

Lowering of symmetry in pyribole structures

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ABSTRACT. The low-symmetry forms of the clinopyroxene structure fit the rules proposed previously (Chisholm, 1981) but the low-symmetry forms of ortho- and proto-pyroxene do not. The rule governing the packing of the tetrahedral chains into layers is therefore revised to take into account the different chain configurations. Starting with simple sequences of . and \times chains (Thompson, Hallimond Lecture 1979, unpubl.) a scheme is proposed for deriving most of the known pyribole structure types and their space groups.

THE crystal structures of the pyroxenes and amphiboles (the 'pyriboles') are made up of 'I-beams', which consist of a strip of M cations sandwiched between two chains of SiO_4 tetrahedra (fig. 1). The tetrahedra in the chains are generally rotated about a^* to improve the fit between the chains of tetrahedra and the coordination polyhedra of the M cations. A simple model for an I-beam allows different rotations of the tetrahedra in the two chains and retains the c -glide symmetry of the pyroxene I-beam (mirror symmetry of amphibole). Such an I-beam will obey a set of symmetry rules (Table I of Chisholm, 1981) which determine the space group of a given arrangement of I-beams.

A model I-beam of this type has been used to derive a reasonable set of pyribole structure types (Chisholm, 1981). Two empirical rules are sufficient to limit the stacking permutations of such I-beams to those commonly observed in nature and others simply related to them: (a) The structure may contain only one kind of I-beam. This restricts us to simple arrangements in which the I-beams differ only in their relative orientation. (b) Only one type of tetrahedral chain may be present in a (100) layer composed of such chains which are the flanges of the I-beams. We may call this the tetrahedral layer packing rule; it expresses the requirement for optimum edgewise packing of the tetrahedral chains into layers \parallel (100).

In my earlier derivation of the pyribole structure types, I noted that several pyroxenes with lower symmetry than the common structures lay outside the scope of the model. These low-symmetry structures are here discussed in more detail for the light they shed on cation ordering and strain relief

mechanisms in the common pyroxene structure types.

Only small structural differences may be needed to lower the symmetry of the common structure types. As will be seen, there are instances of such differences being close to the limit of detection.

Possible variants of the $C2/c$ clinopyroxene structure have been considered by several authors: some deal only with a limited range of possibilities (Burnham *et al.*, 1967; Zussman, 1968; Okamura *et al.*, 1974; Matsumoto *et al.*, 1975) while others derive the full range of possible space groups (Hahn and Behruzi, 1968; Matsumoto and Banno, 1970). Brown (1972) gives the most comprehensive treatment but concentrates mainly on those possibilities with monoclinic symmetry.

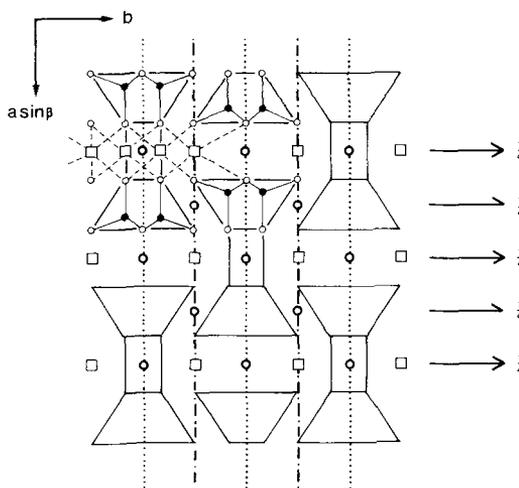


FIG. 1. Arrangement of I-beams in clinopyroxene. In the top left-hand corner is shown one I-beam which consists of a strip of cations (open squares) between two chains of SiO_4 tetrahedra (Si: small filled circles, O: small open circles). Adjacent I-beams (top) are linked via the irregularly coordinated outermost cation of the strip ($M2$). Elsewhere only these cations and the outlines of the I-beams are shown. The symmetry operators of the clinopyroxene space group $C2/c$ are shown in the conventional notation (International Tables for X-ray Crystallography, 1969).

The structural differences which are implied by symmetries lower than the orthopyroxene space group $Pbca$ have been noted by Matsumoto (1974); low-symmetry variants of $Pbcn$ protopyroxene structure have not so far been considered.

In the following discussion it will be convenient to take as the general pyroxene formula



where $M2 = Na, Ca, Mg, Fe^{2+}, Li$ and represents the cation in the irregularly coordinated sites linking adjacent I -beams; $M1 = Mg, Fe^{2+}, Al, Fe^{3+}, Mn$ and represents the octahedrally coordinated cation sandwiched between the tetrahedral chains; $T = Si, Al$ and is the tetrahedrally coordinated cation in the TO_4 chains.

Clinopyroxenes with lowered symmetry. As an aid to understanding the derivation and significance of reduced-symmetry variants, the symmetry operators of the normal clinopyroxene space group, $C2/c$, are shown in relation to the I -beams and their component octahedral strips and tetrahedral chains in fig. 1.

Lowering of the symmetry from $C2/c$ may occur for one or both of the following reasons: (1) For some compositions, cation ordering may be energetically favourable and the ($M1, M2$) and/or T sites will then be subdivided. (2) Strain within the structure may be relieved by deformation involving subdivision of ($M1, M2$) and/or T sites.

