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High Resolution Electron Microscopy of Enstatite. II: Geological Application

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Abstract

A number of polytypes, existing over short intervals of structure, have been observed in enstatites. These include the 27, 36, and 54 Å periodicities, in addition to the well known 9 Å monoclinic enstatite (CLEN) and 18 Å orthorhombic enstatite (OREN) polymorphs. The polytypes, as well as all other features described in this paper, can be explained on the basis of a twinning model. This includes "antiphase boundaries," which we interpret in terms of the normal (100) twin planes stepping across adjacent (100) planes.

Parting planes can be seen in their earliest stages of development as simple extensions of the (100) twin planes. They presumably occur in regions where lattice strains have been most highly localized. These strains can be observed as dark contrast in the electron photomicrographs. Parting is produced by shear plus rotation.

It is possible to distinguish between CLEN that formed by solid state transformation (a) directly from OREN in the absence of shearing, (b) from OREN by shearing, and (c) by temperature quench from the protoenstatite stability field. This is done by measuring the width of CLEN fields within OREN and noting the degree of CLEN twinning. Most meteoritic CLEN formed by shearing.

Introduction

In our previous papers on pyroxenes (Iijima and Buseck, 1975a,b) we demonstrated that twinning is common in Ca-poor pyroxenes; we also confirmed that the polymorphic relation between the orthoenstatite (OREN) and low clinoenstatite (CLEN) structure-types is interpretable on the basis of a twinning model. In Buseck and Iijima (1974) we showed high resolution photomicrographs of enstatite containing coherent intergrowths of OREN and CLEN from the Norton County meteorite. In subsequent studies we have looked at other enstatite specimens. Intimate intergrowths of OREN and CLEN (with one of the phases commonly in plates only a few unit cells wide) occur in all the samples examined, in spite of the fact that published X-ray studies describe Shallowater, Bamble, and Bishopville enstatite as pure OREN (Pollack, 1966, 1968; Morimoto and Koto, 1969). Clearly, the resolution of electron microscopy permits the imaging of details that were previously not detectable.

In this paper we explore the role of twinning in the development of polytypism, anti-phase domains, and parting. We also utilize the results of electron microscopy to interpret the geologic history of specimens containing OREN-CLEN intergrowths.

CLEN can form from OREN in a variety of ways. Turner, Heard, and Griggs (1960) have shown that shearing favors CLEN. It can also be produced experimentally from OREN by heating the latter into the protoenstatite (PEN) stability field, followed by quenching. (On the other hand, although kinetically more difficult, OREN can be produced from CLEN by annealing for several days at temperatures just below 1000°C). Finally, although OREN appears to be favored, the data are contradictory regarding whether OREN or CLEN is stable at low temperatures in the absence of shear (*e.g.*, Grover, 1972). In this paper we suggest a means whereby the question of OREN-CLEN stability can be determined by utilizing CLEN field widths, and the presence and degree of twinning. The procedure will also be helpful in determining if the CLEN was quenched from the PEN stability field, or if it was subjected to shear.

Although these mixtures of CLEN and OREN are clearly disordered, confusion may arise from this term as it has been applied to both physical and chemical features. For example, a recent paper by Dowty and Lindsley (1973) discusses ordering of cations between the $M(1)$ and $M(2)$ octahedral sites of pyroxenes. We prefer to call this *compositional* or *chemical* disorder, distinct from the *structural* or *physical* disorder produced by the mechanical mixing of polymorphs, as described in this paper.

Polytypism

A number of hypothetical polytypes were discussed by Iijima and Buseck (1975b) (hereafter called I&B *I*). The 9 and 18 Å periodicities, corresponding to CLEN and OREN respectively, are well known and have been illustrated in some of the figures in the preceding paper. It would be interesting to investigate other periodicities that might occur in enstatite.

An interesting question arises as to how many repeat units are required to produce a "periodicity" and thus a structure type or a polytype. Using X-ray techniques, the definition can be operational, *i.e.*, a sufficient number of repeats to produce a diffraction peak which can be indexed on the basis of a periodic lattice. Using electron microscopy, where the structures can be imaged directly, such a definition is no longer satisfactory. For this paper we shall call any pattern which is repeated thrice in sequence a periodic pattern, recognizing that statistical fluctuation of a simple stacking sequence can produce such repeats.

The periodic pattern seen in the structure image need not be apparent in the corresponding electron diffraction pattern. The intensities of the diffraction peaks depend on the numbers of polytype clusters or "micro-domains" that are distributed throughout the crystal. The width of the peaks is inversely proportional to the numbers of repeats in a sequence. Consequently, few polytype clusters, each only a few unit cells wide, would result in diffuse peaks of such low intensity as to be extremely difficult to detect and identify. An additional complication is that diffraction patterns are obtained from much larger volumes than are viewed in structure images, and polytypes may be locally distributed. It is true that electron diffraction patterns are very sensitive to structural subtleties, but we suggest that the structure images are still better indicators of local perturbations, and these include short range periodicities. Clearly, the use of such images is a great advantage of electron microscopy over other structural techniques.

Although most enstatite crystals display 9 or 18 Å periodicities parallel to [100], corresponding to CLEN and OREN respectively, we have observed a number of other repeats. Figure 1 shows examples. Figure 1a is of Norton County enstatite which was heated at 1000°C for 7 days and quenched. Figures 1b and 1c are of enstatite from the Steinbach meteorite; these specimens were not heat treated Periodicities of 9, 18, 27, 36, and 54 Å (orders 1, 2, 3, 4 and 6 from Table 1 of I&B *I*) are illustrated.

It is possible to identify the repeat sequences shown in Figure 1, recalling that in any given sequence the designation of "A" or "B" to the first unit in a sequence is arbitrary. The 27 Å repeat is of the type AB_2 (21); the 36 Å repeat corresponds to AB_3 (31). There are two types of 54 Å polytypes: AB_3AB (3111) on the right and AB_5 (51) on the left. (The cell edges of the latter are drawn to correspond to BAB_4 but by translation periodicity this is, of course, equivalent to AB_5.)

Two features are prominent in Figure 1. The first is that in these specimens, as in all that we have observed, CLEN and OREN periodicities predominate. The second, and perhaps more remarkable, is that a number of polytypes occur close to one another: 9, 18, and 54 Å within 100 Å of one another in the case of Figure 1c. It is noteworthy that we did not observe a 45 Å periodicity (we did observe it in individual plates, but not thrice repeated). This aspect is discussed further in the section on "Origin by Protoenstatite Inversion."

Byström (1943) described an enstatite having a 36 Å periodicity, but this has not been confirmed by other workers although Brown, Morimoto, and Smith (1961) discussed a possible explanation. Indeed, a number of papers have been skeptical; we would tend to take his report seriously.

