

## Order-disorder approach to calcioaravaipate, $[\text{PbCa}_2\text{Al}(\text{F},\text{OH})_9]$ : The crystal structure of the triclinic MDO polytype

ANTHONY R. KAMPF,<sup>1,\*</sup> STEFANO MERLINO,<sup>2</sup> AND MARCO PASERO<sup>2</sup>

<sup>1</sup>Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Blvd., Los Angeles, California 90007, U.S.A.

<sup>2</sup>Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italy

### ABSTRACT

The crystal structure of calcioaravaipate,  $\text{PbCa}_2\text{Al}(\text{F},\text{OH})_9$ , was initially solved by direct methods in the monoclinic space group  $A2/m$  ( $R = 12.4\%$ ). Further study demonstrated the OD nature of the structure, and showed that the crystal was twinned. The structure was solved in the triclinic space group  $C\bar{1}$ ,  $a = 7.722(3)$ ,  $b = 7.516(3)$ ,  $c = 12.206(4)$  Å,  $\alpha = 98.86(1)$ ,  $\beta = 96.91(1)$ ,  $\gamma = 90.00(1)^\circ$ ,  $V = 694.8(3)$  Å<sup>3</sup>,  $Z = 4$ , yielding  $R = 5.1\%$  for 1420 reflections with  $F_o > 4S(F_o)$ .

Calcioaravaipate belongs to a family of order-disorder (OD) structures formed by equivalent layers of symmetry  $C2/m$ . Two maximum-degree-of-order (MDO) polytypes are possible. MDO1 results from a regular alternation of stacking operators  $2_{1/2}$  and  $2_{-1/2}$  and yields a monoclinic structure with  $C2/c$ ,  $a = 7.72$ ,  $b = 7.52$ ,  $c = 24.12$  Å,  $\beta = 96.99^\circ$ . MDO2 results from the sequence  $2_{1/2}/2_{1/2}/2_{1/2}/\dots$  and yields a triclinic structure with  $a = 7.72$ ,  $b = 7.52$ ,  $c = 12.21$  Å,  $\alpha = 98.86$ ,  $\beta = 96.91$ ,  $\gamma = 90.00^\circ$ .

The structure of calcioaravaipate is comprised of two kinds of alternating polyhedral slabs parallel to (001). Slab 1 consists of a fluorite-like double layer of edge-sharing ( $\text{CaF}_8$ ) distorted cubes and slab 2 is a composite of face- and edge-sharing ( $\text{PbF}_{12}$ ) polyhedra and outlying ( $\text{AlF}_6$ ) octahedra, the latter sharing faces and edges with the ( $\text{PbF}_{12}$ ) polyhedra, but no elements with one another. Aravaipate and calcioaravaipate share a common fluorite-type layer; however, in aravaipate the presence of  $\text{Pb}^{2+}$  rather than  $\text{Ca}^{2+}$  in this layer results in slabs of strikingly different polyhedral configuration.

### INTRODUCTION

Calcioaravaipate is one of six recently described lead-fluoride minerals from the Grand Reef mine in the Aravaipa mining district of Graham County, Arizona (Kampf et al. 1989; Kampf and Foord 1995, 1996). The mineral was named for its apparent close relationship to aravaipate. In the original description of calcioaravaipate, Kampf and Foord (1996) provided the ideal formula  $\text{PbCa}_2\text{Al}(\text{F},\text{OH})_9$ , which is comparable to that reported by Kampf et al. (1989) for aravaipate,  $\text{Pb}_3\text{Al}(\text{F},\text{OH})_9$ . Kampf (2001) determined the crystal structure of aravaipate and provided the revised ideal formula  $\text{Pb}_3\text{AlF}_9\cdot\text{H}_2\text{O}$  and the symmetry and unit cell:  $P2_1/n$ ,  $a = 25.048(4)$ ,  $b = 5.8459(8)$ ,  $c = 5.6805(7)$  Å,  $\beta = 94.013(3)^\circ$ . The original X-ray diffraction study of calcioaravaipate (Kampf and Foord 1996) yielded an *A*-centered monoclinic cell with  $a = 23.906$ ,  $b = 7.516$ ,  $c = 7.699$  Å,  $\beta = 92.25^\circ$ , which for comparison with aravaipate was also reported as the alternate primitive triclinic cell:  $a = 5.380$ ,  $b = 23.906$ ,  $c = 5.380$  Å,  $\alpha = 91.62$ ,  $\beta = 91.38$ ,  $\gamma = 88.38^\circ$  (transformation matrix  $0 \ -1/2 \ -1/2 \ | \ 0 \ 0 \ | \ 0 \ -1/2 \ 1/2$ ).

We derived a promising structural model by using diffraction data collected with reference to the above mentioned *A*-centered cell and refined it to an acceptable *R*-value (12.4%). However some oddities in the structural results were observed:

a part of the structural arrangement appeared perfectly ordered, whereas another part corresponded to the superposition of two structures with partially occupied sites. This suggested that we carefully consider the peculiarities of the diffraction pattern. In particular we observed that besides the absences due to the *A*-centering (reflections present only for  $k + l = 2n$ ) additional non-space-group absences occurred for the reflections with  $k = 2n$ , which are present only for  $2h + k + l = 4n$ . These absences suggested that order-disorder was present in the mineral. A second peculiarity has to be considered: whereas the reflections with even *k* values present diffraction symmetry  $2/m$ , this is not true for reflections with odd *k* values; the partial enhancement of symmetry is another indicator of the OD character of calcioaravaipate (Merlino 1997).

