CRYSTAL CHEMISTRY OF THE PYROXENES AND PYROXENOIDS

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ABSTRACT

The classification of the crystal structures of the pyroxenes and pyroxenoids according to the repeat unit of the silicate chain is well-known. This system does not, however, differentiate between structures which contain similar types of chains. For example, the pyroxenoids wollastonite (CaSiO₃), parawollastonite (CaSiO₃), bustamite (CaMnSi₂O₆) and pectolite (CaNaH₂Si₂O₇) all have the same chain repeat unit (drierketten), yet are distinctly different; therefore, further structural criteria should be used in their classification. Recent structure determinations and detailed refinements have shown that these structures display additional features which serve to differentiate them from each other.

All of these structures contain sheets of approximately closest-packed oxygen ions. Sheets of approximately octahedrally coordinated cations alternate with sheets of tetrahedrally coordinated Si between sheets of oxygen. Comparison of the structures viewed in this way shows that they are characterized by the following interdependent criteria:
1. Repeat unit of the silicate chains
2. Distribution of cations in the octahedral layer
3. Sharing of edges and corners of octahedra with tetrahedra
4. Coordination of oxygen by cations

Wollastonite, parawollastonite and bustamite are composed of similar octahedral layers and silicate chains which are linked to each other in different ways, while in pectolite the presence of Na and H is reflected in a different distribution of cations in the octahedral layer. Since similar considerations apply to the pyroxenes as well as to other members of the metasilicate group, it is possible to differentiate between any members of this group, and to predict further relations using the above criteria. In addition, previously suggested mechanisms for some polymorphic transitions are found to be somewhat different when the structures are viewed in this way.

INTRODUCTION

The crystal structures of the pyroxenes and pyroxenoids were among the first to be investigated by x-ray diffraction techniques. Warren and Bragg (1928) worked out the structure of diopside and by the early 1930's most of the pyroxenes had been investigated and assigned to a particular structural class. The pyroxenoid structures proved to be more difficult to determine and it was not until almost thirty years later that Buerger (1956) and Mamedov and Belov (1956) solved the structures of pectolite and wollastonite, respectively. Today, the gross features of the structures of a number of these minerals are known (Liebau, 1962) and
attention is shifting toward understanding the reasons for the various relations among them. Detailed refinements of several of these structures have now been completed. It is the purpose of this paper to describe some structural relations which lead both to an improved classification and to an understanding of the crystal chemical relations among these minerals.

**Structural Similarities and Differences**

The structures of the pyroxenes clinoenstatite, pigeonite, and enstatite, and of the pyroxenoids wollastonite, pectolite, bustamite, and rhodonite have been refined.\(^1\) In addition, those of diopside, protoenstatite, parawollastonite and pyroxmangite have been determined but not refined.\(^2\) These structures all have a number of features in common. The structures, like those of micas and amphiboles, may best be described in terms of closest-packing of anions. Oxygen ions, arranged in a two-dimensional closest-packed pattern, form layers which intersect the two principal cleavages at about 45°. Si occupies tetrahedrally coordinated sites between oxygen sheets while the larger cations (e.g., Ca, Mn, Mg) occupy octahedrally coordinated sites. These cations are arranged in alternating layers between sheets of oxygens. Thus layers of Si alternate with layers of large cations.

Tetrahedra all share two vertices to form a continuous chain parallel to the two principal cleavages. Liebau (1962) has shown that these structures differ in the repeat unit along the chain. Thus pyroxenes contain Zwierketten (repeat unit of two tetrahedra), wollastonite, parawollastonite, bustamite, and pectolite Drierketten, rhodonite Fünferketten, and pyroxmangite Siebenerketten.

There are other major differences, however, which lie principally in the distribution of octahedrally coordinated cations within a single layer. This is shown in Fig. 1. Here the different kinds of cation distribution are illustrated for each of the chain types, the structure being represented by

\(^1\) Clinoenstatite, MgSiO\(_3\), and pigeonite, (Ca, Mg, Fe) SiO\(_3\); Morimoto et al. (1960).
Enstatite, MgSiO\(_3\); Lindemann (1961).
Wollastonite, CaSiO\(_3\); Buerger and Prewitt (1961). Also called α-wollastonite or wollastonite 1-Tr.
Bustamite, CaMnSi\(_2\)O\(_6\); Peacor and Buerger (1963).
Rhodonite, CaMn\(_2\)Si\(_2\)O\(_6\); Peacor and Niizeki (1963).

