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# GROWTH HABITS OF CLINOPYROXENE

M. E. FLEET
*Department of Geology, University of Western Ontario, London, Ontario.*

## ABSTRACT

The clinopyroxene crystal structure adequately accounts for the preferential development of the [001]-zone growth forms over the non-'prism' forms, and of $\{\bar{1}11\}$ and $\{001\}$ over $\{111\}$ and $\{\bar{1}01\}$, respectively. [110]* and [010] are shown to be directions of difficult growth and this is consistent with the habits associated with rapid crystallization. The familiar feathery augite dendrites develop parallel to (010), acicular, skeletal grains being merely transverse sections. The available compositional data on sector-zoned clinopyroxene are marked by inconsistencies and a satisfactory explanation for this phenomenon has not yet been presented.

## RÉSUMÉ

La structure cristalline clinopyroxène rend compte adéquatement du développement préférentiel des formes de croissance de la zone [001] par rapport aux formes de non-"prisme", et de $\{\bar{1}11\}$ et $\{001\}$ par rapport à $\{111\}$ et $\{\bar{1}01\}$, respectivement. [110]* et [010] sont démontrés comme étant des indications de croissance difficile et ceci est en accord avec les habitudes associées à une cristallisation rapide. Les dendrites famillières d'augite duveteuse se développent parallèlement à (010); les grains skelettiques aciculaires étant purement et simplement des sections transversales. Les données de composition disponibles sur la clinopyroxène de zone de secteur sont soulignées d'inconsistences et une explication satisfaisante de ce phénomène n'a pas encore été présentée.

(Traduit par le journal)

## INTRODUCTION

The growth habits of clinopyroxene vary quite markedly, covering the entire range of equant, tabular, prismatic, acicular, fibrous, ophitic, skeletal, dendritic and spherulitic. The present paper is largely an examination of the crystal-structure constraints on the crystal growth of clinopyroxene when it is uninhibited by other solid phases. A brief introduction to various concepts of equilibrium and nonequilibrium crystal growth has already been given in a related paper on olivine (Fleet 1975). Aspects of the crystal growth of clinopyroxene considered in the present study are (i) equilibrium forms, (ii) habits associated with rapid crystallization and (iii) sector-zoned clinopyroxene.

## EQUILIBRIUM FORMS

Winchell & Winchell (1951) suggest the following common forms for Ca-rich clinopyroxene: $\{100\}$, $\{010\}$, $\{110\}$, $\{001\}$, $\{\bar{1}01\}$, $\{111\}$, $\{111\}$ and $\{\bar{2}21\}$. A survey of this pyroxene in the mineral collection of the Department of Mineralogy and Petrology, University of Cambridge, revealed one other form, $\{311\}$, well-developed in a diopside from De Kalb, New York. There is a very wide variation in their development although most pyroxene crystals show some degree of elongation parallel to the *c*-axis. Tabular habits may be due to either $\{010\}$ or $\{100\}$, and $\{110\}$ may develop to the exclusion of these pinacoidal forms. The [001]-zone forms may be terminated, dominantly, by $\{001\}$ and $\{\bar{1}01\}$ or $\{\bar{1}11\}$ and $\{111\}$ or by combinations of them. However, the examples given by Winchell & Winchell (1951, Figs. 290 to 293) are fairly representative of the usual combinations of forms. Possible additions to these would be the augite, from Nordmarken, Sweden, which has long prisms with equally-developed $\{100\}$ and $\{010\}$ terminated by $\{001\}$ and $\{\bar{1}01\}$, and skarn diopside from Ala Valley, Piemont, Italy, which has tabular prisms with $\{100\}$ developed more than $\{010\}$, terminated by $\{111\}$, $\{\bar{2}21\}$ and $\{\bar{1}01\}$. The latter are somewhat reminiscent of the platy whiskers of diopside which occur as quench products in certain hydrothermal experiments (MacRae 1974). These are elongate parallel to the *c*-axis and are platy parallel to (100), with width:thickness ratios of about 10:1. In summary then, whilst the 'prism' forms (those in the [001] zone) tend to dominate, only $\{\bar{2}21\}$ and $\{\bar{3}11\}$ of the non-'prism' forms can be considered as less important.

