Bracelets and Pinwheels: A Topological-Geometrical Approach to the Calcium Orthosilicate and Alkali Sulfate Structures

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Abstract

Glaserite, $K_3Na[SO_4]_2$ and its high temperature isotype "silico-glaserite," α-$Ca_2[SiO_4]$; merwinite, $Ca_3Mg[SiO_4]_2$; larnite, β-$Ca_2[SiO_4]$; room temperature β-$K_2[SO_4]$; bredigite, *ca.* $Ca_7Mg[SiO_4]_4$; $K[LiSO_4]$; and palmierite, $K_2Pb[SO_4]_2$ are the bases of the atomic arrangements for over 100 compounds. Some of these compounds are of considerable interest to the cement, blast furnace, brick and fertilizer industries.

The glaserite structure type consists of one large alkali cation which is ideally 12-coordinated by oxygen atoms, six of which define the vertices of an elongate trigonal antiprism and six of which reside in an hexagonal ring in the plane of the large alkali. The tetrahedral grouping around the antiprism defines a "pinwheel" where the apical oxygens point either up (u) or down (d).

The bracelet is a mathematical object, a loop with n nodes involving m symbols, where $m < n$. For the pinwheel, $n = 6$ (an hexagonal ring) and $m = 2$ (u or d). Combinatorially, the total number of distinct bracelets is 13. For any bracelet there is a pinwheel which, idealized, defines the maximum coordination number of the central large alkali. The maximum coordination number is 12-p where $0 \leq p \leq 6$ and where p are the number of tetrahedral apical oxygens coordinating to the alkali. The bracelets can be used to construct, by condensation, ideals of real and hypothetical atomic arrangements found in the $Ca_2[SiO_4]$ polymorphs and many of the alkali sulfates.

The coordination polyhedra of interest include T (tetrahedron); M (octahedron, = p = 6); $X^{[12-p]}$ (which, for $p = 0$, has ideal symmetry $\bar{3}2/m$); $Y^{[10]}$ (point symmetry $3m$) and $F^{[12]}$ (cuboctahedron). Condensation of the bracelets and their associated pinwheels defines the maximum coordination numbers for all the polyhedra in the ideal model. These models can be used to classify known structures and to retrieve hypothetical ones, one of which may correspond to bredigite.

Introduction

In a recent detailed atomic arrangement analysis of merwinite, $Ca_3Mg[SiO_4]_2$ (Moore and Araki, 1972), it became abundantly clear that a review of the calcium orthosilicate structures was necessary in order to advance our knowledge of these related structures. As this review progressed, it became evident that extensive confusion and uncertainty abounds in the literature. This is not surprising in light of the fact that the literature on the subject of calcium orthosilicates is voluminous, largely on account of their crucial importance in the cement, clinker, slag, fertilizer and brick industries.

This paper is not intended to be an exhaustive treatise on the subject, but shall draw from pertinent literature only where that knowledge is imperative in advancing some general geometrical models of these structures. Despite the fact that no less than 100 compounds have been characterized as isotypes of the structure types which have bearing on this discussion, only a handful of papers treat the gen-

eral problem of the structural aspects of calcium orthosilicate polymorphism in detail. The attempts to show structural interrelationships among key compounds have been meager indeed, augmented by the fact that only a few reasonably precise structure refinements of the calcium orthosilicates have been reported. But few papers have attempted to afford the general relationships among these structures and none to my knowledge utilizes the polyhedral approach which shall be the theme of this contribution.

The structure types included in this discussion are merwinite, $Ca_3Mg[SiO_4]_2$; glaserite, $K_3Na[SO_4]_2$, and its high temperature isotype "silico-glaserite", α-$Ca_2[SiO_4]$; larnite, β-$Ca_2[SiO_4]$; room temperature β-$K_2[SO_4]$ and its myriad isotypes; bredigite, α_0'-$(Ca,Mg)_2[SiO_4]$; $K[LiSO_4]$; and palmierite, $K_2Pb[SO_4]_2$.

The Glaserite Model: Its Geometry

All compounds discussed evince a profound hexagonal substructure which, in many instances, has led to obfuscation in the literature regarding identi-

fication by powder diffractometry. Glaserite is the simplest arrangement, the one whose geometry defines the substructure observed in the other compounds. Glaserite, $K_3Na[SO_4]_2$ and the structurally similar aphthitalite, $K_2NaNa[SO_4]_2$, have been investigated by several workers but highly accurate structure refinements appear to be wanting.

The structure of aphthitalite appears as a polyhedral diagram in Figure 1. It derives from the study of Bellanca (1943). The large cation polyhedra, when idealized, consist of three kinds, and illustration of the first two in Figure 2 shall be the key theme in this subject. The glaserite structure was investigated by Gossner (1928) and re-examined by Fischmeister (1962) from the standpoint of cation disorder. One large cation coordination polyhedron (Fig. 2a) consists of a 12-coordinated trigonal antiprism with six additional meridional anions in hexagonal outline, with ideal point symmetry $\bar{3}2/m$. It is identical to the idealized polyhedron discussed by Moore and Araki (1972) about the Ca(1) cation in merwinite. The second large cation coordination polyhedron involves, when idealized, 10 nearest anions which possess $3m$ trigonal symmetry (Fig. 2b). Again, six anions are situated on the vertices of a meridional hexagon, three above share the tetrahedral base and one below the tetrahedral apex. This polyhedron corresponds to the ideals found for the Ca(2) and Ca(3) coordination polyhedra in merwinite. The remaining polyhedron, of point symmetry $\bar{3}2/m$, is a trigonal antiprism, whose ideal is the octahedron. This corresponds to the Mg coordination polyhedron in merwinite. In glaserite, Gossner (1928) ascribes K to this polyhedron, which has been documented by Wyckoff (1965), but it is more likely that Na belongs to this site with the K cations in the 12-coordinated site.

Several geometrical games can be played with the glaserite structure type. If the trigonal antiprism of the 12-coordinated polyhedron is idealized to an octahedron and defined with an edge equal to the tetrahedral edge, the hexagonal close-packed network in Figure 3a results. Geometrically, the apices of the tetrahedra are at the same heights as those of the octahedra, so become second nearest neighbors, and the true coordination number of the central large cation is reduced to 6. In actuality, the ionic radii of the K^+ and S^{6+} cations are propitiously related to assure a close approximation to 12-coordination by oxygens. This is demonstrated by construction in Figure 4. From the ionic radii tables of Shannon and Prewitt (1969), an ideal KO_6 octahedron is constructed
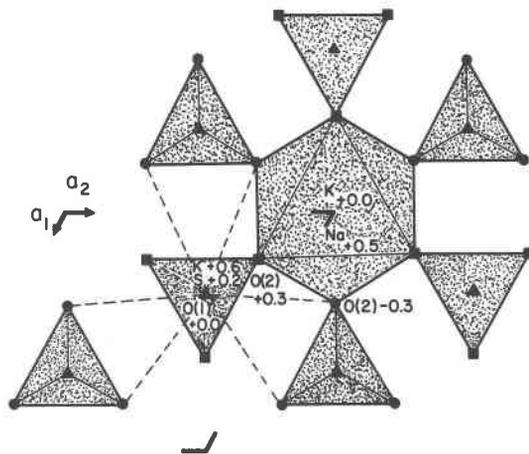
FIG. 1. Polyhedral diagram of the glaserite atomic arrangement. The central trigonal antiprism and six circumjacent tetrahedra are stippled. The KO_{10} arrangement is shown as a spoke diagram.

