THE CRYSTAL STRUCTURE OF TREMBATHITE, $(Mg_{1.55}Fe_{1.43}Mn_{0.02})B_7O_{13}Cl$, A MINERAL OF THE BORACITE GROUP: AN EXAMPLE OF THE INSERTION OF A CLUSTER INTO A THREE-DIMENSIONAL NET

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ABSTRACT

The crystal structure of trembathite, $(Mg_{1.55}Fe_{1.43},Mn_{0.02})B_7O_{13}Cl$, a 8.588(2), c 21.050(6) Å, V 1344.5(1) Å^3, was refined in the space group $R3c$ to an R index of 3.2% based on 1472 observed reflections measured with Mo$K\alpha$ X-radiation. Trembathite is a mineral of the boracite group. In contrast to the cubic boracite structure, it contains only three borate tetrahedra connected *via* one oxygen atom. The borate clusters are connected to each other by single borate tetrahedra. We designate the single borate tetrahedra as *topologically active* and the condensed [B$_4$O] or [B$_3$O] groups as *topologically passive*. Connecting the centers of the topologically active borate tetrahedra results in a three-dimensional net in which the nodes are isostructural to the anion positions of the ReO$_3$ structure-type. The anion position around the central cations in the ReO$_3$ structure-type form chains of corner-sharing octahedra, which we name as *cso*-chains. The same topology with four condensed octahedra [M_4(O,OH)$_4$] (M = Fe, Ge, Mo, Al, Ge) surrounded by six TO$_4$ tetrahedra (T = As, P, Ge) occurs in the structures of pharmacosiderite, K[(FeOH)$_4$(AsO$_4$)$_3$](H$_2$O)$_6$. In both cases, the structure-building principle involves the insertion of clusters of polyhedra into the *cso*-chains.

Keywords: trembathite, crystal structure, electron-microprobe analysis, structure topology.

SOMMAIRE

Nous avons affiné la structure cristalline de la trembathite, $(Mg_{1.55}Fe_{1.43},Mn_{0.02})B_7O_{13}Cl$, a 8.588(2), c 21.050(6) Å, V 1344.5(1) Å^3, dans le groupe spatial $R3c$ jusqu'à un résidu R de 3.2% en utilisant 1472 réflexions observées, mesurées avec rayonnement Mo$K\alpha$. La trembathite est un minéral du groupe de la boracite. Contrairement au cas de la structure cubique de la boracite, elle contient seulement trois tétraèdres de borate liés *via* un atome d'oxygène. Ces agroupements de borate sont interliés par un tétraèdre de borate isolé. Nous appelons le tétraèdre isolé *topologiquement actif*, et les groupes condensés [B$_4$O] ou [B$_3$O], *topologiquement passifs*. L'interconnexion des centres des tétraèdres topologiquement actifs mène à un réseau tri-dimensionnel dans lequel les noeuds rappellent le placement des anions dans les structures de type ReO$_3$. La position des anions autour des cations centraux dans ce type de structure definit une chaîne d'octaèdres à coins partagés, que nous appelons chaînes *cso*. On retrouve la même topologie avec quatre octaèdres condensés [M_4(O,OH)$_4$] (M = Fe, Ge, Mo, Al, Ge) entourés de six tétraèdres TO$_4$ (T = As, P, Ge) dans la structure de la pharmacosidérite, K[(FeOH)$_4$(AsO$_4$)$_3$](H$_2$O)$_6$. Dans les deux cas, le principe de construction des structures implique l'insertion d'assemblages de polyèdres dans les chaînes *cso*.

(Traduit par la Rédaction)

Mots-clés: trembathite, structure cristalline, analyse à la microsonde électronique, topologie de la structure.

