

Structural Hierarchies of Minerals Based on Bond Topology*, 1

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Abstract—Two- and three-dimensional nets are widely used to describe and systematize crystal structures based solely on tetrahedral oxyanions. This approach may also be used to advantage for crystal structures based on polymerization of tetrahedra and octahedra. Thus, the $[^{6}M_2^{[4]}T_2\phi_{12}]$ sheet occurs as a fragment in a wide variety of structures, including silicate, phosphate, and sulfate minerals and several uranium minerals related to metaautunite, $Ca[(UO_2)(PO_4)]_2(H_2O)_6$; sulfosalite, $Na_6[(SO_4)_2]FCl$; natisite, $Na_2[TiO(SiO_4)]$; garnet, $[^{8}M_3^{[6]}M_2T_3O_{12}]$; griphite, $(Mn^{2+}, Ca, Na, Li)_{24}Ca_4Fe_4^{2+}Al_8(PO_4)_{24}F_8$; girvasite, $NaCa_2[Mg_3(OH)_2(PO_4)_2\{PO_2(OH)_2\}(CO_3)](H_2O)_4$; olmsteadite, $K_2[Fe_4^{2+}Nb_2O_4(H_2O)_4(PO_4)_4]$; gainesite, $Na_2[Zr_2Be(PO_4)_4]$; and rhomboclase, $(H_5O_2)[Fe(SO_4)_2(H_2O)_2]$. Trimeric clusters of the form $[M\phi_{11-14}]$, $M = Na, Ca$; $\phi = O, OH, F, Cl$, are common in a group of alkali sulfates and phosphates (and silicates) and occur in sulfosalite, $Na_6(SO_4)_2FCl$; galeite, $Na_{15}(SO_4)_5F_4Cl$; schairerite, $Na_{21}(SO_4)_7F_6Cl$; kogarkoite, $Na_3(SO_4)F$; arctite, $(Na_5Ca)Ca_6Ba(PO_4)_6F_3$; quadruphite, $Na_{14}CaMgTi_4[Si_2O_7]_2[PO_4]O_4F_2$; polyphite, $Na_{17}Ca_3Mg(Ti, Mn)_4[Si_2O_7]_2(PO_4)_6O_2F$; and sobolevite, $Na_{11}(Na, Ca)(Mg, Mn)Ti_4[Si_2O_7]_2(PO_4)_4O_3F_3$. Bond valence considerations suggest that Si analogues of some of these structures should be stable, and several phases of tricalcium silicate, $Ca_3(SiO_4)O$, contain such trimeric clusters. These topological similarities between chemically and paragenetically diverse mineral structures are an important step in the eventual development of structural hierarchies that are based on bond topology (rather than chemical composition).

INTRODUCTION

As discussed in the first talk by Dr. F.C. Hawthorne, we need ways to think about complicated crystal structures in a simple but quantitative fashion if we are to be able to deal with complex environments. In particular, we need to be able to relate mineral structures that are very different in chemical composition, e.g., silicates, sulfates, and phosphates. Here, I consider this problem using two-dimensional nets. The advantage of this method is that it has been used extensively to relate structures, usually of similar chemical type (e.g., zeolites). I will apply this approach to structures of different chemical types (i.e., sulfates, phosphates, silicophosphates, and silicates). This work can be found in more detail in Sokolova and Hawthorne (2001, 2002).

THE 4⁴ PLANE NET

The 4⁴ plane net is an array of vertices of valence four, connected by edges (Fig. 1a). Such nets (or graphs) have been used extensively to describe connectivity (or bond topology) in crystal structures (e.g.,

Wells, 1977; Smith, 1977, 1978, 1979; Hawthorne, 1983; Hawthorne and Smith, 1986a, 1986b, 1988; Schindler *et al.*, 1999). The vertices of the graph may represent polyhedra, and the edges of the graph represent the connectivity of the constituent polyhedra. This approach to the topology of crystal structures has concentrated primarily on linkages of tetrahedra. However, one may color the vertices of a graph to represent different types of polyhedra (including vacancies), giving rise to one-colored (Fig. 1a), two-colored (Fig. 1b), three-colored (Figs. 1c, 1d), and four-colored (Fig. 1e) graphs. In this way, one may examine the topology of crystal structures in which linkage of different types of polyhedra (e.g., tetrahedra and octahedra) is involved. The graphs shown in Fig. 1 all have fairly high plane-group symmetry. Many other lower symmetry graphs are possible, but here we examine only a few high-symmetry representatives.

THE CRYSTAL CHEMISTRY OF THE $[^{6}M_2^{[4]}T_2\phi_{12}]$ SHEET

Minerals with a $[^{6}M_2^{[4]}T_2\phi_{12}]$ Sheet

*Uranium minerals related to metaautunite, $Ca[(UO_2)(PO_4)]_2(H_2O)_6$ (Makarov and Ivanov, 1960), have been described by Burns *et al.* (1996) and Burns*

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¹This article was submitted by the authors in English.

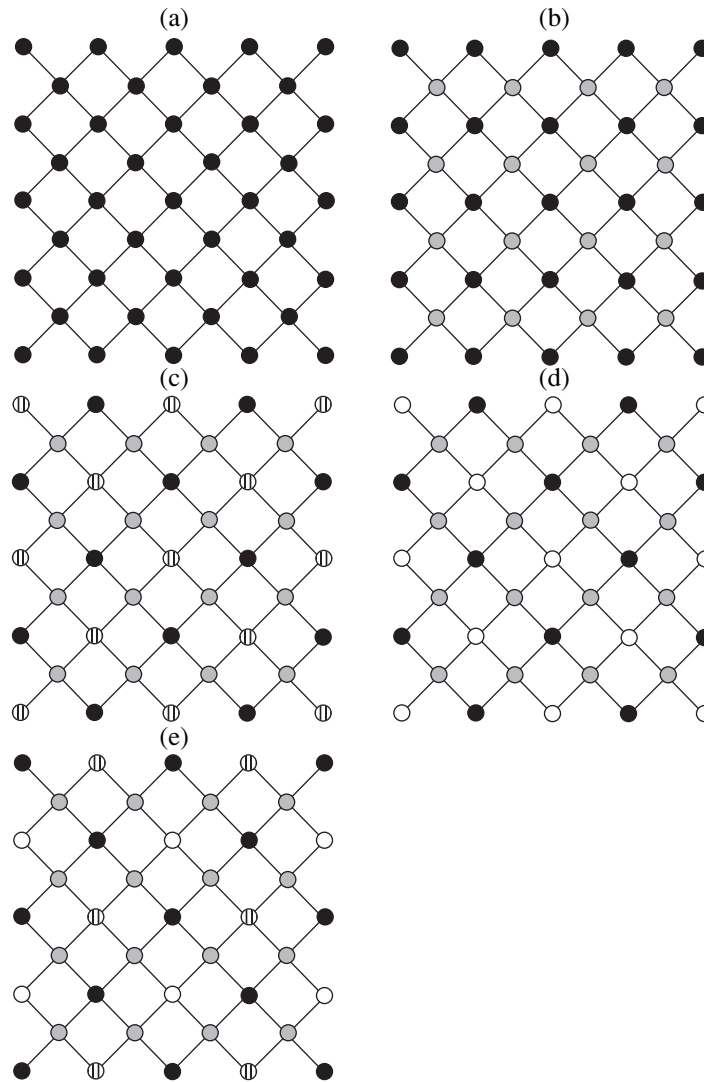


Fig. 1. The 4^4 net: (a) the square 4^4 net; (b) a two-colored 4^4 net; (c) a three-colored 4^4 net; (d) a three-colored 4^4 net in which vertices of one color are replaced by vacancies; (e) a four-colored 4^4 net with equal amounts of vacancies and vertices of the third color.

(1999), who showed that the main structural fragment of these structures is a sheet of $(U^{6+}O_6)$ square bipyramids and (PO_4) or (AsO_4) tetrahedra: $[(UO_2)(PO_4)]$. These minerals are listed in Table 1. The metaautunite sheet is the structural unit in these seven uranium minerals. The U–P sheet in metaautunite (Fig. 2a) is similar to the Na–S sheet in sulfohalite (Fig. 2b).

