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THE CRYSTAL STRUCTURE OF ANGELAITE, $Cu_2AgPbBiS_4$

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Abstract

The crystal structure of angelaite, ideally $Cu_2AgPbBiS_4$, a 12.734(5), b 4.032(1), c 14.633(5) Å, V 751.2(5) Å^3, space group *Pnma*, $Z = 4$, $D_{calc} = 6.89$ g.cm^{-3}, from the Ángela mine, Los Manantiales district, province of Chubut, Argentina, has been solved by direct methods and refined to $R_1 = 6.47\%$ on the basis of 606 unique reflections [$F_o > 4\sigma(F_o)$]; these were collected on a Bruker P3 diffractometer with a CCD detector and Mo$K\alpha$ radiation from a fragment consisting of an intergrowth of angelaite and galena. Angelaite contains a capped trigonal prismatic Pb site, a quasi-octahedral Bi site, a linearly coordinated Cu site, and three triangular sites, one occupied by Ag and two partially occupied by Cu. Angelaite is a homeotype of galenobismutite with the Pb and Bi1 sites of galenobismutite preserved, and the Bi2 site replaced by the combination of Ag and Cu sites described above, which represent a novel type of substitution: ($Ag^+ + 2Cu^+$)-for-Bi^{3+}. Selenium-free galenobismutite from Felbertal (Austria) was refined to the R_1 value of 2.49% to serve as a reference structure related to that of angelaite.

Keywords: angelaite, Cu–Ag–Pb–Bi sulfosalt, galenobismutite, crystal structure.

Sommaire

Nous avons résolu la structure cristalline de l'angelaïte, dont la formule idéale est $Cu_2AgPbBiS_4$, a 12.734(5), b 4.032(1), c 14.633(5) Å, V 751.2(5) Å^3, groupe spatial *Pnma*, $Z = 4$, $D_{calc} = 6.89$ g.cm^{-3}, provenant de la mine Ángela, district de Los Manantiales, province de Chubut, en Argentine, par méthode directes, et nous l'avons affinée jusqu'à un résidu R_1 de 6.47% en utilisant 606 réflexions uniques [$F_o > 4\sigma(F_o)$]; elles ont été prélevées avec un diffractomètre Bruker P3 muni d'un détecteur CCD employé avec rayonnement Mo$K\alpha$ sur un fragment contenant une intercroissance d'angelaïte et de galène. L'angelaïte contient un site Pb trigonal prismatique avec couronne, un site Bi quasi-octaédrique, une site Cu à coordinence linéaire, et trois sites triangulaires, dont un contient l'atome de Ag, et deux à occupation partielle contiennent le Cu. L'angelaïte est un homéotype de la galénobismutite, avec les sites Pb et Bi1 de la galénobismutite intacts, et le site Bi2 remplacé par une combinaison des sites Ag et Cu, décrite ci-haut, ce qui représente un nouveau schéma de substitution: ($Ag^+ + 2Cu^+$)-pour-Bi^{3+}. Nous avons aussi affiné la galénobismutite dépourvue de sélénium provenant de Felbertal, en Autriche, jusqu'à un résudu R_1 de 2.49% pour servir de structure de référence apparentée à celle de l'angelaïte.

(Traduit par la Rédaction)

Mots-clés: angelaïte, sulfosel de Cu–Ag–Pb–Bi, galénobismutite, structure cristalline.

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INTRODUCTION

The relatively small group of Cu–Ag–Bi–Pb sulfosalts, having all these elements present in substantial amounts, with each of them playing its own crystal-chemical role, corresponds to a number of structurally diverse minerals and structural families. If we quote structure papers only, we can mention, besides cupromakovickyite (Topa *et al.* 2008) and other representatives of the pavonite homologous series, neyite (Makovicky *et al.* 2001), berryite (Topa *et al.* 2006), and paděraite (Mumme 1986, Topa & Makovicky 2006). Furthermore, we should mention larosite (Petruk 1972) and arcubisite (Karup-Møller 1976), both still without a known structure. Angelaite is one more unexpected and very interesting contribution to this diverse group. A short report on the results published here was given by Topa *et al.* (2004) at a geological meeting in Florence, Italy.

