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A NOVEL OCTAHEDRAL FRAMEWORK STRUCTURE: GAGEITE

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ABSTRACT

Gageite, ideally $M^{2+}_7(O)(OH)_8[Si_2O_6]$ where M=Mn and Mg, a 13.79(2), b 13.68(2), c 3.279(3) Å, *Pnnm*, $Z=2$, is an octahedral pipe structure. This unusual structure consists of walls of edge-sharing octahedra corner-linked to bundles of edge-sharing octahedra leaving pipe-like channels which run parallel to the c-axis. The octahedral framework has the ideal composition $M^{2+}_7(O)(OH)_{12}$, with the oxide anion octahedrally coordinated by six manganese atoms.

The channels are clogged by disordered silicate tetrahedra which support the framework by a network of hydrogen bonds. The tetrahedra are not geometrically compatible with the arrangement of octahedra, resulting in anomalous behavior of the atoms within the pipes.

INTRODUCTION

Gageite is a highly basic manganese silicate occurring as fibers and warped acicular crystals in open cavities associated with late stage low temperature hydrothermal veins at Franklin, New Jersey. A recent discussion on the crystal chemistry of gageite by Moore (1968a) ended with a promise to analyze the crystal structure, which is now presented.

This interesting mineral is orthorhombic with a 13.79(2), b 13.68(2), c 3.279(3) Å, *Pnnm*, and $Z=2$ for an empirical formula which is approximately $H_8(Mn, Mg)_7Si_2O_{15}$. The acicular habit for gageite with the needle axis parallel to z, is probably a consequence of the very short c-translation relative to a and b.

EXPERIMENTAL

Suitable crystals of gageite for X-ray study are very difficult to obtain. The mineral characteristically occurs as finely matted fibers or bundles, and even when the fibrils are of sufficient size, they tend to be warped and composed of many individuals in near-parallel growth. One specimen, located in the Franklin, New Jersey collection at Harvard University, showed crystals up to 0.1 mm in thickness consisting of basal pinacoid and unit prism. With the kind permission of Prof. C. Frondel, a slightly imperfect needle of 0.009 mm³ volume was secured for structure analysis. 921 independent diffraction spectra of the $hk0$-$hk2$ levels to $2\theta=60°$ were collected on a manual Weissenberg-geometry diffractometer using Zr-filtered Mo radiation. These data were processed to obtain $|F_{obs}|$ after suitable polyhedral transmission-factor correction.

STRUCTURE DETERMINATION

A Patterson projection, $P(uv)$, was prepared and the arrangement of cations was deciphered by the method of vector set analysis applied to octahedral packing models. Since the c-axis dimension suggests an octahedral edge distance, the geometry of octahedral linkages in the xy-plane was assumed limited to shared edge, edge-corner, and corner-corner polyhedral distances. Trial models of octahedral linkages based on the orientation and lengths of vectors within 4 Å in the projection led to a plausible arrangement from which all vectors could be derived and subsequently labelled. The model included four independent octahedral centers, one situated at the cell origin. Refinement of these metal positions gave $R_{hk0}=0.43$, using the scattering curve for Mn^{2+}. An electron density map was prepared based on the signs determined from these metals. All other atoms were clearly revealed including two independent tetrahedral centers. As shown in Figure 1, the background is remarkably free from spurious peaks.

As discussed further on, all atoms were assumed to reside in special positions at $z=0$ or $1/2$ except for two oxygen atoms associated only with the silicate groups. The first refinement, which included variation of cation multipliers, gave $R_{hkl}=0.28$ after three cycles.

