

## STEREOACTIVE LONE-PAIR BEHAVIOR OF Pb IN THE CRYSTAL STRUCTURE OF BIDEAUXITE: $Pb^{2+}_2 Ag^+ Cl_3 F (OH)$

MARK A. COOPER AND FRANK C. HAWTHORNE<sup>§</sup>

*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

STEFANO MERLINO, MARCO PASERO AND NATALE PERCHIAZZI

*Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italy*

### ABSTRACT

The crystal structure of bideauxite,  $Pb^{2+}_2 Ag^+ Cl_3 F (OH)$ , cubic,  $a$  14.1273(6) Å,  $V$  2819.2(4) Å<sup>3</sup>,  $Fd\bar{3}m$ ,  $Z = 16$ ,  $D_{calc} = 6.26$  g.cm<sup>-3</sup>, has been solved by direct methods and refined to an  $R$  index of 2.8% for 324 observed ( $5\sigma$ ) reflections measured with  $MoK\alpha$  X-radiation. There is one unique  $Ag$  site surrounded by an octahedral array of Cl anions, and one  $Pb$  site surrounded by nine anions with a very asymmetrical distribution of bonds and bond-lengths characteristic of stereoactive lone-pair behavior of  $Pb^{2+}$ . Four  $(AgCl_6)$  octahedra link by sharing corners to form an  $[Ag_4Cl_{18}]$  cluster, and these clusters link by sharing corners to form a three-dimensional chequerboard arrangement, with  $[Pb_4 (OH)_2 F_2 Cl_{18}]$  clusters filling the interstices. The structure of bideauxite is not related to those of the paragenetically related minerals boléite and pseudoboléite.

*Keywords:* bideauxite, crystal-structure refinement, hydroxy-chloride.

### SOMMAIRE

Nous avons résolu la structure cristalline de la bideauxite,  $Pb^{2+}_2 Ag^+ Cl_3 F (OH)$ , cubique,  $a$  14.1273(6) Å,  $V$  2819.2(4) Å<sup>3</sup>,  $Fd\bar{3}m$ ,  $Z = 16$ ,  $D_{calc} = 6.26$  g.cm<sup>-3</sup>, par méthodes directes jusqu'à un résidu  $R$  de 2.8% en utilisant 324 réflexions observées en diffraction X ( $5\sigma$ ) mesurées avec rayonnement  $MoK\alpha$ . Il y a un site unique  $Ag$  entouré d'anions Cl définissant un agencement octaédrique, et un site  $Pb$  entouré de neuf anions ayant une distribution très asymétrique de liaisons et de longueurs de liaison, signes d'une paire isolée d'électrons stéréoactifs sur l'ion  $Pb^{2+}$ . Quatre octaèdres  $(AgCl_6)$  sont liés par partage d'un coin pour former un agencement  $[Ag_4Cl_{18}]$ , et ces agencements à leur tour sont liés par partage de coins pour former un réseau tridimensionnel en damier, avec des agencements  $[Pb_4 (OH)_2 F_2 Cl_{18}]$  dans les interstices. La structure de la bideauxite n'a pas de rapport avec celles des minéraux boléite et pseudoboléite de la même paragenèse.

(Traduit par la Rédaction)

*Mots-clés:* bideauxite, affinement de la structure cristalline, hydroxy-chlorure.

### INTRODUCTION

Bideauxite is a lead-silver fluor-hydroxy-chloride mineral,  $Pb_2 Ag Cl_3 (F,OH)_2$ , described by Williams (1970) from the Mammoth - St. Anthony mine, Tiger, Pinal County, Arizona. It is transparent where fresh and becomes lavender on exposure to strong light. It occurs as crystals up to 7 mm in maximum dimension. Bideauxite overgrows crystals of boléite and, in turn, is overgrown by matlockite and leadhillite, with associated sugary anglesite and surficial cerussite (Bideaux 1980). Among the secondary minerals of lead, halides are rare; a typical occurrence is in ancient metallurgical

slags, such as Laurion, Greece. Recently, a similar paragenesis with rare lead oxychlorides was discovered in the Etruscan metallurgical slags of Baratti beach, southern Tuscany, Italy (Franzini & Perchiazzi 1992).

