ROBINSONITE, A NEW LEAD ANTIMONY SULPHIDE*

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Abstract

Crystals of robinsonite are triclinic, with probable space group $P\bar{1}$; $a=16.51$, $b=17.62$, $c=3.97$A, $\alpha=96°04'$, $\beta=96°22'$, $\gamma=91°12'$. Slender prismatic [001], striated [001]; also massive, fibrous to compact. Cleavage was not observed; fracture is irregular; brittle, H 2.5–3. Measured specific gravity: 5.27 (artificial crystals), 5.20, 5.25 (natural fragments), 5.34 (artificial fused material), and 5.28 (indirect determination on natural material). Composition and cell content is $7PbS \cdot 6Sb_2S_3$ with calculated specific gravity 5.40. Strongest x-ray powder lines: 4.08A(6), 3.97(6), 3.41(10), 3.19(6), 3.04(6), 2.74(5), 2.68(5).

Robinsonite occurs as a primary mineral with pyrite, sphalerite, stibnite, and boulangerite in small pieces in oxidized ore bodies at the Red Bird mercury mine, Pershing County, Nevada.

Introduction

In 1943 while investigating quicksilver deposits in Nevada, one of the authors (E.H.B.) collected a sample at the Red Bird mine in Pershing County, Nevada, that he suspected of being zinkenite or jamesonite. He sent it, with several other samples, to Washington for identification. An x-ray powder picture taken by Joseph M. Axelrod of the U. S. Geological Survey Laboratories in Washington did not match any pictures found in the literature. This was subsequently confirmed by Martin A. Peacock of the University of Toronto.

Owing to the pressure of other work, nothing more was done on the problem until 1946, when the powder pattern obtained by Professor Peacock was found to be identical with one of several unidentified patterns obtained by Dr. S. C. Robinson[1] at Queen's University during his investigation of the synthesis of lead antimony sulphides (Robinson 1947, 1948a,b). A small specimen was sent to Queen's University for x-ray study; later some of the same material was analyzed in the U. S. Geological Survey (J. J. F.) and proved to be a mixture of boulangerite and the unknown sulphosalt referred to Robinson as "mineral X" with composition close to $7PbS \cdot 6Sb_2S_3$. In 1950, additional artificial material was prepared at Queen's University.

The name robinsonite is given to this new mineral in honor of Dr. Robinson, whose synthesis made its identification possible.

Occurrence (E. H. B.)

The Red Bird mine, where the robinsonite was found, is one of the less

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productive of several quicksilver mines in Pershing County, Nevada. It is in sec. 33, T. 27 N., R. 34 E., on the south slope of Buffalo Mountain at an elevation of about 5,500 feet, and can best be reached by travel over 23 miles of gravel road extending eastward from Lovelock, Nevada. The geology of the mine is described in a report of the strategic minerals program of the U. S. Geological Survey (Bailey & Phoenix, 1944).

The geology of a large region about the Red Bird mine is not well known, although the local geology has been mapped and studied in detail. The rocks consist of a thick sequence of Upper Triassic and Lower Jurassic sediments, which includes limestone, dolomitic conglomerate, sandstone, and shale, and locally these are intruded by small diabasic dikes believed to be late Jurassic in age. The quicksilver ore bodies in the district occur only in the limestone and dolomite beds, generally along faults of small displacement or beneath shale, and they contain cinnabar as the principal ore mineral.

Much of the ore of the Red Bird mine consists of pulverulent cinnabar closely associated with bindheimite, limonite, goethite, cerussite, hemimorphite, and various oxides of antimony. The primary ore is found in the oxidized ore bodies only in small pieces. It consists of pyrite, sphalerite, stibnite, boulangerite, and the new mineral robinsonite. The gangue minerals identified are quartz, calcite, and tarnowitzite, a plumbian aragonite.

The analyzed sample was obtained from a specimen of approximately oval shape, with major and minor axes about 9 and 5 cm respectively and weighing about 650 g. A slab about 1 cm thick was cut through the center and parallel to the longer axis. The core of the slab, which is composed of boulangerite and robinsonite, is lead gray speckled by small inclusions of quartz, usually rimmed by tiny crystals of pyrite. A few small areas of bindheimite are also seen within the boulangerite-robinsonite mass. This mass is completely rimmed by about a centimeter of the alteration product bindheimite. Small inclusions of minium, the red oxide of lead, are found in the bindheimite.

