

Artroeite, $\text{PbAlF}_3(\text{OH})_2$, a new mineral from the Grand Reef mine, Graham County, Arizona: Description and crystal structure

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ABSTRACT

Artroeite, $\text{PbAlF}_3(\text{OH})_2$, space group $P\bar{1}$, $a = 6.270(2)$, $b = 6.821(3)$, $c = 5.057(2)$ Å, $\alpha = 90.68(2)$, $\beta = 107.69(2)$, $\gamma = 104.46(2)^\circ$, $V = 198.6(2)$ Å³, $Z = 2$, is a new mineral from the Grand Reef mine, near Klondyke, Graham County, Arizona. It occurs as colorless bladed crystals associated with quartz, fluorite, galena, anglesite, and an as yet undescribed mineral of composition $\text{PbCa}_2\text{Al}(\text{F},\text{OH})_9$. Artroeite has a Mohs hardness of about 2.5, a measured density of 5.36(2) g/cm³, and a calculated density of 5.47 g/cm³. It exhibits a perfect {100} cleavage and a good {010} cleavage. Optically it is biaxial (–) with $\alpha = 1.629(1)$, $\beta = 1.682(2)$, and $\gamma = 1.691(2)$. Dispersion is strong, $r > v$. The six strongest powder diffraction lines are [$d(I, hkl)$] 4.42₁₀₀($\bar{1}01$), 3.221₄₀(101), 2.595₇₀($1\bar{2}1, 021$), 2.190₆₅(201, 012, 030), 2.030₅₀(022), 2.015₄₀($\bar{2}30$) Å.

The structure was solved by direct methods and refined to $R = 0.022$ using X-ray diffractometer data (1096 independent reflections). In the structure, edge-sharing dimers of $\text{AlF}_3(\text{OH})_3$ octahedra link together by bonds to Pb atoms to form approximately close-packed layers parallel to (10 $\bar{1}$). The layers are linked to one another by one Pb-F bond and two H bonds per formula unit. Pb is coordinated to 6 F and 3 O atoms. Three F ligands are associated with the same Al octahedral face and correspond to much longer bonds. It is probable that the lone pair electrons are situated on that side of the Pb atom. The structure is compared with those of acuminite and tikhonenkovite.

INTRODUCTION

Kampf et al. (1989) described the new minerals grandreefite, $\text{Pb}_2\text{SO}_4\text{F}_2$, pseudograndreefite, $\text{Pb}_6\text{SO}_4\text{F}_{10}$, laurelite, $\text{Pb}(\text{F},\text{Cl},\text{OH})_2$, and aravaipaite, $\text{Pb}_3\text{AlF}_6 \cdot \text{H}_2\text{O}$, from a single vug found in the oxidized zone of the Grand Reef mine, an epithermal Cu-Pb-Ag deposit in the Aravaipa mining district of Graham County, Arizona. Acidic supergene sulfate-rich solutions are thought to have dissociated Pb and F from layers of earlier-formed galena and fluorite that envelop the vug. The layers of galena and fluorite apparently also served as a barrier preventing Cu^{2+} from entering the vug.

A specimen containing a similar vug, collected in the same portion of the mine by Michael Shannon in 1981 and set aside as an unknown, was provided to the authors in 1992 by David Shannon. Although it did not contain any of the previously described minerals, it yielded two more new Pb-F species, one of which is described herein, including a determination of its crystal structure. The other new mineral is still under study.

The new mineral is named artroeite in honor of Arthur Roe (1912–1993) of Tucson, Arizona. Art Roe was an avid collector of microscopic minerals (micromounts) and a prolific author and lecturer to the amateur mineralogi-

cal community. He provided volunteer curatorial assistance to the mineral collections of the U.S. National Museum of Natural History, the Arizona-Sonora Desert Museum, and the University of Arizona. Art Roe served as professor and as chairman in the Chemistry Department at the University of North Carolina (1939–1959) and was the first director of the Office of International Science at the National Science Foundation. The mineral and name were approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. The holotype specimen is in the collection of the Natural History Museum of Los Angeles County (Cat. no. 39338).

