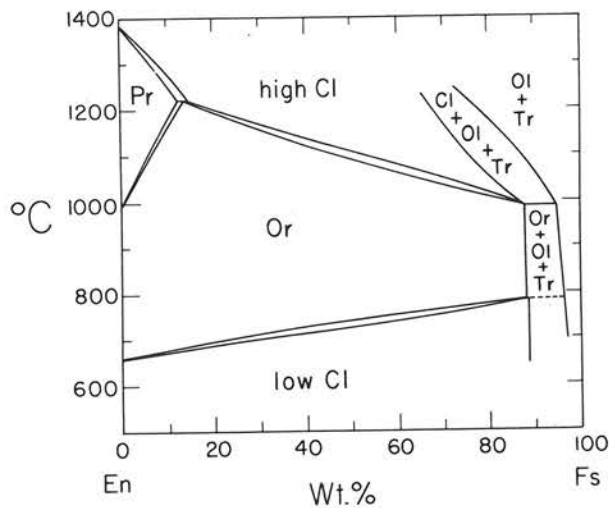


FIG. 5. Hypothetical phase diagram in the system  $MgSiO_3$ - $FeSiO_3$  for low pressures as given by Kuno (1966). See text for meaning of high- and low- clinopyroxene. Pr protopyroxene; Or orthopyroxene; Ol olivine; Tr tridymite.

in terrestrial rocks in the light of experimental data. His hypothetical phase diagram (Fig. 5) is notable for distinguishing two types of clinopyroxene. Unaware of the work of Perrotta and Stephenson (1965), Kuno assigned the names high and low clinopyroxene to Mg,Fe monoclinic pyroxenes believed to occur stably at temperatures respectively higher and lower than those for orthopyroxene. The high clinopyroxene was identified with pigeonite and clinohypersthene occurring as phenocrysts in volcanic rocks, and in some plutonic rocks: the low clinopyroxene was identified with material produced synthetically from orthopyroxene under high pressures and low temperatures. Kuno was surprised at the absence of low clinopyroxene from lower-temperature metamorphic rocks and "suggested that the stability field of low clinopyroxene found at high pressures does not extend to the low pressure range but instead its place is taken by that of an unrecognized form of orthopyroxene." He did not provide any evidence for a structural difference between high and low clinopyroxene, nor did he give any valid indication of a new form of orthopyroxene. If the speculations of Smith (1969) are correct, Kuno's high clinopyroxene is structurally continuous with the high clinoenstatite of Perrotta and Stephenson, and the structural difference between Kuno's high and low form results from a phase inversion with symmetry change from  $P2_1/c$  to  $C2/c$ .

Since (1) low clinoenstatite is extremely rare in metamorphic rocks, where it appears only in the special environment of kink bands, and (2) laboratory synthesis indicates the strong effect of shearing stress, Kuno's assignment of a stability field to low clinoenstatite seems to be unnecessary. Hence the remainder of this section of the review will concentrate on results obtained at high temperature.

The systematic heating studies of the Mg,Fe pyroxenes (Bowen and Schairer, 1935) were hampered by the difficulty of obtaining equilibrium, by the special requirements for minimizing oxidation of iron, and by lack of observations *directly* at elevated temperatures. Figure 6 is a TX section at atmospheric pressure for quenched samples whose iron was held in the ferrous state either by heating in an iron crucible, or by heating in evacuated silica capillaries. The relations for Fe-rich compositions are complex involving olivine and silica minerals; these complexities are largely eliminated by application of pressure as shown by

Lindsley (1965) and by Akimoto *et al.* (1965). The transition between ortho- and clino-pyroxene was determined by heating natural orthopyroxenes. Specimens of intermediate composition inverted only in the presence of NaF flux. No reversal from clino- to ortho-pyroxene was obtained. However since a decrease of only  $10^\circ C$  changed the reaction velocity of ortho to clino from complete transformation in an hour or so to no change at all in many hours, Schairer and Bowen believed that they were dealing with a reversible transformation and that the equilibrium transformation temperature was close to the observed sharp change in reaction velocity. All the clinopyroxene was shown by optical study to be polysynthetically twinned. The boundary between the two polymorphs in partly transformed grains was sharp. The transformation started at edges and corners of grains. From later results it can be deduced that for the  $MgSiO_3$  composition, the clinoenstatite inverted from protoenstatite upon quenching. The inversion temperature given by Bowen and Schairer is about  $100^\circ C$  higher than that given by Sarver and Hummel, and  $150^\circ C$  higher than given by Atlas (1952). Since Bowen and Schairer did not obtain phase reversal, probably their higher temperature results merely from lack of equilibrium. If this is true for  $MgSiO_3$  composition, it is probably also true for Fe-bearing compositions. Since there are no convincing experimental data on whether proto- or clino-pyroxene is the high-temperature form for hypersthene compositions, it must not be assumed uncritically that the twinned clinohypersthene indicates inversion from a proto form. Later on it will be shown that twinned clinohypersthene should result no matter what is the high-temperature phase.

An apparently important observation by Bowen and Schairer (1935) concerning the reaction mechanism is that although in the Mg-rich orthopyroxenes there was a tendency for the clinopyroxene to retain the prism zone of the original orthopyroxene, generally "a single crystal or crystal fragment" "transformed into an aggregate of several grains of monoclinic pyroxene of random orientation with respect to each other and to the original orthorhombic substance." This implies a major recrystallization rather than a simple epitaxial transformation. However it should be noted that NaF flux was used. Perhaps a complex transformation occurs involving fluor-amphibole.

Recently Dallwitz, Green and Thompson (1966) found that a porphyritic volcanic rock from Papua contains abundant phenocrysts of multiply-twinned clinoenstatite and less common

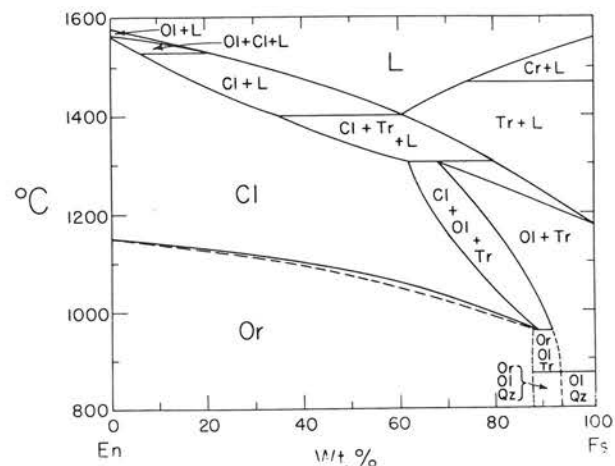


FIG. 6. The  $MgSiO_3$ - $FeSiO_3$  section of the  $MgO$ - $FeO$ - $SiO_2$  system as determined by Bowen and Schairer (1935). Ol olivine; Cl clinopyroxene; L liquid; Tr tridymite; Cr cristobalite; Or orthopyroxene; Qz quartz.



phenocrysts of orthopyroxene (bronze composition). Some phenocrysts are mixtures of clino- and ortho-pyroxene separated by a distinct boundary. Microprobe analyses showed that clinoenstatite ranges from  $En_{92}$  to  $En_{87}$  (mole %) and contains very little  $Wo$  molecule (less than 0.5%). The orthoenstatite ranges from  $En_{87}$  to  $En_{78}$  with higher  $Wo$  contents averaging about 1½ percent. Dallwitz *et al.* interpreted the twinned clinoenstatite as a metastable inversion product from a primary protoenstatite solid solution on the basis of the multiple twinning, the orthorhombic morphology of the twinned clinoenstatite, and the lower  $Wo$  content. The latter criterion checks with the lower  $Wo$  content of protoenstatite found to coexist with orthoenstatite in the synthetic system En-Di (Boyd and Schairer, 1964). Much earlier, Foster (1951) had obtained X-ray powder patterns of the proto type for a natural bronzite of uncertain composition heated in air at 1300°C, and had observed inversion to the clino form upon quenching.

For more iron-rich compositions, the evidence concerning the type of pyroxene stable at high temperatures is strongly indicative but not definitive. Since pigeonite crystals do not show polysynthetic twinning, since they show augite exsolved on both the (100) and (001) planes, since they appear to have monoclinic morphology, and since the diffuseness of the ( $h+k$ ) odd reflections in some pigeonites can be interpreted on the basis of a high-temperature precursor with space group  $C2/c$ , it is natural to claim that the high-temperature form is monoclinic (see Poldervaart and Hess, 1951; Brown, 1957, 1968; Kuno, 1966; Morimoto and Tokonami, 1969a). However Yoder, Tilley and Schairer (1964) reported only Opx for Mg,Fe compositions in isothermal sections down to 1050°C. The situation is complicated by the possible effects of solid solution with  $CaSiO_3$  molecule and of hydrostatic pressure. Güssregen (1964) prepared pigeonite from dry melts obtained by briquetting oxides at 1450°C subsequently held at temperature for 12–18 hours. The pigeonite was identified by X-ray diffraction. For the time being, it will be assumed that under most circumstances, a monoclinic pyroxene is stable at high temperatures, but that a protopyroxene might also occur.

Boyd and Schairer (1964) proposed two schematic sets of inversion relations between the three forms of  $MgSiO_3$  (Fig. 7). Others are possible. Based on new experimental data for high clinoenstatite (Perrotta and Stephenson, 1965; Schwab, 1968), the third set of relations is worth serious consideration.

In the absence of detailed laboratory syntheses, Kuno used petrologic observations to estimate the  $TX$  curves separating the fields of the various polymorphs. Some volcanic rocks contain phenocrysts of pigeonite whereas others contain phenocrysts of hypersthene. Occurrence, in the magma bulk composition, of components other than those strictly belonging to the system  $MgO-FeO-SiO_2$  can cause the solidus temperature to fall several hundred degrees below that for a pure dry system at low pressure. The extrusion temperature of some active lavas has been measured. Using these temperatures, Kuno estimated the temperature of the transition curve (strictly a two-phase field) between clino- and ortho-pyroxene (Fig. 5). His estimate ranges from 30–70°C higher than that given by Schairer and Bowen (1935). These estimates are not strictly comparable since pigeonites contain much more Ca in solid solution than do the inverted orthopyroxenes of Schairer and Bowen. Although Kuno states that the measured extrusion temperature of a lava should be somewhat lower than that at which the phenocrysts crystallized, I suggest that the opposite is possible because of exothermic oxidation reactions proceeding during eruption.

Brown (1968) heated selected natural pyroxenes enclosed in iron capsules contained in piston-cylinder equipment; other techniques were also used. The most complete results were for an orthopyroxene with augite lamellae of bulk composition

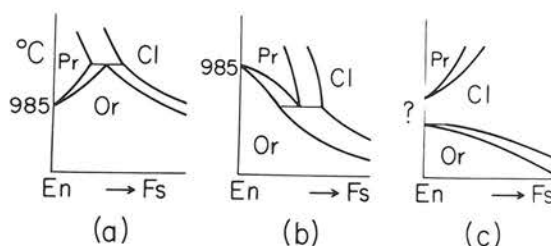


FIG. 7. Hypothetical TX relations between the stability fields of proto-, clino- and ortho-pyroxene near the enstatite composition on the En-Fs join at low pressures. The first two diagrams were proposed by Boyd and Schairer (1964). The third diagram is a new one which might apply if clinoenstatite has a field of stability between those of ortho- and proto-enstatite.

$Wo_{0.9}En_{48.2}Fs_{42.9}$  (mole %). Conversion to clinopyroxene (examined after quenching) was obtained above 1000°C at zero pressure and about ~1150°C at 20 kbar. Some reversals were obtained at lower temperature, but the inversion curve was not definitely located. The slope of the tentative transition curve indicates that the clinopyroxene has lower density than the orthopyroxene. Perhaps this indicates that the clinopyroxene is in the high form analogous to high clinoenstatite.

Brown made many runs at atmospheric pressure using sealed silica tubes. Powdered rock acted as a flux permitting inversion to occur at lower temperature. An iron-rich pigeonite ( $Wo_{0.4}En_{39.2}Fs_{52.4}$ ) yielded a reversal from ortho- to clino-pyroxene near 980°C. Exsolution of augite occurred prior to inversion upon cooling.

Brown presented several convincing arguments against the existence of a stable proto phase at high temperature for pigeonite compositions: (1) protoenstatite favors lower Ca content than the amounts found in pigeonite (2) protopyroxenes have been synthesized only for Mg-rich compositions at low pressure (3) morphological data can be interpreted in terms of phase changes.