using $r_{K^+} = 1.38$ Å and $r_{O^{2-}} = 1.40$ Å. This results in an ideal octahedral edge distance, $l = 3.93$ Å. For a regular octahedron, the altitude, h, normal to opposing faces would be $(l/2) \tan 60° \sin 70° 32' = 0.825\, l$. Thus, $h = 3.24$ Å. Now, define the tetrahedral edge =
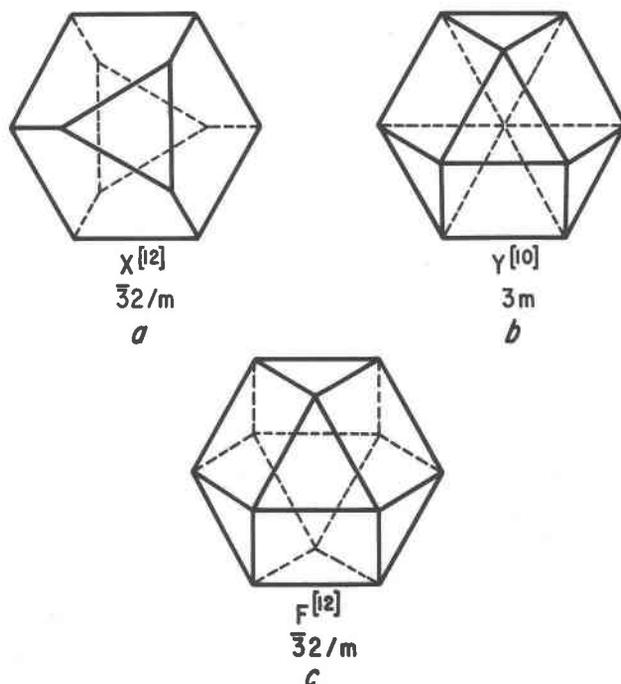
FIG. 2. Three large cation coordination polyhedra. a. $X^{[12]}$, consisting of trigonal antiprism (triangles) and six meridional anions. b. $Y^{[10]}$, which occurs above and below tetrahedra. c. $F^{[12]}$, the cuboctahedron.
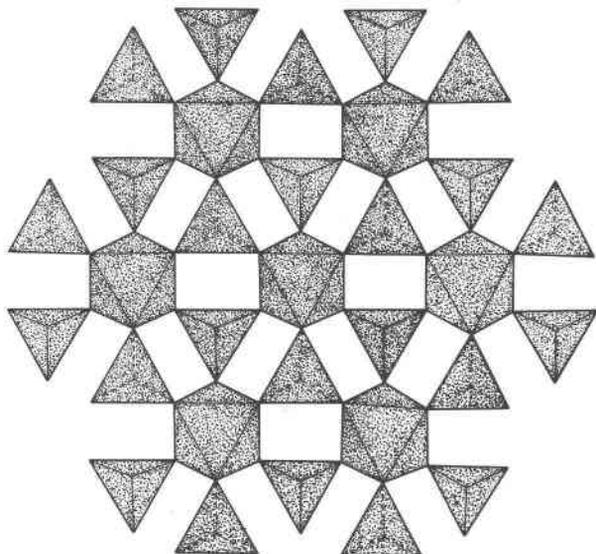
FIG. 3a. Condensation of trigonal antiprisms and circumjacent tetrahedra to form the sheet of $X^{[12]}$ polyhedra.
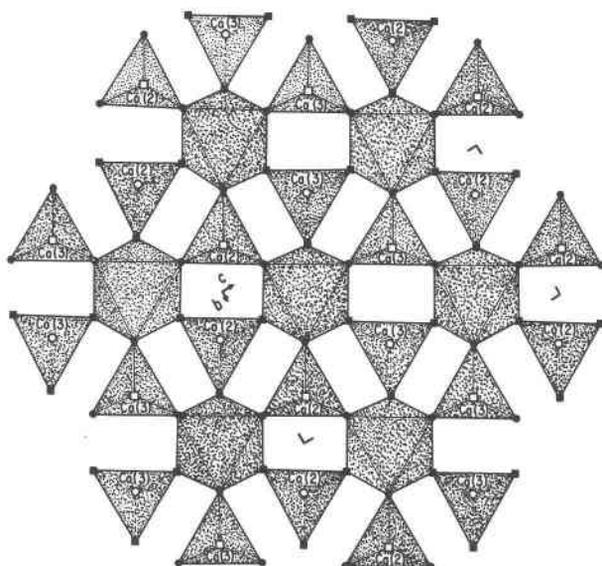
FIG. 3b. Condensation of trigonal antiprisms (=octahedra) and tetrahedra to form the sheet of MgO_6 octahedra and SiO_4 tetrahedra in merwinite. The merwinite cell is outlined.

$l/2$; this results in the six circumjacent tetrahedral apices around the central octahedron situated in the plane of the large cation at the octahedral center. Define the distance from the octahedral center to its vertex = L. The distance from the octahedral center to the tetrahedral apex in the plane would be $L' = (\sqrt{2}/\sqrt{3})L + (\sqrt{2}/\sqrt{6})L = 1.063L$. It is clear

that this ideal model closely approximates the 12–coordinated polyhedron, where the meridional distances are only slightly longer than the apical octahedral distances.

In the actual glaserite structure, the KO_{12} polyhedron is significantly distorted, such that the "octahedral" component is elongated to a trigonal antiprism. Such an arrangement can be appreciated in Figure 1, where the approximate O(2) coordinates would lead to an estimated altitude $h \sim 0.600 \times 7.3$ Å = 4.4 Å, a very significant dilation from the 3.2 Å altitude computed on the basis of ionic radii and the ideal octahedron. This accommodates the geometrical problem encountered in Figure 4. A tetrahedron whose edge is only half that of the ideal octahedron would be too small for the O—O' tetrahedral interatomic distance which would be 3.93 /2 = 1.96 Å. The actual tetrahedral edge is approximately 20 percent larger than the geometrical construction and contributes to further dilation of the ideal "octahedron" into an elongate trigonal antiprism.