<div align="center">SYNTHETIC MATERIAL (L. G. B.)</div>

Robinson (1948a,b) obtained material, referred to as "mineral X" and giving an x-ray powder pattern identical with that of the mineral described here, by pyrosynthesis from the elements, by hydrosynthesis from alkaline solutions, and by heat treatment (below the melting point) of hydrosynthetic crystals of fuloppite and zinkenite. The material is described as follows:

"The artificial crystals are acicular to bladed, longitudinally striated, and without visible end faces. They are terminated by irregular fracture, and there is no evidence of cleav-

age. In polished section . . . strongly anisotropic, the polarization colors are bluish gray, creamy white and brownish gray; the standard etch reactions are the same as those given by Short (1940) for boulangerite. Distinction is possible with practise by the use of 1:1 KOH solution which etches mineral X in four minutes, boulangerite in ten minutes.

"The molal ratios obtained by means of the Cambridge polarograph for mineral X are Pb:Sb=3.3:6.5 and 4.2:7.9; both are near the proportions in $PbS \cdot Sb_2S_3$ as in zinkenite, and not far from $7PbS \cdot 6Sb_2S_3$."

In 1950 new fusions of Pb, Sb, and S in the proportions of $7PbS \cdot 6Sb_2S_3$ were made at Queen's in evacuated silica-glass tubes. The resulting crystalline buttons appeared homogeneous in polished section and revealed only the x-ray powder pattern of robinsonite. In these fusions the vitreosil tubes of 7-mm bore were kept as short as possible and the whole tube heated in a furnace to prevent condensation of volatiles at the colder end of the tube. This new artificial material has now been analyzed (Table 5).

Physical Properties (J. J. F.)

The specific gravity of the new mineral was necessarily determined by an indirect procedure, because robinsonite is in intimate association with boulangerite, as shown in Fig. 1, and with other materials (quartz, pyrite) that are insoluble in HCl. Using a fused-silica Adams-Johnston
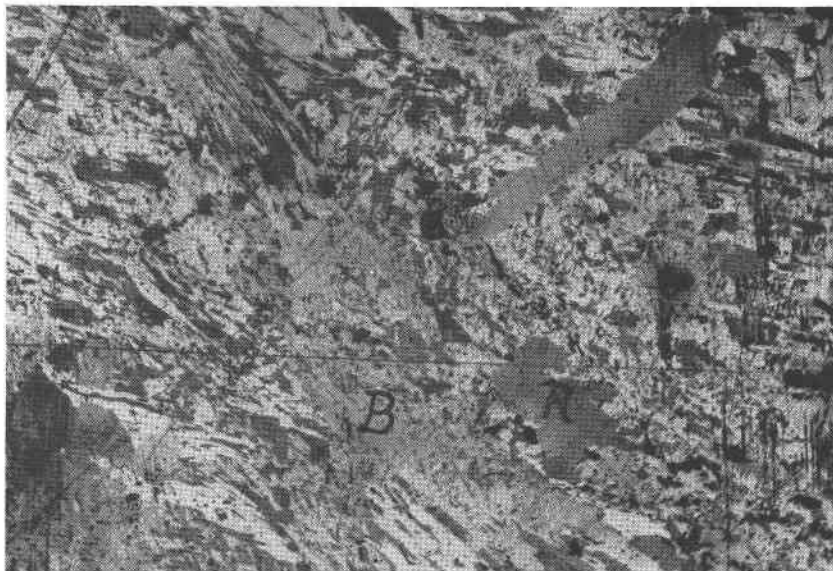

FIG. 1. Photomicrograph of polished section of robinsonite and boulangerite etched with 40% KOH solution applied for 4 minutes. Magnification 100×. The robinsonite (dark) marked "R" on the photograph, is etched; the boulangerite (light), marked "B," is not etched under these conditions. The small black areas are pits in the section.

pycometer of 5-ml capacity, the specific gravity of the sample was determined and found to be 4.790. The "Insol in HCl" portion (19.14% of the sample) was then obtained and its specific gravity (2.762) measured in the same manner. The specific gravity of boulangerite, 6.2, was taken from the literature. From these figures and from the percentages of the three constituents—robinsonite, boulangerite, and insoluble—the specific gravity of robinsonite was computed to be 5.28 at 4° C.

Robinson (1947, 1948b) measured several small samples of the artificial crystals on a Berman balance and found the specific gravity to be 5.27. A similar determination on a fragment from a natural specimen, which did not show boulangerite in polished section or by x-ray, yielded the value 5.20 (Robinson, 1947).

The new artificial material analyzed here (Table 5) gives a specific gravity of 5.34, which is in good agreement with the values given above. The hardness, 2.5–3, the bluish lead-gray color, and the metallic luster are the same as those of boulangerite.

