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Palermoite, $SrLi_2[Al_4(OH)_4(PO_4)_4]$: Its Atomic Arrangement and Relationship to Carminite, $Pb_2[Fe_4(OH)_4(AsO_4)_4]$

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Abstract

Palermoite, $SrLi_2[Al_4(OH)_4(PO_4)_4]$, space group *Imcb*, *a* 11.556(5), *b* 15.847(7), *c* 7.315(4) Å, $Z = 4$, is structurally related to carminite, $Pb_2[Fe_4(OH)_4(AsO_4)_4]$. $R(hkl) = 0.090$ for 1471 non-equivalent reflections. Both contain the same $[M^{3+}{}_4(OH)_4(TO_4)_4]^{4-}$ octahedral and tetrahedral slabs oriented parallel to {010}. They are distinguished by the link to symmetry-equivalent slabs across the glides at $b = 1/4$. The space group *Amaa* for carminite shares the same subgroup (*Pmaa*) with palermoite. In both structures, the octahedra form chains of edge-linked dimers which are corner-linked to symmetry-equivalent dimers resulting in the composition $M^{3+}{}_2(O)_7(OH)_2$. One-eighth of the tetrahedral oxygens are not bonded to the octahedra.

Polyhedral interatomic averages are ^{VIII}Sr–O 2.62 Å, ^{VI}Al–O 1.91 Å, ^{IV}Li–O 2.13 Å, ^{IV}P(1)–O 1.53 Å and ^{IV}P(2)–O 1.54 Å. Local isomorphism of all atoms excepting Li and Pb(2) occurs: the Li atoms are split into twice the equipoint rank number as Pb(2) and possess lower point symmetry.

Introduction

Palermoite occurs locally in moderate abundance as small striated prismatic colorless crystals at its type locality, the Palermo No. 1 pegmatite, near North Groton, New Hampshire. It was originally described by Mrose (1953), who proposed the formula (Li, Na)$_4$SrAl$_9$(PO$_4$)$_8$(OH)$_9$, $Z = 2$, and the unit cell parameters *a* 7.31 Å, *b* 15.79 Å, *c* 11.53 Å with the space group *Immm*. Another chemical analysis by Frondel and Ito (1965) led to the proposed formula (Li, Na)$_2$(Sr, Ca) Al$_4$(PO$_4$)$_4$(OH)$_4$, $Z = 4$, with the refined cell parameters *a* 7.315(4), *b* 15.849(9), *c* 11.556(6) Å. Meanwhile, Strunz (1960) proposed an isotypic relationship between palermoite and carminite, $PbFe^{3+}{}_2(AsO_4)_2(OH)_2$. To reconcile the rather complex formula of Mrose and the similarity in the crystal cell parameters between palermoite and carminite, he proposed the formula $SrAl_2(PO_4)_2(OH)_2$.

Despite similarities in the cell dimensions, we were puzzled by the difference between the body-centered cell for palermoite and the end-centered cell for carminite. Atomic positions based on the crystal structure analysis of carminite by Finney (1963) could not be isomorphically transformed into the palermoite cell since the space groups are neither isomorphic nor is one a subgroup of the other.

Experimental

Palermoite single crystals collected at the type locality by P.B.M. were submitted to single crystal X-ray study. In addition, a qualitative electron probe scan detected Sr, Al, P, and only minor Ca (< 1%). The extinction criteria, from films and single crystal diffractometer, suggested the space groups *I2cb* or *Imcb*, in disagreement with *Immm* proposed by Mrose (1953). Doubly terminated crystals and the three-dimensional crystal structure analysis support the centrosymmetric space group *Imcb*.