INTRODUCTION

Boracite-type phases have the general formula M_3[B$_7$O$_{13}$]A, where M stands for Mg, Cr, Mn, Fe, Co, Ni, Zn, Cd, and A represents F, Cl, I, Br, S, OH and NO$_3$ (Burzo 1993). The framework is a complex network of corner-sharing borate polyhedra with M cations and A anions located in the interstices. Most phases show a first-order ferroelectric → ferroelastic transition between a high-temperature cubic phase ($F\bar{4}3c$) and a low-temperature orthorhombic phase ($Pca2_1$) (Schmid

& Tippmann 1978). During cooling from the high-temperature cubic phase to the lower-symmetry phases (Schmid 1994), complex twin-domains form. The lowering of symmetry is accompanied by a change in coordination of one B atom, which is triangularly coordinated in space group $Pca2_1$ (Dowty & Clark 1973). In the cubic form, the M site is in octahedral coordination with two *trans* A anions (Ito *et al.* 1951, Sueno *et al.* 1973); in space group $Pca2_1$, one A anion is closer to the M cation, forming a pyramidal [4+1] coordination. Iron-rich compounds show space-group

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symmetry $R3c$, with a structural arrangement similar to that in compounds with space group $Pca2_1$, but with a different arrangement of the equivalent units (Dowty & Clark 1973).

Trembathite was first described by Burns *et al.* (1992) as a mineral of the boracite group with the general formula $(Mg,Fe)B_7O_{13}Cl$. The ratio Mg/Fe is greater than 1.0, and the structure has space-group symmetry $R3c$. This distinguishes trembathite from congolite $(Fe,Mg)B_7O_{13}Cl$, the Fe-analogue with space-group symmetry $R3c$ (Schmid 1970, Dowty & Clark 1973, Mendoza-Alvarez *et al.* 1985), and the low-temperature structure of boracite $(Mg,Fe)B_7O_{13}Cl$ with a small Fe/Mg value and space-group symmetry $Pca2_1$ (Dowty & Clark 1973). Burns & Carpenter (1996, 1997) described in detail the phase relations of the boracite minerals with respect to changing Fe/Mg and temperature.

Here, we present results of the first single-crystal structure-refinement of trembathite, and we show the topological analogy of the boracite structure with the ReO$_3$ structure-type (Meisel 1932) by insertion of [B$_4$O] groups into a three-dimensional net.

EXPERIMENTAL

The trembathite sample is from the Baulby potash mine, Loftus, Cleveland, England; this is only the second locality for trembathite. A pink cube with an edge length of approximately 2 cm was crushed and examined with a polarizing microscope. The occurrence of large single-crystal domains in twinned boracite crystals was reported by Schmid (1970) and Dowty & Clark (1973). One single-crystal domain of trembathite was identified by its uniform optical properties in this work. The crystal was mounted on a Nicolet $R3m$ automated four-circle diffractometer. Twenty-six reflections were centered using graphite-monochromated MoKα X-radiation; the resulting cell dimensions are given in Table 1. A total of 679 symmetry-independent reflections was measured ($3 \leq 2\theta \leq 60°$), with index ranges $-12 \leq h \leq 0$, $-10 \leq k \leq 10$, $0 \leq l \leq 26$, according to the

method of Burns *et al.* (1994). The intensity data were corrected for absorption (psi-scan method), Lorentz, polarization and background effects, and reduced to structure factors. A reflection was considered observed if its magnitude exceeded five standard deviations above background, based on counting statistics.

Refinement of the crystal structure

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The SHELXS system of programs (Sheldrick 1990) was used for this work.

The structure was refined in the space group $R3c$ using the positional coordinates of Dowty & Clark (1973). The final cycles of refinement involved all variable positional parameters, anisotropic-displacement factors and the site-scattering parameter for the M site. The structure converged to an R index of 3.0%. The anisotropic displacement factors of the $B(1)$ atom were non-positive definite, and so we refined the isotropic displacement factor for $B(1)$. For comparison, we transformed the cell to the orthorhombic and cubic boracite cells and we refined the structure in the space groups $Pca2_1$ and $F\bar{4}3c$, respectively. Both models refined to an R index of 27%, which showed clearly that the space-group symmetry $R3c$ is correct. Final atomic positions are listed in Table 2. Selected interatomic distances and

TABLE 1. EXPERIMENTAL DATA FOR TREMBATHITE $(Mg_{1.55}Fe_{1.43}Mn_{0.02})B_7O_{13}Cl$

a (Å)	8.588(2)	crystal system	hexagonal
c	21.050(6)	crystal size (mm)	0.21 x 0.17 x 0.02
V (Å^3)	1344.5(1)	No. I	1472
Z	6	No. of unique $|F|$	679
μ (mm^{-1})	2.96	No.of $|F_o| > 5\sigma F$	429
D(calc) (g/cm^3)	3.225	R_m (%)	3.0
space group	$R3c$	R (%)	3.2
		wR (%)	2.6