X-RAY MEASUREMENTS (L. G. B.)

Robinson (1948b) described the artificial crystals of "mineral X" [=robinsonite] as "acicular to bladed, longitudinally striated, and without visible end faces. They are terminated by irregular fracture, and there is no evidence of cleavage." From Weissenberg photographs about the axis of elongation, Robinson obtained dimensions for a triclinic unit cell. Previous experience with triclinic crystals has indicated that the

TABLE 1. LATTICE DIMENSIONS OF ROBINSONITE[1]

	Rotation and Weissenberg (Robinson, 1948b)	Precession camera	
		Measurements	Calc. values
$d(100)$	—	16.40 A	
$d(010)$	—	17.52	
$d(001)$	—	3.92	
α^*	84°25′	83°46′	
β^*	83°11′	83°28′	
γ^*	87°52′	88°07′	
a	16.5 A	16.3 A	16.51 A
b	17.7	17.7	17.62
c	3.99	3.97	3.97
α	95°22′	96°17′	96°04′
β	96°39′	96°40′	96°22′
γ	92°06′	—	91°12′

[1] Using CuKα, 1.5418 A and mass factor, 1.6602.

values of α and β are subject to some error when obtained from films about one axis (c) only. Therefore the cell dimensions of Robinson's original crystal were redetermined with the precession camera.

The crystal was first adjusted with the needle axis, c, as the precessing axis. The zero and first-level films yielded values for $d(100)$, $d(010)$ and γ^*, and using the orientation of the pattern on the film, the crystal was readjusted with (100) normal to the spindle of the camera. Several trial cone-axis films were used to locate the b axis as precessing axis and the angle between this axis and the needle axis, read on the drum of the precession camera, is a rough value for α. The zero-level film about b yielded values for $d(100)$, $d(001)$ and β^*. The a axis was located and used as the precessing axis in a similar way, yielding values for $d(010)$, $d(001)$ and α^*. The measurements from the precession films are given in Table 1 together with the values obtained by Robinson (1948b) from the rotation and Weissenberg films about c. The measured spacings and starred angles were obtained directly from zero-level precession films about each axis. These measurements yielded the final calculated values in the last column. The measured values of a, b, and c that were obtained from cone-axis films (in column 2) are not very accurate. The measured values of α and β were read on the drum of the camera and represent the angle through which the crystal was turned from c-axis precession position to the b- and a-axis position respectively.

The natural material, unfortunately, is quite unsuitable for single-crystal study. However, several x-ray powder photographs show patterns that are identical with patterns of the artificial material. One natural crystal fragment yielded a rotation pattern with rather poor diffraction spots that is identical with the rotation pattern from artificial crystals. The crystal was too poor to yield Weissenberg pictures.

The x-ray powder pattern for robinsonite is given by Robinson (1948b). In Table 2 the intensities, measured θ°, and d values are listed for the natural material measured on the original film taken by Professor Peacock at the University of Toronto in 1944 and for the artificial crystals averaged from two visibly identical films taken by Robinson in 1947. The measured spacings agree with one or more calculated spacings down to a spacing of 3.0, and the intensity I (W) of the diffractions for each set of planes observed on Weissenberg and precession camera films is given in the last column. The film of the natural material is very heavily exposed and the films of the artificial crystals are rather lightly exposed; this difference in exposure would probably account for slight differences in intensities. The close similarity clearly establishes the identity of the natural and artificial materials.

TABLE 2. ROBINSONITE—$7PbS \cdot 6Sb_2S_3$: X-RAY POWDER PATTERN

Triclinic $P\bar{1}$; $a = 16.51$, $b = 17.62$, $c = 3.97$ A, $\alpha = 96°04'$, $\beta = 96°22'$, $\gamma = 91°12'$, $Z = 1$