Ca-rich clinopyroxene has the diopside structure in which the Si,O tetrahedra form single chains arranged in pairs parallel to the *c*-axis so that the $M(1)$-site coordination octahedron

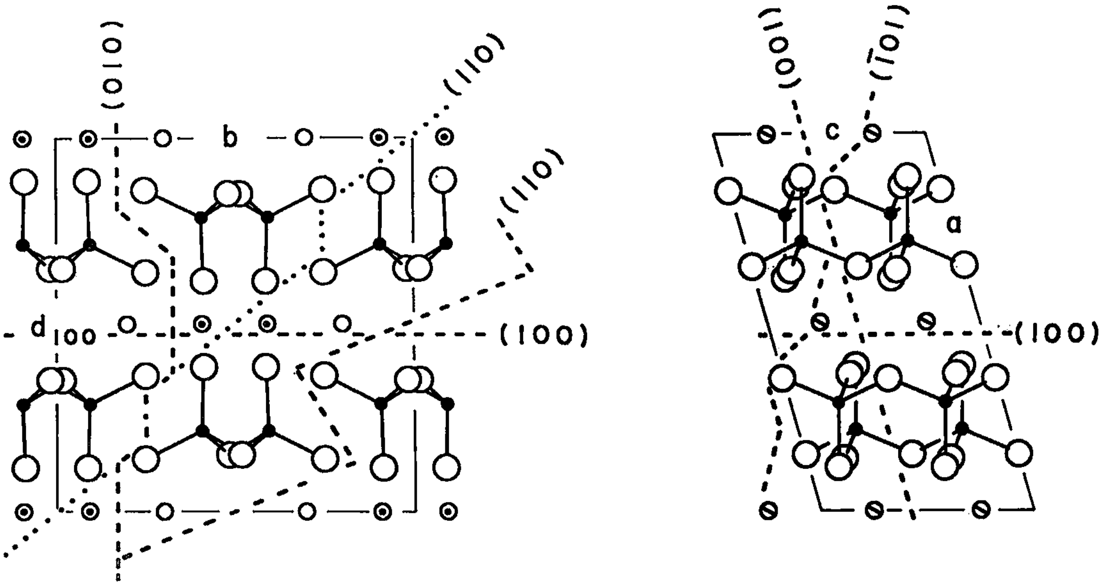

FIG. 1. The crystal structure of diopside showing the probable compositions of faces of {110}, {010}, {100}, {001} and {$\bar{1}$01} (dashed lines) and the possible composition of faces of {110} (stippled lines): $M(1)$ atoms, medium circles with dot; $M(2)$ atoms, medium open circles; overlapping $M(1)$, $M(2)$ atoms, medium circles with bar; Si, small closed circles; O, large open circles.

and the $M(2)$-site coordination polyhedron are formed, respectively, largely by apical and basal oxygens (Fig. 1). The stereochemistry of the $M$-site cations has been discussed by Fleet (1974). The $M(2)$ cations are eight-fold coordinated and hence, for cations of the same valence, $M(2)$-O bonds are proportionately weaker than $M(1)$-O bonds. There are no direct lateral bonds between the Si,O tetrahedral chains which are the dominant feature of the structure and, as is well-known, the resulting voids are responsible for the good {110} cleavage. The structure also allows for easy cleavage on {010} and to a lesser extent on {100}. These cleavages are imperfect only because stress in the plane normal to the $c$-axis is relieved so readily by rupture parallel to {110}.

The existence of the common forms of Ca-rich clinopyroxene can be rationalized quite satisfactorily assuming that possible crystal faces are those which have a minimum surface energy (with few unsatisfied bonds) and which do not have marked growth steps. The probable growth surfaces of {100}, {010} and {110} are shown in Figure 1a. A second growth surface for {110} is also shown. However, although it is slightly stepped, the former is the more probable since it interrupts largely relatively-weak $M(2)$-O bonds: this point is particularly significant for $M(2)^{+}$ $M(1)^{3+}$ pyroxene. Also, the greater development of the 'prism' forms suggests that the Si,O tetrahedral chains are parallel to a direction of easy growth and that it is the bridging role of the cations in the $M$ protosites (terminology after Nakamura, 1973) that retards growth normal to the $c$-axis. $M(2)$ will be less efficient as bridging cations in the {110} growth surfaces than $M(1)$ since they are associated with larger and more irregular polyhedra which are less likely to develop in a way leading to continuation of the structure. Because the Si,O tetrahedral chains are 'added' laterally to the faces of {010} (Fig. 1a), the bonding between these growth layers is minimal. Thus both [110]* and [010] could be directions of relatively difficult growth. The probable growth surfaces of the non-'prism' forms (Figs. 1b and 2) must all include terminated Si,O tetrahedral chains. The growth surfaces of {001} and {101} are apparently quite similar. Both contain equal numbers of $M(1)$ and $M(2)$ protosites. However, because the $M$-site polyhedra are tilted forward in the clinopyroxene structure, the $M$-protosite polyhedra in the {001} growth surfaces are formed largely of oxygens attached to the crystal (the $M(1)$ polyhedron having five crystal oxygens and the $M(2)$ having six). This is a factor which tends to inhibit further growth, since it reduces the surface energy, and thus provides an explanation for the

