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GOLD-BEARING ARSENOPYRITE OF THE PEZINOK ANTIMONITE DEPOSIT

(*Figs. 15, Tabs. 3*)

Abstract: Arsenopyrite of the Pezinok antimonite deposit has been attracting attention of geologists for ten years since more attention is paid to the discovered As : Au correlation. The main knowledge on the gold-bearing arsenopyrite generation is summarized and the possibility of studying sulphidic minerals by means of an electron scanning microscope and energy-dispersion analyser is mentioned in the paper. The results obtained are compared with those of an electron microanalyser and the outcomes of thermoelectric voltage measurements of the studied mineral are given.

Резюме: Арсенопирит из сурьмяного месторождения Пезинок является в центре внимания геологической общественности больше десяти лет, с тех пор уделяется повышенное внимание обнаруженной корреляции As : Au. В статье подытоживаются основные информации о золотоносной генерации арсенопирита. Отмечаются возможности исследования сульфидных минералов растровым электронным микроскопом и энерго-дисперсионным анализатором. Сравниваются результаты полученные электронным микроанализатором и приводятся результаты измерения термоэлектрического напряжения исследованного минерала.

Arsenopyrite is the principal As-bearing mineral at the Pezinok deposit. Mrákava (1977) gives the Sb : As ratio of 2 : 1.14 at the deposit. The occurrence of arsenopyrite is not mentioned in older literature. Munda (1944 in Cambel, 1959) infers its presence only from the As content of the antimony ores.

Cambel (1950, 1959) has described only one arsenopyrite generation at the Pezinok deposit, which crystallized from solutions of the oldest quartz-pyrite-arsenopyrite period. According to Cambel (1959) arsenopyrite sometimes originates by replacement of syngenetic or hydrothermal pyrite. Cambel, however, does not remember this alleged statement. He only stated pyrite anisotropy due to an increased As content in pyrite, but apparatuses available at that time could not have proved it. Dadák (1983) has described high Sb contents (up to 9.17 %) in some arsenopyrites of the Pezinok deposit.

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The presence of two arsenopyrite generations at the deposit has been noted for the first time by Polák — Rak (1979). Later it turned out that the idiomorphic fine-grained arsenopyrite I has a larger, and often separate, spatial distribution independent from the main carbonate-antimonite mineralization (Polák — Rak, 1979; Dadák, 1983). As this arsenopyrite is not associated with antimony minerals it is only rarely mined and therefore remained unnoticed for a long time.

Andráš (1983) pointed out that the gold-bearing fine-grained idiomorphic arsenopyrite I originated in the course of the oldest (quartz-arsenopyrite) hydrothermal period. It may represent an independent mineralizing stage, the products of which are highly sericitized black quartz lenses with gold-bearing arsenopyrite and pyrite impregnations. Andráš (1983) gives an average Au content of 110 ppm in arsenopyrite and 57 ppm in pyrite (Andráš et al., 1987).

Sampling and investigation methodics

All gold-bearing arsenopyrite I samples have been taken at the Pezinok deposit in the adit Budúcnosť. Samples of the granular coarse-grained arsenopyrite II come from the Antimony adit.

Samples chosen for further investigations have been studied first by means of a polarizing microscope and electron microanalyser. Later, in the following stage of the investigation, the samples have been crushed. The flotation concentrate has been cleaned visually using a binocular microscope. Quantitative spectrochemical (arsenopyrite I) and atomic absorption spectrometric (arsenopyrite II) analyses have been carried out afterwards. Principal investigations have been performed by an electron scanning microscope JSM-840 and X-ray electron microanalyser Superprobe 733 (Jeol), Edax PV-9100 and X-ray emission analyser NZ-854 of the Geochemical Department of the Hungarian Academy of Sciences in Budapest.

The illustrated composition (phase composition) facilitates homogeneity and inclusion studies. Combination of the information on the morphology and composition of the same mineralogical individual is an asset.

Point quantitative analyses (analysed by an additional energy-dispersion analyser) have been added to these data.

Thermoelectric voltage has been measured by an adapted ore microscope MIN 9 on ore mineral polished sections in measurement points of the microanalyser NZ-854. The methodics is described in detail by Ďurža (1981) and Gajdoš — Ďurža (1981).