For a full understanding of the subsequent steps it seems proper to introduce first the order-disorder (OD) description of calcioaravaipate, and then to discuss the solution and refinement of the structure. For an appraisal of the OD theory and its relevance in the structural characterization of minerals, the reader is referred to Āurovič (1997, and references therein) and Merlino (1997).

### OD DESCRIPTION OF CALCIOARAVAIPAITE

For a better understanding of the OD features of calcioaravaipate, reference will be made in this section to a monoclinic cell with  $a = 7.72$ ,  $b = 7.52$ ,  $c = 23.96$  Å,  $\beta = 92.21^\circ$ , obtained from the cell of the original X-ray diffraction study

\* E-mail: akampf@nhm.org

(Kampf and Foord 1996) by interchanging the  $\mathbf{a}$  and  $\mathbf{c}$  vectors, thus passing from an  $A$ -centered to a  $C$ -centered cell. We summarize here our observations from the X-ray diffraction patterns, with special attention to the systematic absences: (1) for all reflections, it holds that those with  $h + k = 2n + 1$  are absent. This is of course due to the  $C$ -centered cell; (2) for the reflections with  $k = 2n$ , further systematic absences occur for  $h + k + 2l \neq 4n$ . The extinction rule (2) becomes a normal space-group extinction rule for the set of reflections with  $k = 2K$  (and hence  $h = 2H$ ). These reflections define a reciprocal lattice with vectors  $\mathbf{A}^*$ ,  $\mathbf{B}^*$ ,  $\mathbf{C}^*$  ( $\mathbf{A}^* = 2\mathbf{a}^*$ ,  $\mathbf{B}^* = 2\mathbf{b}^*$ ,  $\mathbf{C}^* = \mathbf{c}^*$ ;  $A = 3.86$ ,  $B = 3.76$ ,  $C = 23.96$  Å,  $\mathbf{b} = 92.21^\circ$ ). For these reflections (the so-called “family reflections” in the OD terminology) the extinction rule (2) becomes:  $HKL$  reflections are absent for  $H + K + L \neq 2n$ , which corresponds to an  $I$ -centered lattice.

For a proper development of the OD approach it is more convenient to transform the  $I$ -centered “family cell” into an  $A$ -centered cell through the transformation matrix  $[-1\ 0\ 0\ | 0\ -1\ 0\ | 1\ 0\ 1]$ , which gives  $A = 3.86$ ,  $B = 3.76$ ,  $C = 24.12$  Å,  $\mathbf{b} = 96.99^\circ$ , space group symmetry  $A12/m1$ . The centrosymmetric character has been observed by looking at the intensity distribution of the family reflections.

For a complete description of any OD family, the metrics and symmetry of the OD layer ( $I$ -operations; the structural features of the OD layers will be addressed below, in conjunction with the description of the structure of calcioaravaipaite) as well as the operations which convert a layer into the adjacent one ( $S$ -operations) must be defined. These operations are called *partial operations* (POs) in the OD terminology, since they are not necessarily valid for the whole structure.

The preliminary structural results clearly pointed to OD layers characterized by basic vectors  $\mathbf{a}$ ,  $\mathbf{b}$  (translational vectors of the layer:  $a = 2A = 7.72$  Å,  $b = 2B = 7.52$  Å) and  $\mathbf{c}_0$  (not a translation vector:  $c_0 = C/2$ , 12.06 Å;  $\mathbf{b} = 96.99^\circ$ ).

As regards the  $I$ - and  $S$ -symmetries of the OD layers it is useful to recall that they must be compatible with each other and be in keeping with the space group symmetry of the family structure. The OD theory indicates the correct procedures to be applied (Dornberger-Schiff and Fichtner 1972), which in the present case lead to the symbol:

$$C \quad 1 \quad 2/m \quad (1) \\ \{ 1 \quad 2_{1/2}/c_2 \quad (1) \}$$

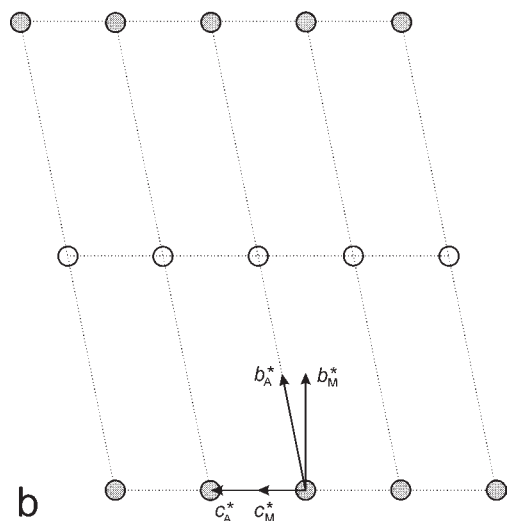
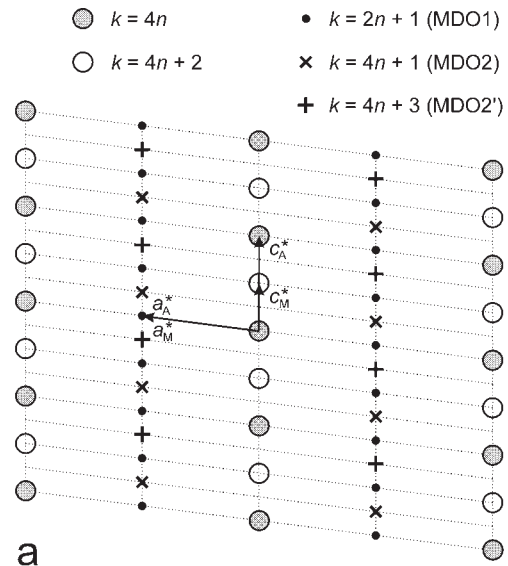
where the first and the second row indicate the  $I$ - and  $S$ -POs, respectively, and the brackets indicate the direction of missing periodicity.

