

THERMOMETRY OF ARSENOPYRITE-PYRITE MINERALIZATION IN THE DÚBRAVA ANTIMONY DEPOSIT (WESTERN CARPATHIANS)

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Abstract: Arsenopyrite occurs at the Dúbrava antimony deposit (Central Slovakia) in quartz veins together with pyrite. Arsenopyrite is also found as impregnation around quartz veins in granodiorites and migmatites. On the basis of analysis of arsenopyrite by electron microprobe the average content of arsenic (in atomic %) in arsenopyrite is 31.67, which indicates temperature of formation about 425 °C, resp. 395 °C. These data are compared with the analysis obtained by X-ray diffractometer: the average As atomic % is 31.72, indicating temperatures about 400–430 °C. Microthermometric measurements made on fluid inclusions in quartz associated with arsenopyrite-pyrite mineralization gave temperatures about 325 °C. All the above mentioned temperature measurements revealed that the sulphide mineral formation in Dúbrava began at a high temperature.

Key words: arsenopyrite geothermometer, homogenization temperature of fluid inclusions, hydrothermal vein deposit, Western Carpathians.

Introduction

The composition of arsenopyrite, $\text{FeAs}_{1\pm x}\text{S}_{1\pm x}$, is the most refractory of common sulphides, which, together with its wide range of As/S atomic ratio, makes it a potentially useful geochemical tool for determining the environmental conditions of its formation. Clark (1960) was the first one to propose the use of arsenopyrite composition as a potential geothermometer. Barton (1969) provided important information about the Fe-As-S system by measuring with pyrrhotite indicator method and also contributed a number of univariant curves in the Fe-As-S system. The validity of these curves has been confirmed by Kretschmar and Scott (1976).

In the Dúbrava antimony deposit arsenopyrite is associated mainly with pyrite. According to Kretschmar and Scott (1976), atomic weight percent of As in arsenopyrite coexisting with pyrite is a direct function of the temperature of formation and it is slightly affected by variations in pressure. This aspect of arsenopyrite geothermometer is in very good agreement with the conditions at the Dúbrava deposit. The authors applied here the arsenopyrite geothermometer for deciphering the temperature of formation of the Dúbrava deposit.

The arsenopyrite geothermometer has been successfully applied by many workers, such as Either et al. (1976), Berglund and Ekström (1980), Deb and Bhattacharya (1980), Scratch et al. (1984), Sundblad et al. (1984), Radvanec and Bartalský (1988) and others.

Mineralogical-paragenetical characteristics of the Dúbrava deposit

Quartz veins with sulphide mineralization in the Dúbrava deposit are lying in Variscan granodiorite and partly in migmatite (Fig. 1). According to Chovan (1990), the mineralization occurred at the Dúbrava deposit in two stages. The older stage is characterised by quartz-pyrite veins with scheelite. The younger sulphidic phase consists of four mineralization periods. The oldest are quartz veins with arsenopyrite-pyrite (first period), later on, sphalerite, zinkenite, stibnite were formed (second period) and subsequently dolomite, tetrahedrite (third period) and in the last part of the depositional process, barite veins (fourth period) were formed with carbonate and a small amount of sulphides.

Arsenopyrite is the characteristic mineral of the first period of the second ore formation stage at the deposit. Arsenopyrite is associated with pyrite and quartz (Fig. 2), which is an assemblage observed commonly at the deposit. Arsenopyrite is found in quartz veins, frequently with sulphides of the second ore formation stage and it is also often present in the form of veinlets in the host rocks. Arsenopyrite is also disseminated in the surrounding rocks (Fig. 3) and occurs as well as a relic in the third period of mineralization, associated with tetrahedrite.

All types of arsenopyrite observed at the deposit are thought to be genetically related, having been deposited at the beginning of the formation of sulphidic mineralization.