The pinwheel. The key to the relationship of glaserite with the other structures discussed herein is the disposition of the tetrahedra about the octahedral
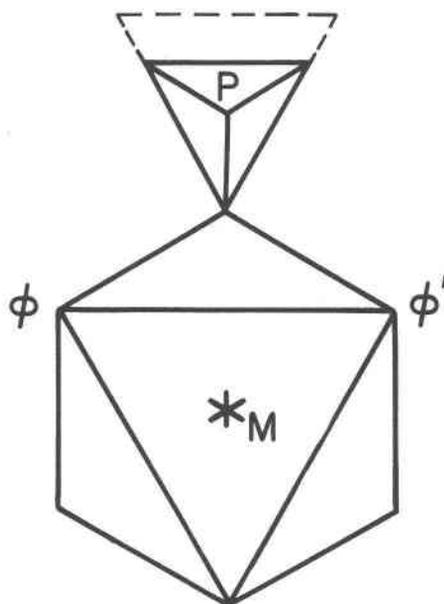
FIG. 4. Construction of MO_6 trigonal antiprism (=octahedron) and one of the circumjacent tetrahedra where the tetrahedral edge is half the octahedral edge. ϕ are the octahedral vertices, P the tetrahedral apex. The dashed line approximates the [SO_4] tetrahedron when M = K^+.

component of the KO_{12} polyhedron. This grouping, featured in Figure 5a, defines a cluster with point symmetry $\bar{3}2/m$ and I shall refer to it as the "pinwheel". Condensation of such pinwheels leads to the diagram in Figure 3a. We have encountered the complement of this pinwheel in the close–packed slab of the merwinite structure, where six SiO_4 tetrahedra are grouped around the MgO_6 octahedron as depicted in Figure 5b. Condensation of this pinwheel leads to the hexagonal close–packed sheet in Figure 3b. Such an arrangement is complementary to the glaserite arrangement since the six tetrahedral vertices are as far removed as possible from the octahedral core and cannot be associated in the inner coordination sphere. To derive and describe the other structures in this paper, we shall engage in a topological exercise utilizing bracelet theory.

The Pinwheel Bracelets

There does not appear to be a strict mathematical definition for the term "bracelet," but Gardner (1969) applies the term to a cyclic chain involving symbols which shall be manipulated in a combinatorial way. Thus, a bracelet is defined as a cyclic collection of n-beads or nodes involving m symbols where $m < n$. It is also to be noted that the bracelets may possess the property of complementarity, that is, where the interchange of symbols for some m leads to further solutions.[1]

The pinwheel grouping is reduced to a bracelet problem in the following manner. In any pinwheel, tetrahedral apices point either up (u) or down (d). Thus, the symbols are distributed at the nodal points of an octahedron and the possible combinations, including complements, are derived. We set $n = 6$ and $m = 2$. The complements in this case are derived by a $60°$ rotation of the symbols in their proper order. The solutions are $6u = 1$; $5u + 1d = 2$; $4u + 2d = 4$; $3u + 3d = 6$, with 13 possible arrangements in all. These arrangements are depicted in Figure 6. They are symbolized by the combination $(u + d)_r$, where $(u + d)_{r'}$ indicates its complement.

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[1] Some definitions are in order. Depending on their utility, nodes may represent vertices of a polyhedron, the center of a polyhedron, *etc.* Connections between nodes are branches (for example, edges of a polyhedron). If nodes and branches are connected such that tracing a path without retracing one's steps leads to the starting point then the chain of nodes and branches is cyclic and constitutes a loop. In this study, each node has a symbol ascribed to it (in this case, either "u" or "d").
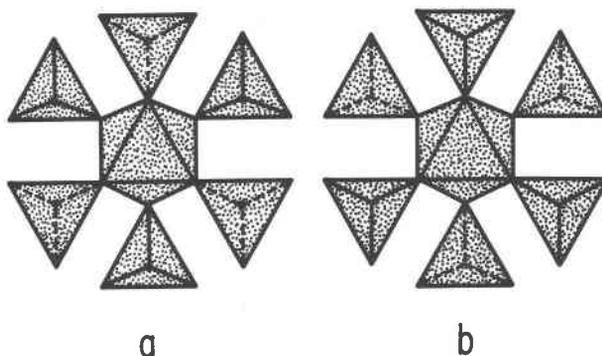
FIG. 5. a. Pinwheel for the $X^{[12]}$ cation in glaserite. b. Pinwheel for the $Mg^{[6]}$ octahedron in merwinite.

Now, the geometrical restriction is imposed on the pinwheels thus derived. We consider only those tetrahedral altitudes which conform to the glaserite model, that is, the height of the tetrahedron from base to opposing vertex is exactly half the height of the trigonal antiprism. Thus, associated with each bracelet configuration in Figure 6 are tetrahedral apical positions which may potentially be coordinated to the central large cation. For convenience of visualization, potentially coordinating apical positions are drawn as bold disks.

It is necessary to discuss complementarity of the bracelets in terms of the glaserite structure. As Figure 1 reveals, the repeat distance normal to the hexagonal outline is the repeat of the pinwheel and its complement above. In the ideal construction, the central large cation at level $z = 0$ possesses a bracelet whose complement corresponds to the ideal coordination of the central large cation at $z = 1/2$. Thus, for any specified bracelet and its associated pinwheel, the complementary pinwheel occurs above and specification of any one leads to the other. It is also worthy to note that $(4 + 2)_a$ and $(4 + 2)_b$ each possesses a self-complement, where the central large cations at both levels would possess the same ideal configuration. The remaining large cations situated above and below the tetrahedron are automatically defined: in the ideal arrangement, they coordinate to six oxygens associated with the trigonal antiprism, to the three oxygens of the tetrahedral base, and to the tetrahedral vertex, resulting in an ideal coordination number of 10.

Discussion of the Structures

The pinwheels derived from the bracelets can now be used as modules for constructing hypothetical structures. Such an approach is reminiscent of the

(5+1)a   (4+2)c   (3+3)b

(5+1)a′   (4+2)c′   (3+3)b′

(4+2)a =(4+2)a′   (3+3)a   (3+3)c

(4+2)b =(4+2)b′   (3+3)a′   (3+3)c′

(6+0)a
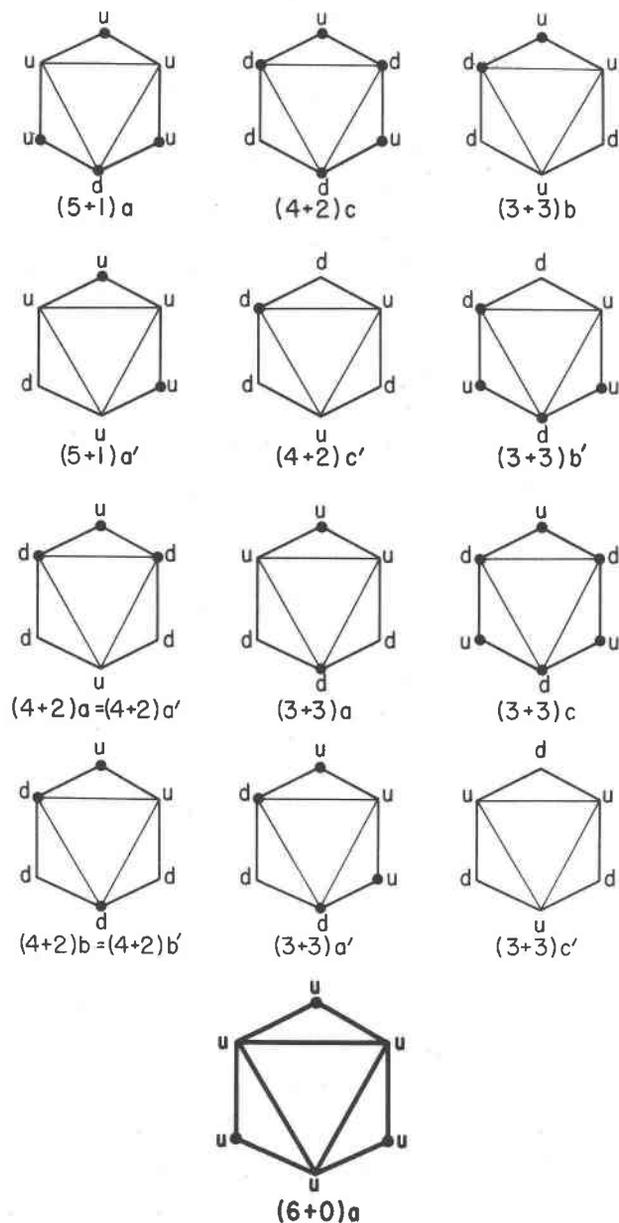
FIG. 6. The thirteen distinct bracelets involving six nodes and two symbols distributed over trigonal antiprismatic vertices. Solid disks represent tetrahedral apices coordinating to the central large cation.