Refinement of the cell parameters on a PICKER automated diffractometer afforded *a* 11.556(5), *b* 15.847(7), *c* 7.315(4) Å. We selected the standard axial convention for the orthorhombic system to which the space group *Imcb* conforms and accepted the cell contents $4[SrLi_2Al_4(OH)_4(PO_4)_4]$. Other salient details: graphite monochromatized Mo$K\alpha_1$ radiation ($\lambda = 0.7093$ Å); maximum $\sin\theta/\lambda = 0.80$; twenty second background counting times; scan rate 1.0°/minute; half angle scan 1.8°. The thick prismatic crystal, of maximum dimension 0.12 mm, was not corrected for absorption. The equivalent reflec-

TABLE. 1. Palermoite: Atomic Coordinate and Isotropic Thermal Vibration Parameters*

Atom	Point group	Mult.	x	y	z	B(Å^2)	Atom	Point group	Mult.	x	y	z	B(Å^2)
Sr	222	4	0.2500	0.5000	0.5000	0.80(2)	P(2)	m	8	.0000	.4576(1)	.7731(2)	.50(2)
Pb(1)	222	4	.2500	.5000	.5000		As(1)	m	8	.000	.457	.760	
Li	m	8	.5000	.2851(11)	.2723(21)	2.20(24)	O(3)	m	8	.0000	.3993(3)	.6107(6)	.98(7)
Pb(2)	2/m	4	.5000	.2500	.2500		O(3)	m	8	.000	.386	.606	
Al	1	16	.1307(1)	.3727(1)	.1374(2)	.56(2)	O(4)	m	8	.0000	.4014(3)	.9502(6)	.76(6)
Fe	1	16	.136	.378	.131		O(2)	m	8	.000	.405	.968	
P(1)	2	8	.2500	.2922(1)	.5000	.45(2)	O(5)	1	16	.1083(3)	.4857(2)	.2275(4)	.69(4)
As(2)	2	8	.250	.289	.500		O(1)	1	16	.115	.482	.260	
O(1)	1	16	.1438(3)	.2632(2)	.0387(4)	.75(5)	OH(1)	m	8	.0000	.3363(3)	.2606(6)	.62(6)
O(5)	1	16	.145	.272	-.013		OH(1)	m	8	.000	.334	.241	
O(2)	1	16	.2257(3)	.3515(2)	.3389(4)	.59(4)	OH(2)	2	8	.2500	.4117(3)	.0000	.87(6)
O(4)	1	16	.241	.348	.326		OH(2)	2	8	.250	.430	.000	

* *Estimated standard errors refer to the last digit. The atomic parameters of carminite in Finney (1963), appropriately reoriented, are shown for comparison.*

tions (*hkl*) and (*h$\bar{k}$l*) were averaged, yielding 1471 independent *F* (obs), which were obtained through standard computational procedures.

Determination and Refinement of the Structure

Three-dimensional Patterson synthesis indicated strong vector densities at 0 *v* 0; 1/2 *v* 0; 0 *v* 1/2; and 1/4 *v* 1/4. Symmetry restrictions led to rapid determination of the Sr, Al, P(1), and P(2) positions. The β- and γ'syntheses of Ramachandran and Srinivasan (1970) led to unambiguous resolution of all non-hydrogen atoms.

Four cycles of full-matrix, least-squares refinement based on isotropic thermal vibration parameters, full site occupancies, secondary extinction correction with $c_o = 0.428 \times 10^{-6}$ (Zachariasen, 1968) and anomalous dispersion correction for Sr, Al, and P led to

$$R(hkl) = \frac{\Sigma\,\big||F(\text{obs})| - |F(\text{calc})|\big|}{\Sigma\,|F(\text{obs})|} = 0.090$$

for all 1471 reflections. The final atomic coordinates and the isotropic thermal vibration parameters are presented in Table 1. Table 2 lists the structure factor data.[1]

Description of the Structures

The formula $SrLi_2[Al_4(OH)_4(PO_4)_4]$ (here idealized) proposed by Frondel and Ito (1965) is confirmed. Although the structures of palermoite and carminite are closely related, the two crystals do not exhibit an isotypic relation. Figure 1 features the symmetry diagrams of the space groups *Imcb* (palermoite) and *Amaa* (carminite) down the *c* axis in the conventional *b* > *a* > *c* orthorhombic setting. The essential difference between the two is a *c* glide at *b* = 1/4 in

