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MODULAR MINERALOGY IN THE CUSPIDINE GROUP OF MINERALS

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ABSTRACT

The crystal structures of the minerals in the cuspidine–wöhlerite–låvenite group can be described in terms of two kinds of modules whose connections form the structures of the various phases: "octahedral walls" four columns wide and running along *c*, and diorthosilicate groups. The octahedral walls are interconnected by corner sharing to create a framework that is the common feature in all the structures of the family. There are various ways to distribute the Si_2O_7 units, which serve to strengthen the framework. Ten different structure-types were derived, within fixed cell dimensions ($a \approx b \approx 10.5$ Å, $c \approx 7.3$ Å). One of these structure-types, with topological symmetry $P2_1/a$, is shown by cuspidine and låvenite, both with space-group symmetry $P2_1/a$, as well as by niocalite, in which the space-group symmetry is lowered to Pa by the ordering of the octahedral cations. Another structure-type, with topological symmetry $P2_1$, is shown by wöhlerite. The enumeration of the possible structure-types was successfully applied to determine the unknown structures of other natural phases in the group: hiortdahlite I and II, baghdadite, and a natural phase from the Burpala Massif, USSR. The disorder phenomena commonly occurring in these minerals, such as domain structure, micro-scale twinning, and stacking faults, can be interpreted on the basis of the "modular" structure.

Keywords: cuspidine group, modular mineralogy, diorthosilicate groups, wöhlerite, låvenite, hiortdahlite I and II.

SOMMAIRE

La structure cristalline des membres de la famille cuspidine - wöhlerite - låvenite peut s'exprimer par deux sortes de modules, dont les connexions définissent la structure des diverses espèces: des "parois octaédriques" d'une largeur de quatre colonnes parallèles à *c*, et des groupements diorthosilicatés. Les parois octaédriques sont interliées par partage d'arêtes, ce qui crée le réseau commun à la structure des membres de cette famille. Il y a plusieurs façons d'agencer les unités Si_2O_7, qui servent à renforcir le réseau. Dix structures différentes ont été dérivées, ayant toutes des paramètres réticulaires fixes ($a \approx b \approx 10.5$ Å, $c \approx 7.3$ Å). Une de ces structures, de symétrie topologique $P2_1/a$, caractérise la cuspidine et la låvenite, qui partagent le groupe spatial $P2_1/a$, aussi bien que la niocalite, dont la symétrie du groupe spatial est réduite à Pa par la mise en ordre des cations des sites octaédriques. Une autre structure, ayant la symétrie topologique $P2_1$, est adoptée par la wöhlerite. Nous avons déterminé, par l'énumération des types de structures possibles, la nature des structures non connues d'autres exemples naturels de la famille, par exemple, hiortdahlite I et II, baghdadite, et une espèce naturelle du massif de Burpala, en URSS. Le désordre, phénomène répandu dans cette famille, implique une structure en domaines, des macles submicroscopiques, et des défauts d'empilement, que nous interprétons à la lumière d'une structure "modulaire".

(Traduit par la Rédaction)

Mots-clés: groupe de la cuspidine, minéralogie modulaire, groupements de diorthosilicates, wöhlerite, låvenite, hiortdahlite I et II.

INTRODUCTION

We were prompted to study the group of minerals related to cuspidine, låvenite, and wöhlerite by our investigations of guarinite, which was found on Vesuvius by Guiscardi (1857) and studied by Zambonini & Prior (1909). We found that the crystals of guarinite are characterized by the existence of various domains, a complete understanding of which can only be obtained once we have understood the structural relationships among the various phases in the cuspidine family. This family of minerals is structurally characterized by the presence of walls of octahedra, four columns wide, that run parallel to [001]. The walls are interconnected both directly by corner sharing, and through Si_2O_7 groups, each group being linked to three walls. Figure 1 gives a schematic representation of the structural features common to the whole group, as seen along the *c* axis, namely along the walls of octahedra.

The different minerals in the group display triclinic or monoclinic symmetry and can be described, in the simplest way, by the formula $X_{16}(Si_2O_7)_4(O,OH,F)_8$, where X denotes cations with various possible charges and radii, characterized by octahedral to roughly octahedral coordination. For example, cuspidine, with only calcium cations in octahedral coordination, has the chemical formula $Ca_{16}(Si_2O_7)_4F_8$, space group $P2_1/a$, *a* 10.906, *b* 10.521, *c* 7.518 Å, β 109.3° (Saburi *et al.* 1977).

The various minerals in the family differ according to the following basic features: 1) Structural feature: the diorthosilicate groups may be connected to the walls of octahedra in different ways. For example, the Si_2O_7 groups, indicated as A and F in

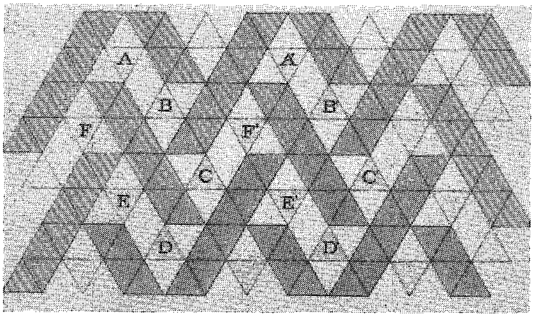


FIG. 1. Schematic polyhedral view along *c* of the structure of the minerals in cuspidine–låvenite group. Octahedral walls are shaded; diorthosilicate groups are lettered.

Figure 1 and linked to the same octahedral column, may be connected to the same octahedron or to succeeding octahedra. 2) Crystal-chemical feature: different cations, with different possible distributions, may be located in the octahedral sites.

The two features are in some way related to each other; we should expect, and in fact it was verified in all the structures so far determined for the members of this family, that the diorthosilicate groups are not linked to the edges of octahedra that contain relatively small cations, such as Zr^{4+}, Ti^{4+} and Nb^{5+} (Mellini & Merlino 1979, Mellini 1981, 1982). However, it is convenient to tackle the two features separately, and subsequently to take their relationships into account.