Red Bird mine, Nevada			Artificial crystals			Artificial single crystal		
I	θ(Cu)	d(meas.)	I	θ(Cu)	d(meas.)	(hkl)	d(calc.)	I(W)
1/4	6.0°	7.4 A	1/4	6.0	7.4 A	($\bar{2}10$)	7.522	w
						(210)	7.333	w
1/2	7.4	6.0	1/2	7.3	6.1	($\bar{2}20$)	6.082	m
						(220)	5.885	w
1/2	8.15	5.44	1/2	8.15	5.44	(300)	5.469	w
						(130)	5.443	w
—	—	—	1/2	8.6	5.16	(310)	5.156	w
1/2	10.2	4.35	1	10.1	4.40	(040)	4.378	w
8	11.0	4.04	7	10.9	4.08	(400)	4.100	w
						($\bar{3}30$)	4.055	s
						(410)	3.963	s
8	11.35	3.92	7	11.2	3.97	(330)	3.923	m
						($\bar{1}20$)	3.916	m
6	11.75	3.79	5	11.7	3.80	(240)	3.810	s
						($\bar{2}01$)	3.706	w
6	12.15	3.66	6	12.1	3.68	($\bar{2}11$)	3.692	s
						(420)	3.666	s
						(050)	3.502	s
5	12.85	3.47	3	12.75	3.49	($\bar{3}40$)	3.474	w
						(150)	3.449	m
						($\bar{4}30$)	3.408	s
						(150)	3.402	m
10	13.15	3.39	10	13.05	3.41	($\bar{2}11$)	3.398	m
						(201)	3.391	s
						($\bar{3}01$)	3.374	s
						($\bar{1}31$)	3.307	w
						(121)	3.295	m
—	—	—	1/2	13.6	3.28	(211)	3.264	m
						($\bar{2}31$)	3.261	m
						(250)	3.260	w
6	14.05	3.18	6	14.0	3.19	(510)	3.205	s
						($\bar{2}50$)	3.183	s
						(221)	3.054	s
						($\bar{4}40$)	3.041	s
8	14.75	3.03	6	14.7	3.04	(520)	3.039	s
						(301)	3.028	m
						($\bar{3}31$)	3.018	s

Red Bird mine			Artificial			Red Bird mine			Artificial		
I	θ(Cu)	d(meas.)	I	θ(Cu)	d(meas.)	I	θ(Cu)	d(meas.)	I	θ(Cu)	d(meas.)
—	—	—	1	15.1°	2.96 A	3	23.05°	1.969 A	1/2	23.0°	1.973 A
2	15.55	2.88 A	1	15.45	2.89	6	24.45	1.862	2	24.45	1.862
2	15.95	2.81	1/2	15.85	2.82	4	25.55	1.787	2	25.5	1.791
8	16.25	2.75	8	16.35	2.74	2	26.7	1.716	1	26.55	1.725
8	16.8	2.67	7	16.7	2.68	1/2	27.75	1.656	1/2	27.65	1.661
1	17.35	2.59	3	17.35	2.59	1	29.15	1.583	1	29.05	1.588
—	—	—	1/2	17.75	2.53	2	32.15	1.449	—	—	—
2	19.3	2.33	3	19.2	2.34	2	35.05	1.342	1	35.05	1.342
2	19.85	2.27	1/2	19.9	2.26	1	36.2	1.305	1/2	36.05	1.310
1	20.75	2.18	1/2	20.6	2.19	1	37.15	1.276	1/2	37.05	1.279
—	—	—	1	21.25	2.13	1	38.15	1.248	—	—	—
4	21.4	2.11	3	21.6	2.09	2	40.0	1.199	—	—	—
3	22.1	2.05	1	22.2	2.04	1	53.8	0.955	—	—	—
1/2	22.55	2.01	—	—	—	1/2	58.25	0.907	—	—	—

Chemical Composition (J. J. F.)

A sample of the specimen was prepared for chemical analysis by breaking up into pea-sized pieces selected portions of a sawed slab about a centimeter thick, care being taken to avoid areas of high quartz content. This material was then ground to pass an 80-mesh sieve and that retained on 200 mesh was freed of quartz with methylene iodide. The heavy portion was washed free of methylene iodide with acetone and then allowed to dry in air at room temperature. This material was used for the chemical analysis and the determination of the specific gravity.

TABLE 3. Chemical Analysis of Robinsonite and Boulangerite from Nevada
[Joseph J. Fahey, analyst]

	Per Cent
Pb	36.72
Hg	0.13
Sb	27.44
As	0.48
S	15.15
H_2O	0.90
Insol. in HCl	19.14
	99.96