PROVENANCE

Angelaite occurs in polymetallic ore of the Ángela cluster of mines, situated in the Los Manantiales ore district, near the city of Gastre, province of Chubut, Argentina (Brodtkorb & Paar 2004, Topa *et al.* 2010). The ore mineralization is structurally controlled and emplaced into calc-alcaline andesitic to dacitic rocks of Late Jurassic age. Three different stages of mineralization were observed. The first stage is characterized by abundant base-metal sulfides such as sphalerite, galena and chalcopyrite, associated with pyrite and lesser amounts of arsenopyrite, bornite, betekhtinite, matildite and acanthite. Angelaite is a member of this association. It occurs as microscopic inclusions in galena, with trace amounts of aikinite, miharaite and wittichenite (Topa *et al.* 2010). The second stage is dominated by hematite and Au–Ag–Te mineralization. A reopening of the veins during the third stage was accompanied by the precipitation of a sulfide assemblage and native gold. The mineralization is epithermal (230–390°C), and results from an intermediate-sulfidation environment. These data are discussed in detail by Topa *et al.* (2010), who include all original references and the historical notes on this species.

The crystal structure of a selenium- and chlorine-free natural galenobismutite, $PbBi_2S_4$, used as a reference structure in this study, was refined on a material from the Felbertal deposit in Hohe Tauern, Austria. It was collected in the orebody K3, mine level ~950 m above sea level. The associated minerals are cosalite, eclarite, lillianite, heyrovskyite and vikingite. The present investigation required a recent refinement of the structure of galenobismutite, because the last refinements of that structure were published by Pinto *et al.* (2006a) on a crystal of selenium-bearing galenobismutite, by Pinto *et al.* (2006b) on selenium- and chlorine-containing material, and by Olsen *et al.* (2007) on synthetic material in a diamond-anvil cell.

EXPERIMENTAL

Chemical analyses

Quantitative chemical data for angelaite and galenobismutite were obtained with a JEOL Superprobe JXA–8600 electron microprobe, installed at the Department of Geography and Geology, University of Salzburg. The apparatus was operated at 25 kV and 35 nA; measurement time was 15 s for peak and 5 s for background counts. The following standards and X-ray lines were used: natural $CuFeS_2$ (chalcopyrite, Cu$K\alpha$), natural PbS (galena Pb$L\alpha$), synthetic Bi_2S_3 (Bi$L\alpha$, S$K\alpha$) and Ag metal (Ag$L\alpha$). We sought both Se and Te, but neither was detected. The raw data were corrected with the on-line ZAF–4 procedure.

The results for angelaite, obtained from eight grains in two polished sections of the holotype specimen, show invariably a close-to-ideal composition and only minor variation of the chemical composition. Average results of 23 electron-microprobe analyses on eight grains gave: Cu 16.74(0.32), Ag 13.40(0.15), Pb 27.80(0.58), Bi 26.62(0.45), S 15.97(0.21), total 100.54(0.51) wt.%. The empirical formula, $Cu_{2.07}Ag_{0.97}Pb_{1.05}Bi_{1.00}S_{3.91}$, is based on nine atoms per formula unit, resulting in $Cu_2AgPbBiS_4$ ($Z = 4$) as the ideal formula of angelaite. The ideal formula requires Cu 16.31, Ag 13.84, Pb 26.58, Bi 26.81 and S 16.46, total 100.00 wt.%.

Electron-microprobe analyses of galenobismutite from Felbertal gave Pb 27.8(1), Bi 55.2(1), Sb 0.14(5), and S 17.10(5), total 100.2(2) wt.%. The resulting chemical formula is $Pb_{1.01}Bi_{1.98}S_4$, virtually identical with $PbBi_2S_4$.

Single-crystal X-ray diffraction

For our single-crystal investigation, several grains of angelaite were extracted from the galena matrix (Fig. 1). They were investigated with a Bruker AXS P3 diffractometer equipped with a CCD area detector using graphite-monochromated Mo$K\alpha$ radiation. We found an irregular fragment measuring approximately 0.02 × 0.04 × 0.07 mm to be suitable for structural investigation in spite of the presence of a minor amount of galena. Experimental data are listed in Table 1. We used the SMART (Bruker AXS 1998a) system of programs for unit-cell determination and data collection, SAINT+ (Bruker AXS 1998b) for the calculation of integrated intensities, and XPREP (Bruker AXS 1998c) for empirical absorption correction based on pseudo Ψ-scans. The space group *Pnma*, proposed by the XPREP program, was accepted. The structure of angelaite was solved by direct methods (program SHELXS of Sheldrick 1997a) and difference-Fourier syntheses (program