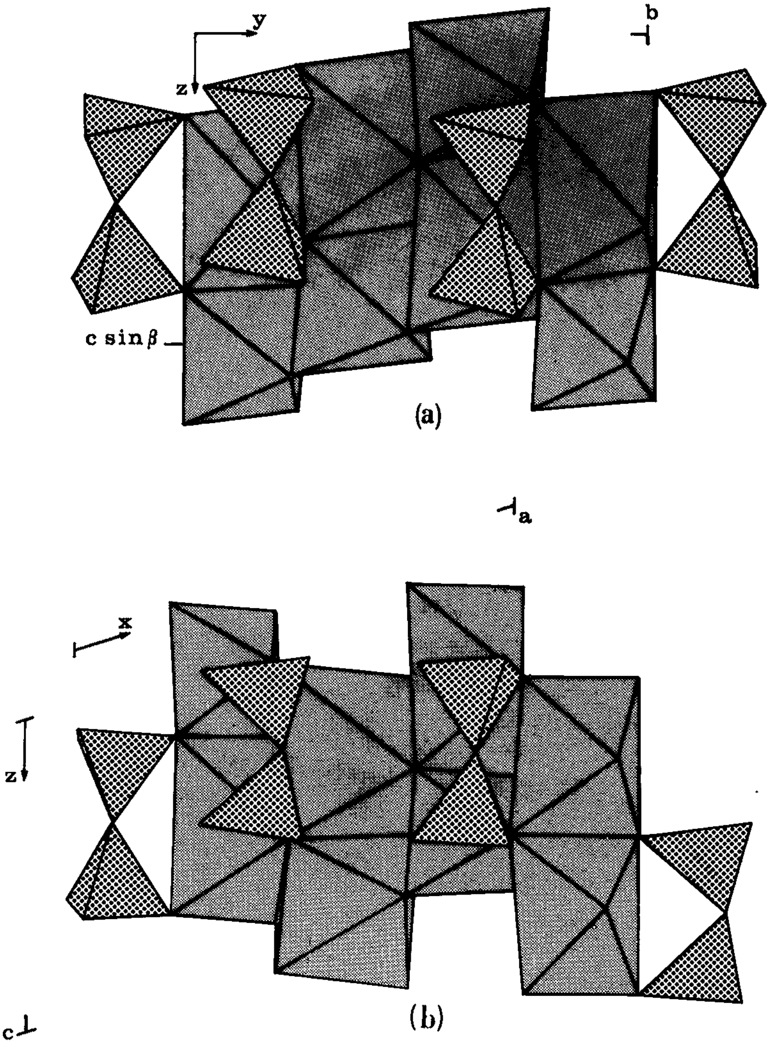


FIG. 2. Octahedral walls and clinging Si_2O_7 groups in låvenite (a) and wöhlerite (b).

The Ten Different Topologies

Figure 2a shows the wall of octahedra in the crystal structure of låvenite (Mellini 1981); Figure 2b shows the wall present in wöhlerite (Mellini & Merlino 1979). Comparison of the two structures shows that Si_2O_7 groups are connected to the walls in two different ways. Our aim is to determine all of the topologically distinct ways to make such connections within the framework of cell dimensions of 10 × 10 × 7.3 Å.

Figure 2 shows that Si_2O_7 groups linked to adjacent columns (for example the pairs *A–B* and *D–E* in Fig. 1) differ in height by *c*/4, whereas Si_2O_7 groups linked to the same column, on opposite sides of the wall (for example the pairs *A–F* and *C–D* in Fig. 1), are either located at the same height, as in Figure 2a, or differ in height by *c*/2, as in Figure 2b. These are the composition rules by which the two basic modules, namely Si_2O_7 groups and walls of octahedra, fit to each other to form the various possible patterns.

In what follows we shall indicate the height of the Si_2O_7 groups by giving the height, in *c*/8 units, of the bridging oxygen atom in the diorthosilicate groups, with respect to a plane normal to the *c* axis. To enumerate all the truly distinct combinations, we may place, without loss of generality, the first and second Si_2O_7 groups, *A* and *B*, at ⅛ and -⅛, respectively, thus also fixing the position of the reference plane.

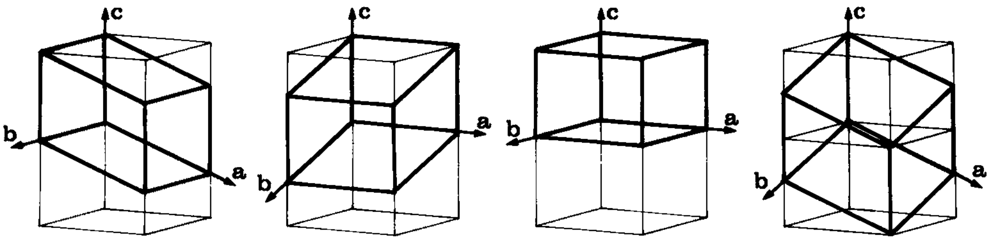
TABLE 1. THE SIXTEEN POSSIBLE [illegible] ASSEMBLE OCTAHEDRAL WALLS AND Si_2O_7 GROUPS ACCORDING TO THE COMPOSITION RULES

	A	B	C	D	(E)	F	A'	TS
1	1/8	-1/8	-1/8	-1/8	1/8	1/8	-3/8	$P12_1/a1$
2	1/8	-1/8	-1/8	-1/8	1/8	-3/8	-3/8	$Bb11$
3	1/8	-1/8	-1/8	3/8	-3/8	1/8	-3/8	$A1a1$
4	1/8	-1/8	-1/8	3/8	-3/8	-3/8	-3/8	$P\bar{1}$
5	1/8	-1/8	3/8	-1/8	1/8	-3/8	-3/8	$P12_1/n$
6	1/8	-1/8	-1/8	-1/8	1/8	1/8	1/8	$P2_1/b11$
7	1/8	-1/8	-1/8	-1/8	1/8	-3/8	1/8	$P12_11$
8	1/8	-1/8	-1/8	3/8	-3/8	1/8	1/8	$P2_111$
9	1/8	-1/8	-1/8	3/8	-3/8	-3/8	1/8	$P\bar{1}$
10	1/8	-1/8	3/8	-1/8	1/8	-3/8	1/8	$P2_1/n11$
2'	1/8	-1/8	3/8	-1/8	1/8	1/8	-3/8	
3'	1/8	-1/8	3/8	3/8	-3/8	-3/8	-3/8	
4'	1/8	-1/8	3/8	3/8	-3/8	1/8	-3/8	
7'	1/8	-1/8	3/8	-1/8	1/8	1/8	1/8	
8'	1/8	-1/8	3/8	3/8	-3/8	-3/8	1/8	
9'	1/8	-1/8	3/8	3/8	-3/8	1/8	1/8	

The ten distinct structures, with the corresponding topological symmetry, and the six additional symmetry-related patterns are listed.

