Rotated and extended model structures in amphiboles and pyroxenes

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SUMMARY. The model for the amphibole and pyroxene structures based on close-packed oxygen layers introduced by Thompson is investigated systematically. It is shown that different features of it can best be understood in terms of three different symbolisms: the O and S rotations of tetrahedra; the A, B, C stacking notation for close-packed layers; and the c, h notation for the relationship of close-packed layers to their neighbours. The possible stacking arrangements and their space-groups are derived systematically. Relationships between the close-packed, fully rotated, model and the extended chain model are discussed, and some important drawbacks in the former model are pointed out, especially in connection with real amphibole structures.

THE original structure determinations of pyroxenes and amphiboles (Warren and Bragg, 1928; Warren, 1929; Warren and Modell, 1930) were all described in terms of fully extended silicate chains. In the case of the amphiboles, the double chain consists of a sequence of hexagonal rings of SiO_4 tetrahedra, and in the case of pyroxenes the single chain is half of this. In the structure of crocidolite, Whittaker (1949) demonstrated that the tetrahedra have a measure of rotation away from the fully extended configuration, and this has been found, in varying degrees, in all the many detailed pyroxene and amphibole structures determined since that date.

Thompson (1970) observed that topographically equivalent model 'pyribole' structures can be generated by continuing to rotate the tetrahedra further from their positions in the extended chains. Rotation through 30° brings the oxygens into a geometric array which is truly close-packed, reducing the octahedral to tetrahedral edge ratio from $2:\sqrt{3}$ (fully extended) to $1:1$ (fully rotated). In

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these fully rotated structures, all polyhedra (including, for amphiboles, both $M4$ and A sites) are regular octahedra or tetrahedra.

Thompson's proposals were developed in more detail for amphiboles by Papike and Ross (1970), and for pyroxenes by Papike et al. (1973). Two types of tetrahedral rotation are distinguished: S-rotation, where 'a tetrahedron rotates so that the triangular face normal to the rotation axis turns towards the same orientation as that of the nearest parallel faces of the three octahedra to which the tetrahedron is linked', and O-rotation, where the faces point in the opposite direction. These rotations are illustrated in fig. 1.

The basic building unit of the amphibole or pyroxene structure is the I-beam (the term is due to Papike and Ross, 1970) in which a pair of tetrahedral chains combine to form octahedral sites between the apical oxygens. In the close-packed model, this I-beam is a strip from a set of four close-packed oxygen layers: the adjacent strips in the four layers are formed from the 'lower' and 'upper' halves of further I-beams meeting back-to-back. Such an I-beam has an 'orientation' or directionality that is introduced along its length by the orientation of the octahedra. This directionality was defined by Papike and Ross (1970) as positive if the lower triangle faces of the octahedra point along the positive direction of the c-axis, and negative in the converse case. Application of this definition, however, depends on an independent criterion to specify the positive direction of the c-axis, and this is a problem that will be discussed below.

Thompson noted a restriction on the ways in which O- and S-rotated I-beams can stack together. I-beams are stacked together in a staggered fashion, so that a particular pair of oxygen

layers joined by tetrahedral cations consists of alternate strips that form the 'top' and 'bottom' of *I*-beams. If two adjacent tetrahedral strips are identically related (rotationally as *S* or *O*) to the octahedral strips to which they are joined, then those octahedral strips (one above and one below the tetrahedral layer) must be identically directed; if the rotations are different then the octahedra must be oppositely directed. Thompson referred to this restriction as a 'parity rule'.
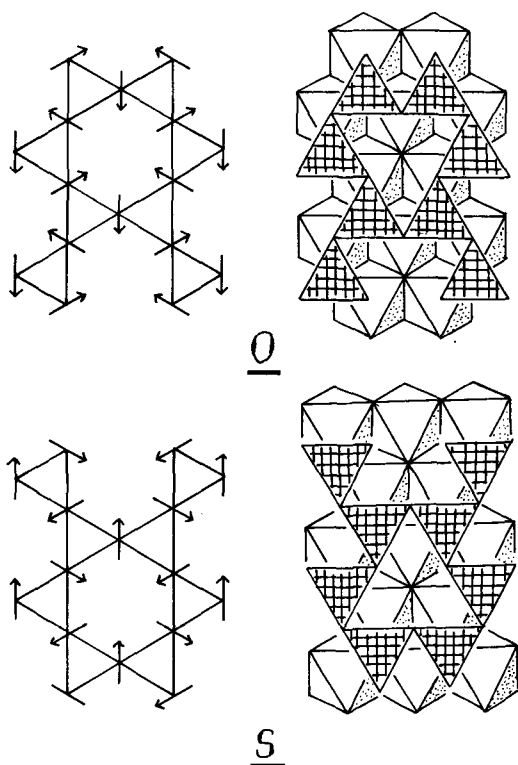

FIG. I. *O*-rotation chain (top diagram) and *S*-rotated chain (lower diagram) related to the extended chain (outline diagrams, left-hand side). Arrows on extended chains indicate direction of tetrahedral movement.

It was observed by Papike *et al.* (1973) that, if repeated throughout the structure, 'a complete *S*-rotation results in hexagonal close-packing of oxygen atoms (*ABABAB*) and a complete *O*-rotation in cubic close packing of oxygen atoms (*ABCABC*)'. This paper presents an analysis of the matter in this form. We believe that discussion in terms of close-packed structures has considerable

advantages over the description in terms of *O*- and *S*-rotations, and + and − octahedral directionality, to which nevertheless it has a one-to-one relationship. The advantages are: it combines these two features in a single self-consistent description; it incorporates the 'parity rule' as a necessary corollary which requires no separate explanation; and it makes possible a complete discussion of the subject without the need for complex structural diagrams.