Both Canadian (MC and FCH) and Italian (SM, MP and NP) groups have long-term interests in the crystal chemistry of lead-(copper) oxide-hydroxy-chloride minerals (Hawthorne 1985, Hawthorne & Groat 1986, Cooper & Hawthorne 1995, Merlino *et al.* 1993, 1994, 1995, 1996, Pasero & Perchiazzi 1996, Kutzke *et al.* 1999). In view of our interest in these minerals, both groups have solved the structure of bideauxite; we present the joint results here.

<sup>§</sup> E-mail address: frank\_hawthorne@umanitoba.ca

## EXPERIMENTAL

The samples of bideauxite used for this work are from the type locality. For the Canadian study, a pale-lavender crystal of high optical clarity was ground into a thin plate (of arbitrary orientation) in order to minimize the number of reflections affected by complete attenuation of the beam due to absorption by the crystal; the indices of the plate were determined after collection of the X-ray intensity data. The crystal was mounted on a Siemens P4 automated four-circle diffractometer, and all 48 Laue-equivalents of reflection 2 8 12 at  $2\theta \approx 43^\circ$  were centered to determine the cell dimension (Table 1) and orientation matrix using graphite-monochromatized  $\text{MoK}\alpha$  X-radiation. Intensity data were collected using  $\theta$ - $2\theta$  scans, with a variable scan-rate inversely proportional to the peak intensity, and with minimum and maximum scan-rates of 2.0 and  $29.3^\circ/2\theta/\text{min.}$ , respectively. A total of 11,795 reflections was measured over the range  $4 < 2\theta < 70^\circ$ , with index ranges  $\bar{2}\bar{2} < h < 22$ ,  $\bar{2}\bar{2} < k < 22$ ,  $\bar{2}\bar{2} < l < 22$ . Two standard reflections were monitored every 58 reflections; there were no significant changes in their intensities during data collection. Subsequent to the collection of the nor-

mal intensity data, psi-scan data were collected every  $4^\circ$  of psi on 15 reflections distributed over the complete  $2\theta$  range. The faces of the plate were indexed, and a psi-scan absorption correction was done, reducing  $R(\text{azimuthal})$  from 21.7 to 3.0%. All reflections with a plate-glancing angle of  $\leq 20^\circ$  were rejected (as having excessively large path-lengths through the crystal), leaving 6851 reflections. These data were then corrected for Lorentz, polarization and background effects, and reduced to structure factors; of the 337 unique reflections [with  $R(\text{merge}) = 2.6\%$ ], 324 were classed as observed ( $|F_o| > 5\sigma F$ ).

For the Italian study, intensity data were collected with a Siemens four-circle diffractometer. The unit-cell parameter (Table 1) was determined by least-squares refinement of  $2\theta$  values of a set of 20 reflections. Experimental conditions were: room temperature, 50 kV, 40 mA, graphite monochromatized  $\text{MoK}\alpha$  X-radiation. A total of 1158 intensities was measured in the range  $4^\circ \leq 2\theta \leq 60^\circ$ ,  $0 \leq h, k, l \leq 19$ ; scan mode  $\omega$ - $2\theta$ , scan width (in  $\theta$ ) 0.8%, scan speed  $2^\circ/\text{min.}$  An absorption correction was done according to the method of North *et al.* (1968), on the basis of  $\Psi$ -scan measurements on 15 reflections. The measured intensities were reduced by Lorentz and polarization effects to a set of 233 unique reflections.