study of Smith and Rinaldi (1962) who generated cells based on parallel 4- and 8-membered tetrahedral loops, and used these solutions to clarify the geometrical ideals of the feldspars, harmotome and paracelsian structures.

Despite the fact that 13 distinct pinwheels exist, the possible combinations in periodic arrays appear to be quite limited. This derives from the symbols
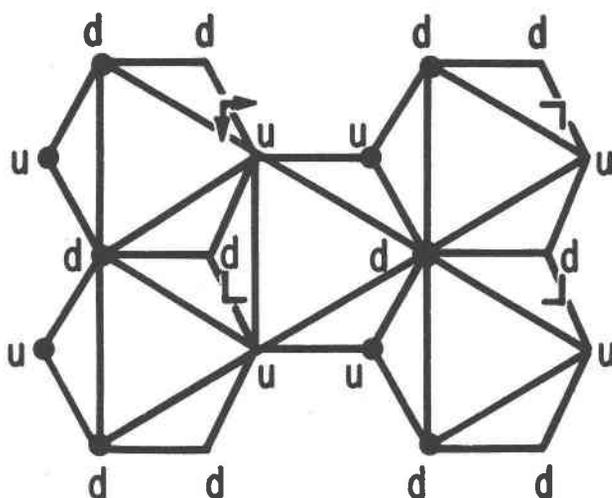
FIG. 7. Condensation of the $(4 + 2)a = (4 + 2)a'$ bracelets to form a periodic array.

initially used when the first pinwheel is constructed, which limit to some extent the symbols permissible for the adjacent bracelets. Some modules, such as $(3 + 3)_c$ and $(4 + 2)_a$, lead to simple arrangements with small cells, others do not. For example, $(3 + 3)_a$ must always be used in combination with some other bracelet at the same level to generate a repeating pattern.

It is only necessary to specify the connection of bracelets corresponding to one level along the pinwheel repeat axis. This is clear since the complementary solution at $z + 1/2$ is automatically defined and that the remaining large cation sites above
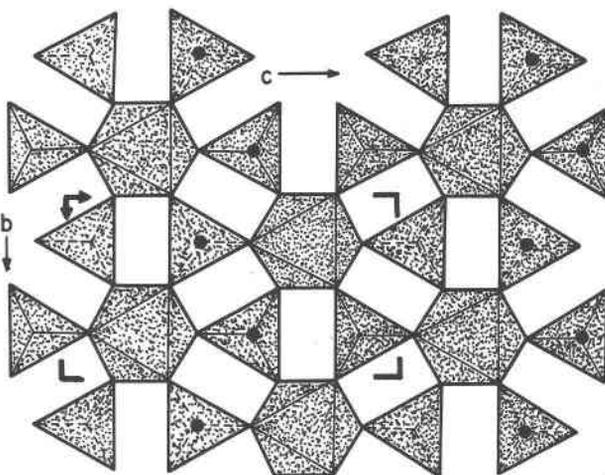
FIG. 8. Condensation of pinwheels corresponding to Figure 7.

and below the tetrahedra are dictated by the orientations of those tetrahedra.

Consider the bracelet $(4 + 2)_a$ which has a self-complement. Figure 7 reveals that the condensation of the bracelets of the same kind corresponds to the nodal points of the hexagonal tessellation. The symbols around any hexagon are identical to any other hexagon within the repeat unit. This solution appears in Figure 8. It has formula unit $4M_2[TO_4]$ and possesses the space group *Pnma* for the geometrical ideal. In the inorganic world, it corresponds to the atomic arrangement of room temperature $K_2[SO_4]$.

Glaserite. The glaserite structure is derived from the bracelet $(3 + 3)_c$ and possesses ideal 12-coordination. Its complement above, $(3 + 3)_{c'}$, possesses a coordination polyhedron which is a trigonal antiprism. It is evident why the K atom was placed in the $(3 + 3)_c$ location and Na in $(3 + 3)_{c'}$, reversed from the inferred ordering scheme suggested by Gossner (1928).

The crystal cell criteria for glaserite, $KNaK_2[SO_4]_2$ are $a = 5.65$ and $c = 7.29$ A. This is compared with "silico-glaserite," α-$Ca_2[SiO_4]$, the high temperature calcium orthosilicate polymorph: Douglas (1952) reports $a = 5.46$ and $c = 6.76$ A.

Room temperature $K_2[SO_4]$ (β-$K_2[SO_4]$) and larnite (β-$Ca_2[SiO_4]$). The structure of room temperature $K_2[SO_4]$ (also called β-$K_2[SO_4]$) was determined by Robinson (1958); in addition, the isotypes $Cs_2[CrO_4]$ (Miller, 1938) and $K_2[CrO_4]$ (Zachariasen and Ziegler (1931)) were investigated from a structural standpoint. Wyckoff (1965) lists 47 compounds belonging to this structure type.

For β-$K_2[SO_4]$, the crystal cell criteria are $a = 7.46$, $b = 5.78$, $c = 10.08$ Å, space group *Pnma*, $Z = 4$. The a–direction is the pinwheel repeat and $b = 5.78 \sim c/\sqrt{3} = 5.82$ Å emphasizes the pseudo–hexagonal character of the x–axis projection. These values are to be compared with $a = 5.65$ and $c = 7.29$ Å reported by Gossner (1928) for glaserite.