Further discussion of the stability of pigeonite and hypersthene is beyond the scope of this paper since it would involve prolonged consideration of the phase relations in the En-Di-Hd-Fs quadrilateral, and the even more complex relations between olivine, pyroxene, feldspar, iron ores, etc.

**Physical properties.** In this review only cell dimensions and refractive indices will be considered out of the myriad physical properties. For several decades optical properties, and later on cell dimensions, were used for identification and for estimation of the chemical composition of pyroxenes. Over the last few years there has been a growing realization that these physical properties depend on the temperature-pressure history of the pyroxene as well as on the bulk composition. Not only does the site preference of the  $M$ -cations change, but there may be visible or submicroscopic exsolution. Unfortunately almost all data on the physical properties of pyroxenes have been obtained at room temperature and atmospheric pressure. Smith (1969) contends that pyroxenes should have unusual thermal expansion, which for some culminates in a high-low inversion. Interpretation of the thermodynamic functions depends critically on the cell volume, and on implications concerning vibrational contributions to the entropy.

Fortunately detailed review of the cell dimensions of orthopyroxenes near the En-Fs join is not necessary since Smith, Stephenson, Hey and Howie (1969) published a critical review of the literature, and provided a detailed statistical analysis of the relations between chemical composition and new measurements of cell dimensions. Briefly they found:

1. Metamorphic and plutonic specimens yielded smaller dimensions than volcanic specimens, after correction for the differences in minor element content. This difference was ascribed to a lower site preference of the latter in accordance with the evidence from Mössbauer resonance studies.

2. Cell dimensions for the slowly-annealed specimens could not be expressed accurately by a regression relation based on ideal solid solution between  $\text{MgSiO}_3$  and  $\text{FeSiO}_3$ . Either a single parabolic relation or a pair of linear relations for two ideal solid solutions,  $\text{MgSiO}_3\text{-Mg}_{0.5}\text{Fe}_{0.5}\text{SiO}_3$  and  $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{SiO}_3\text{-FeSiO}_3$ , is needed. The latter pair is consistent within the large experimental uncertainty with the strong site preference found by resonance and diffraction methods.

3. Cell dimensions yielded correlations with the minor-element concentrations of Al and Ca (determined by electron microprobe analysis) which agree semi-quantitatively with predictions based on simple ionic theory.

4. Prediction of the contents of Mg, Fe, Al and Ca just from the three cell dimensions are of low accuracy even for specimens known to have strong site preference. The data suggested that the attainable accuracy is no better than 0.04, 0.02 and 0.01 for the Mg, Al and Ca cation contents expressed as a decimal fraction of the total of  $M$  cations. (These estimates are expressed roughly as a standard deviation, but the original paper must be consulted for the statistical details). For volcanic specimens, the variable site preference causes additional uncertainty in estimates of chemical composition.

There are innumerable papers dealing with the refractive indices of orthopyroxenes, but undoubtedly the data suffer from the same problems as those found for the cell dimensions.

The cell dimensions and optical properties of clinopyroxenes near the En and Fs join are subject to considerable uncertainty. Unfortunately many natural specimens contain exsolved augite, not always optically visible. In addition, the site preference of the  $M$  cations, and the domain texture responsible for the diffuse ( $h+k$ ) odd reflections, are variable. Consequently the sparse experimental data cannot bear more than a qualitative or semi-quantitative relation to the bulk chemical composition. Brown (1967) reviewed the available data reaching the pessimistic conclusion that for pigeonite time is better spent on chemical analysis of separated material than on optical measurements referred to dubious determinative charts.

Smith *et al.* (1968) reviewed the evidence whether Mg, Fe orthopyroxenes form an ideal solid solution series, beginning with the pioneering work of Ramberg and DeVore (1951). Briefly the physical data suggest:

1. There is no single ideal solid solution series across the whole composition range.
2. Slowly cooled natural specimens yield site preferences which indicate a near approach to two separate solid-solution series, and yield cell dimensions consistent with Vegard's rule for each series. However, the site preferences are not complete, indicating some deviation towards a single solid solution series.

Theoretically, one may expect some deviation from an ideal solid-solution for Fe-rich members. Davis in Jambor and Smith (1964) proposed that magnetic interactions between iron atoms in olivine could lead to a break in the relation between cell dimensions and chemical composition. Such a break was not established experimentally. The nature of the proposed magnetic interactions in pyroxenes is being investigated by Hafner and co-workers.

3. Some of the minor elements, Ca, Al and Mn, occur at concentration levels high enough to confuse attempts to determine the extent of non-ideality in natural orthopyroxenes. This problem is perhaps especially severe for those Fe-rich members which contain much Mn, and those Mg-rich members containing much Al.

There are very few data on the thermal expansion of the

Mg, Fe pyroxenes. For convenience these data together with new speculations will be discussed later in relation to the phase relations.

#### NEW CONSIDERATIONS

##### *Crystal structures:*

1. *Orthoenstatite.* The 3- $D$  least-squares structure refinement of orthoenstatite by Morimoto and Koto (priv. commun.) provides interatomic distances with a standard deviation near 0.01 Å. The details of the distortions of the coordination polyhedra are close to those found by Burnham (1967) for orthoferrosilite, and by Ghose (1965) for an orthohypersthene. Consequently the atomic coordinates of orthoenstatite can be considered known to an accuracy (*i.e.*  $3\sigma$ ) of about 0.03 Å in each interatomic distance. The Fourier refinement by Lindemann (1961a) yielded the same atomic topology, but the atomic coordinates are quite different from those of Morimoto and Koto.

2. *Low clinoenstatite.* There is a severe difference between the two structures proposed for low clinoenstatite at room temperature. Using 2- $D$  Fourier syntheses followed by 2- $D$  least-squares methods, Morimoto, Appleman and Evans (1960) determined the atomic coordinates of a twinned clinoenstatite obtained by heating an orthoenstatite from the Bishopville meteorite (the same source used by Morimoto and Koto). The resulting interatomic distances were assigned standard deviations ranging from 0.04 Å for  $M\text{-O}$  to 0.07 Å for  $\text{O-O}$  distances. Crystal-chemically the distances are compatible with the more accurate data obtained for pigeonite (Morimoto and Güven, 1968) and clinoferrosilite (Burnham, 1967) when account is taken of the difference between Mg and Fe cations.

The other data for clinoenstatite, by Lindemann (1961a), are quite different from those of Morimoto *et al.* Since no details were given of the X-ray method, the quality of the underlying data cannot be judged. The atomic coordinates in Lindemann's Table 3 are remarkable in that all but the  $z$ -coordinates of the MgI and MgII atoms obey the requirements of  $C2/c$ . The  $z$ -coordinates of MgI and MgII are 0.247 and 0.253, thus being displaced only 0.02 Å from the special coordinate 0.25 in  $C2/c$ . These deviations from  $C2/c$  are so small that the intensity of reflections of type ( $h+k$ ) odd would be much below the observational limit. Nevertheless Lindemann claimed to observe extra reflections from which he deduced the space group  $P2_1/n$ . Morimoto *et al.* (1960) found that reflections of type ( $h+k$ ) odd obeyed the restrictions for  $P2_1/c$ . Stephenson, Sclar and Smith (1966) were able to index the powder pattern of synthetic clinoenstatite using the restrictions for  $P2_1/c$ , while a new examination shows that the  $d$  corresponding to the reflections 302 and 102 cannot be explained by reflections which obey  $P2_1/n$ . The cell dimensions of clinoenstatite listed by Lindemann (1961b) *viz.*:  $a$ , 9.612(5);  $b$ , 8.820(5);

TABLE 1. SELECTED CELL DATA FOR PYROXENES

Name	Composition	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta$	$V(\text{\AA}^3)$	Space group	Temperature
Orthoenstatite <sup>a</sup>	Pure $MgSiO_3$	18.2249 (13)	8.8149 (8)	5.1746 (8)	—	831.30 (14)	$Pbca$	RT
Low clinoenstatite <sup>a</sup>	Pure $MgSiO_3$	9.6065 (11)	8.8146 (7)	5.1688 (6)	108.335 (9)	415.46 (9)	$P2_1/c$	RT
High clinoenstatite <sup>b</sup>	$(Mg_{.95}Ca_{.05})SiO_3$	9.864 (6)	8.954 (4)	5.333 (3)	110.03 (4)	442.5 (5)	$C2/c?$	1100°C
Protoenstatite <sup>c</sup>	Near $MgSiO_3$	9.252 (2)	8.740 (1)	5.316 (1)	—	429.9 (1)	$Pbcn?$	RT
Diopside <sup>d</sup>	Pure $CaMgSi_2O_6$	9.748	8.924	5.251	105.67	439.8	$C2/c$	RT
Orthoferrosilite <sup>e</sup>	Pure $FeSiO_3$	18.431 (4)	9.080 (2)	5.238 (1)	—	876.7 (5)	$Pbca$	RT
Clinoferrosilite <sup>e</sup>	Pure $FeSiO_3$	9.7085 (8)	9.0872 (11)	5.2284 (6)	108.432 (4)	437.6 (1)	$P2_1/c$	RT

<sup>a</sup> Stephenson, Sclar and Smith (1966).

<sup>b</sup> Smith (1969).

<sup>c</sup> New refinement of data by Smith (1959).

<sup>d</sup> Nolan and Edgar (1963).

<sup>e</sup> Burnham (1966).

$c$ , 5.201(5) Å;  $\beta$  71° 50(5)' are close to the values determined by Morimoto *et al.* and Stephenson *et al.*, thereby ruling out a possible transformation of axes to turn an  $n$ -glide plane into a  $c$ -glide plane. Since interatomic distances for Lindemann's structure are qualitatively similar to those in diopside, it seems likely that the atomic coordinates were obtained merely by a topologic analogy. The Lindemann structure must be wrong.

3. *High clinoenstatite.* There are no definitive data on the crystal structure of high clinoenstatite, as discussed in the literature review.

Table 1 compares cell dimensions of the various enstatite polymorphs. Even when account is taken of the 5 percent substitution of Mg by Ca in the high clinoenstatite, the volume of the latter phase at 1100°C is remarkably high, surpassing that of protoenstatite and diopside at room temperature. Smith (1969) pointed out that the  $c$  dimension of high clinoenstatite indicates full extension of the silicate chains, and proposed that as the temperature rises the Mg2 atoms vibrate with increasing amplitude thus simulating the inherently larger Ca atoms of diopside. Perhaps the Mg2 atoms oscillate from side to side of the cavity in a manner analogous to the interpretation proposed for the Ca atoms in anorthite by Smith and Ribbe (1969). Such increased vibration could be combined with straightening of the silicate chain, thus resulting in a structure similar to that of diopside. It would not be unreasonable for such an expanded structure to have the symmetry  $C2/c$ .

Smith proposed that pigeonite also undergoes a high-low inversion, and that the high form is isostructural with high clinoenstatite. Previously Morimoto and Tokonami (1968a) had interpreted diffuse ( $h+k$ ) odd reflections in pigeonite as the result of inversion of a high temperature form with space group  $C2/c$  to a domain texture of low temperature form with  $P2_1/c$ .

In the remainder of this paper, it will be assumed that all Ca-poor clinopyroxenes probably undergo a rapid, reversible inversion to a high form of symmetry  $C2/c$ . This high form should have extended silicate chains, and probably

will have M2 atoms vibrating in a large cavity similar to that occupied by Ca atoms in diopside.

4. *Protoenstatite.* The structural data for protoenstatite are rudimentary, and much more work is required. Unfortunately there are severe technical difficulties caused by the high temperatures at which protoenstatite is stable, and the strong tendency for inversion at the lower temperatures at which X-ray study is technically easier. A critical review of the available data is necessary.

Atlas (1952) prepared protoenstatite by heating anthophyllite. The resulting X-ray patterns showed that the single crystal contained an oriented aggregate of protoenstatite related by a common  $c$  axis. Earlier, Thilo and Rogge (1939) noted weak layer lines halfway between the main layer lines of a similar transformed specimen and gave  $c = 10.48$  Å. Atlas preferred to interpret the weak layer lines as the result of a subsidiary preferred orientation on [011] additional to the preferred orientation on [001], and decided that  $c$  is 5.25 Å, similar to all other pyroxenes. Partial indexing of the X-ray powder pattern of a protoenstatite obtained by heating  $MgSiO_3$  glass at 1300°C for 1 day without a flux yielded inaccurate cell dimensions  $a$  9.25,  $b$  8.92,  $c$  5.25 Å. Atlas did not find it necessary to double the values of  $a$  or  $b$  for either the single crystal or powder data. In addition he found that the single crystal reflections could be indexed by using the restrictions of  $Pbc-$ . He proposed a hypothetical structure but did not test it by comparing calculated and observed intensities. The model actually has space group  $Pbcn$ , not the stated  $Pbc2$ .