\(^2\) Diopside, CaMgSi\(_2\)O\(_6\); Warren and Bragg (1928).
Protoenstatite, MgSiO\(_3\); Smith (1959).
Parawollastonite, CaSiO\(_2\); Tolliday (1958). Also called β-wollastonite or wollastonite-2M.
Pyroxmangite, (Mn, Fe, Ca, Mg) SiO\(_3\); Liebau (1959).
Fig. 1. Distributions of octahedrally coordinated cations for each type of silicate chain. The larger circles are arranged in a hexagonal pattern with the solid circles representing occupied sites. Silicate chains are represented by the smaller solid circles connected by lines and projected onto the plane of the octahedrally coordinated cations.

a layer of Si and a layer of large cations projected onto a plane parallel to the sheeting. Closest-packed oxygen ions are omitted for simplicity. Large shaded circles represent occupied octahedrally coordinated sites, while the large open circles represent vacant sites, all within a single layer. Occupied tetrahedral sites in the layer above are represented by smaller circles connected by a line to indicate the nature of the chain. Tetrahedra have vertices pointing down, shared with octahedra.

Several features are at once evident:

1. The distribution of filled octahedral sites differs in each. However, in each type, octahedra share edges to form bands which parallel the silicate chains. In wollastonite, the band is composed of three continuous chains of edge-sharing octahedra. In rhodonite and pyroxmangite, chains of octahedra 10 and 8 octahedra long, respectively, are joined in an offset manner to form the band.
2. By assuming a specific chain type, the distribution of octahedrally coordinated cations may be determined from a consideration of bond strengths. Indeed, this was accomplished in the redetermination of the structure of rhodonite. In this way it is possible to predict further structure variations.
3. Liebau has noted that the chain type is a function of cation size. Thus the average size of the octahedrally coordinated cations increases in pyroxene through pyroxmangite, rhodonite and wollastonite. The idealized diagram shows that a section of chain \( n \) tetrahedra long, where \( n \) is the repeat unit along the chain, in wollastonite, pyroxmangite, and rhodonite, is similar to that of pyroxenes. Thus as cation size increases above that required for the stability of the pyroxene structure, the chain length in common with pyroxenes decreases.
**Consideration of Individual Structures**

*Clinoenstatite.* Figure 2 is the first of several diagrams which show the structures of the minerals under consideration, in this case that of clinoenstatite, projected onto a plane parallel to the sheeting. A portion of a layer of Si tetrahedra is shown over a plane of octahedra. The unit translations within this plane are shown at the lower left. Tetrahedra are omitted in the upper half of the diagram to permit the underlying octahedral sheet to be more clearly seen. The band of octahedra extending parallel to the silicate chain is shown on the right. It is separated from the band on the left by a rift of unoccupied octahedrally coordinated sites. Except in pectolite, this latter feature is common to all of these structures, all of which have different distributions of cations forming the bands, as noted above. Considerable distortion of the closest-packed oxygen framework occurs along this rift. Nevertheless, an approximately closest-packed arrangement is retained.

A second feature is shown by the left-hand chain of tetrahedra, which has vertices pointing up. The bases of these tetrahedra parallel the rift in the octahedral sheet, and knit parallel bands together. There is a second chain below the rift, with vertices down, which also serves to knit the bands together. Thus the rift of unoccupied sites is enclosed by two

![Fig. 2. The clinoenstatite structure projected onto a plane parallel to the octahedral sheeting. Unit translations are shown in the lower left of the figure. A single octahedral layer and a portion of the adjacent tetrahedral layer are shown.](image-url)
parallel back-to-back silicate chains. This feature is known in the pyroxenes, but will also be shown to be present in all of the pyroxenoid structures.