REFINEMENT

The multipliers permitted an approximate choice of scattering curves, which were applied to the octahedral species in the following manner: $0.83\ Mg^{+}+0.17\ Mn^{+}$ for $M(1)$, $0.59\ Mg^{+}+0.41\ Mn^{+}$ for $M(2)$, and $1.00\ Mn^{+}$ for $M(3)$ and $M(4)$. The wet chemical analysis of gageite reported by Palache (1928) suggested that the octahedral sites consist essentially of manganese and magnesium, with a Mn:Mg atomic ratio of 3·3:1. The present assignment of scattering curves led to a ratio 2·5:1, based on the site multiplicity refinements. The scattering factor data were obtained from MacGillavry and Rieck (1962). The two independent Si sites, which cannot be fully occupied because of steric hindrance, were initially assumed to be half empty and their population densities were obtained by varying the multipliers. Prior to refinement, 309 reflections were excluded. They were either of zero intensity or the background error amounted to more than 25 percent of the peak intensities.

Two cycles of coordinate refinement followed by two cycles of full-matrix coordinate and isotropic temperature factor refinement gave $R_{hkl}=0.17$ for 612 "nonzero" reflections and 0.21 for all 921 reflections.

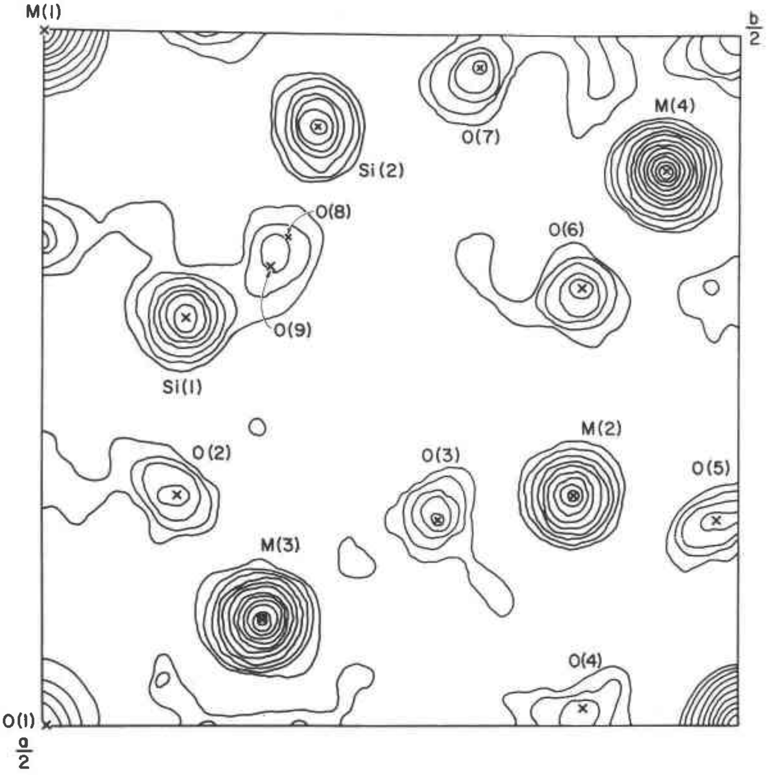

FIG. 1. Electron density map, $\rho(xy)$, of gageite, based on the signs from octahedral cations only. The final atomic coordinates are presented.

These refinements included varying the multipliers of O(8) and O(9) which are bonded to the silicon atoms only. The final multipliers of all other species were obtained from the equipoint rank numbers, assuming completely occupied sites, and applied prior to temperature factor refinement.

Finally, a three-dimensional difference synthesis was obtained. Despite the relatively poor reliability index, there was no indication of incorrectly placed, incompletely shifted, or omitted atoms. Atomic coordinates and isotropic temperature factors are given in Table 1 and the $F_{obs} - |F_{calc}|$ data appear in Table 2.[1]

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[1] To obtain a copy of Table 2, order NAPS Document #00479 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting $1.00 for microfiche or $3.00 for photocopies, payable to ASIS-NAPS.