We may now impose the constraints on the cell dimensions as follows: a) the vector that connects the position of the *B* and *D* groups must be equal to the vector that connects the positions of *A* and *E* groups; therefore, the height of *E* is fixed at ⅛ or ⅝, depending on the height of *D*, − ⅛ or ⅜; b) the heights of the groups *B′*, *C′*,....*F′*, are tied to the height of *A′*, which may be ⅛ and − ⅜.

Within these metrical constraints, the application of the composition rules leads to the sixteen possibilities listed in Table 1. Close scrutiny of the six-



Type of unit cell	I	II	III	IV
Unit cell parameters	a= 10.93Å	a= 10.3 Å	a= 10.3 Å	a= 10.93Å
	b= 10.3 Å	b= 10.93Å	b= 10.3 Å	b= 10.93Å
	c= 7.3 Å	c= 7.3 Å	c= 7.3 Å	c= 7.3 Å
	α= 90°	α= 109.5°	α= 90°	α= 109.5°
	β= 109.5°	β= 90°	β= 90°	β= 109.5°
	γ= 90°	γ= 90°	γ= 90°	γ= 83.6°

FIG. 3. The four kinds of unit cell.

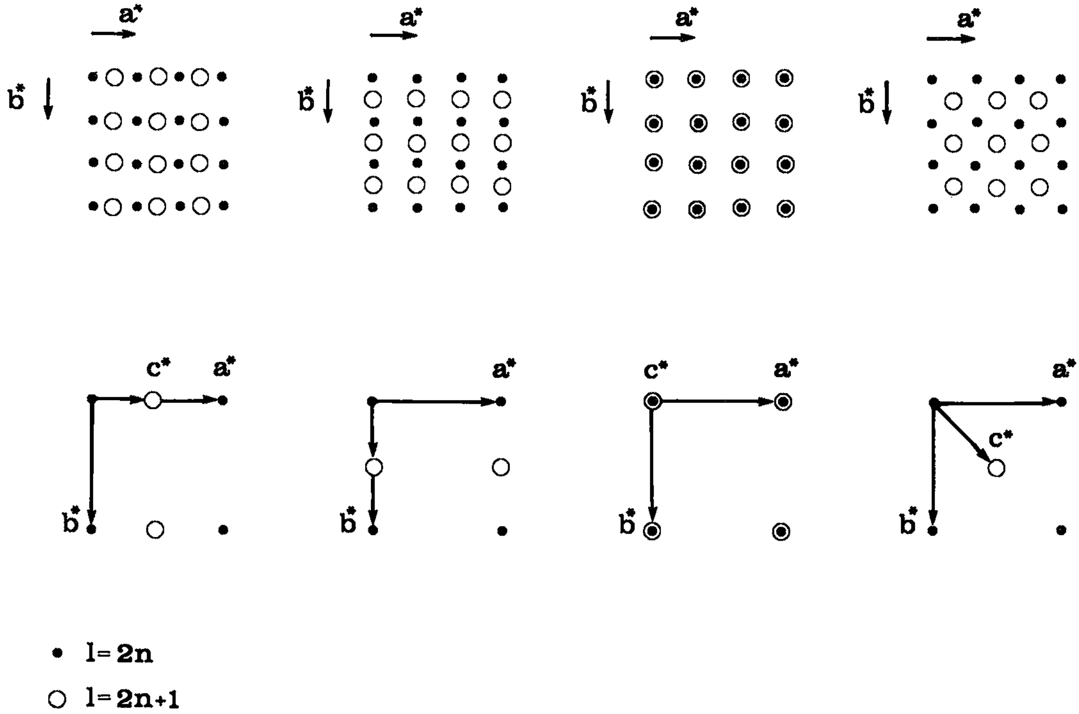


FIG. 4. The four kinds of diffraction patterns and the corresponding reciprocal unit-cells.

teen patterns indicates that only ten are unique (numbered from 1 to 10 in Table 1). Among the six exclusions, 7′ and 8′ are in enantiomorphous relationship with 7 and 8, respectively, whereas 2′, 3′, 4′ and 9′ are symmetry-related to 2, 3, 4 and 9, respectively.

THE FOUR KINDS OF UNIT CELL

At this point it seems useful to give the unit-cell dimensions of the ten distinct patterns, leaving the space-group symmetries for discussion in a later section.

As stated, for all structures the *c* translation period is measured along the length of the walls of octahedra. Its value, 7.3 Å, corresponds to a periodicity of the whole structure every third octahedron. The *a* translation is given by the vector that connects the Si_2O_7 groups at the *A* and *A′* positions, whereas the *b* translation is given by the vector that connects the Si_2O_7 groups at the *A* and *E* positions (Fig. 1). It is easy to obtain the metrical features of the unit cells corresponding to the different structures listed in Table 1 by comparing, for each case, the relative levels of the Si_2O_7 groups at the *A*, *A′* and *E* positions: as both Si_2O_7 groups at *A′* and *E* may be either at the same level as that in the *A* position, or located *c*/2 from it, four distinct kinds of cell are obtained, as represented in Figure 3. In the same figure, the approximate values of the parameters in the different cells are reported; they were calculated assuming $c = 7.3$ Å, $d_{100} = 10.3$ Å, $d_{010} = 10.3$ Å, as indicated by the unit-cell constants of the known phases in this structural group.