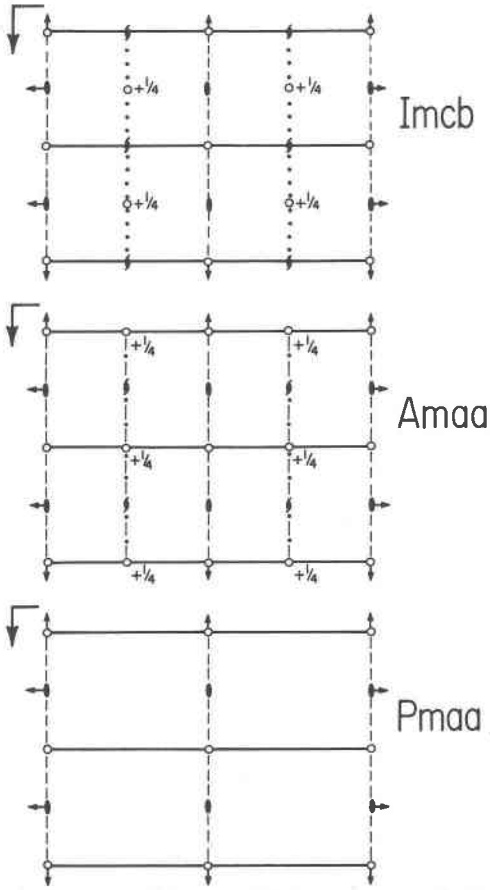

FIG. 1. Symmetry diagrams of the space groups *Imcb, Amaa,* and *Pmaa* in standard cell orientation (down the *c* axis). The first two groups apply to palermoite and carminite respectively. The third group is the subgroup common to the first two.

[1] To obtain a copy of Table 2, order document number AM-75-003-B from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D. C. 20006. Please remit $1.00 for the microfiche.

palermoite which is replaced by a *n* glide at $b = 1/4$ in carminite. Accordingly, the screw axis at (0 1/4 *z*) and the inversion at (1/4 1/4 1/4) in *Imcb* is translated by (1/4 0 0) to create *Amaa*. The two-fold rotations at (1/4 *y* 0); (1/4 0 *z*); (*x* 0 0); the *a*-glide at $c = 0$; the *a*-glide at $b = 0$; the mirror plane at $a = 0$; and the inversion at (000) remain invariant in the two space groups. This corresponds to the mutual subgroup *Pmaa* (D^3_{2h}), shown at the bottom in Figure 1.

The palermoite and carminite structures (Fig. 2) both contain the same $[M^{3+}_4(OH)_4(TO_4)_4]^{4-}$ octahedral (*M*) and tetrahedral (*T*) slab oriented parallel to {010}. The structures are distinguished by the links to symmetry equivalent slabs across the *c* glide at $b = 1/4$ in the former and the *n* glide at $b = 1/4$ in the latter. In fact, taking the symmetry operations which are invariant in the two space groups, the pairs of linked slabs between $1/4 < b < 3/4$ are isomorphous in the two structures. For this reason, the atomic coordinates for palermoite and carminite in Table 1 are compared within this bound. It is seen that all the parameters and their equipoint rank numbers and point symmetries are similar, with the exception of Li in palermoite and Pb(2) in carminite. The Li atom possesses an equipoint rank number of 8, point symmetry *m*, and two degrees of freedom in the atomic coordinates. Pb(2) possesses rank number 4, point symmetry $2/m$, and no degrees of freedom.

Palermoite and carminite contain the same type of *M*–O octahedral chain. In palermoite it consists of an edge-linked dimer which is corner-linked at the same level to symmetry equivalent dimers (see Fig. 2). The chains, which run parallel to the *a* axis, have composition $Al_2(Op)_7(OH)_2$, where Op are oxygens that belong to PO_4 tetrahedra. One-eighth of the tetrahedral oxygens, namely O(3) in both structures, do not bond to the trivalent octahedrally coordinated cations. The points of condensation of the octahedral chains include OH(1), OH(2), and O(4) in palermoite, each of equipoint rank number 8.