The point symmetry of the $(4 + 2)_a$ pinwheel is m and the structure reported by Robinson (1958) is shown as a polyhedral diagram in Figure 9. The K atoms at the two levels are split away from the ideal pinwheel center, with K at $z = 0$ oriented in the direction *toward* the three oxygen atoms at tetrahedral apices. I also note that the pseudo-trigonal antiprism oxygens in that direction are *dilated* whereas those at the opposing vertices are *compressed*. This suggests an approximation of $6 + 3 = 9$-coordination.
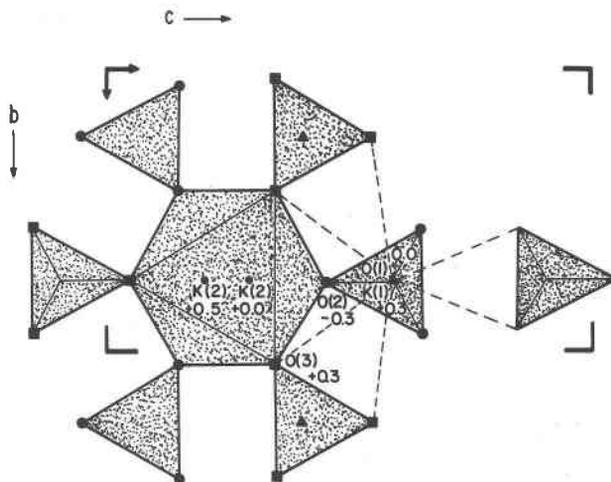
FIG. 9. Polyhedral diagram of the room temperature $K_2[SO_4]$ structure. Compare with Figure 8. The KO_{10} polyhedron $(= Y^{[10]})$ is shown as a spoke diagram.

Unfortunately, Robinson did not present complete interatomic distance data, but such information can be found for the structure of the $(NH_4)_2[WS_4]$ isotype reported by Sasvári (1963). The $(NH_4)^+$ cation grouped in the pinwheel possesses 9 nearest neighbor S atoms with N-S ranging from 3.10 to 3.58 A. The remaining (NH_4)-S polyhedron, which is situated above the tetrahedral base, possesses, as expected, 10-coordination with $N(1)$-S ranging from 3.47 to 3.96 A. The Sasvári article is also noteworthy in that it is one of the few in which an attempt has been made to discuss these structures on a more general basis.

The larnite, β-$Ca_2[SiO_4]$, structure was reported by Midgley (1952) as a distorted β-$K_2[SO_4]$ structure. The crystal cell parameters are $a = 5.48$, $b = 6.76$, $c = 9.28$ A, $\beta = 94°33'$, $P2_1/n$. The comparison with β-$K_2[SO_4]$ is evidently $a_1 = b_\beta$, $b_1 = a_\beta$, $c_1 = c_\beta$. The space group of larnite is the subgroup of *Pnma* in the proper orientation. Larnite is topologically equivalent to β-$K_2[SO_4]$ but is geometrically distorted in such a manner to violate the mirror plane of the ideal arrangement in Figure 8. The explanation appears to be a matter of compromise between *ideal* geometry (see Figure 4) and *actual* coordination number. The evidence appears in Midgley's interatomic distance tables. Ca(2), which is in the pinwheel, possesses only 8-coordination with Ca-O 2.36-2.80 A, and Ca(1) above the tetrahedral base possesses 6 inner coordination spheres ranging from 2.30-2.75 A and 6 outer co-
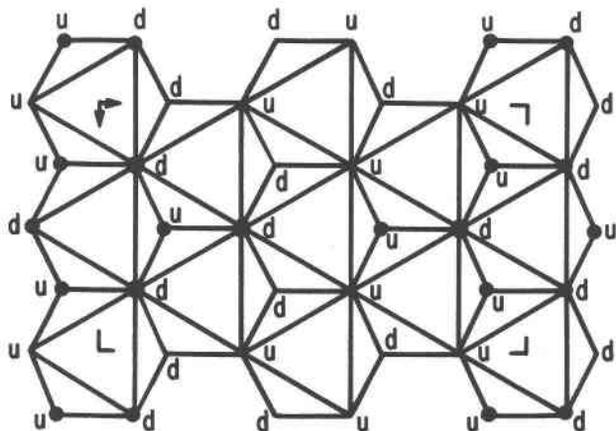
FIG. 10. Condensation of bracelets in Figure 6 which may correspond to the bredigite arrangement.

ordination spheres from 2.98-3.56 Å. It is clear from this discussion that the ideal arrangements are approximated in crystals only when an approach to the geometrical ideal in Figure 4 is evident. Briefly, controlling factors are the ionic radius ratio of the large cation to the small tetrahedrally coordinated cation, a point which shall be discussed in greater detail further on.

Bredigite (α_0'-Ca$_2$ [SiO$_4$]): An Attempt At Postulating Its Structure

Evidently, no three-dimensional solution of the bredigite atomic arrangement has been reported. This is not surprising in light of its large cell with fairly low symmetry. Douglas (1952) presented a detailed single crystal investigation on the compound, which is also called α_0'-Ca$_2$[SiO$_4$]. She reports $a = 10.93$, $b = 6.75$, $c = 18.41$ Å, space group
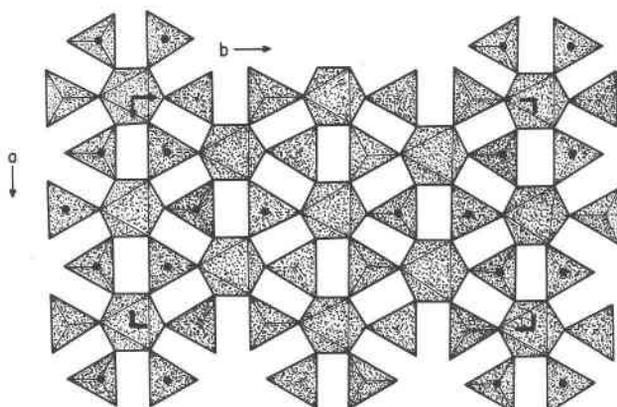
$Pmnn$, $Z = 16$. These values are essentially those of the "ideal" β-K$_2$[SO$_4$] equivalent of β-larnite, but with doubled a and c axes. It is clear that the pinwheel repeat direction is the b-axis. Douglas' study appears to be a careful investigation and she points out the cell relationship with β-K$_2$[SO$_4$]. In addition, she notes that the intensity distribution indicates a centrosymmetric crystal.

A structure for bredigite is postulated which is consistent with the cell criteria of Douglas and which is derived directly from the bracelet combination which allows $Pmnn$ symmetry. Figure 10 is a condensation diagram of the bracelets which lead to ideal symmetry $Pmnn$, and Figure 11 is the corresponding condensation of pinwheels which effectively is an idealized model of the proposed structure. It is made up of 2Ca in the bracelet $(3 + 3)_a$, 2 Ca in $(3 + 3)_{a'}$, 2Ca in $(3 + 3)_c$, 2Ca in $(3 + 3)_{c'}$ and 8 Ca in $(4 + 2)_a$. Figure 6 reveals that the ideal coordination numbers would be 8, 10, 12, 6, and 9 respectively. This would suggest a bredigite composition Ca$_{28}M_2M_2'$[TO$_4$]$_{16}$ where M and M' are smaller "impurity" cations of maximum coordination numbers 6 and 8, respectively. This would suggest a solid solution range of Mg^{2+} for Ca^{2+} between (Ca$_{1.75}$Mg$_{0.25}$) and (Ca$_{1.88}$Mg$_{0.12}$), where the upper bound is Mg^{2+} in the $(3 + 3)_{c'}$ environment. This range is close to compositions of synthetic bredigite reviewed by Biggar (1971). The remaining 16 Ca are in the positions above and below the tetrahedra and are automatically defined from the bracelets specified beforehand. Their coordination numbers average 10.

