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THE COMPOSITION OF THE LEAD SULPHANTIMONIDE, ROBINSONITE

J. L. JAMBOR AND A. G. PLANT
Geological Survey of Canada, Ottawa

ABSTRACT

Robinsonite was defined originally as $Pb_7Sb_{12}S_{25}$, but alternative formulae have been proposed on the basis of recent syntheses. These formulae are examined critically by comparison of compositions and calculated densities with the results of new microprobe analyses of synthetic robinsonite and of material from the type specimen. The theoretical formula of robinsonite may be $Pb_4Sb_6S_{13}$.

RÉSUMÉ

La robinsonite a été définie auparavant comme $Pb_7Sb_{12}S_{25}$, mais d'autres formules basées sur de récentes synthèses ont été proposées. Ces formules sont examinées de façon critique en comparant des compositions et des densités calculées avec les résultats de nouvelles analyses, à l'aide de la microsonde, de robinsonite synthétique et de matériel du spécimen type. La formule théorique de la robinsonite pourrait être $Pb_4Sb_6S_{13}$.

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INTRODUCTION

The lead sulphantimonide known now as robinsonite was synthesized originally by Robinson (1947, 1948a,b), and natural material, from the Red Bird mine, Pershing County, Nevada, was described and named by Berry *et al.* (1952). Based mainly on apparently homogeneous syntheses, and agreement between measured and calculated densities, the formula $Pb_7Sb_{12}S_{25}$ was assigned to the mineral.

The second occurrence of robinsonite, at Madoc, Ontario, was reported by Jambor (1967b), who noted that microprobe analyses of the Madoc mineral and of robinsonite in a fragment from the type specimen gave comparable results that differed substantially from the requirements of the theoretical formula (Table 1). The subsequent discovery and analysis of bismuthian robinsonite from Salmo, B.C. (Jambor & Lachance 1968) supported the earlier microprobe work, thereby also suggesting that the formula $Pb_7Sb_{12}S_{25}$ is incorrect.

TABLE 1. MICROPROBE ANALYSES OF NATURAL AND SYNTHETIC ROBINSONITE

	1	2	3	4			5	6			7	8	9	10	11
Wt. %				(a)	(b)	Average		(a)	(b)	Average		Theoretical $Pb_3Sb_4S_9$	Theoretical $Pb_4Sb_6S_{13}$	Theoretical $Pb_6Sb_{10}S_{21}$	Theoretical $Pb_7Sb_{12}S_{25}$
Pb	45.5	41.5	42.6	41.1	42.5	41.8	42.9	41.1	42.3	41.7	42.2	44.49	41.94	39.67	39.06
Sb	35.4	20.0	35.5	36.2	37.4	36.8	38.0	36.4	37.5	37.0	38.0	34.86	36.97	38.85	39.35
Bi	-	22.0	-	-	-	-	-	-	-	-	-	-	-	-	-
S	20.5	18.0	20.9	21.0	21.6	21.3	21.1	20.8	21.6	21.2	21.1	20.65	21.09	21.48	21.59
Total	101.4	101.5	99.0	98.3	101.5	99.9	102.0	98.3	101.4	99.9	101.3	100.00	100.00	100.00	100.00
Recalculated to 100%															
Pb	44.87	40.89	43.03		41.84		42.06		41.74		41.66	44.49	41.94	39.67	39.06
Sb	34.91	19.70	35.86		36.84		37.35		37.04		37.51	34.86	36.97	38.85	39.35
Bi	-	21.68	-		-		-		-		-	-	-	-	-
S	20.22	17.73	21.11		21.32		20.69		21.22		20.83	20.65	21.09	21.48	21.59

