The crystal structure of aravaipaite

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ABSTRACT

The crystal structure of aravaipaite, $Pb_3AlF_9 \cdot H_2O$, monoclinic, $P2_1/n$, $a = 25.048(4)$, $b = 5.8459(8)$, $c = 5.6805(7)$ Å, $\beta = 94.013(3)°$, $V = 829.7(2)$ Å^3, $Z=4$, was solved by direct methods and refined by full-matrix least-squares techniques to $R = 0.049$ for 1170 observed reflections $[F_o > 4\sigma(F_o)]$ and $R = 0.089$ for all 1820 reflections collected using Mo$K\alpha$ X-radiation and a CCD-based detector. The structure of aravaipaite contains a square-packed layer of F atoms on either side of which are bonded Pb atoms in a fluorite (β-PbF_2)-type configuration. This layer parallel to {100} serves as a template to which on both sides are attached AlF_6 octahedra and $PbF_6(H_2O)_2$ polyhedra. The resulting thick slabs are connected via Pb-O-Pb and Al-F-Pb bonds. The two nonequivalent Pb atoms in the fluorite-type layer are each coordinated to 11 F atoms and exhibit typical lone-pair behavior.

Aravaipaite was originally reported to be triclinic. The structure analysis yielded the new mono-clinic cell provided above and required the following revisions in the mineral's description. Morphology: forms {100} and {401}; lamellar on {100}. Twinning: polysynthetic on {100}. Cleavage: {100} perfect micaceous, {011} good, {010} and {001} fair. Density (calc.): 6.703 g/cm^3. Optical orientation: X = b; Z ∧ a = 24° in the obtuse angle β. A powder pattern calculated from the structure data is also provided.

INTRODUCTION

Aravaipaite is one of six new lead-fluoride minerals from the Grand Reef mine in the Aravaipa mining district of Graham County, Arizona; the others are grandreefite, pseudo-grandreefite, laurelite, artroeite, and calcioaravaipaite (Kampf et al. 1989; Kampf and Foord 1995; Kampf and Foord 1996). The solution of the structure of grandreefite (Kampf 1991) and the partial solution of the structure of pseudograndreefite have shown these minerals to contain layer fragments of the β-PbF_2 (fluorite) structure. Based upon cell dimensions, Kampf et al. (1989) and Kampf and Foord (1996) suggested that the minerals aravaipaite and calcioaravaipaite probably also contain such layer fragments. The present study was undertaken to determine the crystal structure of aravaipaite.

EXPERIMENTAL METHODS

Cell determination

Single-crystal X-ray diffractometer studies were conducted on a thin tabular crystal fragment of aravaipaite from the Grand Reef mine provided by William W. Pinch. The fragment showed no evidence of twinning under either optical or diffraction study. This study showed aravaipaite to be monoclinic, rather than triclinic as originally reported by Kampf et al. (1989). The poor quality and twinning of the crystals used in the original study contributed to the misinterpretation of the crystal symmetry. The new cell parameters refined from the peak positions ob-

tained from the structure data collection are provided in Table 1 along with the original cell parameters. Also reported in Table 1 are other descriptive data which require revision in light of the new cell.

Structure determination

X-ray intensity data were collected using a Bruker PLAT-FORM 3-circle goniometer equipped with a 1K SMART CCD detector. A full sphere of three-dimensional data were collected. Fifty duplicate frames acquired at the end of the data collec-

TABLE 1. Descriptive data for aravaipaite

	This study*	Kampf et al (1989)
Cell parameters	Monoclinic, $P2_1/n$	Triclinic, $P1$ or $P\bar{1}$
	$a = 25.048(4)$ Å	$a = 5.842(2)$ Å
	$b = 5.8459(8)$ Å	$b = 25.20(5)$ Å
	$c = 5.6805(7)$ Å	$c = 5.652(2)$ Å
		$\alpha = 93.84(4)°$
	$\beta = 94.013(3)°$	$\beta = 90.14(4)°$
		$\gamma = 85.28(4)°$
	$V = 829.7(2)$ Å^3	$V = 827(2)$ Å^3
	$Z = 4$	$Z = 4$
Morphology	forms {100} and {401}; lamellar on {100}	forms {010} and {041}; lamellar on {010}
Twinning	polysynthetic on {100}	polysynthetic on {010}
Cleavage	{100} perfect micaceous, {011} good, {010} and {001} fair	{010} perfect micaceous, {100}, {001}, {101} and {10$\bar{1}$}
Optical orientation	X = b; Z ∧ a = 24° in the obtuse angle β	Euler angles: $\phi = 67°$, $\psi = 60°$, $\theta = 76°$
Density (calc)	6.703 g/cm^3	6.37 g/cm^3

* Morphology, twinning, and optical orientation were obtained by transforming the data reported by Kampf et al. (1989); cleavage data are based on new observations; density is based on structural formula.