A most intriguing question arises as to the significance of pyroxene polytypes. It is probable that the free energy differences between different polytypes is small, consistent with other crystals showing such stacking multiplicities (Verma and Krishna, 1966). Consequently, discrete stability fields may be hard to define, if they exist at all. Also, the persistence of pyroxene polytypes of order greater than 2 has yet to

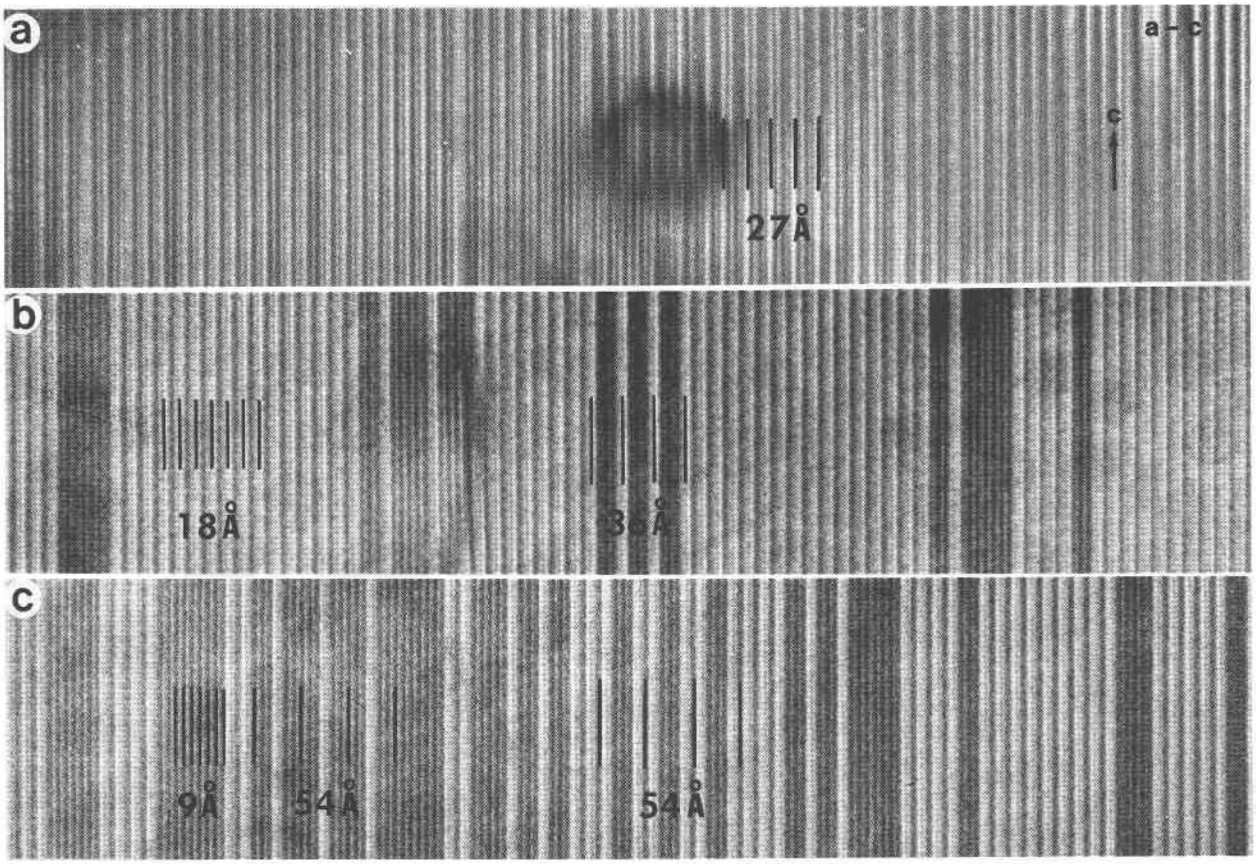

FIG. 1. Enstatite polytypes. Examples as seen in *a-c* electron images of meteoritic samples: (a) enstatite heated to 1000°C, from the Norton County chondrite. (b) and (c) are from the Steinbach mesosiderite.

be demonstrated. If they should turn out to be abundant, and can be correlated with geological history, then the polytypes will serve as an additional means whereby pyroxenes can be used to help unravel the crystal's history.

Twin Offsets and "Anti-Phase Boundaries"

Swinging Twin

I&B *I* have provided several illustrations of (100) twins. In this section we present examples of slight variations, cases where twin planes "swing" or "step" across the crystal. The first case, observed in *a-c* projections, is little understood and so considered only briefly. The second case, visible in *a-b* projections, is discussed in more detail.

Figure 2 shows a (100) twin plane that steps across its CLEN matrix. The steps are spaced at ~100Å intervals parallel to *c* and ~9Å parallel to *a*, equal to one unit cell of CLEN. Crystals that contain such features are relatively rare, and are heavily twinned in the "normal" (100) fashion. The (100) twins are, however, discontinuous across the stepped twin plane.

Twin planes can be observed in *a-b* projections (*e.g.*, Fig. 6 of I&B *I*). Another example is given in Figure 3. Regions A are separated from B by twin planes; note that the (010) fringes are offset by $b/2$ on either side of these boundaries, revealing the *b*-glide relation. The two areas marked B are separated by two twin planes (one "plate" of OREN) so that the (010) fringes on opposite sides are in exact register ($b/2 \times 2$).

A complication arises along the boundary labelled y-y′, roughly parallel to [110], the typical pyroxene cleavage direction. The (100) planes on either side are offset by $a/2$. This can be viewed as another reflection of the "extra" plate, one-half cell wide, that results from twinning on (100) (lower left insert, Fig. 6 of I&B *I*).

The regions on either side of boundary y-y′ are in apparent twin relation to one another. This is in accord with the observation that twin plane x-x′

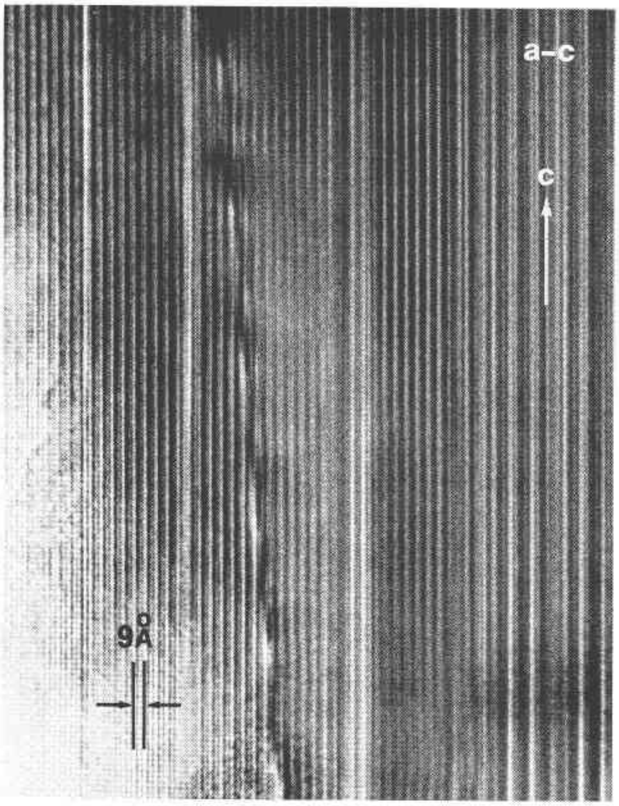

FIG. 2. *a-c* electron image of heated and quenched Bamble enstatite showing a number of twin planes. In the central part of the photograph the planes "step" across the crystal in *en echelon* fashion at ~100 Å intervals.

changes directions, stepping across the (100) planes of the crystal, in a trajectory outlined by boundary y-y′.