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{1/2}$, $w = 1$

TABLE 2. ATOMIC POSITIONS AND DISPLACEMENT PARAMETERS (x 10^3) FOR TREMBATHITE

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M	0.7015(1)	0.8501(3)	0	10(1)	5(1)	8(4)	−2(1)	−5(5)	6(1)
B(1)	0.101(1)	−0.102(1)	0.1448(3)	8(1)*					
B(2)	−0.169(1)	0.169(1)	0.0884(4)	12(5)	6(5)	12(3)	−3(5)	−2(5)	5(3)
B(3)	2/3	1/3	0.1069(4)	10(3)	10(3)	2(4)	0	0	5(1)
O(1)	0	0	0.1620(3)	8(2)	8(2)	8(3)	0	0	4(1)
O(2)	0.7463(5)	0.6412(5)	0.0274(2)	7(2)	6(2)	6(2)	−3(1)	−3(1)	3(2)
O(3)	0.6383(5)	0.0433(6)	−0.0306(2)	9(2)	6(2)	5(2)	−1(1)	−2(1)	3(2)
O(4)	0.7766(5)	0.9761(5)	0.0848(2)	9(2)	1(2)	7(2)	−2(1)	−2(1)	2(1)
O(5)	0.4934(5)	0.6660(5)	−0.0562(2)	13(2)	5(2)	9(1)	1(2)	1(2)	7(1)
Cl	0	0	−0.0626(1)	13(1)	13(1)	12(1)	0	0	6(1)

* Isotropic

TABLE 3. SELECTED DISTANCES [Å] AND ANGLES [°] IN TREMBATHITE

M–O(2)	2.095(6)	O(2)–M–O(4)	94.0(2)
M–O(3)l	2.088(6)	O(3)b–M–O(5)	87.9(2)
M–O(4)	2.020(4)	O(2)–M–O(5)	87.8(2)
M–O(5)	2.066(4)	O(2)–M–O(3)b	175.6(1)
M–Cla	2.581(2)	O(4)–M–O(3)b	89.3(2)
M–Clc	3.507(2)	O(3)b–M–Cla	92.0(1)
		O(2)–M–Cla	90.3(1)
		O(5)–M–Cla	110.7(1)
		O(4)–M–Cla	102.3(1)
B(1)–O(3)e	1.45(1)	O(1)–B(1)–O(3)e	108.4(8)
B(1)–O(2)d	1.44(1)	O(1)–B(1)–O(2)d	110.9(6)
B(1)–O(4)f	1.48(1)	O(1)–B(1)–O(4)f	107.2(9)
B(1)–O(1)	1.56(1)	O(3)e–B(1)–O(2)d	110.3(9)
<B(1)–O>	1.48(1)	O(3)e–B(1)–O(4)f	110.1(9)
		O(2)d–B(1)–O(4)f	109.8(8)
B(2)–O(3)g	1.46(1)	O(3)g–B(2)–O(2)k	109.7(6)
B(2)–O(2)h	1.44(1)	O(3)g–B(2)–O(5)j	107.6(7)
B(2)–O(4)	1.48(1)	O(3)j–B(2)–O(4)i	110.9(6)
B(2)–O(5)j	1.50(1)	O(2)h–B(2)–O(5)j	112.8(9)
<B(2)–O>	1.47(1)	O(2)h–B(2)–O(4)i	110.2(7)
		O(5)j–B(2)–O(4)i	105.4(6)
B(3)–O(5)k,l,m ×3	1.379(2)	O(5)k,l–B(3)–O(5)m	119.7(2)

a: 1+*x*, 1+*y*, *z*; b: *x*, 1+*y*, *z*; c: ⅙+*x*, ⅚+*y*, ⅚+(*z*–½);
d: –⅔+*x*, –⅙+(*x*–*y*), ⅚+(*z*–½); e: ⅓–*y*, ⅔–*x*, *z*; f: 1–*y*, *y*–*x*, *z*;
g: –⅔+*x*, –⅙+(*x*–*y*), ⅚+(*z*–½); h: *y*–*x*, 1–*x*, *z*; i: –1+*x*, –1+*y*, *z*;
j: ⅓–*y*, ⅔–*x*, ⅚+(*z*–½); k: 1+(⅙–*y*), ⅔–*x*, ⅚+(*z*–½);
l: ⅙+(*y*–*x*), –⅙+*y*, ⅚+(*z*–½); m: ⅙+*x*, ⅚+(*x*–*y*), ⅚+(*z*–½)

