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Pyroxene-pyroxenoid polysomatism revisited: A clarification

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ABSTRACT

Previous discussions of the pyroxenoid and clinopyroxene crystal structures have noted the polysomatic relationship between them, in which pyroxenoids with chain periodicities greater than three contain both pyroxene-like (P) and wollastonite-like (W) modules. However, disagreement exists in the published literature as to whether the P modules of pyroxenoids are, in fact, structurally equivalent to those of pyroxenes. By examining the structural attributes of the P modules of pyroxmangite, we show that they correspond to slabs of clinopyroxene cut parallel to $(1\bar{1}\bar{1})_{cpx}$ and oriented in pyroxmangite parallel to $(001)_{pyd}$. This orientation is identical to that observed in pyroxene-pyroxenoid intergrowths.

INTRODUCTION

Structural relationships between the single-chain pyroxenes and pyroxenoids are well known. Pyroxenoid silicate chains contain offset tetrahedra whose frequency determines the chain periodicity, which in all cases is greater than the characteristic two-tetrahedra repeat of pyroxenes. The prototype tetrahedral chain configuration containing offsets occurs in wollastonite, whose tetrahedral repeat periodicity is three. In longer chain pyroxenoids, one or more pyroxene-like tetrahedral pairs separate the wollastonite-like triplets. Thus, five-repeat rhodonite tetrahedral chains contain alternating pyroxene-like pairs and wollastonite-like triplets, whereas in seven-repeat pyroxmangite chains, two pyroxene-like pairs are inserted between each wollastonite-like triplet. Because similar structural analogies can be extended to the octahedral bands, the various pyroxenoids were recognized as members of a polysomatic series by Thompson (1978), who, following Koto et al. (1976), pointed out that all their structures consist of pyroxene-like (P) and wollastonite-like (W) slabs or structure modules. Any pyroxenoid structure can be generated (approximately) by stacking these two modules in the appropriate ratio: rhodonite, with chain periodicity five, contains . . . WPWPWP . . . , or ⟨WP⟩, whereas pyroxmangite is ⟨WPP⟩, and so forth.

More detailed structural analyses (Pinckney and Burnham, 1988a, 1988b) support this analysis of pyroxenoid structures at the atomic level. For example, the W portions of the longer period pyroxenoids closely resemble the wollastonite structure, described as the stacking sequence ⟨W⟩. Similarly, the inner octahedra of the octahedral bands of pyroxenoids closely resemble the M1 sites of pyroxenes, and the outer octahedra, the M2 sites (Pinckney and Burnham, 1988a), both in configuration and site chemistry. Furthermore, the P modules in the various pyroxenoids are very similar to each other because of the correspondence among M-site coordination polyhedra, their connections with each other, and the Si tetrahedra (Ohashi and Finger, 1975; Veblen, 1991). However, there is some disagreement in the published literature as to whether P modules would form a true pyroxene structure when stacked in the absence of W modules. Previous discussions have relied either upon arguments concerning the metrical relationships between the unit cells and lattices of pyroxenes and pyroxenoids (e.g., Koto et al., 1976; Angel, 1986b) or upon experimental observations of intergrowths between pyroxenes and pyroxenoids (e.g., Ried, 1984). In this paper, we examine the structural configuration of a typical pyroxene-like portion of a pyroxenoid, and we show that this P module resembles very closely a $(1\bar{1}\bar{1})$ slab of clinopyroxene structure. Thus, contrary to some previous assertions (Angel, 1986a, 1986b), clinopyroxenes can be considered members of the polysomatic series of pyroxenoids.