Four different diffraction-patterns can be expected to correspond to the four kinds of unit cell. We shall consider, in this section, only the geometrical positions of the reciprocal-lattice points in the four patterns (the symmetry aspects of the intensity distributions are discussed in the next section). All the structures in the family have a common (001) projection if we disregard the differences in the distribution of cations in the walls of octahedra and the consequent distortions from the ideal structure. Moreover, as the network of octahedra shows a *c*/2 pseudotranslation and the Si_2O_7 groups at *A*, *B*, *C*,... can assume at most two different heights, *c*/2 apart, the diffraction patterns of the various structures of the family will be very similar with regards to the reflections with $l = 2n$, and quite different only for the reflections with $l = 2n + 1$. Figure 4 shows the diffraction patterns of the four kinds of unit cell, together with the four reciprocal cells, which have common a^* and b^*, but different c^* translations.

To make an unambiguous distinction among the four types of diffraction patterns, in particular to distinguish between I and II, it is necessary to consider the difference between *a* and *b* translations. This is not possible on the basis of the geometrical features, as d_{100} and d_{010} distances are similar. However, the distinction is simple if we take into account the distribution of intensities of the reflections. Figure 5 shows a *hk*0 precession photograph, taken using a crystal of hiortdahlite II, with of *a** and *b** directions indicated. The allocation of the diffraction pattern of any crystal under study to one of the four kinds represented in Figure 4 is then possible by comparing *hk*0 and *hk*1 diffraction photographs.

TOPOLOGICAL AND TOPOCHEMICAL SYMMETRY OF THE POSSIBLE STRUCTURES

The concepts of topological and topochemical symmetry were introduced by Smith (1970) and used by Gottardi (1979) in discussing the causes of the reduction of symmetry in framework silicates. In the present work, which deals with structures consisting of walls of octahedra and disilicate groups (Fig. 1), the topological symmetry denotes the symmetry of the structure "when idealized into its most regular shape by movements which leave intact the topologic relationships between nodes" (Smith 1970), as shown in Figure 1, assuming identical cationic populations in all the octahedral sites.

Within the assumed metrical constraints, the topological space-group symmetries for the ten possible structures are given in Figures 6 to 9. Each figure gives the distribution of symmetry operators for structures with a similar kind of unit cell. The structures are consistently seen along the *z* direction, with *x* and *y* across and down, respectively. Table 2 summarizes the main results by giving the full symbol of the topological space-group symmetry and the unit-cell parameters for each structure. All the structures have a unit-cell volume of 774.5 Å^3, except for structures 2 and 3, which have a doubled unit-cell volume. However, the latter are *B*- and *A*-centered, respectively, and the corresponding primitive cells have parameters that do not violate the metrical constraints that we assumed. Note that as we have fixed the unit-cell orientation relative to the scaffolding of the octahedral walls, nonstandard unit-cell and space-group symbols may result for some structures.

To complete our discussion and to build a comprehensive framework in which the various minerals in the family can be located, we have to consider the reduction in symmetry due to the distribution of cations in the walls of octahedra. The possibly reduced symmetry may be called the topochemical symmetry, using, in our context, the term suggested by P.B. Moore (in Smith 1970) to describe the idealized symmetry of a tetrahedral framework where the chemical occupancy of the nodes is considered. For example, in structure-type 1, centrosymmetric walls of octahedra are repeated through *a* glides, so that the overall topological symmetry is $P12_1/a1$; such a symmetry applies to cuspidine $Ca_{16}(Si_2O_7)_4F_8$, whose topochemical symmetry obviously coincides with the topological one, as only calcium cations occupy the walls. Låvenite also has $P12_1/a1$ topochemical symmetry. However, various cations are distributed in its walls, as indicated by its chemical formula $M_4(Na,Ca)_8(Zr,Nb)_4(Si_2O_7)_4O_4F_4$, where *M* represents (Mn, Fe, Ca, Ti), but their distribution is still centrosymmetric (Mellini 1981).

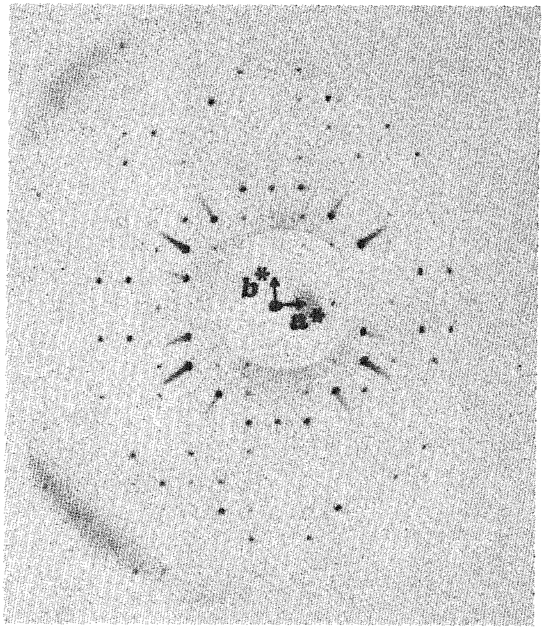


FIG. 5. An *hk*0 precession photograph of hiortdahlite II from Kipawa, Quebec.

In contrast, niocalite $Ca_{14}Nb_2(Si_2O_7)_4O_6F_2$ presents a noncentrosymmetric distribution of cations in the walls of octahedra, owing to the ordering of Ca *versus* Nb cations (Mellini 1982), whereas successive walls in the *x* direction are still symmetry-related through *a* glides; thus, the topochemical symmetry is reduced to $P1a1$.

The topochemical symmetry $P12_11$ is realized when the walls of octahedra characterized by a noncentrosymmetric distribution of cations are related by 2_1 screw axes. Finally, topochemical symmetry $P\bar{1}$ results when two independent walls exist in the unit cell, each wall being characterized by a centrosymmetric distribution of cations. From single-crystal studies, Aarden & Gittins (1974) found that hiortdahlite from the Kipawa alkaline complex, Que-