TABLE 1. GAGEITE. ATOMIC COORDINATES, ISOTROPIC TEMPERATURE FACTORS AND MULTIPLIERS

	x	y	z	B	M
$M(1)=0.83$ Mg$+0.17$ Mn	0	0	½	0.42(12)	1
$M(2)=0.59$ Mg$+0.41$ Mn	0.3382(4)	0.3847(4)	½	.81(8)	2
$M(3)=1.00$ Mn	.4227(3)	.1520(3)	0	1.16(6)	2
$M(4)=1.00$ Mn	.1013(3)	.4493(3)	0	.79(6)	2
Si(1)	.2111(7)	.0974(7)	½	.32(15)	1
Si(2)	.0684(7)	.1952(7)	0	.17(15)	1
O(1)	½	0	0	1.52(45)	1
O(2)	.3316(15)	.0940(15)	½	1.57(36)	2
O(3)	.3411(12)	.2860(13)	0	.75(27)	2
O(4)	.4901(15)	.4029(15)	½	1.50(35)	2
O(5)	.3505(15)	.4895(15)	0	1.27(33)	2
O(6)	.1879(12)	.3904(12)	½	.77(27)	2
O(7)	.0176(14)	.3060(14)	0	1.28(32)	2
O(8)	.1556(26)	.1799(26)	0.323(15)	.29(58)	1.2
O(9)	.1928(36)	.1475(37)	.024(22)	1.30(1.00)	0.8

DISCUSSION OF THE STRUCTURE

Four octahedral centers and seven oxygen atoms in the asymmetric unit define a new kind of octahedral framework structure. This structure consists of walls of edge-sharing octahedra three octahedra wide connected by corner-sharing to bundles of octahedra which are comprised of two fused walls of edge-sharing octahedra, each wall component of two octahedra in width. The walls and bundles run parallel to z, the fiber axis, and their mode of linkage results in large open channels or "pipes" which also run parallel to z (Fig. 2).

This octahedral structure is related to the structures of hollandite (Byström and Byström, 1950), psilomelane (Wadsley, 1953), and fluoborite (Takéuchi, 1950) which also are pipe structures. The most remarkable difference is the presence of octahedral bundles, which as fragments of the rocksalt structure afford a new octahedral arrangement for Mn-O octahedra in open structures. Six divalent cations in these bundles octahedrally coordinate to one oxygen atom, thus requiring it to be truly an oxide anion (O^{2-}) for electro-neutrality.

The stoichiometry for the hypothetically neutral framework is $M^{2+}{}_7(O)(OH)_{12}$. Average M-O distances are $M(1)$-O 2.10, $M(2)$-O 2.13, $M(3)$-O 2.21, and $M(4)$-O 2.22 Å (Table 3). Thus, if $M(1)$ and $M(2)$ are predominantly Mg^{2+} and $M(3)$ and $M(4)$ essentially Mn^{2+}, these distances are consistent with the electron densities observed on the Fourier map and the site occupancy factors obtained during the stages of multi-