"Anti-Phase Domains"

The aforementioned features are interesting in light of published descriptions of anti-phase domains. In 1969 Morimoto and Tokonami hypothesized that diffuse reflections appearing on single crystal X-ray photographs of pigeonite were produced by an anti-phase domain structure. Such structures in terrestrial and lunar pyroxenes have been confirmed by subsequent electron microscope studies (Champness, 1973; Phakey and Ghose, 1973; Champness *et al,* 1971; Christie *et al,* 1971). These indicate that anti-phase domains are a relatively common feature of pyroxenes.

Figure 4b shows marked offset of fringes. It has a similar appearance to an anti-phase boundary and thus, as a working hypothesis, we will first consider it as resulting from anti-phase domains. Because of the possible confusion with twinning, ambiguities arise when this analogy is considered in detail. Therefore, this model will then be reconsidered on the basis of a twinning model, providing what we believe is a more accurate correspondence to our photographs.

Figure 4a is a high resolution photomicrograph of an *a-b* section containing such fringes, with $\frac{a+b}{2}$ representing the offset. An explanation of this feature that is consistent with an anti-phase domain character is shown schematically in Figure 5a. The symbols are those used by Morimoto (1974), where the (001) projections of Si(*A*) and Si(*B*) chains are represented as ∪, ∩, V, and Λ. The boundary, shown as a dashed line along the discontinuity, is in steps two chains wide parallel to *b*.

The trace of the boundary in Figure 4 is roughly parallel to [110], as it is in Figure 5. However, we have observed other orientations, and it can be easily shown that such boundaries can occur at a variety of orientations, depending on the width of steps parallel to *a* and *b*. Note that in Figure 5 the steps are not all of equal width.

Anti-phase domains can be described in terms of a translation vector, *R*. A twin glide plane also is partly described in terms of a translation vector, and the two vectors can be equivalent. The situation in enstatite is not clearcut, as consideration of Figure 5a reveals. The boundary is shown as occurring between chains of the same type, (Si(*A*) or Si(*B*)), but this is ~2.3 or 6.8 Å ($a/4$ or $3a/4$) removed from the position of the *b*-glide plane (in the center of the Si(*A*) chains) along which twinning normally occurs. Thus, we have an apparent situation where the boundary and twin plane can be parallel, but very slightly displaced from one another.

Another problem arises with the anti-phase model described above. It provides no explanation why the boundaries lie close to a (100) twin plane, although this is invariably the case in the crystals that we have examined.

An alternate model is to explain the fringe offset entirely on the basis of twinning. This is shown schematically in Figure 5b. Here the steps must be in multiples of two chains parallel to *a*. This is because twinning *is restricted to* the Si(*A*) chains. The sketch and model are fully consistent with our observations. Further, in Figure 3, region A is in a twin relationship to *B*, not only across the (100) boundary x-x′ but also across y-y′. Thus, we conclude, on the basis of direct structure imaging using high resolution microscopy, that the offset fringes in these enstatite specimens are best explained by regular twinning instead of by an anti-phase boundary.

Parting

Parting is a phenomenon that is mentioned in every elementary course in mineralogy, but one which has received little, if any, attention in the recent literature. Macroscopically, it is generally not possible to determine whether the planar features in a given specimen are produced by cleavage or parting. The result for the individual wishing to distinguish between them is commonly a certain sense of frustration and confusion.

The conventional difference between parting and cleavage is that, although both are crystallographically controlled, parting occurs along only certain planes within a crystal (*e.g.*, Ford, 1932; Tertsch, 1949). These particular planes commonly are the composition planes of twins. In the case of certain pyroxene crystals, and especially the Bamble specimen described in this study, parting along (100) (Figs. 6 and 7) is far more pronounced than the typical "rectangular" {110} cleavage of pyroxene.

Electron microscopy is useful for understanding the development of parting. Ignoring the possible effects of exsolved phases or impurities, parting commonly occurs when a crystal has been strained, as by shearing. Figure 8a shows an *a-b* section of such a crystal, in which portions near the edge have been displaced.

Differences in contrast in Figure 8a provide information regarding parting. The line parallel to *b* (arrows) abruptly separates regions having great differences in contrast. As contrast is produced by Bragg diffraction, the differences indicate slightly differing crystallographic orientations on opposite sides of this trace of the parting plane. The dark band located at the end of the parting plane is a bend con-

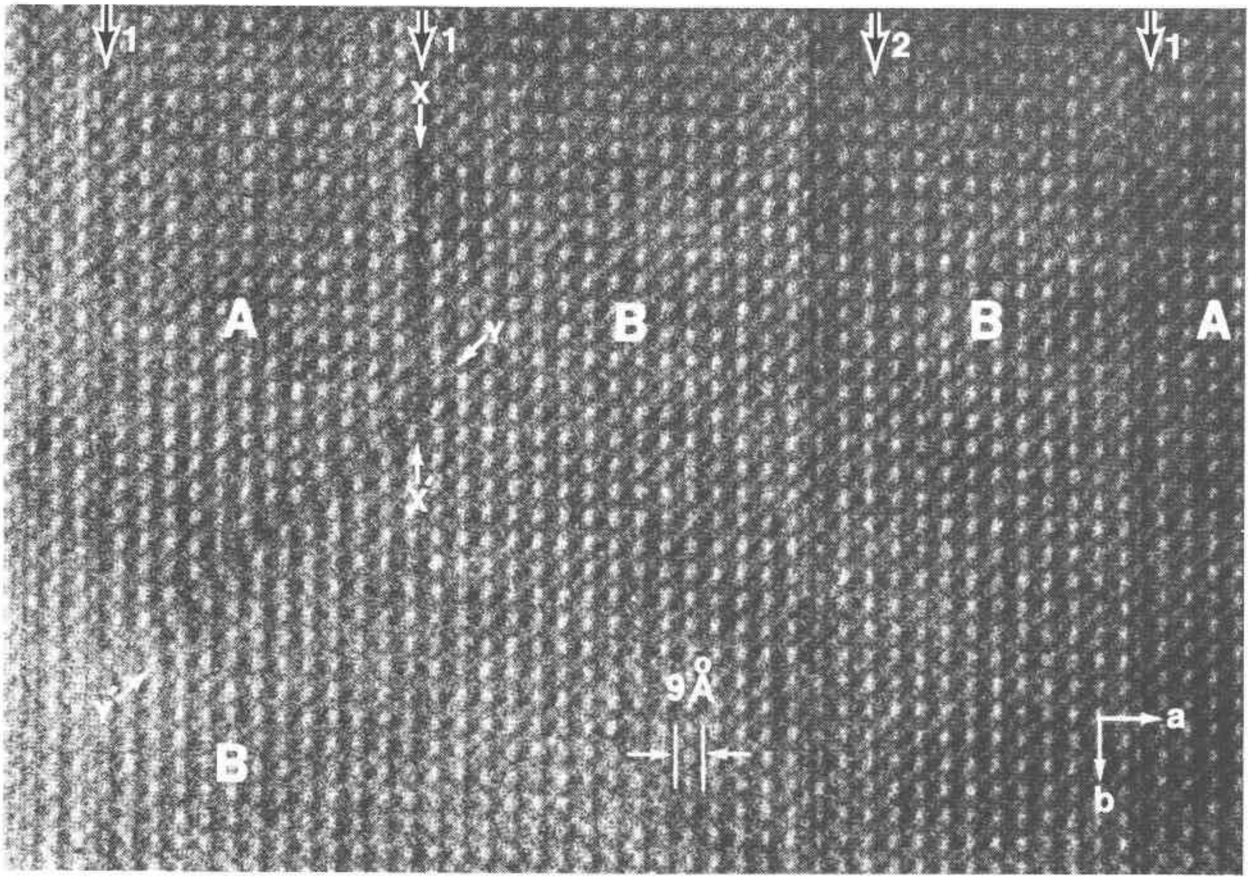

FIG. 3. Stepped twin planes in heated and quenched Bamble enstatite seen in *a-b* projection. Note the fringe offsets along traverses x-x' and y-y', parallel to (100) and (110), respectively (best seen by holding the photograph horizontally at close to eye level). The position of single and double (100) planes are marked by arrows 1 and 2 at the top of the figure. Regions A and B are in twin relationships.