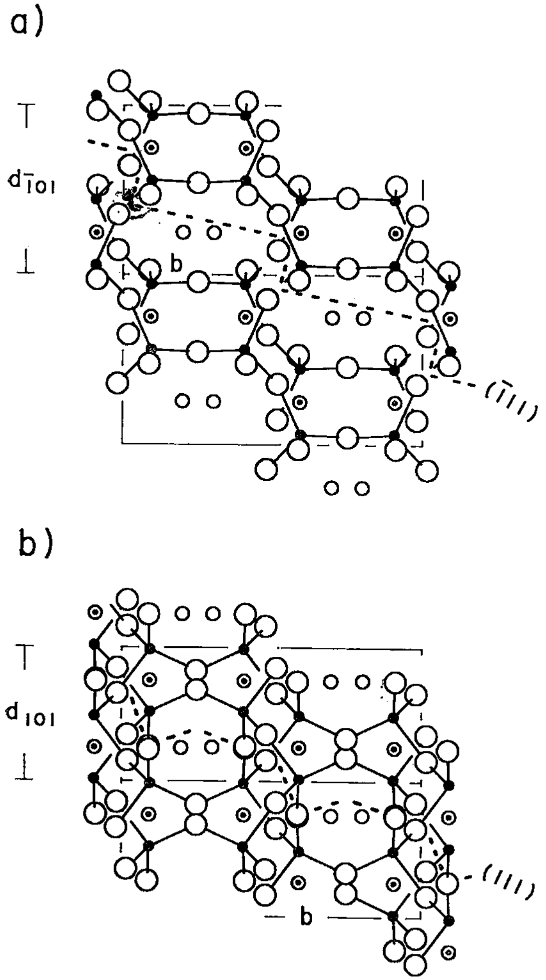

FIG. 2. The crystal structure of diopside projected onto (a) $d_{\bar{1}01},b$ plane and (b) $d_{101},b$ plane showing the probable compositions of faces of $\{\bar{1}11\}$ and $\{111\}$: symbols as in Figure 1.

better development of {001}. Also, the {001} cleavage results in the breaking of fewer bonds than a hypothetical $\{\bar{1}01\}$ cleavage. The projections of the diopside structure in the $d_{\bar{1}01},b$ and $d_{101},b$ planes are also quite similar (Fig. 2). The probable growth surfaces of $\{\bar{1}11\}$ and {111} are slightly 'stepped' and are formed essentially of $M(2)$-protosite polyhedra and terminal Si,O tetrahedra as suggested in Figure 2, the $M(2)$-protosite cations tending to inhibit subsequent growth. The $M(1)$ octahedra in the growth layers of $\{\bar{1}11\}$ and {111} are in varying states of completion. The two non-equivalent $M(1)$ octahedra in {111} have four and five crystal oxygens, respectively. However, the growth layer of $\{\bar{1}11\}$ has one complete $M(1)$ octahedron and one with five crystal oxygens which must favour development of this form, especially for alkali and aluminous pyroxenes. The $\{\bar{2}21\}$ growth layer (not illustrated) is not stepped and includes equal numbers of $M(1)$- and $M(2)$-protosite polyhedra formed largely of crystal oxygens.