Brown et al. (1961) have described the relations between the various forms of MgSiO₃. They show how similar units may be stacked in two different ways to yield stacking sequences which are different in clinoenstatite, enstatite and protoenstatite, and which may be extended to yield additional ordered sequences, as well as disordered sequences. This is due, basically, to the fact that the structures are based on closest packing. Adjacent planes of oxygen ions may be placed in two different relative orientations. This in turn yields two different arrangements for the resulting octahedrally coordinated voids which Mg occupies between the sheets of oxygen ions.

Diopside. It is well known that there are two monoclinic pyroxene type structures, exemplified by clinoenstatite (space group $P2_1/c$) and diopside (space group $C2/c$). Clinoenstatite has two cation positions occupied by two small cations (Mg) in more or less regular octahedral coordination, while diopside has one small cation (Mg) in octahedral coordination and one in eight-fold coordination (Ca). The structure of diopside is shown in Fig. 3 for comparison with that of clinoenstatite. The band of

![Fig. 3. The diopside structure presented in the same orientation as the clinoenstatite structure of Fig. 2.](image)
"octahedra" is less well defined here, since the coordination of Ca approaches 8 rather than 6. Ca occupies the sites on the borders of the band of octahedra whereas Mg occupies the inner sites. This distribution minimizes the distortion of the band caused by the large radius of the Ca ion, just as in the Ca-Mg amphiboles. The same distribution of the large Ca ion is also found in rhodonite, and will be discussed below. In diopside the tetrahedra all share two edges with Ca polyhedra as can be seen in the left-hand chain of tetrahedra, whereas each shares only a single edge with Mg octahedra in clinoenstatite. This result may be modified upon refinement of the diopside structure.

Wollastonite. The wollastonite structure is shown in Fig. 4. Here the octahedra share edges to form bands A, B and C which are three octahedra wide. The octahedra in the center of the bands are fairly regular, but those on either side are distorted. An important feature of each band is that centers of symmetry lie halfway between the Ca in the center column of octahedra. This is in contrast to bustamite where the Ca and Mn of the center column lie directly on the centers of symmetry. Six silicate chains share corners or edges with a band of octahedra.

Prewitt and Buerger (1963) have discussed how pseudomonoclinic sub-
cells in the wollastonite structure are joined to produce an overall triclinic symmetry. Although it is not easy to see in Fig. 4, the bands each have a vertical two-fold screw axis through the centers mentioned above normal to pseudomirror planes which lie halfway between the centers. These symmetry elements are not continuous from band to band and consequently the overall symmetry is triclinic.

Parawollastonite. Although no refinement is available for this structure, it is likely that the only difference between it and that of wollastonite is in the way in which the octahedral bands are joined by the tetrahedral chains. Figure 5 is a diagram of the parawollastonite structure. Bands A and B are identical to bands A and B in Fig. 4. Band C, however, is linked to band B in a different way. This is possible because the $\frac{1}{2} \ b$ separation of the oxygens along the edge of the bands permits two possible linkages without introducing appreciable strain into the structure. If one assumes that such a “fault” can be introduced, then it will be continued in layers above and below the layers of Fig. 5 with the net effect of a $\frac{1}{2} \ b$ shift on (100). Note also that $b$ is normal to [101] in Fig. 5. This is not so in Fig. 4.

By making use of two-dimensional optical analogs of the wollastonite-parawollastonite problem, Willis (1958) has shown that the diffuse

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**Fig. 5.** Parawollastonite in the same orientation as wollastonite in Fig. 4. Note that the relative positions of bands A and B are the same in both structures.
streaks one so often sees in wollastonite single-crystal x-ray photographs are a result of the “faults” discussed above. It should be possible to extend this treatment to three dimensions by means of calculations with a digital computer.

Bustamite. Bustamite and wollastonite have been compared by Peacor and Prewitt (1963). The bustamite structure shown in Fig. 6 is similar to that of wollastonite. The Ca and Mn in bustamite are distributed in the same pattern as are the Ca in wollastonite, but in bustamite the cations in the central columns of the bands lie on centers of symmetry instead of between them. In order to conform to this difference in symmetry, some of the silicate chains in bustamite are shifted by $\pm \frac{1}{2} b$ with respect to those in wollastonite.