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tion indicated that no significant decay had taken place. The measured intensities were corrected for Lorentz and polarization effects using the program SAINT and an empirical absorption correction was applied using the program SADABS.

The SHELXL97 software (Sheldrick 1997) was used for the determination and refinement of the structure. The metal atoms (Pb and Al) and several of the F atoms were readily located by direct methods. The positions of the remaining F and O atoms were obtained from subsequent difference-Fourier

syntheses. In subsequent refinement cycles, anisotropic displacement parameters for all non-H atoms were refined. Hydrogen atoms could not be located, but hydrogen bonds were surmised based upon valence-bond and geometrical considerations.

Table 2 gives the details of the collection and refinement, Table 3 the final fractional coordinates and equivalent isotropic displacement parameters, Table 4 the anisotropic displacement parameters, Table 5[1] the observed and calculated structure factors, Table 6 interatomic distances and angles, Table 7 the bond valences, and Table 8 the powder pattern calculated from the structure data.

DESCRIPTION OF THE STRUCTURE

The structure of aravaipaite contains a square-packed layer of F atoms on either side of which are bonded Pb atoms in a fluorite (β-PbF$_2$)-type configuration. This layer parallel to {100} serves as a template to which on both sides are attached AlF$_6$ octahedra and PbF$_6$(H$_2$O)$_2$ polyhedra. The resulting thick slabs are connected via Pb-O-Pb and Al-F-Pb bonds. The structure down [010] is shown in Figure 1.

Fluorite (β-PbF$_2$)-type layer

The fluorite (CaF$_2$) structure consists of square close-packed layers of F atoms with Ca atoms in alternating pockets above and below. Each Ca atom, sandwiched between successive F layers, is coordinated to eight F atoms at the corners of a cube. The edges of the resulting cubic unit cell are $a = 5.463$ Å. In isostructural β-PbF$_2$, the lattice expands uniformly ($a = 5.940$ Å) to accommodate the larger Pb atoms and the F atoms are "forced" farther apart.

The fluorite-type layer parallel to {100} in aravaipaite (Fig. 2) has layer dimensions $b = 5.8459$ and $c = 5.6805$ Å. The smaller dimensions compared to those in β-PbF$_2$ can be envisioned as resulting from a shift by the Pb atoms (Pb2 and Pb3) away from the plane of the F atoms (F7 and F8), thereby allowing the F atoms in the layer to move closer together.

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[1]For a copy of Table 5, document item AM-01-067, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site (http://www.minsocam.org or current web address).

TABLE 2. Data collection and structure refinement details for aravaipaite

Diffractometer	Bruker SMART Platform CCD
X-ray radiation / power	Mo$K\alpha$ ($\lambda = 0.71073$ Å) / 50 kV, 45 mA
Temperature	301(2) K
Absorption coefficient	60.948 mm^{-1}
F(000)	1400
Crystal size	$0.10 \times 0.10 \times 0.02$ mm
Frame number / width /time	2100 / 0.3° in ω / 30 s
θ range	1.63 to 28.22°
Index ranges	$-26 \leq h \leq 30, -3 \leq k \leq 7, -7 \leq l \leq 3$
Reflections collected	3600
Independent reflections	1820 [R_{int}* = 0.0384]
Reflections, $F_o > 4\sigma(F_o)$	1170
Completeness to $\theta = 28.22°$	89.0%
Refinement method	Full-matrix least-squares on F^2
Parameters refined	127
R_{int} before / after abs. corr.	25.0 / 13.3%
GooF†	0.954
R indices [$F_o > 4\sigma(F_o)$]	$R(F)$‡ = 0.049, w$R(F^2)$§ = 0.115
R indices (all data)	$R(F)$ = 0.089, w$R(F^2)$ = 0.131
Largest diff. peak / hole	$+4.03 / -3.54$ $e/$Å^3

* $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})| / \Sigma[F_o^2]$.
† GooF = S = $\{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$.
‡ $R(F)$ = $\Sigma| |F_o| - |F_c| | / \Sigma|F_o|$.
§ w$R(F^2)$ = $\{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.
   $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where P is $[2F_c^2 + \text{Max}(F_o^2, 0)] / 3$.

