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Lead-antimony sulfosalts from Tuscany (Italy). III. Pillaite, $Pb_9Sb_{10}S_{23}ClO_{0.5}$, a new Pb-Sb oxy-chloro-sulfosalt, from Buca della Vena mine

PAOLO ORLANDI [1*], YVES MOËLO [2], ALAIN MEERSCHAUT [2]
and PIERRE PALVADEAU [2]

[1] Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italy
[2] Laboratoire de Chimie des Solides, Institut des Matériaux J. Rouxel, UMR CNRS 6502,
2 rue de la Houssinière, 44322 Nantes Cedex 3, France

Abstract: The new mineral pillaite, $Pb_9Sb_{10}S_{23}ClO_{0.5}$, an oxy-chloro-sulfosalt, has been found at Buca della Vena mine in the Apuan Alps, northern Tuscany, Italy. It crystallized in small fractures of dolomitic lenses in massive Fe-Ba ore, together with many Pb-Sb sulfosalts, among which the oxy-sulfosalt scainiite. Pillaite occurs as black acicular crystals with metallic lustre, elongated // [010], up to 1 cm long and less than 0.1 mm thick. The mineral is brittle, opaque; $VHN_{50} = 175$ kg/mm^2, $d_{calc} = 5.77$ g/cm^3. In reflected light it shows a weak anisotropy and bireflectance, and rare red internal reflections. Electron-microprobe analysis (wt. %): Pb 49.07, Sb 30.36, Cu 0.16, S18.73, Cl 0.98, O (crystal structure) 0.21, Sum 99.51. Empirical formula: $Pb_{9.30}Sb_{9.80}Cu_{0.10}S_{22.94}Cl_{1.06}O_{0.5}$; ideally: $Pb_9Sb_{10}S_{23}ClO_{0.5}$. Pillaite is monoclinic, space group *C2/m*, $a = 49.65(3)$ Å; $b = 4.150(4)$ Å; $c = 21.91(1)$ Å; $\beta = 99.76(5)°$; $V = 4449(10)$ Å^3; $Z = 4$. The strongest lines of the X-ray powder diffraction pattern are (d (Å), I_{obs}, hkl): 4.14 (27) (205), 3.88 (20) ($\underline{12}01$), 3.621 (26) ($\bar{4}06$, $\underline{12}02$), 3.548 (40) ($\bar{1}204$, $\bar{1}005$), 3.480 (100) (206), 3.249 (24) ($\bar{1}205$), 2.956 (47) ($\bar{5}15$, $\underline{16}01$, $\bar{1}206$, 514), 2.780 (22) ($\underline{13}10$, 515). Pillaite belongs to the zinkenite group. Like for dadsonite and other chloro-sulfides, the formation of this mineral is related to a high chlorinity of the hydrothermal solution, but also to the oxygen fugacity, as for scainiite.

Key-words: pillaite, new mineral, sulfosalt, lead, antimony, oxy-chloro-sulfide, Tuscany, Italy.

Introduction

The Buca della Vena Fe-Ba deposit shows a complex mineralogy, with many rare minerals (Orlandi & Checchi, 1986). Recently two new Pb-Sb sulfosalts were discovered; the first one, scainiite, $Pb_{14}Sb_{30}S_{54}O_5$, has been described by Orlandi *et al.* (1999). This study presents the second one, pillaite, $Pb_9Sb_{10}S_{23}ClO_{0.5}$. This new mineral species and its name have been approved by the IMA-CNMMN (vote n° 97-042). The name of this mineral honours the late Professor Leopoldo Pilla (Venafro, 1805 - Curtatone, 1848), one of the most important Italian vulcanologist and mineralogist in his time. In 1842 he hold the first chair of mineralogy and geology in the Pisa University; he constituted an important collection of minerals and rocks from Monte Somma, Vesuvius, now preserved in the Natural History Museum of Pisa University. The type material of pillaite has been deposited at Museo di Storia Naturale e del Territorio, Università di Pisa, Via Roma 103, I-56011 Calci (PI), Italy (catalogue numbers: 15524-15525).

1. Occurrence and paragenesis

Pillaite was found at the Buca della Vena mine, a small Fe-Ba deposit in the Apuan Alps (northern Tuscany, Italy), from which another new Pb-Sb sulfosalt, scainiite, has been described (Orlandi *et*

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*e-mail: orlandi@dst.unipi.it

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al., 1999); for all the informations on the geology of the mine we refer to this article. Pillaite occurs in thin late extensional calcite veins, which cut either the Ba-Fe ore body, or the phyllites and dolomitic limestones in which the ore body is hosted.

