

## THE CRYSTAL STRUCTURE OF BILLINGSLEYITE, $\text{Ag}_7(\text{As},\text{Sb})\text{S}_6$ , A SULFOSALT CONTAINING $\text{As}^{5+}$

LUCA BINDI<sup>§</sup>

*Museo di Storia Naturale, Sezione di Mineralogia, Università di Firenze, via La Pira 4, I-50121 Firenze, Italy, and  
 C.N.R., Istituto di Geoscienze e Georisorse, Sezione di Firenze, Via La Pira 4, I-50121 Firenze, Italy*

ROBERT T. DOWNS

*Department of Geosciences, University of Arizona, Tucson, Arizona 85721-0077, U.S.A.*

SILVIO MENCHETTI

*Dipartimento di Scienze della Terra, Università di Firenze, via La Pira 4, I-50121 Firenze, Italy*

### ABSTRACT

We have characterized a portion of cotype billingsleyite,  $\text{Ag}_7(\text{As},\text{Sb})\text{S}_6$ , a rare  $\text{As}^{5+}$ -bearing sulfosalt from the silver ores of the North Lily mine, East Tintic district, Utah, USA, by single-crystal X-ray diffraction and electron-microprobe analysis. We found billingsleyite to be structurally identical to synthetic  $\text{Ag}_7\text{AsS}_6$ . It is cubic, space group  $P2_13$ , with a cell parameter  $a = 10.4760(8) \text{ \AA}$ ,  $V = 1149.7(2) \text{ \AA}^3$ , and  $Z = 4$ . Electron-microprobe analyses gave the following formula:  $(\text{Ag}_{6.94}\text{Cu}_{0.04}\text{Fe}_{0.01})_{\Sigma 6.99}(\text{As}_{0.87}\text{Sb}_{0.13})_{\Sigma 1.00}\text{S}_{6.01}$ . The crystal structure has been solved and refined to  $R = 1.64\%$ . It consists of  $(\text{As}^{5+},\text{Sb}^{5+})\text{S}_4$  tetrahedra and Ag polyhedra (2-, 3- and 4-fold coordinated) forming a three-dimensional network. We present structural relationships with other natural and synthetic thioarsenates and thioantimonates.

*Keywords:* billingsleyite,  $\text{As}^{5+}$ -bearing sulfosalt, crystal-structure refinement, chemical analysis, cotype specimen.

### SOMMAIRE

Nous avons caractérisé une portion de l'échantillon cotype de la billingsleyite,  $\text{Ag}_7(\text{As},\text{Sb})\text{S}_6$ , sulfosel rare contenant  $\text{As}^{5+}$ , provenant du minerai d'argent à la mine North Lily, district de East Tintic, au Utah, par analyse en diffraction X sur monocristal et par analyse chimique avec une microsonde électronique. La structure de la billingsleyite est identique à celle du composé synthétique  $\text{Ag}_7\text{AsS}_6$ . C'est un minéral cubique, groupe spatial  $P2_13$ , avec un paramètre réticulaire  $a = 10.4760(8) \text{ \AA}$ ,  $V = 1149.7(2) \text{ \AA}^3$ , et  $Z = 4$ . Les résultats d'analyses chimiques indiquent la formule empirique  $(\text{Ag}_{6.94}\text{Cu}_{0.04}\text{Fe}_{0.01})_{\Sigma 6.99}(\text{As}_{0.87}\text{Sb}_{0.13})_{\Sigma 1.00}\text{S}_{6.01}$ . Nous en avons résolu la structure cristalline et nous l'avons affiné jusqu'à un résidu  $R$  de 1.64%. La structure contient des tétraèdres  $(\text{As}^{5+},\text{Sb}^{5+})\text{S}_4$  et des polyèdres renfermant Ag à coordinence 2, 3 et 4, pour former une trame tri-dimensionnelle. Nous précisons les relations structurales avec les thioarsénates et les thioantimonates naturels et synthétiques.

(Traduit par la Rédaction)

*Mots-clés:* billingsleyite, sulfosel contenant  $\text{As}^{5+}$ , affinement de la structure, analyse chimique, échantillon cotype.