DESCRIPTION

Occurrence and paragenesis

Artroeite is found on a single specimen in a 15 × 5 mm quartz-lined vug in association with anglesite and another new mineral of composition $\text{PbCa}_2\text{Al}(\text{F},\text{OH})_9$. The second new mineral occurs as colorless tabular crystals, as a massive cavity filling, and as inclusions up to 10 μm in length in artroeite crystals. An intergrowth of fluorite and galena completely envelopes the vug. The galena is partially altered to anglesite. Linarite and mus-

TABLE 1. Descriptive characteristics of artroeite

Chemical data	
PbO	67.5 (67.0–68.0)*
Al ₂ O ₃	15.6 (15.5–15.7)*
F	16.1 (15.8–16.5)*
H ₂ O	6.0
O ≡ F	6.8
Total	98.4
	Pb std: synthetic PbS
	Al std: kyanite
	F std: synthetic phlogopite
	H ₂ O by TGA (loss between 300 and 400 °C)
	empirical formula: Pb ₁ Al _{1.01} F _{2.80} OH _{2.20}
	decomposes rapidly in cold 1:1 HCl forming white precipitate
Cell data**	
Triclinic, <i>P</i> $\bar{1}$	<i>a</i> = 6.270(2) Å α = 90.68(2)°
PbAlF ₃ (OH) ₂ ; Z = 2	<i>b</i> = 6.821(3) Å β = 107.69(2)°
<i>V</i> = 198.6(2) Å ³	<i>c</i> = 5.057(2) Å γ = 104.46(2)°
Morphology	
Habit: blades elongate on <i>b</i> and flattened on {10 $\bar{1}$ }	
Maximum crystal size: 1 × 0.7 × 0.04 mm	
Forms: {100}, {010}, {001}, {10 $\bar{1}$ }, {011}, {11 $\bar{1}$ }, {121}	
Twinning: common – by rotation on [010] with C.P. {100}	
Physical properties	
Color: colorless	cleavage: {100} perfect; {010} good
Streak: white	tenacity: brittle
Luster: vitreous	fracture: chonchoidal
Hardness: 2½	density: 5.36(2) _{meas} †; 5.43 _{calc} g/cm ³
Optical properties	
Indicatrix: biaxial	2 <i>V</i> : 41(2) _{meas} ‡; 42 _{calc}
Sign: (–)	dispersion: <i>r</i> > <i>v</i> , strong
α = 1.629(1)	<i>X</i> Δ <i>c</i> = 10° in acute β
β = 1.682(2)	<i>Y</i> Δ <i>a</i> = 42° in acute γ
γ = 1.691(2)	<i>Z</i> Δ <i>b</i> = 50° in obtuse γ

* Electron microprobe (ARL-SEM-Q); averages and ranges for 10 analyses.

** Four-circle data, 25 reflections ($2\theta = 18$ – 22°).

† Berman balance, toluene at 25 °C.

‡ Spindle stage.

covite are only present outside of the fluorite-galena envelope. Artroeite probably resulted from the reaction of acidic supergene solutions with galena and fluorite and was the last mineral to form in this assemblage.

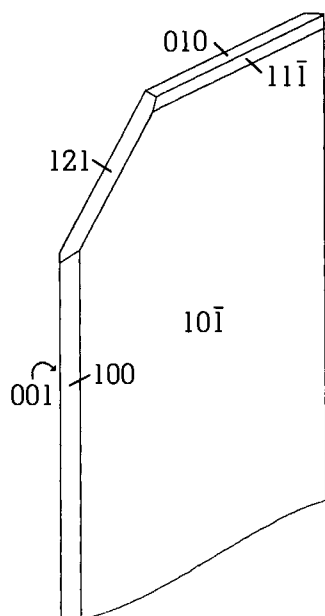


Fig. 1. Orthographic projection of an artroeite crystal.