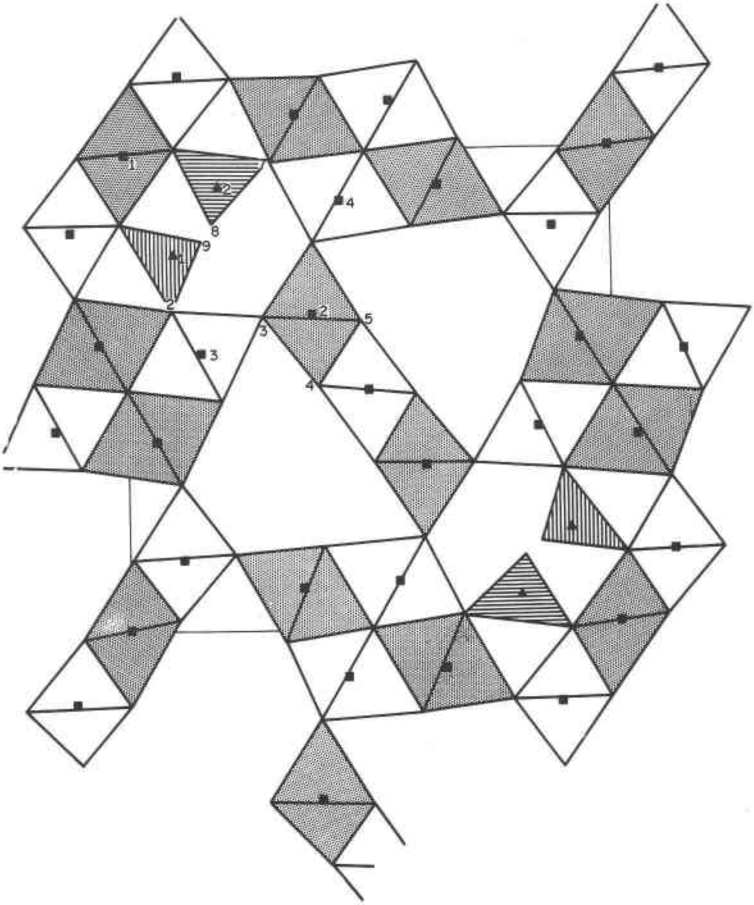

FIG. 2. Polyhedral diagram of the gageite crystal structure down the z axis. Octahedra at $z=\frac{1}{2}$ are stippled. The disordered tetrahedra are drawn in two of the four equivalent open pipes.

plier refinement. The O-O′ distances associated with the $M(1)$ and $M(2)$ octahedra which make up the wall three octahedra in width range from 2.67 to 2.79 Å for shared edges and 3.11 to 3.28 Å for unshared edges.

Distances associated with the octahedral bundles offer some interesting features. The octahedrally coordinated oxide anion takes part in 4[$M(4)$-O(1)] bonds of 2.26 Å and 2[$M(3)$-O(1)] bonds of 2.34 Å. These distances are consistently longer than the mean Mn^{2+}-O octahedral distance of 2.21 Å observed in other structures, conforming to the expected strong cation-cation repulsions about this anion center. Resulting from

TABLE 3. GAGEITE. INTERATOMIC DISTANCES[a]

M(1)		*M*(2)		*M*(3)		*M*(4)	
4 *M*(1)–O(4)	2.11(3)	2 *M*(2)–O(3)	2.12(3)	2 *M*(3)–O(2)	2.21(3)	2 *M*(4)–O(6)	2.18(3)
2 *M*(1)–O(5)	2.07(3)	2 *M*(2)–O(5)	2.18(3)	2 *M*(3)–O(7)	2.171(3)	2 *M*(4)–O(1)	2.262(6)
		1 *M*(2)–O(4)	2.11(3)	1 *M*(3)–O(1)	2.336(6)	1 *M*(4)–O(2)	2.18(3)
		1 *M*(2)–O(6)	2.07(3)	1 *M*(3)–O(3)	2.15(3)	1 *M*(4)–O(7)	2.27(3)
average	2.10 Å		2.13		2.21		2.22
4 O(4)–O(4″)[b]	2.67(6)	2 O(3)–O(5)[b]	2.79(4)	2 O(2)–O(7)[b]	2.91(4)	2 O(1)–O(6)[b]	2.99(3)
2 O(4)–O(5)[b]	2.79(4)	2 O(4)–O(5)[b]	2.79(4)	2 O(2)–O(3)	3.10(4)	2 O(6)–O(7)	3.09(4)
2 O(5)–O(4″)	3.11(4)	2 O(3)–O(6)	3.03(4)	2 O(1)–O(2)[b]	3.12(3)	2 O(1)–O(2)	3.12(3)
2 O(4)–O(4′)	3.28(6)	2 O(3)–O(4)	3.08(4)	2 O(1)–O(7)[b]	3.13(3)	2 O(1)–O(7)[b]	3.13(3)
2 O(4′)–O(4″)	3.28(6)	2 O(5)–O(6)	3.09(4)	2 O(3)–O(7)	3.18(4)	2 O(2)–O(6)	3.24(4)
		1 O(3)–O(3′)	3.28(6)	1 O(7)–O(7′)	3.28(6)	1 O(1)–O(1′)[b]	3.28(–)
		1 O(5)–O(5′)	3.28(6)	1 O(2)–O(2′)	3.28(6)	1 O(6)–O(6′)	3.28(6)
	2.97		3.01		3.12		3.14
Si(1)							
2 Si(1)–O(9)	1.72(9)						
1 Si(1)–O(5)	1.70(4)						
1 Si(1)–O(2)	1.66(4)						
	1.70						
Si(2)		Hydrogen bonds					
2 Si(2)–O(8)	1.62(6)	O(9)–O(3)	2.79(10)				
2 Si(2)–O(4)	1.72(4)	O(8)–O(6)	2.97(7)				
1 Si(2)–O(7)	1.67(4)						
	1.66						

[a] Estimated standard errors in parentheses.