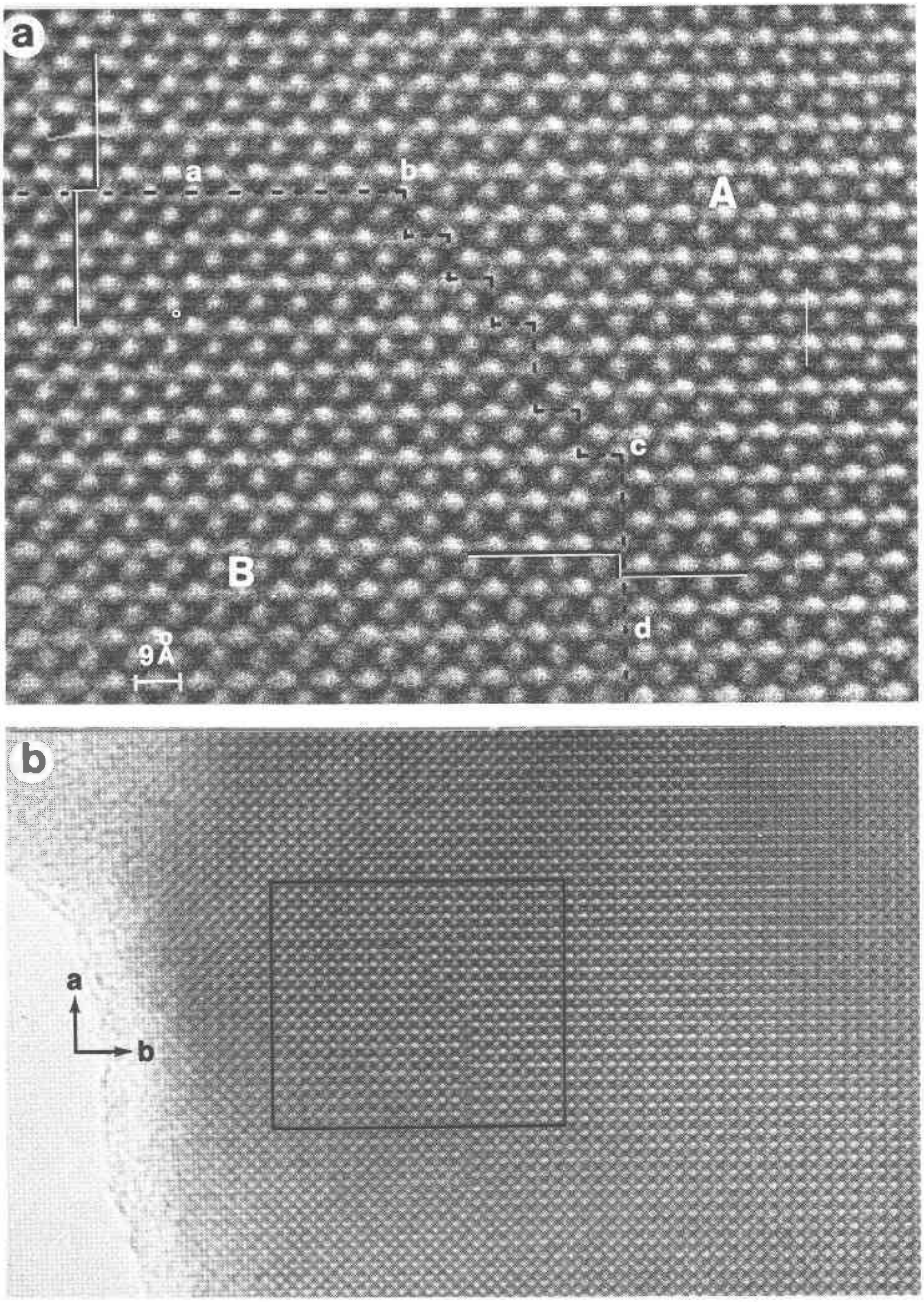

FIG. 4. Offset of fringes in an *a-b* projection of Bamble enstatite. The area enclosed by the rectangle in (b) is shown at greater magnification in (a). The fringe offsets between areas A and B occur along the dotted line *a-b-c-d*. The heavy black and white lines show the offset.

tour, confirming the gradual change in orientation of the crystal around an axis roughly parallel to *a*. Figure 8b illustrates a possible model of incipient parting resulting from shearing plus slight rotation.

The same initiation of parting can also be observed in *a-c* sections. Figure 7b shows such an orientation, and contains two parallel parting planes lying along (100). These planes are roughly coextensive with faults defined by twin planes that are closely adjacent to one another and define one plate of OREN. Note

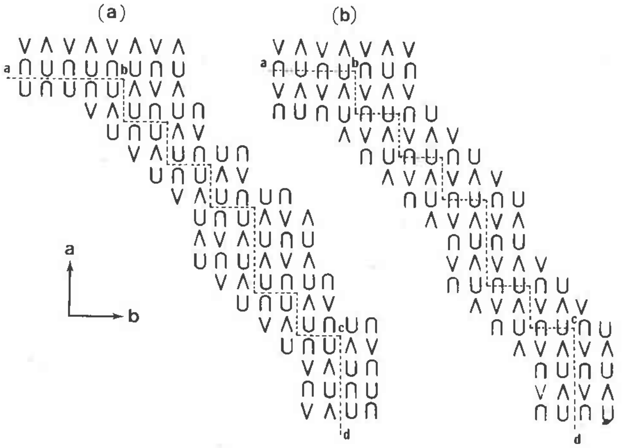

FIG. 5. Schematic model to explain the fringe offsets of Figure 4. The U's correspond to Si(A) chains and the V's to Si(B) chains, pointing alternatingly toward + and $-a$. The dashed line outlines the discontinuity separating the domains in the antiphase model (a) and the twins in our proposed twinning model (b). See text for details.

that the parting planes extend from the edge of the crystal, as expected. If the shearing that produces this parting is more pronounced, the separation extends further into the crystal.

In these photographs and, indeed, in all of our observations, parting planes seem to lie along twin planes. This is in agreement with the standard explanations given in mineralogical texts that parting planes are crystallographically controlled, but can only occur along special, localized planes within a given crystal.

An interesting question arises relevant to the development of parting. The Bamble material is predominantly OREN, but the fact that it contains such a pronounced parting suggests that it was once subjected to a shearing stress. Turner *et al* (1960) showed that shearing at elevated temperatures encourages the OREN → CLEN transformation. We thus conclude that the Bamble material was deformed. Supporting this, as explained below, is the fact that all of the CLEN regions are in the same twinning orientation. Further, Figure 8 shows that rotation has occurred in addition to simple shearing parallel to a principal crystallographic direction. Such rotation may be an integral part of the development of parting.

