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ADDITIONAL DATA ON ROBINSONITE

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ABSTRACT

Robinsonite has been found in two localities at Vall de Ribes, Spain. Refinement of the X-ray powder-diffraction patterns gave a 16.519(2), b 17.641(2), c 3.971(1) Å, α 96.12(2), β 96.32(2), γ 91.15(1)°. Electron-microprobe analyses of several grains gave a PbS/Sb_2S_3 ratio ranging from 1.32 to 1.44 (mean 1.37). From the analyses and a comparison of calculated and measured densities, the proposed formula for robinsonite is $4PbS \cdot 3Sb_2S_3$.

Keywords: robinsonite, sulfantimonide, sulfosalt, Spain (Vall de Ribes).

SOMMAIRE

Nous avons trouvé la robinsonite en deux endroits à Vall de Ribes (Espagne). L'affinement des paramètres à partir de clichés de poudre donne a 16.519(2), b 17.641(2), c 3.971(1) Å, α 96.12(2), β 96.32(2), γ 91.15(1)°. Les analyses à la microsonde, portant sur plusieurs grains, montrent un rapport PbS/Sb_2S_3 allant de 1.32 à 1.44 (moyenne 1.37). Ces résultats et la comparaison des densités (mesurées et calculées) indiquent pour la robinsonite la composition $4PbS \cdot 3Sb_2S_3$.

(Traduit par la Rédaction)

Mots-clés: robinsonite, sulfantimoniure, sulfosel, Espagne (Vall de Ribes).

INTRODUCTION

Robinsonite is a very rare mineral, and data on natural material are scarce. The crystallographic determination was done by Berry *et al.* (1952) using single-crystal methods from a synthetic compound. The material from Red Bird mine, Pershing County, Nevada, gave similar X-ray powder patterns. Berry *et al.* proposed the formula $7PbS \cdot 6Sb_2S_3$ for the mineral, based mainly on a comparison of calculated and measured densities. Jambor (1967) reported robinsonite from Madoc, Ontario, but the microprobe analyses gave a composition of $3PbS \cdot 2Sb_2S_3$. Jambor & Lachance (1968) reported bismuthian robinsonite from Dodger tungsten mine, Salmo, British Columbia, and gave X-ray powder data from a film. Microprobe analyses gave the formula $8.92PbS \cdot 6(Sb,Bi)_2S_{2.68}$. Jambor & Plant (1975) critically discussed the chemical compositions and deduced the formula $4PbS \cdot 3Sb_2S_3$ for robinsonite, based on microprobe analyses of synthetic material and material from the Red Bird mine, and on a comparison of compositions and calculated densities.

Nevertheless, information on natural robinsonite is still sparse. The present communication furnishes further data, based on the natural occurrence of this mineral at two different localities at Vall de Ribes, Eastern Pyrenees, Spain. The two localities are in the outermost zone of a As–(Bi–Au–Cu)–Sb vein area described by Ayora & Phillips (1981). Robinsonite is found intergrown with quartz in association with sphalerite, boulangerite, zinkenite and stibnite.

X-RAY POWDER DATA

The parameters of robinsonite were obtained from an X-ray powder diffractogram by least-squares refinement of 22 diffraction maxima (Table 1), which were indexed starting from the parameters given by Berry *et al.* (1952). Sodium chloride and quartz were used as internal standards, and the refinement was done with the computer program AFFMAIL, kindly provided by the Laboratoire de Cristallographie et Physique Cristalline, Université de Bordeaux, France.

Most intense reflections have indices ($hk0$), suggesting that robinsonite has a cleavage parallel to 001. As a result, c, α and β parameters show higher relative error.

MICROPROBE ANALYSES

Analyses of 25 different grains from seven polished sections were obtained with the Geoscan Mk–II electron microprobe at the Department of Geological Sciences, University of Durham, U.K. Each result in Table 2 is the mean of three analyses on different points of the same grain. The microprobe was operated