Sulfohalite, $Na_6[(SO_4)_2]FeCl$, is a Na sulfate of cubic symmetry (Sakamoto, 1968). This structure can also be described as a combination of two parallel sheets: (1) a sheet of (NaO_4FCl) octahedra at $z = 0.0$ and 0.5 , sharing common vertices, edges, and faces; (2) a sheet of (NaO_4FCl) octahedra at $z = 0.25$ and 0.75 , linked to (SO_4) tetrahedra through common vertices. As sulfohalite is cubic, these two sheets form two types of framework in the structure. A sheet of (NaO_4FCl) octahedra and (SO_4) tetrahedra is shown in Fig. 2b. This

sheet is based on the two-colored 4^4 net (Fig. 1b) and can be characterized by a cluster of two octahedra and two tetrahedra: $[[^{6l}M_2^{4l}T_2\phi_{12}]]$, where ^{6l}M is a [6]-coordinated cation (i.e., Na), ^{4l}T is a [4]-coordinated cation (i.e., S), and ϕ are anions (i.e., O, F, and Cl). In sulfohalite, this cluster has the composition $[Na_2S_2O_{10}FCl]^{8-}$ (Table 1).

Natisite, $Na_2[TiO(SiO_4)]$, is a (Na–Ti) orthosilicate and a high-temperature polymorph of $Na_2TiO(SiO_4)$ (Nyman *et al.*, 1978). In the crystal structure of natisite, there is one type of $[[^{6l}M_2^{4l}T_2\phi_{12}]]$ sheet of (TiO_5) square pyramids and (SiO_4) tetrahedra (Fig. 2c), and the pyramids point alternately up and down relative to the plane of the sheet. In the natisite structure, Ti is [5]-coordinated, in contrast to [6]-coordinated Na in sulfohalite, and thus there are two anion vacancies per sheet unit:

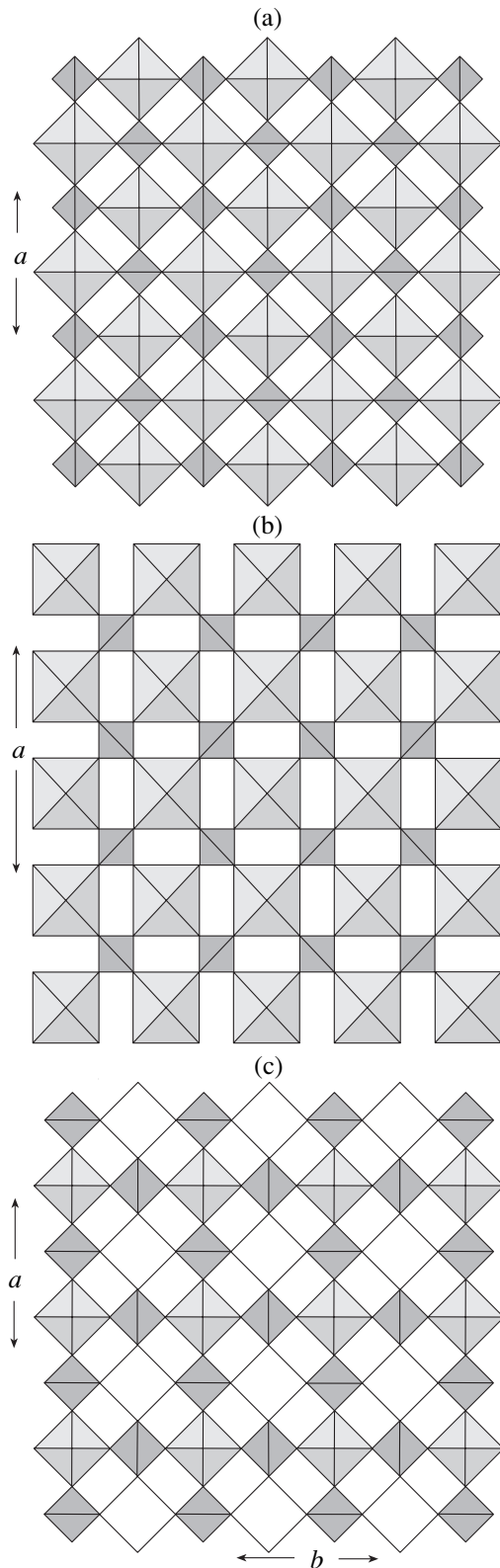


Fig. 2. The $[^6M_2[^4]T_2\phi_{12}]$ sheet in the crystal structure of (a) metaautunite, (b) sulfohalite, and (c) natisite. ($U\phi_6$) square bipyramids (metaautunite), ($Na\phi_6$) octahedra (sulfohalite), and Ti [5]-coordinated polyhedra (natisite) are white; (PO_4), (SO_4), and (SiO_4) tetrahedra are gray.

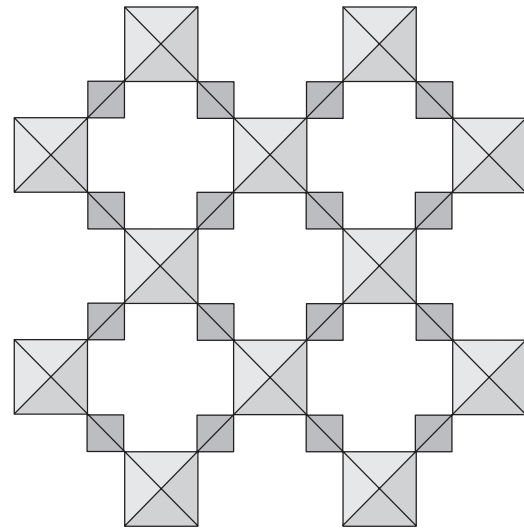


Fig. 3. Hypothetical sheet with a $[^6M[^4]T_2\phi_{10}\square_2]$ unit.

$[Ti_2Si_2O_{10}\square_2]^{4-}$. Note that the sulfohalite and natisite sheets are components of frameworks. There are several synthetic compounds of the same structure type as natisite; these are listed in Table 1.

Paranatisite, $Na_4[TiO(Ti,Fe^{3+})(O,OH)(SiO_4)_2]$, is characterized by three types of $[^6M_2[^4]T_2\phi_{12}]$ sheet (Sokolova and Hawthorne, 2002). In natisite, [5]-coordinated Ti occupies only one M site. In paranatisite, [5]-coordinated Ti and [6]-coordinated Na occupy two M sites and the sheets have the composition $[TiNaSi_2O_{10}\square_2]^{10-}$. The third sheet in the paranatisite structure is similar to the sulfohalite sheet, as it contains [6]-coordinated Na and has the composition $[Na_2Si_2O_{10}\square_2]^{7-}$ (Table 1); this sheet is more distorted than the sulfohalite sheet.

Minerals with a $[M^6]\square[^4]T_2\phi_{10}\square_2$ Sheet

We noted above that a three-colored net (Fig. 1c) corresponds to a sheet with three types of cations. If vacancies (\square) are regarded as a type of cation, the net is also a three-colored 4^4 net (Fig. 1d) (or a two-colored 8^4 net). A hypothetical sheet based on such a vacancy-containing 4^4 net is shown in Fig. 3. Each second octahedron is missing, and the sheet unit is transformed into $[^6M^6]\square[^4]T_2\phi_{12}\square_2$. There are several minerals with this type of sheet as a structural fragment: minerals of the garnet group, griphite, girvasite, olmsteadite, johnwalkite, rhomboclase, and gainesite.

Garnet group. There are 16 minerals in the garnet group with the general formula $A_3B_2(SiO_4)_3$, $[^8]A = Ca, Fe^{2+}, Mg, \text{ and } Mn^{2+}$; $[^6]B = Al, Cr^{3+}, Fe^{3+}, Mn^{3+}, Si, Ti, V^{3+}, \text{ and } Zr$. Spessartine, $Mn_3Al_2(SiO_4)_3$, represents this group in Table 1 (Verkhovskii *et al.*, 1970). In the garnet structure, B octahedra and (SiO_4) tetrahedra form the sheet shown in Fig. 4a. The presence of the vacancy in

Table 1. Selected minerals and synthetic compounds with the $[{}^6M_2 {}^4T_2\phi_{12}]$ sheet

