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DISTRIBUTION OF SILVER AND BISMUTH IN BANSKÁ ŠTIAVNICA ORE VEINS

(Tabs. 5)

A b s t r a c t: Discrimination of both elements in the Štiavnica veins depends on the primary mineralization zoning, and at the same time, silver shows the indirect and bismuth direct dependency on thermality. The largest amount of silver came from the uppermost (Au-Ag) paragenetic zone and mainly in the form of Ag Sb-sulphosalts. In the intermediate (Pb-Zn) zones both elements occur exclusively in the isomorphic form in sulphides, mainly in galenite. The most part of bismuth occurs in the deepest (Cu) zone in the form of Cu-Bi and Cu-Pb-Bi and rarely also in Ag-Bi sulphosalts.

Р е з ю м е: Распределение обоих элементов в штиавницких жилах зависит от первичной зональности минерализации, и одновременно, серебро проявляет непрямую и висмут прямую зависимость от термальности. Самое большое количество серебра происходит из высшей (Au-Ag) парагенетической зоны и особенно в форме Ag, Sb сульфосолей. В середних (Pb—Zn) зонах оба элементы находятся лишь в изоморфной форме в сульфидах, главным образом в галените. Чаще всего висмыт находится в самой глубокой (Cu) зоне в форме Cu—Bi и Cu—Pb—Bi и редко также в Ag—Bi сульфосолях.

The importance of both elements under consideration seems substantially different for Štiavnica ore veins. While silver was the main mining product in the past, the existence of bismuth has, in fact, been unknown, until lately.

Distribution of silver and bismuth in Štiavnica ore district exhibits strong dependence on primary zoning of mineralization. Its regularities have been sufficiently known so far (K o d ě r a, 1963), therefore, only a brief characteristics will be given.

In Štiavnica veins, two essential types of zoning can be found:

a) the monoascending, occurring exclusively within individual mineralization periods and closely related to thermality and

b) the polyascending, being the consequence of regular space functioning of the individual mineralization periods within the deposit. Combination of mono- and polyascending zoning results in *complex zoning,* in which several paragenetic zones can be distinguished and on the basis of their spatial distribution it is possible to state the whole character of zoning in the deposit. The zones manifest as follows (in the surface — depth trend):

1. The zone enriched in Ag and Au — it formed the surfacemost parts of the veins, it had been exploited years ago, therefore, its detailed characteristics does not seem necessary.

2. The upper Pb—Zn zone — it is characteristic by polymetallic mineralization of older ore-bearing period and quartz—carbonate mineralization of the younger ore-bearing period. The zone reaches the depth of 150—200 m.

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3. The lower Pb—Zn zone is characterized by polymetallic mineralization in both ore-bearing periods with vertical extent 300—400 m.

4. The copper zone — only the products of the youngest periods (4—6) are present, whilst the ore-bearing period seems to be the only one in quartz — chalcopyrite development. Its depth is over 500 m.

The following sections of this paper are concerned with distribution of silver and bismuth with regard to the mentioned paragenetic zones.

Silver

The Štiavnica veins offered a considerable amount of silver in the past. High ore contents — over 1000 g/t appeared in subsurface parts of veins, ie. in zone anriched in silver and gold. The majority of silver occurred in the form of individual Ag minerals, particularly Ag—Sb sulphosalts — stephanite, polybasite, Ag—As sulphosalts — proustite and pearceite; argentite and silver were also present. A part of them originated probably as a secondary product of the processes in oxidized and cementation zones. Only a small part from the total silver content in this paragenetic zone occurs as isomorphic admixture in sulphides, mainly in galenite. When passing to the upper and the lower Pb—Zn zones, considerable decrease of silver can be observed. The values of silver contents are only some tens g/t. It is due to the fact that individual Ag minerals are hardly traceable in these paragenetic zones. The whole content occurs in common sulphides, mostly in galenite, in which the Ag contents vary within the range 100 to 1000 ppm, sporadically also more, and at the same time, with the depth (growing thermality) its content gradually decreases. In both other main sulphides — sphalerite and chalcopyrite the silver contents are substantially lower. The distribution of silver in galenite, sphalerite and chalcopyrite in individual mineralization periods and paragenetic zones, is listed in Table 1 (values are given in arithmetic means).