Depending on the nature of the cation ordering or strain relief, the symmetry will be lowered to a subgroup of $C2/c$. Following Brown (1972), there are 15 subgroups (10 monoclinic, 5 triclinic) which correspond to topologically distinct variants of the clinopyroxene structure:

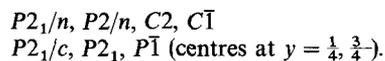
$2/m$: $P2_1/c, P2_1/n, P2/c, P2/n$
m	: Cc, Pc, Pn
2	: $C2, P2_1, P2$
$\bar{2}$: $C\bar{1}$
	: $P\bar{1}$ (centres at $y = 0, \frac{1}{2}$)
	: $P\bar{1}$ (centres at $y = \frac{1}{4}, \frac{3}{4}$)
1	: $C1, P1$.

The unit cell of the $C2/c$ structure is retained throughout with the same origin; unconventional space group symbols are used and an unconventional choice of origin is made, wherever either is necessary.

Although an I -beam may no longer conform to the simple model used to derive the common structure types, the packing of tetrahedral chains into layers should still, to a first approximation, control which structures are likely to occur, i.e. the tetrahedral layer packing rule should still hold.

Adjacent tetrahedral chains in the layers $\parallel (100)$ are related by the screw diad axes and by the centres

of symmetry at $y = \frac{1}{4}, \frac{3}{4}$ (fig. 1). One of these symmetry operators is retained in seven subgroups and in these the tetrahedral layer packing rule is obeyed:



Of these, the last three contain two types of tetrahedral chain and correspond to the low clinopyroxene structure and its subgroups.

$P2_1/n, P2/n, C2$, and $C\bar{1}$ are therefore possible subgroup symmetries for the high clinopyroxene structure type. These are the four possible ordering schemes for calcium Tschermak's pyroxene derived directly by Okamura *et al.* (1974) from the requirement that the structure should have only one type of tetrahedral chain.

Equivalent $M1$ and $M2$ positions in $C2/c$ are related by the c -glide planes and by the centres at $y = 0, \frac{1}{2}$. Only in $P2/n$ and $C2$ are both these symmetry operators absent and ordering of the $M1$ and $M2$ cations over subdivided sites is only possible in these two of the four subgroups. The tetrahedra are related only by the c -glide plane in $C2/c$ and the T sites are therefore subdivided in all four subgroups. Examples of three of the four possible clinopyroxene subgroups have been reported.

Probably the best established low-symmetry space group is $P2/n$ for the omphacites (Matsumoto *et al.*, 1975; Curtis *et al.*, 1975; Phakey and Ghose, 1973) in which the $M1$ ($Mg, Fe^{2+} - Al, Fe^{3+}$) and $M2$ ($Ca - Na$) cations are ordered.

Okamura *et al.* (1974) reported additional weak reflections suggesting Al, Si ordering in space group $C2$ for synthetic calcium Tschermak's pyroxene. Structure refinement, however, did not reveal any departure from $C2/c$ with a random Al, Si distribution. Short range order or a fine-scale domain structure may mask departures from the average $C2/c$ structure.

In his study of α -spodumene ($LiAlSi_2O_6$), Graham (1975) reported extra weak reflections consistent with space group $C2$, which could not be fully accounted for by multiple diffraction or included impurities. For the synthetic analogue $LiAlGe_2O_6$, space group $P2_1/n$ has been reported (Hahn and Behruzi, 1968).

Lindemann (1961*a, b*) has described two $MgSiO_3$ phases produced by thermal decomposition of talc, having space group $P2_1/n$. Smith's (1969) re-examination of the unit cell data clearly shows that these phases are not clinoenstatite and protoenstatite as Lindemann proposed. Nevertheless, the evidence for a $P2_1/n$ $MgSiO_3$ structure may still be valid. The cell dimensions of Lindemann's phases are similar to those of low clinoenstatite

and it seems possible that lowering of symmetry from $C2/c$ (high clinoenstatite) to $P2_1/n$ may provide an alternative strain relief mechanism to the more usual formation of low clinoenstatite with space group $P2_1/c$.

These last three compositions, $\text{LiAlSi}_2\text{O}_6$, $\text{LiAlGe}_2\text{O}_6$, and MgSiO_3 , do not have any scope for cation ordering beyond that of the $(M2)(M1)T_2O_6$ structural formula. The lowered symmetry in these cases can only be the result of strain relief within the structure, particularly around the $M2$ site which links adjacent tetrahedral chains. In the MgSiO_3 and $\text{LiAlSi}_2\text{O}_6$ structures, the Mg and Li cations on the $M2$ site have irregular six-fold coordination. There is probably more strain associated with the $M2$ sites in these than in the Na and Ca clinopyroxenes where the $M2$ cations are in irregular eightfold coordination.

No example of a clinopyroxene with space group $C\bar{1}$ has been reported. This space group has the same extra reflections as $C2$ and can be distinguished from that group only by (a) the symmetry of the intensity distribution and (b) any slight departures of α and γ from 90° . Any departure from $C2/c$ is likely to be small and may be masked by short-range order or fine-scale domain structure. $C\bar{1}$ is thus particularly difficult to distinguish from $C2$; is it possible that some specimens described as $C2$ are in fact $C\bar{1}$?

Strain relief in clinopyroxene. The simplest ways in which the $C2/c$ clinopyroxene structure may lower its symmetry to relieve strain are summarized in Table I. (1) and (2a) are believed to be alternative mechanisms, (2a) being the more common. (2b) and (2c) are not known to occur as equilibrium phases; they both violate the tetrahedral layer packing rule, which seems to control which possibilities occur.

Because of the behaviour of ortho- and proto-pyroxenes (see below), it is worth examining in more detail the operation of the tetrahedral layer packing rule in clinopyrriboles.