Mineral	Formula	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Sp. gr.	Z	Orientation of sheet(s)	Unit $[{}^6M_2 {}^4T_2\phi_{12}]$			Ref.	
								<i>M</i> ₂	<i>T</i> ₂	ϕ_{12}		
Sulfohalite	Na ₆ [(SO ₄) ₂]FCl	10.150	<i>a</i>	<i>a</i>	<i>Fm3m</i>	4	(100) _↷	[Na	Na	S ₂	O ₁₀ FCl] ⁸⁻	(1)
Natisite ¹	Na ₆ [TiO(SO ₄)]	6.480	<i>a</i>	5.107	<i>P4/nmm</i>	2	(001)	[Ti	Ti	Si ₂	O ₁₀ □ ₂] ⁴⁻	(2–5)
Paranatisite ²	Na ₄ [TiOTiO(SiO ₄) ₂]	9.181	4.800	9.811	<i>Pmc2₁</i>	2	(100) _↷	1[Ti	Na	Si ₂	O ₁₀ □ ₂] ⁷⁻	(6, 7)
								2[Na	Na	Si ₂	O ₁₀ □ ₂] ¹⁰⁻	
Metauranocircite ³	Ba[(UO ₂)(PO ₄) ₂](H ₂ O) ₆	9.789	9.882	16.868	<i>P2₁/a</i>	4	(001)	[U	U	P ₂	O ₁₂] ²⁻	(8)
Threadgoldite ⁴	Al[(UO ₂)(PO ₄) ₂](OH)(H ₂ O) ₈	20.168	9.847	19.719	<i>C2/c</i>	8	(100)	[U	U	P ₂	O ₁₂] ²⁻	(9)
Metatorbernite	Cu[(UO ₂)(PO ₄) ₂](H ₂ O) ₈	6.972	<i>a</i>	17.277	<i>P4/n</i>	2	(001)	[U	U	P ₂	O ₁₂] ²⁻	(10)
Metaautunite	Ca[(UO ₂)(PO ₄) ₂](H ₂ O) ₆	6.96	<i>a</i>	8.40	<i>P4/nmm</i>	1	(001)	[U	U	P ₂	O ₁₂] ²⁻	(11)
Saleeite	Mg[(UO ₂)(PO ₄) ₂](H ₂ O) ₁₀	6.951	19.947	9.896	<i>P2₁/c</i>	2	(010)	[U	U	P ₂	O ₁₂] ²⁻	(12)
Abernathyite ⁵	K[(UO ₂)(AsO ₄)](H ₂ O) ₃	7.176	<i>a</i>	18.126	<i>P4/ncc</i>	4	(001)	[U	U	As ₂	O ₁₂] ²⁻	(13–17)
Metazeunerite ⁶	Cu[(UO ₂)(AsO ₄) ₂](H ₂ O) ₈	7.105	<i>a</i>	17.704	<i>P4₂/nmc</i>	2	(001)	[U	U	As ₂	O ₁₂] ²⁻	(18, 19)
Synthetic comp.	K ₄ [(UO ₂)(PO ₄) ₂]	6.985	<i>a</i>	11.865	<i>P4₂/nmc</i>	2	(001)	[U	□	P ₂	O ₁₀ □ ₂] ⁴⁻	(20)
Garnet ⁷	Mn ₃ [Al ₂ (SiO ₄) ₃]	11.650(1)	<i>a</i>	<i>a</i>	<i>Ia3̄d</i>	8	(100) _↷	[Mn	□	Si ₂	O ₁₀ □ ₂] ¹⁰⁻	(21)
Griphite	(Mn ²⁺ , Ca, Na, Li) ₂₄ Ca ₄ Fe ₄ Al ₈ (PO ₄) ₂₄ F ₈	12.205(8)	<i>a</i>	<i>a</i>	<i>Pa3</i>	1	(100) _↷	[Al	□	P ₂	O ₁₀ □ ₂] ⁷⁻	(22)
Girvasite ⁸	NaCa ₂ [Mg ₃ (OH) ₂ (PO ₄) ₂]{PO ₂ (OH) ₂ }(CO ₃)](H ₂ O) ₂	6.552(3)	12.25(3)	21.56(2)	<i>P2₁/c</i>	4	(001)	[Mg	□	P ₂	O ₉ (H ₂ O)□ ₂] ⁶⁻	(23)
Olmsteadite	K ₂ [Fe ²⁺ Nb ₂ O ₄ (H ₂ O) ₄ (PO ₄) ₄]	7.512(1)	10.000(3)	6.492(2)	<i>Pb2₁m</i>	1	(100)	[Nb	□	P ₂	O ₁₀ □ ₂] ⁵⁻	(24)
Johnwalkite	K ₂ [Mn ²⁺ Nb ₂ O ₄ (H ₂ O) ₄ (PO ₄) ₄]	7.516(4)	10.023(8)	6.502(4)	<i>Pb2₁m</i>	1	(100)	[Nb	□	P ₂	O ₁₀ G ₂] ⁵⁻	(25)
Rhomboclase ⁹	(H ₅ O ₂)[Fe(SO ₄) ₂](H ₂ O) ₂]	9.724(4)	18.333(9)	5.421(4)	<i>Pnma</i>	4	(010)	[Fe	□	S ₂	O ₈ (H ₂ O) ₂ □ ₂] ²⁻	(26, 27)
Gainesite	Na ₂ [Zr ₂ Be(PO ₄) ₄]	6.567(3)	<i>a</i>	17.119(5)	<i>I4₁/amd</i>	2	(001)	[(ZrBe ₂ □ ₂)	P ₂		O ₁₀ □ ₂] ^{5B}	(28)

Note: ¹ The first structural data on a synthetic analogue of natisite (2) is quoted. Isostructural synthetic compounds are Li₂TiOSiO₄ (3), Na₂TiOGeO₄ (4), Li₂VOSiO₄ (5).

² Isostructural synthetic compound is Na₂(TiO)[SiO₄] (7).

³ $\gamma = 89.95^\circ$.

⁴ $\beta = 110.71^\circ$.

⁵ Isostructural synthetic compounds are NH₄[(UO₂)(AsO₄)](H₂O)₃, KH₃O[(UO₂)(AsO₄)₂](H₂O)₆ (13); [(UO₂)H(PO₄)](H₂O)₄ (14); K[(UO₂)(PO₄)](D₂O)₃ (15); ND₄[(UO₂)(PO₄)](D₂O)₃ (16); [(UO₂)D(AsO₄)](D₂O)₄ (17).

⁶ Isostructural synthetic compound is Li[(UO₂)(AsO₄)₂](D₂O)₄ (19).

⁷ As an example, spessartine is given.

⁸ $\beta = 89.48(5)^\circ$.

⁹ Isostructural synthetic compound is (H₅O₂){In[SO₄]₂(H₂O)₂} (27).

↷ indicates permutation: thus, (100) ↷ = (100), (010), (001).

References: (1) Sakamoto (1968); (2) Nyman *et al.* (1978); (3) Ziadi *et al.* (1994); (4) Verkhovskii *et al.* (1970); (5) Rangan *et al.* (1998); (6) Sokolova and Hawthorne (2002); (7) Ziadi *et al.* (1996); (8) Khosrawan-Sazedj (1982a); (9) Khosrawan-Sazedj (1982b); (10) Stergiou *et al.* (1993); (11) Makarov and Ivanov (1960); (12) Miller and Taylor (1986); (13) Ross and Evans (1964); (14) Morosin (1978); (15) Fitch and Cole (1991); (16) Fitch and Fender (1983); (17) Fitch *et al.* (1983); (18) Hanic (1960); (19) Fitch *et al.* (1982); (20) Linde *et al.* (1980); (21) Sawada (1999); (22) Rinaldi (1978); (23) Sokolova and Egorov-Tismenko (1990); (24) Moore *et al.* (1976); (25) Dunn *et al.* (1986); (26) Mereiter (1974); (27) Tudo *et al.* (1979); (28) Moore *et al.* (1983).