Remaining in the structures are pockets at (1/4 1/2 1/2); and (1/2 1/4 1/4), each of equipoint rank number 4. Both non-equivalent polyhedra are distorted cubes and accommodate Pb(1) and Pb(2) in carminite. Although Sr in palermoite is isomorphic to Pb(1) in carminite, the Li atoms in palermoite are split into two equivalences, the coordination polyhedron being a distorted tetrahedron. The polyhedral environments about Pb(2) and Li are shown as projections down the *a* axis in Figure 3. These regions are non-isomorphic as they do not

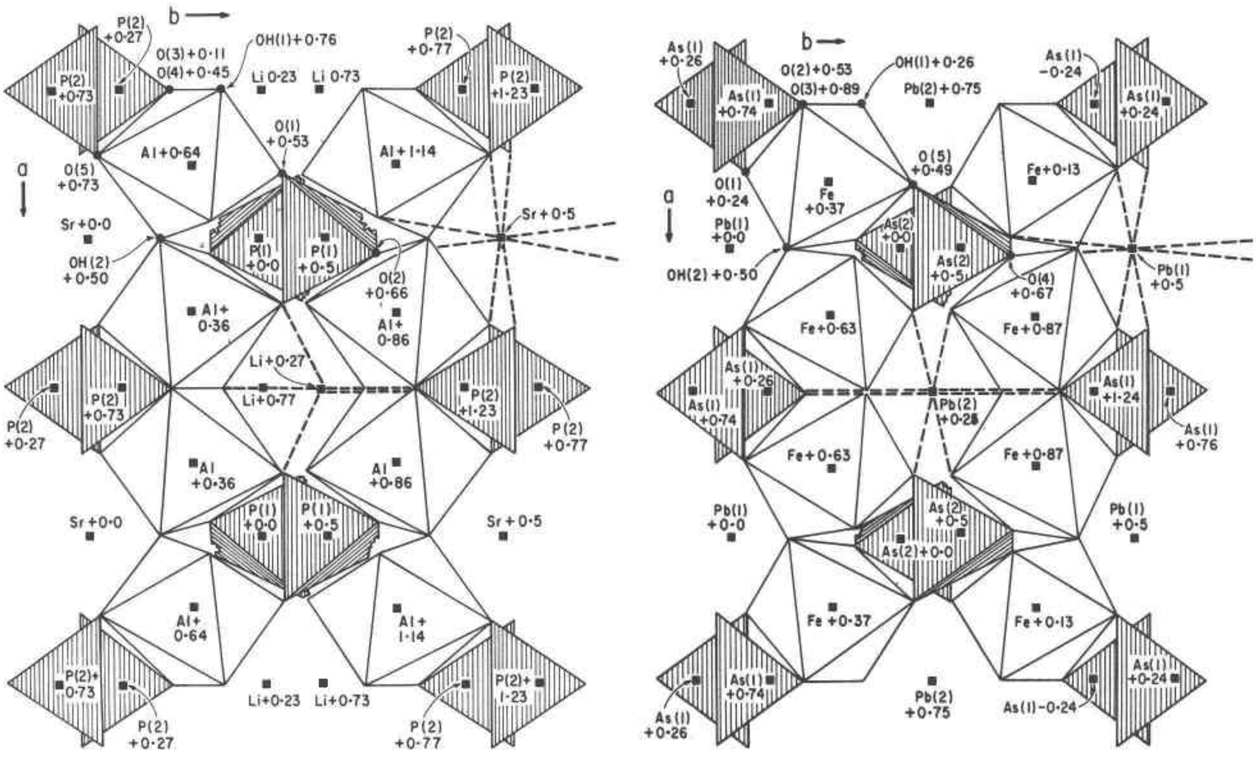

FIG. 2. Polyhedral diagrams of palermoite (left) and carminite (right) structures down the *c* axis. The outline $a \times b/2$ is shown. Heights are given as fractional coordinates in *z*. The Pb–, Sr–, and Li–O bonds are dashed in.

possess the same point symmetry in the two structures.