According to the above symbol, layers with symmetry  $C2/m$  can be stacked along  $\mathbf{c}$  according to either of the two operators  $2_{1/2}$  and  $2_{-1/2}$  (twofold rotation coupled with a transla-

tion of  $+\mathbf{b}/4$  or  $-\mathbf{b}/4$ , respectively). Pairs of layers related by either of the two operations are geometrically equivalent.

It can be shown that, for whatever sequence of operators  $2_{1/2}$  and  $2_{-1/2}$ , the family reflections ( $h$  and  $k$  even) are identical in position, intensity, and sharpness. The other reflections ( $h$  and  $k$  odd) depend on the stacking sequence. In cases of completely disordered sequences, continuous streaks along  $\mathbf{c}^*$  are observed.

Among all possible ordered stacking sequences (each of them actually corresponding to a definite polytype of calcioaravaipaite), there are two in which not only couples, but also triples (quadruples, ...,  $n$ -ples) of adjacent layers are geometrically equivalent. These are the so-called MDO (maximum degree of order) structures. In this case we have two MDO polytypes: (1) MDO1 results from a regular alternation of  $2_{1/2}$  and  $2_{-1/2}$  as stacking operators. In this case a monoclinic structure is obtained with  $a = 7.72$ ,  $b = 7.52$ ,  $c = 24.12$  Å,  $\mathbf{b} = 96.99^\circ$ ,



**FIGURE 1.** (a) The reciprocal lattice of calcioaravaipaite, as seen along  $\mathbf{b}_M^*$ , featuring both family reflections ( $h$ -even, large black and unshaded circles) and superstructure reflections ( $h$ -odd, smaller symbols). The positions of the latter depend on the sequence of layers. In the figure the reflections corresponding to MDO1 (the monoclinic polytype), MDO2, and MDO2' (the triclinic polytype in both twinned orientations) are given. (b) The  $(0kl)$  reciprocal lattice plane. ▶

and space group  $C2/c$ ; (2) MDO results from the sequence  $2_{1/2} / 2_{1/2} / 2_{1/2} / \dots$ , i.e. a single operator constantly active. In this case a triclinic structure is obtained with  $a = 7.72 \text{ \AA}$ ,  $b = 7.52 \text{ \AA}$ ,  $c = 12.21 \text{ \AA}$ ,  $\alpha = 98.86^\circ$ ,  $\beta = 96.91^\circ$ ,  $\gamma = 90.00^\circ$ , and space group  $C\bar{1}$  (the sequence  $2_{-1/2} / 2_{-1/2} / 2_{-1/2} / \dots$  gives rise to a structure in twin relationship).

A comprehensive picture of the diffraction features of the two MDO polytypes of calcioaravaipate is presented in Figure 1.

### CELL DETERMINATION AND CRYSTAL STRUCTURE SOLUTION

Single-crystal X-ray diffractometer studies were conducted on a thin tabular crystal fragment of calcioaravaipate from the type specimen (LACMNH 39338). The fragment was carefully chosen in an attempt to avoid the ubiquitous twinning exhibited by the mineral and showed no evidence of twinning under either optical or diffraction film study. Initial diffractometer study showed the cell to be monoclinic and consistent with that reported by Kampf and Foord (1996).

Structure data collection was performed with a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD detector. A sphere of three-dimensional data were collected. Fifty duplicate frames acquired at the end of the data collection indicated that no significant decay had taken place. The cell parameters refined from the peak positions obtained from the structure data collection were:  $a_0 = 23.965(8) \text{ \AA}$ ,  $b_0 = 7.516(3) \text{ \AA}$ ,  $c_0 = 7.722(3) \text{ \AA}$ ,  $\beta_0 = 92.208(6)^\circ$ . The extraction of the reflections from the data collection frames was made using this unit cell. 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.

SHELXL97 software (Sheldrick 1997) was used for the determination and refinement of the structure. Direct methods were applied and a partially correct structural model was obtained ( $R = 12.4\%$ ). After recognition of the OD nature of calcioaravaipate, it was clear that the intensity measurements were made on a twinned triclinic crystal. To facilitate the analysis of the structure using the OD approach, a new  $C$ -centered triclinic cell was chosen. This cell is provided in Table 1 along with the corresponding primitive triclinic cell and the original  $A$ -centered monoclinic cell of Kampf and Foord (1996). Also reported in Table 1 are other descriptive data which require revision in light of the new cell.