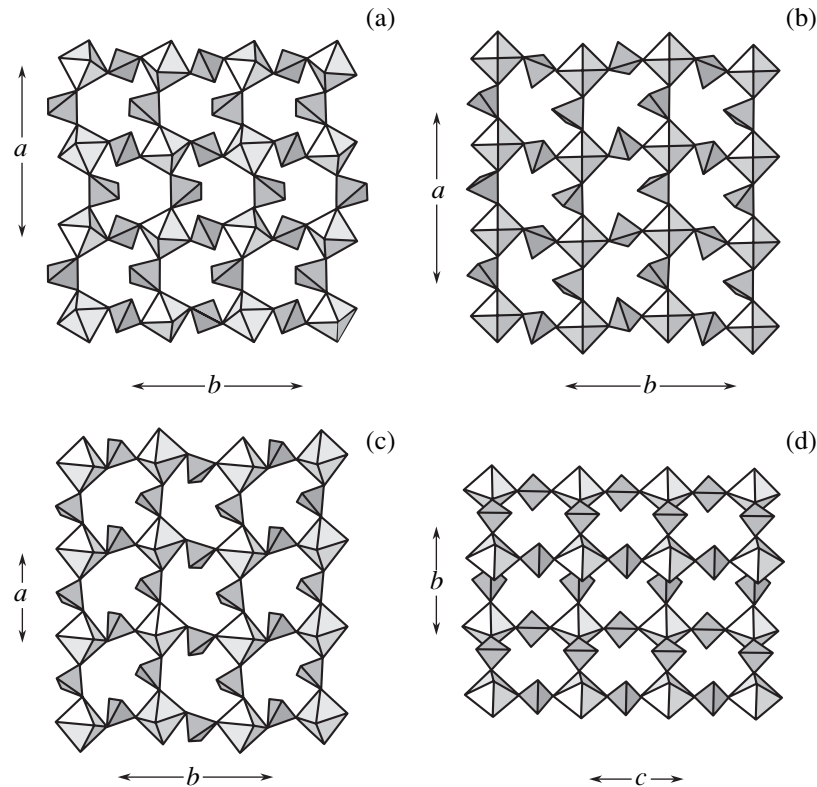


Fig. 4. The $[{}^6M\Box^{[4]}T_2\phi_{10}\Box_2]$ sheet in the crystal structure of (a) spessartine, (b) graphite, (c) girvasite, and (d) olmsteadite. ($Al\phi_6$) (spessartine and graphite), ($Mg\phi_6$) (girvasite), and ($Nb\phi_6$) (olmsteadite) octahedra are white; (SiO_4) (spessartine) and (PO_4) (graphite, girvasite, and olmsteadite) tetrahedra are gray.

the corresponding 4^4 net allows two of the four (SiO_4) tetrahedra to rotate around a line connecting the two nearest octahedra. Thus, the garnet $[{}^6M\Box^{[4]}T_2\phi_{10}\Box_2]$ sheet is more distorted (i.e., has lower plane-group symmetry) than the $[{}^6M_2\Box^{[4]}T_2\phi_{12}]$ sheets in Figs. 2a–2c. In the cubic structure of garnet, three $[{}^6B\Box^{[4]}Si_2\phi_{10}\Box_2]$ sheets intersect each other at right angles to form a framework.

Graphite, $(Mn^{2+}, Ca, Na, Li)_{24}Ca_4Fe_4^{2+}Al_8(PO_4)_{24}F_8$ (Rinaldi, 1978), has two types of framework: (1) one formed of (AlO_6) octahedra and (PO_4) tetrahedra and (2) one formed of (FeO_6) octahedra, (CaO_6F_2) cubes, and (PO_4) tetrahedra. Here, the first framework is of special interest, as it is formed by three $[{}^6Al\Box^{[4]}P_2\phi_{10}\Box_2]$ sheets similar to the $[{}^6B\Box^{[4]}Si_2\phi_{10}\Box_2]$ sheet in the garnet structure. The $[{}^6Al\Box^{[4]}P_2\phi_{10}\Box_2]$ sheet (Fig. 4b) is topologically identical to the garnet sheet and differs only in minor rotations of the polyhedra.

Girvasite, $NaCa_2[Mg_3(OH)_2(PO_4)_2\{PO_2(OH)_2\}(CO_3)](H_2O)_4$, is a good example of an exception to Pauling's (fifth) rule of parsimony (Pauling, 1960). The structure of girvasite consists of heteropolyhedral layers parallel to (001) and joined by hydrogen bonds (Sokolova and Egorov-Tis-

menko, 1990). The $[{}^6Mg\Box^{[4]}P_2\phi_{10}\Box_2]$ sheet (Fig. 4c) is the central part of the layer and is topologically identical to the sheets in garnet and graphite.

Olmsteadite, $K_2[Fe_4^{2+}Nb_2O_4(H_2O)_4(PO_4)_4]$ (Moore *et al.*, 1976) and *johnwalkite*, $K_2[Mn^{2+}NbO_4(H_2O)_4(PO_4)_4]$ (Dunn *et al.*, 1986), were described as phosphates with $[M_2^{2+}Nb_2O_4(H_2O)_4(PO_4)_4]^{6-}$ chains. One can also describe these structures in terms of the $[{}^6M\Box^{[4]}T_2\phi_{10}\Box_2]$ sheet: $[Nb\Box^{[4]}P_2\phi_{10}\Box_2]^{5-}$ (Fig. 4d), in which an (NbO_6) octahedron shares *cis* vertices with (PO_4) tetrahedra, in contrast to *trans* vertices in the sheets discussed above. This pattern of sharing results in a pronounced buckling of the sheet in the (001) plane (Fig. 4).

Rhombochase, $(H_5O_2)[Fe(SO_4)_2(H_2O)_2]$ (Mereiter, 1974), is of special interest here. In its structure, the $[Fe\Box^{[4]}S_2O_8(H_2O)_2\Box_2]^{2-}$ sheet consists of ($Fe^{2+}O_6$) octahedra and (SO_4) tetrahedra (Fig. 5a); each (FeO_6) octahedron shares *cis* vertices with two (SO_4) tetrahedra, with the latter above or below the plane of the sheet. The rhombochase sheet is the most contorted of all the sheets discussed here (Fig. 5b). The synthetic compound $K_4[(UO_2)(PO_4)_2]$ has a similar sheet (Linde *et al.*, 1980).

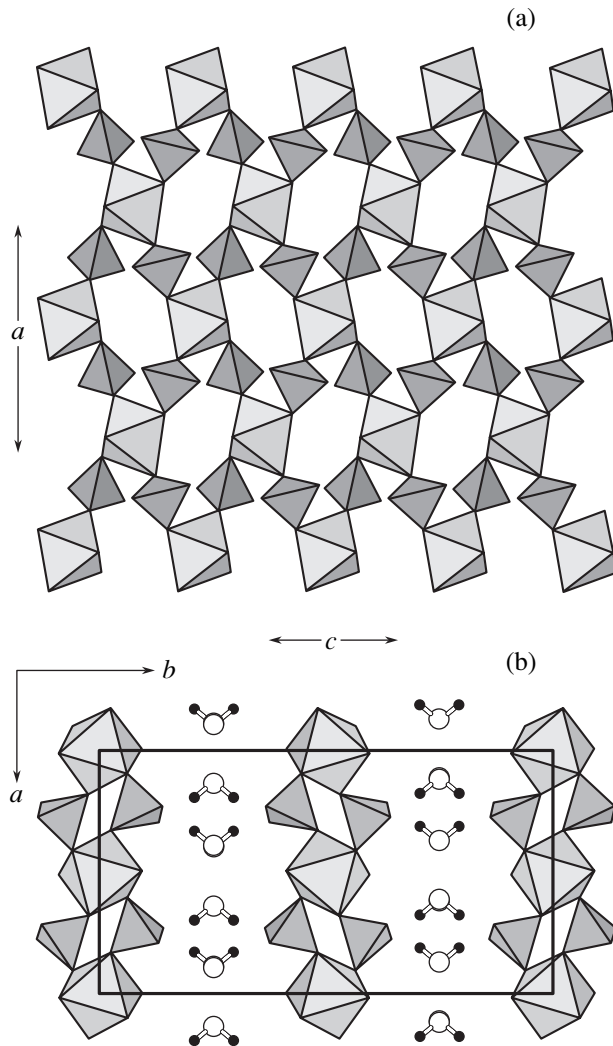


Fig. 5. The crystal structure of rhomboclase: (a) the sheet $[\text{Fe}\square\text{S}_2\text{O}_8(\text{H}_2\text{O})_2\square_2]^{2-}$ viewed down $[010]$ and (b) the $[001]$ projection of the crystal structure; (H_2O) groups of the structural unit are omitted for clarity; note that the central H atoms of the interstitial (H_5O_2) groups were not located in the refinement, and hence only the terminal (H_2O) groups are shown. $(\text{Fe}^{2+}\phi_6)$ octahedra are white, S tetrahedra are gray, and interlayer (H_2O) groups are shown as white (O) and black (H) circles.