TABLE 4. CHEMICAL COMPOSITION OF THE TREMBATHITE AND CONGOLITE FRAGMENTS OF THE LARGE SINGLE CRYSTAL EXAMINED IN THIS WORK

	Trembathite (n = 3)	Congolite Max. Mg	Congolite Min.Mg
MgO	14.27	12.22	10.06
MnO	0.37	0.38	0.36
FeO	23.51	26.62	29.45
CaO	0.01	0.01	0.02
Cl	8.00	8.00	8.14
B₂O₃*	55.67	55.14	54.28
Cl₂O	–1.81	–1.81	–1.84
Total	100.02	100.57	100.48
Mg²⁺	1.55	1.34	1.12
Mn²⁺	0.02	0.02	0.02
Fe²⁺	1.43	1.64	1.84
Cl⁻	0.99	1.00	1.03
B³⁺	7.00	7.00	7.00
O²⁻	13.01	13.00	12.97
Mg/(Mg+Fe)	0.52	0.45	0.38

* B_2O_3 was calculated as 7.0 *apfu* (atoms per formula unit)

angles are shown in Table 3. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

ELECTRON-MICROPROBE ANALYSIS

Subsequent to the collection of the X-ray intensity data, the crystal fragment used, together with one additional larger fragment from the same 2 cm crystal, were mounted and carbon-coated for chemical analysis with a Cameca SX–50 electron microprobe operating in the wavelength-dispersion mode with an excitation voltage of 15 kV and a specimen current of 20 nA. The following standards were used: dolomite (Mg, Ca), tugtupite (Cl) and siderite (Mn, Fe). Data reduction was done according to the $\phi(\rho Z)$ method (Pouchou & Pichoir 1984, 1985); the chemical composition (mean of three points) is given in Table 4. The unit formula was calculated on the basis of 14 anions, assuming stoichiometric B.

RESULTS

Refinement of the site-scattering parameter for the *M* site gave an Mg/(Mg + Fe) value of 0.51, which agrees very well with the value of 0.52 determined by electron-microprobe analysis of the single crystal

(trembathite, Table 4). The chemical formula based on results of the chemical analysis is $(Mg_{1.55}Fe_{1.43},Mn_{0.02})B_7O_{13}Cl$. A second crystal shows the chemical composition of congolite (Table 4), with variation in the Mg/(Mg + Fe) from 0.38 to 0.45. Variation of Mg/Fe was also described by Burns *et al.* (1992) in trembathite crystals from the type locality: Salt Springs potash deposit in Sussex, New Brunswick. Those crystals showed variation in Mg/(Mg + Fe) from 0.74 to 0.51. The crystal-structure refinement shows distances and angles (Table 3) similar to those of congolite (Dowty & Clark 1973).

TOPOLOGY OF THE PARENT CUBIC-BORACITE STRUCTURE

Fundamental Building Block (FBB)