In these veins pillaite is associated with many other acicular lead sulfosalts: scainiite, zinkenite, boulangerite, robinsonite, tintinaite, sorbyite and additional still uncompletely characterized compounds. The morphological features of all these acicular sulfosalts are very similar, and a distinction between the different minerals is not possible macroscopically, but only by testing every crystal by X-ray diffraction methods. Other minerals associated with pillaite are sphalerite, cinnabar, galena, andorite, bournonite, tetrahedrite, chalcostibite, gersdorffite, barite, cerussite and stibiconite.

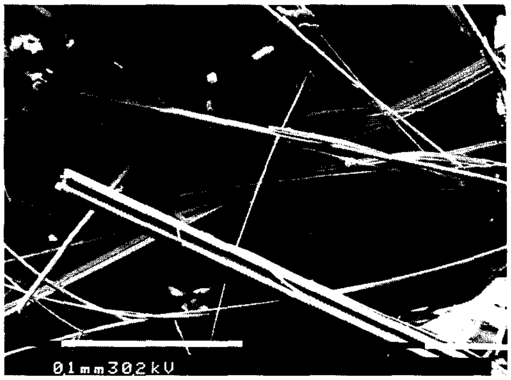

Fig. 1. Scanning electron microscope image of pillaite fibers.

2. Appearance and physical properties

Pillaite occurs as small acicular crystals (Fig. 1), of black color and metallic lustre, elongated // [010], up to 1 cm long and 0.1 mm thick. These fibers are brittle, with irregular fracture, and no distinct cleavage; streak black to dark brown. Density could not be measured, due to the small size of individual crystals; $d_{calc.} = 5.77$ g/cm^3.

In reflected light, pillaite shows weak anisotropy and bireflectance, and rare red internal reflections; pleochroism was not observed. Specular reflectance in air and oil has been measured from 400 to 800 nm on a unique sub-isotropic section (40 x 15 μm) perpendicular to the elongation (Table 1). Fig. 2 represents the two reflectance curves of pillaite, in comparison to those of dadsonite (Cervelle *et al.*, 1979 and 1993). Reflectance curves are very similar, but with reflectance values of pillaite about 4 % below those of the minimum reflectance curves of dadsonite. This general decrease of the reflectance values may be due principally to the higher chlorine content of pillaite, together with the presence of a small amount of oxygen: these two anions, more electro-negative than sulfur, will slightly increase the optical band gap of pillaite relatively to that of dadsonite, with a general shift of the optical spectrum toward higher energies, that is toward shorter wavelengths.

The calculated refractive index *n* is around 4, but with aberrant negative values of k^2. Due to the minute size of the selected fiber section, the selected area for measurement in oil was relatively large (and larger than in air), and some relief effect at the contact with the resin may have induced a small shift of reflectance data in oil, thus produc-

Table 1. Reflectance (%) of pillaite (sub-isotropic basal section) from 400 to 800 nm in air and oil.

λ (nm)	R_{air}	R_{oil}	λ (nm)	R_{air}	R_{oil}	λ (nm)	R_{air}	R_{oil}	λ (nm)	R_{air}	R_{oil}
400	37.0	21.25	500	35.4	19.25	600	32.7	17.65	700	30.5	15.40
410	35.3	20.30	510	35.1	19.45	610	32.9	17.50	710	31.0	15.00
420	37.7	19.80	520	34.7	19.25	620	32.8	16.85	720	29.6	15.05
430	36.3	20.00	530	34.4	18.95	630	32.8	16.90	730	29.3	14.60
440	36.0	20.50	540	34.9	18.60	640	32.4	16.75	740	29.4	14.40
450	36.7	20.40	550	34.2	18.75	650	32.7	16.45	750	27.4	14.50
460	35.9	20.50	560	34.2	18.35	660	31.9	16.10	760	28.0	14.35
470	35.7	20.10	570	34.5	18.15	670	31.9	16.15	770	27.4	13.75
480	35.4	20.00	580	34.4	18.15	680	31.5	16.05	780	27.0	14.05
490	35.3	19.75	590	34.0	17.60	690	31.0	15.55	790	26.0	13.60
									800	22.8	13.35
470	*35.7*	*20.10*	***546***	*34.5*	*18.70*	***589***	*34.0*	*17.60*	***650***	*32.7*	*16.45*

Polishing method: 600/1200 mesh carborundum (paper); 6, 3, 1 and ¼ diamond on cloth; final buffing with Cr_2O_3 on cloth. LEICA DMR microscope with objectives FLUOTAR 20x/0.50 POL (air) and OEL 50x/0.85 (oil). Microscope photometer: Leica MPV-SP, monochromator: Δλ = 2 nm. Standard: SiC (NPL n°50).