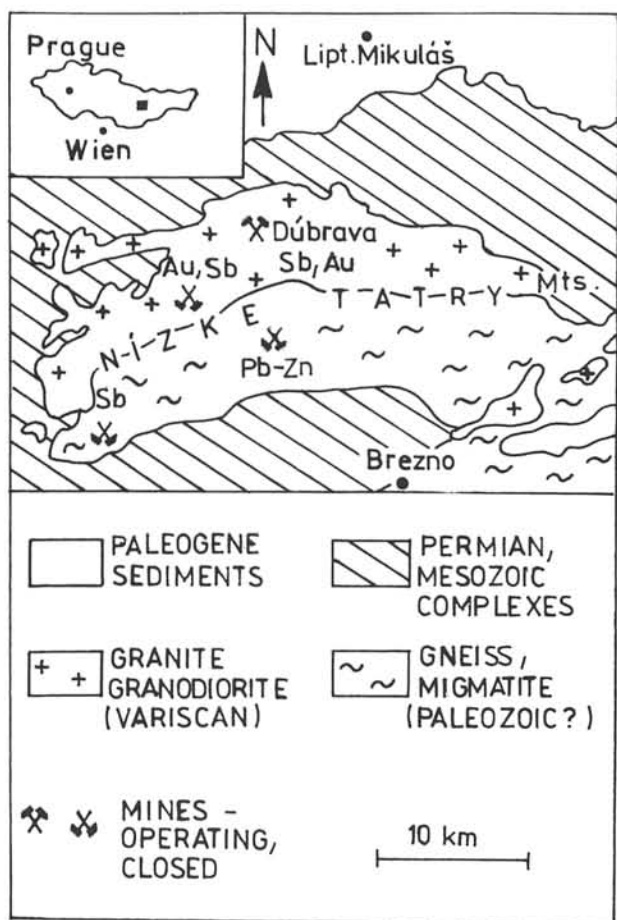


Fig. 1. Simplified geological map of the Nízke Tatry Mts.

Generally, arsenopyrites in the studied samples are in close proximity to pyrites, which indicates that during the formation of this type of association, f_{S_2} was constant (Berglund and Ekström 1980). Arsenopyrite is texturally present in the rhombic form of individual grains and also as crystalline aggregates. Grains are often fractured and healed by younger minerals.

Analytical methods

For temperature estimation, we selected arsenopyrite samples from two mine adits in central and southern part of the deposit, approximately at the same horizontal plane. The distance between the sample collection sites was about 2 km. The arsenopyrite samples were prepared as polished sections and later we studied their mineral assemblages. During the petrographic study we observed that pyrite-arsenopyrite-quartz were in equilibrium in the mineral paragenesis.

The samples of arsenopyrites were analysed by electron microprobe Jeol Superprobe 733, at following operating conditions: the accelerating voltage was 25 kV, detection current 3.5×10^{-4} A. The standards used in analysis were pure arsenopyrite mineral for As, Fe, S and pure metal for Ni, Co, Au and Sb. The authors performed 21 analyses on 6 samples. The quality of analysis has been verified by atomic absorption spectrometry at the Dionýz Štúr Institute of Geology.

The samples of arsenopyrites were also analysed by X-ray diffractometer DRON UM-1. Cu/Ni filter was used in the diffractometer, with a diaphragm of 2-0, 5-2 at

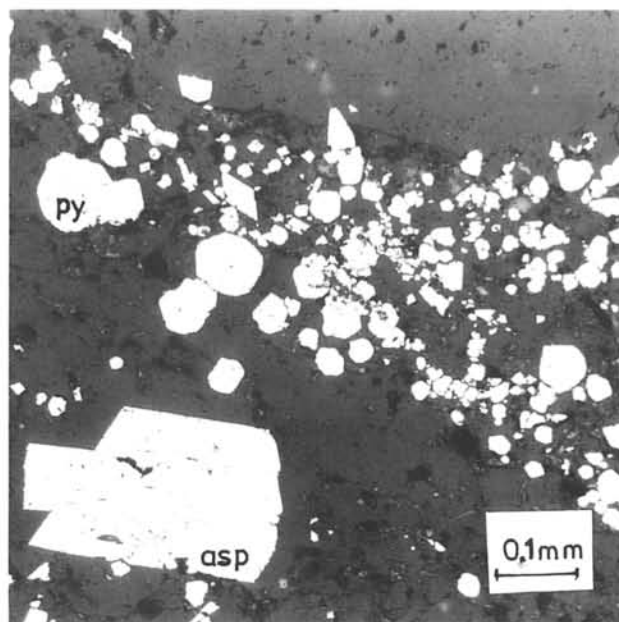


Fig. 2. Association of pyrite (py) and arsenopyrite (asp) in the quartz vein, southern part of deposit, reflected light, polished section.

