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## BILLINGSLEYITE, A NEW SILVER SULFOSALT

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### ABSTRACT

Billingsleyite is a new silver sulfosalt from the North Lily mine, East Tintic district, Utah. It is associated with argentite, tennantite, bismuthinite, galena and pyrite. Analysis gave Ag 75.59, Cu 0.02, Fe 0.06, As 5.73, Sb 1.50, S 16.28, insol. 0.61, total 99.79, corresponding to  $\text{Ag}_7(\text{As}_{0.86}\text{Sb}_{0.14})\text{S}_6$ . The mineral occurs as fine-grained aggregates with a dark lead-gray color and metallic luster; slightly sectile.  $H=2\frac{1}{2}$ . Billingsleyite is isostructural with synthetic  $\text{Ag}_7\text{SbS}_6$  (space group  $C222_1$ ;  $a=14.96$  Å,  $b=14.99$ ,  $c=10.56$ ; density = 6.00) and synthetic  $\text{Ag}_7\text{AsS}_6$  ( $a\sim b\sim 14.82$  Å,  $c=10.48$ ; density = 5.90). A complete series extends between these end-components; synthetic  $\text{Ag}_7(\text{As}_{0.5}\text{Sb}_{0.5})\text{S}_6$  has  $a\sim b\sim 14.88$  Å,  $c=10.53$ ; density 5.96. The natural material has  $a\sim b\sim 14.8$  Å,  $c=10.4$ ; density =  $5.92\pm 0.02$  (meas.). Indexed X-ray powder diffraction data are cited. In addition to the syntheses by the writers, both end-compositions have been synthesized by Gaudin and McGlashin (1938) and Hall (1965), and  $\text{Ag}_7\text{AsS}_6$  by Roland (1965). The name is given after Paul Billingsley (1887-1962), mining geologist who discovered the North Lily mine and in 1930 collected the only known specimens.

### INTRODUCTION

The mineral here described was found in 1930 in the North Lily mine in the East Tintic mining district, Utah. The North Lily mine was discovered in 1927 by Paul Billingsley (1887-1962), American mining geologist, and the mineral is named in his memory.<sup>2</sup> Brief observations on the geology and mineralogy of the mine are given by Billingsley and Crane (1933) and by Lovering (1949). Billingsleyite is believed<sup>3</sup> to have occurred in a body of high-grade silver ore containing tennantite, bismuthinite, pyrite and galena that was stoped in the Ophir shale above the 1200 level in 1930. Only a few small specimens collected by Bil-

<sup>1</sup> Mineralogical Contribution No. 452.

<sup>2</sup> Headley, M. C. (1964). Name approved by the Commission on New Minerals and Mineral Names, IMA.

<sup>3</sup> Personal communication: Mr. V. D. Perry, Chief Geologist, The Anaconda Company, September, 1957.

lingsley and transmitted by Mr. Robert D. Hoffman to the Harvard Museum appear to have been preserved. Pearceite has been said to occur in this orebody, but the material may have been billingsleyite. We have identified pearceite, however, in ores from other locations in the Tintic district.

#### PHYSICAL PROPERTIES

Billingsleyite occurs as fine grained aggregates with a dark lead-gray color and a metallic luster. The mineral is slightly sectile; it is not malleable, but under heavy pressure in a mortar and pestle crushes to form polished aggregates. The hardness is  $2\frac{1}{2}$ ; the scratch made by a knife blade has a bright metallic luster and a silvery color. The mineral has a more marked metallic character than does pearceite-arsenpolybasite, and tends to lead-gray rather than to iron-black in color. The density of the analyzed natural material as measured on the Berman microbalance varied from 5.6 to 5.9. The variation undoubtedly is caused by minute open pores visible locally in the grains. The higher values,  $5.92 \pm 0.02$ , overlap the values 5.92 interpolated for the present composition from the measured and calculated values of the synthetic end-compositions of the solid solution series,  $\text{Ag}_7\text{AsS}_6$ - $\text{Ag}_7\text{SbS}_6$ , to which billingsleyite belongs (Table 1).

In polished section the mineral is homogeneous. Small areas of argentite were noted in some sections, and the stronger diffraction lines of argentite were observed on some X-ray powder patterns taken of bulk samples.