The selection of reflections to be used for the refinement was made in the following way. First, the original indices were transformed according to:  $h = -l_0$ ,  $k = -k_0$ ,  $l = h_0/2 + k_0/4 + l_0/4$ . The reflections with  $k_0$  (and  $h_0$ ) =  $2n$ , which correspond to the "family reflections" according to the OD theory, were placed into one batch. The other reflections, namely those with  $k_0$  (and

TABLE 1. Descriptive data for calcioaravaipate

	Centered cell This study	Reduced cell This study	Original cell Kampf and Foord (1996)
Cell parameters	Triclinic, $C\bar{1}$ $a = 7.722(3) \text{ \AA}$ $b = 7.516(3) \text{ \AA}$ $c = 12.206(4) \text{ \AA}$ $\alpha = 98.86(1)^\circ$ $\beta = 96.91(1)^\circ$ $\gamma = 90.00(1)^\circ$ $V = 694.8(3) \text{ \AA}^3$ $Z = 4$	Triclinic, $P\bar{1}$ $a = 5.388(3) \text{ \AA}$ $b = 5.388(3) \text{ \AA}$ $c = 12.206(4) \text{ \AA}$ $\alpha = 91.22(1)^\circ$ $\beta = 101.17(1)^\circ$ $\gamma = 91.55(1)^\circ$ $V = 347.4(3) \text{ \AA}^3$ $Z = 2$	Monoclinic, $A2$ , $Am$ , or $A2/m$ $a = 23.906(5) \text{ \AA}$ $b = 7.516(2) \text{ \AA}$ $c = 7.699(2) \text{ \AA}$ $\beta = 92.25(2)^\circ$ $V = 1382.2(4) \text{ \AA}^3$ $Z = 8$
Morphology	Forms: {001} dominant; {110}, {110}; elongate on [110]	Forms: {001} dominant; {100}, {010}; elongate on [100]	Forms: {100} dominant; {011}, {011}; elongate on [011]
Twinning	Contact on {001}	Contact on {001}	Contact on {100}
Cleavage	{001} good	{001} good	{100} good
Optical	$Y \oplus b$ ; $Z \dot{Y} c = 10^\circ$ in the acute angle $b$	$Y \oplus [110]$ ; $Z \dot{Y} c = 10^\circ$ in the acute angle between $c$ and $[110]$	$Y = b$ ; $Z \dot{Y} c = 73^\circ$ in the obtuse angle $b$

$h_0$ ) =  $2n + 1$ , were placed in a second batch. Note that half of the latter were not considered, since they belong to the other twin individual and, after the transformation of the indices, had a fractional  $l$  index. The two batches were empirically adjusted to the same scale: all the reflections in the first batch (to which both twin individuals did contribute) were multiplied by 0.57, this factor representing the fraction of the first twin individual.

The refinement was completed in space group  $C\bar{1}$  with anisotropic displacement parameters for all atoms and converged to  $R1$  (conventional  $R$  factor) = 5.11% for 1420 reflections with  $F_o > 4S(F_o)$ . A final difference Fourier map did not indicate any likely H atom sites and the displacement parameters for the F sites did not conclusively show that any were occupied by O. For comparison, a refinement was also conducted using the reflections corresponding to the second twin individual. In this latter case, the family reflections were multiplied by 0.43, and the final reliability indices were just a little bit worse ( $R = 5.4\%$ ) than in the former case.

Table 2 gives the details of the data collection and structure refinement, Table 3 the final fractional coordinates and equivalent isotropic displacement parameters, Table 4 the anisotropic displacement parameters, Table 5<sup>1</sup> the observed and calculated structure factors, Table 6 interatomic distances, and Table 7 the bond valences. The structure of calcioaravaipate along [110] is shown in Figure 2 with atomic positions labeled.

## DISCUSSION OF THE STRUCTURE

### Anion site occupancies

From EPMA and TGA data Kampf and Foord (1996) derived the empirical formula  $Pb_{1.02}Ca_{2.05}Al_{1.04}[F_{7.97}(OH)_{0.76}O_{0.27}]$  based on 9 anions. This suggests that one of the nine F sites in the structure may be occupied by the O atom of an OH group, resulting in the ideal formula  $PbCa_2AlF_8(OH)$ . As mentioned

<sup>1</sup>For a copy of Table 5, order Document AM-03-024 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 2.** Data collection and structure refinement details for calcioaravaipate

Diffractometer	Bruker SMART Platform CCD
X-ray radiation/power	MoK $\alpha$ ( $\lambda = 0.71073$ Å)/50 kV, 45 mA
Temperature	298(2) K
Absorption coefficient	25.99 mm <sup>-1</sup>
F(000)	860
Crystal size	0.08 $\times$ 0.06 $\times$ 0.02 mm
Frame number/width/time	1271 / 0.3° in $w$ / 30 s
q range	1.70 to 28.27°
Index ranges	-10 $\leq h \leq$ 10, -7 $\leq k \leq$ 9, -16 $\leq l \leq$ 12
Reflections collected	2189
Independent reflections	1557 [ $R_{int}^* = 0.050$ ]
Reflections, $F_o > 4s(F_o)$	1421
Completeness to $q = 28.29^\circ$	90.1%
Refinement method	Full-matrix least-squares on $F^2$
Parameters refined	119
GooF <sup>†</sup>	1.102
$R$ indices [ $F_o > 4s(F_o)$ ]	$R(F) \ddagger = 5.1\%$ , $wR(F^2) \S = 12.6\%$
$R$ indices (all data)	$R(F) \ddagger = 5.6\%$ , $wR(F^2) \S = 12.8\%$
Extinction coefficient	0.0011(4)
Largest diff. peak/hole	+4.61 / -3.73 e <sup>-4</sup> Å <sup>-3</sup>