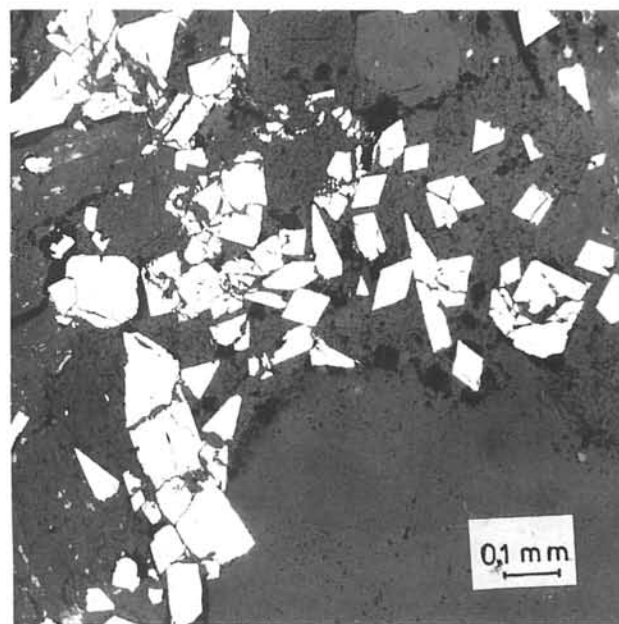


Fig. 3. Impregnated arsenopyrite in altered rock, central part of deposit, reflected light, polished section.

40/20 kV/mA. The time was constant for each analysis – 5 seconds, with 10 impulse current.

Samples of quartz associated with arsenopyrite-pyrite mineralization have been studied for fluid inclusions. The fluid-inclusion microthermometry measurements were carried out on a Leitz heating-freezing stage with attached Carl Zeiss Jena microscope.

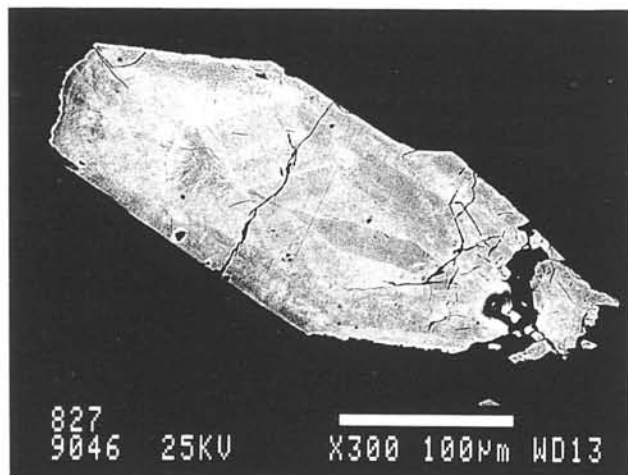
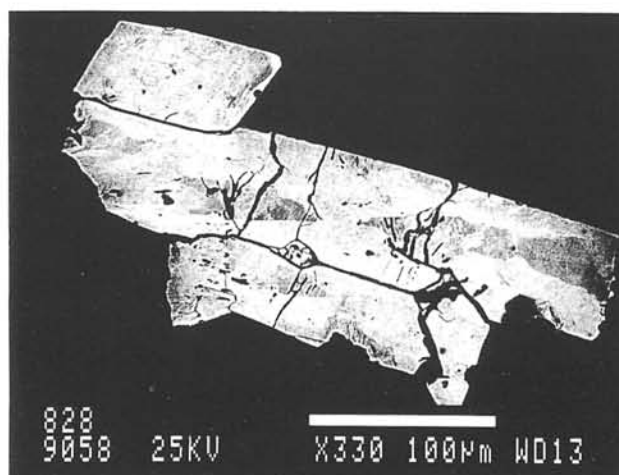
Results and discussion

The chemical composition of arsenopyrite analysed by electron microprobe is listed in Table 1. Only those analyses are presented in which antimony content is below 1 wt.%. The

Table 1. Electron microprobe analysis of arsenopyrite.