TABLE 1. MISCELLANEOUS INFORMATION FOR BIDEAUXITE

	CH	MPP
a (Å)	14.1273(6)	14.1376(9)
Sp. Gr.	$Fd\bar{3}m$	$Fd\bar{3}m$
crystal size (mm)	0.05 x 0.34 x 0.38	0.12 x 0.13 x 0.10
Radiation	MoK $\alpha$ /Graphite	MoK $\alpha$ /Graphite
No. of intensities	11795	1158
No. of intensities remaining after $20^\circ$ glancing angle	6851	—
No. of F	337	233
No. of $ F_o $	324 ( $> 5\sigma F_o $ )	189 ( $> 4\sigma F_o $ )
$R(\text{azimuthal})$ %	21.7 - 3.0	—
$R(\text{merge})$ %	2.6	9.7
$R(\text{obs})$ %	2.8	3.8
$wR(\text{obs})$ %	2.8	—
$wR_2$	5.3	8.9
$\mu\text{m}$ ( $\text{mm}^{-1}$ )	51.5	51.3
$D_c$ ( $\text{g.cm}^{-3}$ )	6.26	6.25
Cell content: 16 $[\text{Pb}^{2+}_2 \text{Ag}^- \text{Cl}_3 \text{F}(\text{OH})]$		

## STRUCTURE SOLUTION AND REFINEMENT

Ionized scattering curves for all species, with corrections for anomalous dispersion, were taken from the International Tables of Crystallography, Vol. 4 (1992) except for  $\text{O}^{2-}$ , which was taken from Azavant & Lichanot (1993).  $R$  indices are of conventional form and are expressed as percentages. The Siemens SHELXLT PLUS PC version system of programs (Canada) and SHELXS86 (Sheldrick 1986) and SHELXL93 (Sheldrick 1993) (Italy) were used throughout this study. The structure was solved by direct methods in space group  $Fd\bar{3}m$ , followed by subsequent cycles of least-squares refinement and difference-Fourier synthesis. Full-matrix least-squares refinement of all variables for an anisotropic displacement model converged to  $R$  and  $wR$  indices of 2.8(3.8) and 2.8(8.9)%, respectively.

TABLE 2. ATOMIC POSITIONS AND DISPLACEMENT FACTORS ( $\times 10^4$ ) FOR BIDEAUXITE\*

Site	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{\text{eq}}$
Pb	0.22185(1)	x	x	206(1)	$U_{11}$	$U_{11}$	-38(1)	$U_{23}$	$U_{23}$	206(1)
	0.22192(4)	x	x	303(4)	$U_{11}$	$U_{11}$	-40(2)	$U_{23}$	$U_{23}$	303(4)
Ag	1/2	1/2	1/2	340(3)	$U_{11}$	$U_{11}$	101(3)	$U_{23}$	$U_{23}$	340(2)
	0	0	0	446(8)	$U_{11}$	$U_{11}$	110(9)	$U_{23}$	$U_{23}$	446(8)
Cl	0.8380(2)	1/8	1/8	360(9)	219(5)	$U_{22}$	-14(6)	0	0	266(4)
	0.8375(4)	1/8	1/8	444(27)	317(14)	$U_{22}$	-2(19)	0	0	360(10)
O(1)	0.0548(2)	x	x	158(14)	$U_{11}$	$U_{11}$	-12(9)	$U_{23}$	$U_{23}$	158(8)
	0.0539(5)	x	x	243(24)	$U_{11}$	$U_{11}$	-5(28)	$U_{23}$	$U_{23}$	243(24)

\* CH values upper line, MPP values lower line

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN BIDEAUXITE

	CH	MPP
<i>Pb</i> -O(1)a	x3 2.420(2)	2.431(5)
<i>Pb</i> -Cl/b	x3 3.174(1)	3.174(2)
<i>Pb</i> -Cl/c	x3 3.311(2)	3.319(4)
< <i>Pb</i> -φ>	2.968	2.974
<i>Ag</i> -Cl/d	x6 2.789(1)	2.788(2)
O(1)-O(1)e	2.679(11)	2.639(26)

a:  $\bar{x}+1/4, \bar{y}+1/4, z$ ; b:  $\bar{x}+1, \bar{y}+1/2, \bar{z}+1/2$ ;  
 c:  $\bar{x}+5/4, \bar{y}+1/4, z$ ; d:  $\bar{x}+5/4, \bar{y}+3/4,$   
 $\bar{z}+1/2$ ; e:  $\bar{x}, \bar{y}, \bar{z}$

TABLE 4. BOND-VALENCE\* ( $\nu_{ij}$ ) TABLE FOR BIDEAUXITE

	<i>Pb</i>	<i>Ag</i>	$\Sigma$
O(1)**	$x_1^1$ 0.39 $x_1^1$ -		1.2
Cl	$x_1^1$ 0.18 $x_2^2$ -	$x_6^1$ 0.15 $x_2^2$ -	0.9
	$x_3^1$ 0.12 $x_2^2$ -		
	2.07	0.9	