TABLE 2. X-ray powder diffraction data for artroeite

<i>l</i> _{obs}	<i>d</i> _{obs}	<i>d</i> _{calc} *	<i>l</i> _{calc}	<i>hkl</i>	<i>l</i> _{obs}	<i>d</i> _{obs}	<i>d</i> _{calc} *	<i>l</i> _{calc}	<i>hkl</i>
15	6.57	6.575	13	010			2.033	9	2 $\bar{1}$ 2
10	5.74	5.759	12	100	50	2.030	2.032	24	022
30	5.04	5.048	32	$\bar{1}$ 10			2.022	8	1 $\bar{3}$ 1
15	4.79	4.796	16	001			2.022	12	230
100	4.42	4.442	100	$\bar{1}$ 01			2.013	25	$\bar{1}$ 22
35	4.05	4.063	50	0 $\bar{1}$ 1	40	2.015	2.012	9	1 $\bar{1}$ 2
20	3.88	3.898	37	$\bar{1}$ 11			1.934	11	211
20	3.84	3.854	46	110	30	1.932	1.927	10	220
20	3.70	3.710	24	011			1.891	8	320
5	3.480	3.496	5	$\bar{1}$ 11	15	1.889	1.888	5	130
35	3.267	3.288	29	020	10	1.826	1.828	6	112
40	3.221	3.251	40	$\bar{1}$ 20	25	1.808	1.810	13	3 $\bar{1}$ 1
<5	3.170	3.218	50	101			1.803	7	302
30	2.940	3.173	6	$\bar{1}$ 11	10	1.746	1.748	6	222
		2.909	19	201	20	1.707	1.705	10	140
30	2.880	2.879	29	200	10	1.670	1.670	8	311
<5	2.674	2.675	3	111			1.639	4	132
70	2.595	2.599	30	021	10	1.639	1.635	7	203
		2.591	24	121			1.609	5	202
30	2.511	2.515	14	$\bar{1}$ 02	15	1.605	1.602	5	041
		2.506	22	$\bar{1}$ 21			1.599	6	003
20	2.454	2.474	12	$\bar{2}$ 11			1.596	5	231
		2.450	22	$\bar{2}$ 21	10	1.590	1.592	4	122
20	2.404	2.412	9	210			1.589	3	013
20	2.334	2.398	13	002	10	1.515	1.513	4	123
10	2.245	2.242	7	$\bar{1}$ 12			1.512	4	041
		2.192	18	030	10	1.497	1.501	4	241
		2.187	9	012			1.495	5	331
65	2.190	2.183	15	212	15	1.456	1.456	4	341
		2.182	6	201	5	1.428	1.452	4	232
<5	2.082	2.089	8	121			1.426	4	431
		2.071	15	311			1.393	3	142
25	2.068	2.066	10	221	25	1.388	1.389	4	123
		2.064	7	131			1.387	4	023
							1.386	5	231

Note: 114.6-mm Gandolfi camera, CuK α (Ni-filtered) radiation, observed intensities visually estimated, calculated intensities obtained from structure data.

* Calculated from the cell parameters given in Table 1.

Mineral data

A drawing of a single crystal of artroeite is provided as Figure 1, and the descriptive characteristics are provided in Table 1. X-ray powder diffraction data are given in Table 2.

CRYSTAL STRUCTURE DETERMINATION

Most details of the data collection and refinement are given in Table 3. Data were corrected for Lorentz and

TABLE 3. Details of data collection and refinement for artroeite

Diffractometer: Huber	$\mu = 429.85 \text{ cm}^{-1}$
Radiation/monochromator: MoK α /Gr	Absorption correction by Gaussian integration
$2\theta_{\text{max}} = 60^\circ$	Face (distance in mm):
Scan type: $\theta/2\theta$	001(0.040), 100(0.055),
Scan width: 3.0°	10 $\bar{1}$ (0.015), $\bar{1}$ 01(0.015),
Scan duration: 3°/min	010(0.030), 0 $\bar{1}$ 0(0.030),
Standards: 3/100 ref.	121(0.040), $\bar{1}$ 0 $\bar{1}$ (0.055)
Total reflections: 2310	$R_{\text{obs}}^* = 0.100$, $R_{\text{w obs}} = 0.119$
Unique reflections: 1155	$R_{\text{int}}^{**} = 0.033$, $R_{\text{w int}} = 0.043$
$R_{\text{merge}} = 0.033$	$R = 0.022$, $R_{\text{w}} = 0.031$
No. data [$F_o > 6\sigma_F$]: 1096	

* Prior to absorption correction.