<sup>§</sup> E-mail address: luca.bindi@unifi.it

## INTRODUCTION

Billingsleyite, ideally  $\text{Ag}_7\text{AsS}_6$ , is a rare  $\text{As}^{5+}$ -bearing sulfosalt first found at the North Lily mine, East Tintic district, Utah, USA, and reported by Frondel & Honea (1968) during a study of the ore minerals of the silver deposit. The mineral, dark lead-gray in color, was found in small fine-grained aggregates usually associated with argentite, tennantite, bismuthinite, galena and pyrite. Billingsleyite has been reported also from the Clara mine, Oberwolfach, Germany (Blass & Graf 2000) and from the La Guitarra mine, Temascaltepec de González district, Mexico (Camprubí *et al.* 2001). Blass & Graf (2000) limited their study to a SEM-EDX characterization of the new occurrence and reported that the Sb content in the German billingsleyite is very low (as in the type-locality specimen; Frondel & Honea 1968). On the other hand, Camprubí *et al.* (2001) reported a very high content of Sb replacing As (up to 0.7 atoms per formula unit, *apfu*) for the Mexican billingsleyite; indeed, these authors labeled the mineral as "Sb-billingsleyite", and it could represent a new species. However, it is important to note that for both the new occurrences, billingsleyite was not analyzed by X-ray diffraction, and the mineral species was identified only on the basis of the results of chemical analyses.

From a crystallographic point of view, billingsleyite was originally reported as being orthorhombic (on the basis of a powder-diffraction investigation), space group  $C222_1$ , with  $a \approx b = 14.82 \text{ \AA}$  and  $c = 10.48 \text{ \AA}$  (Fronde l & Honea 1968). Later, by considering the close analogy between the powder pattern reported for the mineral (Fronde l & Honea 1968) and that given for synthetic  $\text{Ag}_7\text{AsS}_6$  (Blachnik & Wickel 1980), Bayliss (1990) proposed that the diffraction pattern originally given for billingsleyite should be interpreted in terms of a cubic lattice with  $a = 10.481(4) \text{ \AA}$  and space group  $P2_13$ . Finally, using single-crystal X-ray data, Pertlik (1994) solved and refined the crystal structure of synthetic  $\text{Ag}_7\text{AsS}_6$  in space group  $P2_13$  and confirmed the hypothesis formulated by Bayliss (1990).

Despite the structural results obtained by Pertlik (1994) indicating cubic symmetry of synthetic  $\text{Ag}_7\text{AsS}_6$ , a careful structural study on natural billingsleyite has not been reported so far. To help resolve the concerns related to the structure of billingsleyite, we present crystal-structure data for cotype billingsleyite, together with a crystal-chemical comparison with other  $\text{As}^{5+}$ -bearing sulfosalts occurring in nature.

## OCCURRENCE AND CHEMICAL COMPOSITION

The sample of billingsleyite is from the collection of the RRUFF project (deposition No. R070350; <http://rruff.info/R070350>), donated by Mike Scott, and originally obtained directly from Russell M. Honea. It represents grains of the cotype sample from the North Lily mine, East Tintic District, Utah County, Utah,

USA. This mine and the billingsleyite samples were discovered by Paul Billingsley, an American mining geologist to whom the mineral billingsleyite is dedicated. Geological data for the North Lily mine were summarized by Billingsley & Crane (1933) and by Lovering (1949). The sample consists only of billingsleyite, without any associated minerals. Billingsleyite forms fine-grained aggregates with a dark lead-gray to black color and a metallic luster. It does not contain any inclusions or intergrowths with other minerals.

The chemical composition was determined on the same crystal fragment as the structural study using wavelength-dispersive analysis (WDS) with a JEOL JXA-8600 electron microprobe. Concentrations of major and minor elements were determined at a 20 kV accelerating voltage and a 40 nA beam current, with 15 s counting time. For the WDS analyses, the following lines were used:  $\text{SK}\alpha$ ,  $\text{FeK}\alpha$ ,  $\text{CuK}\alpha$ ,  $\text{ZnK}\alpha$ ,  $\text{AsL}\alpha$ ,  $\text{SeL}\alpha$ ,  $\text{AgL}\alpha$ ,  $\text{SbL}\beta$ ,  $\text{TeL}\alpha$ ,  $\text{AuM}\alpha$ ,  $\text{PbM}\alpha$ ,  $\text{BiM}\beta$ . Zinc, Se, Te, Au, Pb and Bi were found to be below the detection limit of the instrument. The estimated analytical precision (wt%) is:  $\pm 0.50$  for Ag,  $\pm 0.30$  for S,  $\pm 0.15$  for As,  $\pm 0.05$  for Sb and Cu,  $\pm 0.01$  for Fe. We made use of the following standards: native elements for Cu, Ag, Au, and Te, galena for Pb, pyrite for Fe and S, synthetic  $\text{Sb}_2\text{S}_3$  for Sb, synthetic  $\text{As}_2\text{S}_3$  for As, synthetic  $\text{Bi}_2\text{S}_3$  for Bi, synthetic ZnS for Zn, and synthetic  $\text{PtSe}_2$  for Se. The crystal fragment is homogeneous within analytical error. The chemical data, together with their standard deviations, are reported in Table 1. On the basis of 14 atoms, the formula of billingsleyite can be written as  $(\text{Ag}_{6.94}\text{Cu}_{0.04}\text{Fe}_{0.01})_{\Sigma 6.99}(\text{As}_{0.87}\text{Sb}_{0.13})_{\Sigma 1.00}\text{S}_{6.01}$ , and compares well with the original results reported by Frondel & Honea (1968),  $\text{Ag}_7(\text{As}_{0.86}\text{Sb}_{0.14})\text{S}_6$ .