It is natural to ask whether there could be a parawollastonite type bustamite, whether CaSiO$_3$ could have the bustamite arrangement, or whether bustamite could be disordered to form a wollastonite-like structure. If the parawollastonite structure is correct, it is unlikely that there could be a “parabustamite” because the upper oxygens on the right-hand side of the bustamite bands do not conform closely enough to the substructure along $b$. This is a result of ordering of Ca and Mn ions. That is, there is only one way to link adjacent bands unless the structure is severely distorted from what must be the equilibrium configuration.
Since it can be shown that the relative arrangement of chains in bustamite arises directly as a result of Ca, Mn ordering, it seems quite likely that at high temperatures, with disordering of Ca and Mn, that bustamite would invert to a wollastonite-type structure. For the same reason, it seems unlikely, although still possible, that CaSiO$_3$ could have the bustamite-type structure as a variant.

Gard and Taylor (1960), in a paper on the structure of foshagite, proposed possible stacking modifications of CaSiO$_3$ which are similar to bustamite and the hypothetical parabustamite. They compare the relative stabilities of these modifications with those of wollastonite and parawollastonite on the basis of the coordination of Ca$_3$ (Gard and Taylor's Ca$_1$). Ca$_3$ in wollastonite is equivalent to Ca$_2$ and Mn$_2$ in bustamite (Peacor and Prewitt, 1963). Essentially, the argument is that in CaSiO$_3$ structures with the wollastonite and bustamite arrangements, Ca$_3$ would be coordinated by seven oxygens in wollastonite and would be split into two sites in the bustamite-type, one coordinated by eight oxygens, the other by six. Maximum stability would be obtained when all Ca$_3$ ions have the same coordination because, since the extra oxygens (O$_5$) are linked also to two silicons, repulsive forces may exist between Ca$_3$ and these oxygens which allow only one oxygen near the cation in the most stable state.

While this idea may be valid in showing why a bustamite-like CaSiO$_3$ is less stable, the reasons for the stability of bustamite itself are probably more involved. For example, to form an ordered bustamite, Ca$_2$ and Mn$_2$ must lie on centers of symmetry. This then requires that two O$_5$'s be coordinated to either Ca$_3$ or Mn$_3$ in order to maintain the symmetry. In other words, the energy of ordering Ca and Mn may be more important than the second-neighbor coordination of Ca$_2$ and Mn$_2$. However, once the ordered arrangement of Ca$_3$ and Mn$_3$ is obtained, it is more likely that the larger Ca$_3$ would have the higher coordination, which is indeed what is found (Peacor and Prewitt, 1963).

**Pectolite.** The pectolite structure (Prewitt, 1964) is unlike the others which have been discussed here since the Na coordination is not octahedral and hydrogen bonding is present. The Na polyhedron can be described as a distorted square antiprism as shown in Fig. 7. The Ca octahedral bands are two octahedra wide and share edges with the Na polyhedron but not with the silicate tetrahedra. On the other hand, no less than five tetrahedral edges are shared with the Na polyhedron. The silicate chains are quite similar to those in wollastonite.

There is little chance to form parawollastonite or bustamite analogs without a major reorganization of the pectolite structure. There is only one way to join adjacent bands together without introducing strain,
thus eliminating the possibility of the parawollastonite analog. Since it is not possible to form a pectolite octahedral band with the Ca on centers of symmetry, the bustamite equivalent is not a possibility. To tentatively confirm this, Weissenberg photographs were taken of schizolite (CaMnNaHSi$_5$O$_8$) and serandite (Mn$_2$NaHSi$_5$O$_8$). No departure from the basic pectolite pattern was detected except for slight intensity changes due to substitution of Mn for Ca.