FORMULAE ON BASIS OF 3Pb, 4Pb, 6Pb, 7Pb

	Pb_3 Sb	S	Bi	Pb_4 Sb	S	Bi	Pb_6 Sb	S	Bi	Pb_7 Sb	S	Bi
1.	3.97	8.73		5.29	11.65		7.94	17.47		9.27	20.38	
2.	2.46	8.40	1.58	3.28	11.21	2.10	4.92	16.81	3.15	5.74	19.61	3.68
3.	4.25	9.51		5.67	12.68		8.51	19.02		9.93	22.19	
4.	4.50	9.88		6.00	13.17		8.99	19.76		10.49	23.05	
5.	4.52	9.54		6.03	12.72		9.04	19.07		10.55	22.25	
6.	4.53	9.85		6.04	13.14		9.06	19.71		10.57	22.99	
7.	4.60	9.69		6.13	12.92		9.19	19.38		10.72	22.61	
8.	4.00	9.00		--	--		--	--		---	---	
9.	--	--		6.00	13.00		--	--		---	---	
10.	--	--		--	--		10.00	21.00		--	--	
11.	--	--		--	--		--	--		12.00	25.00	

1. Red Bird mine, Nevada (Jambor 1967b)
2. Salmo, B.C. (Jambor & Lachance 1968)
3. Red Bird mine, Nevada (this study)
4. Synthetic #471, GSC
5. Synthetic #471, CANMET
6. Synthetic #472, GSC
7. Synthetic #472, CANMET
8. Theoretical $Pb_3Sb_4S_9$
9. Theoretical $Pb_4Sb_6S_{13}$
10. Theoretical $Pb_6Sb_{10}S_{21}$
11. Theoretical $Pb_7Sb_{12}S_{25}$

Wang (1973) reported that synthetic phase VI ($Pb_4Sb_{10}S_{19}$) of Salanci & Moh (1970) is identical to robinsonite, but with the *x*-ray powder pattern having "some deviation in intensities". Sugaki *et al.* (1973) reported that they obtained homogeneous robinsonite using $Pb_4Sb_6S_{31}$ as a starting composition. Garvin (1973), in a study of synthetic products in the system Pb-Sb-S, concluded that the formula of robinsonite is $Pb_7Sb_{12}S_{25}$; however, Craig *et al.* (1973), proposed, on the basis of their independent study of the same system, that robinsonite is $Pb_6Sb_{10}S_{21}$.

Syntheses

Because of the above discrepancies, syntheses of robinsonite using $Pb_6Sb_{10}S_{21}$ and $Pb_7Sb_{12}S_{25}$ as starting compositions were done at CANMET (the acronym for Canada Centre for Mineral and Energy Technology, known formerly as the Mines Branch). As preparation of stoichiometric, homogeneous Sb_2S_3 proved difficult, pure elements were used as starting materials. Both charges were sealed in evacuated silica tubes, heated at 560°C for 4 days, quenched, ground and pelletized, and reheated at the same temperature for 3 weeks. Polished sections of the final products showed that each polished surface consisted of >99% robinsonite. However, each surface also contained minute interstitial inclusions of an antimony-rich phase, too small to be analyzed accurately, and too sparse to appear on Debye-Scherrer *x*-ray powder patterns or on a film taken with a Nonius Guinier focusing camera. Moreover, the detection of boulangerite in *x*-ray powder mounts prepared from the exterior surfaces of surplus material showed that the polished surfaces were clearly a misleading indication of the degree of homogeneity of the charges.

Microprobe Analyses

The compositions of robinsonite from the Red Bird mine, Nevada, and the two synthetic samples were determined using a MAC electron microprobe, operated at 20 kV and with a specimen current of 0.03 microamperes measured on galena. The following standards and *x*-ray lines were used: natural galena, assumed to be stoichiometric (Pb$M\alpha$ and S$K\alpha$), and antimony metal (Sb$L\alpha$). The synthetic robinsonites were analyzed in duplicate, each analysis being the average of at least 20 spot measurements. Care was taken to avoid the antimony-rich inclusions. *X*-ray intensity data from the homogeneous areas of the samples were corrected using EMPADR VII (Rucklidge & Gasparrini 1969).

In order to minimize analytical uncertainty arising, for example, from the choice of standards and analytical procedure, subsequent independent analyses of the synthetic robinsonites were done with the MAC microprobe in CANMET, using natural galena (for Pb) and stibnite (for Sb and S) as standards. The results, also corrected using EMPADR VII, are given in Table 1, and are in basic agreement with those obtained at the Geological Survey. The microprobe analyses indicate that the formula of robinsonite is neither $Pb_7Sb_{12}S_{25}$ nor $Pb_6Sb_{10}S_{21}$, but is closer to $Pb_4Sb_6S_{13}$ or $Pb_3Sb_4S_9$. Of the latter pair, $Pb_3Sb_4S_9$ is considered to be less reliable because its derivation is based on analyses that were obtained by direct comparison with unanalyzed natural sulphosalt standards (Jambor 1967a).