\* curves from Brese & O'Keeffe (1991)

\*\* O(1) = O<sub>0.5</sub> + F<sub>0.5</sub>

Positional and anisotropic-displacement parameters are given in Table 2, selected interatomic distances, in Table 3, and a bond-valence analysis, in Table 4. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

#### DESCRIPTION OF THE STRUCTURE

##### Cation coordination

There is one unique *Pb* site surrounded by nine anions between 2.42 and 3.31 Å and arranged as a distorted triaugmented trigonal prism. There are three O(1) anions (= OH,F) at 2.42 Å, all lying to one side of the *Pb* site, and six Cl anions at 3.17 (×3) and 3.31 (×3) Å lying to the other side of the *Pb* site (Fig. 1a) This type of asymmetrical coordination is typical for lone-pair-stereoactive Pb<sup>2+</sup>.

Typical coordinations for lead in halide compounds are [8] and [9]. Lead is [8]-coordinated as biccapped

trigonal prisms (or distorted square antiprisms) in laurionite (Cannillo *et al.* 1969), boléite (Rouse 1973), grandreefite (Kampf 1991), paralaurionite (Merlino *et al.* 1993), fiedlerite-1A and fiedlerite-2M (Merlino *et al.* 1994), and penfieldite (Merlino *et al.* 1995). Nine-coordinated lead occurs as monocapped square antiprisms in matlockite (Pasero & Perchiazzi 1996) and phosgenite (Giuseppetti & Tadini 1974), and as tricapped trigonal prisms in cotunnite (Nozik *et al.* 1976), laurelite (Merlino *et al.* 1996), barstowite (Kutzke *et al.* 1999) and in the compound Pb<sub>3</sub>FeCl(OH)<sub>4</sub>(H<sub>2</sub>O) (Pasero *et al.* 1997).

There is one unique *Ag* site surrounded by six Cl anions in an octahedral arrangement with a *Ag*-Cl distance of 2.79 Å, typical of Ag<sup>+</sup>. Overall electroneutrality requires that the O(1) site be occupied by monovalent anions, and this is also in accord with the bond-valence sum at the O(1) site (Table 4).

##### Structure topology

Four (Pbφ<sub>9</sub>) polyhedra (φ: unspecified ligand) link to form a compact cluster (Fig. 1b). The core of the cluster is a tetrahedral array of O(1) anions, and the O(1) and Pb atoms thus occur at the vertices of a distorted