In the highest thermal copper paragenetic zone the content of silver in ores is lower. This is due to the rapid decrease of galenite proportion in ores (from the main mineral to the accessory). Galenite itself does not show marked decrease of silver content, corresponding to increased thermality. On the contrary, certain galenites, mainly those from the 4th mineralization period exhibited strongly increased Ag contents, which considerably exceeded the upper detection limit of quantitative spectral analysis — 1000 ppm. At the same time, these contents were accompanied by increased bismuth content, although, on the whole, both in ores and in galenite itself, these two elements show strong negative correlation.

A special attention was devoted to the mentioned high silver contents accompanied by increased bismuth content, discovered in certain galenites and chalcopyrites in the copper paragenetic zone indicating the presence of individual Ag minerals, so far known only from higher (lower-temperature) paragenetic zones. As a matter of fact, their presence was confirmed with microscopic methods. In certain galenites, sporadically also in chalcopyrites, rarely in quartz, irregular grains, fine-grained aggregates and small veinlets of Ag minerals were found. Their precise identification seems very difficult even with the help of electron microprobe analysis because of very small size (less than 0.01 mm). The analyses are listed in Table 2.

Although the analyses are not definitely reliable (because of size of analyzed grains) and they are treated more as the orientation values, on the basis of analyses it is possible to state the presence of at least two different Ag minerals. However, it is not possible to parallelize them with any of so far known minerals with regard to their chemical composition. Minerals from the bore-hole KOV — 41 (analyses numbers 1.2) should belong to Ag—Cu—Bi sulphosalts, which have been unknown until now. Some of Ag—Bi, Ag—Cu, and/or Cu Bi sulphosalts (matildite, stromeyerite, wittichenite, hodrushite and so on) were most probably submicroscopically intergrowing there.

Table 1

Distribution of silver in galenites, sphalerites and chalcopyrites on the basis of quantitative spectral analyses (in arithmetic means)

Mineral		Galenite			Sphalerite		Chalcopyrite
Miner. period		2	4	6	4	6	4
Upper Pb—Zn parag. zone		420/3	406/4	355/2	28.4/8	23.4/9	53/3
Lower Pb—Zn parag. zone	a	286/3	354/7	230/1	55.5/6	10.4/8	65/4
	b	206/4	250/19	104/1	7.7/9	70.5/4	95/10
Copper parag zone	a	225/4	634/17	260/1	12.6/8	8.3/6	129/26
	b	178/1	397/14		16.7/6		41/12

Table 1, 3: analysed by J. Chudý.

Explanations: values in numerator — arithmetic means in ppm, values in denominator — numbers of analyses.

Table 2

Ag sulphosalts of the 4th mineralization period

No.	Locality / Elements	Bi	Pb	Ag	Cu	S	Σ
1	Bore-hole KOV—41 in m 1036.5	15.5	tr.	50.4	18.5	16.0	100.5
2	— // —	27.4	tr.	34.2	17.9	16.5	96.0
3	Bore-hole EBV—9/90 in m 224	34.1	tr.	49.7	6.1	16.9	106.9
4	Bore-hole VŠ—8 in m 527.5	36.5	tr.	41.6	5.1	22.4	105.7

Table 2, 4, 5: analyzed by J. Krištín using the electron microprobe analyzer JXA — 5A.

On the contrary with the preceding ones, analyses number 3 and 4 show low copper content, therefore, they are probably Ag Bi sulphosalts. The low copper content may be due to the presence of some of Cu sulphosalts (analysis 3) or chalcopyrite (analysis No. 4), where its presence is indicated also by the increased content of sulphur. From Ag Bi sulphosalts pavonite — Ag_2S . . $3Bi_2S_3$ (Ag=21.5 %, Bi=62.5 %, S=16 %) and matildite — Ag_2S . Bi_2S_3 (Ag=28.3 %, Bi=54.8 %, S=16.8 %) are known so far. However, both analyses contain substantially lower Bi and higher Ag contents, therefore, it may be so far unknown mineral from Ag—Bi sulphosalts with the most probable ratio $3Ag_2S$. Bi_2S_3 (theoretical composition being Ag=51.4 %, Bi=33.2 %, S=15.3 %.