It has been shown that the structure of olivine allows a direct qualitative explanation for the relative order of importance of its common crystal forms (Fleet 1975). The clinopyroxene situation is somewhat more complicated, principally because the development of the common forms varies markedly, suggesting that the simple structural controls are not overriding. There is some indication that the development of the non-'prism' forms may be a function of crystal composition and/or chemical environment but the 'prism' forms, in particular, may exhibit a wide variation in development within the same environment. Clearly the factors leading to inhibition or stimulation of growth in these circumstances are little-understood at the present time. However, the crystal structure does favour development of the 'prism' forms over the non-'prism' forms and suggests that, of the latter, the important ones should be {001} and $\{\bar{1}11\}$. These are the forms most frequently noted by investigators; for example, it has been shown that $\{\bar{1}11\}$ is the dominant non-'prism' form of sector-zoned titanaugite (Leung 1974).

## HABITS ASSOCIATED WITH RAPID CRYSTALLIZATION

Fine-grained clinopyroxene is usually elongate parallel to the *c*-axis. Augite and pigeonite in the groundmass of basalts tend to be prismatic and microlites of aegirine-augite and clinoenstatite (Dallwitz *et al.* 1966) are acicular. With more rapid cooling, clinopyroxene in certain mafic and ultramafic rocks develops very intricate shapes; for example, swallow-tailed augite occurs in alkali basalts (Strong 1969) and feathery dendrites or spherulites have been reported in dolerite (Wilson 1948), Apollo 12 basalt (Lofgren 1971), submarine basalt (Bryan 1972) and, with apparently-skeletal, acicular crystals, in spinifex-textured rock (Fleet & MacRae 1975). Spherulitic and acicular clinopyroxenes have been produced in experiments on Apollo 15 quartz-normative basalts (Lofgren *et al.* 1975).

The augite from the high-Mg basalt studied by Fleet & MacRae (1975) has been investigated in more detail. The feathery dendrites (Figs. 3a, e) are always (010) sections giving maximum second-order, green-yellow interference colours. Their radial elements have inclined extinction,