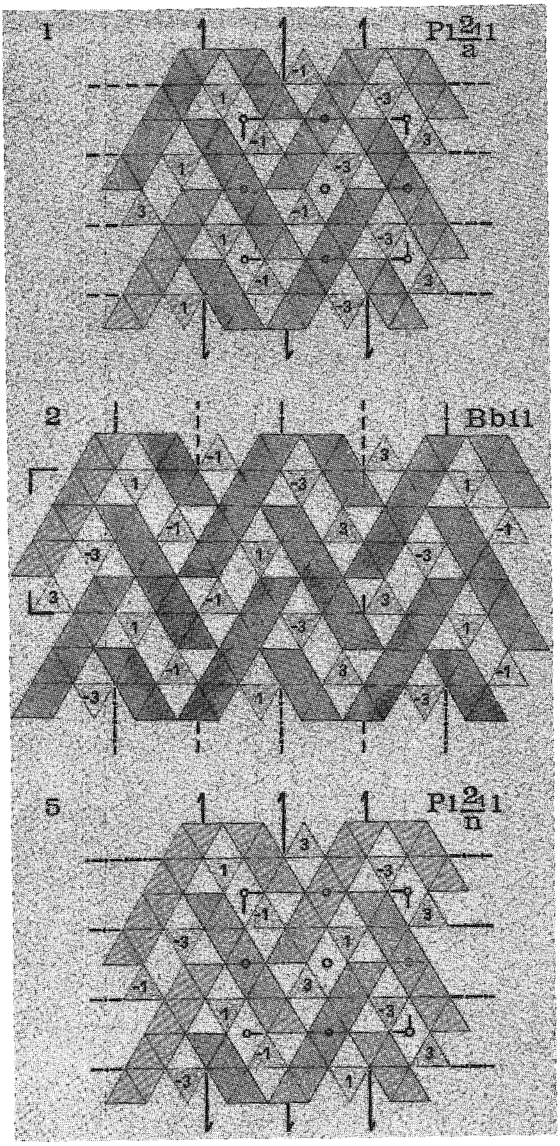


FIG. 6. Structures with cell type I, namely structures 1, 2 and 5 in Table 1.

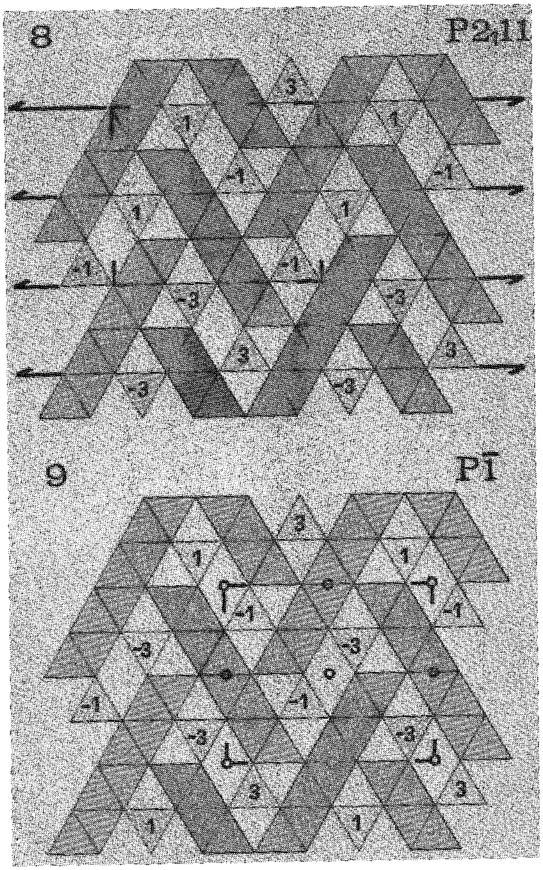


FIG. 7. Structures with cell type II, namely structures 8 and 9 in Table 1.

bec, has triclinic symmetry and unit-cell parameters corresponding to those we have derived for a unit cell of type I. A structural study of the phase confirmed that it has type-1 structure, with topochemical symmetry $P\bar{1}$ (Merlino & Perchiazzi 1987).

The decrease in symmetry due to the ordering of cations in the walls may lead to a doubling of the *c* translation. This happens in janhaugite $(Na,Ca)_{12}(Mn,Fe)_{12}(Ti,Zr,Nb)_8(Si_2O_7)_8O_8(OH,F)_8$. Its structure (Annehed *et al.* 1985) has the same topology as structure-type 1; however, the centrosymmetric walls of octahedra consist of central columns of alternating Mn and Na polyhedra, and lateral columns characterized by the sequence Na–Ti–Mn–Ti–Na.... with a translation period every fifth polyhedron. The walls are related to each other in the *x* direction through *n* glides. The overall topochemical symmetry is $P12_1/n1$, with $c' = 2c$. We may easily sketch other possible structures in which walls of octahedra, with a doubled *c* axis, fit in with Si_2O_7 groups according to structure-type 1, to result in topochemical symmetries $P12_1/a1$, $P\bar{1}$, $P1n1$, $P1a1$.

CRYSTAL CHEMISTRY OF THE CUSPIDINE-LÅVENITE GROUP

The enumeration of the possible structure-types and the corresponding topological symmetries obtained by combining the two basic modules, the walls of octahedra and the disilicate groups, together