The etch reactions are similar to those of pearceite except that KOH solution gives a positive reaction. The appearance and etch reactions of the synthetic antimony analogue of billingsleyite,  $\text{Ag}_7\text{SbS}_6$ , are quite similar to those of stephanite. The mineral is conveniently identified by

TABLE 1. UNIT CELL DIMENSIONS OF SYNTHETIC  $\text{Ag}_7\text{SbS}_6$ - $\text{Ag}_7\text{AsS}_6$

	$\text{Ag}_7\text{SbS}_6$	$\text{Ag}_7(\text{Sb}_{0.5}\text{As}_{0.5})\text{S}_6$	Billingsleyite $\text{Ag}_7\text{AsS}_6$
Space group	$C22_1$		
<i>a</i>	14.96 Å	14.88 Å <sup>a</sup>	14.82 Å <sup>a</sup>
<i>b</i>	14.99	14.88 <sup>a</sup>	14.82 <sup>a</sup>
<i>c</i>	10.56	10.53	10.48
<i>G</i> (meas.)	6.00	5.96	5.90
<i>G</i> (calc.)	6.00	5.96	5.90
<i>Z</i>	8	8	8

<sup>a</sup> Cell edges obtained from powder diffraction data in which there is not sufficient resolution of (*h*00) and (0*k*0) to obtain unique values for *a* and *b*.

its X-ray powder pattern (Table 2). The pattern of the natural material and of the synthetic end-compositions are distinct from those of the isodimorphous pearceite-antimonpearceite and polybasite-arsenopolybasite series (Fron del, 1963), in which Cu is an essential component (Hall, 1967), and from those of other silver sulfosalts.

#### X-RAY CRYSTALLOGRAPHY

Single crystals of the natural material were not available, but fragments adequate for X-ray study by single-crystal methods were obtained from a synthetic crystal of the composition  $\text{Ag}_7\text{SbS}_6$ . Cone-axis precession photographs taken along the  $b$  and  $c$  axes together with 0, 1 and 2 level precession photographs taken perpendicular to these axes established the cell dimensions and space group (Table 1). The cell dimensions for synthetic  $\text{Ag}_7\text{AsS}_6$  and  $\text{Ag}_7(\text{As}_{0.5}\text{Sb}_{0.5})\text{S}_6$  were obtained from the spacings of the (800) or (080) and (006) planes as determined from powder photographs (Table 1). There was not a sufficient separation of the ( $h00$ ) and ( $0k0$ ) reflections on these photographs to obtain unique values for the appropriate cell edges. Indexed X-ray powder data for synthetic  $\text{Ag}_7\text{SbS}_6$ ,  $\text{Ag}_7\text{AsS}_6$  and natural billingsleyite (which has an atomic ratio As:Sb = 6.22:1) are given in Table 2. The powder pattern of the natural material unfortunately is of lower quality than those of the synthetic preparations. Film shrinkage could not be evaluated because of the absence of sharp high angle lines and the cell dimensions obtained are of low precision:  $a \sim b \sim 14.8 \text{ \AA}$ ,  $c \sim 10.4$ .

The pseudotetragonal nature of the orthorhombic cell coupled with the relationship  $c = a/\sqrt{2}$  allows powder patterns of the members of the series to be indexed in terms of an isometric cell using the value  $c_0$  of the orthorhombic cell as the cell edge. The X-ray patterns of these phases somewhat resembles that of silver-rich tetrahedrite, with  $a \sim 10.4 \text{ \AA}$ , and their crystal structure similarly may be derived from that of sphalerite but without vacancies,  $\text{Ag}_7(\text{Sb}_1\text{S}_6)$ . There is also a resemblance in the pattern of billingsleyite to that of argyrodite-canfieldite,  $\text{Ag}_8(\text{Ge},\text{Sn})\text{S}_6$ . These substances are closely related dimensionally. Argyrodite is isometric with  $a \cong 21.1 \text{ \AA}$  (Hahn *et al.*, 1965). The  $\text{Ag}_7(\text{Sb},\text{As})\text{S}_6$  cell, with  $c \cong 10.5 \text{ \AA}$  and  $a = b \cong 15.0 \text{ \AA}$ , has one-fourth the volume of the argyrodite cell and is coincident with the halved [100] and [110] periods of that cell.

The measured densities and the densities calculated from the cited formulas for the synthetic material are in agreement (Table 1). The unit cell dimensions and the density decrease with increasing substitution of Sb by As. There are eight formula-units in the cell.