ANALYSIS

We used the $C\bar{1}$ cell setting for pyroxenoids introduced by Koto et al. (1976), in which closest-packed O planes are parallel to (100) and the tetrahedral chains extend along the **c** axis. In this setting the W and P structure modules are slabs of structure whose boundaries parallel (001). Our analysis uses, as a typical pyroxenoid P module, one from $Mn_{0.97}Mg_{0.02}Ca_{0.01}SiO_3$ pyroxmangite (Pinckney and Burnham, 1988b). Because P modules of all long-chain anhydrous pyroxenoids are identical except for slight variations in bond distances and angles due to chemical substitutions, the conclusions would be the same for any long period pyroxenoid. We selected a slice through

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TABLE 1. Transformation matrices

M1	M2	M3 (= M1·M2)
1 0 0	1 0 1	1 0 1
0 1 1	0 −1 0	0 −1 −1
0 0 1	0 0 −1	0 0 −1

the pyroxmangite structure bounded by planes parallel to (001) at $z \approx 0.4$ and $z \approx 0.7$. This slice contains four Si4, two Si3, and two Si5 tetrahedral sites plus four M3 and four M5 octahedral sites, together with associated O atoms (Fig. 1a). A unit cell for this slice of structure was generated by retaining the a and b axes from the pyroxmangite structure and defining the **c** axis as the average of the chain extension directions [as defined by the bridging OC positions on the (001) faces of the slab] of the four chains within the slice. The resulting structure displays $C1$ symmetry, but is close to being centrosymmetric; its unit cell has the dimensions

$$\begin{aligned} a &= 9.712 \quad b = 10.536 \quad c = 5.209 \\ \alpha &= 122.81 \quad \beta = 102.21 \quad \gamma = 82.95. \end{aligned} \tag{1}$$

The extra periodicity imposed by the new **c**-axis repeat duplicates the bridging O atoms (OCs) close to the (001) faces of the unit cell. Each of these O pairs (separated by 0.32 Å) was therefore replaced with a single O atom at the average position of each pair. This results in slightly distorted Si-O bond lengths (approximately 0.08 Å) and bond angles (approximately 4–5°), but these distortions are not sufficient to invalidate our subsequent conclusions.

The unit cell given in Equation 1, together with the associated atom coordinates, represents a structure built entirely of P modules from pyroxenoids (Fig. 1b). The question is whether this structure closely resembles that of clinopyroxene; this can be addressed by transforming the atom coordinates and the cell into a clinopyroxene-like unit cell. In the next step, the basis vectors of the unit cell given in Equation 1 were transformed by the matrix M1 (Table 1), which is the inverse of that given by Koto et al. (1976) for transforming clinopyroxene to pyroxenoid. The size and shape of the resulting unit cell are clinopyroxene-like:

$$\begin{aligned} a &= 9.712 \quad b = 8.869 \quad c = 5.209 \\ \alpha &= 93.23 \quad \beta = 102.21 \quad \gamma = 88.76. \end{aligned} \tag{2}$$

As discussed by Angel (1986b), however, this unit cell is I centered, as is easily demonstrated by transforming the lattice vector ½,½,0 in Cell 1 into Cell 2 by the transpose of $\mathrm{M1}^{-1}$ (1,0,0/0,1,0/0,−1,1). To produce a conventional C-centered pyroxene unit cell, a further transformation is required. Matrix M2 (Table 1) applied to Cell 2 produces a cell with dimensions

$$\begin{aligned} a &= 10.003 \quad b = 8.869 \quad c = 5.209 \\ \alpha &= 93.23 \quad \beta = 108.39 \quad \gamma = 89.52. \end{aligned} \tag{3}$$