TABLE 3. Atomic coordinates and equivalent isotropic displacement parameters for aravaipaite

	x	y	z	U_{eq}
Pb1	0.06747(4)	0.83423(13)	0.69379(14)	0.0150(2)
Pb2	0.19124(4)	0.82727(14)	0.24796(16)	0.0179(2)
Pb3	0.19100(4)	0.36170(14)	0.72273(15)	0.0156(2)
Al	0.0960(3)	0.3161(11)	0.2001(11)	0.010(1)
F1	0.1124(5)	0.149(2)	0.943(2)	0.026(3)
F2	0.1678(5)	0.368(2)	0.259(2)	0.026(3)
F3	0.0261(5)	0.271(3)	0.141(2)	0.027(3)
F4	0.0847(6)	0.464(2)	0.472(2)	0.024(3)
F5	0.1038(6)	0.055(2)	0.379(3)	0.032(4)
F6	0.0942(7)	0.571(2)	0.033(3)	0.037(4)
F7	0.2542(4)	0.580(2)	0.497(1)	0.012(3)
F8	0.2514(5)	0.577(2)	0.997(1)	0.015(3)
F9	0.1653(6)	0.764(2)	0.683(3)	0.029(4)
O	0.9925(7)	0.778(3)	0.344(3)	0.021(4)

TABLE 4. Anisotropic displacement parameters for aravaipaite

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	0.0178(5)	0.0126(4)	0.0148(4)	0.0012(4)	0.0016(3)	−0.0001(4)
Pb2	0.0179(5)	0.0148(4)	0.0209(4)	−0.0008(4)	0.0009(4)	−0.0010(4)
Pb3	0.0184(5)	0.0139(4)	0.0146(4)	−0.0004(4)	0.0013(3)	−0.0018(4)
Al	0.012(3)	0.011(3)	0.008(3)	0.004(3)	0.002(3)	−0.003(3)
F1	0.014(7)	0.041(8)	0.023(7)	−0.021(7)	0.005(6)	−0.007(7)
F2	0.012(7)	0.029(7)	0.037(8)	−0.004(7)	−0.005(6)	−0.008(6)
F3	0.011(7)	0.053(9)	0.015(6)	0.004(7)	−0.006(6)	−0.003(7)
F4	0.040(9)	0.011(5)	0.021(7)	−0.008(6)	0.003(7)	−0.004(6)
F5	0.038(9)	0.019(6)	0.043(9)	0.018(7)	0.025(8)	0.013(7)
F6	0.045(10)	0.029(7)	0.036(8)	0.014(8)	0.006(8)	0.006(8)
F7	0.003(6)	0.014(6)	0.020(7)	−0.001(5)	0.002(5)	0.004(5)
F8	0.017(7)	0.012(6)	0.016(7)	0.003(5)	−0.003(6)	−0.003(5)
F9	0.033(9)	0.019(6)	0.038(8)	−0.008(7)	0.020(7)	−0.005(6)
O	0.023(9)	0.023(8)	0.018(8)	0.005(8)	0.001(7)	−0.001(8)

TABLE 6. Bond lengths (Å), AlF$_6$ octahedral edge lengths (Å), and bond angles in aravaipaite

Al-F6	1.76		Pb1-F5	2.43	Pb2-F8	2.45	Pb3-F9	2.45		
Al-F3	1.78		Pb1-F9	2.49	Pb2-F7	2.50	Pb3-F8	2.45		
Al-F4	1.81		Pb1-F6	2.52	Pb2-F7	2.51	Pb3-F7	2.46		
Al-F1	1.83		Pb1-F1	2.54	Pb2-F8	2.60	Pb3-F8	2.58		
Al-F2	1.83		Pb1-F4	2.55	Pb2-F9	2.63	Pb3-F7	2.61		
Al-F5	1.84		Pb1-O	2.66	Pb2-F5	2.71	Pb3-F2	2.66		
Al-F	1.81		Pb1-F3	2.66	Pb2-F2	2.75	Pb3-F1	2.71		
F2-F6	2.47	86.9°	Pb1-O	2.72	Pb2-F6	3.04	Pb3-F4	2.99		
F4-F5	2.51	86.8°	<Pb-F>	2.53	Pb2-F1	3.16	Pb3-F7	3.14		
F1-F2	2.54	87.9°	<Pb-O>	2.69	Pb2-F2	3.22	Pb3-F6	3.33		
F2-F4	2.54	88.4°			Pb2-F9	3.25	Pb3-F5	3.35		
F3-F6	2.55	92.0°			<Pb-F>	2.80	<Pb-F>	2.79		
F1-F5	2.56	88.6°								
F2-F5	2.56	88.4°								
F1-F6	2.56	91.2°			O-H1..F4	2.67				
F3-F4	2.57	91.3°			O-H2..F3	2.78				
F4-F6	2.60	93.2°			F3-O-F4	104.8°				
F1-F3	2.60	92.5°								
F3-F5	2.62	92.8°								
F-F	2.56	90.0°								