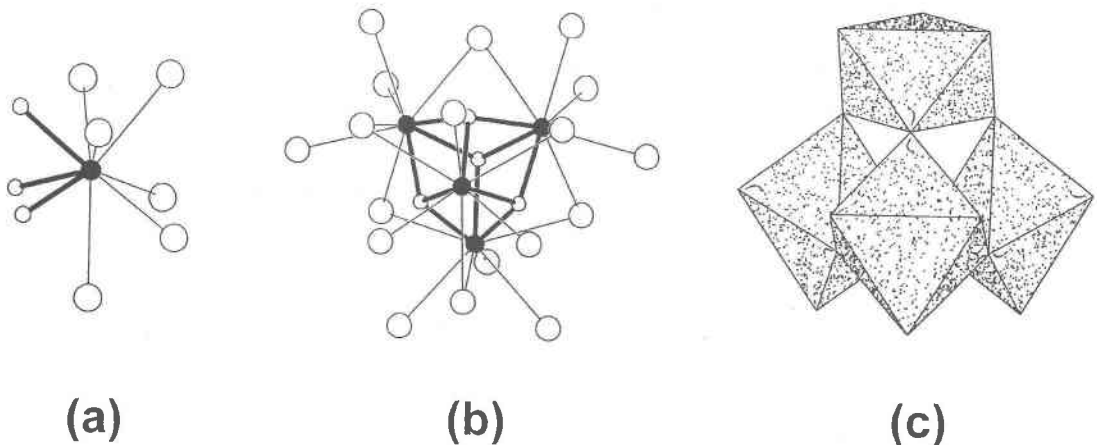


FIG. 1. Elements of the structure of bideauxite: (a) The coordination of the *Pb* site; black circle: Pb<sup>2+</sup>; large unshaded circle: Cl; small unshaded circle: (OH,F); (b) the [Pb<sub>4</sub>(OH,F)<sub>4</sub>Cl<sub>18</sub>] cluster; legend as in Figure 1a; (c) the [Ag<sub>4</sub>Cl<sub>18</sub>] cluster shown as polyhedra; each (AgCl<sub>6</sub>) octahedron is random-dot-shaded.

cube. Each triangular face of anions forms part of one ( $\text{Pb}\phi_9$ ) polyhedron, and the bond-valence requirements of the O(1) anions [ $=(\text{OH})_{0.5} + \text{F}_{0.5}$ ] are approximately satisfied by the three  $\text{Pb}^{2+}$  atoms to which they are bonded (Table 4, Fig. 1b), and the external anions of the cluster are Cl. Four ( $\text{AgCl}_6$ ) octahedra link to form a compact cluster (Fig. 1c) with an octahedral hole at the center. Each Cl anion bounding this octahedral hole links to two Ag atoms.

The structure may be visualized as an array of [ $\text{Ag}_4\text{Cl}_{18}$ ] clusters that join by sharing octahedron corners to form a continuous [ $\text{AgCl}_3$ ] framework analogous to the octahedron framework in pyrochlore (Fig. 2). [ $\text{Pb}_4(\text{OH},\text{F})_4\text{Cl}_{18}$ ] clusters fill the interstices; note that the strongly bonded [ $\text{Pb}_4(\text{OH},\text{F})_4$ ] cluster at the center of each large hole promotes the off-centered geometry required by the lone-pair-stereoactive  $\text{Pb}^{2+}$  cations. If viewed along [100], the two types of clusters are arranged in a three-dimensional chequerboard pattern; a layer through this arrangement is shown in Figure 3.

#### Hydrogen bonding

The O(1) site is occupied by 0.5 F and 0.5 (OH) (Williams 1970), and it can be argued that this occupancy is actually structurally controlled. The H was not detected in this work, but it must lie on the 3-fold axis on the outside of the [ $\text{Pb}_4(\text{OH},\text{F})_4$ ] cluster, approximately 1 Å from the O(1) site. Adjacent [ $\text{Pb}_4(\text{OH},\text{F})_4$ ] clusters have their O(1) anions both lying on the 3-fold

axis with a separation of 2.68 Å, and the H atom lies between the two anions. We suggest that such opposing O(1) anions form the following H-bonded system: O–H...F. This is a linear donor–H...acceptor arrangement, and the donor–acceptor distance is 2.68 Å, a fairly short approach that is normal for linear H-bond systems. Thus, in the [ $\text{Pb}_4(\text{OH},\text{F})_4$ ] cluster, there is a small bond-valence deficiency for F at O(1) and a small bond-valence excess for OH at O(1), in accord with the relative sizes of OH and F [ $r(\text{OH}) > r(\text{F})$ ]. The excess bond-valence at OH is transferred to the adjacent F *via* the H bond, requiring that O(1) be occupied by 0.5 OH + 0.5 F, as is observed. Thus the formula should be written as  $\text{Pb}^{2+}_2 \text{Ag}^+ \text{Cl}_3 \text{F}(\text{OH})$ .

The space group  $Fd\bar{3}m$  corresponds to complete long-range disorder of OH and F, although there is local ordering of H bonds as O–H...F. A number of long-range-order schemes also are possible, leading to a lowering of space-group symmetry to  $Fd\bar{3}$  or  $F\bar{4}3m$  assuming simple schemes of order, or even lower symmetries with more complicated ordered arrangements. However, the existence of such ordered arrangements can only be examined by neutron diffraction.

#### PARAGENESIS

There is no structural relation between bideauxite and the other Pb minerals with which it occurs (Table 5), although boléite, pseudoboléite and cumengéite do show many structural similarities (Giuseppetti *et al.* 1992).