No assertion is made that this is the correct structure for bredigite; the actual structure can only be revealed through careful three-dimensional crystal structure analysis. I only wish to emphasize that an

FIG. 11. Condensation of pinwheels corresponding to Figure 10.

TABLE 1. ALKALI SULFATE STRUCTURES: FORMAL COMPOSITIONS

$T^{[4]}$ = tetrahedron
$M^{[6]}$ = octahedron
$X^{[n]}$ = nodes of $\bar{3}$ 2/m polyhedron
$Y^{[10]}$ = 3 m polyhedron
$F^{[n]}$ = nodes of cuboctahedron

glaserite	$X^{[12]}Y_2^{[10]}M^{[6]}[T^{[4]}O_4]_2$
merwinite (distortion)	$X^{[8]}Y^{[9]}Y^{[8]}M^{[6]}[T^{[4]}O_4]_2$
β-K$_2$SO$_4$	$X^{[9]}Y^{[10]}[T^{[4]}O_4]$
larnite (distortion)	$X^{[6]}Y^{[8]}T^{[4]}O_4$
palmierite	$X^{[12]}Y_2^{[10]}[T^{[4]}O_4]_2$
kalsilite	$F^{[9]}T^{[4]}[T^{[4]}O_4]$

arrangement with *Pmnn* symmetry can be retrieved in the same manner that the ideal *Pnma* arrangement for β-$K_2[SO_4]$ was retrieved with no prior knowledge of its crystal structure. Because of obvious structural relationships among these compounds, particularly evident in projection down the axis normal to the pseudo-hexagonal outline where electron densities would be similar, careful three-dimensional analysis is the only good tool for ascertaining the true arrangement.

Additional Structure Types With Pinwheels

The idealized coordination polyhedra encountered in this study includes the pinwheel polyhedron whose coordination number is at least 6 (the octahedron) and whose possible maximum is 12, when all meridional oxygens are present. It is symbolized as $X^{[n]}$ where $6 < n \leq 12$; for $n = 6$, the resulting octahedron is symbolized as M. The second polyhedron with ideal point symmetry $3m$ is ideally 10-coordinated and shall be symbolized as $Y^{[10]}$. The third polyhedron is the tetrahedron, symbolized as T. Table 1 summarizes the compositions and structures considered in this study; I emphasize that the coordination numbers refer to the *ideal* model and actual crystals may show true coordination numbers which are lower on account of distortion.

Many compounds in the literature have compositions suggesting ordered derivatives of the simpler structure types. For example, among the 47 compounds listed by Wyckoff (1965) representing the β-$K_2[SO_4]$ structure type, are compositions like $KBa[PO_4]$, $KCa[PO_4]$, $NaCa[PO_4]$(low), *etc.* It is instructive to inquire how the alkali and alkali-earth cations are distributed. According to Table 1, the general formula can be written $X^{[9]}Y^{[10]}[TO_4]$ where 9-coordination for X is the ideal number for the $(4 + 2)_a$ pinwheel. Struck and White (1962), in their structure analysis of $KBa[PO_4]$, have established $X = $ Ba and $Y = $ K. Although a structure analysis of $KCa[PO_4]$ has not been done, it is reasonable to assume that $X = $ Ca. We shall note throughout this discussion that the *smaller* cations tend toward the X positions and the *larger* cations toward the Y positions.

Several other structure types are particularly intriguing and are now discussed. Although they do not fall within the restrictions of the structures based on the condensation of pinwheels, similar if not identical coordination polyhedra prevail in their arrangements.
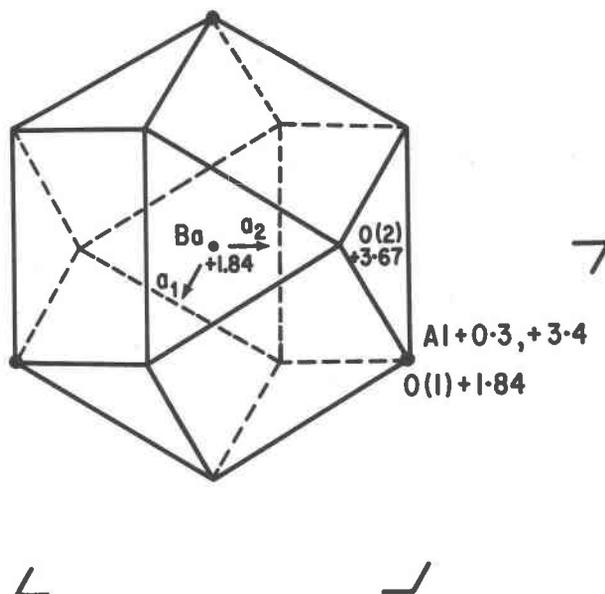
FIG. 12. Coordination polyhedron associated with Ba in $Ba[Al_2O_4]$. Solid disks represent meridional oxygens which coordinate to the central Ba atom. Note that three meridional positions which would complete the cuboctahedron are missing.

The $K[LiSO_4]$ structure type. Some confusion exists in the literature regarding this structure type. Bradley (1925) approximately solved the structure and the polar character of the crystals was well–established. The structure reveals the tetrahedral pinwheel $(6 + O)_a$ and its self-complement. Such an arrangement possesses ideal 9–coordination. In this arrangement, the meridional oxygens are rotated away from the trigonal antiprism. The Li atoms occur in tetrahedral coordination, defining a $[LiSO_4]^{1-}$ tetrahedral framework with space group $P6_3$. When the tetrahedral atoms are identical, the $Ba[Al_2O_4]$ structure results, with space group $P6_322$. Figure 12 presents the disposition of circumjacent oxygen atoms around the central barium atom. In this arrangement, the meridional oxygens are rotated exactly 30° away from the trigonal antiprism. This defines nine of the twelve vertices of a polyhedron, symbolized $F^{[12]}$, featured in Figure 2c. It is ideally the cuboctahedron, an Archimedean solid with 12 vertices, 24 edges and 14 faces, and is a frequent coordination polyhedron in alloy and metal structures when the central atom and its coordinating atoms have similar crystal radii. In addition, it is the coordination polyhedron of an anion with respect to its nearest neighbor anions in ideal cubic close-packing. Movement from the $X^{[n]}$ polyhedron to the $F^{[n]}$ polyhedron is geometrically continuous even though the polydehra