Note: Standard deviations for bond distances are 0.01 to 0.02 for Pb-F, Pb-O and Al-F and 0.02 for F-F and F-O. Standard deviations for bond angles are 0.7 to 0.8°.

TABLE 7. Bond valences for aravaipaite

	F1	F2	F3	F4	F5	F6	F7	F8	F9	O	$\Sigma_c v$
Pb1	0.253		0.183	0.243	0.336	0.265			0.289	0.425	1.993
Pb2	0.048	0.184			0.160	0.066	0.556	0.540	0.237		1.791
Pb3	0.160	0.234		0.075	0.028	0.030	0.520	0.549	0.326		1.923
Al	0.468	0.458	0.532	0.486	0.453	0.554					2.951
H1			0.190							0.810	1.000
H2				0.210						0.790	1.000
$\Sigma_a v$	0.929	0.876	0.905	1.013	0.977	0.914	1.077	1.090	0.852	2.025	

Notes: Constants from Brese and O'Keeffe (1991). Hydrogen bond valence based upon Brown and Altermatt (1985).

TABLE 8. Calculated powder pattern for aravaipaite

I	d	hkl	I	d	hkl
100	12.4930	200	27	2.2615	720
5	5.6922	110	4	2.2365	$\overline{6}$21
10	5.6116	$\overline{1}$01	23	2.1756	$\overline{8}$02
13	5.2949	210	7	2.1341	820
9	4.8454	$\overline{3}$01	6	2.1159	612
6	4.7849	310	3	2.0592	11·0·1
10	4.5396	301	40	2.0360	$\overline{1}$22
9	4.2683	410	11	2.0344	022
4	3.9843	111	18	2.0290	802
8	3.8853	$\overline{5}$01	5	2.0272	$\overline{11}$·1·1
6	3.8128	211	4	2.0241	$\overline{2}$22
3	3.7985	510	11	2.0195	122
32	3.7305	$\overline{3}$11	26	2.0130	920
5	3.6243	501	6	1.9664	821
81	3.5855	311	5	1.9615	12·1·0
46	3.4905	$\overline{4}$11	3	1.9427	130
8	3.3918	610	8	1.9426	$\overline{10}$·0·2
46	3.3336	411	10	1.9422	11·1·1
89	3.2358	$\overline{5}$11	6	1.8925	$\overline{12}$·1·1
54	3.1233	800	5	1.8435	$\overline{10}$·1·2
47	3.0803	511	7	1.8169	12·1·1
9	2.9862	$\overline{6}$11	23	1.7784	$\overline{4}$31
4	2.9292	701	15	1.7726	$\overline{13}$·1·1
12	2.9230	020	3	1.7626	213
46	2.9032	120	3	1.7587	$\overline{4}$13
40	2.8333	002	20	1.7566	431
14	2.8058	$\overline{2}$02	14	1.7333	313
5	2.5977	021	11	1.7305	722
3	2.5650	$\overline{9}$01	16	1.7283	$\overline{5}$13
8	2.5295	$\overline{2}$12	3	1.7104	730