*Chemical Composition.* A chemical analysis of billingsleyite is cited in

TABLE 2. X-RAY POWDER DATA FOR  $\text{Ag}_7\text{SbS}_6$ ,  $\text{Ag}_7\text{AsS}_6$  AND BILLINGSLEYITE

Synthetic $\text{Ag}_7\text{SbS}_6$				Synthetic $\text{Ag}_7\text{AsS}_6$		Billingsleyite	
<i>I</i>	<i>d</i> (meas.)	<i>d</i> (calc.)	<i>hkl</i>	<i>I</i>	<i>d</i> (meas.)	<i>I</i>	<i>d</i> (meas.)
4	6.11	6.11	021	4	6.06	3	6.05
		6.10	201				
2	5.28	5.29	220				
		5.28	002				
1	4.73	4.74	130				
		4.73	310, 112, 221				
1	4.32	4.32	022, 131, 311	1/2	4.29	1	4.27
		4.31	202				
6	3.53	3.53	041, 132, 330	4	3.49	4	3.50
		3.52	401, 312				
5	3.34	3.35	240, 420, 331	3	3.31	2	3.32
		3.34	113				
7	3.19	3.19	023, 241, 421	4	3.16	1	3.16
		3.18	203				
10	3.05	3.06	042	10	3.03	10	3.04
		3.05	402				
5	2.93	2.94	150	5	2.91	4	2.92
		2.93	510, 223, 332				
6	2.83	2.83	133, 151, 511, 242, 422	7	2.80	7	2.82
		2.82	313				
2	2.64	2.65	440	2	2.62	1	2.61
		2.64	004				
1	2.57	2.57	043, 152, 512, 350	1	2.54		
		2.56	114, 403				
6	2.49	2.50	060, 351	7	2.47	8	2.48
		2.49	600, 531, 333, 204				
2	2.43	2.43	061, 601, 243, 423	1	2.40	1/2	2.42
		2.37	260, 620, 442	2	2.36	1	2.36
1	2.37	2.36	224				
4	2.31	2.31	134, 314, 261, 621	3	2.29	3	2.30
		2.26	062, 153	2	2.23	2	2.24
3	2.26	2.25	602, 513				
3	2.16	2.16	044, 404, 262	2	2.14	1	2.16
		2.12	170, 550, 443	2	2.10	1	2.11
2	2.12	2.11	334				
3	2.08	2.08	171, 353, 460, 552	3	2.05	2	2.07
		2.07	115, 244, 711				
5	2.04	2.04	461, 063, 641	4	2.02	3	2.03
		2.03	025, 205, 603				
		1.966	263				
3	1.964	1.965	730	2	1.945	1	1.96
		1.964	154, 712				
		1.963	623				
3	1.932	1.933	462	2	1.912	2	1.92
		1.932	642, 734				
6	1.873	1.874	080	5	1.851	7	1.86
		1.870	830				
1	1.843	1.845	081	1	1.824	1	1.84
		1.841	354, 732, 801				
		1.815	064				
1	1.813	1.814	553, 820	2	1.796	1	1.81
		1.813	713				
		1.789	463				
4	1.788	1.788	821	3	1.771	2	1.78
		1.787	245				

TABLE 2. (Continued)

Synthetic Ag <sub>7</sub> SbS <sub>6</sub>				Synthetic Ag <sub>7</sub> AsS <sub>6</sub>		Billingsleyite	
<i>I</i>	<i>d</i> (meas.)	<i>d</i> (calc.)	<i>hkl</i>	<i>I</i>	<i>d</i> (meas.)	<i>I</i>	<i>d</i> (meas.)
2	1.764	{	1,766 082	1	1.699		
			1,765 660				
			1,764 264				
			1,719 282				
1	1.718	{	1,718 571				
			1,717 373,751				
			1,675 480				
1	1.674	{	1,674 662				
			1,673 840				
2	1.654			2	1.637	1	1.65
1	1.633			1	1.617	1	1.63
1/2	1.615			2	1.579	1	1.59
3	1.595			1	1.562	3	1.555
1/2	1.578			2	1.544	1/2	1.519
3	1.560			1/2	1.511	1	1.497
1	1.529			1	1.482	1	1.436
1/2	1.512			1/2	1.439	1	1.399
1	1.498			1	1.426	1	1.377
1/2	1.482			1/2	1.398	1	1.339
1	1.454			1/2	1.389	1	1.313

Plus additional lines.

<sup>a</sup> Cu radiation, Ni filter ( $\lambda=1.5418 \text{ \AA}$ ), corrected for film shrinkage. Indexing for Ag<sub>7</sub>SbS<sub>6</sub> based on  $a=14.96 \text{ \AA}$ ,  $b=14.99$ ,  $c=10.56$ .

