Canadian Mineralogist
Vol. 20, pp. 97-100 (1982)

RE-EXAMINATION OF ROBINSONITE FROM VALL DE RIBES, SPAIN

J.L. JAMBOR AND D.R. OWENS
CANMET, 555 Booth Street, Ottawa, Ontario K1A 0G1

Abstract

Polished-section study of a robinsonite specimen from Vall de Ribes, Spain, shows that the material consists mainly of intergrown robinsonite and zinkenite. The highest density obtained from an intergrowth fragment is 5.56 g/cm^3, indicating that robinsonite probably has a density of about 5.7 g/cm^3 and that its formula is $Pb_4Sb_6S_{13}$. Zinkenite grains and inclusions associated with robinsonite have the composition $Pb_6Sb_{14}S_{27}$, but a few coexisting inclusions that are also thought to be zinkenite have the composition $PbSb_2S_4$.

Keywords: lead sulfantimonides, robinsonite, zinkenite, density, microprobe analyses, Vall de Ribes, Spain.

Sommaire

L'étude d'une section polie d'un échantillon de robinsonite provenant de Vall de Ribes (Espagne) a révélé que cette matière est principalement composée de robinsonite et de zinckénite en intercroissance. La plus haute densité obtenue à partir d'un tel fragment est de 5.56, valeur légèrement inférieure à celle qui a été déterminée indirectement par Ayora & Gali (1981) pour la robinsonite provenant du même endroit. Ces résultats indiquent que la robinsonite a probablement une densité d'environ 5.7 et que sa formule est $Pb_4Sb_6S_{13}$. Les grains et les inclusions de zinckénite associés à la robinsonite ont une composition de $Pb_6Sb_{14}S_{27}$, mais certaines inclusions co-existantes que l'on croit aussi être de la zinckénite ont la composition $PbSb_2S_4$.

(Traduit par la Rédaction)

Mots-clés: sulfantimonides de plomb, robinsonite, zinckénite, densité, analyse à la microsonde, Vall de Ribes (Espagne).

Introduction

The formula $Pb_7Sb_{12}S_{25}$ was given to robinsonite in the original description by Berry *et al.* (1952), but various alternative compositions, deduced mainly from syntheses, have since been assigned to the mineral. The consensus in recent years seems to favor the formula $Pb_4Sb_6S_{13}$ as proposed by Jambor & Plant (1975). One of the difficulties in discriminating between the recent and original formulas is that their element weight percentages do not differ radically if the elements have been determined by electron microprobe and the raw data have been processed with programs that utilize different correction factors (*cf.*, Pringle 1979).

A critical property for differentiating between the $Pb_4Sb_6S_{13}$ and $Pb_7Sb_{18}S_{25}$ alternatives is density: the first formula gives a calculated value of about 5.74 g/cm^3, whereas the other gives about 5.40 g/cm^3. This criterion was discussed by Jambor & Plant (1975), but the range in measured densities of robinsonite was too great to establish unequivocal correspondence with one specific calculated value. Resolution of the problem seemed possible upon the report of a new occurrence of robinsonite at Vall de Ribes, Spain. This robinsonite, subsequently described by Ayora & Gali (1981), seemed to have considerable potential for a good determination of density, as well as for the first single-crystal X-ray measurements on natural material. Ayora and Gali kindly provided some of their material for these studies.

Sample Preparation

The samples received from Ayora and Gali consisted of a finely powdered sulfosalt concentrate and a rock chip approximately 0.5 x 1.0 x 1.5 cm. The latter, which was the only material studied in detail, consisted largely of quartz with liberal amounts of the sulfosalt at one edge. The sample was cut in three with a low-speed, thin-blade diamond saw, so that each of the resulting wafers contained the sulfosalt edging. The wafers were examined under a binocular microscope, and from each a sulfosalt-rich area containing the smallest amount of quartz was detached. The density of each of the three sulfosalt-rich fragments was determined with a Berman balance prior to mounting in a polished section. Although two of the samples contain visible quartz inclusions, these could not have been removed without appreciable fragmentation of the samples.

Density

The measured density of synthetic robinsonite has been determined as 5.21 to 5.32 (Robinson 1947), 5.34 (Berry *et al.* 1952), 5.41 (Petrova *et al.* 1978), and 5.73 g/cm^3 (Sugaki *et al.* 1973). The first values are appropriate for $Pb_7Sb_{12}S_{25}$, but the last value indicates that the formula is incorrect. There is, however, some question as to whether the highest value was obtained from pure material (Jambor & Plant 1975).