Sample No.	No. of analysis	elements in weight %							elements in atomic %						
		Fe	S	Co	Ni	Au	As	Sb	Fe	S	Co	Ni	Au	As	Sb
1	1	34.68	20.76	0.01	—	0.15	44.71	0.35	33.22	34.64	0.01	—	0.04	31.92	0.15
	2	33.15	21.67	0.06	—	—	44.75	0.78	31.67	36.05	0.06	—	—	31.86	0.03
	3	34.78	21.29	0.01	—	—	43.09	—	33.24	35.44	0.01	—	—	30.69	—
2	∅	34.20	20.90	0.03	—	—	44.18	0.57	32.71	35.37	0.02	—	—	31.49	0.06
	4	34.06	21.60	0.15	—	0.11	43.03	—	32.52	35.93	0.14	—	0.03	30.82	—
	5	34.76	21.40	0.07	—	—	44.75	0.06	32.95	35.33	0.07	—	—	31.61	0.02
	6	33.39	21.27	0.03	—	0.08	44.49	0.72	32.10	35.62	0.03	—	0.02	31.88	0.03
	∅	34.07	21.49	0.09	—	0.10	44.09	0.26	32.52	35.62	0.08	—	0.02	31.43	0.02
3	7	34.54	20.77	0.06	—	—	45.59	0.17	32.94	34.51	0.05	—	—	32.40	0.07
	8	34.91	20.68	0.06	0.01	—	44.45	0.08	33.50	34.57	0.06	0.01	—	31.80	0.03
	9	35.06	20.23	0.01	—	*	43.85	—	34.03	34.21	0.01	—	—	31.73	—
	10	34.58	21.09	0.05	—	*	42.84	—	33.47	35.55	0.05	—	—	30.91	—
	∅	34.77	20.69	0.04	—	—	44.18	0.13	33.48	34.92	0.04	—	—	31.71	—
4	11	34.18	22.12	0.03	0.04	—	44.06	0.13	32.34	36.45	0.03	0.03	—	31.07	0.05
	12	34.73	21.29	0.06	—	—	43.67	0.06	33.16	35.41	0.05	—	—	31.08	0.02
	13	34.84	20.43	0.01	—	*	44.51	0.14	33.60	34.32	0.01	—	—	31.99	0.06
	14	34.53	20.94	0.06	0.01	*	43.25	0.81	33.29	35.18	0.05	0.01	—	31.08	0.03
	15	34.96	21.36	—	—	*	43.07	0.13	33.46	35.68	—	—	—	30.78	0.05
5	∅	34.64	21.17	0.04	0.02	—	43.71	0.25	33.13	35.40	0.03	0.01	—	31.20	0.04
	16	33.36	21.31	0.01	0.04	—	46.32	0.09	31.73	35.31	0.01	0.04	—	32.84	0.04
	17	34.41	21.19	0.01	0.01	—	44.39	0.05	32.93	35.34	0.01	0.01	—	31.66	0.02
	18	32.70	21.90	—	—	—	44.79	0.11	31.35	36.58	—	—	—	32.01	0.05
6	∅	33.49	21.46	0.01	0.02	—	45.16	0.08	32.00	35.74	0.01	0.02	—	32.17	0.03
	19	35.09	21.14	0.01	—	0.02	45.03	0.01	33.26	34.90	0.01	—	0.01	31.81	0.01
	20	35.03	20.83	0.05	0.04	*	44.76	0.06	33.42	34.62	0.05	0.03	—	31.83	0.02
	21	34.32	20.53	0.05	—	*	45.48	0.11	32.97	34.33	0.04	—	—	32.57	0.02
	∅	34.81	20.93	0.03	—	—	45.09	0.06	33.21	34.61	0.03	—	—	32.07	0.01

* not analysed

**Fig. 4.** Zoned arsenopyrite crystal from impregnation in granodiorite. Content of Sb in dark zones is about 1 wt. %. S.E.M. photograph (back scattered electrons).**Fig. 5.** Fractured arsenopyrite crystal with hour-glass texture. S.E.M. photograph (back scattered electrons).

analyses in which antimony content is equal or greater than 1 wt.% (dark zones on Figs. 4 and 5) have been rejected for the purpose of geothermometry. In some samples, cobalt, nickel and gold have been reported, however, in quantities below the permissible limit for the application of arsenopyrite geothermometer.