SHELXL of Sheldrick 1997b). The structure is presented in Figure 2, and the atom labeling in Figure 3. Information about the refinement is given in Table 1; fractional coordinates of the atoms, and isotropic or anisotropic displacement parameters are listed in Table 2. The quality of the structure refinement has been adversely influenced by the unavoidable presence of remnants of galena from which the mineral was extracted, resulting in the R_1 value of 6.5% but, considering the situation illustrated in Figure 1, we were very lucky to find a single bleb of angelaite of workable quality at all. Selected *Me*–S bond distances are presented in Table 3, and selected geometrical parameters for individual coordination polyhedra, calculated with program IVTON (Balić-Žunić & Vicković 1996), are given in Table 4. A table of structure factors for angelaite may be obtained from the Depository of Unpublished Data, on the MAC website [document Angelaite CM48_145]. Refinement data and structure parameters for the reference galenobismutite are given in the right-hand or lower portions of Tables 1–4; the structure is presented in Figure 4 and the atom labeling in Figure 5. A table of structure factors for galenobismutite may be obtained from the Depository of Unpublished Data, on the MAC website [document Galenobismutite CM48_145].

TABLE 1. SINGLE-CRYSTAL X-RAY DIFFRACTION: EXPERIMENTAL AND REFINEMENT DETAILS

	angelaite	galenobismutite
Crystal data		
Chemical formula	$Cu_2AgPbBiS_4$	$PbBi_2S_4$
Chemical formula weight	779.36	753.39
Crystal system	orthorhombic	
Space group	*Pnma*	
a (Å)	12.734(5)	11.742(2)
b (Å)	4.032(1)	4.0814(8)
c (Å)	14.633(5)	14.522(3)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	90.00	90.00
V (Å^3)	751.2(5)	695.9(2)
Z	4	4
D_x (Mg m^{-3})	6.89	7.19
No. of reflections for cell-parameter refinement	954	5952
μ (mm^{-1})	54.82	75.66
Crystal shape	irregular	
Crystal size (mm)	0.02×0.04×0.07	0.02×0.03×0.10
Crystal color	grey metallic	
Data collection		
T_{min}, T_{max}	0.098, 0.563	0.009, 0.070
No. of measured reflections	5918	9588
No. of independent reflections	992	969
No. of observed reflections	606	898
Criterion for observed reflections	$I > 2\sigma(I)$	
R_{int} (%)	33.6	11.8
θ_{max} (°)	28.3	28.3
Range of *h, k, l*	$-16 \leq h \leq 16$ $-5 \leq k \leq 5$ $-19 \leq l \leq 19$	$-15 \leq h \leq 15$ $-5 \leq k \leq 5$ $-19 \leq l \leq 19$
Refinement		
	Refinement on F_o^2	
$R\ [F_o > 4\sigma(F_o)]$ (%)	6.47	2.49
$wR\ (F_o^2)$ (%)	10.03	6.76
S (*GooF*)	0.806	1.065
No. of reflections used	606	898
No. of parameters refined	64	43
Weighting scheme	a = 0.0918, b = 0	a = 0.100, b = 0
	$w=1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max}$	0.000	0.001
$\Delta\rho_{max}$ (e/Å^3)	3.11 (0.79 Å from Bi)	1.92 (1.01 Å from Pb3)
$\Delta\rho_{min}$ (e/Å^3)	–6.46 (0.91 Å from Bi)	–2.67 (0.89 Å from Bi2)
Extinction coefficient	0.0004(3)	none
Source of atomic scattering factors		
	International Tables for X-Ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	
Computer programs		
Structure solution	*SHELXS97* (Sheldrick 1997a)	
Structure refinement	*SHELXL97* (Sheldrick 1997b)	

THE STRUCTURE OF ANGELAITE

Angelaite is orthorhombic, *a* 12.734(5), *b* 4.032(1), and *c* 14.633(5) Å, space group *Pnma*. The structure contains one independent Pb site, one Bi site, three distinct Cu sites and one Ag position (Figs. 2, 3). Two of the copper sites are partially occupied (Table 2). In spite of belonging compositionally to the sulfosalts of Cu and Ag (with Pb and Bi), the closest structural affinities of

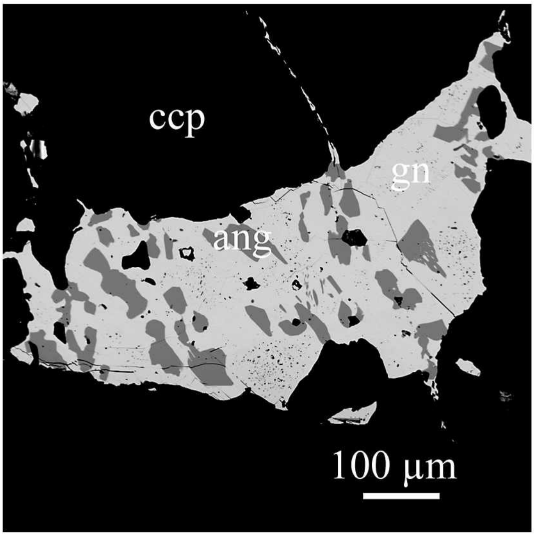

FIG. 1. Large inclusion of galena (gn) in chalcopyrite matrix (ccp) with blebs of angelaite (ang) from the Ángela mine, Argentina. Back-scattered electron image.