The structure of cubic boracite (Ito *et al.* 1951, Sueno *et al.* 1973) consists of a framework of corner-sharing (BO₄) tetrahedra, with interstitial metal and halogen atoms. The *FBB* for this structure (Burns *et al.* 1995) is 4□:[φ]□□□□, showing a central atom of oxygen connected to four (BO₄) tetrahedra. In cubic boracite, the central atom of oxygen occurs at a site with point symmetry 23, and the B(3)–O bond length is 1.693(5) Å (Sueno *et al.* 1973), considerably longer than the grand <[4]B–O> of 1.476 Å in minerals (Hawthorne *et al.* 1996). Significant anisotropic motion of the B(3) and O(1) atoms is observed by diffraction techniques. An infrared spectroscopic study of cubic crystals in the series Mg₃B₇O₁₃Cl–Fe₃B₇O₁₃Cl indicates that there are (BO₃) triangles locally present in the structure (Burns & Carpenter 1997), in contrast to the long-range structure obtained using diffraction techniques. In the
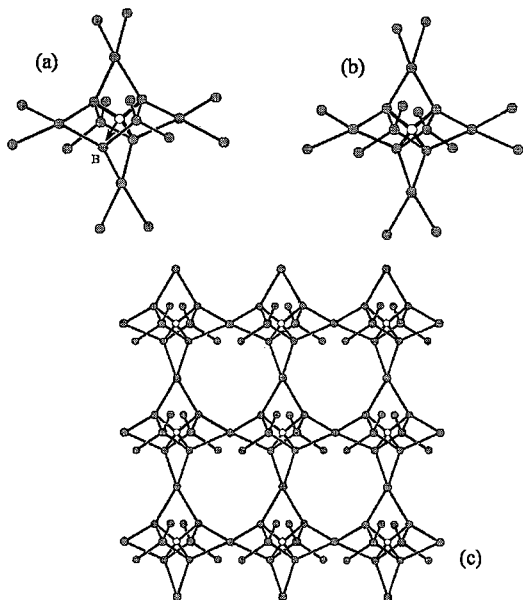
FIG. 1. (a) The [B$_7$O$_{13}$] group of the rhombohedral (or orthorhombic) boracite structure. (b) The [B$_7$O$_{13}$] group of the cubic boracite structure. The core with the [B$_3$O] and [B$_4$O] cluster is shown in heavy lines. All other oxygen atoms have been omitted for clarity. The shift of one B atom from the center in the rhombohedral (or orthorhombic) group is indicated by an arrow. (c) The arrangement of the [B$_7$O$_{13}$] groups in the cubic boracite structure with ReO$_3$ topology.

low-temperature structures, the central atom of oxygen is bonded to three B atoms only, and the borate framework contains both (BO$_4$) tetrahedra and (BO$_3$) triangles. The FBB of both the *Pca2$_1$* and *R3c* structures is Δ6 □:[ϕ]<3 □><3 □><3 □>Δ.

Active and passive borate tetrahedra in a three-dimensional net formed by cso-chains

Another way to describe the structures of high- and low-temperature boracite is to divide them into topologically active and passive borate tetrahedra. Figure 1 shows parts of the [B$_7$O$_{13}$] groups of the boracite structures and the whole topology of the cubic form. For clarity, only the B atoms and the O(1) atom are shown. The difference between the [B$_7$O$_{13}$] groups of the cubic and rhombohedral phases is shown in Figure 1. In the rhombohedral structure, one B atom moves away from O(1), breaking one of the four B–O(1) bonds present in the cubic phase. The inner cores of the groups contain a polymerized [B$_4$O] or [B$_3$O] cluster, respectively (shown in Fig. 1 with bold lines). The groups and the topology of the cubic form show that each [B$_4$O] or [B$_3$O] cluster is connected to adjacent [B$_4$O] or [B$_3$O]

clusters by single borate tetrahedra at each vertex of an octahedron. Connecting the centers of the single borate tetrahedra results in a three-dimensional net, whose nodes are isostructural to the anion positions in the ReO$_3$ structure-type. In the ReO$_3$ structure-type, the anion positions around the central cations form chains of corner-sharing octahedra, which we name *cso*-chains. We designate further the connecting borate tetrahedra as *topologically active*, and the [B$_4$O] cluster as *topologically passive*, because the single (BO$_4$) tetrahedra are the nodes of the *cso*-chain, and the [B$_4$O] or [B$_3$O] clusters are, in a topological sense, only decoration inside the octahedra of the *cso*-chains. To derive the boracite structure, the topologically passive [B$_4$O] clusters are inserted into the centers of the octahedra, each B atom linking to three atoms of oxygen of the topologically active tetrahedra.

Insertion of clusters into the AB$_3$ structure-type

The analogy between the ReO$_3$ framework as an *AB$_3$* structure-type and the three-dimensional boracite net can be expressed as follows: in ReO$_3$, *A* is [6]-coordinated and *B* is [2]-coordinated, whereas in boracite, *A* is a [B$_4$O] cluster surrounded by 6/2 borate tetrahedra. The structure of boracite can thus be written as (Mg$_3$)(Cl) [(B$_4$O)(BO$_4$)$_{6/2}$].