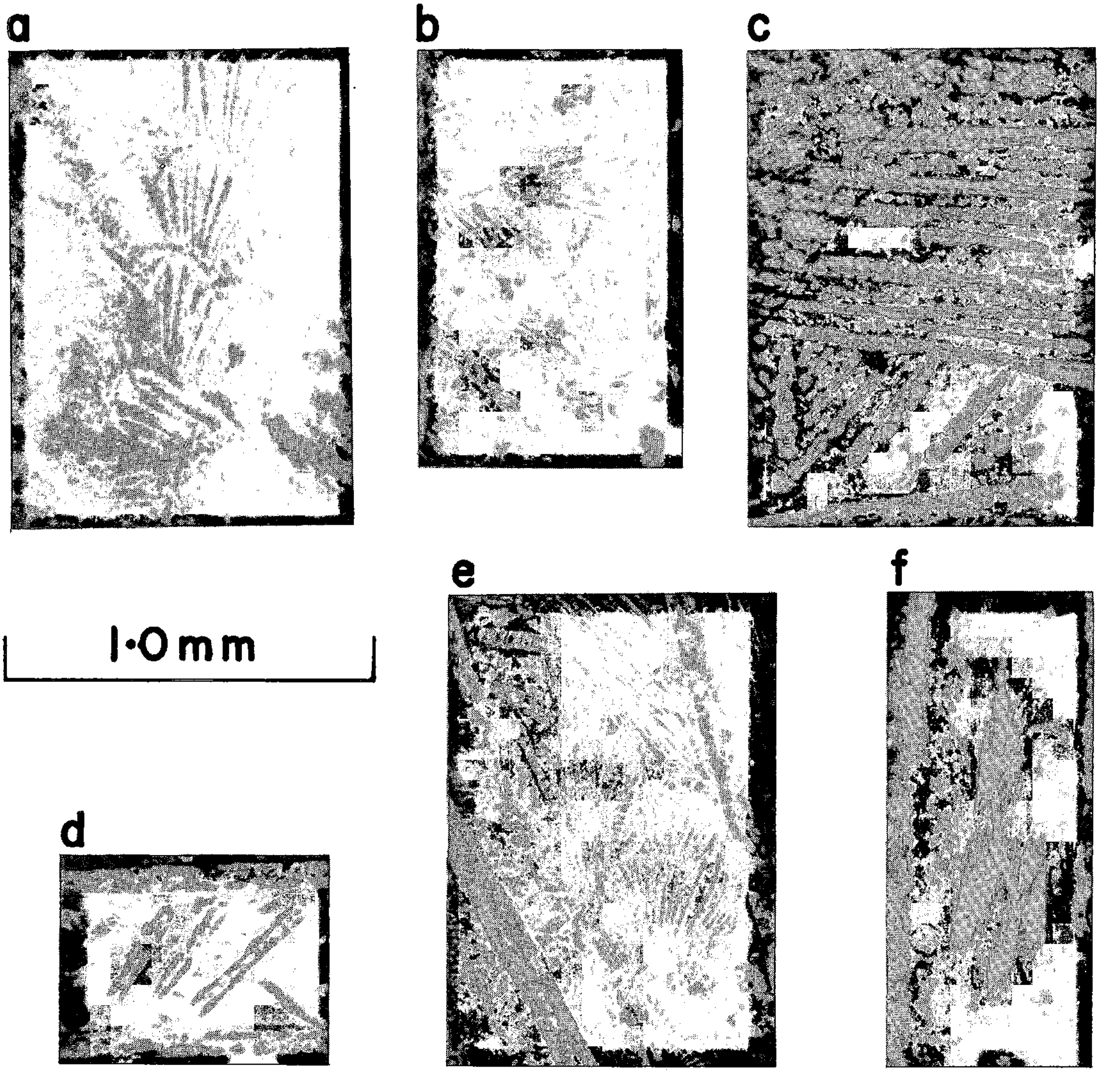

FIG. 3. Photomicrographs of a spinifex-textured rock showing the appearance of augite dendrites parallel to (010) (a and e), and transverse to (010) (b, c, d and e); (f) oblique section of larger skeletal augite grain with whiskery extensions: plain, polarized light.

are elongate parallel to the *c*-axis, and are terminated by apparently-irrational (*h*0*l*) planes (Fig. 3a). They often coalesce to form an inner arcuate element which retains crystallographic continuity with adjacent radial elements. The skeletal, acicular crystals are merely sections of the dendrites cut normal to (010) (Figs. 3b, c, d, e). The crystallographic orientation (and thus the interference colours) varies progressively along their lengths and usually the leading element is an (001) section and the tail element, if elongate, is a near-(100) section. The (001) or near-*c*-axis sections are bounded by the forms {110} and {010}, and are often arrowhead-shaped although larger grains may also form box, spearhead, fleur-de-lis or W shapes. The largest grains, more acicular than dendritic, approach the size and shape of clinoenstatite microlites. The surfaces of the individual crystal elements are often whiskery (Fig. 3f). The whiskers are organized into spherulite-like sprays which pass into and retain crystallographic continuity with the surrounding finer-grained groundmass. They appear to post-date the development of the dendrites and probably represent either a later phase of crystallization from the liquid or devitrification. However, they are occasionally associated with areas of hydrothermal alteration.

The nucleation of new growth layers is a rate-controlling step and thus, during rapid crystallization, crystal development tends to be restricted to directions of easy growth. The shape of the radial crystal elements of the clinopyroxene dendrites is consistent with the evidence presented earlier that the *c*-axis is parallel to a direction of easy growth and that for the 'prism' forms [110]* and [010] are directions of difficult growth. However, the arrangement of the dendrites does suggest that the radial elements originate only after initial clinopyroxene nucleation by growth approximately parallel to [100], which may thicken by further development to become an arcuate element. Once seeded, the radial elements extend out rapidly toward the nutrient. This growth requires the removal of terminal oxygens or, more likely, the breaking of Si-O bonds in the liquid; clearly, however, the addition of Si,O tetrahedral units to existing chains is more efficient than bridging by the *M* atoms. It is possible that growth is facilitated by partial organization of the Si,O tetrahedral chains in the liquid ahead of the crystal-liquid interface.

## SECTOR-ZONED CLINOPYROXENE

Sector zoning in crystals is characterized by the presence of compositionally-distinct pyramidal segments subtended by faces of certain crystal forms. The available data on sector-zoned clinopyroxene can be organized into three separate parageneses: (i) alkalic rocks, (ii) pegmatitic bodies in diabases and tholeiitic basalts, and (iii) lunar rocks. These parageneses are summarized as follows:

(i) titanaugite and aluminous augite show enrichment of Al, Ti, and total Fe in 'prism' sectors ($\{100\}$, $\{010\}$ and $\{110\}$) and enrichment of Si and Mg in non-'prism' sectors ($\{\bar{1}11\}$ and $\{001\}$; Strong 1969; Hollister & Gancarz 1971; Ferguson 1973; Wass 1973; Leung 1974). Ca and Na show no consistent variation. Of the prism sectors, the study of Hollister & Gancarz (1971) indicated a slight preference of Al and Ti for $\{100\}$, and that of Ferguson (1973) suggested a slight preference of Ca for $\{010\}$.