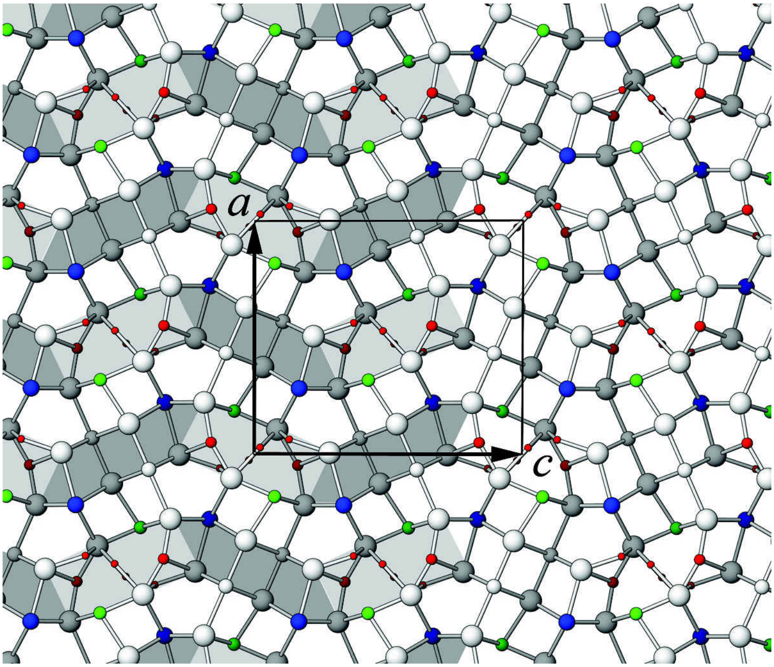

FIG. 2. The crystal structure of angelaite projected upon (010). Shading indicates atoms at two *y* levels, 2 Å apart. Large spheres indicate S atoms; in order of decreasing size, cations are Pb, Bi, Ag, and Cu. The Cu2a and Cu2b sites are partially occupied. The *a* axis is vertical, and the *c* axis, horizontal. The "anti-aikinite" ribbons (grey shading) and the Cu–Ag configurations (lighter shading) are indicated.

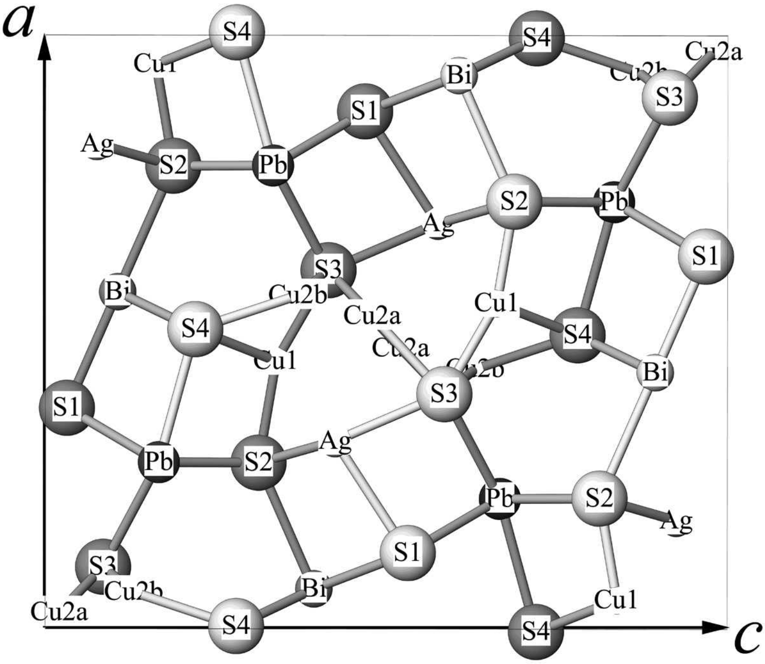

FIG. 3. Atom labeling in the unit cell of angelaite.