Gainesite, end-member $\text{Na}_2[\text{Zr}_2\text{Be}(\text{PO}_4)_4]$ (Moore *et al.*, 1983), is based on an open framework of composition $[\text{Zr}_2\text{BeP}_4\text{O}_{16}]^{2-}$. Within this framework, Be and P show major long-range positional disorder. However, the framework must show short-range order if local bond valence requirements are to be satisfied. The resultant ordered arrangement of a slice through the structure is shown in Fig. 6. The corresponding net (Fig. 6a) is intermediate between the nets of Figs. 1b and 1d, and the sheet involves alternating (BeO_4) tetrahedra and vacancies (Fig. 6b), the tetrahedra forming $[\text{Be}(\text{PO}_4)_4]$ clusters. According to our scheme, this sheet is of the form $[(^{6}\text{Zr}^{4}\text{Be}\square)^{4}\text{P}_4\text{O}_{20}\square_4]^{10-}$ or

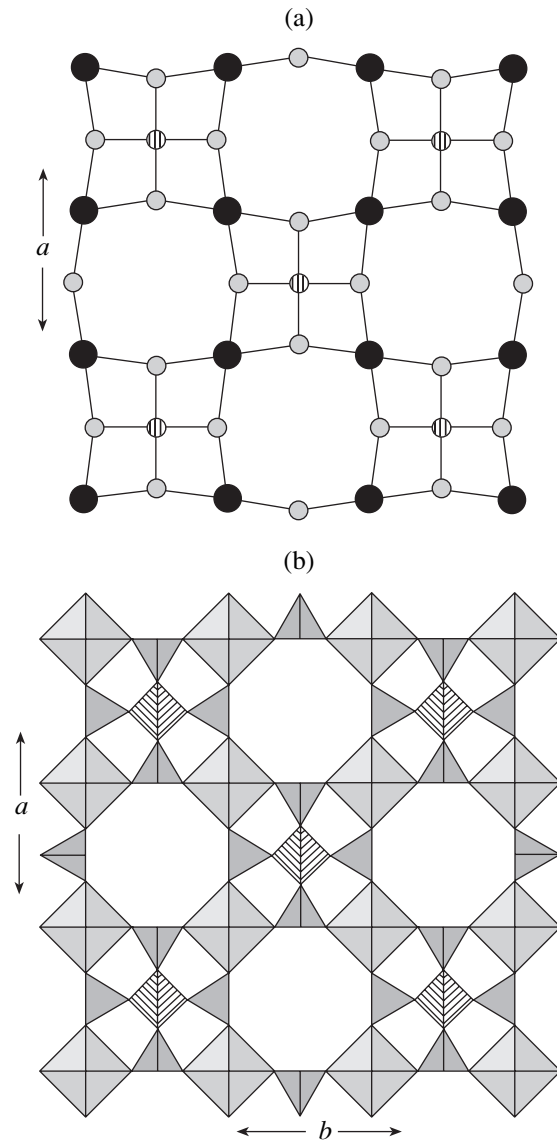


Fig. 6. Gainesite: (a) three-colored 4^4 net; (b) the (001) sheet of Zr octahedra, (PO_4) , and (BeO_4) tetrahedra. $(\text{Zr}\phi_6)$ octahedra are white, and (PO_4) and (BeO_4) tetrahedra are gray and striped, respectively. Colors of the atoms in the net correspond to colors of the polyhedra in the sheet, except for Zr atoms, which are shown as black spheres.

$[(^{6}\text{Zr}^{4}\text{Be}_2\square_2)^{4}\text{P}_2\text{O}_{10}\square_2]^{5-}$. Note that M now involves a tetrahedrally coordinated cation, Be, and also that the bond valence of the Be–O bonds, ~ 0.50 *vu*, is more similar to most octahedrally coordinated cations (Na–O to Al–O are in the range 0.17–0.50 *vu*) than to most tetrahedrally coordinated cations (Si–O to S–O are in the range 1.00–1.50 *vu*).

TRIMERIC CLUSTERS OF ALKALI-CATION COORDINATION POLYHEDRA

We can look at the crystal structure of sulfohalite, described above, in a different way.

Sulfohalite, $\text{Na}_6(\text{SO}_4)_2\text{FCl}$ (Sakamoto, 1968), has cubic symmetry and can be described as a combination of two layers parallel to (001): (1) a layer of $(\text{Na}\phi_6)$ octahedra sharing common vertices, edges, and faces at $z = 0$ and 2 and (2) a layer of $(\text{Na}\phi_6)$ octahedra linked to (SO_4) tetrahedra through common corners at $z = 1/4$ and $3/4$ (Fig. 2b). Figure 7a shows linkage of (NaO_4FCl) octahedra in the layer at $z = 0$. There is a cluster of six $(\text{Na}\phi_6)$ octahedra at the center of the cell, and one at each of the cell corners. If viewed along one of the threefold axes (Fig. 7b), the clusters of octahedra in the structure of sulfohalite now appear as combinations of two trimeric clusters at an angle of 60° to each other. The axis of the cluster along $[111]$ is formed by a sequence of O–F–O atoms with $\langle \text{F–O} \rangle = 2.90 \text{ \AA}$ (Table 2). Thus, the crystal structure of sulfohalite can be described as a framework of coupled trimeric clusters of octahedra.

In this work, we focus on the role of trimeric clusters, particularly the bond topology of the structures with these clusters. Two trimers of octahedra occurring in the crystal structure of nacaphite, $\text{Na}(\text{Na,Ca})_2(\text{PO}_4)\text{F}$ (Sokolova *et al.*, 1989; Sokolova and Hawthorne, 2001), are shown in Fig. 8. The $(\text{Na}_{1/2}\text{Ca}_{1/2}\phi_6)$ octahedra share an edge and also share a face each with the $(\text{Na}\phi_6)$ octahedron; the central axis of each cluster is an edge (formed by two F atoms) that is common to all three constituent octahedra. It should be emphasized that the degree of polymerization of these clusters depends on the content of monovalent anions relative to that of the alkali cations. The *interior* anion receives bond valence from six cations, primarily Na. With increasing content of monovalent anions, clusters can link into a chain. Moreover, to form a cluster, a polyhedron should exhibit only a *cis* configuration of the constituent monovalent anions. In this treatment, we do not include Cl because of its large size (and hence, different structural role) in comparison to F and OH anions.

The occurrence of trimeric clusters of octahedrally coordinated alkali cations in the structures of minerals results from the key role played by alkalis in the structure of these minerals. The presence of a similar cluster in a series of crystal structures indicates its high stability as a structural motif and testifies to a highly alkaline environment of formation. Table 2 lists minerals and synthetic compounds in which such trimeric clusters occur. In all these crystals, there are large amounts of Na (or Na and Ca) and monovalent anions: F, (OH), and Cl. Excluding synthetic compounds, the minerals can be divided into two groups: (1) hydrothermal minerals of hyperagpaitic rocks of the Khibina–Lovozero complex, Kola Peninsula (arctite, kogarkoite, nacaphite, quadruphite, polyphite, and sobolevite) and (2) volcanogenic exhalative minerals from Searles Lake, California (sulfohalite, galeite, and schairerite).

The crystal structures of *galeite*, $\text{Na}_{15}(\text{SO}_4)_5\text{F}_4\text{Cl}$ (Fanfani *et al.*, 1975b); *schairerite*, $\text{Na}_{21}(\text{SO}_4)_7\text{F}_6\text{Cl}$ (Fanfani *et al.*, 1975a); and *kogarkoite*, $\text{Na}_3(\text{SO}_4)\text{F}$, are

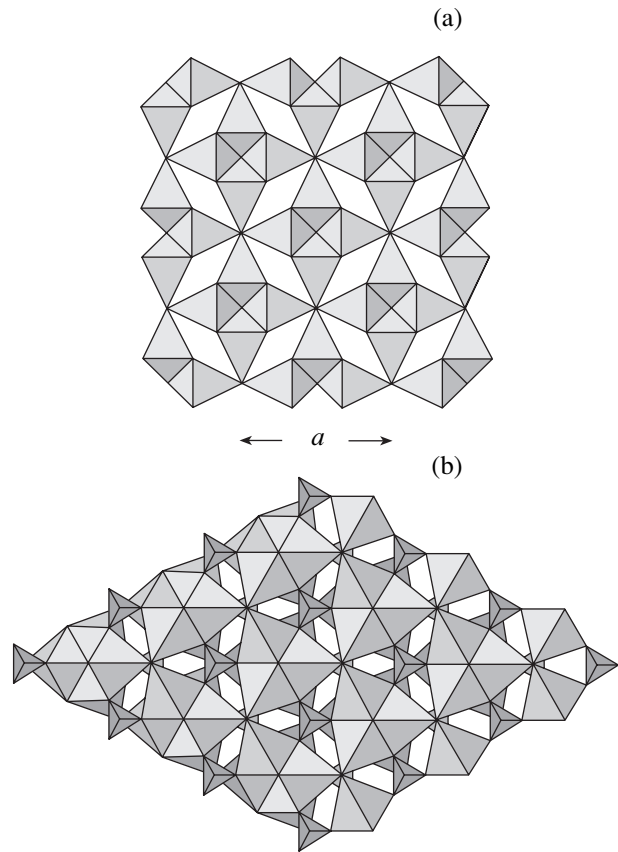


Fig. 7. The crystal structure of sulfohalite: (a) the layer of $(\text{Na}\phi_6)$ octahedra at $z = 0$; (b) the structure viewed down $[111]$; $(\text{Na}\phi_6)$ octahedra are white, and (SO_4) tetrahedra are gray.