The powder data given by Atlas index satisfactorily on an orthorhombic cell of space group  $Pbcn$  with the new cell dimensions given in Table 2, except for the weak line at 3.48 Å and the strong line at 2.66. The weak line at 3.48 does not occur in the pattern given by Smith (1959) for protoenstatite made from pure  $MgSiO_3$  glass. Since Koltermann (1964) also observed this line for protoenstatite made from talc, it may result from some silica-rich impurity. Alternatively it may be a  $\beta$  line associated

TABLE 2. CELL DATA FOR PROTOENSTATITE

Reference	Source	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$\beta$	$V(\text{Å}^3)$	Temperature
Smith (1959) <sup>a</sup>	Pure MgSiO <sub>3</sub> glass	9.252 (2)	8.740 (1)	5.316 (1)	—	429.9 (1)	RT
Atlas (1952) <sup>a</sup>	Natural anthophyllite	9.230 (13)	8.730 (10)	5.311 (4)	—	428.0 (6)	RT
Lindemann (1961c) <sup>b</sup>	Natural talc	9.681 (5)	8.739 (5)	5.202 (5)	71°55 (5)'	418.4	RT
Koltermann (1964) <sup>a</sup>	Natural talc	9.239 (9)	8.734 (8)	5.305 (6)	—	428.0 (5)	RT
Lange & Koltermann (1966) <sup>a</sup>	Natural talc	9.245 (9)	8.75 (3)	5.33 (2)	—	431.3 (7)	20°
Lange & Koltermann	Natural talc	9.34 (4)	8.98 (13)	5.36 (9)	—	449.5 (3.5)	1450

<sup>a</sup> Cell dimensions determined from least-squares refinement of all uniquely indexed reflexions given equal weight. Lange and Koltermann listed only 4  $d$  for 221, 310, 121 and 211.

<sup>b</sup> No  $d$  listed by Lindemann. Single-crystal data taken.

Note that only Smith described a calibration procedure to reduce systematic error. The data of Atlas and of Koltermann appear to have systematic errors varying with the diffraction angle. Hence an unknown systematic error must be added to the above errors.

with the very strong reflexion at 3.16. The calculated (201) line falls at 3.49 Å, but violates the  $c$  glide plane of  $Pbcn$ . The 2.66 line probably is a transcription error for 2.56 since both Smith and Koltermann recorded a strong line at 2.55. The 040, 060 and 004 indices given by Atlas should be (231, 212), (531, 133) and 104.

Smith (1959) indexed an X-ray diffractometer pattern of pure synthetic protoenstatite using an orthorhombic cell with  $a$  9.25,  $b$  8.74 and  $c$  5.32 Å. Only one line (210) violated the conditions for  $Pbcn$ , and this line might actually index as (111) since the discrepancy between observed and calculated  $2\theta$ -values was only 0.06°. Detailed reexamination of the data in Smith's Table 1 shows satisfactory agreement between observed and calculated  $2\theta$ -values, and yielded the improved cell dimensions in Table 2; furthermore, a reasonable percentage of the possible calculated lines actually occurs. The following errors occur: the calculated line at 50.45° is from 232 not 242; the observed line at 1.6598 should be at 1.6880. Smith compared observed intensities with values calculated for the model proposed by Atlas, and made some minor adjustments of the atomic coordinates. The resulting  $R$ -factor of 0.36 (based on intensities *not* amplitudes) is encouraging but not convincing.

Brown and Smith (1963) confirmed that the space group of protoenstatite obeys the restrictions of  $Pbcn$  from single crystal photographs at 1000–1100°C of protoenstatite obtained by heating orthoenstatite from the Norton meteorite. Results could not be obtained at room temperature because of rapid inversion to a disordered clinoenstatite. They also obtained low-accuracy powder diffractometer data at 1400°C of protoenstatite grown from pure MgSiO<sub>3</sub> glass. The key reflections which serve to identify protoenstatite at room temperature were measured at 1350°C, and could be indexed satisfactorily on an orthorhombic cell. Unfortunately a gradual drift with  $2\theta$  of the discrepancy between observed and calculated  $d$  precluded determination of accurate cell dimensions. In addition to the lines ascribed to protoenstatite, three lines occurred whose intensities increased

reversibly as the temperature increased from 1000 to 1440°C. No corresponding reflexions were found on single crystal patterns. The strongest line at 3.03 Å might correspond to the strongest line of high clinoenstatite (3.06 Å) while the other strong lines of high clinoenstatite might be confused with lines of protoenstatite. The situation is unsatisfactory.

Koltermann (1964) obtained a powder pattern of protoenstatite from talc heated to 1270°C. The 4.08 line was ascribed by him to cristobalite impurity, which also could account for the 2.494 line not listed by Atlas or by Smith. The 1.797 line may be a transcription error for 1.807. The 3.51 line is analogous to the 3.48 line in Atlas' pattern. All other lines index satisfactorily using the cell dimensions of Table 2.

Lange and Koltermann (1966) heated talc at 1200°C and observed the X-ray powder diffraction pattern directly at temperatures up to 1450°C. Protoenstatite was observed at 1450°C. They listed  $d$  at 20°C and 1450°C for only four reflexions. From these values the cell dimensions given in Table 2 were calculated.

When account is taken of unrecorded systematic errors of measurement, and of a possible chemical difference between protoenstatite produced from pure MgSiO<sub>3</sub> and from natural specimens of talc and anthophyllite, the simplest explanation of all the available X-ray data is that protoenstatite is orthorhombic and that the space group could be  $Pbcn$ .

However Lindemann (1961c) proposed that  $\gamma$ -MgSiO<sub>3</sub> which he equated with protoenstatite (1961b) is monoclinic with space group  $P2_1/n$  and cell dimensions given in Table 2. Since Lindemann did not give a table of  $d$ , attempts were made to index the data of Atlas, Smith and Koltermann using this monoclinic cell. Success was not achieved without drastic change of the cell dimensions. Of course, the orthorhombic cell resulting from Smith's data can be transformed into a monoclinic cell which explains the powder data equally well. Unfortunately the  $a$ ,  $c$  and  $\beta$  values do not agree with those of Lindemann. Until Lindemann provides an indexing of

TABLE 3. OBSERVED AND CALCULATED REFRACTIVE INDICES

Polymorph	Experimental Values				Experimental $3\sqrt{\alpha\beta\gamma}-1$	Calculated $3\sqrt{\alpha\beta\gamma}-1$
	$\alpha$	$\beta$	$\gamma$	$V(\text{\AA}^3)$		
Orthoenstatite <sup>a</sup>	1.650 (1)	1.652 (1)	1.658 (1)	831.30 (14)	0.653	(0.653)
Clinoenstatite <sup>a</sup>	(1.651)	(1.654)	1.660 (1)	415.46 (9)	.655	.6533
$\gamma$ -enstatite <sup>b</sup>	1.602	1.604	1.611	418.4	.606	.649
Protoenstatite <sup>c</sup>	—	—	—	429.9	—	.631

<sup>a</sup> Stephenson, Sclar and Smith (1966).

<sup>b</sup> Lindemann (1961c).

<sup>c</sup> Table 2.

the powder patterns his data must be suspected. Lindemann stated that the cell dimensions and space group were determined from single crystal patterns of  $\gamma$ - $MgSiO_3$  formed by firing talc, but detailed data were not given.

The refractive indices given by Lindemann are surprisingly low. Table 3 compares observed and calculated refractive indices using the Gladstone-Dale relation. For isotropic polymorphs,  $(n^2 - 1)/(n^2 + 2)$  should be proportional to the density. For anisotropic material,  $n$  can be replaced by  $\sqrt[3]{\alpha\beta\gamma}$ . To a sufficient level of approximation  $(\sqrt[3]{\alpha\beta\gamma} - 1)$  is proportional to the density. Taking orthoenstatite as a standard, mean refractive indices were calculated by use of the cell volume determined by X rays. The observed and calculated values of clinoenstatite are in reasonable agreement, but the observed refractive indices for  $\gamma$ - $MgSiO_3$  are very much lower than the value calculated from Lindemann's cell volume. The discrepancy is so large that either the observed refractive indices or the cell volume, or both sets of data, are wrong.

This calculation also points up a problem with the cell data for protoenstatite proposed by Smith. The predicted mean refractive index for protoenstatite, 1.631, is well below the mean values of 1.653 and 1.655 for ortho- and clino-enstatite. Yet Boyd and Schairer (1964, p. 298) reported that ortho- and proto-enstatite "cannot readily be distinguished by optical methods inasmuch as both have parallel extinction and their indices of refraction are the same within the accuracy obtained by routine microscopic determinations." Furthermore Atlas reported that the refractive indices of protoenstatite differ not more from those of an unheated enstatite than the experimental error of about 0.002. The optic axial angle was observed as about  $+70^\circ$  compared to  $+60^\circ$  for orthoenstatite and  $+53\frac{1}{2}^\circ$  for clinoenstatite. If these statements are rigorously true, the unit cell proposed by Smith for protoenstatite has too great a cell volume. It is possible that the protoenstatites examined by Boyd and Schairer and by Atlas had inverted to clinoenstatite *submicroscopically* thus attaining the higher refractive indices of clinoenstatite while retaining parallel extinction. Obviously detailed optical and single crystal diffraction studies are needed to resolve this anomaly.

Smith (1959) checked the structure model proposed by

Atlas. Since computer programs were not available, the atomic positions were adjusted by hand calculations. Although the space group  $Pbcn$  enforces strict geometrical requirements on the positions of the Mg atoms and the silicate chains, the structural model was geometrically idealized to ease calculation. The resulting structure amplitudes gave reasonable but not convincing agreement with the observed intensities from the diffractometer pattern.

Because of the scepticism about the structure, the data were subjected to a new least-squares refinement with the aid of Mr. S. J. Louisnathan. Since only 27 nonoverlapping intensities were available, a complete refinement was statistically unfeasible. After some preliminary tests of key positional parameters, all 14 positional parameters and the overall scale factor were refined while the  $B$ -values were held constant at arbitrary values. Two extreme weighting schemes were used. In the first scheme, only the 27 nonoverlapping intensities were used, and all the resulting amplitudes were given equal weight. In the second scheme, all 85 possible amplitudes up to the termination of the diffractometer pattern were used. For observed, nonoverlapping reflections, the standard error in  $F_o$  was based on the estimated error of the area of the diffractometer peak. For the strong intensities, a limiting minimum error of  $\sigma(F_o) = 0.1 F_o$  was used because of the possibility of preferred orientation and perhaps extinction. For unobserved reflections,  $pF_o^2$  was taken to be equal to the average  $pF_o^2$  for unobserved reflections; this value increased with decreasing  $d$  because of the Lorentz-polarization factor. Arbitrarily  $\sigma(F_o)$  was taken as equal to  $F_o$ . For overlapping reflections, the intensity was split according to the values calculated for the preceding refinement. Large values were ascribed to  $\sigma(F_o)$  because of the uncertainty. The choice of the weights is essentially a matter of personal judgment and cannot be justified rigorously. However, the two refinements described here do show how the weighting affects the resulting atomic coordinates. Half-ionized atomic form factors were used. Study of the refinements suggested very small  $B$ -values, indicating some experimental error depending on diffraction angle.

Table 4 shows the atomic coordinates resulting from the two refinements. Table 5 lists the interatomic distances for

TABLE 4. ATOMIC COORDINATES FOR PROTOENSTATITE

Atom	Refinement 1 <sup>a</sup>			Refinement 2 <sup>b</sup>			Arbitrary <i>B</i> (Å <sup>2</sup> )
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	
Mg1	0	0.089 (10)	0.75	0	0.092 (3)	0.75	0.2
Mg2	0	.272 (8)	.25	0	.270 (3)	.25	.2
Si	0.289 (5)	.098 (7)	.083 (14)	0.294 (2)	.091 (3)	.063 (5)	.0
O1	.119 (10)	.093 (10)	.105 (23)	.131 (4)	.086 (4)	.086 (8)	.4
O2	.373 (11)	.258 (12)	.084 (20)	.377 (3)	.272 (5)	.037 (7)	.4
O3	.346 (13)	.979 (11)	.262 (25)	.346 (4)	.978 (4)	.284 (10)	.4

<sup>a</sup> Equal weight to all observable lines with unique indices.