X-RAY CRYSTALLOGRAPHY  
AND CRYSTAL-STRUCTURE DETERMINATION

Several crystals of billingsleyite were selected from the RRUFF sample No. R070350. The diffraction quality of the single crystals was initially checked by means of a Bruker P4 single-crystal diffractometer equipped with a conventional point-detector using graphite-monochromatized  $\text{MoK}\alpha$ . The billingsleyite crystals are very brittle and of a soft platy nature. In fact, most of them produced diffraction effects typical of multiple crystallites. A crystal of relatively high diffraction-quality was selected for the structural study.

The data collection was then carried out with an Oxford Diffraction Xcalibur 3 diffractometer, fitted with a Sapphire 2 CCD detector (see Table 2 for details). Intensity integration and standard Lorentz-polarization correction were performed with the CRYSTALIS RED (Oxford Diffraction 2006) software package. The program ABSPACK in CRYSTALIS RED (Oxford Diffraction 2006) was used for the absorption correction. The values of the equivalent pairs were averaged, and the merging  $R$  factor for the data set in Laue class  $m\bar{3}$

TABLE 1. ELECTRON-MICROPROBE DATA FOR THE BILLINGSLEYITE CRYSTAL SELECTED

	1	2	3	4	5	6	mean
Ag wt%	72.09 (0.61)	72.55 (0.58)	73.28 (0.49)	73.00 (0.63)	72.85 (0.56)	73.26 (0.60)	72.84
Cu	0.33 (0.06)	0.22 (0.05)	0.11 (0.03)	0.22 (0.06)	0.29 (0.05)	0.31 (0.05)	0.25
Fe	0.08 (0.02)	0.11 (0.03)	0.03 (0.01)	0.05 (0.02)	0.04 (0.01)	0.07 (0.02)	0.06
As	6.23 (0.14)	6.66 (0.16)	6.01 (0.17)	6.24 (0.18)	6.42 (0.15)	6.37 (0.13)	6.32
Sb	1.53 (0.04)	1.84 (0.05)	1.30 (0.04)	1.51 (0.06)	1.55 (0.04)	1.42 (0.03)	1.53
S	18.95 (0.31)	18.44 (0.28)	19.12 (0.35)	18.54 (0.42)	18.53 (0.38)	18.81 (0.40)	18.73
Total	99.21	99.82	99.85	99.56	99.68	100.24	99.73
Ag <i>apfu</i>	6.87	6.94	6.95	6.99	6.97	6.95	6.94
Cu	0.05	0.04	0.02	0.04	0.05	0.05	0.04
Fe	0.01	0.02	0.01	0.01	0.01	0.01	0.01
As	0.85	0.92	0.82	0.86	0.88	0.87	0.87
Sb	0.13	0.16	0.11	0.13	0.13	0.12	0.13
S	6.08	5.93	6.10	5.97	5.96	6.00	6.01

Standard deviations are shown in parentheses; atomic proportions are calculated on the basis of 14 atoms.