[b] Shared edges.

these polyhedral dilations are edge-sharing distances which are longer than usual whenever the O(1) anion is involved: O(1)-O(2) 3.12, O(1)-O(7) 3.13, O(1)-O(6) 2.99, and O(1)-O(1′) 3.28 Å. The only other unique shared edge for the octahedral bundle is O(2)-O(7) which is 2.91 Å.

The tetrahedra. The pipes in gageite are not open but clogged by disordered silicate groups. These silicate groups, which occur as independent pairs within an asymmetric unit of a pipe, prevent the octahedral framework from collapsing. Each silicon site is approximately half-occupied. Steric hindrance requires that if one asymmetric Si tetrahedral site is occupied, the other neighboring one must be empty. Further, if Si(1) is empty, O(9) must be empty; and if Si(2) is empty, O(8) is empty.

Only the *average* arrangement of silicate tetrahedra can be ascertained in this structure analysis. It is not possible for silicate units to be translationally ordered over a 3.27 Å repeat. It was noted elsewhere (Moore, 1968a) that long exposures of *c*-axis rotation photographs showed continuous weak streaks indicating a trebling of that axis. The relatively high reliability index is partly a result of these disordered groups. It is interesting to note that two other minerals occurring in the same paragenesis with gageite, leucophoenicite and chlorophoenicite, also have disordered tetrahedral groups (Moore, 1967 and 1968b).

The tetrahedral Si-O distances range from 1.62 to 1.72 Å, but the individual estimated standard errors are high (Table 3). The two independent tetrahedra have mean Si-O distances of 1.66 and 1.70 Å, considerably longer than the 1.63 Å distance observed for insular tetrahedra (Smith and Bailey, 1963). These distances should be given little physical meaning since the close proximity of atomic coordinates between the disordered Si(1)-Si(2) and O(8)-O(9) pairs would result in parameter interactions during refinement of these positions.

Hydrogen bonds. The silicate groups support the pipe structure in the following manner: the O(8) and O(9) atoms are involved in hydrogen bonding with O(6) and O(3), respectively, as depicted in Figure 3. The distances O(8)-O(6) 2.97, and O(6)-O(3) 2.79 Å are indicative of hydrogen bonding. The significance of *two* independent disordered silicate groups in each pipe is now understandable: in this manner, the hydrogen bonds are on the average most symmetrically disposed in each pipe, thus maximizing support.

Crystallochemical formula. The geometrical restrictions placed on the disordered tetrahedra by the framework of octahedra result in forced anom-

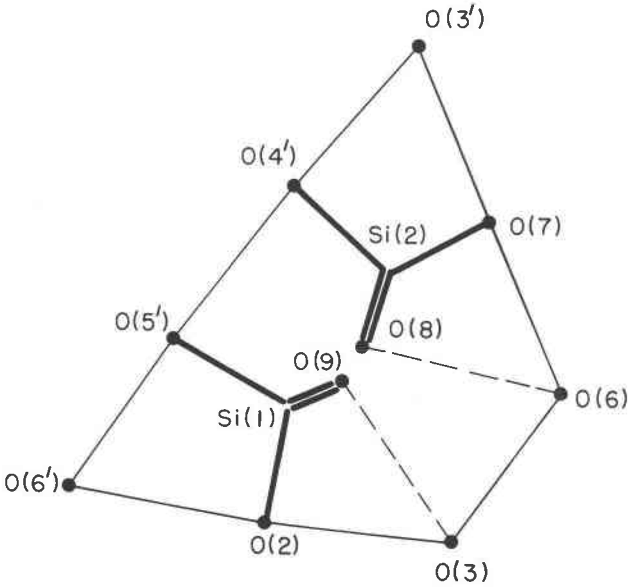

FIG. 3. A cross-section of the pipe in gageite. Dashed lines show the network of hydrogen bonds within a pipe.

alous behavior of these tetrahedra. The tetrahedra are oriented in such a fashion that one edge is parallel to the 3.3 Å axis. Such a repeat distance is unreasonably long for O-O′ edge distances, which are typically about 2.7 Å. This condition corresponds to the anomalous behavior of arsenate tetrahedra found in the paragenetically related chlorophoenicite (Moore, 1968b).