TABLE 2. POSITIONAL AND ATOMIC DISPLACEMENT PARAMETERS FOR ANGELAITE AND GALENOBISMUTITE

ATOM	x	z	sof	U_{eq}	U_{11}	U_{22}	U_{33}	U_{13}
				Angelaite				
Bi	0.06739(8)	0.39411(9)	1	0.0170(4)	0.0205(6)	0.0110(6)	0.0194(8)	0.0007(4)
Pb	0.2193(1)	0.6666(1)	1	0.0294(5)	0.0460(8)	0.0164(6)	0.0259(9)	0.0040(6)
Ag	0.1832(2)	-0.0751(3)	1	0.0388(8)	0.050(2)	0.039(2)	0.028(2)	0.013(1)
Cu1	0.4510(4)	0.3382(5)	1	0.054(2)	0.021(2)	0.104(5)	0.037(4)	-0.010(2)
Cu2a	-0.0274(7)	-0.0209(8)	0.67(2)	0.074(5)	0.042(5)	0.14(1)	0.040(7)	0.008(4)
Cu2b	-0.062(1)	-0.130(2)	0.31(2)	0.042(7)	0.030(9)	0.024(8)	0.07(2)	-0.007(7)
S1	0.3718(5)	0.0317(6)	1	0.018(2)	0.020(3)	0.004(3)	0.031(5)	-0.003(3)
S2	0.2798(5)	0.3128(6)	1	0.017(2)	0.017(4)	0.012(3)	0.024(4)	-0.002(3)
S3	0.1041(5)	0.0851(7)	1	0.020(2)	0.016(3)	0.019(3)	0.028(5)	0.002(3)
S4	-0.0048(6)	0.7198(6)	1	0.020(2)	0.033(4)	0.010(3)	0.018(5)	-0.002(3)
				Galenobismutite				
Bi1	0.06789(3)	0.39037(2)	1	0.0187(1)	0.0204(2)	0.0183(2)	0.0175(2)	0.0020(1)
Bi2	0.10367(3)	0.90512(3)	1	0.0220(1)	0.0243(2)	0.0157(2)	0.0261(2)	0.0011(1)
Pb	0.24877(3)	0.65191(3)	1	0.0259(1)	0.0310(2)	0.0225(2)	0.0241(2)	0.0053(2)
S1	0.3325(2)	0.0137(2)	1	0.0207(5)	0.025(15)	0.019(1)	0.018(1)	0.0010(9)
S2	0.2606(2)	0.2984(2)	1	0.0167(4)	0.018(1)	0.016(1)	0.016(1)	0.0001(8)
S3	0.0528(2)	0.0927(2)	1	0.0173(4)	0.019(1)	0.018(1)	0.015(1)	0.0014(8)
S4	0.0182(2)	0.7125(1)	1	0.0165(4)	0.020(1)	0.017(1)	0.013(1)	-0.0030(8)

sof: site-occupancy factor. Note that $y = 1/4$, $U_{12} = 0$ and $U_{23} = 0$ by symmetry.

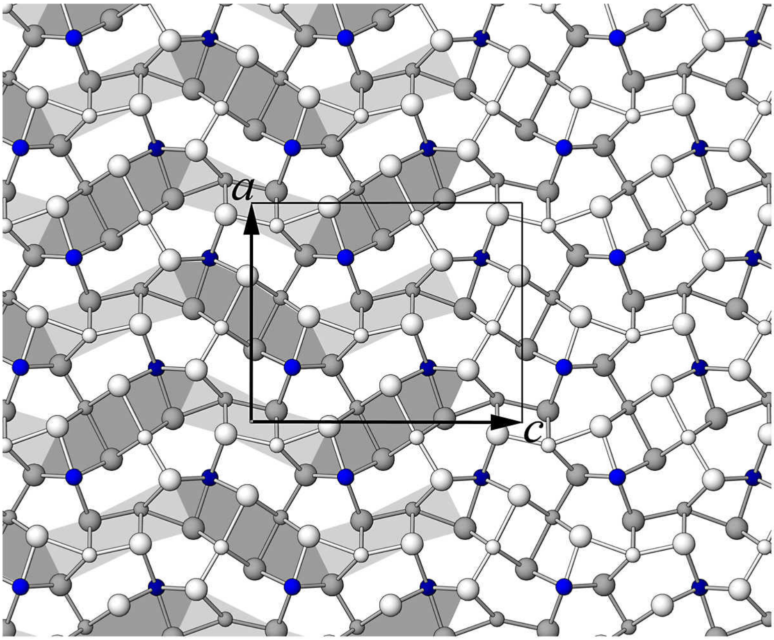

FIG. 4. The crystal structure of galenobismutite, $PbBi_2S_4$ from Felbertal, projected upon (010). Shading indicates atoms at two y levels, 2 Å apart. Large spheres indicate S atoms; in order of decreasing size, cations are Pb and Bi. The a axis is vertical, and the c axis, horizontal. The "anti-aikinite" ribbons (grey shading) and the Bi_2S_6 configurations (lighter shading) are indicated.

angelaite are to galenobismutite, as described in detail below (Figs. 2, 4).