The work of Papike *et al.* (1973) has shown the value of the analysis of pyroxene structures by reference to fully rotated forms. It is unfortunate, however, that they describe these as 'ideal' structural models. Although it is true that in the rotated models the polyhedra become regular, in fact the ideal model is really the extended structure. This is true historically; it is true nomenclaturally, in that Papike *et al.* themselves continue to speak of *O*- and *S*-rotations (that is, rotations away from the extended structure); and it is true phenomenologically, in that all the amphibole chains and 70% of the pyroxene chains that have been described are closer to the extended form than to the fully rotated one. Moreover, all known pyroxene and amphibole structures are compatible with the fully extended model, which predicts a relatively small number of basic pyribole structures; not all are compatible with the fully rotated model (i.e. some amphibole and pyroxene structures exhibit 'parity violations'), and this model predicts a much larger number of complex structures of which only a small proportion have known counterparts.

To avoid confusion between the two concepts of 'ideality', we shall eschew the term entirely and refer explicitly to fully extended and fully rotated models.

The close packed model. In developing the structural model, the first step is to write down the possible stacking sequences for the set of four successive oxygen layers of which a particular *I*-beam is part. Using the standard notation of structural inorganic chemistry (Wells, 1962) the three arrays on which oxygen atoms may be located are denoted *A*, *B*, and *C*. Which is which is arbitrarily defined; we shall consistently assume that in going through the cyclic sequence $A \rightarrow B \rightarrow C \rightarrow A$ there is a shift of one-third of the projected inter-oxygen distance (one-sixth of the *c*-dimension of the amphibole) along the *negative* direction of the amphibole *c*-axis. This is chosen for reasons which will become clear later, in order that the axial orientations shall conform as far as possible to the conventional ones for real amphiboles.

Let a first oxygen layer be *A*. A second must be either *B* or *C*. Following *B* in the second layer, the third layer must be *A* again or *C*; if the second layer

is C, the third must be A again or B. Extending this into the fourth layer we obtain:

1st layer ⠀⠀⠀⠀⠀⠀⠀⠀A

2nd layer ⠀⠀⠀⠀⠀B⠀⠀⠀⠀⠀⠀⠀⠀C

3rd layer ⠀⠀A⠀⠀⠀⠀C⠀⠀⠀A⠀⠀⠀⠀B

4th layer ⠀B⠀⠀C⠀⠀A⠀⠀B⠀⠀B⠀⠀C⠀⠀A⠀⠀C
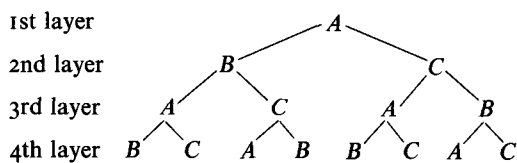
In this 'pyramid' any of the eight routes from the apex to the base yields a valid stacking sequence for close-packed layers. Two further pyramids can be built, starting from B and from C. These need not be considered separately; the changes $A \to B$, $B \to C$, and $C \to A$, which we shall call a 'cyclic permutation', may be interpreted either as a systematic change of the (arbitrary) notation or as a shift of the whole structure along the c-axis, and the structures are crystallographically equivalent.

It can further be seen that there are in fact only three fundamental types of sequence, from which the remaining five can be generated by either cyclic permutation (i.e. replacing A by B, B by C, and C by A throughout), or by reversal of the entire sequence, or by a combination of two or more such operations. For example, sequence $ABCA$ reversed becomes $ACBA$; sequence $ABAB$ can be changed by reversal (to $BABA$), followed by two cyclic permutations, into $ACAC$. Such operations generate crystallographically equivalent sequences differing only in orientation with respect to the chosen axes. The three basic sequences have: (i) the first and last symbols identical and the inner two different, as in $ABCA$; (ii) the first and third symbols identical and the second and fourth identical, as in $ABAB$; (iii) the first and third symbols identical but the second and fourth different, as in $ABAC$, or the reverse of this, as in $ABCB$. This point is considered further below.

In an I-beam, considered as a narrow strip from such a set of four oxygen layers, tetrahedral sites are formed between layers 1 and 2 and between layers 3 and 4, and are occupied by Si, Al, etc. These tetrahedral sites are formed on the same array as the inner oxygen atoms (layers 2 and 3 respectively). Octahedral cations (Mg, Fe^{2+}, etc.) occupy sites between layers 2 and 3 which lie on the array differing from both these layers. Thus if cation arrays (octahedral or tetrahedral) are denoted by lower-case letters we may extend the notation to show the full structure of I-beams formed in a given set of four oxygen layers. For example, in the four layers $ABCB$ the full I-beam is $AbBaCcB$.

The structure of an I-beam is fully defined when the stacking pattern of the four oxygen layers is known. Because a tetrahedral array is always identical with the corresponding inner oxygen array, there is no loss in omitting its symbol. For many purposes the octahedral array symbol may also be omitted; but we retain it for the present and thus represent an I-beam in the form $ABaCB$. This notation is related to that of Papike and Ross (1970) as follows.

Tetrahedron rotation is defined by the three oxygen layers which bound the octahedral layer and the tetrahedral layer under consideration. When all three symbols appear, as in ABC, CAB, etc. the rotation is O (the sequence is that of cubic close packing); if only two symbols appear, as in ABA, CBC, etc., the rotation is S (hexagonal). Tetrahedron rotation is invariant under all symmetry operations (cf. Thompson, 1970).

Octahedral directionality is determined by the relationship between the two oxygen layers which bound the octahedral strip (layers 2 and 3). From the definitions already given, octahedra are positively directed if the symbols of these two layers reading upwards from the lower one to the upper one, are in cyclic order (AB, BC, CA) and negatively if the order is reversed (BA, CB, AC). Any symmetry operation which inverts the order of the array symbols reverses directionality; note that many symmetry operations will move ions on to a different array (see Appendix 2 for a full discussion).

Thus, in terms of the notation of Papike et al., the I-beam $ABaCB$ is seen to have one O-rotated tetrahedral strip ($ABaC$) and one S-rotated ($BaCB$), and the octahedra are positively directed (BaC); we may denote this by the composite symbol $[O + S]$.