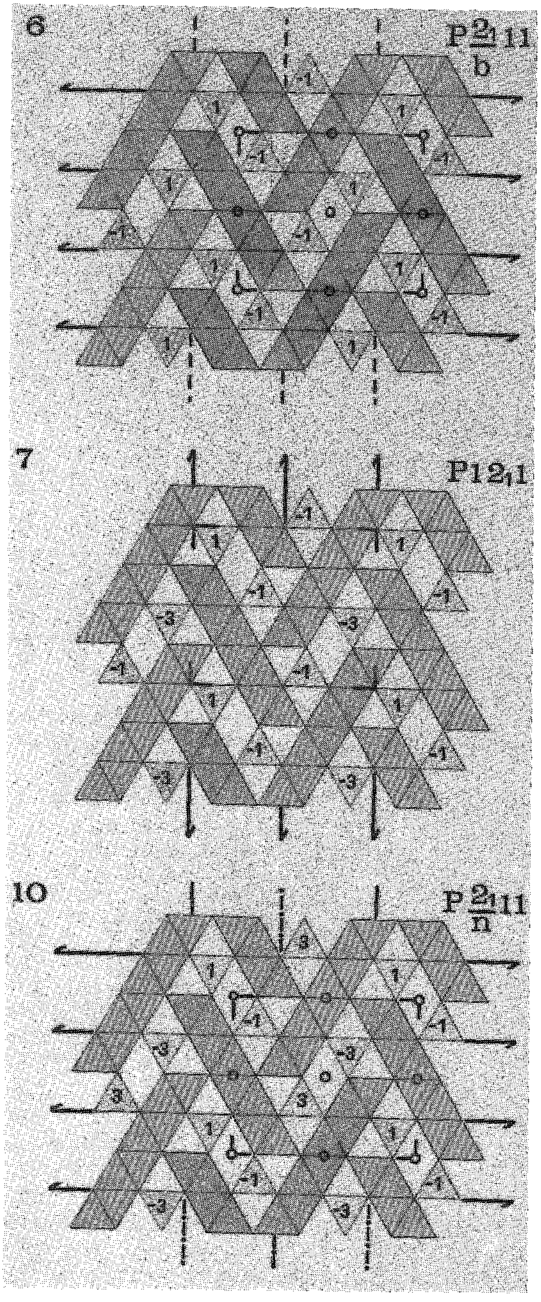


FIG. 8. Structures with cell type III, namely structures 6, 7, 10 in Table 1.

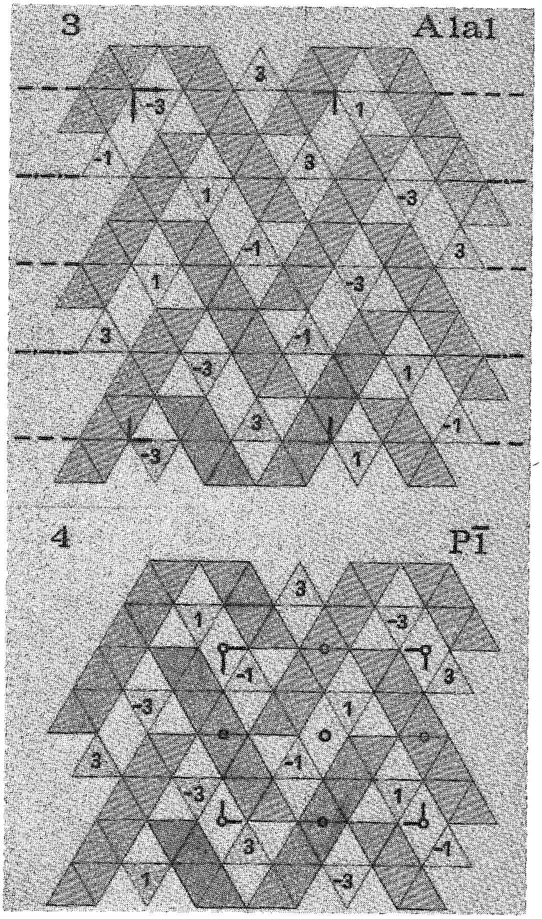


FIG. 9. Structures with cell type IV, namely structures 3 and 4 in Table 1.

with the generation of the relative topochemical symmetries due to the ordering of the octahedral cations, provide the framework in which the various mineral phases of the cuspidine family may be conveniently classified. Such a classification has not only a descriptive power, in showing the structural relationships among the various minerals, but can also be used to make inferences about possible solutions of as yet unknown structures. However, before we apply the concepts just derived to obtain structural information about actual minerals, some basic crystal-chemical features should be considered.

A number of octahedrally coordinated cations, largely different in ionic radius and charge, may be located in the walls. Consider the list of those cations found in appreciable quantities in the known minerals of this family: Na^+, Ca^{2+}, Y^{3+}, Mn^{2+}, Fe^{2+}, Ti^{4+}, Mg^{2+}, Zr^{4+}, Nb^{5+}, Hf^{4+} and rare-earth cations. Two main factors to be taken into account are the dimensions of the coordination polyhedra, largely dependent on the radius of the guest cations, and the repulsive interactions, largely dependent on the charges of the cations located in adjacent sites. These factors give rise to the two following rules, which control the distribution of cations in the walls:

TABLE 2. UNIT-CELL DIMENSIONS, TOPOLOGICAL SYMMETRIES AND NATURAL REPRESENTATIVES FOR THE VARIOUS POSSIBLE STRUCTURAL TYPES.

Type of unit cell	Structures	Cell parameters	Topological symmetry	Natural phases
I	1 5	a = 10.93 Å b = 10.3 c = 7.3 β = 109.5°	$P12_1/a1$ $P12_1/n1$	Cuspidine ($P12_1/a1$) Låvenite ($P12_1/a1$) Niocalite ($P1a1$) Hiortdahlite II ($P\bar{1}$) Janhaugite ($P12_1/n1$, $c'=2c$)
	2	a = 20.6 Å b = 10.3 c = 7.3 α = 90.0°	$Bb11$	
II	8	a = 10.3 Å b = 10.93 c = 7.3 α = 109.5°	$P2_111$	Wöhlerite ($P2_111$)[1]
	9	a = 10.3 Å b = 10.93 c = 7.3 α = 109.5° β = 90.0° γ = 90.0°	$P\bar{1}$	
III	6 10	a = 10.3 Å b = 10.3 c = 7.3 α = 90.0°	$P2_1/b11$ $P2_1/n11$	Baghdadite ($P2_1/b11$)[2] Phase from Burpala[3] ($P2_1/b11$)
	7	a = 10.3 Å b = 10.3 c = 7.3 β = 90.0°	$P12_11$	
IV	3	a = 10.93 Å b = 20.6 c = 7.3 β = 109.5°	$A1a1$	
	4	a = 10.93 Å b = 10.93 c = 7.3 α = 109.5° β = 109.5° γ = 83.4°	$P\bar{1}$	Hiortdahlite I ($P\bar{1}$)

1) Unit-cell parameters in a standard orientation (transformation matrix: 010/100/001) are as follows: a = 10.823, b = 10.244, c = 7.290 Å, β = 109.0°, space group $P12_11$ (Mellini & Merlino 1979).

2) Unit-cell parameters in a standard orientation (transformation matrix: 010/100/001) are as follows: a = 10.42, b = 10.16, c = 7.36 Å, β = 91.1°, space group $P12_1/a1$ (Al-Hermezi et al. 1985).

3) Unit-cell parameters in a standard orientation (transformation matrix: 010/100/001) are as follows: a = 10.12, b = 10.45, c = 7.26 Å, β = 90.04°, space group $P12_1/a1$ (Merlino & Perchiazzi, in prep.).