$$^* R_{int} = S [ \sum (F_o^2 - F_c^2) / \sum F_o^2 ]$$

$$^\dagger \text{GooF} = S [ \sum (F_o^2 - F_c^2)^2 / (n-p) ]^{1/2}$$

$$^\ddagger R(F) = S [ |F_o| - |F_c| ] / \sum |F_o|$$

$$^\S wR(F^2) = \{ S [ \sum (F_o^2 - F_c^2)^2 ] / \sum (F_o^2)^2 \}^{1/2} \quad w = 1 / [s^2(F_o^2) + (aP)^2 + bP]$$

where  $P$  is  $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$

**TABLE 3.** Atomic coordinates and equivalent isotropic displacement parameters for calcioaravaipate

Atom	$x$	$y$	$z$	$U_{eq}$
Pb1	0.74457(6)	0.52709(6)	0.10749(4)	0.0202(2)
Ca1	0.3925(3)	0.6497(3)	0.6144(2)	0.0120(5)
Ca2	0.8932(3)	0.6576(3)	0.6137(2)	0.0118(5)
Al1	0.2511(4)	0.5453(5)	0.1813(3)	0.0142(7)
F1	0.0673(9)	0.5655(9)	0.2648(6)	0.017(1)
F2	0.8449(9)	0.8984(10)	0.2749(6)	0.021(1)
F3	0.1484(11)	0.6981(11)	0.0948(7)	0.030(2)
F4	0.4319(9)	0.5265(11)	0.1002(6)	0.022(1)
F5	0.6474(11)	0.8513(10)	0.0930(7)	0.027(2)
F6	0.3443(9)	0.7371(9)	0.2768(6)	0.019(1)
F7	0.1273(8)	0.6210(9)	0.4991(6)	0.012(1)
F8	0.6201(9)	0.6304(9)	0.5053(6)	0.014(1)
F9	0.6854(10)	0.5714(10)	0.2905(6)	0.021(1)

**TABLE 4.** Anisotropic displacement parameters for calcioaravaipate

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Pb1	0.0207(3)	0.0218(3)	0.0185(3)	0.0027(2)	0.0041(2)	0.0001(2)
Ca1	0.0105(10)	0.0102(10)	0.0160(11)	0.0028(8)	0.0030(8)	0.0001(8)
Ca2	0.0115(10)	0.0082(10)	0.0155(11)	0.0013(8)	0.0017(8)	-0.0009(8)
Al1	0.013(2)	0.014(2)	0.018(2)	0.005(1)	0.003(1)	-0.0003(7)
F1	0.013(3)	0.020(3)	0.020(3)	0.004(3)	0.006(3)	-0.004(3)
F2	0.018(3)	0.028(4)	0.020(3)	0.005(3)	0.004(3)	0.003(3)
F3	0.016(3)	0.015(3)	0.023(4)	-0.006(3)	0.002(3)	0.000(3)
F4	0.030(4)	0.025(4)	0.035(5)	0.013(3)	-0.002(3)	0.004(3)
F5	0.013(3)	0.009(3)	0.014(3)	-0.001(2)	0.002(2)	-0.001(2)
F6	0.016(3)	0.010(3)	0.015(3)	0.000(2)	0.004(2)	0.002(2)
F7	0.019(3)	0.022(4)	0.027(4)	0.013(3)	0.004(3)	0.007(3)
F8	0.027(4)	0.015(3)	0.020(4)	0.003(3)	0.004(3)	-0.003(3)
F9	0.028(4)	0.021(4)	0.029(4)	-0.002(3)	-0.004(3)	-0.008(3)