For natural robinsonite, Robinson (1947) obtained 5.20 g/cm^3, stated as a rough determination on impure material. In their preliminary study of the Vall de Ribes robinsonite, Ayora & Gali obtained 5.35 g/cm^3 by pycnometer measurement of a separate containing an undetermined amount of quartz. Subsequently, or contemporaneously with the present study, Ayora & Gali (1981) chemically determined the silica content of a bulk sample of robinsonite that had given a measured density of 5.11 g/cm^3; they deducted the analytically determined 17.3 wt. % SiO_2 as quartz, and thereby obtained a recalculated density of 5.63 g/cm^3 for robinsonite. However, this value evidently was obtained by an additive procedure: density of mixture = (wt. % quartz x density of quartz) + (wt. % robinsonite x density of robinsonite). Dr. J.A. Mandarino has pointed out (written communication) that the correct equation is: density of mixture = mass of mixture/V, where V is the sum of the volumes of quartz and robinsonite. Solution of the equation using the bulk density and the weight percentages reported by Ayora & Gali (1981) gives a recalculated density of 6.33 g/cm^3 for robinsonite.

The three sulfosalt-rich fragments studied here weighed 11.4, 7.7, and 7.6 mg and gave respective measured densities of 5.23, 5.33, and 5.56 g/cm^3. The highest density was obtained from the sole quartz-free sample. As the Vall de Ribes robinsonite is associated with sphalerite, boulangerite, zinkenite, stibnite, and quartz (Ayora & Gali 1981), contamination by any of these minerals except boulangerite would lead to low measured densities. On the other hand, incorporation of about 20% boulangerite (density 6.2 g/cm^3) and exclusion of other contaminants is necessary for the formula $Pb_7Sb_{12}S_{25}$ to be valid for the sample with the highest measured density.

Microscopy and Microprobe Studies

Polished-section examination of the robinsonite fragments shows that they are similar and are all mixtures of lead sulfantimonides ± quartz. The quartz-free fragment contains a few specks of pyrite, the largest about 20 x 20 μm, and also has a small amount of an unidentified, translucent, antimony-rich oxide that is present mainly in hairline veinlets. However, robinsonite and zinkenite make up about 97–98% of the polished surface. Trace amounts of a phase with the composition $PbSb_2S_4$ occur as minute inclusions, but no boulangerite or other sulfosalts were found.

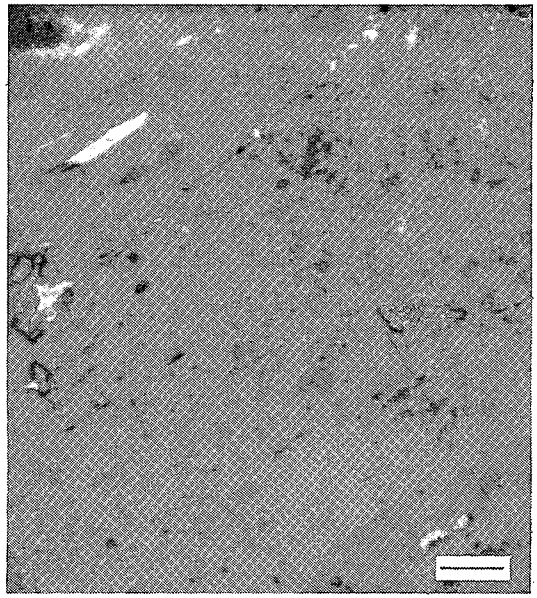

FIG. 1. Matrix of robinsonite riddled with blebs of zinkenite ($Pb_6Sb_{14}S_{27}$) and with irregular grains of pyrite (py) and a row of dark inclusions of the $PbSb_2S_4$ phase (2). Partly crossed nicols, reflected light, air; bar scale represents 0.05 mm.

The largest single grain of robinsonite is only about 0.1 x 0.05 mm, but homogeneous, multigrain areas of the mineral are several times larger. Several grains show indications of a perfect cleavage parallel to the elongation, as has been suggested by Ayora & Gali (1981). Zinkenite occurs as irregular patches intergrown with robinsonite, and in some areas makes up 25 to 50% of the sulfosalts present. Abundantly interspersed among the homogeneous robinsonite grains and the robinsonite–zinkenite intergrowths are inclusion-riddled grains in which the blebs vary from abundant (Fig. 1) to only sparsely disseminated. Except for rare grains of the $PbSb_2S_4$ phase, the inclusions are zinkenite in a host of robinsonite. It is estimated that robinsonite constitutes about ⅔ of the polished surface, with zinkenite making up the bulk of the remainder.