PALMIERITE

$-20.8-$ $\longleftarrow$ Pb $X^{[12]}$

$-16.5-$ $\longleftarrow$ K $Y^{[10]}$

$-12.4-$ $\longleftarrow$ S $T^{[4]}$

C_h

$-8.4-$ $\longleftarrow$ S $T^{[4]}$

$-4.3-$ $\longleftarrow$ K $Y^{[10]}$

$-0.0-$ $\longleftarrow$ Pb $X^{[12]}$
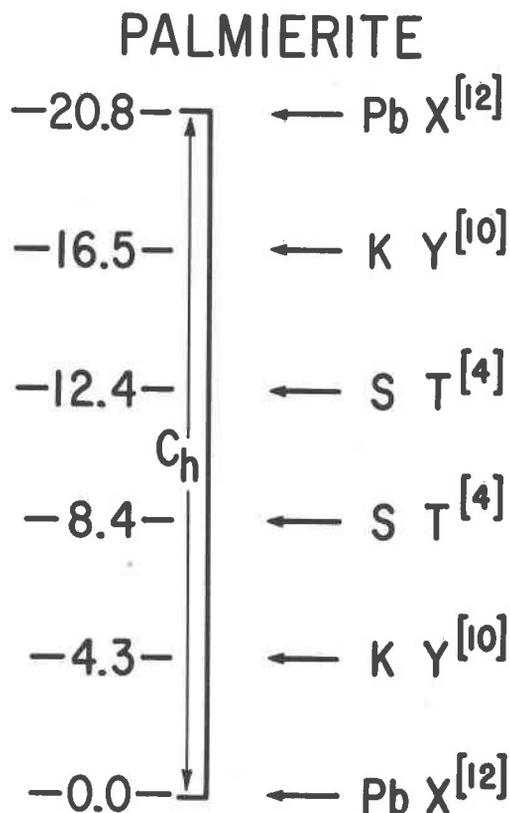
FIG. 13. Stacking sequence in the palmierite arrangement. Heights are given as Ångström units.

are not topologically identical since the former is 3–connected and the latter is 4–connected. This movement is facilitated by rotation of the tetrahedra in the pinwheel about their trigonal axes. Kalsilite, $K[AlSiO_4]$ possesses the $K[LiSO_4]$ structure but oxygen disorder occurs in the structure (Perrotta and Smith, 1965). Wyckoff (1965, p. 113) lists 15 compounds which may possess the $K(LiSO_4)$ structure but it appears more likely that they actually belong to the aphthitalite structure type $(P\bar{3}m1)$ since the "T" atoms are large cations such as Ca^{2+}, Ba^{2+}, K^+ and Na^+.

The palmierite, $K_2Pb[SO_4]_2$ structure type. About 10 compounds crystallize in the palmierite structure type, most notably the alkaline earth ortho–phosphates. This arrangement crystallizes in space group $R\bar{3}m$ and differs from the other structures since the pinwheel and its complement no longer make up the c–axis repeat. As Figure 13 reveals, the sequence along the c_h-axis involves $\cdots X^{[12]}$—$Y^{[10]}$—T—T—$Y^{[10]} \cdots$. The Pb $= X$ cation corresponds to the

$(3 + 3)_e$ pinwheel found in glaserite. The K atoms reside in the Y position with actual point symmetry $3m$. This is yet another example where ordering of different cations leads to site preference of the larger cation in the YO_{10} polyhedron.

The merwinite structure: its topological identity with glaserite. Moore and Araki (1972) have presented an extensive discussion on the geometry of the merwinite ($Ca_3Mg[SiO_4]_2$, $a = 13.25$, $b = 5.29$, $c = 9.33$ Å, $\beta = 91.90°$, $P2_1/a$, $Z = 4$) structure and pointed out its profound pseudo-hexagonal character when idealized (*i.e.,* freed from geometrical distortions). Despite its complicated structure, the present study reveals that merwinite is a distorted equivalent of the glaserite structure, compared with the β-larnite structure as the distorted equivalent of the β-$K_2[SO_4]$ structure. The authors have shown that the geometrical ideal of merwinite can be written $X^{[12]}Y_2^{[10]}M[TO_4]_2$ which is identical to the general glaserite formula. In the actual structure, where X, $Y = Ca^{2+}$, $M = Mg^{2+}$ and $T = Si^{4+}$, the coordination numbers are closer to $X^{[8]}Y^{[9]}Y^{[8]}M[TO_4]_2$.

Figure 14 illustrates the relationship in the stacking of the cations for merwinite and glaserite along the (pseudo-) hexagonal axis. The correspondence in actual heights along the a-axis of merwinite and the c-axis of glaserite is apparent.

Although there is no evidence that a higher temperature polymorph of merwinite exists, it is logical to assume that if such a polymorph occurred, it would possess the glaserite arrangement, just as "silico-glaserite" is the high temperature polymorph of β-larnite. Although Wyckoff (1965) classifies high-$K_2[SO_4]$ and high-$Na_2[SO_4]$ with the $K[LiSO_4]$ structure type, there is no evidence supporting this classification. More logical would be their classification with the aphthitalite (glaserite) arrangement. A self-consistent relationship between the alkali sulfate and calcium orthosilicate structures is evident: at low temperatures, the olivine structure type exists; at intermediate temperatures, the β-$K_2[SO_4]$ structure and its geometrical distortions; and at high temperature the glaserite arrangement prevails. It is noted that the proposed structure of bredigite shares aspects of its structure with both β-$K_2[SO_4]$ and glaserite arrangements and may represent a field of structural transition where properties of both low and high temperature polymorphs are present.
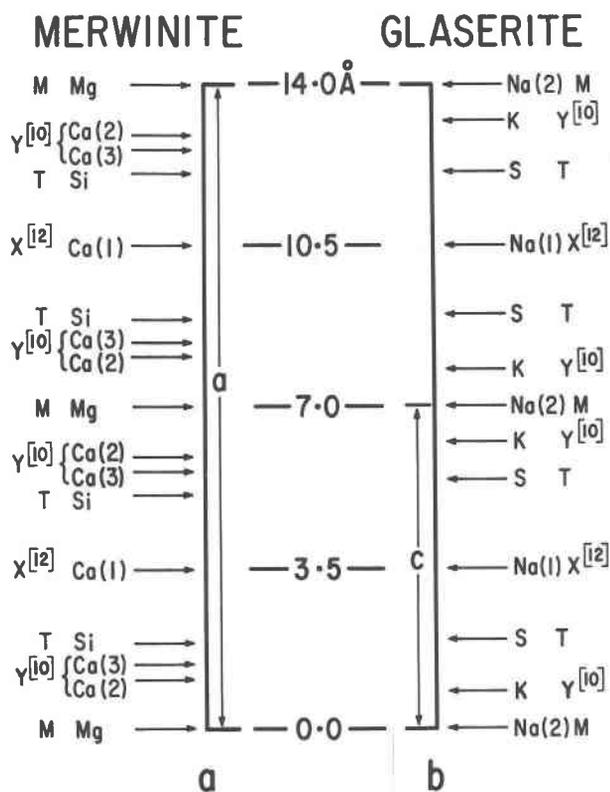
FIG. 14. Comparison of stacking sequences between (a) merwinite and (b) glaserite.