Geological Implications

Structures observable with the electron microscope can aid in interpreting the history of an enstatite specimen. We are here concerned with the relationships between OREN and CLEN and the path by which one forms from the other. Interpretation of the history depends on (a) the width of CLEN fields (= $m9$Å or $n9$Å, where m is any integer and n is an even integer) within an OREN matrix, (b) the presence and degree of twinning of CLEN and, to a lesser extent, (c) the concentration of CLEN within the OREN. These are discussed in more detail below.

As there is abundant experimental evidence for the development of CLEN from or within OREN, this reaction will be considered in detail. There are three known or hypothesized paths by which such a reaction can occur: (a) by inversion from PEN, (b) by shearing of OREN, (c) by slow static transformation (assuming that CLEN is the stable form). Each of these situations can be distinguished by residual features in the sample, as seen by electron microscopy. The relationships are summarized in Table 1.

Clinoenstatite Field Widths

The use of CLEN field widths for interpreting geological history is best done through a consideration of the structural relationships that are involved. Specifically, we are concerned with the Si(A) and Si(B) chains that must always alternate in sequence (parallel to a) in homogeneous OREN and CLEN. (Where they do not alternate, the adjacent similar chains define an anti-phase boundary).

Because of b-glide (pyroxene) twinning we must distinguish between Si(B) and Si(B)′ chains, *i.e.*, chains that are in a twin relationship to one another (see, for example, Fig. 2b of I&B *I*). This difference forms one basis for interpreting origin. The OREN structure demands that adjacent Si(B) chains be in a twin relationship to one another (Fig. 9a). In untwinned CLEN all of the Si(B) chains have the same orientations (Figs. 9b and 9c). Thus, in the one in-

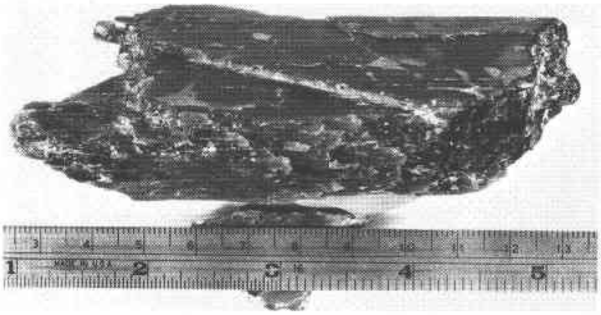

FIG. 6. Photograph of Bamble enstatite showing the striking (100) parting which is prominent along the stepped, flat top and can also be seen in the parallel lines on the edge of the crystal.

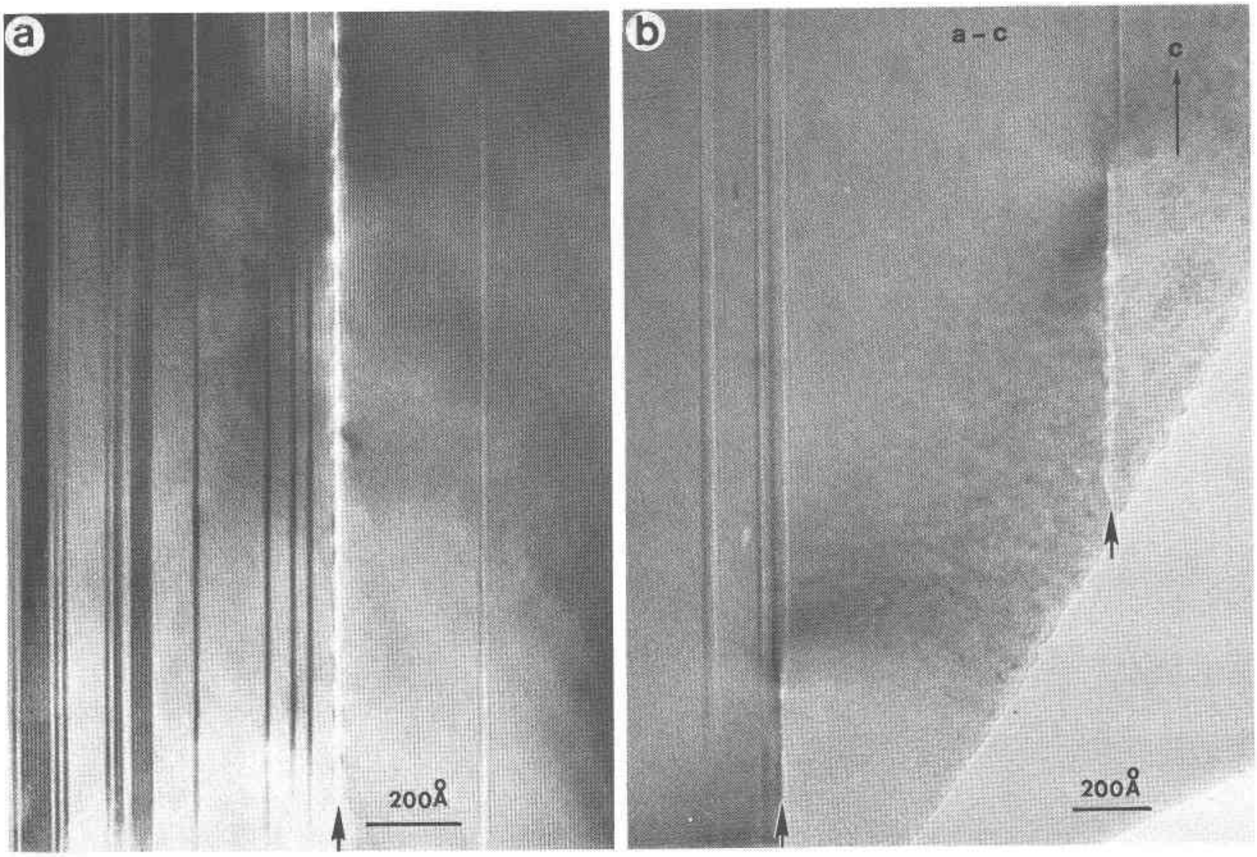

FIG. 7. Electron image of *a-c* sections of heated and quenched Bamble enstatite. The white, slightly irregular vertical zones marked by arrows—one in (a) and two in (b)—are incipient parting planes continuous or almost continuous with twin planes.

stance the spacing between equivalent Si(*B*)-type chains is 18 Å (OREN) and in the other 9 Å (CLEN).

Distinct constraints are placed on CLEN field widths, if CLEN formed directly from OREN. As described in I&B *I*, this transformation can be performed by a slight translation of the Si(*A*) chains parallel to the *c* axis, and by changing the Si(*B*) chains to Si(*B*)′, or vice versa (Figs. 9b and 9c). In a single crystal of OREN, neighboring Si(*B*) type chains form a sequence . . . Si(*B*)–Si(*B*)′–Si(*B*)–Si(*B*)′ . . . In untwinned CLEN, on the other hand, all of the Si(*B*) chains are identical. Thus, CLEN formed directly from OREN must be in fields *n*9 Å wide, where *n* is an even integer.