** Based upon isotropic displacement parameters.

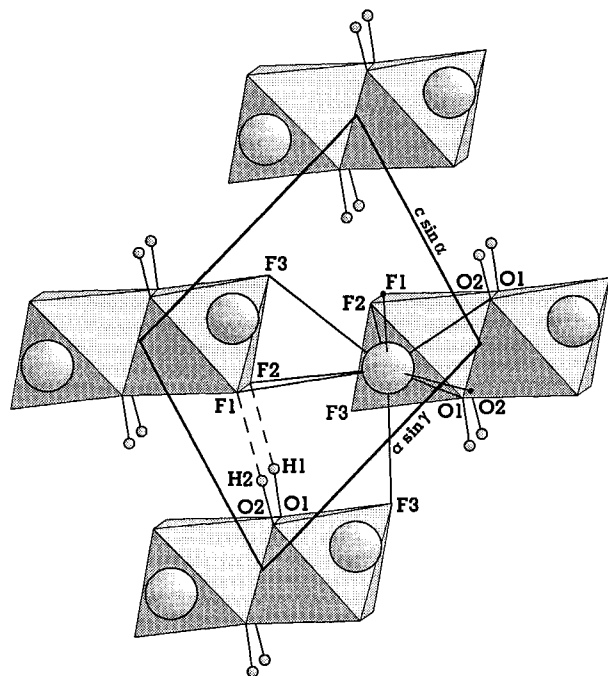


Fig. 2. The atomic structure of artroite projected down [010] showing close-packed layers viewed on edge. Large circles are Pb atoms; small circles are H atoms; black dots indicate anions in octahedra above those shown.

polarization factors. Computations were carried out with the crystallographic computing package from the University of California, Los Angeles. Scattering factors for neutral atoms and anomalous dispersion coefficients were taken from *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). The structure was solved using direct methods.

All atoms are in general positions, and all were assigned full occupancy. F and O were easily discerned on the basis of distances from Al, isotropic displacement factors, and bond valence sums. There was no conclusive evidence for assigning partial O occupancy to any F site, as was suggested by the chemical analysis. H atoms were located from analysis of difference-Fourier maps. The scale factor and the positional and anisotropic displacement parameters of all atoms except H were varied in the final cycle of refinement. Final positional and displacement

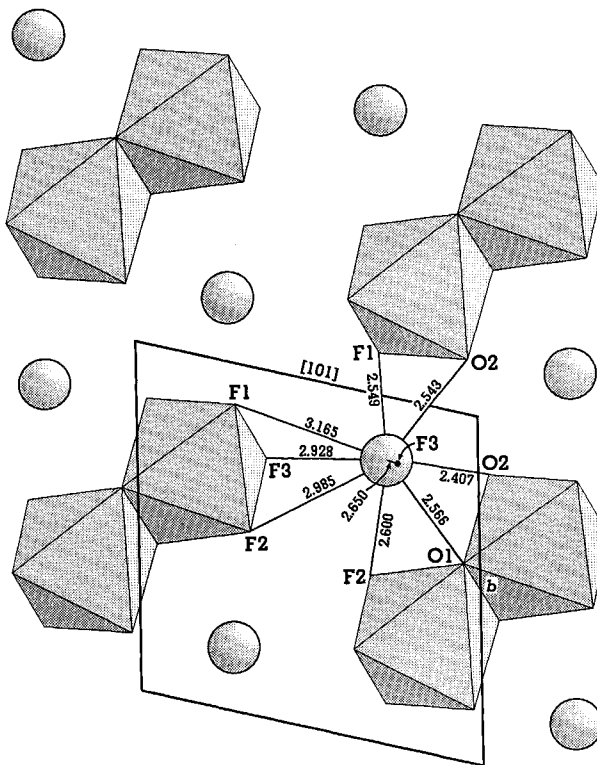


Fig. 3. An approximately close-packed layer in artroite oriented parallel to (101) showing bond distances (Å) to one Pb. Large circles are Pb atoms; black dot indicates F3 in layer above that shown.