The sample (2.0875 g) on which the specific gravity was determined was treated in a 500-ml Erlenmeyer flask with 100 ml of H_2O and 300 ml of concentrated HCl. The flask was placed on a steam bath for one hour and then removed and allowed to remain at room temperature overnight. The solution was then filtered through a weighed Munroe crucible and the residue washed with HCl $(3+1)$. The filtrate plus the washings was made up to 500 ml and aliquots were taken for the determination of Pb and Sb, the former being weighed as $PbSO_4$ and the latter determined by titration with permanganate. The residue on the crucible was washed with NH_4OH $(1+1)$ followed by H_2O to remove the As_2S_3, dried for one hour in an oven at 75° C. weighed, and recorded as "Insoluble in HCl" in the analysis. The ammonia solution was acidified with HCl and the arsenic was precipitated with H_2S, filtered on a Monroe crucible, heated for one hour in an oven at 500° C, and then weighed as As_2S_3. Sulphur was determined by wet oxidation with bromine in nitric acid and weighed as $BaSO_4$ in the usual way. A separate sample was analyzed for Hg, which was collected as an amalgam on a preweighed gold bar. Water was determined by the Penfield method. The figure for water (0.90%) recorded in Table 3 was obtained by deducting the water con-

tained in the insoluble portion (0.24%) from total water (1.14%). The rigorous treatment necessary to obtain the "Insol in HCl" portion probably resulted in a water determination on this portion that is a little low. Hence the figure given for H_2O in the analysis would be correspondingly a little too high, probably by several tenths of one percent.

TABLE 4. PERCENTAGE OF ROBINSONITE AND BOULANGERITE IN THE HCl-SOLUBLE
PORTION OF THE SAMPLE

	Robinsonite $7PbS \cdot 6Sb_2S_3$	Pb and Sb in the sample computed to sulphides and calculated to 100%	Boulangerite $5PbS \cdot 2Sb_2S_3$
PbS	45.1%	52.6%	63.8%
Sb_2S_3	54.9	47.4	36.2
	40.1 ←	100.0	→ 59.9

In Table 4 the formula percentages of PbS and Sb_2S_3 in robinsonite and boulangerite are listed with the determined percentages of these two constituents in the analyzed sample, after calculation to 100%. By computation based on the PbS content, the HCl-soluble portion of the sample (approximately 80%) is found to consist of 40.1% of robinsonite and 59.9% of boulangerite. By computation based on the Sb_2S_3 content, these same percentages (40.1% and 59.9%) of robinsonite and boulangerite respectively are obtained.

The ratio of $Pb:Sb_2 = 7:6$ as reported by Robinson is confirmed by the Pb and Sb_2 determinations made on a sample of synthetic robinsonite (Table 5) that appeared homogeneous in polished section and gave an x-ray powder pattern identical with that given by the natural material. A spectrogram by K. J. Murata showed only negligible quantities of impurities.

TABLE 5. PARTIAL CHEMICAL ANALYSIS OF SYNTHETIC ROBINSONITE
[Joseph J. Fahey, analyst]

		Ratios
Pb	$38.6\% \div 207.21 = 0.1863 \div 0.0262 = 7.11$	7
Sb_2	$37.5\% \div 243.52 = 0.1540 \div 0.0262 = 5.88$	6
Specific gravity = 5.34 at 4° C.		

CONCLUSIONS

Artificial crystals of lead antimony sulphide, "mineral X," prepared by Robinson (1947, 1948a,b) by dry fusion of the elements in vacuo and by hydrosynthesis in a bomb, a fusion in vacuo of the elements in the

proportion 7PbS to $6Sb_2S_3$, and an unidentified mineral from the Red Bird mine, Pershing County, Nevada, all give identical x-ray powder patterns. Robinson gives the composition as $PbS \cdot Sb_2S_3$ or $7PbS \cdot 6Sb_2S_3$. The homogeneous fusion, later analyzed, clearly indicates the latter composition. The crystals are triclinic with $a = 16.51$, $b = 17.62$, $c = 3.97$ A, $\alpha = 96°04'$, $\beta = 96°22'$, $\gamma = 91°12'$. The unit cell contains $7PbS \cdot 6Sb_2S_3$ with calculated specific gravity 5.40, which is in good agreement with the measured values, 5.27, 5.20 (Robinson), 5.34 (artificial fusion), and 5.28 (indirect determination on natural material), thus confirming the cell content.

ACKNOWLEDGMENTS

REFERENCES

BAILEY, E. H., & PHOENIX, D. A. (1944): Quicksilver deposits in Nevada, *Nevada Univ. Bull.*, **38**, no. 5, 159–160, 167–168.

ROBINSON, S. C. (1947): The lead-antimony-sulphur system, mineralogy and mineral synthesis—Ph.D. thesis, *Queen's University, Kingston.*

——— (1948a): Synthesis of lead sulphantimonites: *Econ. Geology*, **43**, 293–312.

——— (1948b): Studies of mineral sulphosalts, XIV—Artificial sulphantimonites of lead, *Univ. Toronto Studies, Geol. Ser.*, **52**, 54–70.