Tetrahedral layer packing in clinopyroxenes. In an idealized, fully extended chain of regular tetra-

hedra, the two non-bridging oxygen atoms will coincide when projected orthogonally on to the c -axis (fig. 2a). When the tetrahedra in a chain are rotated about a^* , these two atoms are separated on the projection on the c -axis by a distance δ (fig. 2b). For a regular tetrahedron,

$$\delta = 2\sqrt{2/3} (T-O) \sin \frac{1}{2} (180^\circ - \text{CRA}) \quad (1)$$

where $(T-O)$ is the tetrahedral bond length and CRA is the chain rotation angle as measured conventionally, i.e. $O3-O3-O3$ for pyroxenes and $O5-O6-O5$ for amphiboles (Veblen and Burnham, 1978).

The actual value of δ for a pyribole structure can be calculated from the atomic coordinates. For pyroxene, the non-bridging oxygen atoms are $O2$ and $O1$ and

$$\delta = (x_{O2} - x_{O1})a \cos \beta + (z_{O2} - z_{O1})c \quad (\text{\AA}) \quad (2)$$

In amphibole, the non-bridging atoms at the edge of the chain are $O4$ and $O2$.

Fig. 3 shows the variation of δ (\AA) with chain rotation angle for pyroxenes and amphiboles, and the line corresponding to equation (1) for regular tetrahedra. How distorted the tetrahedra in a particular structure are is indicated by the departure from the theoretical line and not by the value of δ itself. (Data for the low clino-structure type have been omitted; its behaviour will be considered after that of the proto- and ortho-structure types.

For both clinopyroxene and clin amphibole, the values of δ lie fairly close to the predicted line. The

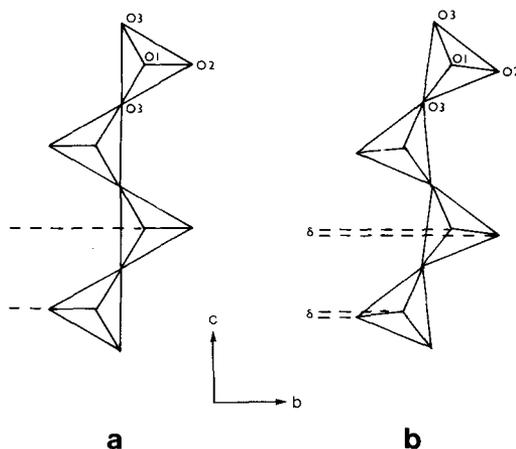


FIG. 2. (a) Chain of regular tetrahedra which are not rotated. The two non-bridging oxygen atoms ($O1$ and $O2$) coincide when projected on to the c -axis (dotted lines). (b) Chain of rotated regular tetrahedra. When projected on to the c -axis (dotted lines), the two non-bridging oxygen atoms are separated by a distance $\delta = 2\sqrt{2/3}(T-O) \sin \frac{1}{2}(180^\circ - \text{CRA})$.

TABLE I. Simple strain relief mechanisms for $C2/c$ clinopyroxene

Mechanism	Resulting space group
(1) Formation of two distinct T sites in the tetrahedral chain with various ordering schemes	$P2_1/n$, $P2_1/n$ $C2$, $C\bar{1}$
(2) Formation of two distinct kinds of tetrahedral chain	
(a) As two kinds of tetrahedral layer	$P2_1/c$
(b) As two kinds of chain within one kind of layer	Cc
(c) As two kinds of I -beam	$P2/c$

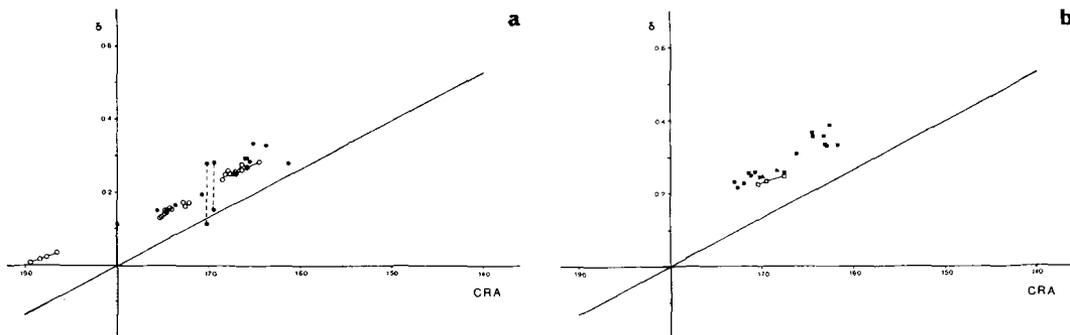


FIG. 3. δ vs CRA plot for (a) clinopyroxenes and (b) clin amphiboles and clinojimthompsonite. Separation along the c -axis, δ (Å), of the non-bridging O atoms plotted against chain rotation angle, CRA. The straight line shows the variation of δ with chain rotation angle expected for regular tetrahedra; the further a point lies away from this line, the greater the distortion of the tetrahedra. Chain rotation angles above 180° correspond to tetrahedral rotations in the opposite sense (S -rotation) relative to the octahedral strip to that usually found (O -rotation). Points for single chains (clinopyroxenes) are shown as circles, for double chains (clin amphiboles) as squares, and for triple chains (clinojimthompsonite) as triangles. Structures determined at high temperature or at a series of temperatures are shown as open circles or squares and joined by lines where space permits. The vertical dashed lines in (a) link the points for the two distinct tetrahedra in the $P2/n$ -omphacite chain. Data for figs. 3, 6, 9, and 10 are taken (a) for pyroxenes, from references in Table A1 of Cameron and Papike (1980), and from Cameron *et al.* (1973), Finger and Ohashi (1976), Gordon *et al.* (1981), Sadanaga *et al.* (1969), Smyth (1973) and (1974b), and Sueno and Prewitt (1976). (b) for amphiboles and triple-chain silicates, from references in Table A1 of Hawthorne (1981), and from Papike *et al.* (1969), Sueno *et al.* (1972) and (1973), and Veblen and Burnham (1978).

distortion of the tetrahedra is certainly much less than in proto-pyribole or in the A-chains of orthopyribole (cf. figs. 6 and 9). The actual values of δ are slightly larger than predicted, as is the case too for the B-chains of orthopyribole. Veblen and Burnham (1978) have ascribed this to a shortening of one of the tetrahedron edges which are shared with the $M2$ coordination polyhedron.