It is to be noted that the definition of octahedron directionality is in the end arbitrary. It depends on the choice of the direction of the c-axis and on the decision as to which of the arrays are denoted A, B, and C; though if a consistent convention is followed, as we have outlined, the results will always be consistent. Consistency in this respect may lead to structures whose space groups or monoclinic cell angles are not those conventionally chosen. Tetrahedron rotation however is not arbitrary, and the results are independent of the choice of the direction of the axis and of notation.

The complete list of possible I-beams, with the alternative forms generated by starting from B and from C arrays, is:

$ABcAB$	$BCaBC$	$CAbCA$	$[S-S]$
$ABcAC$	$BCaBA$	$CAbCB$	$[S-O]$
$ABaCA$	$BCbAB$	$CAcBC$	$[O+O]$
$ABaCB$	$BCbAC$	$CAcBA$	$[O+S]$
$ACbAB$	$BAcBC$	$CBaCA$	$[S+O]$
$ACbAC$	$BAcBA$	$CBaCB$	$[S+S]$
$ACaBA$	$BAbCB$	$CBcAC$	$[O-O]$
$ACaBC$	$BAbCA$	$CBcAB$	$[O-S]$

It can be seen that, ignoring orientation both along c and perpendicular to the layers, there are only three basic I-beam types: $[O \pm O]$, $[O \pm S]$ (or $[S \pm O]$), and $[S \pm S]$. These correspond to the three stacking sequence types. The remaining variation arises from the orientation relative to the chosen axes. For many purposes it is sufficient to consider only this basic set of three I-beams.

At this stage we may already consider one feature which was noted by Thompson (1970) but has not been commented on in detail by Papike and Ross (1970) or by Papike et al. (1973). This is the predominance in nature of O-rotations. All known amphibole chains are O-rotated; in pyroxenes, S-rotation has been found only in spodumene, in low $P2_1/c$ clinopyroxene (considered by Papike et al. (1973) to be metastable), and in $LiVO_3$; and in all these examples rather small cations occupy the $M2$ site (pyroxene structures tabulated in Papike et al. (1973)). Thompson (1970) suggests that the predominance may arise because, in the fully rotated models, the S-configuration involves edge-sharing between octahedra and tetrahedra (at $M4$ and A in amphiboles, and at $M2$ in pyroxenes), whereas O-rotation does not. Violations of the 'parity rule' might arise to avoid edge sharing. We believe that this explanation over-interprets the relationship between the models and the actual structures, and suggest a simpler explanation.

In the fully extended amphibole structure the nearest neighbour of $M3$ outside its own octahedral ligands is $O7$ (the bridging oxygen on the middle line of the double chain). Of all the basal oxygen atoms, $O7$ is also the least well shielded from $M3$ by apical oxygens. In an O-rotated chain, the octahedra of the I-beam necessarily occupy the same array as the basal oxygens of the tetrahedra. Thus O-rotation brings $O7$ closer to $M3$, as it moves into the equivalent position vertically below or above it, with a consequent increase in crystal chemical stabilization. S-rotation, on the other hand, moves $O7$ away from $M3$. Similar considerations apply to all the octahedral cations and appropriate basal oxygen atoms in both amphibole and pyroxene. We suggest that this is a primary factor in the observed preponderance of O-rotation in nature, though other factors such as those cited by Thompson and by Papike et al. may also contribute.[1]

The stacking of I-*beams.* There are two aspects of the stacking of I-beams to be considered: their stacking one on another, parallel to a or to $a \sin \beta$, with back-to-back contact between the chains; and their stacking side by side, in the b–c plane, to complete the coordination of the edge cations and (in

the fully rotated models) individual close-packed layers.

In the fully rotated structures the geometry of the stacking is controlled by the back-to-back contacts. The first oxygen layer of the second I-beam must be a different array from the last layer of the first. Subject to this condition it is possible, using any single type of I-beam, to construct a simple monoclinic stack with one I-beam in the height of the cell (the a-direction, here represented running across the page) having $\beta \neq 90°$, e.g.

$ABcAB \cdot CAbCA \cdot BCaBC$ (I-beam type $[S-S]$)

where the . represents the back-to-back contact between I-beams. Stacks of this kind having monoclinic symmetry but with $\beta = 90°$ may also be constructed, provided one or both of the chains in the I-beam be S-rotated, e.g.

$ABcAB \cdot ABcAB \cdot ABcAB$ (I-beam type $[S-S]$)
$ABcAC \cdot ABcAC \cdot ABcAC$ (I-beam type $[S-O]$)
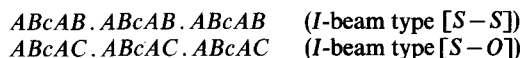
but this cannot be done with $[O \pm O]$ type I-beams because they start and finish with the same array.

The behaviour of fully extended structures is quite different from that of fully rotated ones. In the extended structures, stacking is controlled by edge-to-edge contacts, not back-to-back ones. It is this distinction which most fundamentally limits the usefulness of the fully rotated models in relation to real structures. In fully rotated structures, edge-to-edge contacts are automatically satisfied since the oxygen atoms in adjacent I-beams must lie on continuations of the same close-packed arrays, and possible values of $|a \cos \beta|$ are $2c/3$, $c/3$ or zero. A single stack of extended similarly directed I-beams with optimum back-to-back packing would give $|a \cos \beta| = 5c/12$ (equivalent also to $7c/12$) or $c/12$. In real amphiboles, values of $|a \cos \beta|$ are controlled by edge-to-edge contacts and range from near $c/2$ in tremolite to near $2c/3$ in cummingtonite and zero in protoamphibole.

The continuity of the close-packed arrays in the bc plane in the fully rotated structures is of great importance. Once a single stack of I-beams has been set up in the a-direction, the nature of the I-beams in adjacent stacks sideways (and hence, throughout the entire structure) is defined.

It can easily be shown that there is only one way in which fully rotated tetrahedral strips (i.e. half I-beams) can be placed side-by-side so that the constituent oxygens lie on a pair of coherent close-packed arrays. This is illustrated in fig. 2: the 'arrowheads' of adjacent chains must point in opposite directions, as shown. Any other juxtaposition would lead to a discontinuity in an oxygen layer.