Gold-bearing arsenopyrite occurrences

The arsenopyrite I forms impregnations of small idiomorphic to hypidiomorphic grains or spongy aggregates intergrown with the gold-bearing pyrite II, which accompanies the former (Fig. 1). The arsenopyrite I : pyrite II ratio varies from 5:1 to 10:1. The younger antimony mineralization only very rarely spatially overlaps with the gold-bearing sulphidic one.

Fig. 1. Sample RB-50, disseminated structure of arsenopyrite I (light-coloured) and pyrite II (Py). Magn. 32×, 1 nicol.

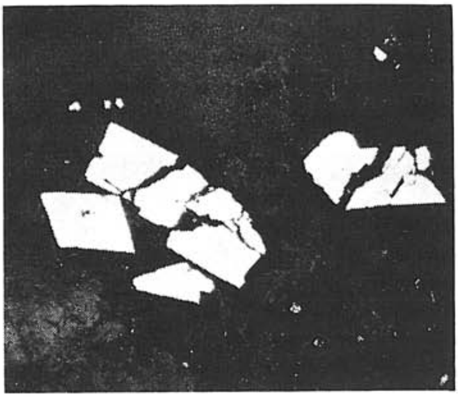


Fig. 2. Sample PA-78, panidiomorphic-grained brecciated texture of arsenopyrite I (light-coloured) in quartz (dark), Magn. 32×, 1 nicol.

The arsenopyrite I is preferentially associated with black quartz lenses or occurs in the surrounding hydrothermally altered rocks of a shale formation in which it forms tiny impregnations (Figs. 1, 2).

Microscopic description

The arsenopyrite is well polishable and is of light yellow to light gray colour. It is marked for very high reflectance and weak bireflectance. Diagnostic etching by nitric acid stains the arsenopyrite colourfully and in the air these coatings gradually get dark. The gold-bearing idiomorphic arsenopyrite I has distinct coloured anisotropic effects (light yellow-brown to dark brown-blue) and high anisotropy can be observed in immersion oil. Zoning sporadically occurs in typical rhombic cross-sections of prismatic crystals.

The arsenopyrite II, that originates by replacement of older pyrite, can be distinguished from the arsenopyrite I for its allotriomorphic grains, different structures and lower reflectance.

Both arsenopyrites I and II are often tectonically fractured and the fissures are usually filled with undulose pressure quartz.

Structures and textures of arsenopyrite ores

There are two basic types of arsenopyrite ore structures at Pezinok:

1. The first structure is nest structure, typical for gold-bearing arsenopyrite I (Figs. 1, 2).

2. Disseminated structure, which is the principal structure of the coarse-grained arsenopyrite ores of younger generation (with Au contents up to O.X ppm). The subtype of brecciated massive structure can be distinguished (Fig. 4).

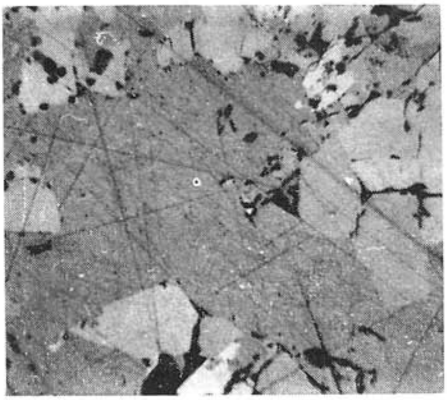


Fig. 3. Sample RB-109, massive structure and allotriomorphic-grained texture of arsenopyrite II. Magn. 32×, x nicols.

Fig. 4. Sample RB-4, brecciated massive structure of arsenopyrite II (light-coloured) in quartz (dark). Magn. 32×, 1 nicol.

There exist also two kinds of textures:

1. Arsenopyrite I forms panidiomorphic to hypidiomorphic textures (Fig. 1)·
2. Arsenopyrite II is granular and occurs in allotriomorphic textures (Fig. 3). The brecciated subtype can be set up in both main types.