One of the curious features of the two structures is the observation that the "X" position at (1/2 1/4 1/4) in palermoite possesses a coordination polyhedron similar to that in carminite, both being distorted cubes. Figure 4 provides the bond distances for "X" in palermoite and Pb(2) in carminite. The position "X", however, still has equipoint rank number 8 since its point symmetry remains *m* and to afford a carminite-like composition would require disordered half-occupied sites over the Pb(2) positions. Since the environments about the X and Pb(2) sites are non-isomorphic, the energetic relationships between the two structures are probably dictated by the charges and ionic radii of the cations competing for the X and Pb(2) environments, as the distinctions in the bonding over the rest of the structures are small.

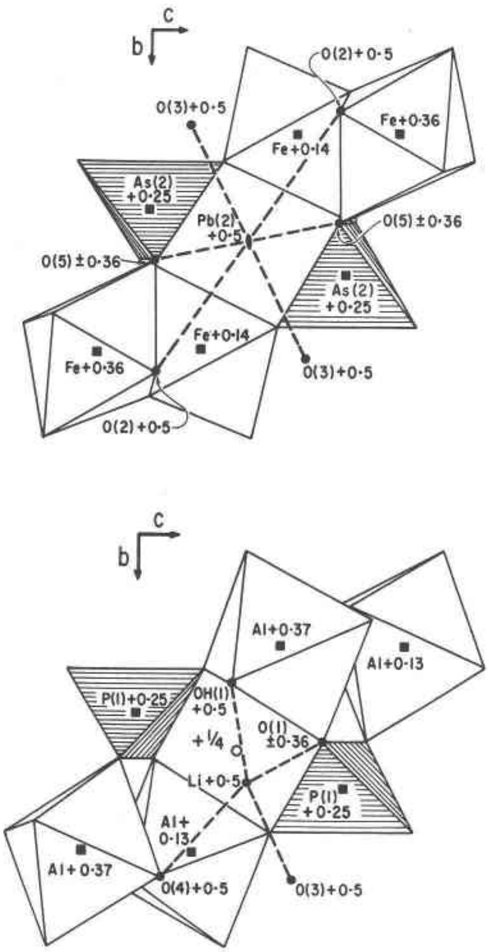

FIG. 3. The polyhedral environments of Pb(2) in carminite (top) and Li in palermoite (bottom) down the *a* axis. The Pb(2) atom resides at (1/2 1/4 1/4). In palermoite, the locus at (1/4 1/4 1/4) is drawn as a circle.

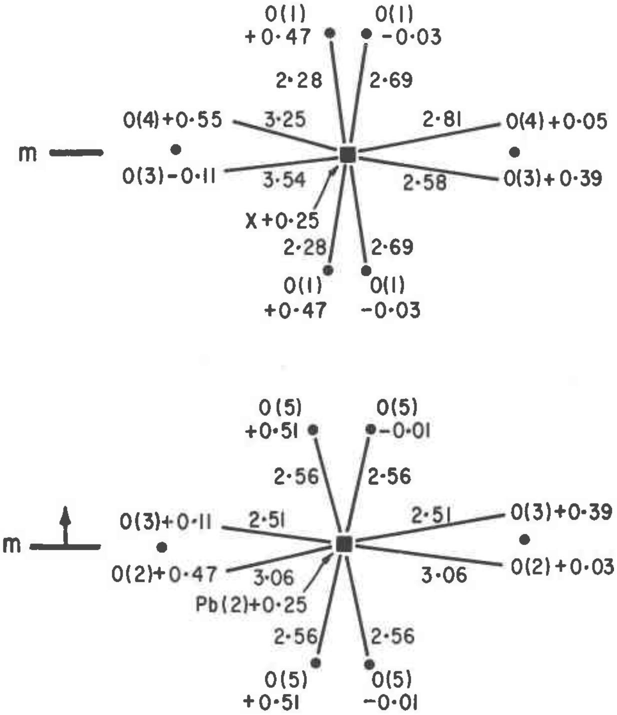

FIG. 4. The "X"–O bonds and Pb(2)–O bonds in palermoite (top) and carminite (bottom). The symmetry elements (*m* and $2/m$ respectively) are shown on the left and apply to the loci of "X" and Pb(2). Bond distances are specified.