Microprobe analyses of the sulfosalts were obtained with a Materials Analysis Company

TABLE 1. MICROPROBE ANALYSES OF VALL DE RIBES SULFOSALTS

	robinsonite		zinkenite	$PbSb_2S_4$ phase
wt %	1*	2	2	2
Pb	42.9	42.6	32.7	37.4
Sb	35.8	36.3	44.4	41.9
Cu	n.d.	n.d.	0.3	0.04
Ag	n.d.	n.d.	0.08	n.d.
S	21.1	21.1	23.0	20.6
	99.8	100.0	100.48	99.94
	23 atoms		47 atoms	7 atoms
Pb	4.11	4.07	5.96	1.08
Sb	5.83	5.90	13.76	2.06
Cu			0.18	
Ag			0.03	
S	13.06	13.02	27.08	3.85
Pb/Sb_2	1.41	1.38	0.87	1.05
Theor.	1.33	1.33	0.86	1.00

*1 and 2 are different fragments used for the density measurements; n.d. is not detected; Bi, As, Cl also not detected

(model 400) instrument operated at 20 kV and a specimen current of 0.03 μA. The standards used were meneghinite (Tuscany) and zinkenite (Wolfsberg) for Pb$M\alpha$, Sb$L\alpha$ and S$K\alpha$, argentopyrite for Ag$L\alpha$, and synthetic $Cu_{11}FeSb_4S_{13}$ for Cu$K\alpha$. For Cu and Ag the 10-second counting periods were increased to 50 seconds so that the limits of detection were 0.06 wt. % for Ag and 0.04% for Cu. Data were processed using a modified version of EMPADR VII (Rucklidge & Gasparrini 1969).

Microprobe analyses of homogeneous robinsonite from two of the fragments used for the density measurements (Table 1) give results similar to those obtained by Ayora & Gali (1981) and close to the formula $Pb_4Sb_6S_{13}$. Judging from the proportion of zinkenite (S.G. 5.30–5.33: Palache *et al.* 1947) in the quartz-free fragment studied here, it seems probable that robinsonite has a density of about 5.7 g/cm^3. For example, if the fragment contains 25 to 35 wt. % zinkenite, the corresponding range for the calculated density of robinsonite is 5.64 to 5.75 g/cm^3.

Cell Dimensions

Attempts to obtain single-crystal data from fragments of the largest homogeneous grain of robinsonite produced only broad lines rather than sharp spots. The effect might be due to multiple slight offsets along the perfect cleavage, but more likely reflects distortion induced during removal from the polished section.

Single-crystal data for robinsonite are based solely on synthetic material, for which three different unit cells have been proposed: *a* 16.51, *b* 17.62, *c* 3.97 Å α 96°04′ β 96°22′ γ 91°12′ (Berry *et al.* 1952); *a* 16.56, *b* 17.69, *c* 3.982 Å, α 91.09°, β 96.46, γ 96.77° (Petrova *et al.* 1978); *a* 32.85, *b* 23.64, *c* 3.97 Å, γ 131°57′ (Wang 1977). Although the symmetries obtained by Berry *et al.* (1952) and Wang (1977) differ, both these lattices can be reduced to dimensionally equivalent monoclinic cells. Similar reduction applied to the triclinic cell of Petrova *et al.* (1978) does not give satisfactory results. More work is needed to demonstrate whether only the monoclinic cell of Wang is valid for all synthetic robinsonite.

Despite the symmetry and parameter variations indicated above, all three robinsonite cells give a calculated density of approximately 5.7 g/cm^3 for $Pb_4Sb_6S_{13}$. Cell volume (2290 Å^3) and $Z(4)$ of the monoclinic cell are double those of the triclinic cells.

$PbSb_2S_4$ Phase

Results of a microprobe analysis of the Vall de Ribes zinkenite are given in Table 1. The composition is close to $Pb_6Sb_{14}S_{27}$, and the very slight departure from stoichiometry correlates well with structural incorporation of copper, as noted by Moëlo (1978, written comm. 1981).

A second phase that also occurs as inclusions in robinsonite is not optically distinctive, and was initially detected on electron back-scatter images. Microprobe analysis of this sparse phase indicates an approximate composition $PbSb_2S_4$ (Table 1); supplementary analyses consistently confirm the excess of Pb + Sb relative to S.

Owing to the small amount and small grain size of the $PbSb_2S_4$ phase, only a poor X-ray powder mount was obtained for the Debye–Scherrer and Gandolfi exposures. Although the powder-diffraction lines are weak, they indicate that the mineral is not twinnite, guettardite, or any of the profusion of compounds of approximate composition $PbSb_2S_4$ that have been synthesized (Sugaki *et al.* 1973, Wang 1973, 1976, Chang *et al.* 1980). Instead, the pattern seems to be mainly that of zinkenite with enlarged cell parameters and possibly some difraction-line shifts.