TABLE 2. CRYSTALLOGRAPHIC DATA FOR THE BILLINGSLEYITE CRYSTAL SELECTED

Crystal data	
Chemical formula	Ag <sub>6.96</sub> Cu <sub>0.02</sub> As <sub>0.88</sub> Sb <sub>0.11</sub> S <sub>6</sub>
Temperature (K)	298
Space group	<i>P</i> 2 <sub>1</sub> 3 (#198)
Cell parameters	<i>a</i> 10.4760(8) Å, <i>V</i> 1149.7(2) Å <sup>3</sup> , <i>Z</i> = 4
Crystal color	black
Crystal shape	block
Crystal size (mm)	0.05 × 0.08 × 0.10
Data collection	
Diffractometer	Oxford Diffraction Excalibur 3
Radiation	MoKα ( <i>λ</i> = 0.71073 Å)
Monochromator	oriented graphite (002)
Scan mode	$\phi / \omega$
$\sin \theta / \lambda_{\max}$ (Å <sup>-1</sup> ), $\theta_{\max}$ (°)	0.672, 28.51
<i>hkl</i> range	-9 ≤ <i>h</i> ≤ 9, -9 ≤ <i>k</i> ≤ 9, -14 ≤ <i>l</i> ≤ 14
No. of reflections	9623
Data reduction	
Absorption correction	multi-scan (ABSPACK; Oxford Diffraction 2006)
No. of independent refl.	902
Criterion for obs. refl.	<i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )
No. of observed refl.	419
<i>R</i> <sub>int</sub>	0.0654
Refinement	
Refinement coefficient	<i>F</i> <sup>2</sup>
No. of refined parameters	46
Weighting scheme	$w = 1 / [\sigma^2(I) + (0.044 \times I)^2]$
<i>R</i> (obs) / <i>R</i> (all)	0.0164 / 0.0191
Diff. Fourier (e <sup>-</sup> / Å <sup>3</sup> )	[-0.52, 0.60]

decreased from 18.30% before absorption correction to 6.54% after this correction. The statistical tests on the distribution of |*E*| values ( $|E^2 - 1| = 0.658$ ) clearly indicate the absence of an inversion center. Systematic

absences (*h*00: *h* = 2*n*) are uniquely consistent with space group *P*2<sub>1</sub>3.

The positions of the Ag atoms, As and three sulfur atoms were determined from three-dimensional Patterson synthesis (Sheldrick 2008). A least-squares refinement on *F*<sup>2</sup> using these heavy-atom positions and isotropic temperature-factors yielded an *R* factor of 10.66%. Three-dimensional difference-Fourier synthesis yielded the position of the remaining sulfur atom. The full-matrix least-squares program SHELXL-97 (Sheldrick 2008) was used for the refinement of the structure. The introduction of anisotropic temperature-factors for all the atoms led to *R* = 1.64% for 419 observed reflections [*F*<sub>o</sub> > 4σ(*F*<sub>o</sub>)] and *R* = 1.91% for all 902 independent reflections with 46 refined parameters (Table 2). In order to check the reliability of the model, the site occupancies of the Ag (*i.e.*, Ag1, Ag2, and Ag3), As and S (*i.e.*, S1, S2, S3, and S4) positions were allowed to vary. The anion sites were found to be fully occupied, and the occupancy factors were then fixed to 1.00. Among the Ag sites, Ag1 was found to show a slightly lower scattering value with respect to that of pure Ag, thus indicating a very minor replacement by lighter elements (*i.e.*, Cu and Fe; Table 3). Arsenic was partially replaced by antimony (Table 3). Scattering factors for Ag, Cu, As, Sb and S were taken from *The International Tables of X-ray Crystallography*, volume IV (Ibers & Hamilton 1974). The inspection of the difference-Fourier map revealed that maximum positive and negative peaks were 0.60 and 0.52 e<sup>-</sup>/Å<sup>3</sup>, respectively.

Experimental details and *R* indices are given in Table 2. Fractional coordinates and isotropic-displacement parameters of atoms are shown in Table 3. In Table 4, we report the anisotropic displacement parameters. A list of the observed and calculated

structure-factors is available from the Depository of Unpublished Data, MAC website [document Billingsleyite CM48\_155].

#### DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Selected distances for the short strong bonds in billingsleyite are given in Table 5, together with those reported for the synthetic  $\text{Ag}_7\text{AsS}_6$  (Pertlik 1994). The crystal structure of billingsleyite (Fig. 1) was found to be topologically identical to that of the synthetic  $\text{Ag}_7\text{AsS}_6$  (Pertlik 1994). It consists of (As,Sb) $\text{S}_4$  tetrahedra and Ag polyhedra forming a three-dimensional framework. In particular, silver adopts various coordinations extending from linear to quasi-tetrahedral (Fig. 2). Atom Ag1 links two sulfur atoms in a linear coordination, with a mean bond-distance of 2.420 Å (Table 5). This value is in excellent agreement with the overall mean  $\langle R(\text{Ag}-\text{S}) \rangle = 2.43$  Å found for the linearly coordinated Ag sites in the pearceite–polybasite group of minerals (Bindi *et al.* 2006, 2007a, 2007b, 2007c, Evain *et al.* 2006). Atom Ag2 is triangularly coordinated by three sulfur atoms with a mean  $\langle R(\text{Ag}-\text{S}) \rangle$  of 2.536 Å (Table 5). This value is in good agreement with both that associated with the Ag(1) position in the crystal structure of stephanite,  $\text{Ag}_5[\text{SISbS}_3]$  (2.54 Å; Ribár & Nowacki 1970), and the Ag position in the

crystal structure of pyrargyrite,  $\text{Ag}_3[\text{SbS}_3]$  (2.573 Å; Engel & Nowacki 1966). Finally, Ag3 adopts a close-to-tetrahedral coordination with a mean  $\langle R(\text{Ag}-\text{S}) \rangle = 2.643$  Å (Table 5), which matches that associated with the Ag(3) position in the crystal structure of stephanite,  $\text{Ag}_5[\text{SISbS}_3]$  (2.68 Å; Ribár & Nowacki 1970).