[1] The bond strength considerations adduced by Hawthorne (1979) are also likely to be of major importance.

In terms of the oxygen-stacking pattern, if the symbols for the first I-beam stack are written on one line then the same symbols written on the next line, but differently divided up, correspond to the adjacent stack. Because the positions of the octa-

First stack: $.ACbAC.BAcBA.CBaCB.ACbAC. = . S + S . S + S . S + S . S + S .$
Second stack: $cAC.ACaBA.BAbCB.CBcAC.ACa = . O . O - O . O - O . O - O . O -$

where the first stack consists of positively directed $[S \pm S]$ I-beams and the second of negatively directed $[O \pm O]$ ones. This structure is monoclinic and by the methods described in Appendix 2 may be shown to have the space group $P2/m$ for an amphibole, $P2/c$ for a pyroxene, both with $\beta = 109.47°$.

Clearly there are an infinite number of structures which could be set up if no limitations existed on the succession of stackings. However, because of the regularity of crystal structures some restrictions

hedral strips (denoted by the lower case letter) and of the back-to-back contacts (denoted by the dot) alternate, the I-beams in the two stacks may be of different kinds, e.g. (giving first the stacking sequence and then the I-beam types):

on the model are reasonable at this point. At the least, the stacking sequence must repeat in a small number of layers. In nature, it appears that a further restriction holds—that all I-beams in a structure are identical except for their orientation—but we do not wish to impose this restriction on the model.

It can be verified, tediously, that there are only four ways of setting up a stack of similar, similarly directed I-beams such that the adjacent stack contains the same basic kind of I-beams. These are:

1. $.ABaCA.BCbAB.CAcBC.ABaCA.$ ... $= . O + O . O + O . O + O . O + O .$
   $bAB.CAcBC.ABaCA.BCbAB.CAc$ ... $= + O . O + O . O + O . O + O . O +$
2. $.ABcAB.ABcAB.ABcAB.ABcAB.$ ... $= . S - S . S - S . S - S . S - S .$
   $cAB.ABcAB.ABcAB.ABcAB.ABc$ ... $= - S . S - S . S - S . S - S . S -$
3. $.ABaCB.ABaCB.ABaCB.ABaCB.$ ... $= . O + S . O + S . O + S . O + S .$
   $cAB.CBcAB.CBcAB.CBcAB.CBc$ ... $= - S . O - S . O - S . O - S . O -$
4. $.ABcAC.BCaBA.CAbCB.ABcAC.$ ... $= . S - O . S - O . S - O . S - O .$
   $cAB.ACaBC.BAbCA.CBcAB.ACa$ ... $= - S . O - S . O - S . O - S . O -$

Structure 1 is monoclinic and the amphibole with this stacking has space group $C2/m$, $\beta = 109.47°$; in fact our choice of conventions of directionality of the c-axis and nomenclature of the layers was designed to ensure that this structure, related to real monoclinic amphiboles, should exhibit this space group and orientation. However, if these conventions are maintained, as they must be for a self-consistent treatment of the subject, then the corresponding pyroxene is $I2/c$ with the same obtuse β; if it were described as $C2/c$ with the same axial directions it

would have an acute $\beta = 74.98°$ or the very large obtuse $\beta = 125.26°$. Structure 2 gives monoclinic amphibole $C2/m$ (pyroxene $I2/c$) with $\beta = 90°$; the opposite centring would involve $\beta = 117.94°$. Structure 3 is orthorhombic $P2_1mn$, pyroxene $P2_1cn$. Structure 4 is monoclinic, amphibole $P2_1/m$, pyroxene $P2_1/c$, $\beta = 109.47°$.

There is one other stacking of similar, similarly directed, I-beams in any one stack, but the adjacent stack then consists of I-beams of a different type.

5. $.ABaCA.CAcBC.BCbAB.ABaCA.$ ... $= O + O . O + O . O + O . O + O$
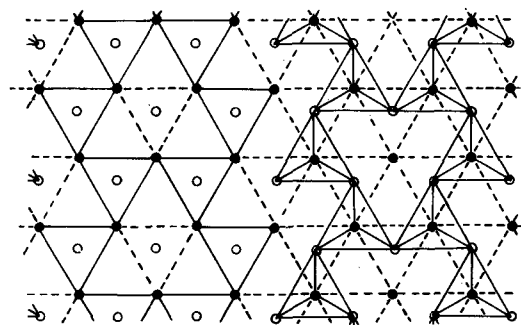 $cAB.CAbCA.BCaBC.ABcAB.CBb$ ... $= S . S - S . S - S . S - S . S$

It gives an amphibole $P2/m$, pyroxene $P2/c$, $\beta = 100.02°$. These five structures have two I-beams per unit cell, since the sequence repeats every I-beam in every stack. From the symbolism these can be seen to exhaust the possibilities for this type of structure. In each stack the first symbol of the second I-beam must differ from the last symbol of the first so that for each of the three types of I-beam (that is $[O \pm O]$, $[O \pm S]$, and $[S \pm S]$) there are two possibilities. Structure 5 combines two of these possibilities so that there are five, not six, in total (the possibilities in adjacent stacks are not independent). The five structures as we have given them are identical to the first five structures listed by Thompson (1970) although not in the same order.

FIG. 2. Side-by-side stacking of fully rotated tetrahedral chains showing how continuous octahedral layers are formed.

All five have equal numbers of O- and S-rotated tetrahedra or exhibit one type of rotation only. All except structure 5 are built from identical I-beams throughout.

The stacking notations. Enumeration of stackings in terms of A, B, C notation, and O, S notation is complicated by the fact that equivalent stackings may be obtained with the symbols in inverse order or starting at a different point in the sequence, and their descriptions in one or both of these symbolisms may look different. So far, we have considered only structures in which each stack contains only one type of I-beam, uniformly oriented (orientation, in this sense, means that for example $[O+S]$ is considered different from $[O-S]$ and from $[S+O]$). To consider structures in which I-beams within a stack differ in type or orientation makes the task of enumeration much greater. We therefore describe a much simpler way of deriving these structures.