Coordination polyhedra

The topologically bicapped trigonal prism of Pb is so strongly asymmetric (the Pb–S distances in the caps are 2.958 Å and 3.887 Å) that it can also be considered a monocapped one. Together with the slightly asymmetric coordination octahedra of Bi (bond distances vary from 2.717 Å to 2.955 Å), these prisms form a distant

TABLE 3. BOND DISTANCES IN THE POLYHEDRA OF ANGELAITE AND GALENOBISMUTITE

				Angelaite				
Bi –			Pb –			Ag –		
S1	2.717(7)		S2	2.940(7)	×2	S3	2.551(11)	
S4	2.734(6)	×2	S4	2.958(8)		S2	2.641(6)	×2
S1	2.952(6)	×2	S1	3.050(6)	×2	S1	2.865(8)	
S2	2.955(7)		S3	3.247(6)	×2	S4	3.839(9)	
			S4	3.887(8)				
Cu1 –			Cu2a –			Cu2b –		
S2	2.212(8)		S3	2.283(13)		S3	2.184(9)	×2
S3	2.250(9)		S3	2.429(7)	×2	S4	2.323(26)	
S4	2.745(8)	×2	S4	3.805(15)		S3	3.790(24)	
				Galenobismutite				
Bi1 –			Pb –			Bi2 –		
S2	2.628(2)		S4	2.847(2)		S3	2.746(2)	×2
S4	2.724(1)	×2	S2	2.950(2)	×2	S3	2.789(2)	
S1	2.956(2)	×2	S1	3.018(2)	×2	S4	2.972(2)	
S1	3.095(2)		S3	3.214(2)	×2	S2	3.018(2)	×2
			S4	3.726(2)		S1	3.115(2)	

TABLE 4. POLYHEDRON CHARACTERISTICS IN THE CRYSTAL STRUCTURES OF ANGELAITE AND GALENOBISMUTITE

1	2	3	4	5	6	7	8	9
				Angelaite				
Bi	6	2.845	0.069	0.193	0.996	96.448	30.500	2.863
Pb	8	3.152	0.124	0.327	0.798	131.197	54.360	1.878
Ag	5	2.919	0.176	0.441	0.580	104.225	17.373	1.024
Cu1	4	2.396	0.237	0.556	1.000	57.632	6.652	0.918
Cu2a	4	2.762	0.516	0.887	1.000	88.289	7.202	0.754
Cu2b	4	2.762	0.520	0.889	1.000	88.289	7.202	1.125
				Galenobismutite				
Bi1	6	2.856	0.016	0.284	0.985	97.577	30.560	2.956
Bi2	7	2.915	0.100	0.217	0.953	103.768	35.340	2.803
Pb	8	3.100	0.044	0.318	0.844	124.771	51.687	2.065

The polyhedron characteristics used were defined by Balić-Žunić & Makovicky (1996) and Makovicky & Balić-Žunić (1998): 1) atom label, 2) coordination number, 3) radius r_s of a circumscribed sphere, least-squares fitted to the coordination polyhedron, 4) "volume-based" distortion u = [V(ideal polyhedron) – V(real polyhedron)]/V(ideal polyhedron). The ideal polyhedron has the same number of ligands, 5) "volume-based" eccentricity $ECC_V = 1 - [(r_s - \Delta)/r_s]^3$; Δ is the distance between the center of the sphere and the central atom in the polyhedron, 6) "volume-based" sphericity $SPH_V = 1 - 3\sigma_r r_s$; σ_r is a standard deviation of the radius r_s, 7) volume of the circumscribed sphere, 8) volume of the coordination polyhedron, 9) bond-valence sum.