**Rhodonite.** Fig. 8 shows the structure of rhodonite (Peacor and Niizeki, 1963) to be similar to those of the preceding minerals. The band of octahedra is formed of chains of edge-sharing octahedra 10 octahedra long, joined through further edge sharing in a staggered manner to form the band. The rift of unoccupied sites is more irregular here, but is still defined by two back-to-back silicate chains. One coordination polyhedron on the border of the band is an irregular polyhedron of seven oxygen ions. This site is occupied by Ca while Mn is distributed over the remaining sites. The Ca polyhedron is thus on the edge of the band, as in diopside. A similar situation may be expected in pyrosmangite, and a refinement of this structure is now planned, in part to confirm this result. In rhodonite, tetrahedra-octahedra edge sharing is again illustrated by the left-hand silicate chain. Five such edges are shared, three by the Ca coordination polyhedron.

**Babingtonite.** The structure of babingtonite (Ca$_2$Fe$^{2+}$Fe$^{3+}$HSi$_5$O$_8$) is as yet unknown, but work is now in progress on its solution. The similarity
of composition between rhodonite and babingtonite, and the similarity of $b$-axis Weissenberg photographs suggests that babingtonite contains $\text{Fünferketten}$, not double $\text{Fünferketten}$ as suggested by Liebau (1956). Thus the structure may be related to that of rhodonite as the structure of pectolite is to that of wollastonite, i.e., hydrogen plays similar roles in each, and the distributions of large cations within available octahedrally coordinated sites differ.

**Polymorphism**

Several polymorphic transitions between members of this group of structures are well known. For example, bustamite and johannsenite (diopside structure) are high and low temperature modifications of CaMnSi$_2$O$_6$ respectively, while Ca-rich rhodonite and bustamite are similarly related. Dent Glasser and Glasser (1961) concluded in a study of the inversion of rhodonite to wollastonite (bustamite?) that Si-O bonds were broken and reformed, whereas the octahedral sheet merely underwent distortion. By comparing the structures of wollastonite and rhodonite, as described above, it is clear that this picture is over-simplified. Since the morphology of the crystals used by Dent Glasser and Glasser remained unchanged after inversion, and since the distribution of

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**Fig. 8.** The rhodonite structure projected onto a plane parallel to the octahedral sheets.
both Si and large cations in the close-packed frameworks differs, the
mechanism of inversion between pyroxene and pyroxenoid structures
must involve:

1. The breaking of both Si-O and cation-O bonds.
2. Redistribution of some of these cations.
3. Retention of the basic packing framework of oxygen anions.

Bonding

As Cruickshank (1961) has pointed out, reliable interatomic distances
and angles for the silicates have been rather scarce, primarily because so
many silicate structures were solved before high-speed digital computers
became available. Any theory of bonding which attempts to explain
differences of bond lengths on poor experimental data or on incomplete
analysis of atom coordination is likely to be in error. For example,
Voronkov (1961) uses the wollastonite structure as an example of un-
balance in Si-O-Si bridges and quotes Si-O distances of 1.48 Å and 1.76 Å
for this particular linkage. Prewitt and Buerger (1963), however, found a
maximum deviation of 0.02 Å (1.65–1.67 Å) in the Si-O-Si bridges of wol-
lastonite. Even the maximum deviation (0.10; 1.57–1.67 Å) of Si-O dis-
tances found by Buerger and Prewitt is considerably less than that
quoted by Voronkov.

The errors in accuracy of the interatomic distances and angles which
have been obtained from many least-squares refinements are probably
somewhat greater than is indicated by the computed standard devi-
ations. In addition, experience has shown that interatomic distances and
interbond angles obtained from refinement of two-dimensional data may
be quite different from those obtained using three-dimensional data. The
distances reported by Buerger and Prewitt (1963) for pectolite which re-
sulted from a refinement of relatively crude two-dimensional data differ
considerably from those obtained by Prewitt (1964) who used three-
dimensional counter-diffractometer data. Nevertheless, it is encouraging
that consistent results have been obtained by different investigators
working with different compounds as in the case of bustamite and
wollastonite. The discussion below deals with the results of refinement of
these and other minerals and points out considerations which should be
understood when one tries to explain the bonding on a theoretical basis.