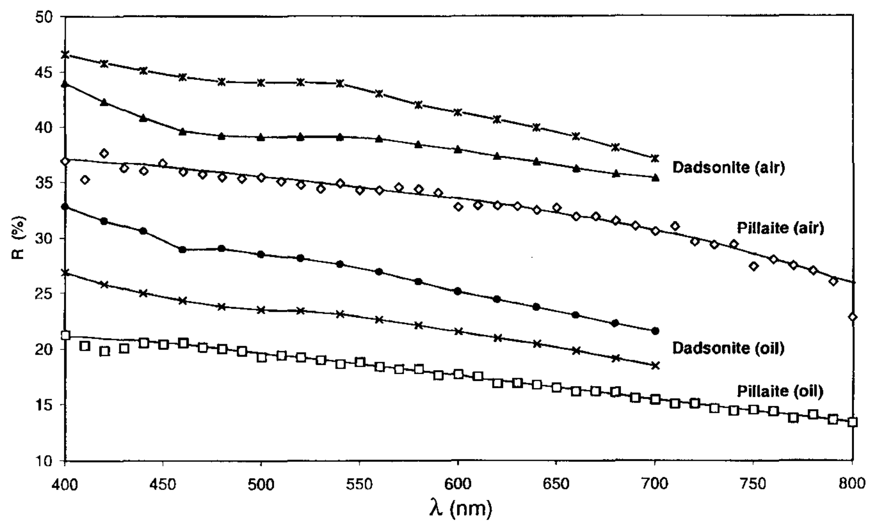

Fig. 2. Reflectance curves of pillaite in air and oil.

ing wrong values of k^2 (more sensitive than the refractive index n to measurement error – Embrey & Criddle, 1978).

3. Chemistry

Two samples were analysed with distinct electron microprobes (Table 2). For analysis No. 2 (mean of 13 spot analyses – same crystal as for reflectance measurements and crystal structure study), dadsonite (ideally: 0.36 wt.% Cl – Moëlo, 1979) was used together with pyromorphite as a secondary standard for Cl; it clearly revealed a chlorine content of 0.98 wt.% in pillaite. The presence of oxygen was not checked, and this anion was detected laterly through the reexamination of the crystal structure (Meerschaut *et al.*, accepted). There is half an oxygen atom p.f.u., that is around 0.2 wt.% oxygen, corresponding to the detection limit of EPMA (Orlandi *et al.*, 1999). Taking into account the crystal structure, the empirical formula of pillaite is $Pb_{9.30}Sb_{9.80}Cu_{0.10}S_{22.94}Cl_{1.06}O_{0.5}$ (Table 2, No. 2). After subtraction of minor Cu (Cu + Pb → Sb), and of the excess of Cl over 1 (Pb + Cl → Sb + S), the reduced formula is $Pb_{9.14}Sb_{9.96}S_{23}ClO_{0.5}$, and the ideal structural formula $Pb_9Sb_{10}S_{23}ClO_{0.5}$ (which contains 0.93 wt.% chlorine and 0.21 wt.% oxygen).

Pillaite is the first known oxy-chloro-sulfosalt, and the fourth well-defined natural chloro-sulfosalt, after dadsonite (Moëlo, 1979), ardaite (Breskovska *et al.*, 1982) and playfairite (Jambor *et al.*, 1982; Moëlo, 1983). There exist other natural or synthetic Pb-Sb chloro-sulfosalts with a low chlorine content (Moëlo *et al.*, 1989): An uncompletely studied chlorine-bearing sulfosalt, "mineral C", from the Pb-Sb sulfosalt deposit of Les Cougnasses (Hautes-Alpes, France), is very close to pillaite. It contains 0.90 wt.% Cl, and its structural formula, calculated on the basis of S + Cl =

Table 2. Electron microprobe analysis of pillaite, compared to those of "mineral C" (Moëlo *et al.*, 1989) and synthetic Phase V (Bortnikov *et al.*, 1979).