Morphology of gold-bearing arsenopyrite I crystals

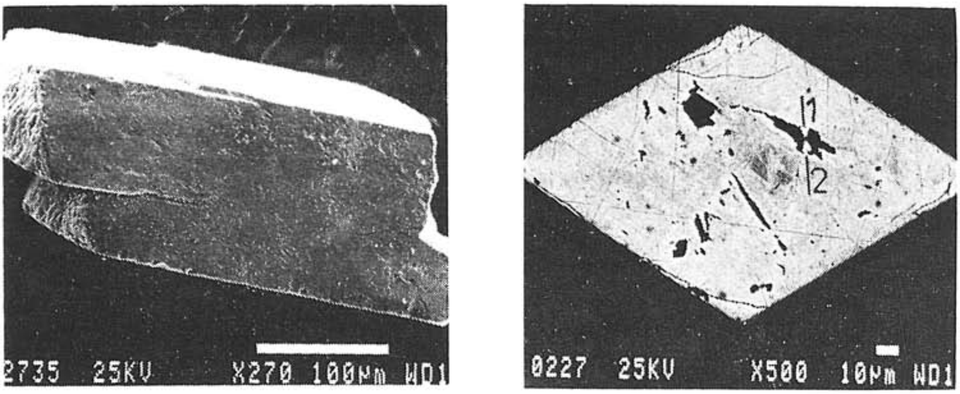
The arsenopyrite I forms small, commonly 0.05—0.15 mm, but exceptionally 0.5—1.5 mm long, idiomorphic (Fig. 5a) and hypidiomorphic (Figs. 6a, 7a) prismatic grains. The crystals are often tectonically fractured (Fig. 8a) exhibiting signs of corrosion on the margins (Figs. 6a, 7a). Various compound crystals (Fig. 9a), especially crossed compounds (Fig. 10a) and star triplets (Fig. 11a) are characteristic.

Study of mineral homogeneity

Already the homogeneity study by means of reflected electrons (composition) by the X-ray microanalyser Jeol Superprobe 733 discovered differences between the arsenopyrites I and II. Unlike the arsenopyrite II, the arsenopyrite I is markedly inhomogeneous mainly because of locally increased Sb contents at the expense of As. This dependence is documented by arsenopyrite I compositions supplemented with Sb and As diagrams (Figs. 12, 13) and an arsenopyrite II composition (Fig. 14a). A micrograph (Fig. 14b) illustrates homogeneous As distribution in the arsenopyrite II.

The arsenopyrite I inhomogeneity can be observed also in compositions made by the scanning microscope (Figs. 5b—11b).

4 grains (Figs. 5a, 8a—10) of two samples (RB-46 and RB-49) have been chosen for a detailed study by means of the electron scanning microscope and the NZ-854 X-ray emission analyser.



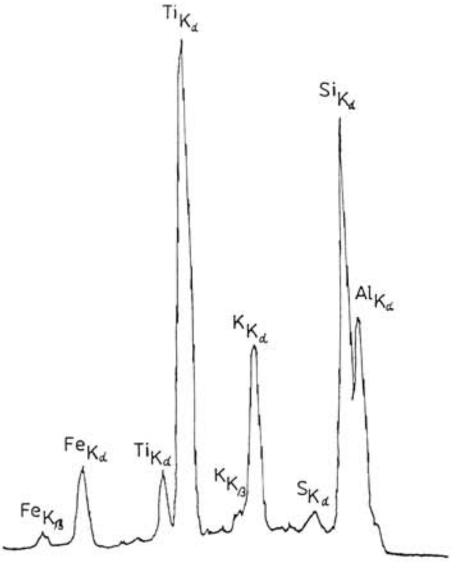


Fig. 5. Sample RB-49; a) arsenopyrite I morphology; b) composition of arsenopyrite I, point qualitative analyses: 1: Si, Al, K, Fe, S, 2: Si, Al, K, Fe, Ti; c) line diagram of Ti distribution.

Much attention has been paid to qualitative analysis of inclusions in the arsenopyrite I of the sample RB-46 (Fig. 5a). In the studied inclusion (Fig. 5b) the qualitative analyses confirmed presence of Si, Al, K, S and Fe in the point 1 and Si, Al, K, Ti and Fe in the point 2. The line diagram of a Ti mineral at the point 2, carried out by the NZ-854 X-ray emission analyser, makes it possible to suppose that the mineral concerned is rutil in an other, exactly unidentified, silicate mineral.