A peculiar feature of the structure of billingsleyite is the presence of the  $(\text{As}^{5+}, \text{Sb}^{5+})\text{S}_4$  tetrahedra. Indeed, a very limited number of natural sulfosalts correspond to thioarsenates [ $\text{As}^{5+}$ : enargite ( $\text{Cu}_2\text{CuAsS}_4$ ), fangite ( $\text{Ti}_3\text{AsS}_4$ ), and luzonite ( $\text{Cu}_3\text{AsS}_4$ )] or thioantimonates ( $\text{Sb}^{5+}$ : famatinite,  $\text{Cu}_3\text{SbS}_4$ ). Moreover, there is only one structural study of sulfosalts minerals having mixed  $(\text{As}^{5+}, \text{Sb}^{5+})$  tetrahedral positions reported in the scientific literature [*i.e.*, luzonite,  $\text{Cu}_3(\text{As}_{0.64}\text{Sb}_{0.36})\text{S}_4$ ; Marumo & Nowacki 1967]. In Figure 3, we have plotted the  $\langle R[(\text{As}, \text{Sb})-\text{S}] \rangle$  distances for several natural (open circles) and synthetic (crosses) thioarsenates and thioantimonates, together with the data of the billingsleyite crystal studied here (filled square). The equation obtained from the linear fit of the data,  $\langle R[(\text{As}, \text{Sb})-\text{S}] \rangle$  (Å) = 2.409(7) – 0.240(8)(As content in *apfu*) ( $R = 0.993$ ), allows a determination of the As content directly from the bond-distances obtained from the structure refinement. If we observe a mean  $\langle R[(\text{As}, \text{Sb})-\text{S}] \rangle$  bond distance in the tetrahedral group that is greater than 2.289 Å (calculated with As content = 0.50 *apfu*), then

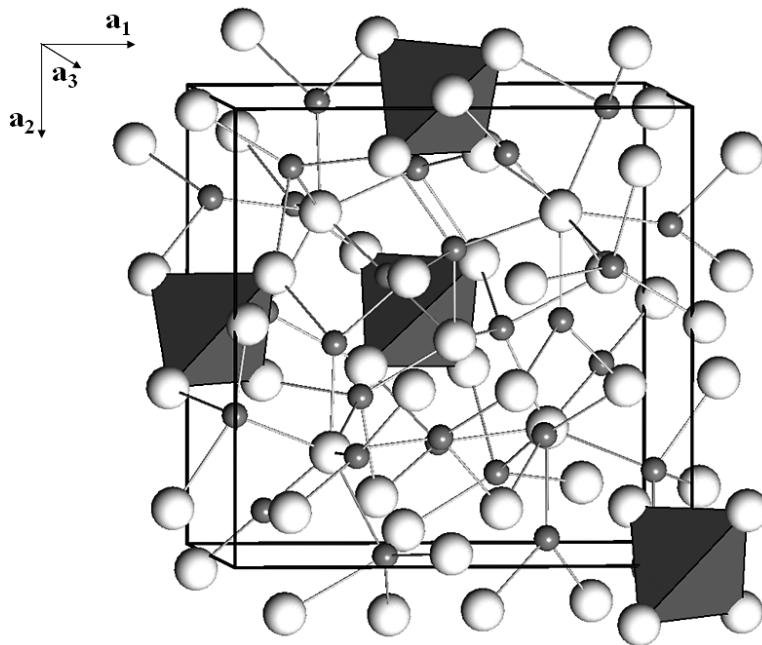


FIG. 1. The crystal structure of billingsleyite projected down [001]. Gray and white circles represent Ag and S atoms, respectively. The  $(\text{As}, \text{Sb})\text{S}_4$  units are depicted as dark gray tetrahedra. The unit cell and the orientation of the structure are outlined.

the mineral will be Sb-dominant. This could provide an important test for potential new mineral species belonging to the thioarsenates–thioantimonates group. In this context, a careful structural analysis of the Sb-rich Mexican billingsleyite described by Camprubí *et al.* (2001) would be worthy of study to verify if it is actually the Sb analogue of billingsleyite.