An example (Fig. 9d) shows where one Si(*B*)′ chain in OREN (*cf* center of Fig. 9a) is changed to an Si(*B*) chain. This results in a CLEN region, 18 Å wide, surrounded by OREN; the latter has suffered no change. An example of a crystal showing CLEN fields that are *n*9 Å wide is given in Figure 10a.

Origin by Protoenstatite Inversion

CLEN formed by inversion of PEN may originally have been OREN (reaction: OREN → PEN → CLEN + OREN), or have formed directly (PEN → CLEN + OREN). In either case the CLEN fields within OREN-CLEN intergrowths are distinct. The SiO_3 chains in PEN are structurally equivalent. During cooling of PEN there is an equal probability that any given chain will assume either the Si(*A*), the Si(*B*), or Si(*B*)′ configurations. Nucleation will presumably occur simultaneously in many places throughout the crystal and, depending on the configuration of adjacent chains, will produce fields of OREN and CLEN. There is no constraint on the physical widths of the CLEN fields surrounded by OREN, except that they must be *m*9 Å wide. In this case 9 Å is, of course, the CLEN unit cell repeat parallel to *a*. The absolute widths of the CLEN and OREN fields would be related to the cooling rate from the PEN stability field. Slower cooling would presumably produce more extensive regions of OREN.

An example of a crystal containing OREN regions that may have formed from different nuclei is shown in Figure 9e. The regions at opposite ends along *a* are out of phase; this can be best seen by comparing the Si(*B*) chains to those in homogeneous OREN (Fig. 9a). The two OREN regions are separated by a CLEN field 27 Å wide, *i.e.*, *m*9 Å ($m = 3$). This is a consequence of the reversal of the relative positions of the Si(*B*) and Si(*B*)′ chains in the OREN region on the right. Such a transition is energetically more difficult than one producing fields *n*9 Å wide; it is therefore less common, and likely only for high temperature transitions.

Another feature of the CLEN produced from PEN is that such a transition would not favor one twin orientation over another. Thus, owing to random nucleation, it would be twinned. Such twinning could occur within a single field of CLEN. It might also be manifested by a twin relationship between CLEN fields separated by OREN.

Bamble enstatite that has been heated in the laboratory into the PEN stability field and then quenched will serve as an example. The electron diffraction patterns are streaked and the electron images show intimate intergrowths of OREN and CLEN. Based on its former existence as PEN, we would predict such Bamble enstatite to be strongly twinned with the CLEN fields divided between *n*9 Å and ($n + 1$)9 Å widths. This is indeed observed (Fig. 10b), confirming the PEN → CLEN + OREN origin, and showing that the reaction OREN → PEN was only partly reversed on cooling. Similar effects occur in Norton County enstatite that was heated in the laboratory into the PEN stability field (Fig. 10c). Note that in Figure 10 CLEN field widths, rather than polytypes as in Figure 1, are outlined.

Papua enstatite has a similar history. It occurs in a volcanic rock and consists primarily of CLEN. Dallwitz, Green, and Thompson (1966) suggest that the CLEN was produced by inversion of primary PEN. Consistent with this origin, we observed that these crystals are strongly twinned. Unfortunately, an insufficient amount of OREN was present to permit determination of CLEN field widths. We hypothesize that the crystals cooled sufficiently slowly to allow the CLEN to grow at the expense of OREN, thereby accounting for the relatively small amounts of OREN that are present.

Reid, Williams, and Takeda (1974) recently described the Steinbach pyroxene as containing intergrowths of OREN and CLEN structure (compositionally, it is a bronzite rather than an enstatite but this does not affect the reasoning). As our papers show, such intergrowths are common and, indeed, to be expected. In light of their data the interpretation of Reid *et al* that the pyroxene formed from an original OREN-PEN assemblage is reasonable. We have examined pyroxene from another Steinbach sample and confirm their observation that the pyroxene consists of intergrowths of the OREN and CLEN type (as well as other polytypes—see Figures 1b and c). All of the CLEN fields, however, are *n*9 Å wide, inconsistent with an origin as quenched PEN, and suggesting that the CLEN formed directly from OREN.

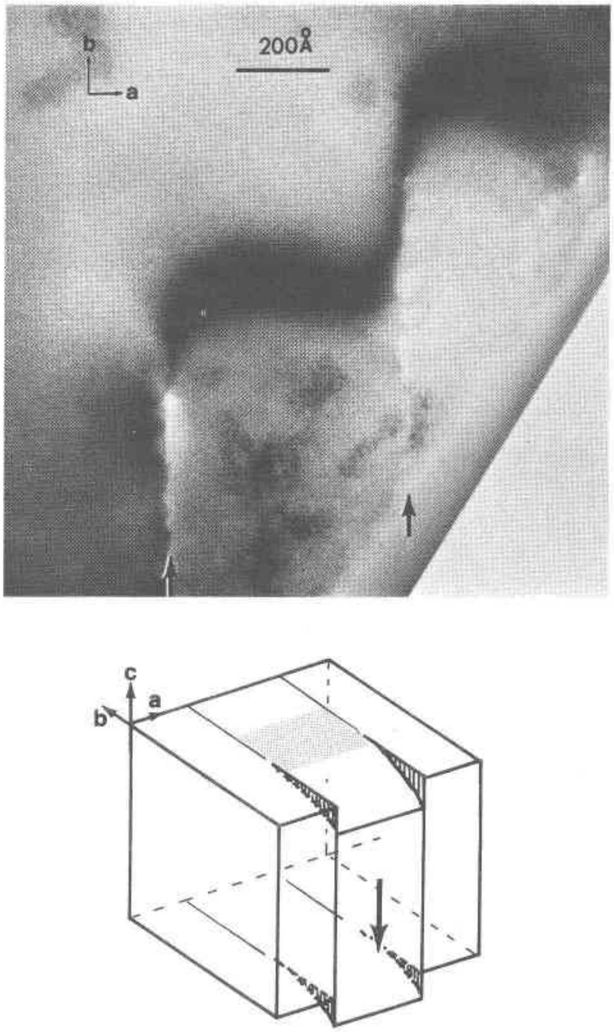

FIG. 8. (a) Parting in Bamble enstatite as seen in an *a-b* section. The black bands are bend contours. (b) Diagrammatic explanation of features seen in (a). As in Figure 7, parting is parallel to (100).

TABLE 1. Characteristics of the OREN → CLEN Reaction, Depending on Origin
(See text for details.)

	CLEN Field Widths		Twins	CLEN	
	n 9Å	$(n+1)$ 9Å	Same Orientation	Concentration	Examples
1. PEN inversion; high temperature	Yes	Yes	No	High	Papua Norton Co. (artificially heated) Bamble (artificially heated)
2. Shearing; moderate to low temperature					
a) homogeneous shear	Yes	No	Yes	High*	Bamble, Shallowater, Bishopville, Norton Co.**
b) inhomogeneous shear (*e.g.*, shock)	Yes	No	No	High	
3. Static; moderate to low temperature	Yes	No	No	Low	

**assuming much shearing*
***In any given crystal fragment only one CLEN twin orientation was observed. We cannot be certain that the same orientation holds from grain to grain and thus this assignment to group 2(a) is, of necessity, tentative. It is likely that observation of larger, ion thinned samples would place at least some of the meteorites in group 2(b). Variations in grain to grain crystal orientation,* e.g. *Klosterman and Buseck (1973), will also affect the twin orientations.*

Philpotts and Gray (1974) describe a bronzite that, based on external morphology, they conclude originally crystallized with the CLEN structure. A high resolution electron microscopy study would presumably quickly confirm or disprove such an origin.