**TABLE 6.** Selected bond distances (Å) in calcioaravaipate

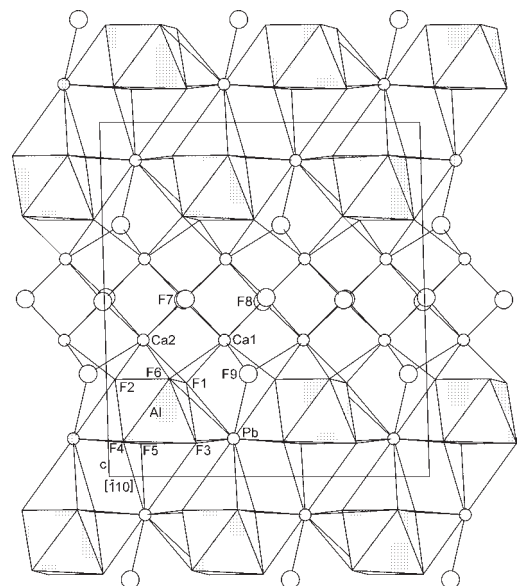
Pb1-F9	2.308(7)	Ca1-F9 <sup>e</sup>	2.287(7)
Pb1-F4	2.405(7)	Ca1-F8	2.321(7)
Pb1-F3 <sup>a</sup>	2.558(8)	Ca1-F7	2.331(7)
Pb1-F5	2.575(8)	Ca1-F2 <sup>f</sup>	2.357(7)
Pb1-F4 <sup>b</sup>	2.702(8)	Ca1-F8 <sup>e</sup>	2.365(7)
Pb1-F1 <sup>c</sup>	2.943(7)	Ca1-F7 <sup>g</sup>	2.366(7)
Pb1-F5 <sup>d</sup>	2.950(8)	Ca1-F1 <sup>g</sup>	2.402(7)
Pb1-F3 <sup>b</sup>	2.974(9)	Ca1-F6 <sup>g</sup>	2.463(7)
Pb1-F2	3.229(8)		
Pb1-F6 <sup>a</sup>	3.258(7)	<Ca1-F>	2.362
Pb1-F5 <sup>a</sup>	3.393(9)		
Pb1-F3 <sup>c</sup>	3.403(8)	Ca2-F9 <sup>f</sup>	2.307(7)
		Ca2-F8 <sup>f</sup>	2.311(7)
<Pb1-F>	2.892	Ca2-F7 <sup>e</sup>	2.316(7)
		Ca2-F8	2.342(7)
Al1-F3	1.798(8)	Ca2-F6 <sup>f</sup>	2.354(7)
Al1-F6 <sup>h</sup>	1.799(8)	Ca2-F1 <sup>e</sup>	2.399(7)
Al1-F5	1.799(8)	Ca2-F7 <sup>c</sup>	2.406(7)
Al1-F4	1.799(8)	Ca2-F2 <sup>f</sup>	2.486(8)
Al1-F2 <sup>h</sup>	1.800(7)		
Al1-F1	1.838(7)	<Ca2-F>	2.365
<Al1-F>	1.806		

Notes: Symmetry code for equivalent positions: a =  $x + 1/2, y - 1/2, z, b = -x + 1, -y + 1, -z, c = x + 1, y, z, d = -x + 3/2, -y + 3/2, -z, e = -x + 1, -y + 1, -z + 1; f = -x + 3/2, -y + 3/2, -z + 1; g = -x + 1/2, -y + 3/2, -z + 1; h = x - 1/2, y - 1/2, z.$

**TABLE 7.** Bond valence balance for calcioaravaipate

	F1	F2	F3	F4	F5	F6	F7	F8	F9	$S_{cV}$
Pb	0.085	0.039	0.078	0.363	0.229					0.472 1.837
			0.024	0.163	0.025					
Ca1	0.220	0.249				0.187	0.267	0.274		0.300 1.983
							0.243	0.243		
Ca2	0.222	0.175				0.251	0.278	0.282	0.285	1.970
Al	0.453	0.502	0.505	0.503	0.503	0.503	0.218	0.259		2.969
$S_{aV}$	0.980	0.965	0.847	1.029	0.840	0.977	1.006	1.058	1.057	

Note: Constants from Brese and O'Keeffe (1991).

**FIGURE 2.** The structure of calcioaravaipate viewed along [110]. Stippled octahedra are AlF<sub>6</sub>, small shaded circles are Pb, small unshaded circles are Ca, large unshaded circles are F.

above, the structure refinement provided no conclusive evidence for assigning O to any F site. Of the nine (F,OH) sites in calcioaravaipate, labeled generically "F" in our refinement, seven are linked to four cations in roughly tetrahedral arrangements, and consequently are unlikely to accommodate any significant amount of OH. The other two sites (F4 and F9) are linked to three cations only, making them more likely to be occupied at least in part by OH. Also favoring F4 and F9 as the repositories for OH is the fact that these are the only sites exhibiting significant bond valence oversaturation (1.029 and 1.057 v.u., respectively).

The possible hydrogen-bond receptors in the vicinity of F4 are F4, F9, F3, and F5 at 2.75, 2.83, 2.97, and 2.98 Å, respectively. Despite the greater distances, F3 and F5 seem favored as the receptors because of their significant bond undersaturation (0.846 and 0.841 v.u., respectively). The possible hydrogen-bond receptors in the vicinity of F9 are F8, F6, F2, F4, F2, F6, and F1 at 2.70, 2.79, 2.79, 2.82, 2.91, 2.91, and 3.00 Å, respectively. Since F1, F2, and F6 are bond undersaturated (0.980, 0.965, 0.977 v.u.), they are seen to be more likely receptors.

In summary, it is likely that OH groups in calcioaravaipate are split between the F4 and F9 sites and that each of these sites participates in hydrogen-bonding to two or more other F atom sites. Furthermore, it is likely that hydrogen-bonding serves to mitigate bond valence imbalance. A better chemical formula for calcioaravaipate could be  $\text{PbCa}_2\text{AlF}_7(\text{F,OH})_2$ ; however, because of the lack of certainty in assigning OH groups to specific sites and in knowing how much OH might be accommodated in any site, we recommend that the ideal formula for calcioaravaipate continue to be written  $\text{PbCa}_2\text{Al}(\text{F,OH})_9$ .