In the over-all structure, each layer of oxygen atoms is in a local arrangement that is of hexagonal or cubic type according as its neighbours in adjacent layers lie on the same array as each other or on different ones. Following Wells (1962), we denote these types of layers by h or c, though we do not imply as much by this notation as does Wells, who requires that a sphere in any c-type layer shall have identical environments, at all distances, to those of all other c spheres, and similarly for h spheres. We shall use the c, h notation to refer only to the configuration of the immediately adjacent oxygen layers in a structure.

It is also necessary to distinguish which layers are linked by tetrahedral and which by strips of octahedral cations, and we shall indicate the general position of the latter by . (corresponding to both the position of the . and the lower case letter which we have used in the A, B, C notation).

To convert A, B, C notation into c, h notation is straightforward. Structures 1 to 5 become $.cc.cc.$, $.hh.hh.$, $.hc.hc.$, $.hh.cc.$, and $.hc.ch.$ respectively in their first stacks (as written above); in the second stacks structures 1, 2, and 3 are the same, but structures 4 and 5 give $.cc.hh.$ and $.ch.hc.$ respectively.

This notation has both advantages and disadvantages compared with the A, B, C notation. It represents more clearly the underlying pyribole structure. For example, to move from one I-beam stack to the next we simply remove a pair of symbols from one end of the sequence, and add them on at the other (compare the examples in the previous paragraph). Cyclic permutation of the A, B, C notation does not alter the corresponding c, h notation, nor does it alter the type and orientation of the I-beams; reversal of the A, B, C sequence reverses the c, h sequence and the I-beam sequence. The c, h notation does not provide a representation of octahedron directionality, and it is this which makes it easier to manipulate. It is however less easy to appreciate the detailed structure in c, h notation. For example, it is not obvious that sequences $.cc.ch.$ and $.ch.hh.$ do not represent possible structures of the same type as structures 1 to 5. It is only when a translation is made into A, B, C notation that it is seen that they repeat after eight layers rather than four. Because of the symmetry effect at an h layer, it is impossible for the repeating unit to contain an odd number of h's.

However, with only two symbols it is much easier to exhaust the possibilities for structurally distinct sequences (i.e. those which give different I-beams). It is shown in Appendix 1 that in addition to the five sequences that repeat in four layers, there are a further twenty-two that repeat in eight layers (two I-beams). Once these have been derived they can be translated into equivalent (though not unique) A, B, C and O, S notations. Table I gives the results of this analysis: for consistency, the first two symbols of all A, B, C sequences are AB; alternative A, B, C notations merely start at a different layer or reverse the whole sequence or both.   •

In Table I the two orthorhombic structures can be identified with those listed by Thompson (1970), as can the two with space group $P2_1/m$ and equal numbers of O- and S-rotated chains, and the one with space group $P2_1/m$ and a ratio of $O:S = 3:1$. The two remaining structures listed by Thompson cannot be uniquely identified with particular members of this complete list.

More complex sequences, repeating after $4n$ layers ($n > 2$), could be derived in the same way.

The 'parity' rule. Papike and Ross (1970) state that 'Thompson's parity rule is violated in protoamphibole and in the A layers of orthoamphibole' (in orthoamphibole the two tetrahedral chains in the I-beam, not being symmetrically equivalent, are distinguished as A and B; this symbolism has no relationship to the A, B, C stacking notation). They give the I-beam sequences as $+, -, +, -$ in protoamphibole and $+, +, -, -$ in orthoamphibole, the structures having all O-rotations. In this notation alternate symbols relate to I-beams in adjacent stacks, which are different in protoamphibole and the same in orthoamphibole. Thus in protoamphibole the sequences are (in our notation)

first stack: $.\ O+O\ .\ O+O\ .$
second stack: $-\ O\ .\ O-O\ .\ O-$

with the sequence repeating in four oxygen layers, and in orthoamphibole they are

first stack: $.\ O+O\ .\ O-O\ .$
second stack: $+\ O\ .\ O-O\ .\ O+$

with an eight-layer repeat.