On the basis of short Ag–Ag separations, Pertlik (1994) suggested that there are Ag–Ag bonds in

TABLE 3. BILLINGSLEYITE: WYCKOFF POSITIONS, SITE-OCCUPANCY FACTORS, FRACTIONAL ATOMIC COORDINATES, AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{Å}^2$ )

Atom	Wyckoff	s.o.f.	x	y	z	$U_{eq}$
As	4a	0.886(5)	0.99834(7)	0.99834(7)	0.99834(7)	0.0202(6)
Sb	4a	0.114	0.99834(7)	0.99834(7)	0.99834(7)	0.0202(6)
Ag1	4a	0.979(4)	0.39542(6)	0.39542(6)	0.39542(6)	0.0198(4)
Cu1	4a	0.021	0.39542(6)	0.39542(6)	0.39542(6)	0.0198(4)
Ag2	12b	1	0.23157(6)	0.02321(5)	0.25897(6)	0.0212(2)
Ag3	12b	1	0.34660(5)	0.82461(6)	0.98492(6)	0.0217(2)
S1	4a	1	0.5304(2)	0.5304(2)	0.5304(2)	0.0213(8)
S2	4a	1	0.8763(2)	0.8763(2)	0.8763(2)	0.0213(9)
S3	4a	1	0.2638(2)	0.2638(2)	0.2638(2)	0.0219(8)
S4	12b	1	0.1226(2)	0.8731(2)	0.1085(2)	0.0241(5)

TABLE 4. ANISOTROPIC DISPLACEMENT PARAMETERS  $U_{ij}$  ( $\text{Å}^2$ ) FOR BILLINGSLEYITE

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
As	0.0202(6)	0.0202(6)	0.0202(6)	-0.0004(3)	-0.0004(3)	-0.0004(3)
Sb	0.0202(6)	0.0202(6)	0.0202(6)	-0.0004(3)	-0.0004(3)	-0.0004(3)
Ag1	0.0198(4)	0.0198(4)	0.0198(4)	-0.0004(3)	-0.0004(3)	-0.0004(3)
Cu1	0.0198(4)	0.0198(4)	0.0198(4)	-0.0004(3)	-0.0004(3)	-0.0004(3)
Ag2	0.0208(4)	0.0215(3)	0.0214(4)	-0.0001(3)	-0.0001(3)	0.0003(3)
Ag3	0.0213(4)	0.0220(4)	0.0220(4)	-0.0001(3)	-0.0002(3)	-0.0001(3)
S1	0.0213(8)	0.0213(8)	0.0213(8)	0.0009(9)	0.0009(9)	0.0009(9)
S2	0.0213(9)	0.0213(9)	0.0213(9)	-0.0002(9)	-0.0002(9)	-0.0002(9)
S3	0.0219(8)	0.0219(8)	0.0219(8)	0.0002(9)	0.0002(9)	0.0002(9)
S4	0.025(1)	0.025(1)	0.023(1)	0.0005(9)	0.0012(9)	0.001(1)

TABLE 5. MAIN INTERATOMIC DISTANCES ( $\text{Å}$ ) FOR BILLINGSLEYITE AND SYNTHETIC  $\text{Ag}_7\text{As}_6\text{S}_6^*$

(As,Sb)	-S4	2.179(2)	[2.174]	(Ag,Cu)1	-S3	2.389(4)	[2.409]
	-S4	2.179(2)	[2.174]		-S1	2.450(4)	[2.428]
	-S4	2.179(2)	[2.174]	<(Ag,Cu)1	-S>	2.420	[2.419]
	-S2	2.214(3)	[2.194]				
<(As,Sb)	-S>	2.188	[2.179]				
				Ag3	-S1	2.517(1)	[2.514]
Ag2	-S4	2.503(2)	[2.509]		-S2	2.577(1)	[2.577]
	-S3	2.543(2)	[2.535]		-S4	2.728(2)	[2.728]
	-S4	2.563(2)	[2.569]		-S3	2.750(1)	[2.750]
<Ag2	-S>	2.536	[2.538]	<Ag3	-S>	2.643	[2.642]

\* Data on synthetic  $\text{Ag}_7\text{As}_6\text{S}_6$  (Pertlik 1994) are given in square brackets for comparison.