It is proposed that the O(8) and O(9) general atomic positions are only one-fourth occupied on the average and that each of these atoms is shared by two tetrahedra, resulting in disordered chains of tetrahedra running parallel to the *z*-axis. Thus, equivalent positions across the mirror planes would be the average location of an oxygen atom shared by two silicon atoms. The framework oxygens O(2), O(4), O(5) and O(7) are also shared by the disordered half-occupied silicon atoms and accordingly they are on the average $1/2\ O^{2-}+1/2\ OH^{-}$. In any event, the individual tetrahedra cannot be strictly insular since there is no way of relating the terminal oxygen atoms along the *z*-axis to only one silicon atom while maintaining the cell contents of four silicon atoms.

So far, no mention has been made of the possibility of noncentrosymmetry in gageite. The octahedral framework is by itself centrosymmetric but any lack of centrosymmetry among atoms in the pipes would distort

TABLE 4. ELECTROSTATIC VALENCE BOND STRENGTH COMPUTATIONS (Σ) FOR GAGEITE

Gageite. Franklin, New Jersey				$M^{2+}_7(O)(OH)_{12}$	
Multiplicity			Σ		Σ
1	O(1)	O^{2-}	2.00	$4M(4)+2M(3)$	2.00
2	O(2)[a]	$\frac{1}{2}O^{2-}+\frac{1}{2}OH^-$	1.50	$2M(3)+M(4)+\frac{1}{2}Si(1)^b$	1.00
2	O(3)	OH^-	1.00	$2M(2)+M(3)$	1.00
2	O(4)[a]	$\frac{1}{2}O^{2-}+\frac{1}{2}OH^-$	1.50	$2M(1)+M(2)+\frac{1}{2}Si(2)^b$	1.00
2	O(5)[a]	$\frac{1}{2}O^{2-}+\frac{1}{2}OH^-$	1.50	$2M(2)+M(1)+\frac{1}{2}Si(1)^b$	1.00
2	O(6)	OH^-	1.00	$2M(4)+M(2)$	1.00
2	O(7)[a]	$\frac{1}{2}O^{2-}+\frac{1}{2}OH^-$	1.50	$2M(3)+M(4)+\frac{1}{2}Si(2)^b$	1.00
~1	O(8)	O^{2-}	1.00	$Si(2)+Si(2)'^b$	—
~1	O(9)	O^{2-}	1.00	$Si(1)+Si(1)'^b$	—

[a] If Si is absent, then $\frac{1}{2}O^{2-}\rightarrow\frac{1}{2}OH^-$.

[b] Absent in $M^{2+}_7(O)(OH)_{12}$.

the framework atoms away from the mirror planes at $z=0$ and 1/2. One test would be to refine the z-parameters of all atomic sites in the space group *Pnn*2. Unfortunately, the inferior quality of the data and the addition of 14 more variable parameters doesn't warrant such a test. Like chlorophoenicite, all interatomic distances and distortions among the octahedral framework atoms conform to expected values, supporting the centrosymmetric model in this study. Further support is gained from the similar convergences noted for refinement of the zero-level data alone compared with the full set of three-dimensional data. If the framework atoms did not reside on mirror planes at $z=0$ or 1/2, then the *R* indices would diverge at higher levels. Finally, the difference synthesis did not show any evidence of parameter splitting across the mirror planes for the framework atoms. Thus, anomalous behavior of atomic positions is essentially confined to the regions within the pipes.