	Pillaite		Min. C	Phase V
wt.%	**No. 1**	**No. 2**		
Pb	47.30	49.07	46.56	48.19
Sb	31.80	30.36	30.46	28.83
As			0.88	
Cu	0.18	0.16	0.09	
Ag			0.85	
S	20.54	18.73	19.83	17.72
Cl	n.a.	0.98	0.90	1.26
O	n.a.	0.21*		
Total	99.82	99.51	99.57	95.40
Atomic proportions (S + Cl = 24 at.)				
Pb	8.55	9.30	8.37	9.49
Sb	9.79	9.80	9.28	9.66
As			0.43	
Cu	0.10	0.10	0.05	
Ag			0.32	
S	24	22.94	23.04	22.55
Cl		1.06	0.96	1.45
O		0.5		

No. 1: ARL-SEMQ microprobe (Modena University); No. 2: Cameca SX 50 microprobe (BRGM-CNRS-University, Orléans). *: according to crystal structure. Analytical conditions: see Orlandi *et al.* (1999). n.a.: not analysed.

24 at., gives $Pb_{9.01}(Sb, As)_{9.44}S_{23.04}Cl_{0.96}$ (after subtraction of minor metals, Cu (see above), and Ag according to Ag + Sb → 2 Pb). Nevertheless, the X-ray powder pattern for "Mineral C" is significantly different from that of pillaite. Due to the very fine and heterogeneous nature of the product from Les Cougnasses, it is not possible to decide whether "mineral C" is effectively pillaite (but with an X-ray powder diagram obtained from a close, but different area of the studied sample), or a distinct, unknown phase. The other closest natural chloro-sulfosalt is dadsonite, $Pb_{23}Sb_{25}S_{60}Cl$, with a lower Cl content (~ 0.4 wt.%). A synthetic Phase V, obtained at 350°C by Bortnikov *et al.* (1979), is richer in Cl and Pb, with the hypothetic structural formula $Pb_{9.49}Sb_{9.66}S_{22.55}Cl_{1.45}$ (1.26 wt.% Cl).

4. Crystallography and crystal chemistry

Table 3 gives the X-ray powder pattern of pillaite. Single-crystal studies (Weissenberg, precession, 4-circle diffractometer and Image Plate system) indicated first (IMA proposal) a triclinic symmetry, space group $P\bar{1}$, with a = 24.90(3) Å, $2b$ = 8.28(1) Å, c = 21.92(3) Å, α = 90.19(7)°, β = 99.67(6)°, γ = 94.86(9)°, V = 4438(18) Å^3 and Z = 4. Nevertheless, reexamination of the crystal structure, with the detection of an additional atom position, half-filled by oxygen, led to a monoclinic symmetry, with space group $C2/m$, and a = 49.65(3) Å, b = 4.150(4) Å, c = 21.91(1) Å, β = 99.76(5)°, V = 4449(10) Å^3 and Z = 4.

Like for dadsonite (Moëlo, 1979), a Bragg photograph obtained by rotating the crystal along the elongation axis reveals a very weak $2b$ superstructure (Fig. 3). However, the refinement of unit-cell parameters from the powder diagram could be performed only on the basis of the reduced b parameter.

The crystal structure of pillaite will be presented in a separate paper (Meerschaut *et al.*, accepted); Fig. 4 shows the projection of half of the unit cell along b. This crystal structure shows a specific chlorine site, at the center of a pseudo-ternary

Table 3. X-ray powder diffraction pattern of pillaite.