<sup>b</sup> All reflections with weights assigned according to estimated uncertainty.

the three polyhedra. Table 6 lists observed and calculated  $F^2$  for the first refinement, and Table 7 the structure amplitudes for the second refinement together with the estimated values of  $\sigma(F_o)$ .<sup>1</sup> To save space, individual errors have not been calculated for the distances, but typically for refinements 1 and 2, the least-squares calculations yield  $\sigma(\text{Si-O})$  near 0.10 and 0.04 Å, respectively. If confidence limits are taken at  $3\sigma$ , the uncertainty levels are near 0.3 and 0.12 Å, respectively.

Figure 8 shows the *c*-axis projection of protoenstatite, and Figure 9 the details of the coordination polyhedra. In discussing the structure there are two major questions: first, is the structure correct, and second, are the distortions of the polyhedra meaningful? Since a father is usually over-proud of his offspring, I am probably optimistic in thinking that there is no serious conflict between observed and calculated intensities for the present model. None of the interatomic distances in Table 5 is inconsistent, within the derived error limits, with values expected from crystal chemical analogy with related structures. Nevertheless I think that it can be reasonably claimed that the agreement between observed and calculated amplitudes and intensities in Tables 6 and 7 is not as good as might be expected. The

<sup>1</sup>To obtain a copy of Tables 6 and 7, order NAPS Document #00452 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting \$1.00 for microfiche or \$3.00 for photocopies.

stronger intensities which should have good statistics do not yield better than moderate agreement. However, the calculated values for unobserved reflections are almost all below the estimated detection limits. One unobserved reflection (312) in Table 7 has a medium calculated value, but this reflection may be masked by the  $\alpha_2$  component of (331). Perhaps there is preferred orientation on (110) since the observed values for 220, 330 and 440 are higher than the calculated values.

The second question is also hard to answer. The second refinement yielded lower standard deviations than the first one, but its weighting scheme is so strong that one is sceptical of the significance of the errors. Qualitatively, I suggest that both sets of distances in Table 5 be considered. The distances in Figures 8 and 9 are the mean values for the two refinements. Even when the large errors are considered, some of the apparent distortions may be meaningful. The Mg1 polyhedron is a regular octahedron within experimental error. The Mg2 polyhedron is an irregular octahedron with distortions similar to those found in clino- and ortho-enstatite. The Mg2-O3 distance seems to be genuinely longer than the other distances. All shared edges are short (Fig. 9): the edge between Si and Mg2 polyhedra is 2.6, those between Mg1 and Mg2 polyhedra are 2.8 and 2.8 Å. Nonbonding oxygen contacts are not listed in Table 5, but all values are reasonable.

Until new data are obtained this crystal structure will be used in further discussions of the paper. Mr. J. R.

TABLE 5. INTERATOMIC DISTANCES (Å) FOR TWO REFINEMENTS OF THE PROTOENSTATITE STRUCTURE

Atoms	First	Second	Atoms	First	Second	Atoms	First	Second
Si-O1	1.58	1.51	Mg1-O1	2.19	2.16	Mg2-O1	2.06	2.19
Si-O2	1.60	1.76	Mg1-O1'	2.08	2.16	Mg2-O2	2.15	1.94
Si-O3	1.51	1.61	Mg1-O2	1.99	1.99	Mg2-O3	2.30	2.31
Si-O3'	1.91	1.67	O1-O1'	3.12	3.06	O1-O1'	2.69	2.98
O1-O2	2.76	2.81	O1'-O1''	2.96	3.00	O1-O2'	2.81	2.73
O1-O3	2.47	2.44	O1'-O1'''	2.69	2.98	O1-O2	2.86	2.70
O1-O3'	2.85	2.62	O1-O2	3.06	3.17	O1-O3	3.49	3.59
O2-O3	2.63	2.90	O1'-O2	2.93	2.76	O2-O3	2.70	2.58
O2-O3'	2.70	2.58	O1''-O2	2.81	2.73	O2'-O3	3.80	3.77
O3-O3'	2.68	2.69	O2-O2'	2.94	3.20	O3-O3	2.85	2.87

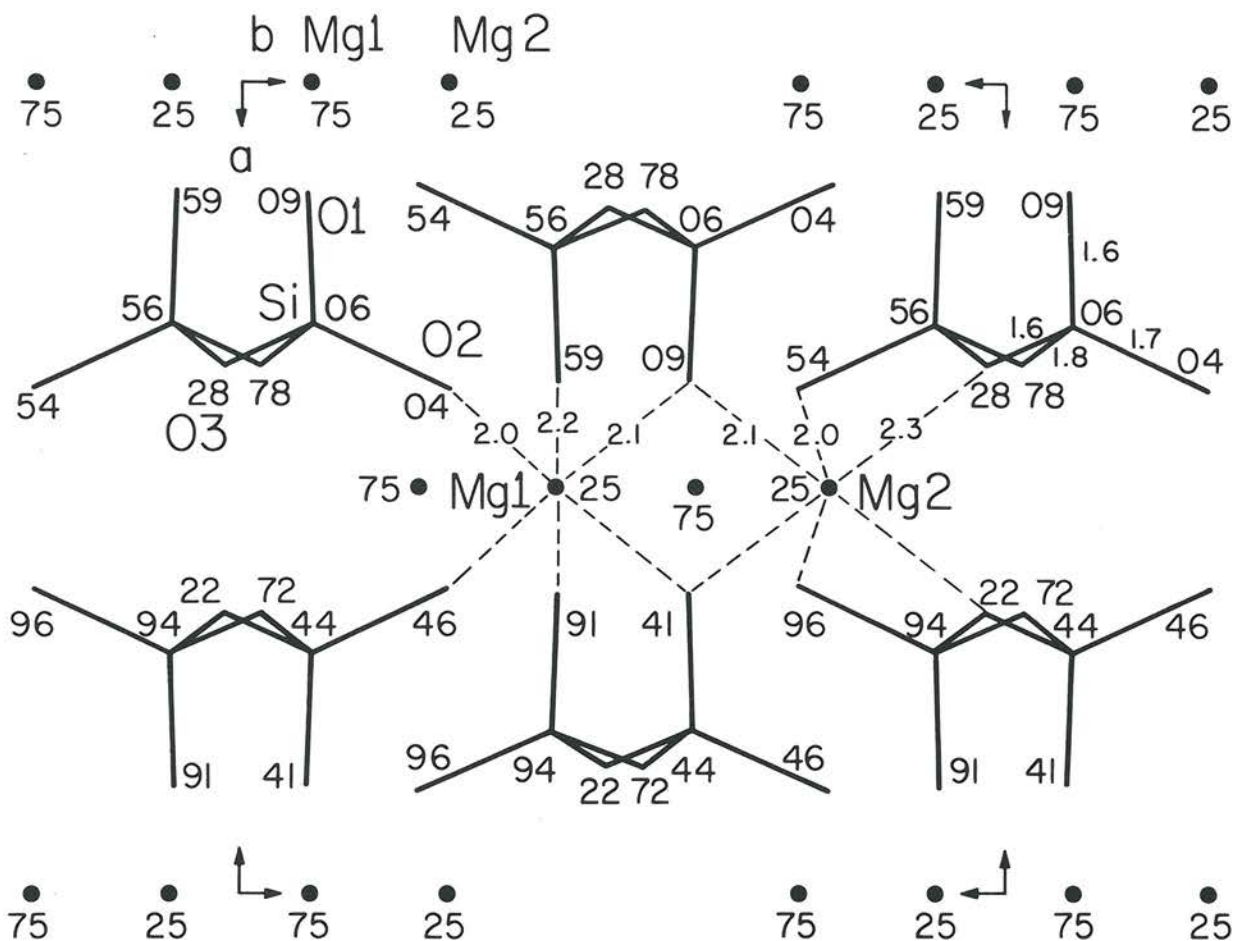


FIG. 8. Refined crystal structure of protoenstatite shown on the c-axis projection, with heights shown as percentages of  $c$ .

Smyth is currently measuring intensities for a single crystal of protoenstatite held above  $1100^{\circ}C$ .

To conform to the nomenclature proposed for clinopyroxene by Burnham *et al.* (1967), the  $Mg_1$  and  $Mg_2$  of

Smith (1959) were switched to  $Mg_2$  and  $Mg_1$ . The Si and O atoms were already analogous, but the suffix notation is changed e.g.  $O_1$  becomes  $O1$ .

Von Gehlen (1962) argued that the crystal structure

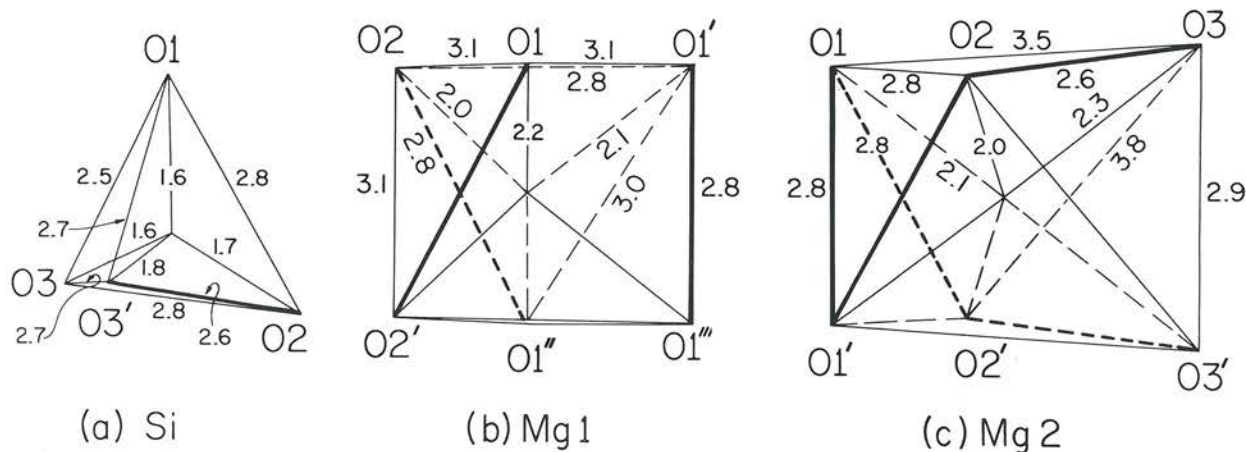


FIG. 9. The coordination polyhedra in protoenstatite. Shared edges are shown by heavy lines.

of protoenstatite must be wrong since the preferred orientation of protoenstatite formed by firing talc at 1300 and 1400°C could not result from an orthorhombic structure. He claimed that the peaks were consistent with Lindemann's monoclinic cell for  $\gamma$ -enstatite. Contrary to von Gehlen's claims of a very good planar orientation, his Figure 4 shows X-ray peaks with a half-width of 20–40°. His attempted resolution of a complex peak into two peaks is unconvincing. Furthermore there is a possibility that high clinoenstatite rather than protoenstatite nucleates first. In addition, there may be complex epitaxial relations between talc and pyroxene which complicate the situation. The results of Atlas (1952) are instructive. In an appendix von Gehlen argues that clinoenstatite did not form as an intermediate. Furthermore he states that because Lindemann's proposed models for clinoenstatite and protoenstatite are closer to each other than are the structures determined by Morimoto *et al.* and by Smith, they provide a better reason for easy transformation of protoenstatite into clinoenstatite upon grinding. Actually Lindemann's models differ only by  $\sim 0.2 \text{ \AA}$  in the  $z$ -coordinates of his O(V), O(VI) and Mg(I). This difference is so small that the transformation would be displacive in character. Although the transformation is easy, the experimental data suggest that it involves a significant activation energy. The Smith model for protoenstatite can transform to the Morimoto *et al.* model for clinoenstatite by an *auto-epitaxial* transformation involving a moderate activation energy.