There have been numerous discussions as to whether zinkenite is $PbSb_2S_4$ or $Pb_6Sb_{14}S_{27}$, but only recently has the crystal-structure character of the mineral been defined (Portheine & Nowacki 1975, Lebas & Le Bihan 1976). The latter authors concluded that the formula of zinkenite is $Pb_{1+n}Sb_{4-n}S_7$ with $0.50 \leq n \leq 0.67$. This variability corresponds to a composition range from $Pb_6Sb_{14}S_{27}$ to $PbSb_2S_4$. Thus the simplest conclusion is that the two extreme limits of zinkenite composition are represented in coexisting inclusions in the Vall de Ribes robinsonite. However, neither Portheine & Nowacki (1975) nor Lebas & Le Bihan (1976) discussed the structural role of copper in zinkenite, whereas Moëlo's (1978) data indicate that zinkenite specimens with high Pb/Sb atomic ratios should be the most enriched in minor elements. Even though Moëlo's results do not extend along the full composition range to Pb/Sb = 0.5, the minor-element relationship introduces an additional uncertainty about the identification of the Vall de Ribes $PbSb_2S_4$ inclusions because these are almost copper-free (Table 1).

Acknoledgements

The writers are pleased to acknowledge the generosity of Carles Ayora and Salvador Gali, who provided the Vall de Ribes material. Technical assistance at CANMET was given by J.H.G. Laflamme and E.J. Murray, and X-ray examination of the robinsonite fragments was done by A.C. Roberts of the Geological Survey of Canada. The comments and unpublished data provided by Y. Moëlo, Orléans, France, are much appreciated. The writers also grateful to J.A. Mandarino of the Royal Ontario Museum, Toronto, for detection of the flaw concerning the additive procedure to recalculate density and for permission to use this information here.

References

Ayora, C. & Gali, S. (1981): Additional data on robinsonite. *Can. Mineral.* **19**, 415-417.

Berry, L.G., Fahey, J.J. & Bailey, E.H. (1952): Robinsonite, a new lead antimony sulphide. *Amer. Mineral.* **37**, 438-446.

Chang, L.L.Y., Walia, D.S. & Knowles, C.R. (1980): Phase relations in the systems $PbS–Sb_2S_3–Bi_2S_3$ and $PbS–FeS–Sb_2S_3–Bi_2S_3$. *Econ. Geol.* **75**, 317-328.

Jambor, J.L. & Plant, A.G. (1975): The composition of the lead sulphantimonide, robinsonite. *Can. Mineral.* **13**, 415-417.

Lebas, G. & Le Bihan, M.-T. (1976): Etude chimique et structurale d'un sulfure naturel: la zinckénite. *Soc. franç. Minéral. Crist. Bull.* **99**, 351-360.

Moëlo, Y. (1978): Minor constituents of acicular lead sulphantimonides; their part in conditions of formation of these sulphosalts. *Int. Mineral. Assoc., XI Gen. Meet. (Novosibirsk)* **1**, 138 (abstr.).

Palache, C., Berman, H. & Frondel, C. (1947): *The System of Mineralogy. I.* John Wiley & Sons, New York.

Petrova, I.V., Kaplunnik, L.N., Bortnikov, N.S., Pobedimskaya, E.A. & Belov, N.V. (1978): Crystal structure of synthetic robinsonite. *Dokl. Akad. Nauk SSSR* **241**, 88-90 (in Russ.).

Portheine, J.C. & Nowacki, W. (1975): Refinement of the crystal structure of zinckenite, $Pb_6Sb_{14}S_{27}$. *Z. Krist.* **141**, 79-96.

Pringle, G.J. (1979): Electron microprobe analysis of a seleniferous bismuth sulphosalt: correction for matrix effects. *Geol. Surv. Can. Pap.* **79-1C**, 111-115.

Robinson, S.C. (1947): *Lead–Antimony–Sulphur System: Mineralogy and Mineral Synthesis.* Ph.D. thesis, Queen's Univ., Kingston, Ontario.

Rucklidge, J.C. & Gasparrini, E. (1969): EMPADR VII. Specifications of a computer program for processing electron microprobe analytical data. *Dep. Geol., Univ. Toronto.*

Sugaki, A., Shima, H. & Kitakaze, A. (1973): Synthetic sulfide mineral (V).*Tech. Rep. Yamaguchi Univ.* **1**, 183-194.

Wang. N. (1973): A study of the phases on the pseudobinary join $PbS–Sb_2S_3$. *Neues Jahrb. Mineral. Monatsh.*, 79-81.

——— (1976): Crystallography. *In* Experimental and Descriptive Ore Mineralogy (G.H. Moh, ed.). *Neues Jahrb. Mineral. Abh.* **128**, 167-175.

——— (1977): The symmetry of robinsonite. *Neues Jahrb. Mineral. Monatsh.*, 501-503.

Received October 1981, revised manuscript accepted December 1981.