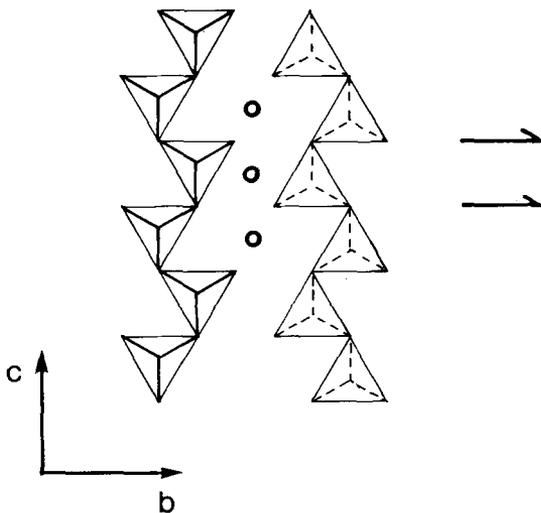


FIG. 4. Optimum packing of chains of fully rotated tetrahedra is achieved if adjacent chains are related by screw diad axes $\parallel b$ or by centres of symmetry as indicated.

It is significant that the points in fig. 3 lie approximately parallel to the theoretical line. The point for $\text{LiFe}^{3+}\text{Si}_2\text{O}_6$ (chain rotation angle 180°) shows the distortion in a fully extended chain. A roughly similar distortion occurs in all the clinopyriboles of fig. 3, even when the sense of the tetrahedral rotation is reversed (chain rotation angles greater than 180°) as in spodumene (discussed further below). The distortion of the tetrahedra evidently has little effect in the clinopyriboles.

The packing of the chains is therefore dominated by the requirements of fitting together chains of rotated tetrahedra. Optimum fit is achieved if adjacent chains are related by screw diad axes $\parallel b$ and/or by centres at $y = \frac{1}{4}, \frac{3}{4}$ (fig. 4). All the chains in a layer must then be identical and for this reason the tetrahedral layer packing rule holds. Subject to this rule, strain can be relieved by mechanism (1) or (2a) (Table I), consistent with observation.

Lowered symmetry in protopyroxene. Fig. 5 shows the symmetry of space group $Pbcn$ in relation to the I -beams and the possibilities for lowered symmetry in protopyroxene are summarized in Table II.

Strain relief mechanisms (1) and (2a) obey the tetrahedral layer packing rule but no example of either is known. The only known low-symmetry variant of protopyroxene is the protoenstatite of Smyth (1971) with space group $P2_1cn$. This is the only simple possibility which violates the tetra-

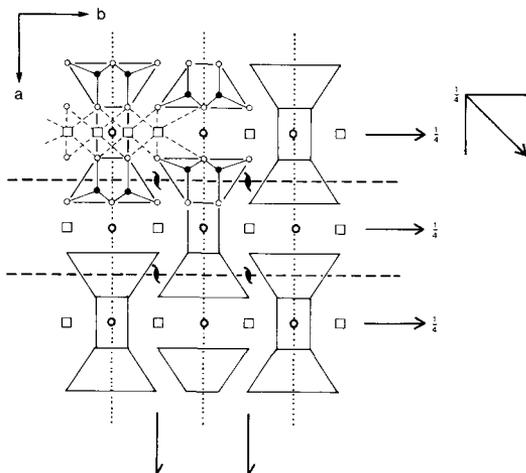


FIG. 5. Arrangement of *I*-beams in relation to the symmetry operators of the protopyroxene space group *Pbcn* shown using the same symbols as fig. 1.

hedral layer packing rule, which therefore requires closer examination. The rule is also violated by the *P2₁ca* orthopyroxene space group (see below).

The values of δ and the chain rotation angle for protopyriforms are shown in fig. 6. The points do not lie parallel to the theoretical line as they would if rotation of the tetrahedra were predominant. Nor do the points cluster along the δ -axis as they would if the tetrahedra were distorted but not appreciably rotated. In the protopyriforms, the tetrahedra are both distorted and rotated through a moderate to large angle.

Chisholm (1981) considered the packing together of chains of tetrahedra which were distorted but not rotated. For minimum strain, adjacent chains have to be related by a *b* glide plane \perp *a* in pyroxene (*n* glide plane in amphibole) and/or a screw diad axis \parallel *c* (fig. 7) and this symmetry requirement leads to the tetrahedral layer packing rule.