6	2.5272	221	10	1.7051	13·1·1
3	2.5028	$\overline{3}$21	4	1.6995	$\overline{6}$31
10	2.4986	10·0·0	4	1.6975	413
4	2.4576	321	4	1.6917	$\overline{6}$13
4	2.3313	$\overline{5}$12	14	1.6818	$\overline{9}$22
3	2.3102	412	5	1.6030	922
8	2.2975	10·1·0	5	1.5616	16·0·0
12	2.2698	602			
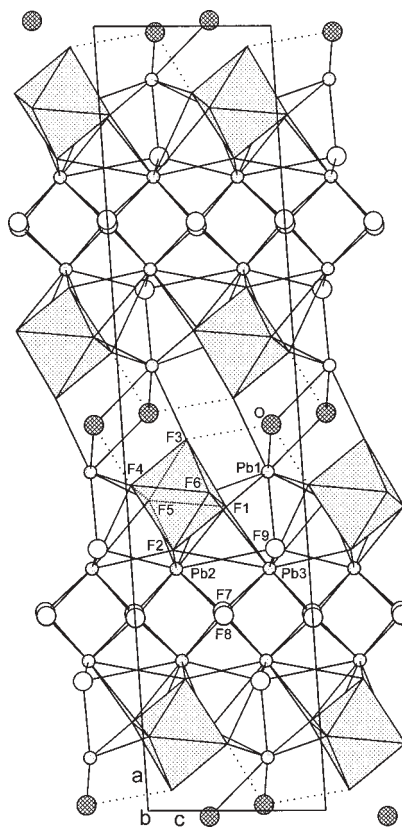
FIGURE 1. The structure of aravaipaite viewed along the *b* axis. Stippled octahedra are AlF$_6$, small shaded circles are Pb, large unshaded circles are F, large cross-hatched circles are O (H$_2$O), dotted lines are presumed hydrogen bonds.
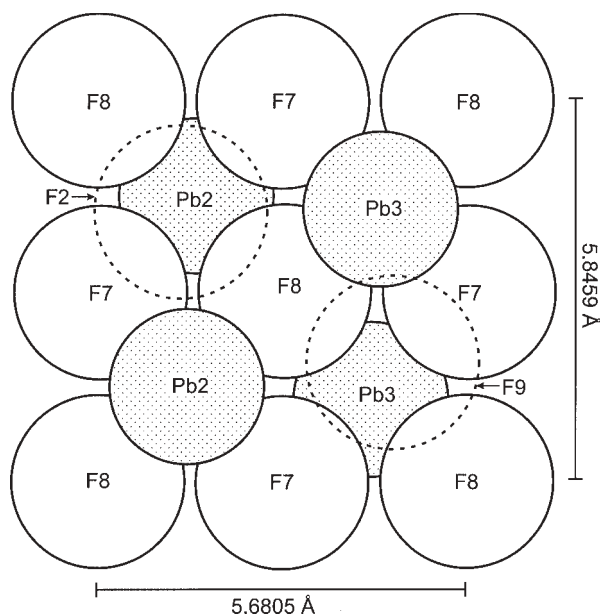
FIGURE 2. The fluorite-type layer parallel to {100} in aravaipaite. Broken circles indicate the positions of non-layer F9 and F2 atoms. Circles are drawn to scale [R(Pb^{2+}) = 1.19 Å, R(F$^-$) = 1.33 Å].

The fluorite-type layer in aravaipaite not only defines the *a* and *c* cell parameters, it also provides a foundation or template for the organization of the other structural elements. The pockets between the Pb2 and Pb3 atoms above and below the square-packed layer of F atoms (see Fig. 2) are alternately occupied by isolated F atoms (F9) and apical F atoms (F2) of the AlF$_6$ octahedra. The opposite apex (F3) of the octahedron is thus constrained to point approximately away from the fluorite-type layer. The Pb1 atoms then nestle between the AlF$_6$ octahedra.

AlF$_6$ octahedron

In the AlF$_6$ octahedron, the Al-F bonds range from 1.76 to 1.84 Å and the F-Al-F angles range from 86.8 to 93.2°. The F6, F3, and F4 atoms, forming the same octahedral face, corre-

spond to the three shortest Al-F bonds (1.76, 1.78, and 1.81 Å, respectively). The Al atom is, therefore, shifted toward this side of the octahedron and especially toward the F6-F3 edge. The shift is away from the Pb2 and Pb3 atoms of the fluorite layer and the non-layer Pb1, suggesting that cation-cation repulsion may be responsible.