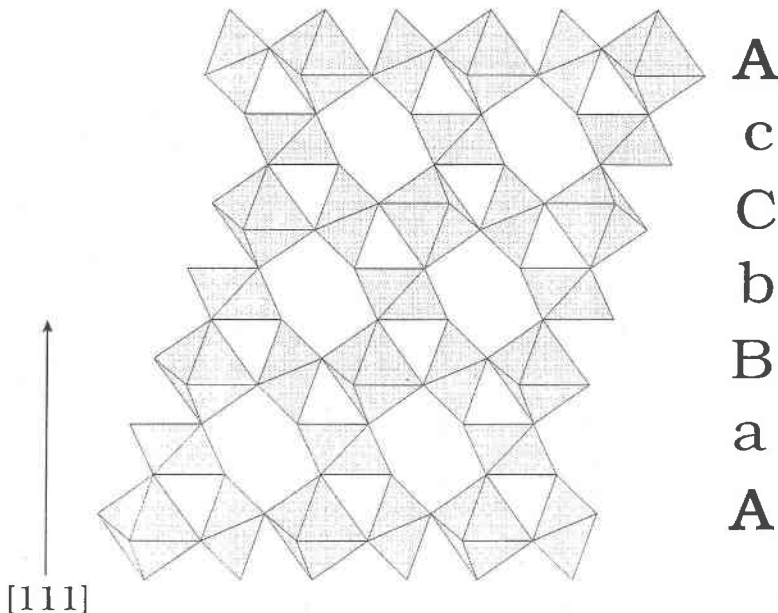


FIG. 2. The [ $\text{AgCl}_3$ ] pyrochlore-like framework in bideauxite; legend as in Figure 1.

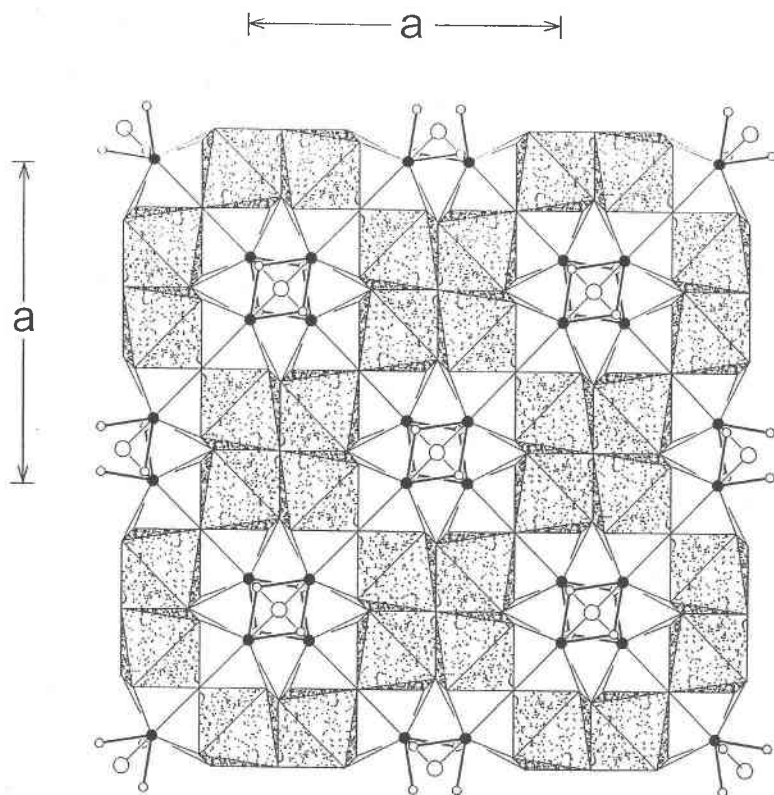


FIG. 3. The crystal structure of bideauxite projected down [001]; legend as in Figure 1.

However, there are strong paragenetic relations among these minerals.