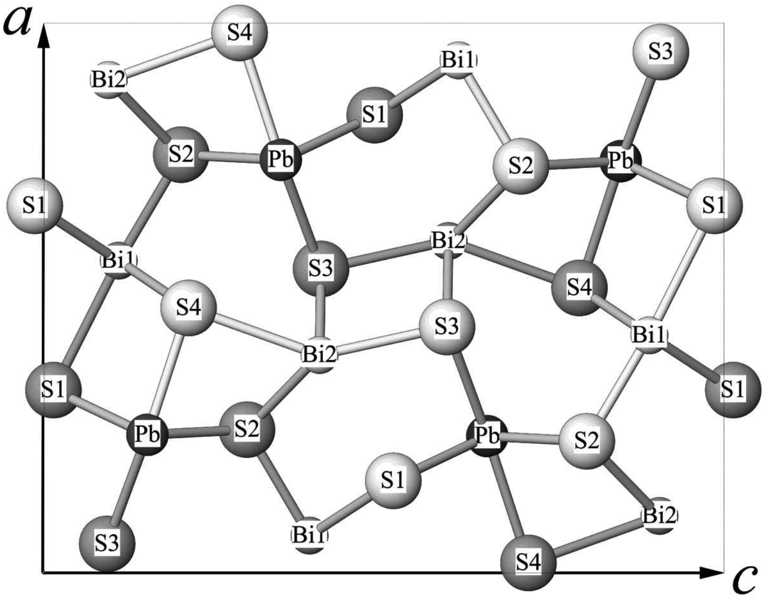

FIG. 5 Atom labeling in the unit cell of galenobismutite.

analogy to "aikinite-like" ribbons, with Cu1 sites laterally attached to them. However, the position of Pb and Bi, respectively, and the coordination type of the inner and terminal cations in the ribbon, are interchanged in comparison with the true ribbon of aikinite, creating an "anti-aikinite" motif. The position of these "anti-aikinite" ribbons in angelaite is illustrated in Figure 2 and in galenobismutite in Figure 4. An approximation to this type of ribbon, with octahedral coordinations twisted, is present in paděraite (Mumme 1986, Topa & Makovicky 2006).

The Cu1 site is a bent linear coordination with two additional, longer Cu–S contacts (Table 3). In character as well in distances, it is close to the Cu7 coordination polyhedron in paděraite, which has its Cu–S distances equal to 2.13 and 2.22 Å, and 2 × 2.83 Å. These values are to be compared with our results, 2.212 Å, 2.250 Å, and 2 × 2.745 Å. The partially occupied Cu2a and Cu2b sites, and the Ag site (Figs. 2, 3), have trigonal planar coordination. The values of interatomic distances for Cu2a and especially for the minority position, Cu2b, may be partly distorted because the S positions involved are averages of those for which the given Cu site is occupied and those for which it is empty.

All monovalent cations are concentrated into a small structural volume in the interior and on the surfaces of a column of paired, much distorted (half-flattened, half-extended) octahedra sharing a common edge (Fig. 2). The shortest Cu1–Cu2a distance is 2.80 Å. The Cu2a–Cu2a distance (2.22 Å) indicates that two adjacent Cu2a positions cannot be occupied simultaneously, unless a positional displacement of Cu2a along the [010] channel takes place. Thus, the 66% occupancy of these sites appears unrealistic; on the one hand, this "excess" occupancy may reflect an admixture of Ag (refined as pure Cu) in this site. This would imply, however, the opposite situation for the Ag site. On the other hand, U_{22} of Cu2a is unusually high, suggesting shifts along the channel axis. The Cu1–Ag and Cu2a–Ag distances are 2.93 Å and 2.78 Å, respectively. The distances 2.7–2.8 Å are typical for the weak cation–cation interactions of these metals. The statistically one-third-occupied triangular-coordinated site Cu2b has a short but still acceptable Cu1–Cu2b distance, equal to 2.51 Å, expressing the statistical and disordered nature of both Cu sites. Unidimensional ionic conduction parallel to the 4 Å axis appears probable at the temperatures of formation.

Relation to galenobismutite and its isotypes

There exists a fascinating modular analogy between angelaite and galenobismutite. Angelaite appears to be a fully (Cu, Ag)-substituted version of galenobismutite according to the scheme $2Bi^{3+} \rightarrow 4Cu^{+} + 2Ag^{+}$ in one unit cell, or $Bi^{3+} \rightarrow 2Cu^{+} + Ag^{+}$ for one Bi site.

The Pb position in angelaite corresponds fully to the asymmetric bicapped trigonal prism of Pb in galenobismutite, and the Bi position in angelaite corresponds to the square pyramidal (elongate octahedral) pure Bi1 site in galenobismutite. Comparison of these polyhedra indicates that the polyhedron volume of Pb in galenobismutite is equal to 51.7 Å^3, whereas it is 54.4 Å^3 for the presumably pure Pb site in angelaite. For the elongate Bi1 octahedron, these values are 30.6 Å^3 and 30.5 Å^3, respectively. The volume of the "Bi2" polyhedron in galenobismutite, 35.3 Å^3, is slightly smaller than that expected for octahedral Pb. It has a close analogy in the total volume of the Ag atom in angelaite, situated in about the same position. Therefore, the volume of the circumscribed sphere is 103.8 Å^3 and 104.2 Å^3, respectively, for these two polyhedra, although they are not strictly identical. The respective configurations may be inspected in Tables 3 and 4, as well as in Figures 2 and 4.