*Enstatite polymorphs considered as polysynthetic structures.* Warren and Modell (1930) suggested that the orthorhombic unit cell of enstatite (hypersthene) is essentially two monoclinic cells joined through a  $b$ -glide plane on (100). Ito (1935) questioned whether the enstatite structure results from a statistical twinning (*i.e.* irregularly spaced twin planes) or whether a regularly repeated "twinning" is involved. He pointed out the difficulty of an experimental distinction. Ito (1950) in a collection of papers devoted to submicroscopic twinning developed a theory of regularly-twinned space groups, and assigned the name *polysynthetic structures*. He refined the atomic coordinates of a hypersthene, and went on to show that the monoclinic subunit has symmetry  $P2_1/c$  rather than the  $C2/c$  of diopside. Morimoto (1956) and Bown and Gay (1957) found that natural Mg-poor pyroxenes actually have symmetry  $P2_1/c$ , while Morimoto *et al.* (1960) produced a detailed structure for clinoenstatite and pigeonite based on this space group. Morimoto and Koto (priv. commun.) considered their refined structure of orthoenstatite to be an exact twin of clinoenstatite. Burnham (1967) mathematically "twinned" his refined structure of clinoferrrosilite and found that it compared closely with his refined structure of orthoferrrosilite. He suggested that orthoferrrosilite contains do-

mains within which the unit cells are "made up of double monoclinic units related exactly by the  $b$  glide, but between which there is a spatial mismatch due to structural adjustments that are apparently necessary to effect the glide operation." He stated that this hypothesis was supported by the apparent atomic displacement factors ( $B$ -values) which are two to three times larger in the ortho variety. However Morimoto and Koto did not find abnormally large  $B$ -values for orthoenstatite.

The availability of accurate data permits a more accurate test of Ito's hypothesis than was available earlier. Figure 10a shows the hypothetical relationship between the ortho- and clino-cells, while Figure 10b compares transformed clinoferrrosilite with orthoferrrosilite. Table 8 gives the transformations between clinopyroxene and hypothetical orthopyroxene based on the geometry of Figure 10a. It should be noted that for an ideal transformation the cell dimensions bear the following relationships:  $a_o = 2a_c \sin \beta^*$ ;  $b_o = b_c$ ;  $c_o = c_c$ . Table 9 shows that these relationships are not obeyed exactly for ferrrosilite; however, the difference is close to the experimental error. Probably there is a genuine difference between the cell volumes of enstatite since the refractive indices via the Gladstone-Dale relation also indicate a lower density for orthoenstatite. The transformations of Table 8 refer to unit cells which fit exactly at point  $p$  of Figure 10b, but do not fit exactly at point  $q$ . Table 10 compares atomic coordinates of ortho- and clinoferrrosilite. The differences between observed and theoretical values for clino-ferrrosilite are small and at first sight hardly greater than the observed errors. Close study of Figure 10b however reveals an important relation. The coordinates for the atoms of the B silicate chain fit more closely than those of the A chain. This is precisely what should result if distortions occur which decrease with the distance from those atoms which have drastic changes of position. The addition of the  $b$ -glide plane causes relative movements of  $M$  atoms directly bonded to atoms of the A silicate chains, but does not affect  $M$  atoms bonded to the B silicate chains. It is concluded that *isochemical* clino- and ortho-pyroxenes are *not* related exactly by regular operation of a  $b$ -glide plane on an identical unit. Rather it is concluded that the transformation causes small distortions interpretable in terms of chemical interactions between distant atoms.

Such a structural distortion is reasonable from the viewpoint of chemical stability. If clino- and ortho-pyroxenes were related by an exact transformation it would imply that only chemical interactions between first neighbors affect the thermodynamic energy functions and that the polymorphs have equal stability at absolute zero. There would be no reason why one polymorph should occur in preference to the other. Pyroxenes should occur as a random intergrowth with the glide operation occurring randomly (as originally considered by Ito). Although pyroxenes with disordered stacking are not uncommon (Brown and Smith, 1963),



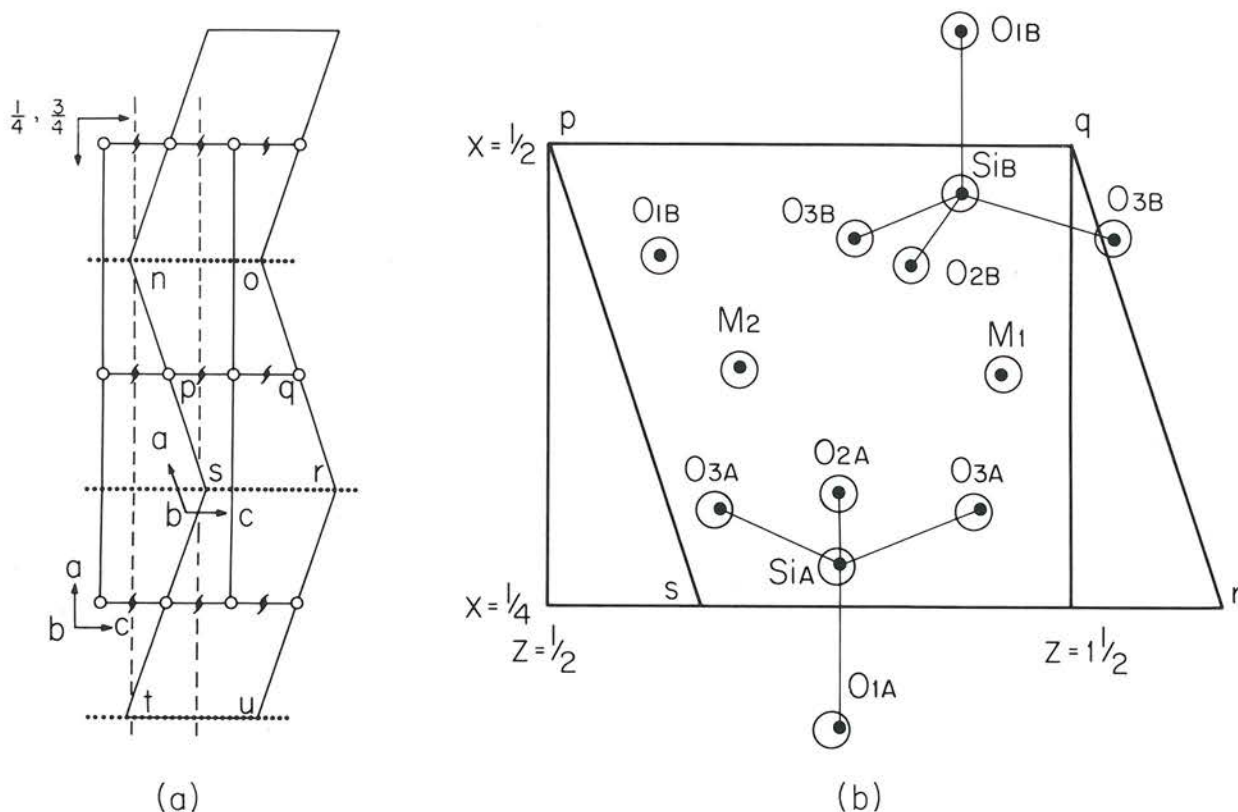


FIG. 10(a). Relation between the unit cells of ortho- and clino-pyroxene. The unit cell of orthopyroxene is outlined by the rectangle, and the glide planes in the space group  $Pbca$  are shown by conventional symbols. An equivalent unit cell of clinoenstatite is shown at  $nors$ . The centers of symmetry at  $p$  and  $q$  mark the overlapping points of the two unit cells. The second unit cell of clinoenstatite  $rstu$  is related to the first one by the  $b$  glide plane.

(b). Comparison of the coordinates of clinoferrosilite with transformed orthoferrosilite. The parallelogram  $pqrs$  is the same as the one in Fig. 10a. The atomic coordinates are given in Table 10. Dots, clino; center of circles, ortho.

the experimental evidence favors ordered orthopyroxene as the stable phase under low-temperature hydrostatic conditions. At higher temperatures, experimental evidence for  $(Mg,Fe)SiO_3$  favors ordered clinopyroxene as a stable phase, but the evidence is less clear.

The specific case of pyroxene suggests that the more general case of polytypism be considered. Ito's concept of a *polysynthetic structure* is merely an example of one-dimensional polymorphism, or polytypism, in which the same basic unit is stacked differently along one axis while retaining the same lattice repeats in the plane perpendicular to the axis. In a survey monograph, Verma and Krishna (1966) discussed the various theories concerning the occurrence, growth and relative stability of polytypes. For some polytypes, e.g.  $SiC$ , there is no

evidence of a distortion caused by a different stacking scheme. Pyroxene provides an example of distortion of the basic unit occurring in isochemical polytypes. Probably a similar distortion occurs in mica polytypes, but careful structural study of *isochemical* polytypes has not yet been achieved. Perhaps distortion occurs in *all* polytypes, but only in a few is the distortion large enough to be demonstrated experimentally, and large enough to result in a clearly-defined thermodynamic stability field.

The observation of a structural distortion between the subunits of pyroxene polytypes does not mean that Ito's idea of unit-cell twinning is invalid. In simple

TABLE 9. COMPARISON OF CELL DIMENSIONS OF PYROXENE POLYTYPES

Name	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$
Transformed clinoenstatite	18.238 (2)	8.8146 (7)	5.1688 (6)	830.92 (18)
Orthoenstatite	18.2249 (13)	8.8149 (8)	5.1746 (8)	831.30 (14)
Transformed clinoferrosilite	18.421 (2)	9.0872 (11)	5.2284 (6)	875.2 (2)
Orthoferrosilite	18.431 (4)	9.080 (2)	5.238 (1)	876.7 (5)

TABLE 8. TRANSFORMATION OF ORTHO TO CLINO PYROXENE<sup>a</sup>

$$x_c = (x_o - \frac{1}{4}) a_o / (a_c \sin \beta^*) \cong 2(x_o - \frac{1}{4})$$

$$y_c = y_o b_o / b_c \cong y_o$$

$$z_c = \frac{1}{2} + z_o + (x_o - \frac{1}{2}) a_o \tan \beta^* / c_c$$

<sup>a</sup> Subscripts  $o$  and  $c$  refer to ortho and clino.

TABLE 10. TRANSFORMATION OF ORTHO TO CLINO FERROSILITE<sup>a</sup>

Atom	Ortho-Fs			Theoretical Clino-Fs			Observed Clino-Fs		
	x	y	z	x	y	z	x	y	z
M1	0.3759 (1)	0.6542 (2)	0.8755 (5)	0.2518 (2)	0.6542 (2)	0.2297 (5)	0.2508 (2)	0.6533 (1)	0.2255 (3)
M2	.3775 (1)	.4854 (2)	.3660 (5)	.2550 (2)	.0146 (2)	.2221 (5)	.2570 (2)	.0142 (1)	.2233 (3)
SiA	.2719 (2)	.3386 (5)	.0498 (6)	.0438 (4)	.3386 (5)	.2818 (6)	.0447 (2)	.3386 (3)	.2924 (4)
SiB	.4735 (2)	.3342 (5)	.7878 (6)	.5530 (4)	.8342 (5)	.2433 (6)	.5538 (2)	.8339 (3)	.2393 (4)
O1A	.1862 (4)	.3387 (11)	.0410 (14)	.8724 (8)	.3387 (11)	.1723 (15)	.8711 (6)	.3397 (7)	.1856 (10)
O2A	.3106 (4)	.4955 (10)	.0558 (16)	.1212 (8)	.4955 (10)	.3333 (17)	.1246 (6)	.4953 (6)	.3351 (11)
O3A	.3020 (4)	.2355 (9)	.8159 (18)	.1040 (8)	.2645 (9)	.5833 (19)	.1054 (5)	.2660 (5)	.5986 (10)
O1B	.5609 (4)	.3371 (12)	.7871 (14)	.3782 (8)	.8371 (12)	.1413 (15)	.3786 (6)	.8354 (7)	.1387 (10)
O2B	.4346 (4)	.4783 (9)	.6934 (17)	.6308 (8)	.9783 (9)	.3834 (18)	.6330 (6)	.9813 (6)	.3856 (11)
O3B	.4491 (4)	.2041 (8)	.5862 (18)	.6018 (8)	.7041 (8)	.4736 (19)	.6036 (5)	.7011 (6)	.4758 (10)

<sup>a</sup> Errors in brackets to same significance level as coordinate. The errors for the theoretical clino-Fs were obtained just from the listed errors for ortho-Fs combined independently according to the equations in Table 8. Errors in the cell dimensions were neglected. All observed data from Burnham (1967).

twinning, distortion should always exist at the twin boundary even though the structure away from the boundary is undistorted. In orthopyroxene, the entire structure corresponds to boundary regions!