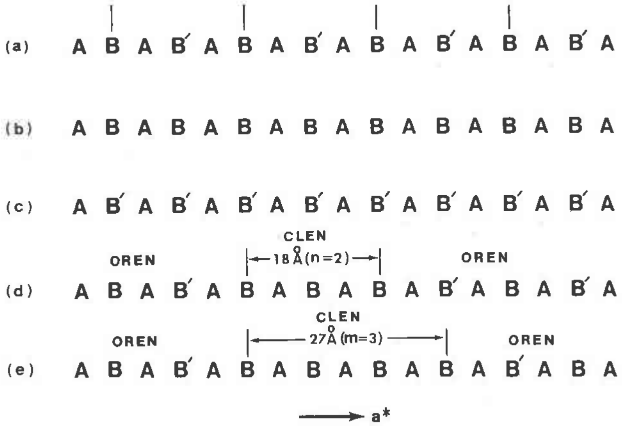

FIG. 9. Schematic representation of a variety of enstatites and enstatite intergrowths. A, B, and B' represent Si(A), Si(B), and Si(B)′ chains, respectively. The horizontal direction is parallel to a. (a) represents pure OREN; (b) and (c) pure CLEN, but in twin relationships to one another; (d) corresponds to an intergrowth of CLEN, 18 Å wide (n = 2), within OREN. Comparison with (a) shows the OREN is in phase on either side of the CLEN field. (e) represents a CLEN field 27 Å wide (m = 3); in this instance the OREN is out of phase across the CLEN field. This is characteristic of intergrowths formed from PEN.

Origin by Shearing

Turner *et al* (1960) suggested that CLEN is a good stress indicator and numerous subsequent studies have confirmed that it can be produced from OREN by shearing. Such a reaction occurs at temperatures below the PEN stability field and thus is represented as OREN → CLEN. In this instance the CLEN fields would have to be n9 Å wide.

The twinning in CLEN produced by shearing is also distinctive. If partial dislocations occur regularly throughout the OREN structure, then an applied shear stress will cause them to migrate in such a fashion as to leave behind CLEN "plates." Most or all of these plates would have the same crystallographic orientations. We therefore predict that naturally or artificially sheared material will contain minimal twinning, *i.e.*, CLEN with few "stacking faults" will result.

A few twins could occur if the shear stress were not distributed homogeneously across the crystal. This could then result in local, internal shear couples having a sense opposite to the couple external to the crystal and could thereby produce localized regions twinned in an opposite sense from the crystal as a whole.

A related effect has been observed in what we believe to be grinding artifacts in Bamble enstatite that was converted to CLEN by heating in the laboratory. In this instance subsequent grinding ap-

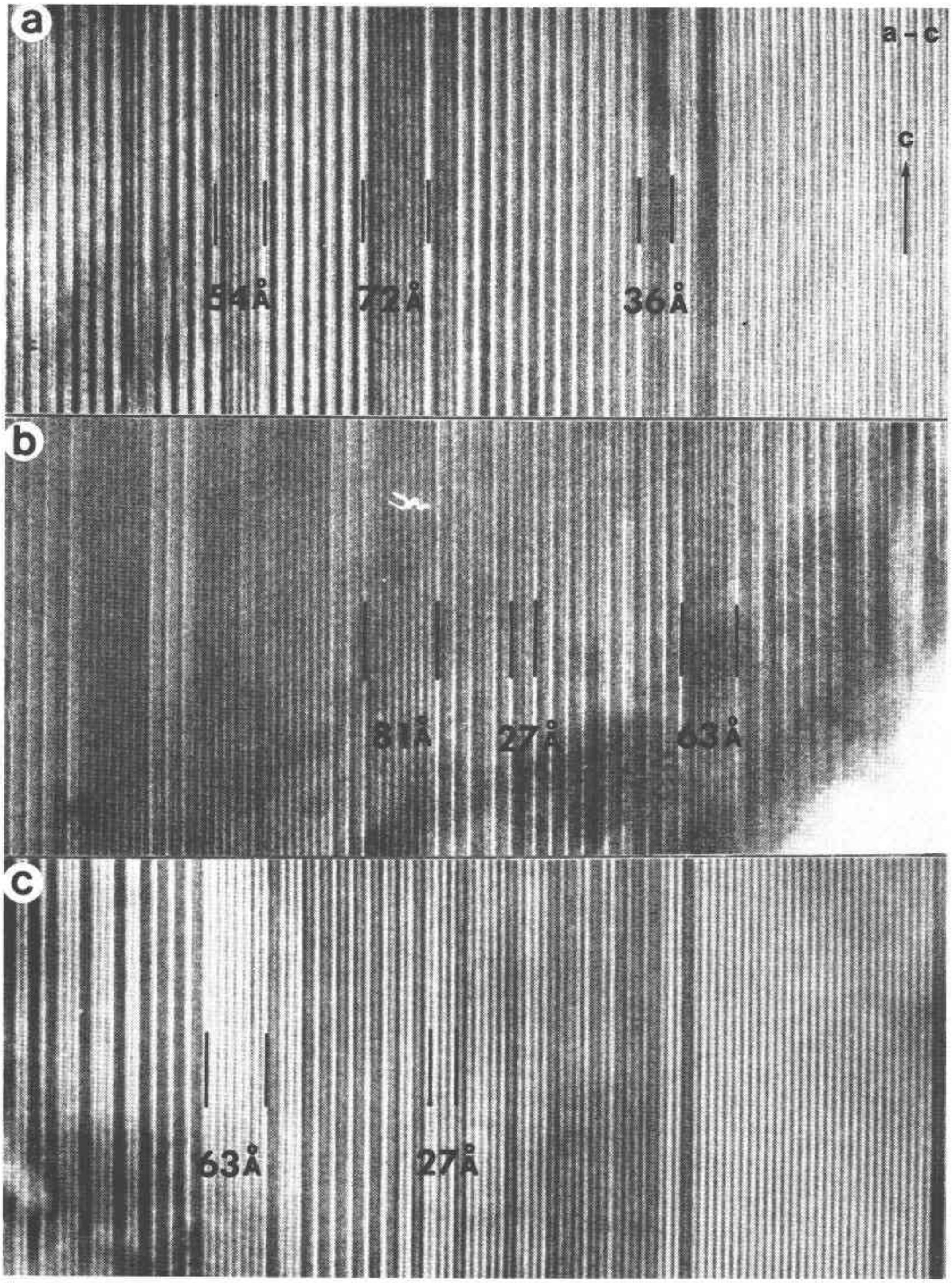

FIG. 10. Fields of CLEN of varying width (and origin) within OREN. (a): Bamble OREN containing CLEN fields with $n = 4$, 6, and 8. (b) and (c): Bamble and Norton County enstatites that have been heated in the laboratory and quenched, containing CLEN fields with $m = 3$, 7, and 9.

parently produced OREN near the edge of the CLEN crystal fragment. This would appear to be anomalous in view of the data of Turner *et al* (1960) and Coe and Müller (1973). Shearing encourages the reaction OREN → CLEN rather than the reverse. Nonetheless, it is clear that if a given shear couple produced CLEN having a particular orientation, then reversal of the shear directions may result in reversal of the CLEN orientation, *i.e.,* twinning. If such twinning only occurs on an extremely limited scale, it is conceivable that a single "plate" or disc of OREN might be produced within CLEN. Although we have not observed them, similar features could conceivably develop naturally and care will be required to identify them.