TABLE I. *Stacking sequences for amphiboles*

Stacking sequence	A, B, C notation (first stack)	I-beam types		β	Space group
		1st stack	2nd stack		
Sequences repeating in four layers					
$hh.hh.hh.hh.$	$AB.AB.$ (rep)	$*S-S.S-S.$	$S-S.S-S.$	$90°$	$C2/m$
$hh.cc.hh.cc.$	$AB.AC.(B\tilde{})$	$*S-O.S-O.$	$O-S.O-S.$	$109.47°$	$P2_1/m$
$hc.hc.hc.hc.$	$AB.CB.$ (rep)	$*O+S.O+S.$	$O-S.O-S.$	ortho	$P2_1mn$
$hc.ch.hc.ch.$	$AB.CA.(C\tilde{})$	$O+O.O+O.$	$S-S.S-S.$	$100.02°$	$P2/m$
$cc.cc.cc.cc.$	$AB.CA.(B\tilde{})$	$*O+O.O+O.$	$O+O.O+O.$	$109.47°$	$C2/m$
Sequences repeating in eight layers					
$hh.hh.hh.cc.$	$AB.AB.AB.AC.(B\tilde{})$	$S-S.S-O.$	$S-S.O-S.$	$100.02°$	$P2_1/m$
$hh.hh.hc.hc.$	$AB.AB.AB.CB.$ (rep)	$S-S.O+S.$	$S-S.O-S.$	$90°$	Pm
$hh.hh.ch.hc.$	$AB.AB.AC.AC.(B\tilde{})$	$S-S.S+S.$	$S-O.O-S.$	$100.02°$	$P2/m$
$hh.hh.hc.ch.$	$AB.AB.AB.CA.(C\tilde{})$	$S-S.O+O.$	$S-S.S-S.$	$95.05°$	$P2/m$
$hh.hh.cc.cc.$	$AB.AB.AC.BA.(C\tilde{})$	$S-S.O-O.$	$S-O.O-S.$	$95.05°$	$P2/m$
$hh.hc.hh.hc.$	$AB.AB.CB.CB.$ (rep)	$S-S.S+S.$	$O+S.O-S.$	ortho	$P2_1ma$
$hh.hc.hh.ch.$	$AB.AB.CB.CA.(C\tilde{})$	$S-S.S+O.$	$O+S.S-S.$	$95.05°$	$P2_1/m$
$hh.hc.hc.cc.$	$AB.AB.CB.AC.(B\tilde{})$	$S-S.O-O.$	$O+S.O-S.$	$100.02°$	Pm
$hh.hc.ch.cc.$	$AB.AB.CA.CB.$ (rep)	$S-S.S-O.$	$O+O.O-S.$	$90°$	Pm
$hh.hc.cc.hc.$	$AB.AB.CA.BA.(C\tilde{})$	$S-S.O+S.$	$O+O.O-S.$	$95.05°$	Pm
$hh.hc.cc.ch.$	$AB.AB.CA.BC.(B\tilde{})$	$S-S.O+O.$	$O+O.S-S.$	$100.02°$	$P2_1/m$
$hh.ch.hc.cc.$	$AB.AC.AC.BA.(C\tilde{})$	$S-O.O-O.$	$S+S.O-S.$	$95.05°$	Pm
$hh.ch.ch.cc.$	$AB.AC.AB.AC.(B\tilde{})$	$*S-O.S-O.$	$S+O.O-S.$	$100.02°$	Pm
$hh.ch.cc.hc.$	$AB.AC.AB.CB.$ (rep)	$*S-O.O+S.$	$S+O.O-S.$	$90°$	$P2_1/m$
$hh.cc.cc.cc.$	$AB.AC.BA.CB.$ (rep)	$S-O.O-O.$	$O-O.O-S.$	$90°$	$P2_1/m$
$hc.hc.hc.ch.$	$AB.CB.AB.CA.(C\tilde{})$	$O+S.O+O.$	$O-S.S-S.$	$95.05°$	Pm
$hc.hc.ch.ch.$	$AB.CB.AC.AB.$ (rep)	$O+S.S+O.$	$O-S.S-S.$	$90°$	$P2/m$
$hc.hc.cc.cc.$	$AB.CB.AC.BA.(C\tilde{})$	$O+S.O-O.$	$O-O.O-S.$	$95.05°$	Pm
$hc.ch.cc.cc.$	$AB.CA.CB.AC.(B\tilde{})$	$O+O.O-O.$	$S-O.O-S.$	$100.02°$	$P2/m$
$hc.cc.hc.cc.$	$AB.CA.BA.CB.$ (rep)	$O+O.O-O.$	$O+S.O-S.$	ortho	$P2_1ma$
$hc.cc.ch.cc.$	$AB.CA.BC.BA.(C\tilde{})$	$O+O.S-O.$	$O+O.O-S.$	$95.05°$	Pm
$hc.cc.cc.ch.$	$AB.CA.BC.AB.$ (rep)	$O+O.O+O.$	$O+O.S-S.$	$90°$	Pm

Notes. In the second column, (rep) indicates that the next I-beam in the sequence is the same as the first; $(B\tilde{})$ or $(C\tilde{})$ indicates that it begins with B or C and repeats by one or by two cyclic permutations respectively. In the third column sequences which contain only one type of I-beam (i.e. all $[O \pm O]$, all $[S \pm S]$, or all $[O \pm S]$ or $[S \pm O]$ are starred.

As may be seen from Table I, there exists an orthorhombic stacking $hc.cc.hc.cc.$ which contains an I-beam stack of type $O+O.O-O$, but the adjacent stack is $O+S.O-S$ and the space group is $P2_1ma$ (not $Pnma$ as in orthoamphibole). In A, B, C notation one equivalent sequence for the ortho-amphibole structure is

first stack: $ABaCA.BAbCB.ABaCA$
second stack: $AB.ACaBA.BCbAB.AC$

which shows that alternate pairs of oxygen layers would not match up as continous close packed layers across the two stacks (cf. fig. 2). The actual orthoamphibole structure, therefore, cannot be related to the fully rotated model.

The attempt by Papike and Ross (1970) to relate the protoamphibole structure to the fully rotated model breaks down at a still more fundamental level. An I-beam of type $[O \pm O]$ always starts and finishes with the same symbol in A, B, C notation (e.g. $ABaCA$). The protoamphibole structure has a four-layer repeat, and in an orthogonal structure this means that all I-beams start with the same symbol. Thus the sequence in the first stack in protoamphibole must be, for example, $ABaCA$. $ABaCA$, and this does not correspond to a close-packed stacking because it contains identical symbols adjacent to one another $(A.A)$. As can be seen from Table I there exist two fully rotated structures that repeat in four layers $(hc.ch.$ and $cc.cc.)$

and contain only $[O+O]$ I-beams in one of their stacks, but both are monoclinic. Thus protoamphibole cannot be related in any way to the fully rotated model. The same is true for protoenstatite if it has the $Pbcn$ space group assumed by Papike and Ross (1970), although as noted by Papike *et al.* (1973) protoenstatite can be related to the fully rotated model if it has the space group $P2_1cn$ proposed by Smyth (1971). It would then have equal numbers of O- and S-rotated tetrahedral chains.

The parity rule is in fact another way of stating that in the fully rotated model close-packed oxygen layers run continuously through adjacent stacks of I-beams. The four orthorhombic structures considered in this section are structures that do not conform to the fully rotated model. If an attempt is made to describe them in terms of that model they exhibit parity violations, but we believe it is more informative to say that the real structures are not intermediate between the fully extended and fully rotated types. They can be discussed in terms of the former but not in terms of the latter.

The 'A-site' in amphiboles. In the extended chain model of an amphibole there is a hexagonal hole directly over the OH group at $O3$. When the tetrahedra begin to rotate in either direction (O or S) this hole becomes trigonal and contracts, but remains exactly over $O3$. In the fully rotated form there is no open hole left, but there is still a depression between three oxygen atoms which is directly over $O3$ and is homologous with the original hole. There is also a similar depression on the mirror-plane of the I-beam, which does not lie over the $O3$ position and does not correspond to the original hole.