An arsenopyrite grain with a distinct zonal pattern and numerous non-ore inclusions can be seen in the composition (Fig. 9a). Unlike the analysis at the point 3 corresponding with arsenopyrite (S, Fe, As), at the points 1 and 2 the qualitative analyses discovered S, Sb and Fe, which indicates that the light-coloured phase is represented by gudmundite (FeSbS).

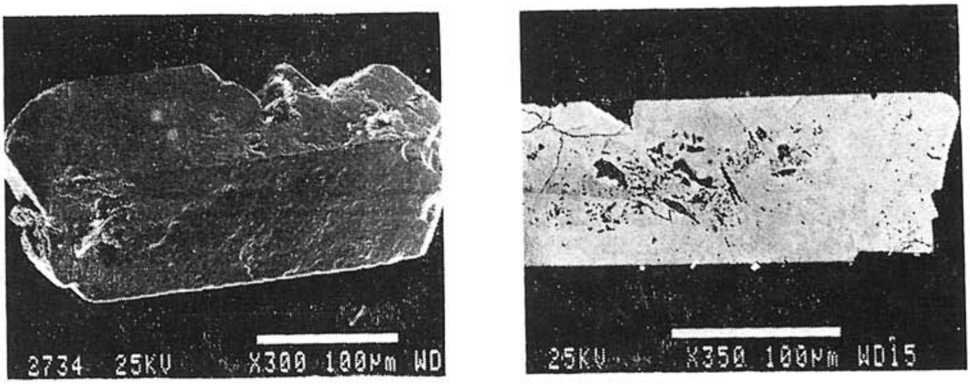


Fig. 6. Sample RB-46; a) morphology of arsenopyrite I; b) composition of arsenopyrite I.

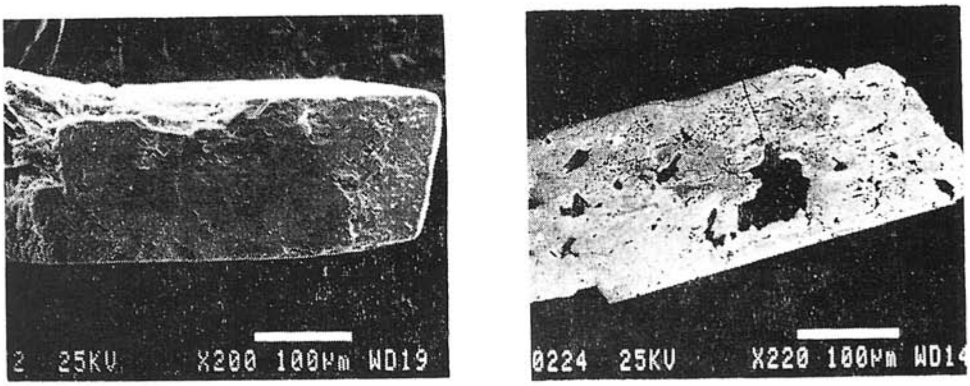


Fig. 7. Sample RB-46; a) morphology of arsenopyrite I; b) composition of arsenopyrite I.

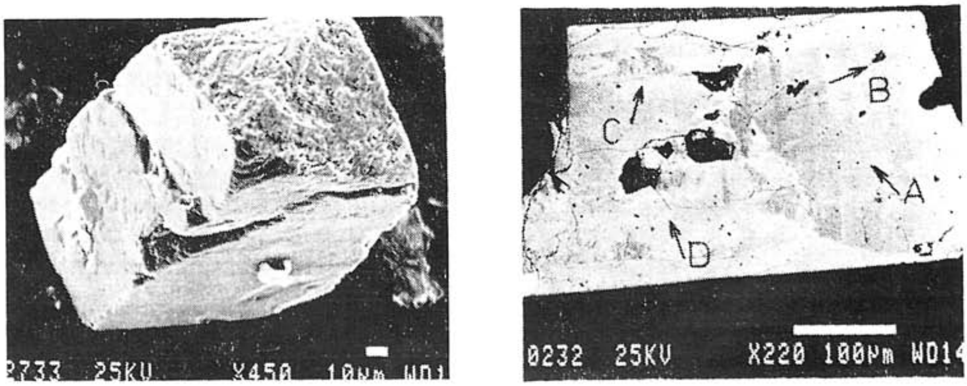


Fig. 8. Sample RB-46; a) morphology of arsenopyrite I; b) composition of arsenopyrite I with location of analysed points (results of point analyses in points A — D are given in Tab. 1).