TABLE 1. X-RAY POWDER DATA FOR ROBINSONITE, VALL DE RIBES, SPAIN

I/I_o	d_{meas}(Å)	d_{calc}(Å)	hkl	I/I_o	d_{meas}(Å)	d_{calc}(Å)	hkl
7	7.528	7.525	$2\bar{1}0$	13	2.345	2.345	460*
7	7.342	7.341	210	13	2.280	2.284	$5\bar{3}1$
7	6.084	6.089	$\bar{2}20$			2.283	$7\bar{2}0$
9	5.464	5.470	300*	11	2.191	2.191	080
9	4.383	4.383	040*			2.191	$6\bar{5}0$
46	4.059	4.059	$3\bar{3}0$*	7	2.163	2.163	$1\bar{8}0$
48	3.966	3.967	410*			2.163	$4\bar{6}1$
20	3.928	3.931	330	17	2.130	2.132	$3\bar{6}1$
		3.923	001			2.128	$2\bar{7}1$
35	3.814	3.815	$2\bar{4}0$*	19	2.057	2.057	$3\bar{8}0$*
13	3.710	3.706	$20\bar{1}$			1.986	$6\bar{4}1$*
35	3.671	3.671	420*	24	1.986	1.985	$1\bar{1}2$
20	3.506	3.506	$0\bar{5}0$*			1.985	$4\bar{7}1$
87	3.440	3.436	$0\bar{3}1$			1.983	$8\bar{2}0$
100	3.410	3.410	$4\bar{3}0$*	17	1.980	1.978	$7\bar{5}0$
48	3.210	3.207	$5\bar{1}0$*			1.978	$1\bar{7}1$
9	3.084	3.083	$2\bar{3}1$	9	1.831	1.833	$2\bar{3}2$
		3.080	$1\bar{4}1$			1.829	212
41	3.043	3.042	$5\bar{2}0$*	11	1.818	1.818	$6\bar{7}0$*
17	3.007	3.007	$1\bar{4}1$*			1.798	$0\bar{5}2$
26	2.902	2.902	$5\bar{3}0$*			1.797	$6\bar{6}1$
13	2.838	2.836	$2\bar{4}1$	20	1.797	1.797	$9\bar{2}0$
24	2.806	2.806	$2\bar{3}1$*			1.796	$5\bar{8}0$
30	2.776	2.776	$0\bar{4}1$*			1.796	$8\bar{5}0$
7	2.735	2.735	600			1.723	$1\bar{6}2$
37	2.689	2.689	$6\bar{1}0$*			1.723	$4\bar{8}1$
43	2.670	2.670	$5\bar{0}1$*	11	1.722	1.723	432
17	2.587	2.587	$5\bar{4}0$*			1.722	$0\bar{4}2$
		2.587	$6\bar{2}0$*			1.721	$3\bar{9}1$
7	2.416	2.418	$3\bar{5}1$	7	1.673	1.673	$0\bar{9}1$
		2.417	$2\bar{7}0$			1.672	412
		2.417	$4\bar{6}0$				
		2.414	$4\bar{4}1$				

* Used in the least-squares refinement. Diffractogram obtained with a proportional counter diffractometer, Cu $K\alpha$ radiation, graphite monochromator, ¼° 2θ/minute, 30 mA, 40 kV. The starting parameters were a 16.51, b 17.62, c 3.97 Å, α 96.07°, β 96.37°, γ 91.20° (Berry *et al.* 1952). The refined cell parameters are a 16.519(2), b 17.641(2), c 3.971(1) Å, α 96.12(2)°, β 96.32(2)°, γ 91.15(1)°.

at 15 kV and with a specimen current of 0.04 mA. The standards and lines used were PbS (Pb $M\alpha$) and Sb_2S_3 (Sb $L\alpha$, S $K\alpha$). The count rate used was the arithmetic mean of five 10-second counting periods. The intensities were corrected using an unpublished program by Dr. A. Peckett, from the above-mentioned department.

Fe, Cu and Zn in amounts less than 0.2 wt. % were detected in some analyses. No Bi or As was found and, as shown in Figure 1, the PbS/Sb_2S_3 ratio ranges from 1.32 to 1.44, with a maximum concentration of values around the mean 1.37.

Density Measurements

A crushed sample consisting of 0.40 g of a fine intergrowth of robinsonite and quartz (other minerals were not detected in the X-ray diffractogram), measured by pycnometer, gave a bulk density of 5.11 g/cm³. The SiO_2 content of a split of 0.10 g of the sample was determined, by atomic absorption analysis, to be 17.3 wt. %. Assuming all the SiO_2 to be quartz, the calculated density of the robinsonite is 5.63 g/cm³.