$I_{obs.}$	$d_{meas.}$	$d_{calc.}$	h	k	l	$I_{obs.}$	$d_{meas.}$	$d_{calc.}$	h	k	l	$I_{obs.}$	$d_{meas.}$	$d_{calc.}$	h	k	l	$I_{obs.}$	$d_{meas.}$
7	14.97	14.982	2	0	1	6	3.305	3.316	12	0	3	2	2.736	2.7341	$\bar{1}$	1	6	8	1.966
4	10.68*	10.796	0	0	2			3.306	$\bar{1}$	1	4			2.7335	$\bar{2}$	0	8	6	1.908
7	7.24	7.236	6	0	1			3.305	4	0	6			2.7308	14	0	4	2	1.879
6	6.64	6.609	2	0	3			3.299	$\bar{9}$	1	0	7	2.693	2.6875	11	1	3	3	1.836
6	5.93	5.915	$\bar{6}$	0	3	24	3.249	3.252	$\overline{12}$	0	5	5	2.634	2.6347	2	0	8	7	1.820
2	4.64	4.656	4	0	4	2	3.197*	3.190	$\overline{14}$	0	4	1	2.519	**				7	1.783
3	4.40	4.381	$\bar{2}$	0	5	6	3.181*	3.172	14	0	2	2	2.486	**				9	1.743
27	4.14	4.135	2	0	5	2	3.163	3.163	3	1	4	8	2.441	2.4459	$\overline{15}$	1	4	7	1.697
4	4.08	4.078	12	0	0	4	3.150#							2.4422	6	0	8	1	1.681
12	3.98	3.975	$\overline{10}$	0	4	3	3.128*	3.123	$\bar{9}$	1	3	13	2.359	2.3597	13	1	4	1	1.654
20	3.88	3.889	12	0	1			*2.998*	*2*	*0*	*7*	5	2.320	2.3190	14	0	6	1	1.640
9	3.84	3.847	$\bar{8}$	0	5	7	2.986	2.996	10	0	5	2	2.283	**				1	1.563
4	3.76	3.762	10	0	3			2.966	1	1	5	8	2.235	2.2341	$\overline{22}$	0	3	1	1.555
26	3.621	3.622	$\bar{4}$	0	6	47	2.956	2.960	$\bar{5}$	1	5	3	2.211	**				2	1.515
		3.618	12	0	2			2.959	16	0	1	6	2.180	2.1804	$\bar{6}$	0	10	2	1.496
40	3.548	3.555	$\overline{12}$	0	4			2.957	$\overline{12}$	0	6	4	2.158	2.1574	16	0	6	6	1.453
		3.549	$\overline{10}$	0	5			2.953	$\bar{9}$	1	4	3	2.076	**				6	1.420
		3.495	*14*	*0*	*0*	8	2.875	2.875	$\bar{7}$	1	5	9	2.057	2.0548	$\overline{24}$	0	3	1	1.388
100	3.480	3.477	2	0	6	22	2.780	2.7881	13	1	0	4	2.037	2.0388	$\overline{24}$	0	0	3	1.369
13	3.365	3.362	14	0	1			2.7723	5	1	5	4	1.996					2	1.339
																		4	1.310

Indexed with: a 49.65(3), b 4.150(4), c 21.91(1) Å ; β 99.76(5)° ; V 4449(10) Å^3. * poorly defined diffraction lines; ** multiple indexing; # non-indexed line. Two $d_{calc.}$ (in italics) were excluded for the refinement.

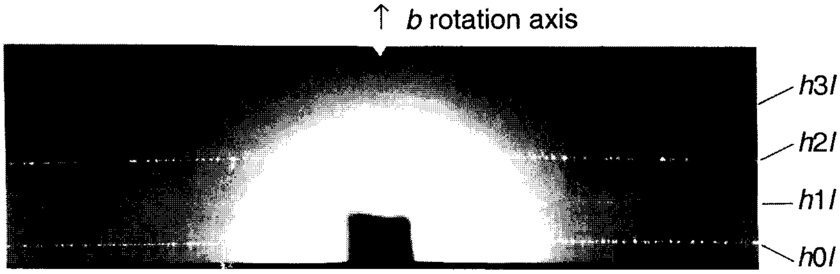

Fig. 3. Bragg photograph obtained by rotation along the elongation axis *b* on pillaite single crystal. *hkl* indexing according to the weak 2*b* superstructure.

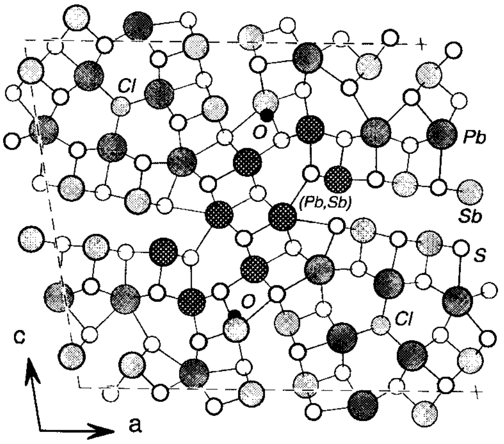

Fig. 4. Projection along *b* of the crystal structure of pillaite (half unit cell *a*/2 x *c*). In order of decreasing size: Pb (medium grey), (Pb, Sb) (cross-hatched), Sb (light grey), Cl (light grey), S (white) and O (black). Oxygen position is half-filled.

axis. The chlorine atom is bonded only with Pb atoms, in a trigonal prismatic coordination. On the contrary, there is an oxygen position, half-filled, which is bonded essentially with antimony, like in the scainiite structure (Moëlo *et al.*, 2000). This selectivity of the chemical bonding of chlorine and oxygen with Pb or Sb, respectively, reflects the stability of $PbCl_2$ (cotunnite) and Sb_2S_2O (kermesite) under natural conditions.