Density of Robinsonite

Robinson (1947) obtained a density of 5.27 g/cm^3 from synthetic robinsonite crystals, and 5.20 g/cm^3 from a fragment of the Red Bird material. Synthetic $Pb_7Sb_{12}S_{25}$ prepared by Berry *et al.* (1952) gave a density of 5.34 g/cm^3, and synthetic $Pb_4Sb_6S_{13}$ prepared by Sugaki *et al.* gave a density of 5.73 g/cm^3.

The cell dimensions of synthetic robinsonite as reported by Berry *et al.* (1952), and partly confirmed by Jambor (1968), yield a cell volume of approximately 1141Å^3. For $Pb_7Sb_{12}S_{25}$, Berry *et al.* obtained a calculated density of 5.40 g/cm^3. Table 2 summarizes calculated densities for various formulae and compares these with densities predicted from the Pb/Sb ratios of the compounds (Jambor 1967a). It is evident that, regardless of the formula selected, the density of robinsonite should be within the range of 5.4-5.8 gm/cm^3. On this basis, Pb_3Sb_4-

TABLE 2. COMPARISON OF COMPOSITIONS AND DENSITIES OF HYPOTHETICAL FORMULAE FOR ROBINSONITE

Formula	PbS/Sb_2S_3	Density (g/cm^3) predicted*	Density (g/cm^3) calc.**	Z	Reference
$Pb_7Sb_{12}S_{25}$	1.17	5.4_6	5.40	1	Berry *et al.* (1952)
$Pb_5Sb_8S_{17}$	1.25	5.5_1	7.43	2	Wang (1973)
$Pb_6Sb_{10}S_{21}$	1.30	5.5_3	4.56	1	Craig *et al.* (1973)
$Pb_4Sb_6S_{13}$	1.33	5.5_5	5.75	2	this study; Sugaki *et al.* (1973)
$Pb_4Sb_{5.67}S_{12.70}$	1.41	5.5_9	5.60	2	Red Bird, this study
$Pb_4Sb_{6.02}S_{12.92}$	1.33	5.5_5	5.75	2	synthetic #471, this study
$Pb_4Sb_{6.07}S_{13.03}$	1.32	5.5_5	5.78	2	synthetic #472, this study
$Pb_3Sb_4S_9$	1.50	5.6_8	6.10	3	-----

* based on PbS/Sb_2S_3 versus density (Jambor 1967a).

** using a cell volume of 1141Å^3.

S_9, $Pb_6Sb_{10}S_{21}$, and $Pb_5Sb_8S_{17}$ are improbable candidates for robinsonite. The original formula proposed by Berry *et al.* (1952) has appropriate densities, but the formula is not supported by the microprobe analyses. Thus, $Pb_4Sb_6S_{13}$ may represent the true theoretical composition of robinsonite, and it may be that previously-measured densities of the mineral gave low values. The excellent correspondence between the measured (5.73 g/cm^3) and calculated (5.75 g/cm^3) densities of $Pb_4Sb_6S_{13}$ synthesized by Sugaki *et al.* (1973) would normally support this formula conclusively; however, the *x*-ray powder pattern given by Sugaki *et al.* contains several weak lines which, though indexable, are considered by the present writers to be extraneous to the pattern of robinsonite.

Conclusions

Microprobe analyses and density considerations indicate that the formula of robinsonite is neither $Pb_7Sb_{12}S_{25}$ nor $Pb_6Sb_{10}S_{21}$, but is close to $Pb_4Sb_6S_{13}$. Although the analytical results for the natural and synthetic phases differ, these differences are not detectable in routine *x*-ray powder diffraction studies. The results of this study suggest that robinsonite is non-stoichiometric and may have a small compositional range. The interpretation of lead sulphantimonide compositions in terms of stoichiometric formulae needs to be treated with a caution not appreciated fully in the past.

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