The atomic percent of iron varies mainly between 31.35 and 34.03, the average being 32.95 (Fig. 6), which indicates that the iron estimates are somewhat too high. The iron content

should be around 33.3 ± 0.7 atomic %, which serves as a good indicator of the quality of analysis (Kretschmar 1973). As observed on Fig. 7, the variation between arsenic and sulphur atomic % follows one trend as the content of arsenic (atomic %) increases, in contrast to this, sulphur atomic % decreases. This type of trend has been observed also by Berglund and Ekström (1980).

At the Dúbrava deposit there are various types of arsenopyrite coexisting with pyrite. The arsenopyrite disseminated in

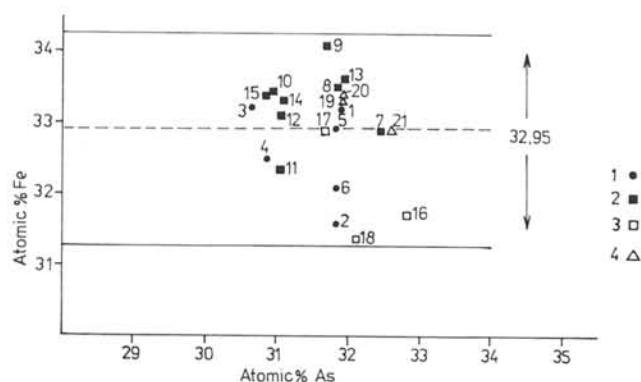


Fig. 6. As/Fe variation in arsenopyrite from Dúbrava deposit.

Note: 1 – analysis No. 1–6, impregnated type; 2 – analysis No. 7–15, vein type; 3 – analysis No. 16–18, veinlet type; 4 – analysis No. 19–21, relict type.

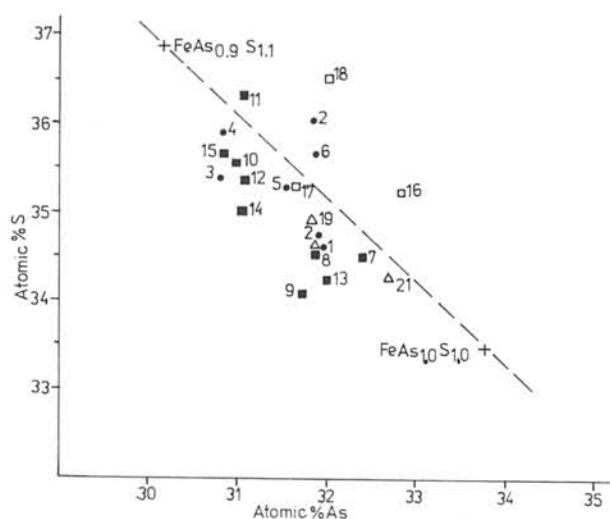


Fig. 7. The As/S variation in arsenopyrite from Dúbrava deposit. For explanation see Fig. 6.

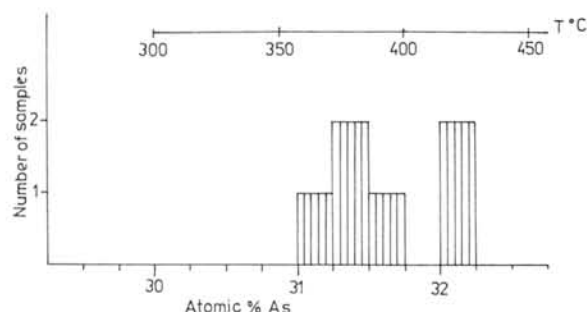


Fig. 8. Histogram of the distribution of As in arsenopyrite (atomic %), which is compared with temperature scale of Sundblad et al. (1984).

altered rocks, closely related to quartz veins, contains between 31.43 and 32.12 atomic % of arsenic (sample No. 1 and 2, Tab. 1). According to Kretschmar and Scott (1976), this composition indicates the equilibrium temperature range of 385–415 °C. This disseminated arsenopyrite with the abovementioned composition comes from the central part of the Dúbrava deposit.