### Coordination of the cations

Aluminum and calcium in the structure of calcioaravaipate have quite regular surroundings.  $\text{Al}^{3+}$  is linked to six anions in regular octahedral coordinations (distances in the range 1.80–1.84 Å and angles in the range 85.8–93.9°). Each of the two  $\text{Ca}^{2+}$  atoms is linked to eight anions defining polyhedra that are slightly twisted cubes, i.e., intermediate between a cube and a square antiprism (distances in the range 2.29–2.49 Å).

Lead is linked to 12 anions in an irregularly shaped polyhedron that can roughly be described as a bicapped pentagonal prism (Fig. 3). Due to the presence of a stereoactive electron lone-pair, the cation is markedly off-center within the polyhedron. The five shortest cation-anion distances, ranging from 2.31 to 2.70 Å, are all on the same side of the polyhedron. The seven longer bonds on the opposite side range in length from 2.94 to 3.40 Å. Twelve-coordinated  $\text{Pb}^{2+}$  is rather uncommon, and to date has been observed in the structures of only 12 lead minerals. In most of these minerals, the 12-coordinated Pb polyhedra are fairly regu-

lar (e.g., icosahedra or augmented prisms; Vacchiano 2000). Calcioaravaipate represents the first known case of lead coordinated by 12 fluorine atoms. In all other reported cases of 12-coordinated  $\text{Pb}^{2+}$ , the coordinating anions are O atoms.

### Polyhedral description of the structure

A polyhedral representation of the calcioaravaipate structure as seen along **b** is provided in Figure 4. In terms of poly-

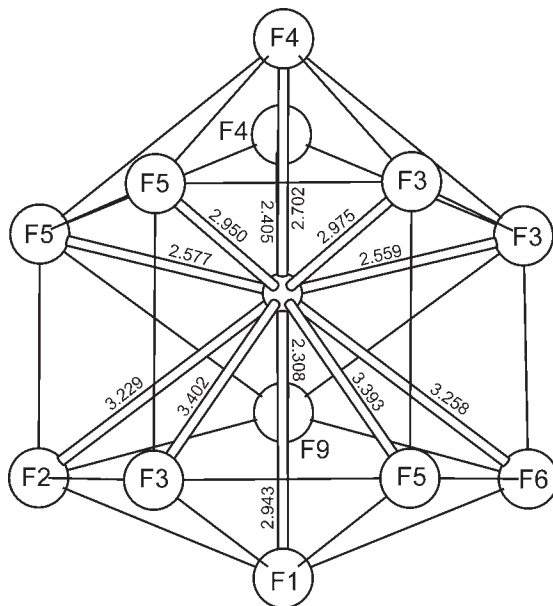


FIGURE 3. Pb coordination in aravaipate with Pb-F bond distances shown.

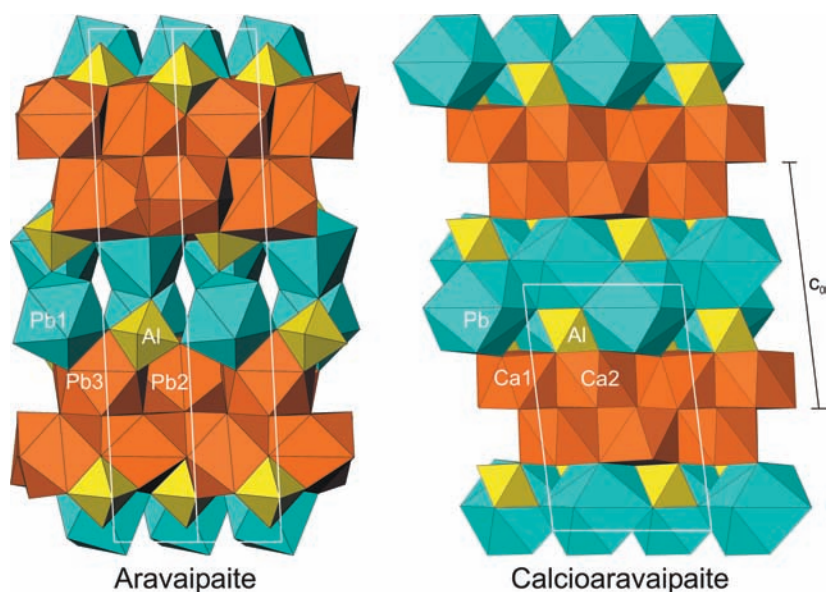


FIGURE 4. Polyhedral representations of the structures of aravaipate (along [011]) and calcioaravaipate (along **b**). The unit cells are outlined. In the case of calcioaravaipate, the  $c_0$  (non-translational) vector of the OD layer is also given.

hedral linkages and general topology, the crystal structure of calcioaravaipate can be viewed as being formed from the regular alternation of two kinds of polyhedral slabs parallel to (001): slab 1 consisting of a double layer of edge-sharing  $\text{CaF}_8$  distorted cubes and slab 2 formed by a composite of face- and edge-sharing  $\text{PbF}_{12}$  polyhedra and outlying  $\text{AlF}_6$  octahedra, the latter sharing faces and edges with the  $\text{PbF}_{12}$  polyhedra, but no elements with one another. At the boundaries between the slabs,  $\text{AlF}_6$  and  $\text{CaF}_8$  polyhedra share F-F edges (2.475 and 2.484 Å, the shortest among all F-F contacts).