When the extended I-beams are stacked together the 'A-site' is formed between the holes in the backs of adjacent I-beams, although the holes are not directly opposite one another (as they are in forming the inter-layer cation site in the micas). In the fully rotated structures one of three things happens depending on the directions of rotations in the I-beams and on their orientation; a depression in one I-beam that is homologous to the original hole may have another such opposite it; it may have a depression of the other kind opposite to it; or it may be occluded by an oxygen atom, in which case two depressions of the other kind will oppose one another. In every case an octahedral site is formed between the backs of the chains, but except in the first case it is not homologous with the A site of the extended structure and cannot be continuously transformed into it by extending the chains.

This can of course be seen on models, but is most simply demonstrated with the symbolism we have already used. In structure 1 we may replace the . between the backs of I-beams by a bold face symbol for the octahedral site between them. It is of course

identical to the symbol for the cation positions in the adjacent stack. Thus we obtain

first stack: $ABaCAcBCbABaCAcBC$
second stack: $ABaCAcBCbABaCAcBC$

It is evident that the 'inter-I-beam' site is everywhere positioned on a similar array to that of the oxygen atoms two layers away to either side. It is therefore directly opposite to the OH groups (at $O3$) which are in those layers, and is analogous to the A site in the extended chain structure. On the other hand in structure 2

first stack: $ABcABcABcABcABcAB$
second stack: $ABcABcABcABcABcAB$

it is equally evident that the situation is quite different. The 'inter-I-beam' sites do not lie opposite the oxygens two layers away and are therefore not analogous to the A sites in the extended model. The residual holes opposite the OH groups are here occupied by basal oxygens of the next I-beam. Finally, in structure 3

first stack: $ABaCBcABaCBcABaCB$
second stack: $ABaCBcABaCBcABaCB$

the 'inter-I-beam' site is analogous to the A site with respect to the I-beam at one side, but not to that at the other. There is no correspondence between the presence or absence of a true A site in a fully rotated structure with the type of rotations which are present. For example, there are true A sites in structure 1, which is wholly of I-beam type $[O+O]$, but not in the stack.

$$ABaCAbCAcBCaBCbABcABaCA$$

which is also wholly of type $[O+O]$. A true A site relationship between the octahedral site and $O3$ arises when the basal oxygen layer of the I-beam is of type c in the stacking sequence in c, h notation.

A true octahedral A site in a fully rotated structure does not share any edges with silicon tetrahedra. The inter-I-beam sites that are not analogous to true A sites share two edges with silicon tetrahedra on each side on which they are wrongly placed. It is a tendency towards this latter situation that was remarked by Papike and Ross (1970) in gedrite; but since the departure from the extended form towards the rotated one is far from complete it is misleading to regard the A site in gedrite as sharing two edges with silicon tetrahedra.

Conclusion. A detailed examination of the fully rotated, close-packed model structures for amphiboles and pyroxenes has demonstrated both the strengths and the weaknesses of the model when compared with the fully extended model. In particular, care is necessary when attempting to use the fully rotated model to explain features observed in real structures. In many ways the fully rotated model does not correspond to the structures of real amphiboles and pyroxenes.

APPENDIX I

Enumeration of stacking sequences

To enumerate the complete set of stacking sequences which repeat in eight oxygen layers (two *I*-beams) or less is not entirely straightforward. We have noted that the repeat unit must contain an even number of c and h type layers, and this is used first to identify sequences which repeat in one *I*-beam (four layers).

There are four two-layer combinations: *hh, hc, ch, cc*. These may be systematically combined to give the following matrix of four-layer combinations (quartets):

hh.hh.	*hh.hc.*	*hh.ch.*	*hh.cc.*
hc.hh.	*hc.hc.*	*hc.ch.*	*hc.cc.*
ch.hh.	*ch.hc.*	*ch.ch.*	*ch.cc.*
cc.hh.	*cc.hc.*	*cc.ch.*	*cc.cc.*

Of these, the following contain odd numbers of c and h symbols: *hh.hc., hh.ch., hc.hh., hc.cc., ch.hh., ch.cc., cc.hc., cc.ch.*. These, which are the off-diagonal elements on the edges of the matrix, repeat not in four layers but in eight (sequences with even numbers of c and h can be generated by writing each one down twice). The remaining eight quartets comprise two unique sequences and three degenerate pairs. Sequence *ch.ch.* is the reverse of *hc.hc.*, and *cc.hh.* of *hh.cc.*. Sequence *hc.ch.* is changed into *ch.hc.* by removing a pair of symbols from one end and adding them on at the other (corresponding to a move into the adjacent *I*-beam stack); this alternative operation also changes *cc.hh.* into *hh.cc.*. Sequences *hh.hh.* and *cc.cc.* are not equivalent to any other. Thus when degeneracy is removed a set of five quartets includes all the possible sequences repeating in four oxygen layers (one *I*-beam). This set may be chosen to be *hh.hh., hh.cc., hc.hc., hc.ch.*, and *cc.cc.*, corresponding to the examples discussed in the text.

The set of sixteen quartets can be used in the same systematic way to generate the complete set of eight-layer sequences. Again sequences which contain odd numbers of h and c repeat not in eight layers but in sixteen, and a considerable number of degenerate sequences are found. Demonstration of degeneracy between eight-layer sequences may require reversal and/or one or more two-layer shifts. It can be verified, tediously, that there are only twenty-two distinct non-degenerate sequences which repeat in eight oxygen layers (two *I*-beams). These are added to the five which repeat in four layers to give the complete set of twenty-seven detailed in Table I.