Inclusions of Ag minerals in copper zone were found out also in galenite from the 6th mineralization period. The electron microprobe analysis (the semiquantitative one) detected only substantial portions of silver and sulphur. It is probably argentite, the quantitative analysis may confirm that. Different character of Ag minerals in the 6th mineralization period within the copper paragenetic zone is closely connected with substantially lower thermality of the 6th mineralization period on the contrary to the 4th period, approximately by 100 °C.

Bismuth

The occurrence of bismuth in Štiavnica ores seems only a very small one. There do not exist any data on bismuth presence in the zone enriched in gold and silver. In the upper and lower Pb—Zn zones bismuth is in isomorphic relation exclusively with galenite of the 4th period, while its amount considerably varies, yet, the maximum average contents occur at the copper zone boundary. The bismuth contents highly increase in the central part of the copper zone, where the part of bismuth occurs heterogeneously as individual Bi minerals. Distribution of bismuth in galenite and chalcopyrite in the individual mineralization periods and paragenetic zones is listed in Table 3 (values are given in arithmetic means).

Individual bismuth minerals have been discovered so far only in the copper paragenetic zone; their occurrence is characteristic for its central part (subzone „b"). From three periods, which form the vein filling, the bismuth minerals have been found only in the 4th and the 5th mineralization periods. None of them is traced in the youngest 6th period. Detected Biminerals in both periods belong to Cu—Bi and Cu—Pb—Bi sulphosalts. Also Ag—Bi sulphosalts occur, but as already mentioned above, only rarely.

Precise identification of Bi sulphosalts is very complicated. As Ag sulphosalts — the main problem lies in small size of the grains, whereas in the case of Cu—Bi and Cu—Pb—Bi sulphosalts, their inhomogeneity — mutual intergrowth, aswell as variable chemical composition of the individual minerals hinders precise identification.

Bi sulphosalts of the 5th mineralization period

Bi-sulphosalts in this period exhibit relatively abundant occurrence at the Rosalia vein, where the copper paragenetic zone reaches the surface and can be followed in vertical extent over 500 m. In deeper parts of the Rosalia vein in the vein filling the 5th mineralization period is occurring in the quartz — hematite development with accessory presence of ore minerals — chalcopyrite, galenite and pyrite. From this vein, the first Bi minerals from the Štiavnica—Hodruša ore district were described: rézbányite (Koděra, 1965) and the new Cu—Bi sulphosalt — hodrushite (Koděra — Kupčík — Makovický, 1970). Bi sulphosalts occur in the oldest part of this mineralization period in aggregates of lath-shaped hematites. They form the lath-shaped and needle-shaped grains and totally irregular aggregates intensively replaced by hematite.

Microscopic characteristics : Bi minerals are of light-creamy colour, the reflectivity being relatively lower than that of galenite, strong anisotropy, the lack of internal reflections. The electron microprobe analyses indicate mutual intergrowth of both sulphosalts, the Cu Bi sulphosalt — hodrushite and that of Cu Pb Bi sulphosalt — aikinite. Hodrushite shows a little stronger anisotropy and also stronger bireflectance in relation to aikinite. Analyses of both minerals are listed in Table 4.

According to the original analysis, hodrushite contains 14.1—15.0 % Cu, 63.8—66.0 % Bi and 21.1—19.1 % S. Bismuth content is nearly identical. Little higher content of copper and sulphur is probably due to submicroscopic ad-

Table 3

Distribution of bismuth in galenites and chalcopyrites on the basis of quantitative spectral analyses (in arithmetic means)

Mineral		Galenite			Chalco-pyrite
Mineral. period		2	4	6	4
Upper Pb—Zn parag. zone		5/3	113/4	0/2	3/3
Lower Pz—Zn parag. zone	a	0/3	28/7	0/1	0/4
	b	0/4	288/19	0/1	9/10
Copper parag. zone	a	8.2/4	7/17	0/1	81/26
	b	0/1	1890/14		65/12

Explanations: values in numerator — arithmetic means in ppm, values in denominator — number of analyses.