We propose that palermoite and carminite structure ideals with compositions $X(1)X(2)M_2(OH)_2(TO_4)_2$ are *combinatorial polymorphs* in the sense defined by Moore (1975).

Bond Distances

Table 3 lists the anions and the coordinating cations in rows and columns. In this manner, the valence bond strengths can be conveniently tabulated and deviations from bond distance averages can be related to deviations in bond strength sums.

One problem immediately arises regarding the coordination of lithium. Although its nearest neighborhood defines a distorted trigonal bipyramid, the valence balances suggest that the true coordination is distorted tetrahedral, the polyhedral vertices including one OH(1), one O(3), and two O(1) atoms.

Interatomic distances are given in Table 4. The Li–O tetrahedral distances range from 1.94 to 2.29 Å, the fifth distance Li–O(4) = 2.46 Å suggesting that the tetrahedral coordination is more likely. We note in addition that a distorted trigonal bipyramid would require that the O(3)–O(4) edge be shared between Li and P(2). The additional distances which obtain from the distorted trigonal bipyramidal model are listed

TABLE 3. Palermoite: Electrostatic Bond Strengths and Their Sums about the Anions*

Anion	Sr^{2+}	Li^{1+}	Al^{3+}	P^{5+}	H(d)	H(a)	Σ	Me-O Sr	Me-O Li	Me-O Al	Me-O P
O(1)		1/4	3/6	5/4			2.00		+	-	0
O(2)	2/8		3/6	5/4			2.00	+		-	0
O(3)		1/4		5/4		1/6	1.67		-		-
O(4)			3/6+3/6	5/4			2.25			+	+
O(5)	2/8		3/6	5/4		½(1/6)	2.08	0		+	0
OH(1)		1/4	3/6+3/6		5/6		2.08		-	-	
OH(2)			3/6+3/6		5/6		1.83			-	

*Me-O refers to distances which are greater than (+), less than (-), or within (0) 2σ of the interatomic error referred to the polyhedral average. H(d) = hydrogen donor, H(a) = hydrogen bond acceptor.

parenthetically in Table 4. The Sr–O polyhedron is a distorted cube with distances between 2.59 and 2.65 Å. The remaining polyhedral distance averages are typical, with the 1.91 Å average for Al–O and 1.53 and 1.54 Å averages for P(1)–O and P(2)–O respectively.

Table 4 also reveals the effects of polyhedral edge-sharing. The SrO_8 cube, for example, shares two

TABLE 4. Palermoite: Interatomic Distances

Al

Al	-OH(2)	1.815(5)Å
	-OH(1)	1.850(5)
	- $O(2)^{i}$	1.868(4)
	- O(1)	1.884(4)
	- O(5)	1.928(4)
	- O(4)	2.089(5)
average		1.906
OH(1)	- O(4)	2.494(7)*
OH(1)	- O(1)	2.596(6)++
OH(2)	- O(5)	2.613(6)
$O(2)^{i}$	- O(5)	2.651(4)✓
OH(2)	- O(1)	2.669(6)
$O(2)^{i}$	-OH(2)	2.671(6)
$O(2)^{i}$	-OH(1)	2.681(6)
OH(1)	- O(5)	2.688(6)
O(4)	- O(5)	2.732(6)
$O(2)^{i}$	- O(1)	2.771(4)
O(1)	- O(4)	2.825(6)
OH(2)	- O(4)	2.916(7)
average		2.692

Hydrogen Bonds

OH(1)...O(3)	2.749(7)
OH(2)...O(5)	2.845(6)

P(1)