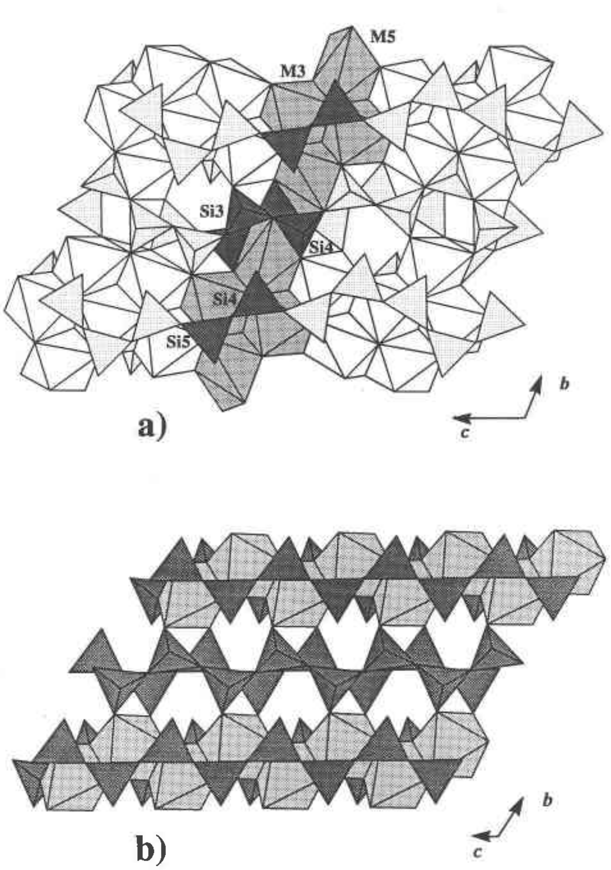

Fig. 1. (**a**) Polyhedral diagram of pyroxmangite projected down **a*** [onto (100)]. One P module, indicated by darker shadings, includes M3 and M5 octahedra and Si3, Si4, and Si5 tetrahedra. Other octahedra are unshaded (M7 not plotted); other tetrahedra are lightly shaded. OC atoms link tetrahedra within chains. Chain repeat of P module is taken as an average of the (Si3 + Si4) tetrahedral repeat and the (Si4 + Si5) tetrahedral repeat. Structure parameters from Pinckney and Burnham (1988b). (**b**) Polyhedral diagram of structure made up entirely of P modules identified in **a**, projected down **a***. Atom coordinates for some atoms have been slightly adjusted as described in text. For clarity, only M3 octahedra and Si tetrahedra are plotted.

This unit cell is closer to that of $MnSiO_3$ clinopyroxene ($a = 9.864$, $b = 9.179$, $c = 5.298$, $\beta = 108.22$; Tokonami et al., 1979); furthermore, most of the resultant atom coordinates approximate $C2/c$ symmetry after the origin is shifted to an approximate inversion center. Figure 2a is a projection onto (100) of the P-module structure in this setting; the equivalence of this structure to that of $MnSiO_3$ pyroxene (Tokonami et al., 1979), shown in the same orientation in Figure 2b, is obvious.

The net transformation of the P module from the pyroxmangite setting to the clinopyroxene setting of Equation 3 is given by matrix M3 (Table 1), which is the product of matrices M1 and M2. Note that the overall transformation takes (001) of pyroxmangite to $(1\bar{1}\bar{1})$ of clinopyroxene. The inverse of matrix M3, (1,0,1/0,−1,1/