Table 4. The analysis is close to the formula Ag<sub>7</sub>(As<sub>0.86</sub>Sb<sub>0.14</sub>)S<sub>6</sub>, with As:Sb=6.22:1 in atomic ratio. The analysis does not unequivocally establish this formula, however, since it is also close in ratios to several other known or hypothetical silver sulfosalts. That the correct formula is in fact Ag<sub>7</sub>(As, Sb)S<sub>6</sub> is established by the structural identity of the natural material with synthetic phases of the composition Ag<sub>7</sub>AsS<sub>6</sub> and Ag<sub>7</sub>SbS<sub>6</sub> found in the system Ag-Sb-As-S by the writers and by Roland (1965), Hall (1965) and Keighin and Honea (1966). These phases also were obtained by Gaudin and McGlashin (1938) but their composition was not then known. The existence of a complete solid solution series between these compositions has been established by the writers. The name billingsleyite is restricted to that part of the solid solution series with As>Sb in atomic percent.

## SYNTHESIS

A synthetic silver sulfarsenide now known to be isostructural with billingsleyite and the antimony analogue of this compound were first synthesized by Gaudin and McGlashin (1938). These authors state that the two phases were stable products only in those experiments containing excess sulfur, and not in experiments lying on the Ag<sub>2</sub>S-As<sub>2</sub>S<sub>3</sub> or Ag<sub>2</sub>S-Sb<sub>2</sub>S<sub>3</sub> joins. The arsenical phase appeared in experiments with

TABLE 3. CHEMICAL COMPOSITION OF BILLINGSLEYITE

	Ag	Cu	Fe	As	Sb	S	Insol.	Total
1	75.59	0.02	0.06	5.73	1.50	16.28	0.61	99.79
2	76.22	0.02	0.06	5.78	1.51	16.41		100.00
3	73.32			6.10	1.90	18.68		100.00
4	77.00			5.76	1.50	15.74		100.00
5	74.86			5.60	1.46	18.08		100.00

1. Billingsleyite, North Lily mine. Jun Ito, analyst, 1956. Bi absent. Traces of Pb, Zn, Mn and Mg found by optical spectrographic analysis.
2. Analysis 1 recalculated to 100 percent after deducting insoluble (quartz).
3. Theoretical weight percentages for  $\text{Ag}_7(\text{As,Sb})\text{S}_6$  with As:Sb=6.22:1 in atomic ratio.
4. Theoretical weight percentages for  $\text{Ag}_{16}(\text{As,Sb})_2\text{S}_{11}$  with As:Sb=6.22:1 in atomic ratio. This composition represents a copper-free member of the pearceite formula-type.
5. Theoretical weight percentages for  $\text{Ag}_{16}(\text{As,Sb})_2\text{S}_{13}$  with As:Sb=6.22:1 in atomic ratio.

excess sulfur and an  $\text{Ag}_2\text{S}:\text{As}_2\text{S}_3$  ratio of about 9:1 was suggested for this phase. Both Roland (1965) and Hall (1966) synthesized  $\text{Ag}_7\text{AsS}_6$  as a stable phase in the system Ag-As-S. The synthesis of the antimony analogue of billingsleyite ( $\text{Ag}_7\text{SbS}_6$ ) is recorded in the sulfur-rich portion of the system Ag-Sb-S by Hall (1965) and Keighin and Honea (1966).

In the present study, billingsleyite and its antimony and mixed arsenic-antimony analogues were synthesized in sealed silica-glass or

TABLE 4. SYNTHESIS OF BILLINGSLEYITE

Number of runs	Composition	Temperature range	Products <sup>a</sup>
4	$9\text{Ag}_2\text{S}:\text{As}_2\text{S}_5+\text{S}$	206°-487°C	blg+arg+S <sub>liq</sub>
4	$8\text{Ag}_2\text{S}:\text{As}_2\text{S}_5+\text{S}$	307°-405°C	blg+arg+S <sub>liq</sub>
8	$7\text{Ag}_2\text{S}:\text{As}_2\text{S}_5+\text{S}$	195°-487°C	blg+S <sub>liq</sub>
4	$5\text{Ag}_2\text{S}:\text{As}_2\text{S}_5+\text{S}$	206°-487°C	blg+pu+S <sub>liq</sub>
4	$8\text{Ag}_2\text{S}:\text{AsSbS}_5+\text{S}$	307°-405°C	blg <sub>ss</sub> +arg+pu <sub>ss</sub> +S <sub>liq</sub>
12	$8\text{Ag}_2\text{S}:\text{Sb}_2\text{S}_5+\text{S}$	200°-405°C	Sb-blg+arg+pr+S <sub>liq</sub>
6	$7\text{Ag}_2\text{S}:\text{Sb}_2\text{S}_5+\text{S}$	320°-397°C	Sb-blg+arg+pr+S <sub>liq</sub>
6	$6\text{Ag}_2\text{S}:\text{Sb}_2\text{S}_5+\text{S}$	320°-397°C	Sb-blg+arg+pr+S <sub>liq</sub>
4	$5\cdot 5\text{Ag}_2\text{S}:\text{Sb}_2\text{S}_5+\text{S}$	270°-351°C	Sb-blg+arg+pr+S <sub>liq</sub>
2	$5\text{Ag}_2\text{S}:\text{Sb}_2\text{S}_5+\text{S}$	345°-397°C	Sb-blg+arg+pr+S <sub>liq</sub>