The paired Bi2 sites of galenobismutite, rather unique among sulfosalts, are replaced by a combination of Cu and Ag in angelaite. However, especially in the case of Cu, this replacement is heterotopical, *i.e.*, the sulfur configurations are preserved but the substituting elements assume sites surrounding, and not identical to, the vacated Bi2 positions (Figs. 2, 4).

The anion topology of the structure survives these substitutions in intact fashion. Geometric adjustments are minor: the position of S3 in the volume surrounded by S2 and S4 of galenobismutite, and the shape of the volume defined by S1–S2–S4–S2–S1–S2–S4–S2 in the center of the unit cell, become more symmetric on insertion of Cu1a and Ag (Figs. 2, 4). The position of Pb is nearly unchanged, whereas the shorter and longer Bi–S bonds that are 'horizontal' in projection on (010) are exchanged, changing the indistinct lone-electron-pair micelle Bi1–Bi1 in galenobismutite into a more tightly bonded configuration, with the lone-electron pair of Bi now oriented outward. The "bent octahedra" Bi2–$(S2)_2$–S4–$(S3)_2$–S3 in galenobismutite (Figs. 4, 5) are vacated. Instead, irregular, asymmetric and broad octahedra Cu1–S2–$(S3)_2$–S3–$(S3)_2$ occur in angelaite (Figs. 2, 3). Atom Cu2a, however, occurs on a level that is *b*/2 displaced from the "original" Bi2 site. As a result of this displacement, the Bi octahedron in galenobismutite and the Cu octahedron in angelaite are rotated by 90° with respect to one another, *i.e.*, they do not occupy the same portion of cell space. The Bi2 polyhedron can also be considered as partly substituted by Ag in angelaite, as suggested above. The unit-cell dimensions and volume reflect these adjustments, especially a change in the *a*:*c* length ratio, from 0.809 in galenobismutite to 0.870 in angelaite. A comparison of these relationships with the rest of the galenobismuthite isotypes (Olsen *et al.* 2007) is presented in Figure 6. Interestingly, the *a*:*c* length ratio of galenobismutite approaches that of angelaite with increasing pressure only very weakly, still being 0.813 at about 9 GPa (Olsen *et al.* 2007).

Geometrical adjustments are still smaller if angelaite is compared with $PbIn_2S_4$ (Krämer & Berroth 1980) and $PbSc_2S_4$ (Shemet *et al.* 2006), both being

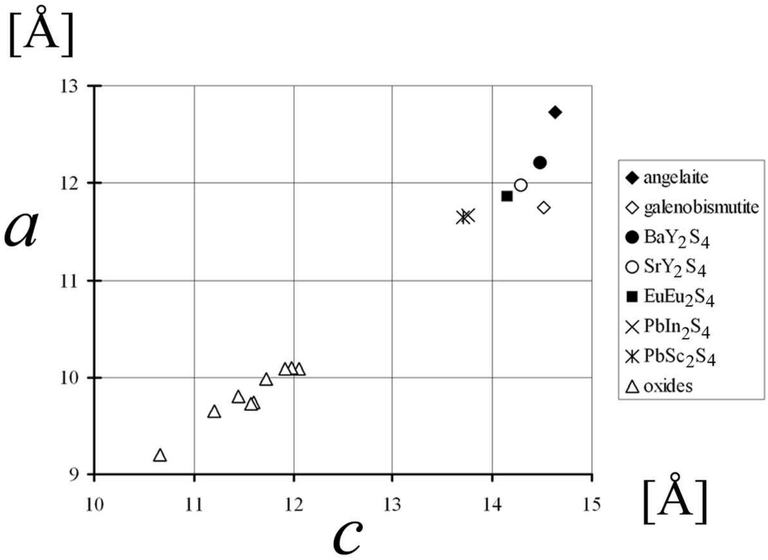

FIG. 6. Ratio of unit-cell parameters of the galenobismutite isotypes and angelaite. Note the non-linear distribution of *a* and *c* data for sulfides, including angelaite. The oxide structures considered were listed by Olsen *et al.* (2007).

galenobismutite-like structures without a lone pair of electrons. A change in the selected longer and shorter bonds in the capped trigonal prisms of Pb is the principal difference in these cases.

Angelaite is a fascinating homeotype of members of the galenobismutite isotypic family, with the Pb and half of Bi sites retained, whereas the unique Bi2 sites of galenobismutite are vacated and replaced heterotopically by Cu and Ag according to the scheme $Bi^{3+} \leftrightarrow 2Cu^+ + Ag^+$.

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