1) The diorthosilicate groups do not link to the edges of polyhedra occupied by small cations, such as Ti^{4+}, Nb^{5+} and Zr^{4+}; instead they link to polyhedra occupied by large cations, such as Ca^{2+} and Na^+. There is little misfit between the length of an edge of a polyhedron hosting Na^+ or Ca^{2+} and the height of the Si_2O_7 group, namely the distance between the two parallel basal faces (4.1 Å), whereas a large misfit would arise for a polyhedron hosting small-radius cations as Ti^{4+} and Nb^{5+}. It is well known that simply on the basis of the dimensional match between Si_2O_7 groups and calcium–oxygen polyhedra, Belov (1961) built up the whole second "chapter" on the crystal chemistry of silicates. The rule is strictly obeyed by all the known structures of this family. It was the apparent exceptions to the rule that prompted Mellini & Merlino (1979) and Mellini (1982) to re-examine the crystal structure of wöhlerite and niocalite, respectively. These authors corrected errors in the previous structural studies and showed that the cation distribution in wöhlerite and niocalite is in perfect agreement with the above-mentioned crystal-chemical rule.

2) In accordance with Pauling's fourth rule (Pauling 1929), high-charge cations are distributed in the walls so as to avoid edge-sharing between the polyhedra they occupy. This rule is more strictly observed the higher the charge and the smaller the radius of the cations involved, from Y^{3+} to Zr^{4+}, Ti^{4+} and, finally, Nb^{5+}.

On the basis of the whole complex of crystallographic and crystal-chemical considerations just developed, we present and discuss the results of Table 2. Listed there are all the known minerals in the cuspidine group, their distribution amongst the various structural types, and for each phase its topochemical symmetry, which results from the ordering of the cations in the walls. Reported in this table are the mineral phases already discussed in the preceding section, namely cuspidine, låvenite, niocalite, hiortdahlite II and janhaugite, characterized by unit cells of type I, as well as wöhlerite, with a unit cell of type II, baghdadite and a natural phase from Burpala, USSR, both with a unit cell of type III, and finally hiortdahlite I, with a unit cell of type IV.

The crystal structure of wöhlerite was determined by Shibayeva & Belov (1962); their results were later amended and refined by Mellini & Merlino (1979), who found that wöhlerite $Na_4Ca_8Zr_2(Nb,Ti)_2(Si_2O_7)_4O_4F_2(O,F)_2$ has a unit cell of type II and a crystal structure of type 8, according to our scheme, with *a* 10.823, *b* 10.244, *c* 7.290 Å, β 109.00°, space group $P12_11$, with *a* and *b* axes interchanged relative to the orientation assumed in the present work.

The actual structure of wöhlerite satisfactorily corresponds to one of the ten possibilities in our scheme. As was stated previously, the important feature of the present scheme of classification is its capability of predicting correct structural arrangements. This capability was successfully tested with hiortdahlite I, hiortdahlite II, and the mineral from Burpala (Merlino & Perchiazzi, in prep.). We shall use these minerals to illustrate the application of the structural classification introduced here to determine unknown structures.

X-ray crystallographic investigations on hiortdahlite crystals from Langesundfjord, Norway, and from Jingera, Australia (Eggleton *et al.* 1979) indicate a unit cell of type IV; therefore two structure-types are possible: type 3, monoclinic $A1a1$, and type 4, triclinic $P\bar{1}$. The diffraction-pattern symmetry and the distribution of the normalized structure-factors indicated space-group symmetry $P\bar{1}$, with measured unit-cell parameters a 11.015, b 10.941, c 7.353 Å, α 109.35°, β 109.88°, γ 83.43°. This indication excludes, for hiortdahlite I, not only the topological symmetry $A1a1$, but also any possible topochemical symmetry obtained as a subgroup of $A1a1$. Consequently, structure-type 4 was assumed to be the correct starting model in the structure determination. Results of a refinement by Merlino & Perchiazzi (1985) ($R = 0.058$ for 2910 reflections) fully confirmed these assumptions and indicated the crystal-chemical formula $(Na,Ca)_4Ca_8Zr_2M_2(Si_2O_7)_4O_2F_4(O,F)_2$, where M represents a mixing site, hosting Zr^{4+}, Ti^{4+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, with an average charge of three.

Hiortdahlite crystals from the Kipawa complex, Quebec, show a unit cell of the type I; they therefore were assigned to a different species (Merlino & Perchiazzi 1987), conveniently defined as hiortdahlite II. As in the preceding case, the measured parameters, diffraction symmetry, and distribution of normalized structure-factors indicate the space-group symmetry $P\bar{1}$. Inspection of Table 2 shows that $P\bar{1}$ may represent the reduced topochemical symmetry of both $P12_1/a1$, structure-type 1, and $P12_1/n1$, structure-type 5. To make a correct choice, we take advantage of the crystal-chemical rules previously introduced.

The chemical composition of hiortdahlite II $Na_{3.3}Ca_{7.87}Zr_2(Y_{0.46}Zr_{0.31}Ti_{0.06}RE_{0.19}Nb_{0.06}Mn_{0.06}Fe_{0.05}Mg_{0.03})_{\Sigma 1.22}(Si_2O_7)_4(OH)_{0.7}O_{0.96}F_{5.26}$ indicates that four sites contain small-radius, high-charge cations in the unit cell. Within a structural scheme of type 5, these cations cannot distribute themselves in the walls so as to satisfy both crystal-chemical rules; on the contrary, a structural scheme of type 1 enables a satisfactory distribution. The choice was easily tested, and its correctness confirmed through a complete structural study by Merlino & Perchiazzi (1987) ($R = 0.069$ for 1793 reflections).