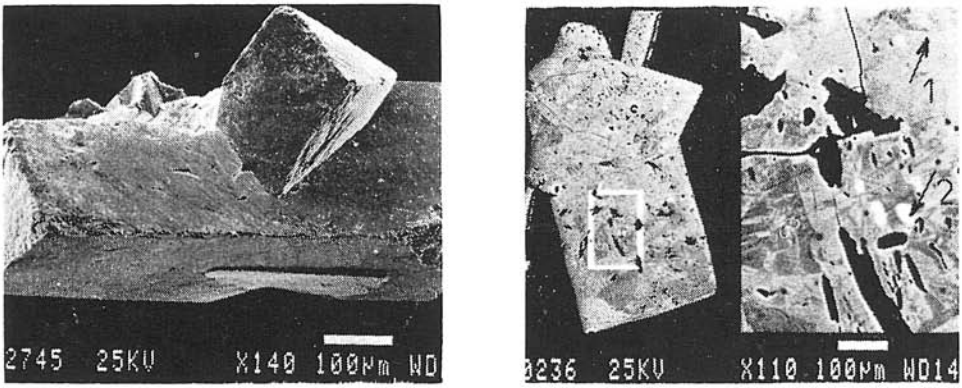


Fig. 9. Sample RB-50, a) morphology of arsenopyrite I; b) composition of arsenopyrite I and magnified detail of the composition, point qualitative analyses: 1: Fe, S, Sb; 2: Fe, S, Sb.

Fig. 10. Sample RB-49, a) morphology of arsenopyrite I; b) composition of arsenopyrite I with location of analysed points (results of point analyses in points E — H are given in Tab. 1.

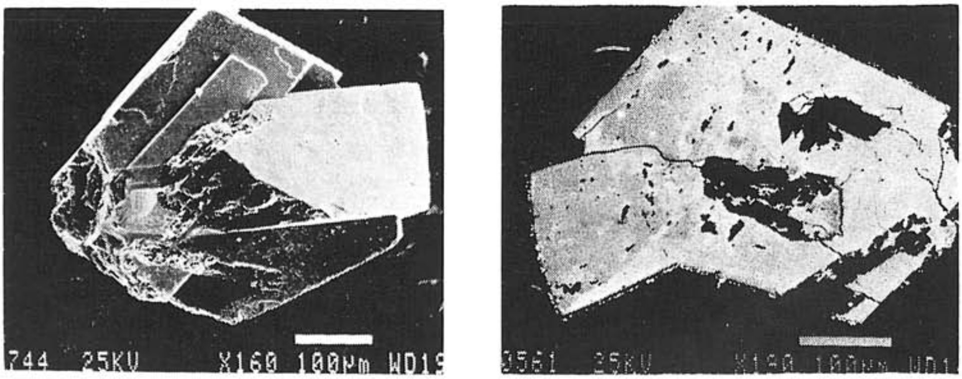


Fig. 11. Sample RB-49; a) morphology of arsenopyrite I, b) composition of arsenopyrite I.

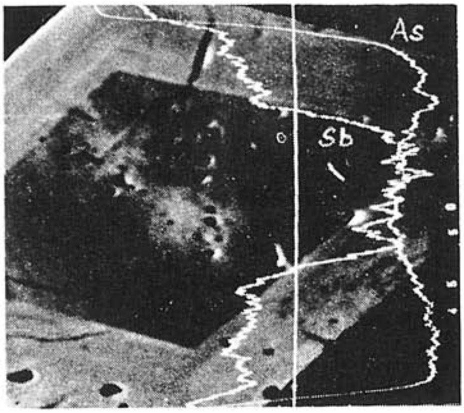


Fig. 12. Simple RB-55, composition of arsenopyrite I, (magn. 300×) and line diagram of As and Sb distribution.