Discussion

Several formulae can be proposed in the PbS/Sb_2S_3 range indicated by the analyses:

TABLE 2. MICROPROBE ANALYSES OF ROBINSONITE FROM VALL DE RIBES, SPAIN

wt.%	1	2	3	4	5	6	7	8	9	10	11	12	13
Pb	42.1	41.7	42.2	41.8	44.9	41.4	43.2	43.2	41.2	42.9	43.0	42.2	42.0
Sb	36.9	36.5	36.6	37.1	36.7	37.0	35.4	36.1	36.7	36.3	35.6	35.6	36.6
S	19.5	20.0	19.4	20.1	19.7	20.7	20.2	20.4	21.1	20.6	19.9	20.6	20.6
Total	98.5	98.2	98.2	99.0	101.3	99.1	98.8	99.7	99.0	99.8	98.5	98.4	99.2
Recalculated to 100%													
Pb	42.7	42.4	43.0	42.3	44.3	41.8	43.7	43.3	41.6	43.0	43.6	42.9	42.3
Sb	37.5	37.2	37.2	37.4	36.2	37.3	35.8	36.2	37.1	36.4	36.2	36.2	36.9
S	19.8	20.4	19.8	20.3	19.5	20.9	20.5	20.5	21.3	20.6	20.2	20.9	20.8

wt.%	14	15	16	17	18	19	20	21	22	23	24	25	
Pb	43.5	42.1	43.0	42.1	42.8	41.6	43.2	43.4	42.4	42.6	42.6	42.7	
Sb	36.3	36.0	36.3	36.2	36.8	37.0	36.5	36.1	36.2	37.1	36.8	36.6	
S	20.6	20.1	20.1	20.5	20.7	20.2	20.6	20.4	20.6	20.8	20.9	20.2	
Total	100.4	98.2	99.4	98.8	99.3	98.8	100.3	99.9	99.2	100.5	100.3	99.5	
Recalculated to 100%													(*)
Pb	43.3	42.9	43.2	42.6	43.1	42.1	43.1	43.4	42.7	42.4	42.5	42.9	41.9
Sb	36.2	36.6	36.5	36.7	36.1	37.4	36.4	36.2	36.5	36.9	36.7	36.7	37.0
S	20.5	20.5	20.3	20.7	20.8	20.5	20.5	20.4	20.8	20.7	20.8	20.3	21.1

(*) Theoretical $4PbS.3Sb_2S_3$

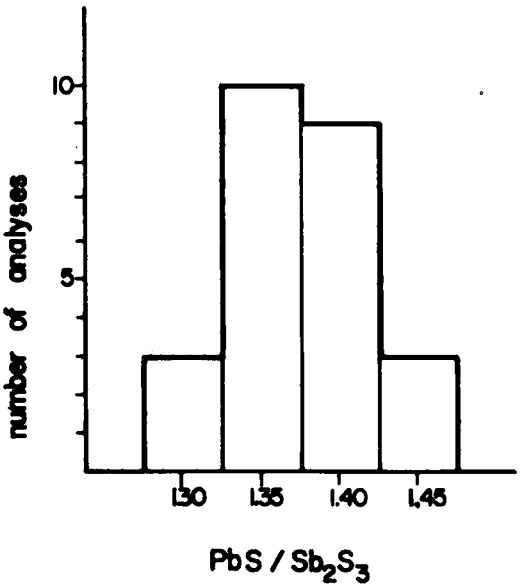

FIG. 1. Histogram showing analyzed compositions of robinsonite from Vall de Ribes, Spain.

(1) $7PbS{\cdot}5Sb_2S_3$ ($PbS/Sb_2S_3 = 1.40$): the calculated density for this formula, using the data in Table 1 ($V = 1143.02$ A^3), would be 4.90 g/cm^3, which is lower than our measured density, making the formula inconsistent. (2) $4PbS{\cdot}3Sb_2S_3$ ($PbS/Sb_2S_3 = 1.33$): the calculated density for this formula, considering $Z = 2$, would be 5.74 g/cm^3, roughly comparable to our measured density of 5.63 g/cm^3. The difference is attributed to systematic errors in the method of estimating density. (3) Although formulae of the type $11PbS{\cdot}8Sb_2S_3$, and higher coefficients, can fit within the PbS/Sb_2S_3 range of the analyses, they would give density values that are too high (more than 7.75 g/cm^3).

The other alternative formula, $7PbS{\cdot}6Sb_2S_3$, has a PbS/Sb_2S_3 ratio of 1.17, too low for the range of compositions indicated by the analyses. The calculated density for this formula would be 5.40 g/cm^3, lower than the measured density. Therefore, according to our analyses of natural material and a comparison of calculated and measured densities, the proposed formula for robinsonite is $4PbS{\cdot}3Sb_2S_3$. This formula is the same as that deduced by Jambor & Plant (1975) from microprobe analyses and from a comparison of compositions and calculated densities of synthetic robinsonites. Nevertheless, it should be noted that the mean of our analyses shows an enrichment of PbS relative to Sb_2S_3 in comparison with this ideal formula. This enrichment in Pb, as well as the systematic low S content of the analyses, could be caused by the effect of the heavy element on the ZAF correction program for matrix effects (Pringle 1979).

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