However, when the tetrahedra in the chain are both distorted and rotated, a difficulty arises. The symmetry requirement for optimum packing of

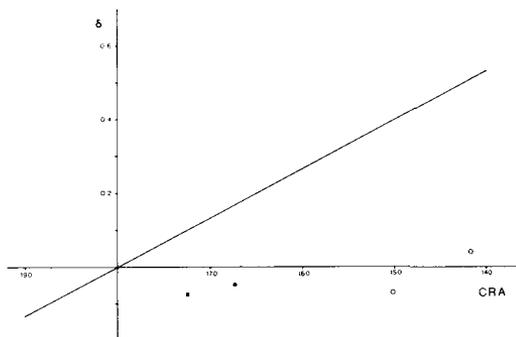


FIG. 6. δ vs CRA plot for protopyroxenes (circles) and protoamphibole (square). The open circles denote the points for protoenstatite at 1100°C. (See caption for fig. 3.)

rotated tetrahedra (fig. 4) differs from that for packing distorted tetrahedra (fig. 7). Not only are these two requirements incompatible as mentioned in the previous paper, they are opposed, i.e. the arrangement which minimizes strain resulting from rotation of the tetrahedra, maximizes the strain resulting from their distortion, and vice versa. When the tetrahedra are both distorted and rotated the minimum strain configuration will be one in which adjacent chains are not related by symmetry and

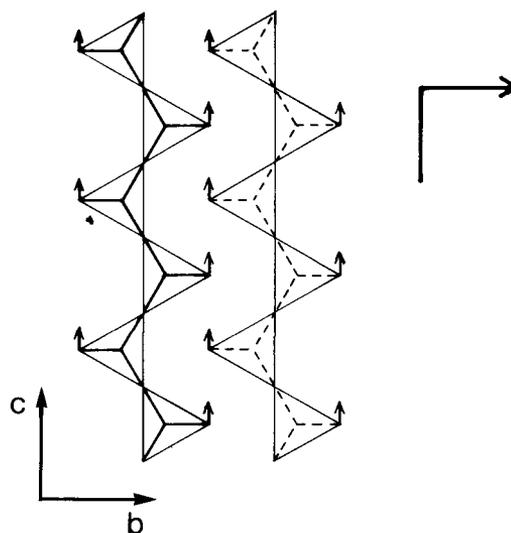


FIG. 7. Optimum packing of chains of tetrahedra which are not rotated but which are distorted by atomic displacements in the *c*-direction (small arrows). Adjacent chains must be related by a *b* glide plane \perp *a* or by a screw diad axis \parallel *c*. Atomic displacements in the *a*- and *b*- directions require adjacent chains to be related by symmetry but do not control the type of symmetry operator (Chisholm, 1981).

TABLE II. Simple strain relief mechanisms for *Pbcn* protopyroxene

Mechanism	Resulting space group
(1) Formation of two distinct <i>T</i> sites in the tetrahedral chain	<i>Pb2n</i> , <i>P2₁22₁</i>
(2) Formation of two distinct kinds of tetrahedral chain	
(a) As two kinds of tetrahedral layer	<i>Pbc2₁</i>
(b) As two kinds of chain within one kind of layer	<i>P2₁cn</i>
(c) As two kinds of <i>I</i> -beam	<i>P2/c</i>

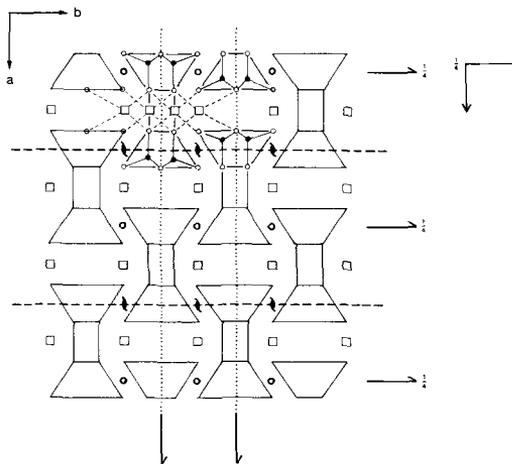


FIG. 8. Arrangement of *I*-beams in relation to the symmetry operators of the orthopyroxene space group *Pbca* shown using the same symbols as fig. 1.

the tetrahedral layer packing rule quoted above is broken. A restatement of the rule will be given later. The space groups for 'low proto-' become $P2_1cn$ (pyroxene) and $P2_1mn$ (amphibole) in the case where the tetrahedra are both rotated and distorted.

Whether strain is relieved by mechanism (2a) or (2b) therefore depends on the configuration of the tetrahedral chain. From fig. 6, the chain distortion and rotation favours (2b) in protopyroxene and probably also in protoamphibole.

Lowered symmetry in orthopyroxene. The same principles can be applied to the two-layer orthopyroxene structure with space group *Pbca* (fig. 8) and the possibilities are summarized in Table III. There is no entry corresponding to (2a) of Tables I and II since there are two types of tetrahedral chain to begin with. The more distorted chains which are related by the *b* glide planes and the 2_1 axes $\parallel c$ are usually referred to as the A chains; those related by the 2_1 axes $\parallel b$ and the centres are the B chains.

Under (2b) (Table III) one might expect to be able to form two types of A chain, or two types of B chain, or both. The rules governing combinations of symmetry operators in fact limit what is possible. For instance, if in *Pbca* one removes from the B chains the centres and 2_1 axes $\parallel b$, one obtains *Pbc2₁* with two types of B chain. But this also leaves two types of A layer each containing its own type of A chain.

When the configuration of the tetrahedral chains in orthopyroxenes is examined (fig. 9), it is found that the A chains are both distorted and rotated

and should lose their *b* glide planes and 2_1 axes $\parallel c$ to relieve strain in the same way as in protopyroxene. The B chains are rotated but not much distorted and 2_1 axes $\parallel b$ and centres should be retained to minimize strain, as is the case in clinopyroxene. When one removes the *b* glide planes and 2_1 axes $\parallel c$ of the A chain layers in *Pbca*, one finds that the 2_1 axes $\parallel b$ and centres of the B layers must vanish at the same time to give space group $P2_1ca$. The B chain symmetry operators could only be retained by lowering the symmetry to monoclinic (space group $P2_1/c$ with $\beta = 90^\circ$). However, $P2_1ca$ would be a possible space group for a 'low orthopyroxene' structure type, if the two types of B chain were accidentally alike. The $P2_1ca$ space group was first reported by Smyth (1974a) and has recently received further confirmation (Harlow *et al.*, 1979; Nord, 1980). Structure refinement of $P2_1ca$ orthopyroxene would provide a good test of the revised tetrahedral layer packing rule (see below) since the results should reveal whether the two types of B chain are alike as predicted above.