Without oxygen, the initial structural formula (IMA proposal) was non-stoichiometric, $Pb_9Sb_{9.7}S_{23}Cl$. Adding the half-filled oxygen position, the final structural formula, $Pb_9Sb_{10}S_{23}ClO_{0.5}$, gives an integer for Sb, and, taking into account the 2*b* superstructure, one obtains the stoichiometric formula $Pb_{18}Sb_{20}S_{46}Cl_2O$.

Like scainiite (Moëlo *et al.*, 2000), pillaite belongs to the group of lead sulfosalts with rod-based, cyclically twinned structures (zinkenite group, Makovicky, 1985, 1993), distinct from the boulangerite family of "rod-layer sulfosalts", to which belongs dadsonite (Makovicky, 1993).

Initially (IMA proposal), the analogy of pillaite with a Pb-Sb fibrous sulfosalt from Mexico ("plumosite" - Fabregat, 1964) was pointed out: ideal formula ($\underline{Pb}$, $Fe)_5Sb_4S_{11}$; monoclinic, space group *C*2/*m*; unit-cell parameters a = 22.16, b = 24.63, c = 8.252 Å, β = 100.97°, V = 4422 Å^3. But here *b* and *c* axes are permuted relatively to those of pillaite. It was finally possible to find the original sample of this "plumosite" (Dr. M.-G. Villasenor-Cabral, Mexico University), but the unit cell of one fiber extracted from this sample corresponded exactly to that of boulangerite: a = 21.57, b = 23.51, c = 8.066 Å, β = 100.71°. As the powder pattern of this "plumosite" is close to that of boulangerite (Berry & Thompson, 1962), clearly Fabregat's "plumosite" is essentially boulangerite. Discrepancy between measured and theoretical unit-cell parameters is difficult to explain: bias due to a calibration error, or selection by Dr. Fabregat of a single crystal distinct from dominant boulangerite? Nevertheless, for the same monoclinic symmetry, permutation between *b* and *c* relatively to pillaite would impose permutation between β and γ, which is not the case for "plumosite" of Fabregat.

5. Conditions of formation

Pillaite has crystallized together with scainiite and other Pb-Sb sulfosalts, at relatively high temperature (over 300°C), in narrow fO_2/fS_2 conditions related to the pyrite-magnetite-hematite buffer (Orlandi *et al.*, 1999). As for other Pb-Sb chloro-sulfosalts (Moëlo, 1979; Moëlo *et al.*, 1989), the formation of pillaite implies a relatively high chlorinity of the hydrothermal solution, but also a specific oxygen fugacity controlled by the pyrite-magnetite-hematite buffer.

Pillaite, $Pb_9Sb_{10}S_{23}ClO_{0.5}$, and dadsonite, $Pb_{23}Sb_{25}S_{60}Cl$, have very close Pb/Sb atomic ratios (ideally 0.90 and 0.92, respectively), but differ by a higher Cl content for pillaite (1 wt.% against 0.4 wt.%), together with minor (but critical) oxygen. In nature, the formation of pillaite, like that of ardaite (~ 4 wt.% Cl – Breskovska *et al.*, 1982), would imply a higher chlorinity of the parent hydrothermal solution, and will be thus more difficult than that of dadsonite. Nevertheless, one may expect to find this oxy-chloro-sulfosalt in some parageneses containing dadsonite.

Conclusion

Pillaite, like scainiite, is a new lead-antimony sulfosalt belonging to the zinkenite group. In this new species, two minor anions, chlorine and oxygen, play an essential role for the stabilization of the crystal structure. The discovery of pillaite and scainiite enlarges the research field for new lead sulfosalts. In both species, the weight percentage of the minor anions (Cl and O) is very low, and may be easily overlooked in a routine chemical analysis; under the ore microscope their optical properties are very close to that of other lead sulfosalts. Thus, careful single-crystal X-ray study coupled with detailed electron-microprobe analysis is the only way to detect such new compounds in nature.

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