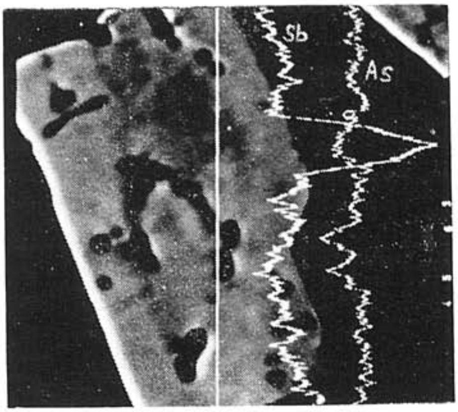


Fig. 13. Sample RB-56, composition of arsenopyrite I (magn. 300×) and line diagram of As and Sb distribution.

Cracks resembling those formed in sulphidic minerals by dehydratation of colloids can be seen in the magnyfied detail.

Chemical composition of arsenopyrite

8 point quantitative analyses by the apparatus Edax PV-9100 have been performed on arsenopyrite crystals (Figs. 8b, 10b). The analysed points are plotted on the grain compositions. The location of the points makes it pos-

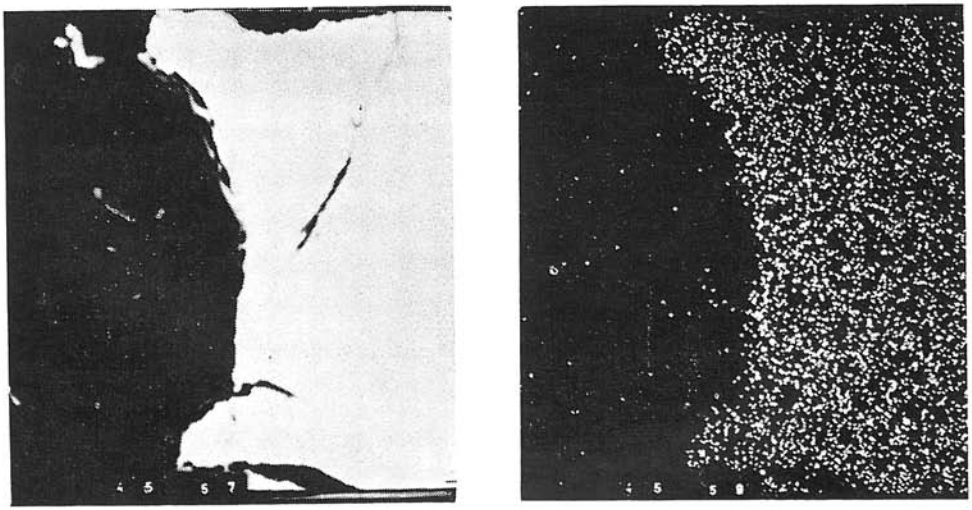


Fig. 14. Sample RB-51; a) composition of arsenopyrite II (light-coloured) and pyrite III (dark) (magn. 300×); b) areal As distribution in arsenopyrite II and pyrite III.

Table 1

Point analyses of arsenopyrite I (electron scanning microscope with X-ray emission analyser NZ-854)

Analysed element		Designation of analysed points							
		A	B	C	D	E	F	G	H
%	Fe	35.13	35.23	34.66	34.97	34.43	35.29	35.11	34.57
	As	41.48	41.77	44.05	44.90	43.92	41.03	41.49	44.96
	S	23.12	23.27	21.05	21.69	21.35	23.87	23.48	21.19
	Sb	1.04	1.25	0.18	0.28	0.15	1.02	0.68	0.16
	Cu	0.01	0.01	0.00	0.02	0.00	0.00	0.01	0.01
	Ag	0.01	0.01	0.00	0.02	0.00	0.00	0.01	0.01
	Σ %	100.79	101.54	99.95	101.86	99.85	101.22	100.77	100.68

Explanations: Analysed points are plotted in Fig. 8b, 10b. Au content in the sample detected spectrochemically is 79 ppm.

Table 2

Average values of point analyses of arsenopyrites I and II by electron microanalyser supplemented with spectrochemical Au analyses

Sample No.		arsenopyrite I			arsenopyrite II	
		RB — 5	RB — 53	RB — 55	PA — 79	RB — 51
%	Fe	34.7874	30.0227	30.9954	35.0353	34.9769
	As	44.9424	47.3034	43.2062	45.3922	46.4675
	S	21.4248	21.4029	19.0375	20.7183	20.2534
	Sb	0.1687	0.0167	0.4043	0.0306	0.0000
	Ni	0.0000	0.0000	0.3297	0.0120	0.0084
	Co	0.0000	0.0662	0.0168	0.0199	0.0649
ppm	Au	155	141	166	0.6	0.4
Σ %		101.3388	98.8260	94.0064	101.1974	101.7711

sible to observe the arsenopyrite I inhomogeneity and chemical composition of individual physical-chemical phases. The results of the analyses are in Tab. 1.