The OD layer has the same translation vectors **a**, **b** as the structure; its third basic vector **c**<sub>0</sub> is shown in Figure 4 [**c**<sub>0</sub> (= **c** + **b**/4) is not a translation vector.] Therefore, the OD layer comprises both slabs described above, extending from the bisection of one double  $\text{CaF}_8$  layer to the bisection of the next.

### Comparison to the structure of aravaipate

Figure 4 shows that the structures of aravaipate and calcioaravaipate both consist of slabs, parallel to (100) in aravaipate and (001) in calcioaravaipate. In each structure, similar layers of F atoms, at  $a = 1/4$  in aravaipate and  $c = 1/2$  in calcioaravaipate, are flanked above and below by cations,  $\text{Pb}^{2+}$  in aravaipate and  $\text{Ca}^{2+}$  in calcioaravaipate, forming fluorite-type layers. As noted by Kampf (2001), these fluorite-type layers appear to serve as templates for the organization of the other structural elements. The  $\text{Pb}^{2+}$  cation, being much larger than the  $\text{Ca}^{2+}$  atom, provides a metrically larger template, leading to striking differences between the polyhedral configurations displayed by the two structures.

The “fluorite-layer” Pb atoms in aravaipate are 11-coordinated, with 7 generally long bonds to F atoms not in the fluorite-type layer (indicating that the lone-pair electrons point away from the fluorite-type layer). These  $\text{PbF}_{11}$  polyhedra present an irregular and more spread out (relative to calcioaravaipate) “surface” of F atoms for bonding to the Al atom and other Pb atoms in the structure. The linkage between the  $\text{AlF}_6$  octahedra and  $\text{PbF}_6(\text{H}_2\text{O})_2$  polyhedra is relatively open. Incidentally, the  $\text{PbF}_{11}$  polyhedra in aravaipate represent the first known case of 11-coordinated  $\text{Pb}^{2+}$  in minerals (Vacchiano 2000).

By contrast, the regular  $\text{CaF}_8$  polyhedra (slightly twisted

cubes) of the fluorite-type layer in calcioaravaipate yield nearly planar arrays of F atoms for bonding to Al and Pb atoms in the adjoining slabs. The twisting of the  $\text{CaF}_8$  cubes appears to be a further accommodation, allowing each  $\text{AlF}_6$  octahedron to include three F atoms (F1, F2, and F6) from this layer with very little deviation from ideal octahedral geometry. One ultimate result is that all of the F atoms in the structure of calcioaravaipate are in well-defined layers parallel to (001).

### ACKNOWLEDGMENTS

Critical and careful reviews by S.V. Krivovichev and A.J. Locock assisted in improving the manuscript. Structure data collection was performed in the X-Ray Crystallography Laboratory of the University of California, Los Angeles, Department of Chemistry and Biochemistry. S. Khan of that laboratory and N. Rotiroti (Department of Earth Sciences, University of Pisa) are acknowledged for technical assistance. Financial support by Istituto di Geoscienze e Georisorse (CNR, Pisa) and by MURST (Cofin 2001) are acknowledged.

### REFERENCES CITED

- Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, B47, 192–197.
- Dornberger-Schiff, K. and Fichtner, K. (1972) On the symmetry of OD-structures consisting of equivalent layers. *Kristall und Technik*, 7, 1035–1056.
- Durovič, S. (1997) Fundamentals of OD theory. In S. Merlino, Ed., *Modular aspects of minerals*, 1, 3–28. EMU Notes in Mineralogy, Eötvös University Press, Budapest, Hungary.
- Kampf, A.R. (2001) The crystal structure of aravaipate. *American Mineralogist*, 86, 927–931.
- Kampf, A.R. and Foord, E.E. (1995) Artroite,  $\text{PbAlF}_3(\text{OH})_2$ , a new mineral from the Grand Reef mine, Graham County, Arizona: Description and crystal structure. *American Mineralogist*, 80, 179–183.
- (1996) Calcioaravaipate, a new, mineral, and associated lead fluoride minerals from the Grand Reef mine, Graham County, Arizona. *Mineralogical Record*, 27, 293–300.
- Kampf, A.R., Dunn, P.J., and Foord, E.E. (1989) Grandreefite, pseudograndreefite, laurelite, and aravaipate: four new minerals from the Grand Reef mine, Graham County, Arizona. *American Mineralogist*, 74, 927–933.
- Merlino, S. (1997) OD approach in minerals: examples and applications. In S. Merlino, Ed., *Modular aspects of minerals*, 1, 29–54. EMU Notes in Mineralogy, Eötvös University Press, Budapest, Hungary.
- Sheldrick, G.M. (1997) SHELXL97. Program for the refinement of crystal structures. University of Göttingen, Germany.
- Vacchiano, D. (2000) *Cristallochimica del piombo e dei minerali contenenti piombo: studi strutturali, analisi termiche, descrizioni statistiche*. Tesi di laurea, University of Pisa, Italy.

MANUSCRIPT RECEIVED MARCH 5, 2002

MANUSCRIPT ACCEPTED NOVEMBER 8, 2002

MANUSCRIPT HANDLED BY PETER C. BURNS