At the Mammoth mine, Tiger, Arizona (Williams 1970, Bideaux 1980), early diaboléite is replaced by boléite and other oxysalt minerals. There is some indication of overgrowth of pseudoboléite on boléite, but this has not been definitely confirmed (Bideaux 1980). Bideauxite overgrows boléite, with no indication of any epitactic relation or preferred orientation. At Boléo, Baja California, Mexico (Bariand *et al.* 1998, Swoboda 1998), boléite is overgrown epitactically by pseudo-

boléite, and pseudoboléite never occurs as isolated crystals. Cumengéite also epitactically overgrows pseudoboléite that epitactically overgrows boléite; cumengéite pyramids are rarely found in direct contact with boléite (Bariand *et al.* 1998).

These relations are synthesized in Figure 4. In the non-oriented replacement sequence diaboléite  $\rightarrow$  boléite  $\rightarrow$  bideauxite, there is a progressive increase of Ag and Cl, and a depletion of Cu. In the epitactic sequence boléite  $\rightarrow$  ( $\pm$ )pseudoboléite  $\rightarrow$  cumengéite, there is depletion in Ag, a slight increase in Cu, and more-or-less constant Cl. Thus there seems to be two distinct paragenetic sequences with differing geochemical trends.

TABLE 5. THE BOLÉITE-GROUP MINERALS

Mineral	Space Group	Cell parameters (Å)	Formula	Ref.
Boléite*	$Pm\bar{3}m$	$a = 15.290$	$Ag_9 Pb_{26} Cu_{24} Cl_{62} (OH)_{48}$	[1]
Bideauxite	$Fd\bar{3}m$	$a = 14.1273$	$Ag Pb_2 Cl_3 (F,OH)_2$	[2]
Cumengéite	$I4/mmm$	$a = 15.065$ $c = 24.436$	$Pb_{21} Cu_{20} Cl_3 (OH)_{10}$	[3]
Diaboléite	$P4mm$	$a = 5.980$ $c = 5.500$	$Pb_2 Cu Cl_3 (OH)_4$	[4]
Pseudoboléite	$I4/mmm$	$a = 15.240$ $c = 30.740$	$Pb_{51} Cu_{24} Cl_{62} (OH)_{48}$	[5]

References: [1] Rouse (1973), [2] this work, [3] Hawthorne & Groat (1986), [4] Cooper & Hawthorne (1995), [5] Giuseppetti *et al.* (1992)

\* The chemical formula of boléite has a net negative charge and therefore cannot be correct; we are currently investigating this issue.

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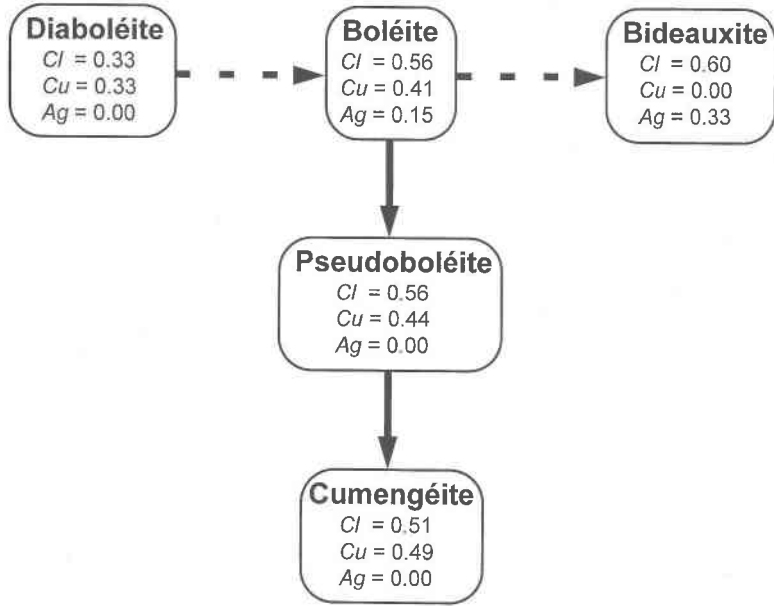


FIG. 4. Crystallization and alteration sequence of selected Pb–Ag–Cu hydroxy-chloride minerals; the Cu, Ag and Cl contents are indicated as follows:  $Cl$  = Cl/(total anions);  $Ag$  = Ag/(total cations);  $Cu$  = Cu/(total cations).

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