billingsleyite. The shortest Ag–Ag contact in our sample is  $R(\text{Ag}2\text{--Ag}3)$ , equal to 2.969  $\text{Å}$ , and only slightly longer than that found in *fcc* Ag metal  $R(\text{Ag--Ag})$ , 2.889  $\text{Å}$  (Suh *et al.* 1988). To investigate this further, we conducted a procrystal electron-density analysis of the billingsleyite structure with the software SPEEDEN (Downs *et al.* 1996). According to Bader (1990) and as reviewed in Gibbs *et al.* (2008) for mineral structures, the existence of stationary points, referred to as bond-critical points, bcp, that occur at local minima,  $\tau_C$ , in

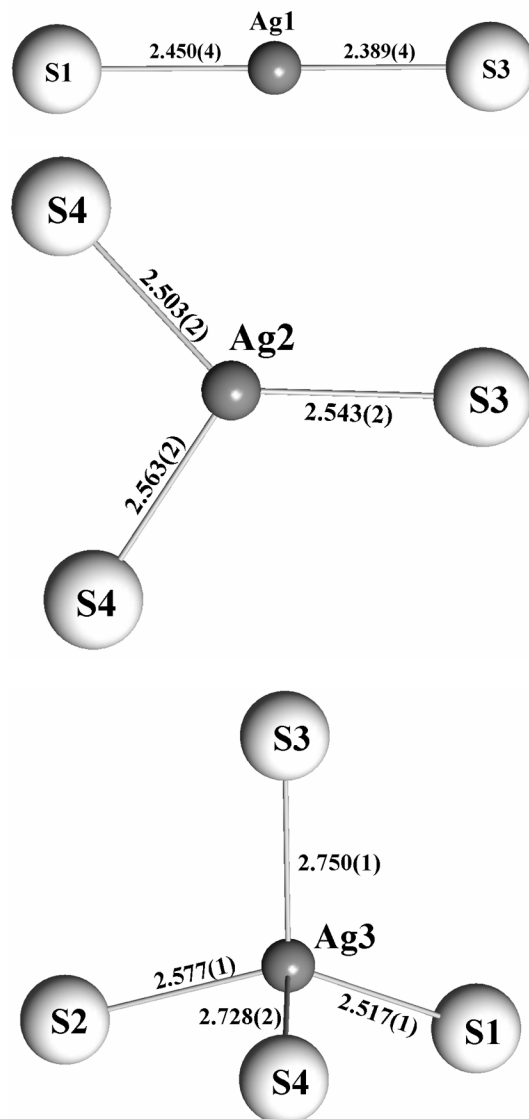


FIG. 2. Coordination polyhedra of the Ag atoms. Colors of atoms as in Figure 1.

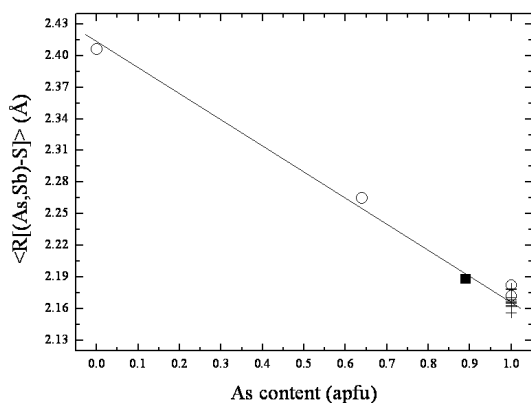


FIG. 3. Relationship between the  $\langle R[(As,Sb)-S] \rangle$  distance (Å) and the As content (apfu) for natural and synthetic thioarsenates and thioantimonates. The filled square refers to our sample of billingsleyite [ $\langle R[(As,Sb)-S] \rangle = 2.188$  Å]. Open circles refer to natural thioarsenates and thioantimonates, as follows ( $\langle R[(As,Sb)-S] \rangle$  distance and reference): enargite,  $Cu_2CuAsS_4$  (2.182 Å; Adiwidjaja & Löhn 1970); fangite,  $Tl_3AsS_4$  (2.170 Å; Wilson *et al.* 1993); luzonite,  $Cu_3(As_{0.64}Sb_{0.36})S_4$  (2.265 Å; Marumo & Nowacki 1967); famatinite,  $Cu_3SbS_4$  (2.406 Å; Garin & Parthé 1972). Crosses refer to synthetic thioarsenates and thioantimonates, as follows:  $Na_3AsS_4 \cdot 8D_2O$  (2.162 Å; Mereiter *et al.* 1982),  $K_3AsS_4$  (2.163 Å; Palazzi *et al.* 1974),  $Tl_3AsS_4$  (2.167 Å; Alkire *et al.* 1984),  $NH_4Ag_2(AsS_4)$  (2.170 Å; Auernhammer *et al.* 1993), and  $Ag_7AsS_6$  (2.179 Å; Pertlik 1994).

the electron-density distribution along the bond path between pairs of bonded atoms is a necessary and sufficient condition to infer that the pair of atoms displays a bonded interaction. Downs *et al.* (2002) demonstrated that the procrystal electron-density model is a useful tool to find bond critical points and provides a good estimate of the electron density,  $\rho(r_C)$ , at the critical points for a large number of oxides.