parameters are given in Table 4, selected interatomic distances and angles are given in Table 5, and observed and calculated structure factors are listed in Table 6.¹

DISCUSSION OF THE STRUCTURE

Structure description

The artroite structure is depicted in Figures 2 and 3. It contains $\text{AlF}_3(\text{OH})_3$ octahedra that share an O1-O1'

¹ A copy of Table 6 may be ordered as Document AM-95-573 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 4. Positional and displacement parameters for artroite

	x	y	z	U_{eq}^*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	0.30975(4)	0.19142(3)	0.20352(5)	0.00960(5)	0.00866(8)	0.00607(6)	0.0140(1)	0.00235(5)	0.00339(7)	0.00156(5)
Al	0.8110(3)	0.3273(3)	0.8364(4)	0.0077(3)	0.0085(5)	0.0047(4)	0.0100(7)	0.0016(3)	0.0031(5)	0.0012(4)
F1	0.7950(8)	0.1378(6)	0.5751(9)	0.0130(8)	0.017(1)	0.0069(8)	0.015(2)	0.0030(8)	0.009(1)	0.0003(9)
F2	0.7407(7)	0.4891(6)	0.5627(8)	0.0104(8)	0.012(1)	0.0081(8)	0.011(2)	0.0043(8)	0.002(1)	0.0028(9)
F3	0.5137(8)	0.2308(7)	0.8113(10)	0.0142(8)	0.009(1)	0.0105(9)	0.023(2)	0.0001(8)	0.006(1)	0.002(1)
O1	0.8629(8)	0.5514(7)	0.0981(10)	0.0094(8)	0.008(1)	0.0073(9)	0.013(2)	0.0027(8)	0.005(1)	0.001(1)
O2	0.8981(8)	0.1432(7)	0.0988(9)	0.0082(8)	0.010(1)	0.0076(9)	0.007(2)	0.0030(8)	0.003(1)	0.0021(9)
H1	0.807	0.509	0.253	0.02						
H2	0.862	0.122	0.255	0.02						