The last opportunity to make use of the predictive power of our model came up during a crystallographic and structural study of crystals of what seems to be yet another member of the cuspidine family. The crystals were found in a sample from Burpala (USSR) kindly donated by Prof. A.P. Khomyakov of IMGRE, Moscow. Various crystals were examined: their diffraction patterns can be interpreted as the superposition of two distinct reciprocal lattices, one corresponding to twinned låvenite domains and the other to domains with a type-III unit cell, the proportions of the two domains being different in the various crystals. Eventually some crystals were found that are free of låvenite domains, thus constituting pure representatives of another phase in this family of minerals. The unit-cell parameters, a 10.455, b 10.117, c 7.256 Å, α 90.04°, and the space-group symmetry $P2_1/b11$, unambiguously indicate the type-6 structure for this phase. The structure determination and refinement fully confirmed the theoretical conclusions (Merlino & Perchiazzi, in prep.). Baghdadite (Al-Hermezi *et al.* 1986) is most probably isostructural with the phase from Burpala, differing from it in chemical composition and unit-cell dimensions.

DISORDER IN THE MINERALS OF THE CUSPIDINE GROUP

The common structural feature in all members is the infinite frame built up by the interconnection of the walls of octahedra; the disilicate groups are linked to this frame in several ways, all of which are geometrically different but energetically nearly equivalent, giving rise to the different types of structure (Table 2, Figs. 6-9). Therefore, it is understandable that disorder phenomena of various kinds, stacking faults, microtwinning, and domain structures can appear. Some of these manifestations were previously mentioned; for example, we hinted at the presence in the same crystal of domains with a låvenite-type structure together with domains having a type-6 structure. Comparison of the two different structure-types shows that both are built up of equivalent layers. In the first one, type 1 (Fig. 6), the layers succeed each other in a direction normal to the (100) plane, with disilicate groups at ⅛, −⅛, −⅜, −⅝,....; whereas in the second one, type 6 (Fig. 8), the succeeding layers have disilicate groups at ⅛ and −⅛. Pairs of adjacent layers in either of these cases are geometrically equivalent. Therefore, we are dealing with two members of a family of infinite possible *OD* structures (Dornberger-Schiff 1956, 1964, 1966); moreover they are the two members of maximum degree of order, *i.e., MDO* members, according to the terminology used in *OD* theory.

Similar structural considerations may easily explain the common twinning in crystals of this group. On this basis, the twinning in niocalite was discussed and documented through HRTEM images by Mellini (1982). It is possible that similar polysynthetic twinning characterizes the structure of the so-called orthorhombic låvenite (Portnov *et al.* 1966), as suggested by Nickel (1966).

It was the observed coexistence of different domains in guarinite crystals that gave us the stimulus for this work. The X-ray-diffraction patterns obtained from crystals of guarinite can be interpreted, on the basis of the present results, as the superposition of reciprocal lattices I, II and IV (Fig. 4): evidence for the presence of one, two, or three types of lattices was shown by different crystals. Further X-ray crystallographic and HRTEM microscopy studies are necessary to identify structural types of the different domains and to obtain a complete understanding of the real structures of guarinite crystals.

BORATES WITH THE SAME OCTAHEDRAL FRAMEWORK

The "octahedral" frame, which is the constant feature in all the structures of this family, appears also in a group of natural and synthetic borate phases, whose structural relationship to the cuspidine family was first indicated by Mamedov & Belov (1964). On the basis of geometrical similarities, those authors proposed structural analogies between diorthosilicates and oxyborates: the disilicate group Si_2O_7 is substituted by two parallel BO_3 groups, with the loss of the bridging oxygen atom; schematically, $(Si_2O_7)^{6-}$ is replaced by $(B_2O_6)^{6-}$. Table 3 reports the chemical composition and cell parameters of five oxyborates, four corresponding to synthetic phases and the last to the mineral warwickite, all of which are built up of walls of octahedra similar to those found in the cuspidine family and similarly assembled. The framework is completed, in all those phases, by trigonal BO_3 groups, which provide a further linking to the walls of octahedra (Takeuchi *et al.* 1950, Moore & Araki 1974, Venkatakrishnan & Buerger 1972). The data in Table 3 point out the relevant differences between oxyborates and disilicate phases:

1) The *a* and *b* unit-cell parameters in oxyborates are shorter than the corresponding parameters in the minerals of the cuspidine family; the sides of the BO_3 triangles are appreciably shorter than the edges of the SiO_4 tetrahedra, the BO_3 sides and SiO_4 edges having the largest influence on the lengths of *a* and *b* unit-cell parameters of oxyborates and disilicates, respectively.

2) The small BO_3 triangles may correctly fit an octahedral frame built up of smaller octahedra than those that build up the walls in the minerals of the cuspidine family. This fact explains why the chemistry of the oxyborates is quite different from that of the structurally analogous disilicates, having relatively small cations such as Mg^{2+}, Fe^{2+}, Co^{2+},.... instead of Ca^{2+}, Na^{+}, Zr^{4+}.... in the walls.

TABLE 3. CHEMICAL COMPOSITION AND UNIT-CELL PARAMETERS OF SOME OXYBORATES

	a	b	c		References
$Mg_2\ Fe^{3+}_2\ (B_2O_6)O_2$	9.427	9.258	3.104	Å	(1)
$Fe^{2+}\ Fe^{3+}\ (B_2O_6)O_2$	9.468	9.243	3.158	Å	(1)
$Ni_2\ Fe^{3+}_2\ (B_2O_6)O_6$	9.351	9.141	3.047	Å	(1)
$Co_2\ Fe^{3+}_2\ (B_2O_6)O_2$	9.395	9.234	3.125	Å	(2)
$Mg_2\ Ti\ (B_2O_6)O_2$	9.358	9.197	3.085	Å	(3)

(1) Bertaut (1950).
(2) Venkatakrishnan & Buerger (1972).
(3) Moore & Araki (1974).

3) The $(Si_2O_7)^{6-}$ for $(B_2O_6)^{6-}$ substitution results in each Si O Si □ Si O Si.... sequence in the [001] direction being substituted by B □ B □ B □ ..., which halves the *c* period of the oxyborates, a halving which, as previously mentioned, appears only as a pseudosymmetry in the diorthosilicates.

4) The Si O Si □ Si O Si □.... sequences in the various positions *A*, *B*,.... (Fig. 1) may present the bridging oxygen atoms at different heights, and we have shown that, within fixed metrical constraints, ten distinct possibilities may be found (Table 2, Figs. 6–9). In contrast, in oxyborates, the B □ B □ B □ B.... sequences are strictly similar to each other, and only one structure, with topological space-group symmetry *Pbnm*, is possible.

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