A similar arrangement occurs in the structure of pharmacosiderite, K[(FeOH)$_4$(AsO$_4$)$_3$](H$_2$O)$_6$, and its many isostructural compounds. Pharmacosiderite consists of a [$^{[6]}$M$_4$(O,OH)$_4$] cluster, with $^{[6]}$M representing Fe, Al, Ge, Mo, *etc.* The four fused octahedra are tetrahedrally arranged and are connected to each other by six TO$_4$ groups (*T* = As, P, Ge, *etc.*) surrounding them in an octahedral arrangement (Buerger *et al.* 1967, Zemann 1959) (Fig. 2). A further example of an ReO$_3$-type structure is the synthetic phase Na$_3$[Zn$_4$O(PO$_4$)$_{6/2}$] (H$_2$O)$_6$ (Harrison *et al.* 1996), with four (ZnO$_4$) tetrahedra (linked in the same way as the [B$_4$O] cluster in boracite) and surrounded by six phosphate tetrahedra. The topologically passive [B$_4$O], [Zn$_4$O] and [Fe$_4$(OH)$_4$] groups are inserted into octahedral units formed by (TO$_4$) tetrahedra (*T* = B, P, As). The octahedral units form *cso*-chains similar to chose in the ReO$_3$ net.

Insertion of clusters in AB$_2$ structure-types

The insertion of clusters into square-planar units was recently described by Schindler & Baur (1997). They showed that in microporous vanadium phosphate compounds (Schindler *et al.* 1997, Khan *et al.* 1996), topologically passive [V$_5$O$_9$] groups are connected to each other by topologically active (PO$_4$) tetrahedra (Fig. 3a). Connecting the topologically active (PO$_4$) tetrahedra yields square-planar four-rings. These square-planar units form twisted square (ts) chains (Smith 1997), which form (in this case) the nets of sodalite (Fig. 3c) (Pauling 1930) and synthetic-zeolite rho (Baur
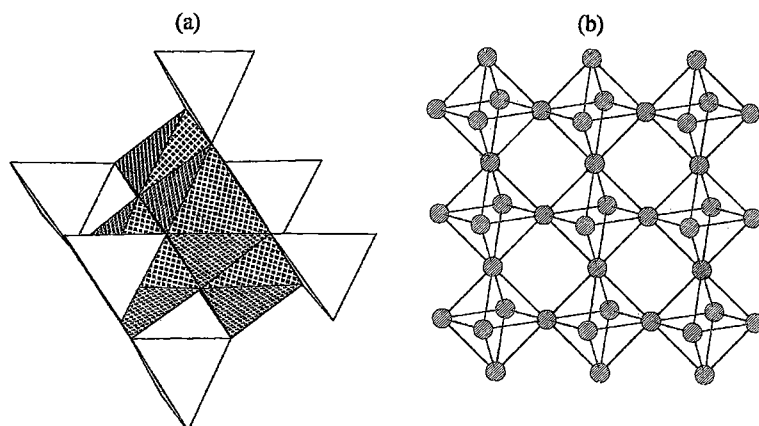
FIG. 2. The $[M_4(O,OH)_4](TO_4)_{6/2}$ group of the pharmacosiderite group. (a) Four fused octahedra, surrounded by an octahedral arrangement of six tetrahedra. (b) The ReO_3 structure-type. The circles indicate the tetrahedron centers of the pharmacosiderite structure.

et al. 1989). The $[V_5O_9]$ clusters are inserted into the square-planar units (Fig. 3b) to form distinct structures such as that shown in Figure 4. Other clusters (*e.g.*, $[M_4O_8]$: Haushalter *et al.* 1989) can be inserted in the same fashion to form microporous structures. The analogy between Si–O frameworks and vanadium phosphates as AB_2 structure-types is apparent; in the silicates, *A* is a [4]-coordinated atom, and *B* is a [2]-coordinated atom, whereas in the vanadium phosphate nets, *A* and *B* each represent clusters of atoms.