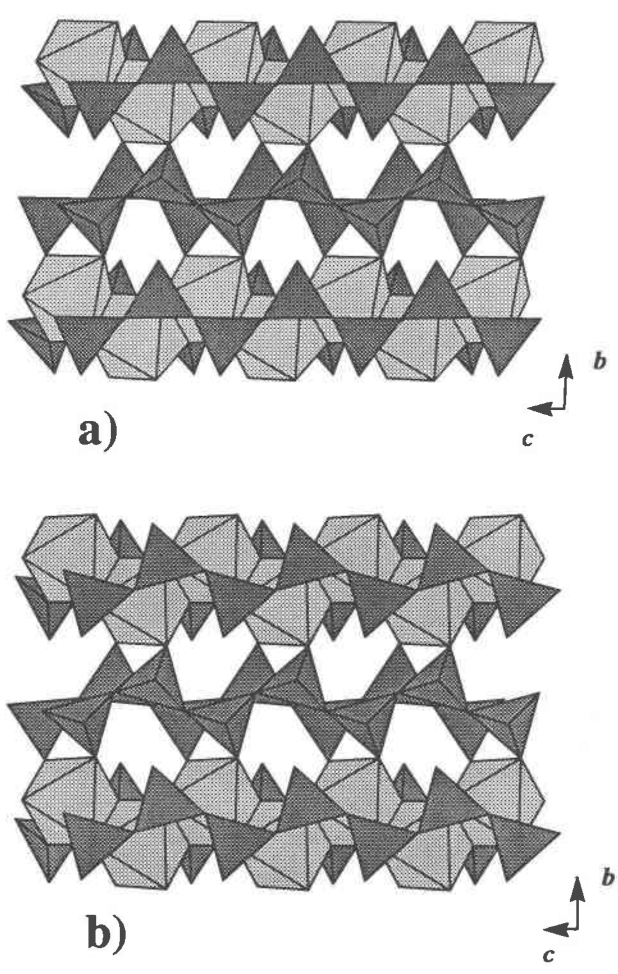

Fig. 2. (**a**) Polyhedral diagram of P-module structure, projected down **a***, with lattice transformed from that of Figure 1b by matrix M3 (Table 1). Structure is triclinic ($C1$), but note close similarity to **b**. This structure is virtually identical to that of true pyroxene. (**b**) Polyhedral diagram of $MnSiO_3$ pyroxene ($P2_1/c$) projected down **a***. For clarity, M2 polyhedra are omitted. Upper chains are B chains, lower ones are A chains. Structure parameters from Tokonami et al. (1979).

0,0,−1), transforms clinopyroxene unit cells into a setting analogous to the $C\bar{1}$ cells of pyroxenoids. The application of this transformation to $MnSiO_3$ clinopyroxene (Tokonami et al., 1979) yields a cell with dimensions

$$a = 9.628 \quad b = 10.598 \quad c = 5.298$$
$$\alpha = 119.99 \quad \beta = 103.29 \quad \gamma = 83.40$$

and to johannsenite ($CaMnSi_2O_6$; Angel, 1984) a cell with dimensions

$$a = 9.992 \quad b = 10.558 \quad c = 5.275$$
$$\alpha = 119.97 \quad \beta = 105.85 \quad \gamma = 82.16.$$

This pyroxenoid-like cell of johannsenite is C centered, unlike that obtained by the transformation of Koto et al. (1976), which is body centered. Furthermore, the new cell for $MnSiO_3$ has $\beta = 103.29°$, far more comparable to the pyroxenoids than the value 108.22° produced by the transformation by Koto et al.

CONCLUSIONS

By analyzing the structure of a P slab from pyroxmangite, which can be considered representative of long-chain pyroxenoid P slabs, we have demonstrated that such slabs correspond to $(1\bar{1}\bar{1})$ slices of the clinopyroxene structure. Clinopyroxene is therefore confirmed as a member of the polysomatic series of pyroxenoids and may be described as the stacking sequence ⟨P⟩. As in all such polysomatic series, the detailed structural correspondence is not exact. On building a pyroxenoid structure from P and W slabs derived from the clinopyroxene and wollastonite structures, some readjustment will occur. Atoms will be displaced slightly from their ideal positions in the isolated structure modules. Indeed, we eliminated some such displacements by averaging the OC positions on the module boundaries. The precise atomic adjustments that occur within individual modules as they abut different neighboring modules lead to the interactions that determine the relative stabilities of the various possible stacking sequences (Price and Yeomans, 1986). The relationship among structural stability, mean cation size, and strain at the module boundaries was analyzed in some detail by Pinckney and Burnham (1988a).

Our demonstration that the P slabs of pyroxenoids are $(1\bar{1}\bar{1})$ slices of the clinopyroxene structure also provides a rationale for the observed orientations of intergrowths of clinopyroxene and pyroxenoid with $\{11\bar{1}\}_{cpx}\|(001)_{pyd}$ (Ried, 1984). The module faces where the stacking sequence changes, $(1\bar{1}\bar{1})_{cpx}$, are members of the form $\{11\bar{1}\}_{cpx}$; thus they are parallel to one possible set of composition planes of observed clinopyroxene and pyroxenoid intergrowths. The same is true for the widely reported chain periodicity faults in clinopyroxene parallel to $\{11\bar{1}\}$ (Ried, 1984; Veblen, 1985; Angel, 1986b).

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