A bcp was located between Ag2 and Ag3 with  $\rho(r_C) = 0.141$   $e/\text{Å}^3$ , indicating a bonded interaction between the two silver atoms. This finding confirms Pertlik's (1994) suspicion of a Ag–Ag bond. In addition, the procrystal analysis showed that As is only bonded to four S atoms, forming an  $AsS_4$  group, and that there are no S–S interactions. However, additional longer Ag–S bonded interactions were located. Atom Ag1 was found to not only have short bonded interactions to S1 and S3, as discussed above, but Ag1 is also bonded to three equivalent S4 atoms with weak Ag–S4 interactions,  $\rho(r_C) = 0.058$   $e/\text{Å}^3$ , at  $R(Ag1-S4) = 3.596$  Å, forming a trigonal bipyramid. Atom Ag2, in addition to the three short strong Ag2–S and the Ag2–Ag3 bonds, was also found to be bonded to S1 at  $R(Ag2-S1) = 3.103$  Å with  $\rho(r_C) = 0.125$   $e/\text{Å}^3$ . Indeed, Ag2 is not coplanar with its three strongly bonded S atoms, but is it out of the plane toward the S1 atom such that the average  $\langle S1-Ag-S \rangle$  angle is  $95.5^\circ$ . These longer Ag–S bonds can be classified as of van der Waals type and appear to be typical of those observed in arsenic oxide and sulfide compounds, as indicated in the study reported by Gibbs *et al.* (2009),

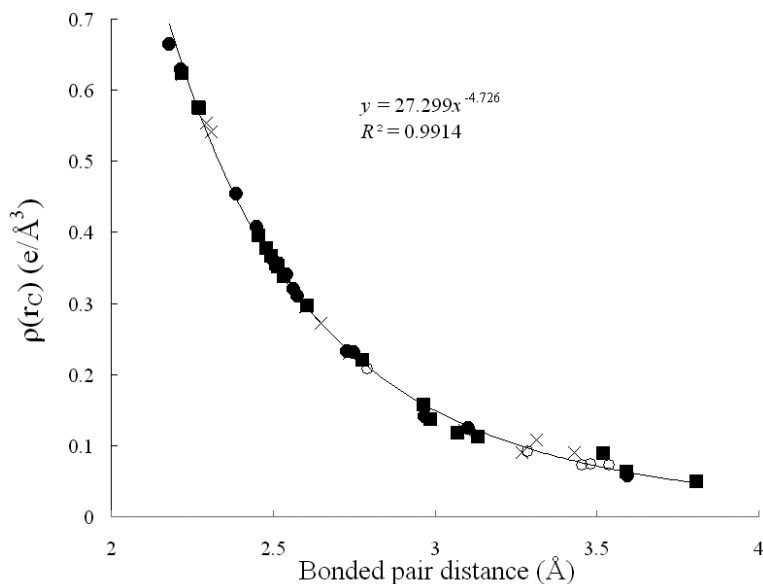


FIG. 4. Bond lengths versus electron density at the bond critical point for the various As–S, As–As, As–Ag, Ag–S, Ag–Ag bonded interactions found in the procrystal electron-density distribution for the sulfosalt minerals billingsleyite (filled circles), xanthoconite (filled squares), trechmannite (crosses) and proustite (open circles).



and can be understood as directed Lewis acid–base pairs. In Figure 4, the values of  $\rho(r_c)$  calculated with the procrystal model are plotted against the interatomic separations for billingsleyite and other silver arsenic sulfosalts including xanthoconite ( $\text{Ag}_3\text{AsS}_3$ ), trechmanite ( $\text{AgAsS}_2$ ), and proustite ( $\text{Ag}_3\text{AsS}_3$ ), representing As–S, As–As, As–Ag, Ag–S, Ag–Ag interactions using structural data from Allen (1985), Matsumoto & Nowacki (1969) and Engel & Nowacki (1968).

In general, these sorts of plots show different trends for different bonded pairs from different rows of the periodic table, e.g., the C–O curve is distinct from the Si–O curve. That the plot for all these different Ag and As bonded interactions shows a single smooth trend demonstrates that these bonds are of the same type.

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