* $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

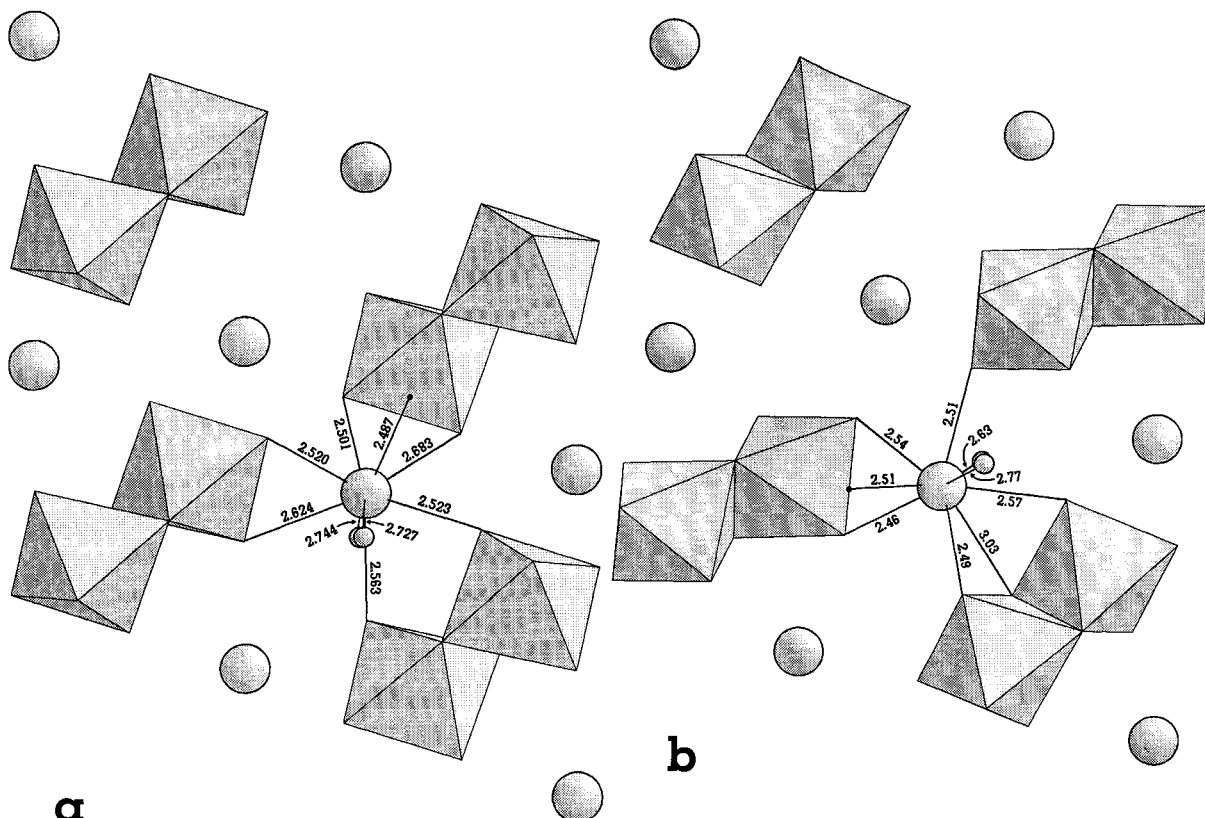


Fig. 4. Puckered layers in (a) acuminite parallel to (010) and (b) tikhonenkovite perpendicular to [100]. Large circles are Sr atoms; small circles are O atoms of H_2O ; black dots indicate anions in octahedra above those shown. Bond distances (\AA) to one Sr are shown.

edge to form $[\text{Al}_2\text{F}_6(\text{OH})_4]^{4-}$ dimers. The structure can be visualized as consisting of approximately close-packed layers oriented parallel to $(10\bar{1})$, composed of Pb atoms and octahedral dimers that are linked by Pb-F and Pb-O bonds. The layers are joined in the third dimension by one Pb-F bond and two H bonds per formula unit.

Following the scheme of Hawthorne (1984), artroeite is classified as a simple aluminofluoride based on a finite octahedral cluster, the aforementioned edge-sharing dimer. Artroeite is most closely related to the $\text{SrAlF}_4(\text{OH})\cdot\text{H}_2\text{O}$ dimorphs, acuminite (Andersen and Ploug-Sørensen, 1991) and tikhonenkovite (Pudovkina and Pyatenko, 1967). In all three of these structures, isolated edge-sharing dimers are linked by bonds to large ninefold-coordinated divalent cations. The layers parallel to $(10\bar{1})$ in artroeite (Fig. 3), parallel to (010) in acuminite (Fig. 4a), and

perpendicular to [100] in tikhonenkovite (Fig. 4b) are remarkably similar in projection; however, in acuminite and tikhonenkovite the layers are markedly puckered.

Al octahedron

In artroeite the three F atoms and three O atoms in each $\text{AlF}_3(\text{OH})_3$ octahedron occupy opposite faces. The Al-F bonds range from 1.779 to 1.800 \AA , and the Al-O bonds range from 1.892 to 1.927 \AA (Table 5). The octahedral angles range from 79.9 to 97.1°. The Al octahedron is somewhat less regular than those in acuminite and tikhonenkovite in that the 1.779- \AA Al-F bond is shorter than any in either of the latter structures and the 1.927 \AA Al-O bond is longer. The Al octahedra in acuminite and tikhonenkovite only have two O ligands, but in all three structures the vertices of the shared edges are occupied by O atoms, and the corresponding O-Al-O angles are the smallest (79.9° in artroeite, 79.8° in acuminite, and 78.5° in tikhonenkovite), the result of the Al^{3+} - Al^{3+} cation repulsion effect.