Based on this interpretation, the crystallochemical formula for gageite is $M^{2+}_7O(OH)_8[Si_2O_6]$, giving an empirical formula $H_8M_7Si_2O_{15}$. This differs from the previously proposed formula (Moore, 1968a) $H_6M_7Si_3O_{16}$, in containing more OH^- and less Si. An electrostatic valence bond strength computation appears in Table 4 for the proposed gageite formula and for the neutral $M_7O(OH)_{12}$ framework.

PIPE STRUCTURES

The term "pipe" structure was first used by Takéuchi for fluoborite. In that structure, walls of edge-sharing Mg—(O, OH) octahedra link to neighboring walls by corner-sharing. Depending on the width of these

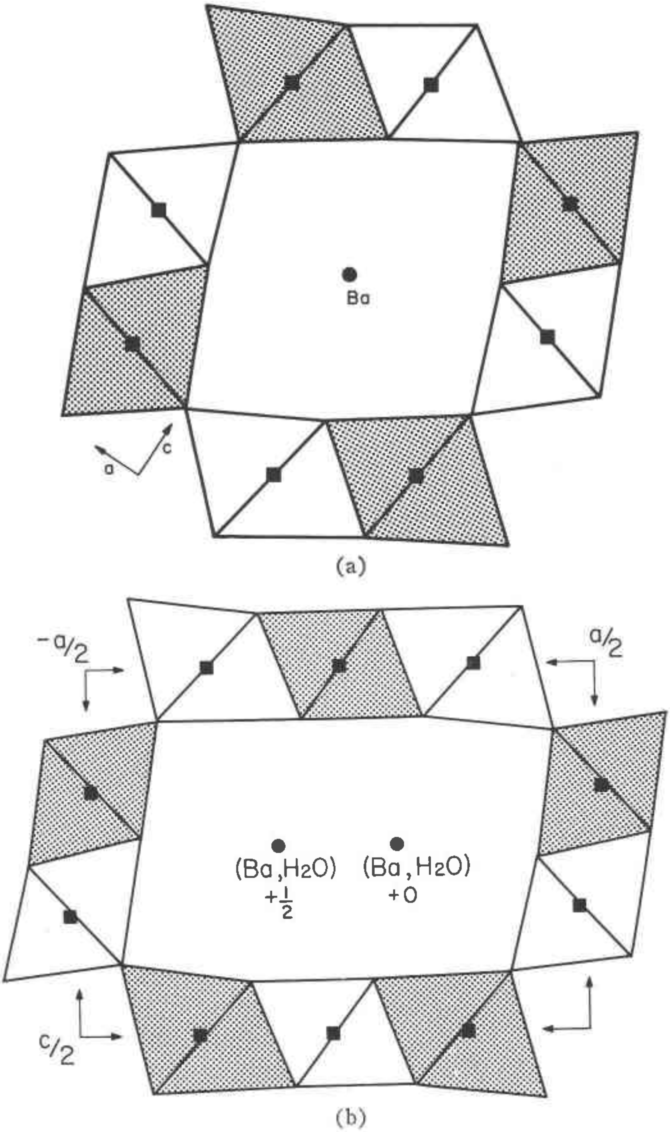

FIG. 4a. Polyhedral diagram of the pipe (a) in the hollandite crystal structure, and (b) in the psilomelane crystal structure.

individual walls, channels or pipes of various dimensions running parallel to the walls result. Octahedral pipe structures are defined here as arrangements of octahedral edge-sharing walls which further link by cor-