Table 4

Bi sulphosalts of the 5th mineralization period

No.	Elements Locality	Bi	Pb	Ag	Cu	S	Σ	Mineral
1	Bore-hole K-5 in m 28	65.20	0.01	0.01	17.925	22.6	105.24	hodrushite
2	—„—	34.96	38.590	0.004	13.825	17.580	104.96	aikinite

mixture of chalcopyrite, which was manifested also in the total sum of analyzed elements.

Aikinite, according to the handbook „Minerals" (1960), shows the following, variation of main element contents: Cu — 14.4—11.3 %, Pb — 35.3—49.3 %, Bi — 30.4—36.2 %, S — 15.7—16.7 %. Comparison with the mentioned analysis manifests identity of Bi portion (34.96 %) and Pb (38.95 %), while increased Cu and S contents probably come from chalcopyrite.

The presence of rézbányite, identified with the help of microscopic methods and powder diffraction patterns, has not been confirmed yet.

Table 5

Bi sulphosalts of the 4th mineralization period

No.	Elements Locality	Cu	Pb	Bi	Ag	S	Σ	Mineral
1	Rosália vein (bore-hole K— 5)	11.608	45.079	25.38	0.009	18.164	100.238	
2	—„—	11.975	45.662	25.77	—	16.634	100.036	A
3	—„—	13.301	44.831	25.96	0.009	19.345	103.442	
4	—„—	44.230	0.002	26.02	1.91	24.80	96.96	B
5	—„—	44.826	0.02	30.35	1.726	25.039	101.945	

Bi sulphosalts of the 4th mineralization period

The presence of Bi sulphosalts in this mineralization period was found out at the Rosalia vein and in several other bore-holes reaching the copper zone. They are less freguently occurring than in the 5th mineralization period. They appear mostly in chalcopyrite, rarely in galenite or independently among the grains of quartz or pyrite. Again, occurrence of two Bi sulphosalts can be observed, which are mutually intergrowing, while their mutual portion is strongly varying. They form irregular and oval grains mostly of size under 0.01 mm, lath-shaped and/or fine-grained aggregates to discontinuous rims at the contact of chalcopyrite and quartz.

Microscopic characteristics: in thick section mineral „A" is grey-coloured with weak creamy tint, it is anisotropic, without stronger bireflectance with reflectivity considerably lower than that of chalcopyrite. On the basis of electron microprobe analysis, it belongs to Cu—Pb—Bi sulphosalts. Mineral „B" is of white colour, similar to galenite, the reflectivity being almost identical with that of chalcopyrite. It shows strong anisotropy and weak bireflectance. It belongs to Cl—Bi sulphosalts.

Chemical composition of both minerals was determined by means of electron microprobe analysis. While in the 5th mineralization period it was possible to identify Bi sulphosalts quite reliably as hodrushite and aikinite, sulphosalts of the 4th mineralization period do not show stronger concordance in chemical composition with any definitely known mineral. The most reliable data, until now, have been gained from the Rosalia vein (bore-hole K-5) and they can be found in Table 5. Since the results of several analyses are very similar, there do not appear analytical errors and/or the mixture of several minerals. Most probably, they are some rare Bi sulphosalts, the chemical composition of which has not been definitely known yet. The possibility of completely new minerals is not out of question.

Mineral „A" belongs to Cu-Pb-Bi sulphosalts and it is ranged among the bournonite group. Its chemical composition is most close to aikinite, yet, the Cu Bi ratio is considerably higher in favour of Pb.

Mineral „B" is probably Cu-Bi sulphosalt, the group of emplectite, which is the most close to wittichenite. Nevertheless, it has higher Cu-Bi ratio in favour of copper, although, certain increase of copper and sulphur contents from the neighbouring chalcopyrite could have taken place in both analyses.

Conclusions

New knowledge on the distribution of silver and bismuth in Štiavnica ore veins, mainly the occurrence in diverse sulphosalt types, provide an interesting topic not only from the mineralogical point of view. Their prevailing concentration in the central part of the copper paragenetic zone can be of economic importance as well. For that reason, it will be necessary to observe systematically the quantitative portion of both elements in ores when exploiting in these parts of veins.

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