2	P(1)	-O(2)	1.534(4)
2		-O(1)	1.535(4)
	average		1.534
1	O(2)	$-O(2)^{iii}$	2.423(4)+
2	O(2)	$-O(1)^{iii}$	2.517(4)
1	O(1)	$-O(1)^{iii}$	2.519(4)
2	O(1)	-O(2)	2.526(4)
	average		2.505

P(2)

1	P(2)	-O(3)	1.506(5)
2		$-O(5)^{iv}$	1.540(4)
1		-O(4)	1.572(5)
	average		1.539
1	O(3)	-O(4)	2.484(7)**
1	$O(5)^{iv}$	$-O(5)^{v}$	2.502(4)
2	O(3)	$-O(5)^{iv}$	2.507(6)
2	O(4)	$-O(5)^{iv}$	2.540(6)
	average		2.513

Sr

4	Sr	- $O(5)^{i}$	2.590(3)
4		- O(2)	2.646(3)
	average		2.618
2	O(2)	- $O(2)^{iii}$	2.423(4)+
4	O(2)	- $O(5)^{i}$	2.651(4)✓
4	$O(5)^{ii}$	- $O(2)^{iv}$	3.317(4)
2	$O(5)^{i}$	- $O(5)^{vii}$	4.012(4)
	average		3.062

Li

1	Li	$-OH(1)^{ii}$	1.94(2)
1		- O(3)	2.00(2)
2		- $O(1)^{ii}$	2.29(2)
(1		- O(4)	2.46(2))
	average		2.13
(1	O(3)	- O(4)	2.484(7)**)
2	$OH(1)^{ii}$	- $O(1)^{ii}$	2.596(6)++
2	$O(1)^{ii}$	- $O(3)^{ix}$	3.110(6)
1	$O(1)^{ii}$	- O(1)	3.323(4)
1	$OH(1)^{ii}$	- O(3)	3.891(7)
(1	$OH(1)^{ii}$	- O(4)	4.014(7))
(2	$O(1)^{ii}$	- O(4)	4.316(6))

*Edge sharing between Al-Al octahedra; +between Sr-P polyhedra; ✓ between Sr-Al polyhedra; **between Li-P polyhedra; ++between Li-Al polyhedra. i = 1/2 -x, 1/2 -y, 1/2 -z; ii = x, 1/2 -y, 1/2 +z; iii = 1/2 -x, y, -z; iv = x, -y, -z; v = -x, -y, -z; vi = 1/2 -x, -y, z; vii = 1/2 -x, 1/2 + y, 1/2 + z; viii = x, 1/2 + y, 1/2 -z; ix = -x, 1/2 -y, 1/2 + z. These equivalences refer to the designated atoms in Fig. 2.

edges with the $P(1)O_4$ tetrahedron and four edges with the AlO_6 octahedra. These smaller more tightly bound polyhedra geometrically restrict the O–O′ shared edges such that the shortest SrO_8 edge distances are associated with $P(1)O_4$ and AlO_6 respectively. The OH(1)–O(4) shared edge between AlO_6 octahedra is 2.49 Å and can be compared with the $O(9)–O(9)^{i}$ shared edge distances (= 2.40 Å) in the structurally related bjarebyite (Moore and Araki, 1974).

Finney (1963) noted a short OH(2)–OH(2) = 2.44 ± 0.13 distance although that distance does not correspond to any cation–oxygen polyhedral edge. In palermoite, the $OH(2)–OH(2)^{vi}$ = 2.80 Å distance is considerably longer.

The proposed hydrogen bonds involve OH(1) . . . O(3) = 2.75 Å and OH(2)–O(5) = 2.84 Å distances. Since O(5) resides in a general position, the hydrogen bond to it is on the average half-occupied. Deviations from average bond lengths can be roughly correlated with degree of undersaturation or oversaturation of cations about anions (Table 3). Thus, O(3), with Σ = 2.25, are all longer than average. OH(1), with Σ = 2.08, has shorter than average bonds, however. At present, we cannot offer a satisfactory explanation for this discrepancy.

Acknowledgments

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