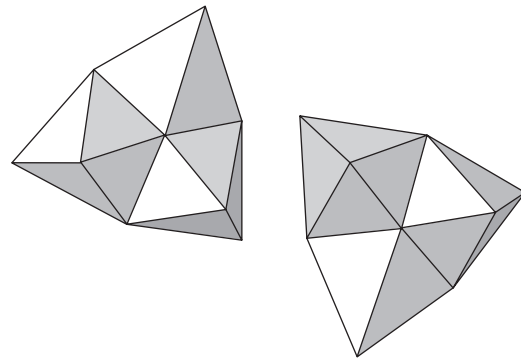


Fig. 8. The two distinct octahedral trimers.

closely related to the crystal structure of sulfohalite (see above). Out of these sulfate minerals, we consider here the crystal structure of kogarkoite.

Kogarkoite, $\text{Na}_3(\text{SO}_4)\text{F}$, occurs both in the Lovozero syenites, Kola peninsula, and in hot-spring deposits at Mount Princeton, Colorado. The crystal structure of kogarkoite has not yet been refined (Pabst and Sharp, 1973), but the structure of the synthetic analogue is known (Fanfani *et al.*, 1980). Its structure consists of

Table 2. Selected minerals and synthetic compounds with clusters of octahedrally coordinated alkali cations

Mineral	Formula	Space group	Z	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	Bonds within octahedral clusters, Å			Ref.
										⟨M(O,F)⟩	common edge		
											⟨An–An⟩	⟨An–O⟩	
Sulfohalite	Na ₆ (SO ₄) ₂ FCl	<i>Fm3m</i>	4	10.071(3)	<i>a</i>	<i>a</i>	–	–	–	2.458	–	2.887	(1)
Galeite	Na ₁₅ (SO ₄) ₅ F ₄ Cl	<i>P31m</i>	3	12.197(4)	<i>a</i>	13.96(1)	–	–	–	2.424	2.803	3.012	(2)
Schairerite	Na ₂₁ (SO ₄) ₇ F ₆ Cl	<i>P31m</i>	3	12.197(4)	<i>a</i>	19.259(1)	–	–	–	2.396	2.890	2.954	(3)
Kogarkoite	Na ₃ (SO ₄)F	<i>P2₁/m</i>	12	18.079(7)	6.958(1)	11.443(2)	–	107.71	–	2.425	3.005	3.166	(4)
Synthetic	(Na _{0.67} Ca _{0.33}) ₃ PO ₄ F	<i>R3m</i>	15	7.0179(7)	<i>a</i>	40.56(4)	–	–	–	2.418	2.849	2.552	(5)
Arctite	(Na ₅ Ca)Ca ₆ Ba[PO ₄] ₆ F ₃	<i>R3̄m</i>	3	7.094(1)	<i>a</i>	41.32(1)	–	–	–	2.446	2.923	2.775	(6)
Nacaphite	Na(Na,Ca) ₂ (PO ₄)F	<i>P1̄</i>	4	5.3232(2)	12.2103(4)	7.0961(2)	90.002(1)	89.998(1)	89.965(1)	2.382	2.382	–	(7)
Synthetic comp.	Na ₂ Fe(PO ₄)(OH)	<i>Pbcn</i>	8	5.227(1)	13.861(5)	11.774(3)	–	–	–	2.360	2.640	–	(8)
Quadruphite	Na ₁₄ Ca ₂ Ti ₄ [Si ₂ O ₇] ₂ [PO ₄] ₄ O ₄ F ₂	<i>P1</i>	1	5.4206(2)	7.0846(2)	20.3641(7)	86.89(1)	94.42(1)	89.94(1)	2.357	2.731	–	(7)
Polyphite	Na ₁₇ Ca ₃ Mg(Ti,Mn) ₄ [Si ₂ O ₇] ₂ [PO ₄] ₆ O ₂ F ₆	<i>P1</i>	1	5.412(2)	7.079(3)	26.56(1)	95.21(4)	93.51(2)	90.10(3)	2.372	2.727	–	(9)
Sobolevite	Na ₁₁ (Na,Ca)(Mg,Mn)Ti ₄ [Si ₂ O ₇] ₂ [PO ₄] ₄ O ₃ F ₃	<i>P1</i>	2	5.4115(7)	7.018(1)	40.62(1)	93.19(2)	90.01(2)	90.00(1)	2.361	2.733	–	(10)

Notes: *M* = (Na,Ca), Na, Ca, Fe²⁺.Axial common edge of the octahedral cluster (triplet); An = univalent anion: F¹⁻, (OH)¹⁻.References: (1) Sakamoto (1968); (2) Fanfani *et al.* (1975b); (3) Fanfani *et al.* (1975a); (4) Fanfani *et al.* (1980); (5) Sokolova *et al.* (1999); (6) Sokolova *et al.* (1984); (7) Sokolova and Hawthorne (2001); (8) Kabalov *et al.* (1974); (9) Sokolova *et al.* (1987b); (10) Sokolova *et al.* (1988).

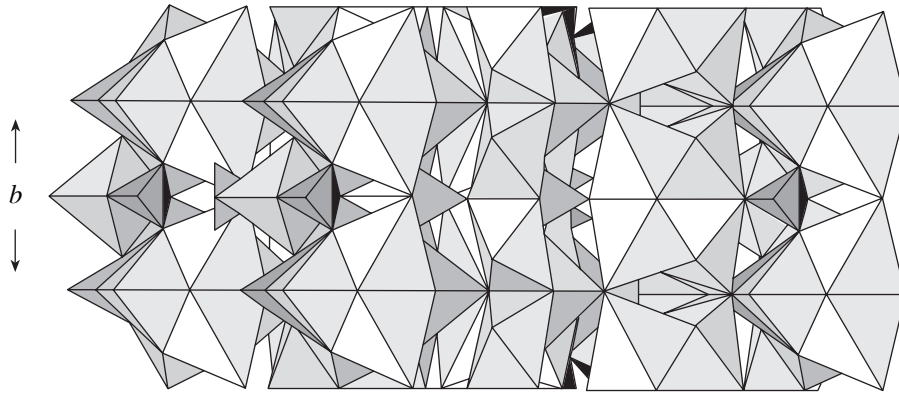


Fig. 9. The crystal structure of synthetic kogarkoite: (a) projected onto (102), (b) projected along [102]; different types of (NaO_4F_2) polyhedra are shown as white, and (SO_4) tetrahedra are dark gray.