Coordination Number and Structure

For an ideal arrangement, if a pinwheel has coordination number $X^{[12-p]}$, where $0 \leqq p \leqq 6$, then its complement has coordination number $X^{[6+p]}$. Pinwheel and complement average to mean coordination number $X^{[9]}$. This is the *maximum* average coordination number for the X polyhedra in glaserite-derivative structures; the actual structures on account of geometrical distortion may possess average coordination number less than this value.

For mixed cations where the differences in ionic radii are considerable (such as Ca^{2+} and Mg^{2+} or K^+ and Na^+), p will tend toward 0 for the larger cation oxygen coordination and the smaller cation will be accommodated in its complementary polyhedron. But it is more difficult to propose an ordering scheme between the $X^{[n]}$ and $Y^{[10]}$ polyhedra. Geometrically, the two polyhedra are similar and the coordination number of Y will tend toward a higher value than n for most structures discussed in this study. A further controlling factor appears to be the cation-cation repulsion effect. It is noted that

the Y polyhedron shares a face with the small highly charged tetrahedral group but the X polyhedron shares faces only with similar large polyhedra of relatively low central positive charge. Even in palmierite, the X polyhedra are shielded from the tetrahedra by the intervening Y polyhedra. Thus, cation-cation repulsions between the T and Y polyhedra are particularly violent and can be minimized in two ways: in the case of cations of same charge but different ionic radius, the larger cation will tend toward the Y polyhedron; and for cations of different charge but similar ionic radius, that cation of lower charge will tend toward the Y polyhedron. Thus, for $KBa[PO_4]$ and $K_2Pb[SO_4]_2$, the K atoms are located in the Y polyhedra. Likewise, in the aphthitalite structure, the larger K^+ cations are located in the Y polyhedra.

Several trends are advanced on the basis of foregoing discussions:

1. For distributions over the X polyhedra for structures involving cations of different crystal radii in $X^{[12-p]}$, p will tend toward 0 for the large cation and will tend toward 6 for the small cation in the complementary pinwheel.

2. For distribution between X and Y, the lower charged cation among cations of similar crystal radius will tend toward the Y polyhedron.

3. For distribution between X and Y, the cation of larger radius among cations of same charge will tend toward the Y polyhedron.

It is worthwhile to note that one of the problems in the study of high temperature polymorphs, especially the $Ca_2[SiO_4]$ structures, is the inversion of such structures upon quenching. Investigators, especially in the cement and blast furnace industries, have empirically observed that the presence of "impurity atoms" can stabilize high temperature $Ca_2[SiO_4]$ structures. Especially good cations for this purpose are Na^+, Mg^{2+}, Sr^{2+} and Ba^{2+}. The explanation for the stabilizing influence of these cations appears straightforward. In structures, where p differs considerably between a pinwheel and its complement, larger cations will order over the sites of low p and the smaller cations over sites of high p. Likewise, in structures where a pinwheel and its complement are identical, ordering will occur between the X and Y polyhedra. Arguing from the opposite direction, it should be possible to select just the right cations to assure the stability of that structure. This emphasizes the pressing need for more accurate refinements of the crystal structures of the

various polymorphs with especial emphasis on the site preferences of the "impurity" cations.

Addendum

During construction of this manuscript while in Australia, I corresponded with Dr Walter Eysel concerning crystals of calcium orthosilicates. He informed me of his studies on $A_2[BX_4]$ and $A_2[BX_3]$ compounds. Upon my return, Dr. Eysel kindly presented me with his doctoral dissertation (Eysel, 1968), which is an extensive study on glaserite and other alkali sulfate compounds, and many of his tabulations on refined cell parameters constitute new information. His study appears to be the most exhaustive review on the $A_2[BX_4]$ and $A_2[BX_3]$ compounds to date. My approach to this problem appears unique and with little duplication of the Eysel study. Accordingly, I submitted this manuscript with but minor alteration and urge interested readers to the outstanding study of Dr. Eysel as well.

Acknowledgments

References

BELLANCA, A. (1943) Sulla struttura dell'aftitalite. *Period. Mineral.* **14**, 1–29.

BIGGAR, G. M. (1971) Phase relationships of bredigite ($Ca_5MgSi_3O_{12}$) and of the quaternary compound ($Ca_6MgAl_8SiO_{21}$) in the system $CaO–MgO–Al_2O_3–SiO_2$. *Cement Concrete Res.* **1**, 493–513.

BRADLEY, A. J. (1925) The crystal structure of lithium potassium sulfate. *Phil. Mag.* **49**, 1225–1237.

DOUGLAS, A. M. B. (1952) X-ray investigation of bredigite. *Mineral. Mag.* **29**, 875–884.

EYSEL, W. (1968) *Kristallchemie Polymorphie und Mischkristallbildung von Silikaten und Germanaten der Verbindungstypur A_2BO_4 und A_3BO_5.* Ph.D. Thesis, Technische Hochschule Aachen.

FISCHMEISTER, H. F. (1962) Röntgenkristallographische Ausdehnungsmessungen an einigen Alkalisulfaten. *Monatsh. Chem.* **93**, 420–434.

GARDNER, M. (1969) Mathematical games: Boolean algebra, Venn diagrams and the propositional calculus. *Sci. Amer.* **220**, 113–114.

GOSSNER, B. (1928) Ueber die Kristallstruktur von Glaserit und Kaliumsulfat. *Neues Jahrb. Mineral. Abt. A Beilage-Band,* **57**, 89–116.

MIDGLEY, C. M. (1952) The crystal structure of β–dicalcium silicate. *Acta Crystallogr.* **5**, 307–312.

MILLER, J. J. (1938) The crystal structure of caesium chromate, Cs_2CrO_4. *Z. Kristallogr.* **99**, 32–37.

MOORE, P. B., AND T. ARAKI (1972) Atomic arrangement of merwinite, $Ca_3Mg[SiO_4]_2$, an unusual dense-packed structure of geophysical interest. *Amer. Mineral.* **57**, 1355–1374.

PERROTTA, A. J., AND J. V. SMITH (1965) The crystal structure of kalsilite, $KAlSiO_4$. *Mineral. Mag.* **35**, 588–595.

ROBINSON, M. T. (1958) The crystal structures of β–K_2SO_4 and of β–K_2PO_3F. *J. Phys. Chem.* **62**, 925–928.

SASVÁRI, K. (1963) The crystal structure of ammonium thiotungstate $(NH_4)_2WS_4$. *Acta Crystallogr.* **16**, 719–724.

SHANNON, R. D., AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.* **B25**, 925–946.

SMITH, J. V., AND F. RINALDI (1962) Framework structures formed from parallel four- and eight-membered rings. *Mineral. Mag.* **33**, 202–212.

STRUCK, C. W., AND J. G. WHITE (1962) The unit cell dimensions and crystal structure of $KBaPO_4$. *Acta Crystallogr.* **15**, 290–291.

WYCKOFF, R. W. G. (1965) *Crystal Structures, Vol. 3, 2nd ed.* John Wiley and Sons, New York. pp. 91–116.

ZACHARIASEN, W. H., AND G. E. ZIEGLER (1931) The crystal structure of potassium chromate, K_2CrO_4. *Z. Kristallogr.* **80**, 164–173.