(ii) Pegmatitic augite tends not to develop non-'prism' sectors (although Smith & Lindsley 1969, have tentatively identified a $\{001\}$ sector). The existing data show no consistent trends except that zoning is largely restricted to the divalent cations. Preston (1966) has reported Ca enriched in the $\{100\}$ sector and Mg and Fe enriched in the $\{010\}$ sector whereas the data of Nakamura (1974) show the opposite enrichment, Mg and Fe in the $\{100\}$ sector and Ca in the $\{010\}$ (and $\{110\}$) sectors.

(iii) There is disagreement on the data for Apollo 11 augite (Hollister & Gancarz 1971). Although, in general, the data for it have similarities with those for titanaugite, an earlier report had suggested that in one specimen Si, Mg and total Fe prefer the $\{110\}$ sector and Al, Ti, Ca and Cr prefer the $\{001\}$ sector (Hargraves *et al.* 1970). Apollo 12 pigeonite has only $\{010\}$ and $\{110\}$ sectors developed with Ca enriched in the latter (Hollister *et al.* 1971) and, as such, is analogous to the pegmatitic augite described by Preston (1966).

It is evident that consistent data only occur for the distribution of certain elements between 'prism' and non-'prism' sectors in Ti- and Al-rich clinopyroxene. However, some of the inconsistencies noted above may have arisen from the misidentification of individual sectors through limited material and anhedral and/or ophitic grains; the identification of non-'prism' sectors ($\{\bar{1}11\}$, $\{001\}$, $\{111\}$ and $\{\bar{1}01\}$) in such circumstances must be virtually arbitrary!

In regard to the probable origin of sector zoning in clinopyroxene, nearly all authorities recognize that the sectors in most larger crystals, from porphyritic and medium- and coarse-grained rocks, developed contemporaneously, as evidenced, for example, by the normal and oscillatory-concentric zoning in titanaugite (Wass 1973), and the normal concentric zoning in pegmatitic augite (Nakamura 1973), and not by the later infilling of hollow sectors as appears to have happened with swallow-tailed groundmass augite (Strong 1969) and pigeonite-augite intergrowths in Apollo 12 basalts (Hollister *et al.* 1971). There is some agreement that sector zoning develops through relatively rapid, non-equilibrium crystallization. However, the growth rate should not exceed the diffusion rate in the liquid as suggested by Wass (1973). Also, diffusion in the liquid phase, between volumes adjacent to different sectors, must be a consequence of sector zoning and cannot be regarded as a cause of it (Leung 1974). It is appreciated by many authors that the crystal structures of growth layers of different forms are not the same and that this is directly related to the selective uptake of elements by the individual sectors. Hollister and co-workers argue that, because of the valence imbalance involved, the substitution of Al for Si will take place preferentially on faces which allow a simultaneous compensating substitution in the $M(1)$ site. However, one would expect that local valence balance around the outermost oxygen atoms in the growth layers would be maintained by adjacent cations in the liquid phase. More significantly, this concept fails to predict the strong enrichment of Si in the non-'prism' sectors of titanaugite and aluminous augite. Nakamura (1973) considers that the coordination polyhedra of the $M(1)$ and $M(2)$ protosites on $\{100\}$ growth layers are more flexible than those on $\{010\}$ growth layers and are able to accept Mg and Fe in excess of equilibrium amounts. Why flexibility of the $M(2)$ protosites should not equally favour enrichment of Ca in the $\{100\}$ growth layers is not discussed. The suggestions for a crystal-chemical control on sector zoning in clinopyroxene are not limited to these two examples, but the common problem facing all of them as unique explanations are the conflicting enrichment trends suggested by the available analytical data. Even the strong enrichment trend for titanaugite and aluminous augite does not persist in any consistent way in clinopyroxene of the other two parageneses and, in fact, is apparently contradicted in at least one instance. Clearly, more systematic analytical work is required, but a satisfactory explanation of sector zoning in clinopyroxene may not be forthcoming until advances have been made in our understanding of the chemistry of solid-liquid interfaces.

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