Pb coordination and the lone pair effect

In artroeite Pb is coordinated by 6 F and 3 O atoms. The Pb-O bonds and three of the Pb-F bonds are within normal limits, ranging from 2.407 to 2.566 \AA and 2.549 to 2.650 \AA , respectively. The other three Pb-F bonds are

TABLE 5. Selected bond lengths (\AA) and angles ($^\circ$) for artroeite

Pb-O2	2.407(5)	Al-F3	1.779(5)	O1-H1	0.972
-O2	2.543(5)	-F2	1.799(4)	H1...F2	1.736
-F1	2.549(4)	-F1	1.800(4)	O1-F2	2.691(6)
-O1	2.566(5)	-O2	1.892(5)	O1-H1-F2	166.9
-F2	2.600(4)	-O1	1.907(5)		
-F3	2.650(5)	-O1	1.927(5)	O2-H2	0.890
-F3	2.928(5)	(Al-F)	1.793	H2...F1	1.800
-F2	2.985(4)	(Al-O)	1.909	O2-F1	2.676(6)
-F1	3.165(5)			O2-H2-F1	167.6

much longer, ranging from 2.928 to 3.165 Å (Table 5). The longer Pb-F bonds are all on the same side of the Pb atom, and the F atoms participating in these bonds are all contained within the same Al octahedral face. The lopsided coordination of Pb is ascribed to the lone pair effect.

Figures 3 and 4 clearly depict the Pb and Sr coordinations in artroite, acuminite, and tikhonenkovite. The Sr coordinations in acuminite and tikhonenkovite differ from the Pb coordination in artroite in three important ways: (1) each Sr bonds to two H₂O groups in lieu of bonding to two octahedral ligands; (2) the Sr coordination polyhedra do not share faces with Al octahedra; and (3) the Sr coordinations are not lopsided, the one long Sr-O bond in tikhonenkovite notwithstanding.

Moore et al. (1993) showed that, when the bonds between the lone pair cation and the anion are disregarded, the relative electrostatic undersaturations of the anions surrounding the lone pair cation predict whether the lone pair effect will be manifested in Pb- ϕ distances and determine in which direction the lone pair cation will shift, relative to the center of its anion coordination polyhedron. The analysis of the Pb coordination sphere in artroite by this approach is complicated by the fact that four of the five distinct anions form two bonds, each of a different length, to Pb. Each of the three F atoms forms one normal-length and one long bond to Pb. Nevertheless, when the bond valences of the anions, listed in Table 7, are considered, after deducing the bond valence contribution by Pb, it is seen that O₂, by far the most undersaturated anion, forms the two shortest bonds to Pb. Furthermore, it is seen in Figure 2 that both Pb-O₂ bonds are roughly on the same side of the Pb atom and the three long Pb-F bonds are on approximately the opposite side of the Pb atom. The Pb can, therefore, be visualized as having shifted off the center position of its coordination polyhedron in the direction of O₂ in response to the high degree of undersaturation of that anion. The lone pair electrons then are localized on the opposite side of the Pb atom in the direction of the long Pb-F bonds.

Although a variety of factors, e.g., temperature, solution chemistry, and activity of H₂O, may serve to determine whether the artroite, acuminite, or tikhonenkovite structure is preferred, the presence of lone pair electrons on the large cation may be crucial to the stability of the artroite structure.

TABLE 7. Bond valences (vu) in artroite

	F1	F2	F3	O1	O2	Total
Pb	{ 0.25 0.05 }	{ 0.21 0.08 }	{ 0.19 0.09 }	0.29	{ 0.45 0.31 }	1.92
Al	0.50	0.50	0.53	{ 0.50 0.47 }	0.52	3.02
H1		0.17		0.83		1
H2	0.17				0.83	1
Total	0.97	0.96	0.81	2.09	2.11	

Note: based upon Brese and O'Keeffe (1991), except for H bonds, which are based on Brown and Altermatt (1985) with O-H 0.95 Å.

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