The underlying cause of the distortion of the A chains can be seen from fig. 13 of Veblen and Burnham (1978). The *O-O* tetrahedron edge shared with the *M2* polyhedron is appreciably shortened and the other *O* atoms adjust their positions away from this edge, making the sense of δ opposite from that expected from the tetrahedral rotation.

The $C2/c \rightarrow P2_1/c$ transformation and the low clinopyroxene structure. The high clinopyroxene structures produced by heating pigeonites (fig. 10) have essentially the same tetrahedral chain configuration as other $C2/c$ clinopyroxenes (fig. 3).

In the transformation to $P2_1/c$, the tetrahedra in the A and B chains become differently rotated (the A and B chains notation is carried over from the orthopyroxenes with the A chain again being

TABLE III. Simple strain relief mechanisms for *Pbca* orthopyroxenes

Mechanism	Resulting space group
(1) Formation of two distinct <i>T</i> sites in the tetrahedral chain	<i>Pb2₁a</i> , <i>P2₁2₁2₁</i>
(2) Formation of two distinct kinds of tetrahedral chain	
(b) (i) Two kinds of B chain in one kind of B layer; two kinds of A chain as two kinds of A layer	<i>Pbc2₁</i>
(ii) Two kinds of B chain in one kind of B layer; two kinds of A chain also in one kind of A layer	<i>P2₁ca</i>
(iii) Two kinds of B chain as two kinds of B layer; two kinds of A chain in one kind of A layer	<i>P2₁/c</i>

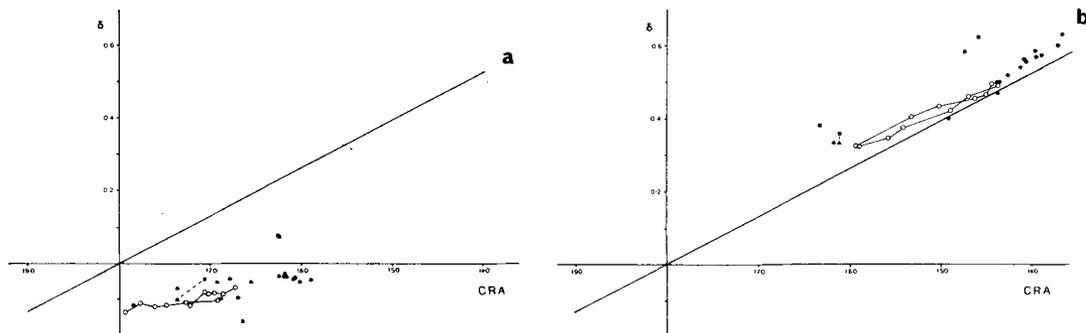


FIG. 9. δ vs CRA plot for (a) A-chains and (b) B-chains of orthopyriboles. Points for single chains (pyroxenes) are shown as circles, for double chains (amphiboles) as squares and for triple chains (jinthompsonite and chesterite) as triangles. The points for the double and triple chains in chesterite are joined by a dashed line. Orthopyroxene structures determined at several temperatures are shown as open circles joined by lines. (See caption for fig. 3.)

the more distorted). The tetrahedra in the A-chain are now rotated in the opposite sense relative to the octahedral strip, i.e. *S*-rotated (see fig. 4 of Chisholm, 1981).

The effect of this is to remove a bridging *O3* atom weakly bonded to *M2* even further from that atom, whose coordination becomes more nearly octahedral. Shortening of shared tetrahedron edges gives the A chain a δ value opposite from that expected from the (*S*-) rotation and makes the A chain analogous to those in ortho- and proto-pyroxene. The increased rotation of the tetrahedra in the B chain removes one bridging *O3* from the *M2* coordination sphere, replacing it with the next one along the chain and giving a tighter *M2* coordination, similar to that in orthopyroxene. This change is described in detail and illustrated by Brown *et al.* (1972).

The δ -values for the A-chain in $P2_1/c$ clinopyroxene do not quite follow the same trend as those for $C2/c$ (cf. figs. 3a and 10). If the distortion of the rotated tetrahedra in the A-chain were large enough, a further lowering of symmetry to *Pc* might be expected, giving two different types of chain in each tetrahedral layer.

In spodumene (fig. 3a), all the chains are similar to A-chains and the *M2* coordination will be even tighter than in $P2_1/c$, resembling that in proto-pyroxene and very suitable for a small cation. This explains why there is no $P2_1/c$ spodumene and no orthorhombic spodumene analogous to the orthorhombic amphibole holmquistite. A Li proto-pyroxene with only A-chains should be possible and does in fact occur (Smyth and Ito, 1977).

Derivation of the pyribole structure types. It is now necessary to summarize the results so far in a set of rules for deriving the pyribole structure types. Our starting point is the first rule proposed

by Chisholm (1981): (a) that the structures may not contain more than one kind of *I*-beam. This could alternatively be stated: that the structures may not contain more than two kinds of tetrahedral chain. These could not then simply be equated with the \cdot and \times chains of Thompson because of the low clino-structure type. But if this is regarded as the product of strain relief in the high clino-type, we can accept Thompson's approach completely and this forms our starting point.