#### Cooperative atomic movement in pyroxene

1. *General.* Movement of single atoms comes under the category of diffusion. Perhaps for petrologists the most interesting such process in pyroxenes is diffusion of Mg,Fe atoms between the M1 and M2 sites as studied kinetically with Mössbauer resonance techniques. Virgo and Hafner (1969) found major changes of distribution after heating times ranging from hours to days at 500–1000°C. These results show that the M cations move much more easily than the Si and Al cations of feldspars. For cooperative atomic movements in pyroxenes a corresponding difference will be assumed for the ease of breaking M–O and Si–O bonds. Two main categories of cooperative movements can be distinguished: (1) transformations which preserve homogeneity of chemical composition, (2) transformations which result in two or more regions of different chemical composition.

In the first category, phase inversions are of particular interest. Since mechanical deformation has a remarkable effect on pyroxenes, phase inversions will be considered in two categories depending on the absence or presence of applied mechanical stress. To some extent this distinction is false since intrinsic mechanical effects result upon heating of any substance merely because of the presence of impurities and defects, and because of temperature gradients and anisotropic thermal expansion. Nevertheless the intrinsic effects are so much smaller than extrinsic effects that they justify a separate category.

The principal transformation involving regions of different chemical composition is exsolution of Ca-poor and Ca-rich pyroxenes from a single pyroxene. This process is often complicated by structural inversion of

one or more of the pyroxenes. Metasomatic alteration of a pyroxene may also come under this category, but is commonly regarded as a minor process.

Since there are no techniques available for observing the actual movement of atoms in pyroxenes, all discussions of cooperative atomic migration are essentially speculative. The most obvious approach is to minimize the estimated energy of broken bonds, but there is no guarantee that this yields the correct mechanism.

2. *Phase inversion without applied mechanical force.* Brown, Morimoto and Smith (1961) suggested a plausible glide mechanism for the transformation of one polymorph into another, and depicted models for the transformation of proto- into either ortho- or clino-enstatite. The BMS suggestion consists of relative translation along [001] in the (100) plane of unbroken silicate chains with breaking of some Mg–O bonds and retention of others. The layers of interlocked silicate chains maintain their integrity except for major changes of Si–O–Si bond angles and minor changes of distances. The transformation could be described as autoepitaxy since part of the structure acts as a template for another part of the structure. The atomic movements could be described by the term *shuffle* used by metallurgists.

There is one problem not considered by BMS. The mechanism implicitly assumes that each entire sheet of silicate chains simultaneously slips over the adjacent sheet. This requires that all atoms in the interface are simultaneously in the intermediate position of high energy. Perhaps a more plausible suggestion is that a transformation wave runs through the interface somewhat analogous to the hump-backed motion of a caterpillar. Since Si–O bonds are stronger than Mg–O bonds, the silicate chains should remain unbroken. Perhaps all Mg–O bonds are broken at the crest of the transformation wave, and regain their coordination by an epitaxial mechanism. Even for this more drastic mechanism, it

seems reasonable to suppose that the silicate layers adopt a new position such that minimum dislocation occurs. Thus the layers should tend to slip into the next position of low energy rather than moving into a more distant position.

Disorder obviously can provide a trigger for this mechanism. Existing stacking faults seem to act in this way, since Brown and Smith (1963) found that D-enstatite (as defined by them) from the Norton meteorite transformed upon heating into protoenstatite much more easily than the O-enstatite from the Bishopville meteorite.

Another crystallographic defect, termination of silicate chains, seems a likely factor, but there is no experimental evidence for its efficacy or otherwise. Although silicate chains are considered crystallographically to be infinite, many pyroxene crystals have cracks cutting across the  $c$ -axis, e.g. the clinopyroxene described by Dallwitz *et al.* (1966). At such terminations, intrinsic mechanical stresses could be focused thereby increasing the energy available for transformation.

The vibrational energy of the atoms should be of great importance for the reaction. Not only does the vibrational energy contribute to the Gibbs function, and hence to determining which particular polymorph is truly stable, but it also affects the kinetics and the nature of the transformation. At low temperatures, atomic vibrations are weak and tend to be independent of each other. At higher temperatures, vibrations are greater and tend to become cooperative. In pyroxene, the thermal agitation of the  $M2$  atom is of particular interest since it occupies a coordination polyhedron which can expand to include additional oxygen atoms. In diopside, the large Ca atom in the  $M2$  site holds apart the silicate chains so that the symmetry is  $C2/c$ . Even so, the silicate chains are kinked. Adoption of the most regular configuration with maximum extension along  $c$  would provide additional space for the Ca atom. In clino- and orthoenstatite at room temperature, the silicate chains are collapsed around the smaller Mg2 atom resulting in symmetry  $P2_1/c$ . Upon heating, the Mg atom should simulate a larger atom and force apart the silicate chains. Smith (1969) suggested that clinoenstatite could adopt the space group  $C2/c$  when the Mg atom begins to vibrate so strongly that it simulates the Ca atoms of diopside, and that the high-low transition in clinoenstatite results from this mechanism. Smith also suggested that orthoenstatite would show similar thermal effects to those of clinoenstatite, though the zig-zag arrangement of the layers of silicate chains should make a high-low transition more difficult.

Thermal vibration ultimately will become so strong that the atomic vibrations become cooperative (see Smith and Ribbe, 1969 for a general description of a similar effect in anorthite). The silicate chains may vibrate in a whip-lash manner.  $M2$  cations may become bonded

temporarily to only the oxygen atoms at one end of the cavity. A domain texture may form in which all  $M2$  cations in one domain are displaced to the left while those in adjacent domains are displaced to the right. This domain texture would be dynamic not static.

The difference between the quench products of enstatite polymorphs may be explained by such a dynamic domain texture. The texture would be very sensitive to grain size and to both physical and chemical defects. Since the texture should depend on temperature, a correlation should exist between the quench products and the heating temperature. I suggest that the experimental evidence for a distinct difference between quench products of enstatite composition above and below the firing temperature of  $1400^\circ\text{C}$  may be explained by the beginning of a different type of thermal vibration. Perhaps whiplash motion of the silicate chains ultimately becomes so strong that the olivine structure with isolated silicate tetrahedra becomes favored thus producing incongruent melting. Obviously other factors are involved, including the structure of the disproportioned liquid.

For *auto-epitaxial* transformations, there are special crystallographic orientational relations which may have petrogenetic significance. All polymorphs formed by such a transformation should have a common (100) plane. Since monoclinic polymorphs have two choices for the  $a$ -axis, the transformation of an orthorhombic to a monoclinic polymorph should result in random twinning for the latter. These remarks have implicitly assumed that each twin domain is large and has no stacking disorder. This assumption need not be valid, and its removal results in stacking disorder for the transformation product. As mentioned earlier, the high-low transition in clinopyroxene provides two possible choices of origin for  $P2_1/c$  in relation to the original  $C2/c$  thus providing the opportunity for out-of-step sequences.

Some specific transformations will now be discussed. Bowen and Schairer (1935) produced twinned clinohypersthene by heating orthohypersthene. The twinning provides no evidence for or against the existence of protohypersthene at the heating temperature since the twinning could result from either (1) transformation from ortho to clino with increasing temperature or (2) transformation from ortho to proto with increasing temperature followed by transformation to clino upon cooling.

Dallwitz *et al.* (1966) stated that phenocrysts of multiply-twinned clinopyroxene (near  $\text{En}_{90}\text{Fs}_{10}$ ) from a Papuan volcanic rock are a metastable inversion-product from primary protopyroxene for reasons given earlier. The possibility will now be examined that the twinning results from inversion of an orthohypersthene to clinohypersthene as a result of rise of temperature during the eruption process.

Dallwitz *et al.* gave a very detailed description of the

pyroxenes, reporting the presence of euhedral phenocrysts of both twinned clinoenstatite and untwinned orthobronzite. Other phenocrysts (their Fig. 5) consist of a composite of untwinned orthobronzite and twinned clinoenstatite with sharp, irregular sector boundaries. The texture is most easily explained by partial, irregular transformation of one mineral into the other. It strongly resembles the description given by Bowen and Schairer of orthopyroxenes inverted in the laboratory. Some of the crystals have feathery terminations which suggest that an inversion took place according to glide on (100) and [001]. Microprobe analyses (Dallwitz *et al.*; Fig. 8) showed that the clinoenstatite ranges from  $En_{92}$ - $En_{87}$  while the bronzite ranges from  $En_{82}$ - $En_{87}$ . In the composite crystals the clinoenstatite tends to be more Mg-rich than the orthobronzite, but undetected chemical zoning may have caused confusion. In addition to the phenocrysts there are microlites of twinned clinoenstatite and calcic pyroxene. Furthermore the phenocrysts may be rimmed by pyroxenes of different composition.

Since there might be mixing of magmas with phenocrysts of different types, and since the temperature-time history of the extrusion might be rather complex, I suggest that the crystallographic evidence for inversion of clinopyroxene from a protopyroxene is inconclusive. Probably the best evidence for the inversion from a protopyroxene lies in the higher Ca content of the orthobronzite compared to the clinoenstatite. However even this evidence could be explained by two different magma sources. The compositional differences between ortho and clino forms coexisting in the same phenocryst are inconclusive because of chemical zoning and uncertain optical identification. Tentatively I suggest that the intergrown crystals of ortho- and clino-pyroxene may have formed upon heating of the former during extrusion, whereas the phenocrysts consisting only of clinoenstatite may have inverted from protopyroxene.

The cooling of protoenstatite produces D-enstatite whose X-ray pattern resembles that of twinned clinoenstatite more than that of orthoenstatite (Brown and Smith, 1963). The presence of strong stacking disorder shows that there is a statistical uncertainty in the direction of glide during the inversion. The diffuse X-ray reflections deserve detailed study to test models which predict the distribution of glide directions. The simplest model consists of a completely random spatial distribution of glide. A more complex model would consider local correlation of glide. Qualitative examination of the X-ray photographs of inverted protoenstatite suggests that there is local correlation of glide since the X-ray patterns resemble that of twinned clinoenstatite more than that of orthoenstatite (Brown and Smith). Nevertheless the evidence is not convincing since orthoenstatite requires correlated zig-zig-zag sequences

whereas clinoenstatite requires only correlated zig (or correlated zag) sequences. Hence in a random sequence of glides, runs which obey correlated zig sequences will be more frequent than runs which obey zig-zig-zag-zag sequences. If statistical analysis confirms the qualitative impression of Brown and Smith, it is possible that the local correlations result from intrinsic shear stress developed during the inversion.

3. *Phase inversion with applied mechanical stress.* Mechanical stress can be resolved macroscopically into hydrostatic and shear components. Submicroscopically even hydrostatic pressure can be resolved locally into shear components because of the presence of structural defects. Most high pressure studies of pyroxenes utilize uniaxial compression in which strong shear stresses should develop. The pseudo-hydrostatic experiment of Munoz (1968) showed quite different results from uniaxial compression experiments.

Shear stress applied as a couple about the  $b$  axis could cause simple glide on (100) with glide direction [001] according to the Brown-Morimoto-Smith mechanism (see Fig. 11). Major changes of Si-O-Si bond angles are also needed. There appears to be no experimental evidence for this mechanism either in synthetic or natural specimens. However it might readily escape detection in polycrystalline aggregates since it could result in a deformation detectable only by a change of external morphology. When crystals are anhedral, the necessary evidence might be completely lacking. The glide mechanism could result in a phase inversion (Fig. 11).