Another example of an AB_2 structure-type is jagowerite $Ba[Al(PO_4)(OH)_2]$ (Meagher *et al.* 1974). It contains edge-sharing pairs of octahedra surrounded by eight tetrahedra, which are the nodes of a net formed by face-sharing distorted cubes. The cubes are arranged as in the CaF_2 structure-type.

CONCLUSION

The description of complex structures, such as boracite and pharmacosiderite, as simple arrangements of complex clusters is elegant and topologically economical. Furthermore, it reinforces the idea (Hawthorne 1994, 1997) that Nature uses a small number of basic arrangements and produces structural diversity by employing a variety of *FBB*s in these arrangements.
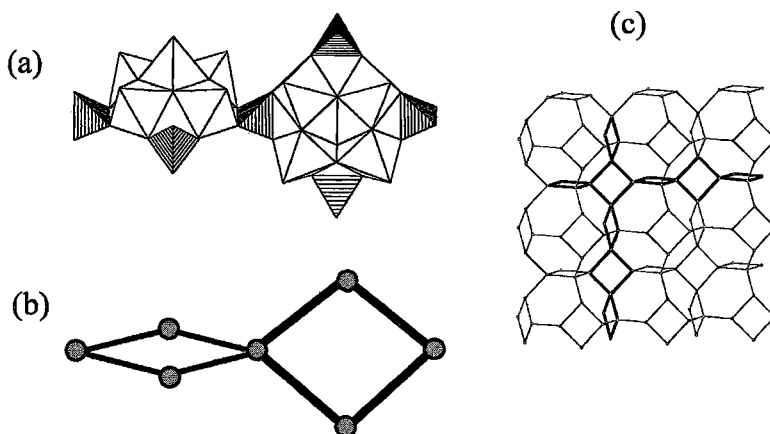
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FIG. 3. (a) The two bridging $[V_5O_9(PO_4)_2]$ units, and (b) two joined square-planar building blocks. (c) The underlying net of sodalite topology (SOD). The tetrahedron centers are indicated by small circles, and two of the twisted chains are highlighted.
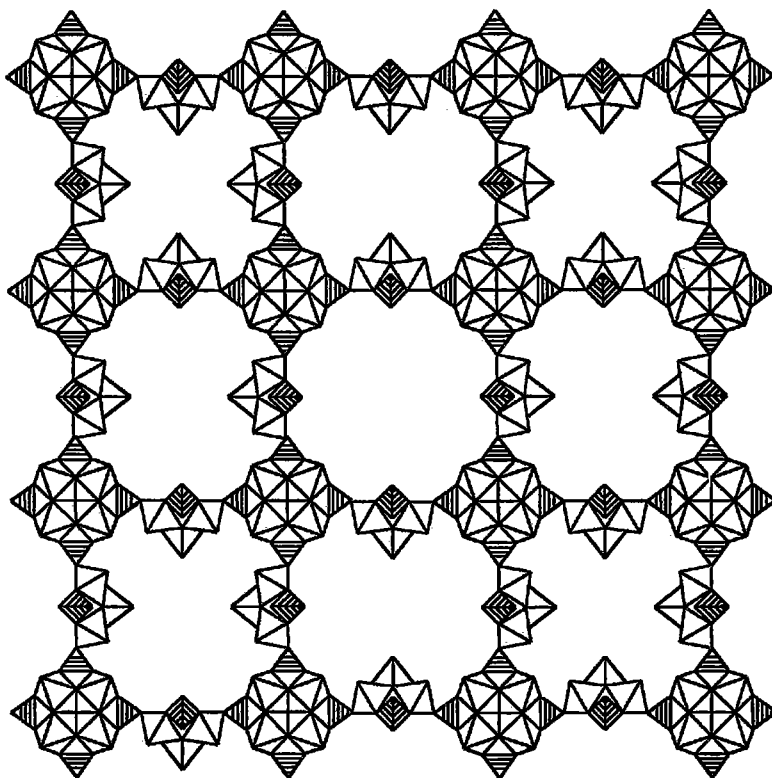
FIG. 4. A possible arrangement of [V₅O₉] groups with the SOD topology (Schindler *et al.* 1997, Khan *et al.* 1996).

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