1. In the pyriboles, there are two types of tetrahedral chain, \cdot chains and \times chains, according as they lie between octahedral strips similarly or oppositely directed. The direction of the octahedral strip is defined by whether, when viewed towards $-a^*$, the lower triangle faces of the octahedra have a corner pointing in the $+c$ or $-c$ direction (Papike and Ross, 1970). The strip direction so defined has no absolute significance since it depends on the choice of axes (Law and Whittaker, 1980) but it does enable us to specify the relative orientation of the octahedral strips and this is all we need to distinguish \cdot and \times chains.

The two types of chain, \cdot and \times , give three simple stacking sequences, $\cdot\cdot\cdot\cdot$, $\times\times\times\times$ and $\cdot\times\cdot\times\cdot\times$, which are those in the three main structure types, clino-, proto-, and ortho-, shown on the top line of Tables IV and V. (This part of the derivation should properly be attributed to Professor J. B. Thompson).

2. The three main structure types may be able to relieve strain (especially if there is a small cation of the *M2* site in pyroxene or the *M4* site in amphibole) by allowing different types of \cdot and \times chain to develop, lowering the symmetry. The way in which this occurs depends on the configuration of the tetrahedral chain.

If the tetrahedra in the chain are rotated but not

appreciably distorted, adjacent chains in the tetrahedral layers must be related by screw diad axes $\parallel b$ or centres of symmetry at $y = \frac{1}{4}, \frac{3}{4}$ for optimum packing. When two distinct kinds of tetrahedral chain occur, the adjacent chains must continue to be equivalent by one of these symmetry operators to maintain optimum packing. The two types of tetrahedral chain must therefore occur as two kinds of tetrahedral layer. This is so for . chains.

If the tetrahedra are distorted but not rotated, adjacent chains must be related by a screw diad axis $\parallel c$ or a b -glide plane $\perp a \sin \beta$ in pyroxene (n -glide $\perp a \sin \beta$ in amphibole). Distortion of the tetrahedra must predominate in the \times chains of proto- and ortho-pyroxene, if they are to have the space group symmetry they do. When two different kinds of tetrahedral chain form, adjacent chains should continue to be related by one of the specified symmetry operators, if the tetrahedra are distorted but not rotated. \times chains do not behave in this way nor is any example of distorted but unrotated chains known.

If the tetrahedra are both rotated and distorted to a significant degree, two kinds of tetrahedral chain must occur next to each other in the same layer if strain is to be minimized. This is so for \times chains.

This section constitutes the restated tetrahedral layer packing rule and its predictions form the second line of Tables IV and V. The first part of the rule (for . chains) corresponds exactly to the 'parity rule' proposed by Thompson (1970). The second part (for \times chains) differs from the parity rule and describes a violation of it, which was recognized as occurring in orthoamphibole by Papike and Ross (1970) and in orthopyroxene by Papike *et al.* (1973).

TABLE IV. Pyroxene structure types

1. Sequence of . and \times chains		
.....	$\times \times \times \times \times \times$	$\cdot \times \cdot \times \cdot \times$
$C2/c$	$Pbcn$	$Pbca$
CLINO-	PROTO-	ORTHO-
2. Relief of strain and lowering of symmetry by allowing different types of . and \times chain, in accordance with the revised tetrahedral layer packing rule		
$P2_1/c$	$P2_1/cn$	$P2_1/ca$
LOW CLINO-	'LOW PROTO-'	LOW ORTHO-
		$P2_1/c^*$
3. Relief of strain and lowering of symmetry by allowing different types of tetrahedral site along the tetrahedral chains, consistent with the revised tetrahedral layer packing rule		
$P2_1/n, P2/n$		
$C2, C\bar{1}^*$		

* No example known.

3. Subject to the requirements of the revised tetrahedral layer packing rule, strain can also be relieved by allowing two kinds of tetrahedral (T) site to alternate along the length of the chains in pyroxenes. Such is already the case in amphiboles. The possible pyroxene space groups make up the third line of Table IV.

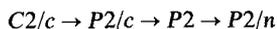
The space groups for clinopyroxene which fit the revised tetrahedral layer packing rule for . chains are taken from Table I(1). Subdivision of the T sites in proto- and ortho-pyroxene leads to the space groups in Table II(1) and III(1). In all these the tetrahedral layer packing rule for \times chains is violated and subdivision of the T sites should therefore not occur in proto- or ortho-pyroxene.

The derivation given above covers most of the pyroxene structure types which are known and all those which occur at all frequently. The only structures in Tables IV and V which are not known to occur are 'low protoamphibole' with space group $P2_1/mn$, 'low orthoamphibole' $P2_1/ma$, 'clinopyroxene' $C\bar{1}$, and the monoclinic structures ($P2_1/c$ and $P2_1/m$) derived from orthopyroxene and orthoamphibole.

Cation ordering. The pyroxene space groups which occur but are not included in Table IV are all specifically associated with the distribution of the $M1$ and $M2$ cations during ordering or exsolution reactions. [The $P2/c$ protoenstatite reported by Lindemann and Wögerbauer (1974) has a unit cell with the same dimensions and symmetry as one derived from the usual $Pbcn$ cell.]

Nord (1980) has described Guinier-Preston zones with $Pbc2_1$ symmetry in orthopyroxenes. The orthopyroxene cell is equivalent to two monoclinic cells related by reflection in (100). $Pbc2_1$ symmetry indicates ordering of Ca in one of the monoclinic cells. Such ordering must be brought about by counter-migration of $M2$ cations (Ca and Mg) between adjacent (100) planes of cations. Heat treatment at 1000–1100 °C leads to nucleation of (100) lamellae of a Ca-rich phase in areas with a high concentration of GP zones; the GP zones are dissolved into the orthopyroxene host where their concentration (and the Ca concentration) is low. This behaviour makes it clear that the $Pbc2_1$ GP zones are associated with segregation of Ca in the early stages of exsolution.