The mechanism of kinking results in a dramatic change of shape which is readily visible since the kink

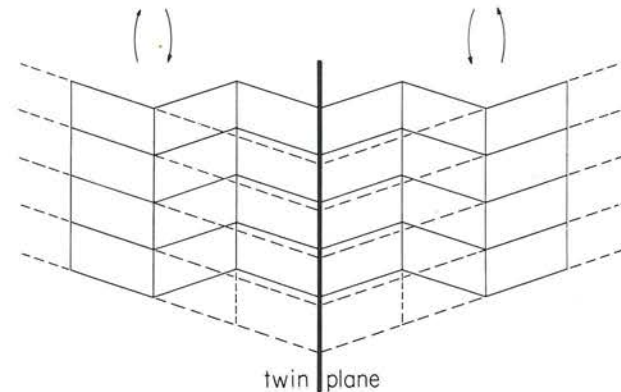


FIG. 11. Schematic diagram of transformation of orthopyroxene into clinopyroxene by simple glide on (100) with glide direction [001]. The herringbone pattern shows the oblique sub-cells which compose the unit cells of orthopyroxene as in Fig. 10. The broken lines show the clinopyroxene cells produced by the transformation. The arrows show the sense of the movement. Opposing senses, as shown here, result in a twin plane on (100). The  $b$  axis is perpendicular to the paper and  $c$  is at the intersection of the paper and the twin plane.

band resembles the upper leg when a person bends his knees. However this analogy is dangerous since it hides the true nature of the mechanism. Hess and Barrett (1949) studied in detail kink banding in single crystals of zinc. They classified kink bands "as a special case of deformation bands. Deformation bands are lamellar regions in crystals and polycrystalline grains within which there has been reorientation by rotation as a result of slip, the amount of rotation increasing gradually with increasing strain." Hess and Barrett developed a complex theory based on movement of dislocations. Undoubtedly the ionic, anisodesmic nature of the pyroxene structure causes differences in the deformation textures and atomic mechanisms from those in metals. In particular there appears to be less curvature in the kink bands of the former, perhaps because the atoms in pyroxene "click" into regular positions more accurately than those of metals. Nevertheless the Hess and Barrett theory seems to be qualitatively applicable to pyroxenes.

Turner, Heard and Griggs (1960) found that kink bands formed in orthoenstatite of a compressed pyroxene consisted of clinoenstatite. They utilized Ito's concept of polysynthetic structures to suggest that shear through  $18\frac{1}{2}^\circ$  could cause the inversion. However they noted that the observed shear angles were rather variable with some reaching as high as  $40^\circ$ . Starkey (1968) used the same idea to predict a shear of  $\sim 18\frac{1}{2}^\circ$  but his diagram uses an incomplete relation between the cells of clinoenstatite and the subcells of orthoenstatite.

Furthermore, the optical data of Trommsdorff and Wenk indicate strongly that the monoclinic orientation used by Starkey is incorrect. Unfortunately the optical orientation of clinoenstatite is not known with complete certainty and there is a small chance that the optic symmetry axis  $Z$  occurs in the acute rather than the obtuse crystallographic oblique angle. Using the most likely optical orientation (*e.g.* Atlas, 1952), the clinoenstatite in the kink-band should be related to the deformation as shown in Figure 12. Trommsdorff and Wenk made a frequency plot of the kink angles in a natural pyroxene finding a maximum at about  $16^\circ$  with a half-width of about  $10^\circ$ . About one-third of the data consist of kink angles greater than  $30^\circ$  (the angle is here expressed as the angle between (100) planes of the original and kinked material).

At some place in the specimen, buckling occurs probably beginning at an existing complex of dislocations. Because of the uniaxial compression, shortening of the specimen occurs with rotation of material in the kink band flanked by dislocations at the upper and lower boundaries. The buckling results in a couple. For the Brown-Morimoto-Smith model, glide along (100) would result in the orthoenstatite "clicking" into clinoenstatite after silicate chains have moved by  $c/3$  and twisted. Some layers might slip whole units of  $c$  when the cou-

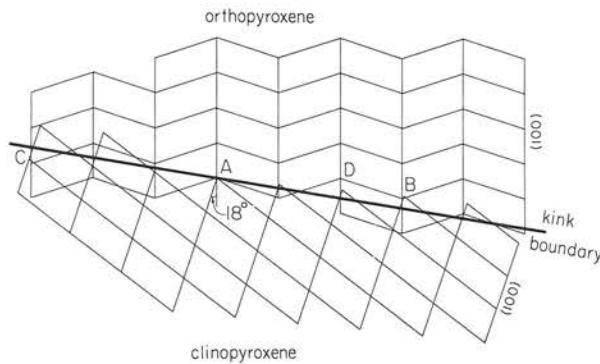


FIG. 12. Possible interpretation of kink-banding in orthoenstatite. Above the kink boundary, the herringbone pattern shows undisturbed orthoenstatite. Below the kink boundary transformation to clinoenstatite occurs. A rotation angle of  $18^\circ$  was chosen arbitrarily on the basis of the observations of Trommsdorff and Wenk (1968); see text. A marks an arbitrary point of coincidence of nodes of the two lattices. B and C denote near-coincidence of nodes displaced three units from A. A rotation angle of  $13^\circ$  would lead to near-coincidence of nodes at D. For both pyroxenes,  $b$  is perpendicular to the plane of the diagram. The traces of (100) are shown.

ple continues to act. But one can suppose that once one layer has "clicked" into the first available position, it is less likely to move another  $2c/3$  than its neighbor is to move  $c/3$ . Hence the transformation should tend to yield a homogeneous deformation. However a space problem results as is shown in Figure 12. The suggestion is now made that although the apparent final and starting positions are related by glides of  $c/3$  plus buckling and rotation, actually the transformation is based on dislocations plus atomic shuffles operating over a boundary region perhaps ten or more unit cells thick. In this region there will be a tendency for dislocations to become regularly spaced and to have Burgers vectors amounting to integral fractions of a lattice repeat. Figure 12 shows that a rotation of  $18^\circ$  yields a near-fit between the ortho- and clino-enstatite for lattice nodes separated by three sub-cells along the kink boundary. Another near-fit can be obtained for the second node when the rotation is  $13^\circ$ . Other angles are possible but these are the most obvious from a visual examination. The data of Trommsdorff and Wenk would be explained by a predominant mixture of these two angles, together with rarer dislocations of even greater magnitude. The misfit between the lattices of ortho- and clino-enstatite could be taken care of at the boundary by flexing of the silicate chains together with irregular coordination of Mg atoms. It is possible that the silicate chains remain unbroken during the kinking. Perhaps strains at the (100) boundaries with exsolved augite trigger the deformation.

Mügge (1898) and Turner *et al.* (1960) observed textural evidence for kink bands in natural orthopyroxene, but the entire sample was orthopyroxene. Turner *et al.*

suggested that inversion back to orthopyroxene had occurred after initial conversion to clinopyroxene. Another possibility is that in natural pyroxene the atomic movements may occur so slowly in response to gradually applied stress that the rotation at dislocation boundaries is immediately counteracted by atomic shuffles resulting in immediate formation of orthopyroxene. In other natural specimens, such as that of Trommsdorff and Wenk, stress acted too rapidly for the atomic shuffles to occur.

The occurrence of gliding in pyroxene has an interesting consequence. As gliding takes place the applied couple is relieved. Hence a rock containing Mg, Fe pyroxene should not be able to store more than a certain amount of mechanical energy, the amount depending on the activation energy for initiation of movement at dislocations. The activation energy for pyroxenes might be less than for minerals whose activation energy depends on breakage of Si-O bands, though protons may act as "catalysts" for the latter.

Kink banding in diopside also utilizes (100) and [001] but the mechanism is different in detail because the orthorhombic polymorph is not stable. Hence dislocations should be related by units of  $c$  not  $c/3$ .

4. *Exsolution.* Both ortho- and clino-pyroxenes near the Mg,Fe join can exsolve augite under appropriate conditions. The resulting orientation relations between host and guest may have genetic significance. Poldervaart and Hess (1951) gave the first comprehensive description based on optical microscopy. Subsequent X-ray study by Bown and Gay (1959, 1960), Morimoto (1966) and Morimoto and Tokonami (1968b) provided definitive identifications, revealed the crystallographic orientation of the phases, and permitted detection of phases too fine for optical resolution. Many workers described the microscopic textures of pyroxenes, in particular Brown (1957, 1967). Determination of chemical composition is difficult even by electron microprobe methods, but valuable results were obtained by Binns, Long and Reed (1963) and Boyd and Brown (1968a, b).

Poldervaart and Hess (1951) proposed that the exsolution texture is governed by minimization of surface energy, which requires that the phases have a common plane. For exsolution of a clino- from an ortho-pyroxene, or vice versa, the only common plane is (100), thus explaining the commonly-observed texture for augite exsolved from hypersthene, or vice versa. For exsolution of clinopyroxene out of a host clinopyroxene, all planes are common, except for dimensional misfit. Poldervaart and Hess went on to propose that the resulting orientation is probably explained by anisotropy of diffusion. Since the easiest movement of  $M$  cations should be parallel to  $c$  in the plane (100) they expected the lamellae to form nearly at right angles to this direction. This conclusion seems to be incorrect geometri-

cally since the premise should result in ellipsoidal regions elongated along  $c$ .

Similar arguments concerning the role of structural misfit and diffusion occur in the extensive literature on feldspar exsolution, which is too complex to quote in detail. For perthite, the irrational contact plane fits nicely with the simple idea that the two lattices have least dimensional misfit at the contact surface. Furthermore, for fine-scale intergrowths the lattices are distorted at the contact such that they have identical translations. A compensation takes place perpendicular to the contact plane. Recently Bollmann and Nissen (1968) developed an elegant mathematical procedure for determining the relative orientation of the two phases when the lattices fit best. This procedure utilizes the expected cell dimensions of isolated macroscopic phases. For feldspars, the cell dimensions change so regularly with composition that estimation of the best fit is easy.

Morimoto (1967) interpreted the cell dimensions of exsolved pyroxene assuming absence of strain, but subsequently Morimoto and Tokonami (1969b) recognized that strain strongly affects the cell dimensions. They developed a theory using a stress-strain tensor, and the assumption of forced deformation parallel to the contact plane and free deformation perpendicular to it. In the absence of data for augite and pigeonite, the elastic constants of another pyroxene, aegirine, were used to calculate the lattice distortion and the strain energy. In pyroxene, augite exsolved on (001) in a pigeonite host should contract 0.6 percent on  $a$  while  $c$  expands 0.2 percent; for exsolution on (100) corresponding figures are expansion of 0.3 percent and contraction of 0.8 percent. Application of reversed values to measured cell dimensions of augites exsolved on (100) and (001) in the same pigeonite yielded identical lattice geometry thereby indicating the same chemical composition. The strain energy was calculated as 0.02 kcal/mole for (001), 0.05 for (100), 0.5 for (010) and 0.3 for (110). Morimoto and Tokonami discussed the effect of hydrostatic pressure, but did not consider the change of cell dimensions with temperature. The above estimates of the strain energy were believed to explain the typical exsolution on (001) with a less common exsolution on (100).

I now try to consider the effect of temperature. There are unfortunately no data on the changes of lattice dimensions of pigeonite, but there are macroscopic thermal expansion data for diopside, augite and the enstatite polymorphs (see next section). Table 11 compares diopside with low clinoenstatite, and an augite with a pigeonite, at room temperature; in addition, diopside at 1000°C is compared with high clinoenstatite at 1100°C. Although Kôzu and Ueda (1933, 1934) did not give for Ca-rich pyroxenes the thermal expansion along  $a$ , it seems reasonable to use that given for  $a^*$  since the expansions for the latter and for  $c$  are closely the same.

TABLE 11. COMPARISON OF CELL DIMENSIONS OF Ca-RICH AND Ca-POOR CLINOPYROXENES

	Room temperature				Source
	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta(^{\circ})$	
Diopside	9.748	8.924	5.251	105.67	Nolan and Edgar (1966) Stephenson <i>et al.</i> (1966)
Low clinoenstatite	9.606	8.815	5.175	108.33	
Difference	-0.142	-0.109	-0.076	+2.66	
% difference	-1.5	-1.2	-1.5	n.a.	
Augite	9.76	8.949	5.250	105.63	Viswanathan (1966 specimen F) Morimoto and Tokonami (1968)
Pigeonite	9.69	8.94	5.227	108.75	
Difference	-0.07	-0.01	-0.023	+3.12	
% difference	-0.7	-0.1	-0.5	n.a.	
High temperature					
Diopside	9.808?	9.073	5.281	?	Kôzu and Ueda (1933)* Smith (1969 at 1100°C)
High clinoenstatite	9.864	8.954	5.333	110.03	
Difference	+0.056?	-0.119	+0.052	n.a.	
% difference	+0.6?	-1.3	+1.0	n.a.	

\* Thermal expansion data applied to cell dimensions of Nolan and Edgar (1966). Expansion of  $a$  estimated from data given for  $a^*$  and  $c$  directions. The sample of Kôzu and Ueda was a natural diopside probably containing several percent of Hd molecule.