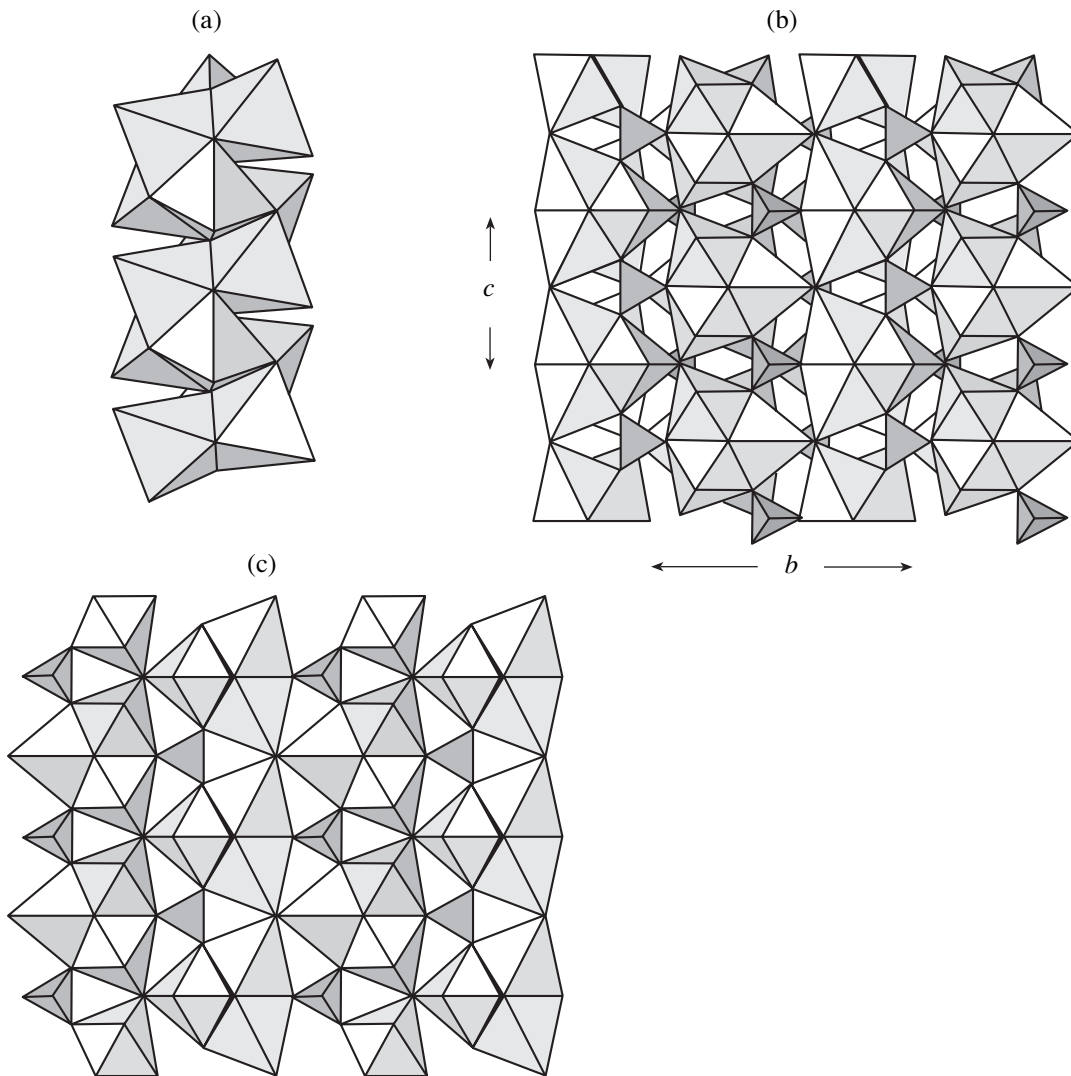


Fig. 10. The crystal structure of nacaphite: (a) the infinite chain of octahedral clusters rotated 60° relative to each other; (b) the crystal structure of nacaphite projected along [100]; (c) an infinite layer at $x \sim 0.25$ consisting of trimeric clusters of octahedra linked by (PO_4) tetrahedra; $(\text{Na}\phi_6)$ and $(\text{M}\phi_6)$ octahedra are white, and (PO_4) tetrahedra are gray.

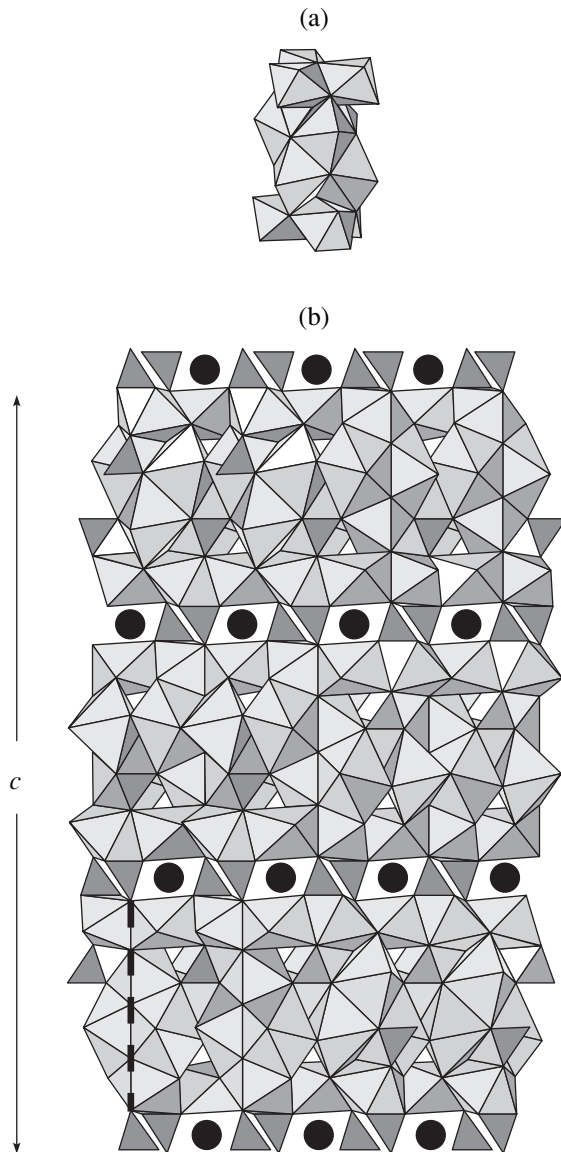


Fig. 11. The crystal structure of arctite, $(\text{Na}_5\text{Ca})\text{Ca}_6\text{Ba}[\text{PO}_4]_6\text{F}_3$: (a) a fragment of the structure, which is a column of four clusters of octahedra linked together, (b) a general view of the structure; [6]- and [7]-coordinated polyhedra are white, (PO_4) tetrahedra are gray, and Ba atoms are shown as black circles. The black dashed line indicates a column of four trimeric clusters linked together.

close-packed $(\text{Na}\phi_6)$ octahedra; in contrast to galeite and schairerite, there are no distorted $(\text{Na}\phi_6)$ octahedra in the structure of $\text{Na}_3(\text{SO}_4)\text{F}$. Figure 9 shows the trimeric clusters in the (102) projection of the structure of $\text{Na}_3(\text{SO}_4)\text{F}$.

Let us now consider the structures of some (Na, Ca) phosphates that have a similar trimeric motif as an important component of their atomic arrangement.

Nacaphite, $\text{Na}(\text{Na,Ca})_2(\text{PO}_4)\text{F}$, has the trimer of octahedra as the key motif in its structure (Sokolova

et al., 1989; Sokolova and Hawthorne, 2001). These *trimeric clusters* link to form a convoluted chain of octahedra (Fig. 10a) that extends in the *a* direction. Clusters adjacent in the chain are rotated $\sim 60^\circ$ relative to each other and connect by sharing both faces and edges. The chain shows pseudohexagonal symmetry described by the 6_3 axis oriented along the sequence of $[\text{F}(1)\text{--}\text{F}(2)]$ common edges that defines the central axis of the chain. Combination of two clusters corresponds to a sequence of two $[\text{F}(1)\text{--}\text{F}(2)]$ edges of 2.679 and 2.668 Å (sum = 5.347 Å), defining the *a* repeat and giving an *a* cell parameter of 5.3232(2) Å.

The chains extend along the *a* axis and link in the (100) plane by sharing octahedron corners (Fig. 10b): triplets of chains are further linked through (PO_4) tetrahedra that point alternately up and down the *a* axis. The (PO_4) tetrahedra share three vertices with octahedra of the same layer and the fourth vertex with three octahedra from the adjacent layer (Fig. 10c). The resultant layer occurs at $x \sim 0.25$ and ~ 0.75 .

Arctite, $(\text{Na}_5\text{Ca})\text{Ca}_6\text{Ba}(\text{PO}_4)_6\text{F}_3$, differs from the other compounds discussed here as it contains Ba in addition to alkali cations (Sokolova *et al.*, 1984). In the structure of arctite, Ba atoms (CN = [12]) are located at $z = 0, 1/3$, and $2/3$. Clusters of alkali cations occur between them (Fig. 11b). There are two unique [7]-coordinated sites in arctite: Ca and *M* ($=\text{Na}_{0.833}\text{Ca}_{0.167}$). Two Ca trimers and two *M* trimers link to form a column along [001] (Fig. 11a). The column of octahedra is centrosymmetric.