Carpenter (1978) and Carpenter and Okay (1978) describe omphacites with space groups $P2/c$ and $P2/n$; textural evidence points to the formation of $P2/n$ omphacite from a high-temperature $C2/c$ (disordered) phase through the sequence of phases



There can be little doubt that the phases with space groups $P2/c$ and $P2$ (not predicted in Table IV)

are metastable intermediate stages in the cation ordering reaction.

Amphiboles. The same principles apply in the amphiboles as in the pyroxenes and the space group possibilities for amphiboles are summarized in Table V. The silicate double chain of amphibole has two *T* and six *O* atomic positions and should be better able to adjust to varying *M* cation sizes than the pyroxene chain with only one *T* and three *O* positions. The strain relief mechanisms should therefore be needed less in the amphiboles and indeed the only example of lowered symmetry is $P2_1/m$ clinoamphibole. For the same reason, the A and B chains in $P2_1/m$ clinoamphibole do not differ so much in their rotation as they do in $P2_1/c$ clinopyroxene (fig. 10).

TABLE V. Amphibole structure types

1. Sequence of . and × chains		
.....	× × × × × ×	. × . × . ×
$C2/m$	Pmn	$Pnma$
CLINO-	PROTO-	ORTHO-
2. Relief of strain and lowering of symmetry by allowing different types of . and × chain, in accordance with the revised tetrahedral layer packing rule		
$P2_1/m$	$P2_1mn^*$	$P2_1ma^*$
LOW CLINO-	'LOW PROTO-'	'LOW ORTHO-'
		$P2_1/m^*$

* No example known.

Triple chain biopyriboles. The distortion and rotation of the tetrahedra in clinojimthompsonite, jimthompsonite and chesterite follow the same trends as the pyroxenes and amphiboles (figs. 3, 9), as would be expected. Clinojimthompsonite and jimthompsonite consist of triple chains only and have the same space groups as the corresponding pyroxenes. Chesterite (orthorhombic) has triple and double A-chains in one layer and triple and double B-chains in the other. Chain multiplicity seems to matter little, but the rotation and distortion of the tetrahedra must be similar for the tetrahedral chains in each layer.

Veblen and Burnham (1978) describe an unnamed mineral which may be a high clino- or low clino-form of chesterite, for which space groups $A2/m$ and Am are predicted. If the former, the tetrahedra in the double and triple chains should fit the trend shown on the plot of δ against chain rotation angle for high clinopyriboles (fig. 3). If the latter, the points for the double chains should lie close to those for $P2_1/m$ clinoamphibole (fig. 10), while the points for the triple chains should be slightly closer together.

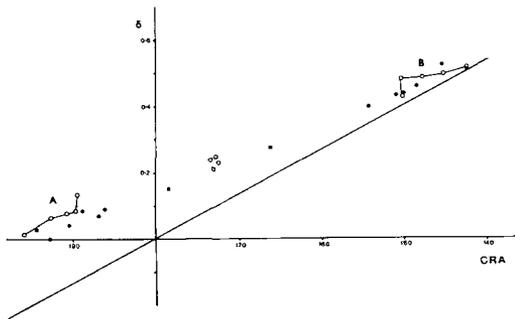


FIG. 10. δ vs CRA plot for $P2_1/c$ clinopyroxenes and the $C2/c$ structures produced from them at high temperature and for $P2_1/m$ cummingtonite and the $C2/m$ structure produced from it. Points for low clinopyroxenes are shown by circles and for low clinoamphibole by squares. Open circles joined by lines refer to the ferro-hypersthene structure at several temperatures. Points for the high-temperature $C2/c$ and $C2/m$ structures are shown as isolated open circles and squares. (See caption for fig. 3.)

Conclusion. The scheme for deriving pyribole structures embodied in the three rules given earlier leads to the space group symmetries summarized in Tables IV and V. Of the predicted structure types, only five are not known to occur: 'low protoamphibole' with space group $P2_1mn$, 'low orthoamphibole' with space group $P2_1ma$, 'clinopyroxene' with space group $C\bar{1}$, and the $P2_1/c$ and $P2_1/m$ structures derived from orthopyroxene and orthoamphibole. Where pyroxene structure types not shown in Table IV are known to occur, they are invariably metastable intermediate phases in cation ordering or exsolution reactions. Otherwise the derivation given in this paper accounts for all the known pyribole structure types.

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Note added in proof. Evidence for lowered symmetry in the pyroxenes rests on the observation of weak reflections which violate the reflection conditions of the normal space group. Sasaki, Matsumoto, and Sawada (1981; *Phys. Chem. Minerals* **7**, 260-7) have shown conclusively that multiple diffraction is entirely responsible for the additional weak reflections suggesting space group $P2_1ca$ for two orthopyroxenes and $C2$ for two spodumenes. The symmetry is thus not lowered from $Pbca$ and $C2/c$ in those cases. Multiple diffraction is shown to be a common phenomenon and almost all earlier reports of lowered symmetry must therefore be called into question.

The structural considerations leading to the revised tetrahedral layer packing rule are not affected by this recent work but the occurrence of some of the predicted low pyroxene structures is in doubt. Space groups $P2_1/c$ for low clinopyroxene and $P2/n$ for omphacite have been confirmed as correct by Sasaki *et al.* But the existence of $P2_1ca$ orthopyroxene, $P2_1cn$ protopyroxene, $P2_1/n$ enstatite, and $C2$ spodumene remains an open question to be resolved by further tests for multiple diffraction in the way that Sasaki *et al.* have shown to be necessary.