Müller (1974) shows a figure of fringes of Bamble enstatite that was sheared in the laboratory. He noted that all of the CLEN fields are even multiples of 9 Å; they are also untwinned. Thus, his example supports our prediction regarding the configuration of enstatite polymorphs resulting from the shear transformation of OREN → CLEN.

Origin by Static Transformation

It is not clear whether OREN or CLEN is the stable phase at temperatures below the PEN stability field (Smith, 1969). The energy differences between the two phases are apparently so small that evidently neither is appreciably more stable than the other; this has resulted in difficulties in resolving the stability question by laboratory experiments.

We would like to suggest a means by which the situation may be resolved. If the CLEN forms from OREN in the absence of shear stresses it must (a) be in fields *n*9 Å wide, and (b) be twinned with each of the twin orientations in approximately equal concentrations. This is because neither twin orientation would be favored during the transition. These constraints are not both necessary for the reverse process wherein OREN forms from CLEN.

Bamble enstatite will serve as an example. Unheated samples consist of relatively pure OREN. The enclosed CLEN fields are all 2, 6, or 8 CLEN unit cells wide, *i.e., n*9 Å (Fig. 10a). This is consistent with CLEN formed by direct transition from OREN. An interesting feature in our sample is that the CLEN all seems to have the same crystallographic orientation. This lack of twinning within CLEN raises the question as to whether the OREN → CLEN transition may have occurred in response to gentle shearing. The strongly developed parting would be consistent with such an origin.

The interpretation of meteoritic samples presents a slight problem. Enstatites from the Norton County, Steinbach, Shallowater, and Bishopville meteorites all have certain features in common. All of the fields of CLEN in OREN are *n*9 Å wide and the CLEN is not appreciably twinned. We believe that the CLEN was produced by shear, and in those meteorites containing much CLEN, this shear was presumably produced by shock impact. The shock origin is consistent with the conclusions of Pollack and Ruble (1964), although the "disordering" is not.

Shearing produced by shock may be inhomogeneous. Further, the shock waves have irregular trajectories in anisotropic materials such as meteorites. Thus, theoretically such waves or series of waves could be resolved into many shear couples of varying orientation. Consequently, we predict that local areas of "reverse" twinning would occur in CLEN produced by shock. X-ray measurements (Pollack and DeCarli, 1969) of artificially shocked enstatite do not reveal such twinned CLEN.

Discussion

Several interesting questions related to enstatite-type phases are raised by the results in this and the previous paper: the meaning of periodicity, the significance of parameters from improved structure refinements, and the relationships between physical and chemical disorder.

The concept of periodicity is fundamental to the study of crystallography, as only periodic objects will diffract radiation. Most structure work has been done with X-rays, for which repeats of the order of several hundred units are required. With electron microscopy, however, repeats of only a few units can be seen. This raises the intriguing question of the minimal number of units required to produce a periodic array. Clearly, the operational definition of the ability to produce X-ray diffraction does not obtain when using electrons, where we can observe as few as two "repeats." We somewhat arbitrarily chose three as the number of repeats needed to define a polytype.

The question of periodicity has an unusual significance for mineralogy. It is generally accepted that a new mineral is defined and characterized on the basis of two parameters: composition and structure. Materials having differing periodicities have differing structures. They are then properly called different minerals, but this potentially opens a Pandora's box. It means that we must distinguish between "periodicities" and "repeats." And yet this may well be an arbitrary distinction based on the historic means of investigating crystal structures.

Using enstatite as an example, it has long been accepted that crystals having 9 and 18 Å *a* periodicities are different minerals (CLEN and OREN). The observation made in this paper that they can occur in plates only one unit wide is "after the fact." Extending this logic, it seems both consistent and reasonable that, *e.g.*, a 27 or 36 Å plate is yet another mineral. The problems of nomenclature, among other things, are formidable. It may be most appropriate to use Zhdanov symbols combined with the mineral name of the simplest sub- or polytype.

It may well be that it is not useful, or even appropriate, to discuss an *a* spacing for materials having such mixed periodicities. Perhaps this is an instance where the concept of unit cell is not applicable. This would then be a structural analog to the chemical case of non-stoichiometry, a feature which used to be thought exceedingly rare, but is now proving more the rule than the exception. This is certainly true as it applies to simple compounds and almost surely will apply to silicates as well when the requisite analytical techniques are used.

There is no question that structure determinations of minerals are highly important. A problem does arise regarding whether attempts at ever more precise X-ray structure refinements are productive on materials that display "mixed phase" intergrowths of the type illustrated herein. The structure-averaging produced by X-rays may simply smooth out and thus conceal such variations in periodicities. In cases such as these it would be appropriate to do high resolution electron microscopy on the crystals preparatory to attempts to do highly precise and accurate structure refinements.

The distinction between compositional and structural disorder was only briefly discussed in the text. The point we wish to make here is that although the differences may be clear in theory, compositional and structural disorder may well be closely related in practice. The case in point in regard to the enstatites is the possibility of chemical variations occurring at physical discontinuities, *e.g.*, within (011) OREN-CLEN boundaries, whereas the coherent (100) boundaries give rise only to structural disorder.

Conclusions

Having established the pervasiveness of enstatite twinning in our previous paper, we here explore its geological significance—actual and potential. Periodic twins or sets of twins at spacings >9 Å parallel to *a* can generate polytypes. Several have been observed in meteoritic enstatite, although they are only of limited areal extent.

In some instances the (100) twin planes "step" across the crystals. Viewed in *a-b* projections the fringes, being offset by $\frac{a+b}{2}$, take on the aspect of anti-phase boundaries. When these are modeled we find that all of the features we observed in enstatite that resemble "anti-phase domains" on the images can be explained by reference to normal (100) twinning. Parting is similarly related to twinning planes; the initiation and further development of parting planes is clearly observable. We suggest that parting may differ from cleavage, not only in its selectively occurring on only certain planes, but that it is produced by shearing plus rotation.

Aspects of the geological history of enstatites can be inferred from the abundance and character of the twinning. This is mainly because CLEN developed directly from OREN—either by static inversion or by shearing—will have different features from CLEN developed from PEN. These features provide a potential means of resolving the question of whether OREN or CLEN is stable in the absence of shear at temperatures below 1000°C.

All of the enstatites, terrestrial and meteoritic, that we have examined contain intergrowths of CLEN and OREN, even those which published reports, based on X-ray data, describe as pure single phases. Moreover, their CLEN fields are untwinned. This suggests that most enstatites have been subjected to at least moderate shear stresses.

The above conclusions are based on work on the Ca-poor pyroxenes. It remains as an interesting possibility that similar data may be relevant to the origin of other minerals. Calcic pyroxenes are a clear possibility. Evans *et al* (1974) described X-ray diffraction features from orthohombic and monoclinic amphiboles that contain features similar to some seen in the enstatites. It may well be that amphiboles, when studied by high resolution electron microscopy, have a similar story to tell.

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