At room temperature the discrepancy between cell edges of the iron-free pair of pyroxenes is greater than that for the iron-bearing ones, especially for  $b$ ; however, the difference in the monoclinic angle is less. The effect of temperature on the pair of Mg-free pyroxenes will be remarkable if Smith's indexing of high clinoenstatite is correct and if the transition from high- to low-clinoenstatite has a critical temperature. The deviations for  $a$  and  $c$  will be reversed, whereas that for  $b$  will stay about the same. There are no data on the monoclinic angle, but probably the deviation does not fall. If one attempts to minimize the deviation between the lattices produced by exsolution of diopside from a clinoenstatite, the indicated contact plane may be different above and below the critical temperature. Below it, all planes containing the  $b$ -axis probably have about an equal deviation, which is less than that of all other contact planes. At high temperature, the situation is complex because two deviations are positive and one negative. Of the simplest low-angle planes, (001) appears to be preferable to (010) and (100) because it has minimum areal distortion. The cleavage plane (110) also appears possible.

For augite exsolving from pigeonite, the situation is also complex. At low temperature, there is a large deviation in  $\beta$ , and probably this remains true at high temperature. If pigeonite goes through a high-low inversion with a big expansion of all three cell dimensions, the nature of the deviations becomes quite different. If the thermal expansion is similar to that of high clinoenstatite, and augite expands like diopside, the corre-

sponding values are:  $a$  9.82, 9.94;  $b$  9.10, 9.08;  $c$  5.28, 5.39 (augite values first). The corresponding percent differences are: +1.2, -0.2, +2.2. For exsolution of augite from such a high pigeonite, the preferred plane should be (001). However small changes of cell dimension might have a major effect and change the plane of minimum deviation. At some temperature during the inversion it is possible that there is essentially no deviation for  $a$  and  $c$  with significant deviations only for  $b$  and  $\beta$ .

Obviously further speculations along this line about the reasons why one plane is preferred to another are still-born, but the preceding discussion shows that the thermal expansion must be measured accurately for a wide range of chemical compositions. In addition the possible effect of variable cation site preference must be considered.

The idea of simple diffusion control does not seem universally applicable since the cations should diffuse most easily in the (100) plane at all temperatures. However atomic vibration may be great enough at high temperatures to permit easy diffusion in all directions, while at low temperatures decreased atomic vibration causes strong anisotropy of diffusion. The predominance of (001) lamellae at high temperature testifies against simple diffusion control, but (100) lamellae might result from anisotropic diffusion. If so, they should predominate at low temperature.

After the lamellae have formed at high temperature, there will be complex changes resulting from differential thermal contraction between the host and guest, especially if an inversion takes place. Two types of in-

inaccurate, but urge the need for new data obtained by X-ray diffraction methods.

If the Sarver-Hummel data are accepted, there are some interesting implications. Protoenstatite has the lowest thermal expansion, and clinoenstatite the largest. This seems reasonable from the viewpoint of the crystal structure. Protoenstatite already has an expanded structure with respect to the other polymorphs, even though the detailed coordinations of the cations are qualitatively similar. The key difference is that the silicate chain of protoenstatite is expanded whereas in the other polymorphs the chains are contracted. With increasing thermal vibration, the chains of clino- and orthoenstatite have more opportunity for expansion. Of course, there are additional atomic movements which complicate the mechanism. Orthoenstatite has more symmetry restrictions than clinoenstatite, and its lower thermal expansion may result from interaction between other than first or second neighbors (see section on Ito's concept of polysynthetic structures).

If one accepts that there is a high-low transition in clinoenstatite near 1000°C, and that the indexing of the powder pattern of high clinoenstatite by Smith (1969) is correct, one can suggest that the thermal expansion of clinoenstatite has a discontinuity (Fig. 13) analogous to that of quartz. This discontinuity should be associated with the endothermic heat effect detected by Schwab (1968). There is some uncertainty in the Ca-content of the high clinoenstatite, but it is insufficient to seriously affect the major difference in cell volume between high- and low- clinoenstatite. The data of Rigby and Green (1942) for clinoenstatite indicate no discontinuity in the expansion up to 1200°C, and hence reveal no evidence for an inversion to high clinoenstatite. Perhaps their clinoenstatite actually consisted mostly of protoenstatite, which inverted to clinoenstatite when a sample was crushed for optical examination.

Kôzu and Ueda (1934) also measured the thermal expansion of several augites finding somewhat lower volume expansion than for diopside. The data indicate smaller expansion on  $a^*$  and  $b$  and greater expansion of  $c$  for augite with respect to diopside.

No data on the thermal expansion of Mg,Fe orthopyroxene or on pigeonite were located.

*Phase equilibria.* Most of the pertinent experimental results have been discussed in the literature review, and this section will be brief.

1. *Pure MgSiO<sub>3</sub>.* It is commonly assumed that orthoenstatite inverts to protoenstatite without the intervention of clinoenstatite. However it can reasonably be asserted that the evidence is inconclusive. Sarver and Hummel (1962) converted ortho- to proto-enstatite in 1 hour as observed directly in a high-temperature diffractometer; on the basis of these and other data they gave an inversion temperature of 1042°C. A 2 percent LiF

flux was used. Atlas (1952) using runs of about one week fluxed by LiF or NaF obtained complex quench products from the range 975–995°C using various starting materials. Examination of the runs was made at room temperature. The results are not inconsistent with an inversion of ortho- to proto-enstatite at about 985°C if the observed clinoenstatite is solely the result of inversion from protoenstatite. To resolve the problem, it seems desirable to construct rugged furnaces which can be plugged into an X-ray camera or diffractometer. Then samples could be held for prolonged times and X-rayed at regular periods to observe the rate of attainment of equilibrium. In the absence of such results, one can only presume that orthoenstatite inverts directly to protoenstatite as given in Figure 14.

There is no good reason to doubt that the field for protoenstatite extends up to the incongruent melting point.

The question whether ortho- or clino-enstatite is the stable form at low temperature is debatable. Certainly on the basis of experimental data quoted earlier, it can be asserted plausibly that clinoenstatite synthesized at low temperature and high temperature is the consequence of applied shearing stress. Thus under hydrostatic conditions, one might claim that orthoenstatite is the truly stable form at all temperatures below the inversion temperature to protoenstatite, and that clinoenstatite is always metastable. However I now wish to propose that clinoenstatite might indeed be the stable form at low temperatures, but at such low temperatures as to be kinetically unreachable using strictly hydrostatic conditions.

The thermal expansion data combined with cell dimensions measured at room temperature suggest that clinoenstatite is denser than orthoenstatite up to about 200°C, but then becomes less and less dense. These data are very tentative and require experimental confirmation; in particular, the temperature of 200°C is very uncertain even if the present data are free of systematic errors.

Although the density is not related to either the internal energy or the Gibbs function, the reversal of density is intriguing and suggests that the bonding properties of the two structures are changing in a subtle manner. Is it possible that the internal energy of clinoenstatite falls below that of orthoenstatite at some temperature not necessarily the same as the one at which the densities are equal? Only experimentation can tell—in particular, high-accuracy calorimetry would be desirable.

If the density reversal occurs below 600°C, the contention of Stephenson, Sclar and Smith (1966) must be changed. They argued that their measurements of cell dimensions made at room temperature supported the positive slope on a  $PT$  diagram found by Sclar *et al.* (1964) for the ortho-clino inversion. If ortho is denser



than clino at 600°C, the slope should be negative assuming the pressure coefficient is equal for both polymorphs.

2.  $MgSiO_3$ - $FeSiO_3$  join. Figure 14 displays the available data, and shows a possible set of relations for low pressures. The old data of Bowen and Schairer (1935) for natural low-Ca pyroxenes must be wrong since their inversion temperature for pure  $MgSiO_3$  was given as 1150°C, some 100–150°C higher than the later values of Atlas and Sarver and Hummel. Brown (1968) obtained an ortho-clino reversal for natural pigeonite. Since pigeonite accepts more Ca in solid solution than does orthohypersthene, the inversion in the Ca-free system should be at a higher temperature. Thus one might propose that the true inversion curve (actually two curves separated by a two-phase field) should lie below the Bowen-Schairer curve but above the Brown reversal. Kuno (1966) relied on temperature measurements of four magmas containing orthopyroxene phenocrysts to set a lower limit to a transition curve. Brown (1968) showed that the temperature of the ortho-clino transition increased with pressure, in accordance with the predictions made here if clinopyroxene goes into an expanded form at high temperature. Consequently the transition temperature at low pressures should be below that for crystals growing at depth in a magma. In addition, during eruption oxidation reactions may raise the magma temperature. Since there is no good evidence as yet for protoenstatite accepting  $FeSiO_3$  in solid solution to a level greater than about 13 mole percent (Dallwitz *et al.*, 1966), the set of phase relations that accommodate most easily to the available data is shown in Figure 14.

Even if this set of relations is correct, it has only semi-quantitative value for petrogenesis since the effects of Ca and of pressure should be quite large. Obviously detailed synthesis studies are needed for a variety of compositions over a range of pressures and temperatures. Missing from the diagram is a curve representing the supposed critical temperature between high- and low- clinopyroxene. Perhaps this inversion so changes the thermodynamic properties of clinopyroxene that the inversion curve is close to the truly stable inversion of clino- to ortho-pyroxene. For complete description of the phase relations, isopleths of the cation site preference will be needed.

3.  $MgSiO_3$ - $CaMgSi_2O_6$  join. The studies of Atlas (1952) and of Boyd and Schairer (1964) showed that the high-low inversion of clinoenstatite observed by Per-

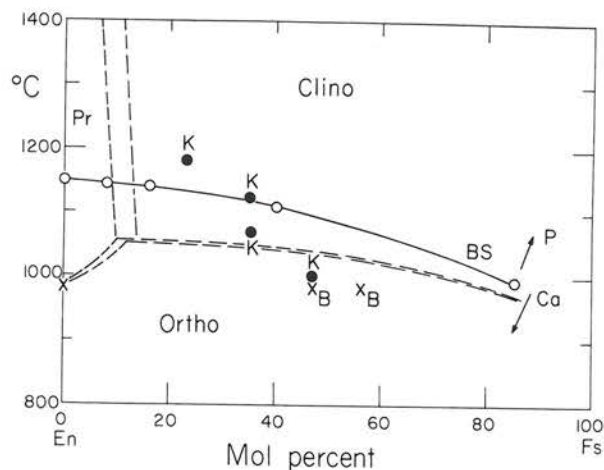


FIG. 14. Possible phase relations at the Mg-rich end of the  $MgSiO_3$ - $SiO_3$ - $FeSiO_3$  join at low pressure.

The curve marked BS represents the upward inversion of ortho- to clino-pyroxene as determined by Bowen and Schairer (1935): the circles show the Mg,Fe ratio of the five samples. The crosses marked B show the conversion of pigeonite to orthohypersthene as obtained by Brown (1968). The four points marked K show the compositions of four orthopyroxenes which exist as phenocrysts in magmas whose extrusion temperature was measured, see Kuno (1966).

The broken lines represent a hypothetical set of phase relations. The effects of pressure and calcium should be as shown by the arrows marked P and Ca.

rotta and Stephenson (1965) must have been metastable for compositions  $En_{90}Di_{10}$  and  $En_{85}Di_{15}$ , and perhaps also for  $En_{100}$ . In addition, there is the possibility of contamination by forsterite and cristobalite (Smith, 1969). Nevertheless since neither Atlas nor Boyd and Schairer observed protoenstatite directly at temperature, there is the possibility that the clinoenstatite solid solution observed as a quench product might be a primary phase rather than inverted from protoenstatite. It is desirable that X-ray data be obtained at temperature for samples held for long periods of time. Perhaps such X-ray data would clarify the unresolved difference between clinoenstatite solid solution resulting from runs made at 1365 and 1395°C (Boyd and Schairer, Fig. 7).

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*Note added in proof:* Joseph R. Smyth converted an orthopyroxene,  $\sim En_{90}Fs_{10}$  (mole %), into a twinned crystal of clinopyroxene. This clinopyroxene inverted from  $C2/c$  to  $P2_1/c$  between 700 and 800°C, thus confirming the postulated high-low

transition. In addition, the  $c$  axis common to the twinned clinopyroxene was found to lie at about 30° from the  $c$  axis of the original orthopyroxene. Consequently the pyroxene chains must have broken up and re-formed in a new direction.

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