<sup>a</sup> blg = billingsleyite, blg<sub>ss</sub> = billingsleyite solid solution, Sb-blg = antimony analogue of billingsleyite, arg = argentite, pu = proustite, pu<sub>ss</sub> = proustite solid solution, pr = pyrrargyrite, S<sub>liq</sub> = sulfur liquid. Vapor present in all experiments.

pyrex tubes containing appropriate amounts of the elements and heated at predetermined temperatures. To reduce vapor space and prevent oxidation the excess volume in each tube was filled with a solid glass rod having a diameter slightly less than that of the tube, and the tube was then evacuated. Starting materials were reagent grade silver metal, reagent grade antimony powder, "purified" arsenic powder, and U.S.P. grade sulfur powder. The powdered arsenic was purged of oxides by heating it in a stream of nitrogen to temperatures above that of volatilization for  $\text{As}_2\text{O}_3$ . In the experiments tabulated in Table 4 an amount of sulfur twice that required by stoichiometric ratios of the sulfides was used, so that all products are in equilibrium with excess sulfur. After weighing, the starting materials were mixed thoroughly in an agate mortar and placed as one-half to one gram charges in glass tubes as described above. After evacuation the tube was sealed approximately two inches above the charge with an oxy-acetylene flame. Continuous temperature records were obtained by use of chromel-alumel thermocouples connected to a Leeds and Northrup recorder. Fluctuations in line voltage resulted in a maximum variation of  $\pm 7^\circ\text{C}$  from the temperature set for the experiment. All experiments were water quenched to room temperature immediately on removal from the furnace.

Products of the various experiments are tabulated in Table 4 along with starting compositions and the heating temperatures. It may be noted that billingsleyite and its antimony analogue form over a wide compositional range. Argentite crystals formed quite readily in many of the runs, both dispersed throughout the charge and as segregated masses at the bottom of the charge. Heating times for the syntheses varied from 2 weeks at the higher temperatures (above  $400^\circ\text{C}$ ) to 34 weeks for the lower temperature experiments (near  $200^\circ\text{C}$ ). The reaction rates were significantly slower at temperatures below  $300^\circ\text{C}$ , and extended heating times were found necessary for more or less complete reaction of the early-formed  $\text{Ag}_2\text{S}$  with the other components of the runs. Larger crystals (to 1 mm) of the billingsleyite analogues were formed only in runs of long duration.

While most of the arsenic runs equilibrated, the products of the antimony-bearing runs represent disequilibrium assemblages of four condensed phases (or five phases including vapor)<sup>1</sup>, and it was not possible in the present study to prepare  $\text{Ag}_7\text{SbS}_8$  as the single silver-bearing phase. Further work on equilibrium relations in the Ag-Sb-S system is in progress and will be reported at a later date. It should be emphasized that X-ray and specific gravity measurements reported in this paper for

<sup>1</sup> Five phases can only occur at an invariant point in a three component system.

the antimony analogue of billingsleyite were obtained from large, homogeneous single-crystals and thus do not represent mixtures. The phase  $\text{Ag}_7\text{SbS}_6$  has also been prepared by heating natural stephanite ( $\text{Ag}_5\text{SbS}_4$ ) in the presence of excess sulfur in an evacuated tube to temperatures above its decomposition at  $197^\circ\text{C}$ . The products of this reaction are pyrargyrite and  $\text{Ag}_7\text{SbS}_6$ . In the absence of sulfur, stephanite breaks down to argenite plus pyrargyrite. Thus the present data support the conclusions of Gaudin and McGlashin (1938) and Hall (1966) that sulfur in excess of that required on the  $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$  join is required, that this phase contains pentavalent antimony and that its composition plots off the argentite-stibnite join.

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