Tab. 2 compares point quantitative analyses by Edax PV-9100 with data obtained by point quantitative analyses by the electron microanalyser. Spectrochemically detected Au contents are supplemented. In Tab. 2, arsenopyrite II analyses are also given so that the chemical compositions of the arsenopyrites I and II could be compared.

Arsenopyrite enrichment of the order 0.0X % (400—500 ppm) Sb has been described from the area Keno Hill in Canada and Yellowknife by Boyle (1965). The possibility of mutual As-Sb replacement in arsenopyrite has been mentioned by Picot — Johan (1982), but arsenopyrite enrichment by 0.X (in individual point analyses even by over 9 %) has been first described by Dadák (1983) from the Pezinok deposit. Comparison of Tab. 1 and 2 indicates that only the gold-bearing arsenopyrite I is enriched in Sb and it contains less As than the arsenopyrite II.

All the deposits cited are those of gold without an independent antimony mineralization, which suggests that the arsenopyrite I origin is not directly related to the formation of the principal antimony or that the arsenopyrite I originated in different conditions than the arsenopyrite II.

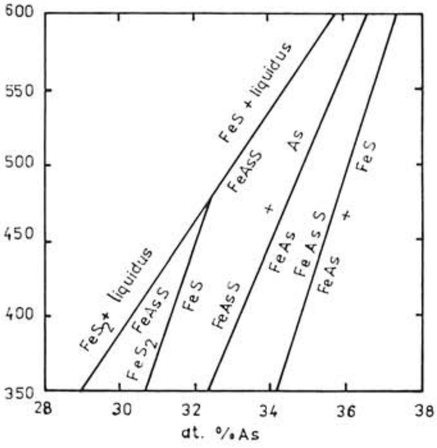


Fig. 15. Phase diagram of dependence of As atomic percentage on temperature (Kretschmar, 1973).

Conditions of arsenopyrite formation in mineral association with pyrite are shown in Barton's (1969) scheme, which has been worked out in detail by Kretschmar (1973, Fig. 15). It is based on the change of the temperature and As atomic percentage in the system. According to this scheme the arsenopyrite I could have originated only at temperatures under 500 °C and low As concentrations (29—33 %). Kretschmar also notes that such an arsenopyrite contains less As than arsenopyrite formed together with loellingite. This conclusion is supported by data in Tab. 1 and 2 showing that the arsenopyrite I formed in association with pyrite contains less As than the arsenopyrite II formed in association with pyrite and loellingite.

Thermoelectric voltage of the arsenopyrite I

The arsenopyrite I may have various types of conductivity according to which p-, p-n and n-arsenopyrites can be distinguished. The conductivity type depends mainly on deviations of the mutual ratio of the basic elements from the theoretic composition and character of various admixtures.

Table 3

Results of thermoelectric voltage measurements α/μ V(deg) in arsenopyrite I

Sample No.	Designation of analysed point	Fig. No.	α/μ V(deg)
RB — 49	A B C D	8b	— 111.5 — 115.1 — 141.7 — 135.6
RB — 49	E F G H	10b	— 136.4 — 169.9 — 145.5 — 112.6
RB — 46		6b	— 191.3
RB — 50		9b	— 133.9

The only element, the content of which in arsenopyrite can exceed 0.5 % is cobalt (Fleischer, 1955). Because cobalt replacing iron acts as a donor, cobalt-rich arsenopyrite has conductivity of the type n. Other admixtures can be nickel (donor) and antimony (neutral). Sulphur replacing arsenic is donor and arsenic replacing sulphur is acceptor. Therefore the arsenic-poor arsenopyrite I has conductivity of the type n. This arsenopyrite is marked for low thermoelectric voltage values (Tab. 3). The average value of the arsenopyrite I thermoelectric voltage is 139.35 V/deg.