Interatomic Distances. Many of the interatomic distances and interbond
angles for the refined pyroxenes and pyroxenoids are given in the basic
references listed in the beginning of this paper and will not be reproduced
in full here. There are, however, some interesting comparisons which
should be made. Fig. 9 is a schematic drawing of the silicate chains in
pectolite, wollastonite, and bustamite. It can be seen from this figure that, in general, the Si-O distances in the Si-O-Si bridges are larger (∼1.66 Å) than the remaining distances (∼1.60 Å). A similar situation exists in rhodonite where the average distances are 1.64 Å and 1.60 Å, respectively. There are, however, some exceptions, and it is worthwhile to see if these exceptions can be explained. One exception is the Si₁-O₉-Si₂ bridge in which the Si-O distances are considerably different for each example.

The smaller Si-O₉ distances in bustamite are probably due to the fact that the Ca around O₉ are considerably farther away than they are in wollastonite. The difference in the Si₁-O₉ and Si₂-O₉ distances in pectolite can be justified in a somewhat more indirect manner. Referring to Fig. 9, the Si₁-O₉ distance is rather large. The hydrogen bond in pectolite, however, lies between O₉ and O₄. Refinement of H parameters indicates that it is closer to O₄ than to O₉, thus giving an explanation for the large Si₁-O₉ distance. This could in turn explain the unbalanced Si₁-O₉-Si₂ bridge. This type of argument is of course qualitative and could be wrong. It does
show, however, that detailed structural information should be examined before searches for more theoretical explanations of bonding are undertaken.

The average Si-O and Ca-O distances for pectolite, wollastonite, bustamite, and rhodonite are quite similar, considering the distortions of the various polyhedra.

<table>
<thead>
<tr>
<th>Average Distance</th>
<th>Pectolite</th>
<th>Wollastonite</th>
<th>Bustamite</th>
<th>Rhodonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O</td>
<td>1.628 Å</td>
<td>1.626 Å</td>
<td>1.623 Å</td>
<td>1.628 Å</td>
</tr>
<tr>
<td>Ca-O</td>
<td>2.370</td>
<td>2.387</td>
<td>2.388</td>
<td>—</td>
</tr>
</tbody>
</table>

**Edge-Sharing.** One of the most interesting features of the pyroxene and pyroxenoid structures is the way in which the tetrahedra and octahedra share edges. The fact that this occurs in all of the structures is perhaps not widely recognized and is probably one of the main reasons for the difficulty various investigators had in trying to solve the pyroxenoid structures by trial-and-error methods. For example, in wollastonite the Si₃ tetrahedron shares two of its edges with two Ca octahedra. Two of the three oxygens involved are coordinated by two Si and one Ca, while the other oxygen is coordinated by one Si and 3 Ca. This type of coordination occurs in all the other pyroxenoids and also in the pyroxenes. These coordinations fall into three categories except in pectolite where the presence of H makes the problem more complex. The three types of oxygen coordination are (where M is Ca, Mn, Mg or Fe):

1. O coordinated by one Si and two M
2. O coordinated by one Si and three M
3. O coordinated by two Si and one M

Generally, the average Si-O distance for any one structure increases for type 1 through type 3 oxygen. The same feature is also found with respect to M-O distances. This correlation is readily explained through a consideration of the relative electrostatic bond strengths for the three oxygen types. This sort of comparison should probably not be carried too far, but it is a necessary consideration when correlating interatomic distances.

**Classification**

To propose an overall classification of the pyroxenes and pyroxenoids would be premature at this time since some of these structures are still unknown. The variables upon which a classification should be based have been considered above, however, and are summarized in the following list.

2. Variation in oxygen close-packing sequence, resulting in varying
relative distributions of octahedral and tetrahedral sites, e.g., clinoenstatite vs. enstatite.

3. Retention of basic closest-packing sequence with similar octahedral site occupancy. Relation of silica chain distribution to octahedral site occupancy may vary, e.g., wollastonite vs. parawollastonite.

4. Retention of basic closest-packing sequence with varying octahedral site occupancy, e.g., wollastonite vs. pectolite.

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References


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