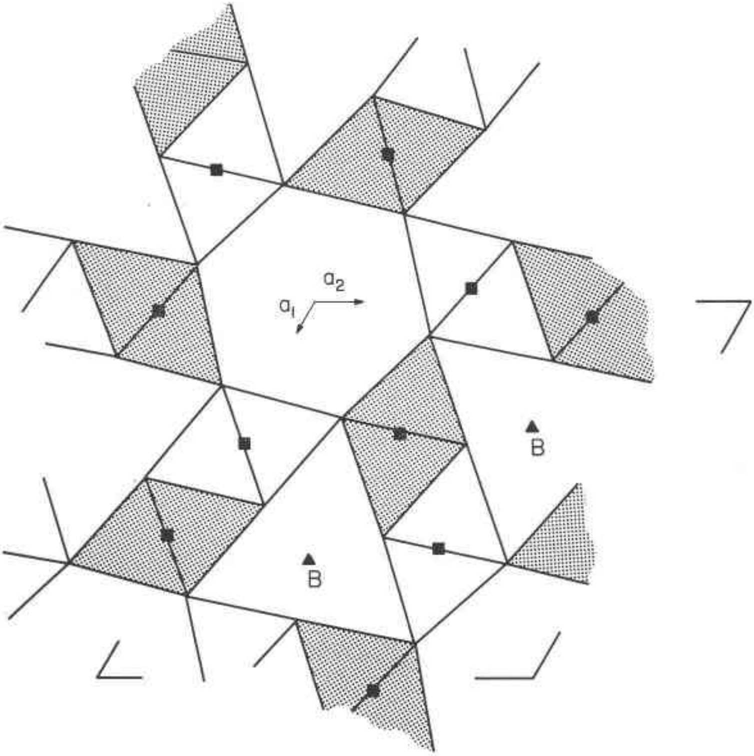

FIG. 5. Polyhedral diagram of the pipe in the fluoborite crystal structure. The centers of the boron atoms are also depicted.

ner-sharing to leave open channels geometrically large enough for passage of small molecular units (such as water molecules) or geometrically permitting large-cation base exchange within the channels. These channels may or may not be clogged; despite the disordered silicate groups in the gageite channels, its octahedral topology warrants it as a member of the octahedral pipe structures.

One interesting consequence of the pipe structures is the framework property of the linked octahedra. Analogous to the tektosilicates, SiO_2, the entire framework is neutral. *In sensu stricto*, the octahedral framework structures are not equivalent topologically to tektosilicates since both corner- and edge-sharing occur in the former.

In the octahedral pipe structures known so far, each anion is associated with three cations. Thus, *M* is 4+ when the anion is O^{2-} and 2+ when the anion is OH^-. This is clearly understood in the crystal structures of hollandite and psilomelane (Figs. 4a and 4b). If the pipes weren't occupied by large cations (such as K^+ and Ba^{2+}) and water molecules, their composition would be that of a neutral framework, *i.e.* $M^{4+}O_2$. This criterion is also satisfied by fluoborite, $Mg_3(BO_3)(F, OH)_3$ (Fig. 5) since in this structure three octahedral cations coordinate to one anion. The hypothetically boron-free fluoborite is $Mg_3(F, OH)_6$.

As stated earlier, the neutral gageite framework is $M^{2+}{}_7(O)(OH)_{12}$. The ratio M:(O, OH) is not 1:2 because of the presence of the octahedral bundles; consequently, the quadrivalent neutral oxide analogue cannot exist, unless one anion has charge 4^-. In this respect, gageite differs from the other pipe structures.

Emphasis has been placed on these pipe structures because many other members probably exist. All of the members mentioned above have fibrous habits, with the fiber axis defining the length of the octahedral edge and the axis of the pipes. For this reason, other likely members may be sussexite, wiserite, woodruffite, and todorokite.

CLASSIFICATION

Any standard crystallochemical classification of gageite would be ambiguous since it does not appear to be obviously and unequivocally related to any mineral group. Though I suggested that gageite and harstigite might be related (Moore, 1968a), new data on harstigite (Moore, 1968c) show that the latter mineral is derivative of the aminoffite structure type. Thus, there is no crystallochemical relationship between the two minerals.

It is clear that unusual structure types like gageite would only make sense in a topological classification rather than the standard crystallochemical ones. Topological classification would fully utilize the hierarchy of structure types; unfortunately, the mathematical formalism which would define the ground rules is not yet available. Until then, taxonomic mineralogists will have to decide more or less arbitrarily whether gageite belongs to the psilomelane group, the hydroxides, the borates (under fluoborite), or the silicates.

ACKNOWLEDGMENT

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