Favorov et al. (1972) have found that n-arsenopyrite is associated with minerals, the formation of which requires a higher sulphur potential in the solutions, while p-arsenopyrite occurs together with minerals that cannot exist by a higher sulphur potential.

Conclusion

The study of the gold-bearing arsenopyrite I has proved that, besides increased Au contents, it differs from the younger arsenopyrite II also in structural and textural elements, crystal morphology, increased Sb contents, decreased As contents, inhomogeneous Fe, As and S distributions and numerous inclusions of non-ore minerals. Thermoelectric voltage study of the arsenopyrite I has discovered that it is of type n. The study also pointed out different formation conditions of the arsenopyrites I and II and that the arsenopyrite I was formed of solutions with a higher sulphur potential than the arsenopyrite II.

The comparison of the results obtained by the electron scanning microscope and energy dispersion analyser with those obtained by X-ray electron microanalyser make it possible to regard them as comparable and recommend the study of sulphidic minerals by this non-traditional method, too.

Translated by Ľ. Böhmer

REFERENCES

ANDRÁŠ, P., 1983: Problémy genézy antimónového a zlatého zrudnenia na ložisku Pezinok. Manuscript, Geol. Inst. of SAS, Bratislava, 158 pp.

ANDRÁŠ, P. — RAJNOHA, J. — HRNČÁROVÁ, M., 1987: Gold distribution in sulphide and non-ore minerals at the Pezinok — Kolársky vrch deposit. Geol. Zbor. Geol. carpath. (Bratislava), 38, 5, pp. 585—591.

BARTON, P. B., 1969: Termochemical study of the system Fe-Zn-S. Geochim. Cosmochim. Acta (London), 33, pp. 841—857.

BOYLE, R. W., 1965: Geology, geochemistry and origin of the lead-zinc-silver deposits of the Keno-Hill — Galena Hill area, Yukon territory. Bull. Geol. Surv. Can. (Ottawa), 111, 302 pp.

CAMBEL, B., 1939: Hydrotermálne ložiská v Malých Karpatoch, mineralógia a geochémia ich rúd. Acta geol. geogr. Univ. Comen. Geol. (Bratislava) 3, 338 pp.

CAMBEL, B., 1950: Malokarpatské rudné ložiská v oblasti Pezinok—Pernek. Geol. Sbor. (Bratislava), I, 1.

DADÁK, V., 1983: Antimonem bohatý arzenopyrit z ložiska Pezinok v Malých Karpatoch. Čas. Mineral. Geol. (Praha), 23, 1, pp. 89—92.

ĎURŽA, O., 1981: Elektrické vlastnosti niektorých sulfidických minerálov v závislosti na ich chemizme. Manuscript, Geofond, Bratislava, 111 pp.

FAVOROV, V. A. — KRASNIKOV, V. I. — SYCHUGOV, V. S., 1972: Nekotorye faktory opredeľajuščija izmenčivosť poluprovodnikovych svojstv pyrita i arzenopyrita. Izv. AN SSSR, Ser. geol. (Moskva), 11, pp. 72—84.

FLEISCHER, M. V., 1955: Minor elemente in some sulphide minerals. Econ. Geol. (Lancaster, Pa.), 50, pp. 970—1024.

GAJDOŠ, V. — ĎURŽA, O., 1981: Merný elektrický odpor, koeficient usmernenia a diferenciálne termoelektrické napätie niektorých rudných minerálov. Miner. slov. (Bratislava), 13, 3, pp. 263—268.

KRETSCHMAR, U., 1973: Phase relations involving arsenopyrite in the system Fe-As-S and their application. Thes. Univ. Toronto (Toronto), 100 pp.

MRÁKAVA, F., 1977: Popis ložiska Sb Pezinok—Cajla. Manuscript, Ore Mines, Pezinok.

PICOT, P. — JOHAN, Z., 1982: Atlas of ore minerals. B.R.G.M. Elsevier, 458 pp.

POLÁK, S. — RAK, D., 1979: Zlato v antimonitovom ložisku v Pezinku. Miner. slov. (Bratislava), 11, 6, pp. 553—554.

VOJTKEVICH, G. V. et al., 1965: K voprosu o prirode termoelektričeskogo effekta v mineralach. Dokl. Akad. nauk SSSR (Moskva), 162, 1, pp. 169—172.

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