Related Minerals

Quadruphite, $\text{Na}_{14}\text{CaMgTi}_4[\text{Si}_2\text{O}_7]_2[\text{PO}_4]_4\text{O}_4\text{F}_2$ (Sokolova *et al.*, 1987a, Sokolova and Hawthorne, 2001); *polyphite*, $\text{Na}_{17}\text{Ca}_3\text{Mg}(\text{Ti,Mn})_4[\text{Si}_2\text{O}_7]_2(\text{PO}_4)_6\text{O}_2\text{F}_6$ (Sokolova *et al.*, 1987b); and *sobolevite*, $\text{Na}_{11}(\text{Na,Ca})(\text{Mg,Mn})\text{Ti}_4[\text{Si}_2\text{O}_7]_2(\text{PO}_4)_4\text{O}_3\text{F}_3$ (Sokolova *et al.*, 1988), are closely related to other minerals of the lomonosovite group. All three structures consist of two types of blocks, TS (titanium silicate) and AC (alkali cations) (Sokolova, 1998; Sokolova and Hawthorne, 2001). By analogy with nacaphite, there are infinite chains of trimeric clusters of octahedra in the structures of these minerals. In the structure of quadruphite, there is one infinite chain of trimeric clusters along the *c* axis. In the structure of polyphite, two infinite chains of octahedral clusters are joined together along the *c* axis. The structure of sobolevite corresponds to two quadruphite-like unit cells that differ in the chemical composition of the TS and AC blocks. The P : Si ratio varies from 1 : 1 in quadruphite and sobolevite to 3 : 2 in polyphite.

BOND VALENCE CONSIDERATIONS

These trimeric clusters occur in Na sulfates and (Na, Ca) phosphates. An O site in any structure with trimeric clusters of octahedra is characterized by four nearest neighbors: three [6]-coordinated cations and

one [4]-coordinated cation (P or S). In a sulfate structure, the central O atom receives $\sim 1.5 \nu u$ from S and needs $0.5 \nu u$ from the three neighboring cations. It receives $\sim 3 \times 1/6 = 0.5 \nu u$ from three ^{61}Na atoms. In a phosphate structure, an O atom receives $\sim 1.25 \nu u$ from P and needs $\sim 0.75 \nu u$ from the three adjacent cations. A value of $0.25 \nu u$ from an adjacent cation requires partial substitution of Na by a divalent cation, usually Ca. For a silicate structure of this type, the central O atom would receive $\sim 1.00 \nu u$ from Si and would need $\sim 1.00/3 = 0.33 \nu u$ from each of the three adjacent cations, e.g., ^{61}Ca . Thus, we can conclude that silicate members of this group of structures are possible.

Possible Silicate Analogues

We can assume that, for a silicate structure containing such a trimeric unit, dominance of divalent cations at the alkali sites is necessary. In a silicate structure, an oxygen atom receives $\sim 1.00 \nu u$ from Si^{4+} and needs $\sim 1.00 \nu u$ (in total) from three nearest neighbors. A value of $\sim 0.33 \nu u$ from one nearest-neighbor cation requires [6]-coordinated or [7]-coordinated Ca. Consider replacing Na by Ca and P by Si in a trimeric phosphate structure. Substitution of F for O should be possible as this anion receives bond valence from six adjacent alkali cations. The substitution $2\text{Na} + \text{Ca} + \text{P} + \text{F} \longleftrightarrow 3\text{Ca} + \text{Si} + \text{O}$ produces the formula $\text{Ca}_3[\text{SiO}_4]\text{O}$. This compound is well known as the most important constituent of portland cement clinker, tricalcium silicate: $3\text{CaO} \cdot \text{SiO}_2$. It crystallizes in several polymorphic modifications of triclinic, monoclinic, orthorhombic, and hexagonal symmetry (Regourd, 1964). Three polymorphs are strongly pseudorhombohedral, with hexagonal axes of $a = 7.0 \text{ \AA}$, $c = 25.0 \text{ \AA}$ (Jeffery, 1952). The pseudosymmetrical polymorph with $R3m$ symmetry corresponds quite well with the triplet Na sulfate and (Na, Ca) phosphate structures. In this structure, three unique [7]-coordinated Ca atoms form two types of triplets, $[\text{Ca}_3\text{O}_{15}][\text{Ca}(1)]$ and $[\text{Ca}_3\text{O}_{12}][\text{Ca}(2)$ and $\text{Ca}(3)]$, in the ratio 1 : 2. In the $[\text{Ca}_3\text{O}_{15}]$ triplet, (CaO_7) polyhedra share a common edge, as described above for sulfates and phosphates. In the $[\text{Ca}_3\text{O}_{12}]$ triplet, they have a central common vertex. Linkage of three clusters is shown in Fig. 12a. There are three types of oxygen atom in this structure: O atoms of the first type receive $2 \nu u$ from three Ca atoms and a Si atom, O atoms of the second type receive bond valence from the six nearest Ca atoms; and O atoms of the third type receive bond valence from one Si and four Ca atoms. For the latter case, two Ca–O bonds are short (about 2.3 \AA) and two Ca–O bonds are long (about 3.0 \AA). The crystal structure of $\text{Ca}_3[\text{SiO}_4]\text{O}$ can be split into nine layers (three of them unique) formed by different types of clusters (Fig. 12b).

For the synthetic compound $\text{Ca}_3[\text{SiO}_4]\text{O}$, triclinic, $a = 11.670 \text{ \AA}$, $b = 14.240 \text{ \AA}$, $c = 13.720 \text{ \AA}$, $\alpha = 105.5^\circ$, $\beta = 94.3^\circ$, $\gamma = 90.0^\circ$, $P\bar{1}$, $Z = 18$ (Golovastikov *et al.*,

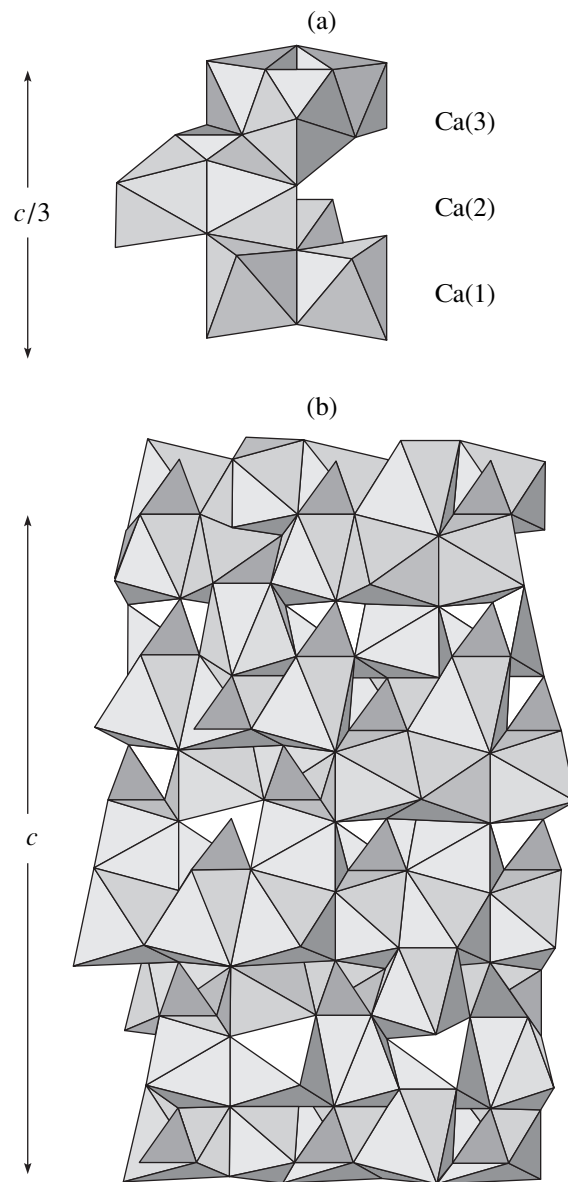


Fig. 12. $\text{Ca}_3[\text{SiO}_4]\text{O}$: (a) linkage of three trimeric clusters involving Ca; (b) general view; (CaO_7) polyhedra are white, and (SiO_4) tetrahedra are gray.

1975), the octahedral triplet $[\text{Ca}_3\text{O}_{11}]$ occurs. In this triplet, each octahedron shares two common faces with adjacent octahedra. Calcium is [6]- and [7]-coordinated; (CaO_n) polyhedra are linked to each other through common vertices, edges, and faces, and zigzag chains of (CaO_n) polyhedra extend through the structure. In the crystal structure of triclinic $\text{Ca}_3[\text{SiO}_4]\text{O}$, triplets of octahedra occur as *islands* in a wild (dis)array of Ca polyhedra. Moreover, an infinite layer of Ca triplets has been previously described for arctite. These arguments suggest that the occurrence of a mineral similar to the pseudosymmetrical polymorph of $\text{Ca}_3[\text{SiO}_4]\text{O}$ is possible.

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