Pb polyhedra

Pb1 is coordinated to eight ligands, six F atoms, and two O atoms of H$_2$O groups. Five of the F atoms (F1, F3, F4, F5, and F6) represent corners shared with five different AlF$_6$ octahedra. The remaining ligand is an "isolated" F atom (F9) not contained in the fluorite-type layer. The Pb1-F distances range from 2.43 to 2.66 Å with an average of 2.53 Å and the Pb1-O distances are 2.66 and 2.72 Å, average 2.69 Å. Pb1 is not shifted in its coordination polyhedron, indicating that the Pb^{2+} lone electron pair is not stereoactive. The Pb-F and Pb-O distances are consistent with those found in other Pb-F/O coordinations in which Pb^{2+} directional inert-pair ("lone-pair") electrons are not a factor. For example, the PbF$_4$O$_4$ polyhedron in grandreefite exhibits Pb-F distances between 2.39 and 2.71 Å, average 2.55 Å, and Pb-O distances between 2.54 and 2.84 Å, average 2.70 Å. The Pb1 polyhedron (PbF$_6$O$_2$) in aravaipaite (Fig. 3) approximates a bicapped trigonal prism, similar to the PbF$_4$O$_4$ polyhedron in grandreefite. The bond valence sum for Pb1 is 1.99 v.u., very close to the ideal value.

Both Pb2 and Pb3 are coordinated to eleven F atoms at distances ranging from 2.44 to 3.35 Å. In each coordination, there are four short bonds to F7 and F8 atoms in the fluorite-type layer and one additional short bond to F9, the only other F atom not in the AlF$_6$ octahedron. These short bonds are all within the range 2.44 to 2.63 Å. Except for one additional long Pb2-F9 bond (3.24 Å), all other Pb-F bonds are to F atoms in the AlF$_6$ octahedra and these Pb-F distances range from 2.66 to 3.35 Å. The Pb2 polyhedron shares the F1-F2-F5 face with one AlF$_6$ octahedron (at Pb-F distances of 3.16, 3.22, and 2.71 Å, respectively) and the F2-F6 edge with another (at 2.75 and 3.04 Å, respectively). The Pb3 polyhedron shares the F1-F2-F6 face with one AlF$_6$ octahedron (at 2.71, 3.14, and 3.33 Å, respectively) and the F2-F4-F5 face with another (at 2.66, 2.99, and 3.35 Å, respectively). The bond valence sums for Pb2 and Pb3
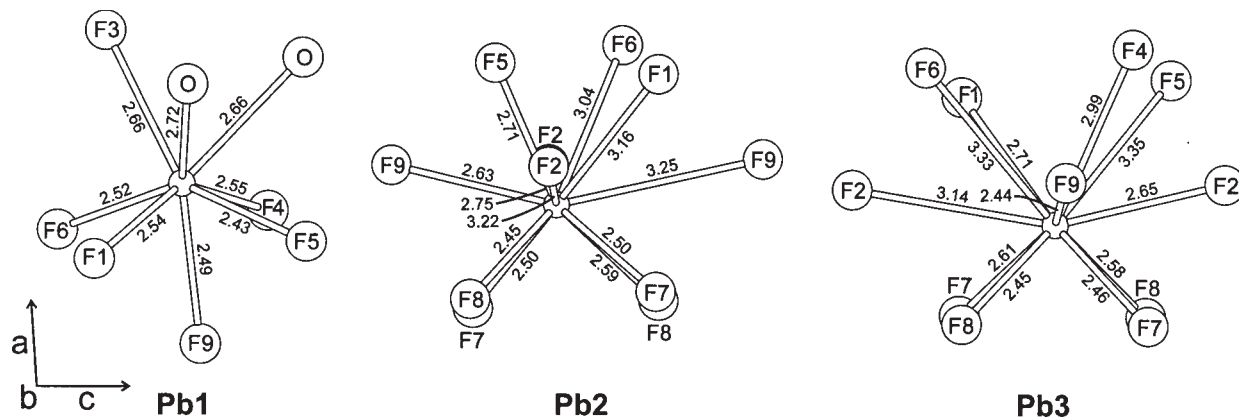

FIGURE 3. Pb coordinations in aravaipaite with Pb-F and Pb-O bond distances shown. Orientations are the same as in Figure 1.

are 1.79 and 1.92 v.u., respectively. In both cases, extending the Pb-F bond distance limit would bring the bond valence sums only slightly closer to the ideal value. The coordinations of Pb2 and Pb3 become twelve if the additional bonds Pb2-F2 (3.54 Å) and Pb3-F9 (3.56 Å) are included.

As described above, Pb2 and Pb3 are effectively shifted significantly off-center in their coordination polyhedra. Such behavior is typical of Pb atoms with lone-pair electrons. The positions of Pb2 and Pb3 suggest that their lone-pair electrons are directed away from the fluorite-type layer and toward the interlayer region containing the AlF_6 octahedra and Pb1 polyhedra.

ACKNOWLEDGMENTS

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