APPENDIX 2

Determination of space group

Information about the space group of a model structure can be determined from the (O, S) representation. The structure can be shown to be orthorhombic or monoclinic, and for a primitive unit cell the full space group can be derived. For centred cells it is not possible to decide *a priori* between *I*- and *C*-centred conventions: *C*-centred is normally chosen. We consider three features of the structures, and the effect upon them of the various symmetry operations. Tetrahedral rotation is invariant under all symmetry operations. The octahedral direction may be changed, and the order of the symbols may be reversed; for example, $[S-O]$ may become $[S+O]$, $[O-S]$ or $[O+S]$, or may be unchanged. Symmetry operations may move atoms on to a different array, or may interchange layers in the structure, or both. As an example, if an *AB* octahedron is rotated about an axis parallel to *b* through the centre of the octahedron (a *C* position), the top octahedron face (*B* array) rotates into the bottom position and the atoms move on to the *A* array. Similarly *A* (bottom) becomes *B* (top). An *I*-beam *BABC* subjected to this rotation would become *CABA*, changing from $[S+O]$ or $[O+S]$, although the octahedron is still *AB*.
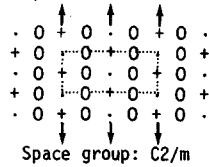
Table A1 lists the effect of 180° rotation and reflections on all the possible orientations of different *I*-beams. Note
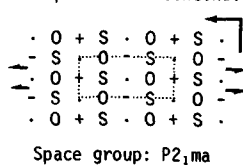
TABLE A1

Operation	180° Rotation about			Reflection perpendicular to		
	a	*b*	*c*	*a*	*b*	*c*
$[O+O]$ becomes	$[O-O]$	$[O+O]$	$[O-O]$	$[O-O]$	$[O+O]$	$[O-O]$
$[O+S]$ „	$[O-S]$	$[S+O]$	$[S-O]$	$[S-O]$	$[O+S]$	$[O-S]$
$[S+S]$ „	$[S-S]$	$[S+S]$	$[S-S]$	$[S-S]$	$[S+S]$	$[S-S]$
$[S+O]$ „	$[S-O]$	$[O+S]$	$[O-S]$	$[O-S]$	$[S+O]$	$[S-O]$
$[O-O]$ „	$[O+O]$	$[O-O]$	$[O+O]$	$[O+O]$	$[O-O]$	$[O+O]$
$[O-S]$ „	$[O+S]$	$[S-O]$	$[S+O]$	$[S+O]$	$[O-S]$	$[O+S]$
$[S-S]$ „	$[S+S]$	$[S-S]$	$[S+S]$	$[S+S]$	$[S-S]$	$[S+S]$
$[S-O]$ „	$[S+O]$	$[O-S]$	$[O+S]$	$[O+S]$	$[S-O]$	$[S+O]$

Values of the angle β in the monoclinic structures can be determined from the number of layers in the repeat unit and the first *A, B, C* symbol of the next repeat unit, and these are included in Table I in the text. The same β values apply to both amphiboles and pyroxenes, but the space groups of the latter all have *c* in place of *m*, perpendicular to the *y*-axis, and the two pyroxenes with centred space groups are in the setting *I2/c* for these values of β. If the description is to remain consistent with the octahedral signs they can only be changed to *C*-orientation with obtuse β if this angle is changed to 117.94° for *hh.hh.* and to 125.26 for *cc.cc.*.
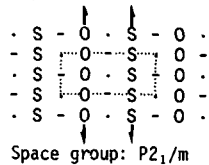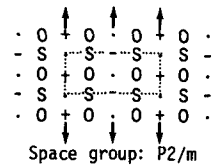
Example 1: cc.cc.cc.cc.

```
    ↑   ↑   ↑
 · O + O · O + O ·
 + O ┌─O─+─O─┐ O +
 · O + O · O + O ·
 + O └─O─+─O─┘ O +
 · O + O · O + O ·
    ↓   ↓   ↓
```
Space group: C2/m

Example 2: hc.hc.hc.hc.

```
                       ←
 · O + S · O + S ·┐
 ─· S ┌─O─···─S─┐ O ─
 ─· O + S · O + S ·→
 ─· S └─O─···─S─┘ O →
 · O + S · O + S ·
```
Space group: P2₁ma

Example 3: hh.cc.hh.cc.

```
    ↑   ↑
 · S ─ O · S ─ O ·
 ─ S ┌─O─···─S─┐ O ─
 · S ┊ O · S ┊ O ·
 ─ S └─O─···─S─┘ O ─
 · S ─ O · S ─ O ·
    ↓   ↓
```
Space group: P2₁/m

Example 4: hc.ch.hc.ch.

```
    ↑   ↑   ↑
 · O ┊ O · O ┊ O ·
 ─ S ┌─S─···─S─┐ S ─
 · O ┊ O · O ┊ O ·
 ─ S └─S─···─S─┘ S ─
 · O ┊ O · O ┊ O ·
    ↓   ↓   ↓
```
Space group: P2/m

Example 5: hh.hh.hc.hc.

```
 · S ─ S · O + S · S ─ S ·
 ─ S ┌─S─···─S─v─O─···─S─┐ S ─
 · S ┊ S · O + S · S ┊ S ·
 ─ S └─S─···─S─v─O─···─S─┘ S ─
 · S ─ S · O + S · S ─ S ·
```
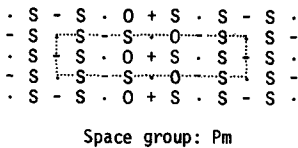Space group: Pm

FIG. 3. Examples showing the determination of space groups of amphiboles from the (O, S) notation. Note that the mirror plane present in all amphiboles is omitted from the diagrams for the sake of clarity. Examples 1–4 have four layers (one I-beam) and example 5 has eight layers (two I-beams) in the repeat unit. The unit cell is shown by a dotted outline; the a-axis is horizontal and the b-axis down the page.

that the I-beam type is not changed by reflection perpendicular to B; this is the mirror plane which is present in all amphiboles (the c-glide plane in pyroxenes).

With the information in Table A1 we can write down the symmetry elements of any structure by inspection if a portion of it is displayed in (O, S) notation, and hence determine the space group. Fig. 3 shows five examples for amphiboles (for clarity, the mirror plane perpendicular to b is not represented as it is present in all structures).

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