Another type of arsenopyrite coexisting with quartz and pyrite in quartz veins has a composition of 31.2 to 31.71 atomic % As. This composition has been reported from the southern part of the deposit (sample No. 3 and 4), indicating the temperature range of 365–400 °C. The composition of arsenopyrite from the southern part, which is the veinlet type (sample No. 5), is 32.17 atomic % As, which indicates temperature around 419 °C. The arsenopyrite sample consisting of relic grains with tetrahedrite mineralization from the central part of the deposit (sample No. 6) contains 32.07 atomic % As, which indicates a temperature of 410 °C.

All over the deposit, the atomic % of arsenic in arsenopyrite ranges as a rule between 30.69–32.84, with an average of 31.67 (Tab. 1). In Fig. 8 the atomic % of arsenic in arsenopyrite is plotted against the temperature scale proposed by Sundblad et al. (1984). There is one distinct group showing high temperature, since the average temperature is approx. 395 °C. According to Kretschmar and Scott (1976), the arsenic atomic % in arsenopyrite corresponds to approx. 425 °C, which can be seen as well on Fig. 9, showing mineral assemblages.

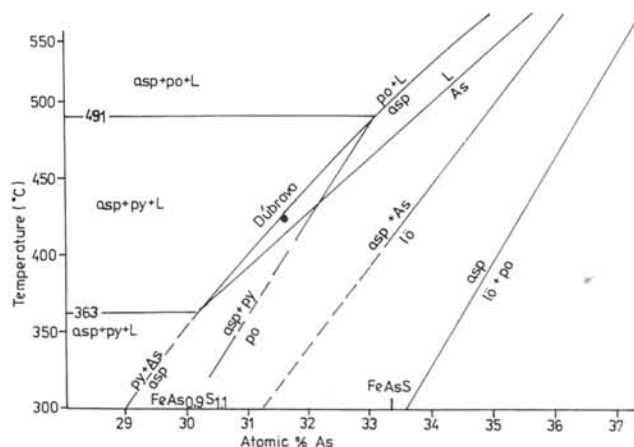


Fig. 9. The varying composition of arsenopyrite as a function of temperature with different mineral assemblage (modified after Kretschmar and Scott 1976).

The symbols of minerals are denoted as follows: asp-arsenopyrite, lö-löllingite, py-pyrite, po-pyrrhotite, As-arsenic, L-liquid.

For the purpose of verification of electron microprobe analyses of arsenopyrite we carried out X-ray diffraction study of one sample (No. 3). The atomic % of arsenic has been calculated by the equation given by Kretschmar and Scott (1976), which is as follows:

$$\text{As (atomic \%)} = 866.67 \times d_{131} - 1381.12$$

where As stands for arsenic. The average value of d_{131} from three analyses is 1.6302 Å, which gave 31.72 atomic % of arsenic, corresponding to temperature of about 430 °C.

Microthermometric measurements were made on quartz from arsenopyrite mineralization at the Dúbrava deposit. The fluid inclusions in quartz have approximately the size of below $10\text{ }\mu\text{m}$ in diameter. Temperature measurements were made on 50 inclusions.

The homogenization temperature of quartz associated with arsenopyrite indicates the temperature range from $232\text{ }^{\circ}\text{C}$ to $349\text{ }^{\circ}\text{C}$. On Fig. 10 it can be seen that there are two distinct populations of fluid inclusions. A small number of inclusions shows a temperature peak of about $260\text{ }^{\circ}\text{C}$, while a large number of inclusions with CO_2 in the gaseous phase shows a peak about $325\text{ }^{\circ}\text{C}$ ($308\text{--}349\text{ }^{\circ}\text{C}$). According to the authors' opinion, older inclusions are very significant from the genetic point of view.

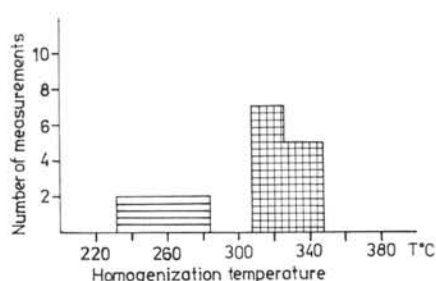


Fig. 10. Histogram of homogenization temperature (T_H) for quartz from arsenopyrite-pyrite mineralization in Dúbrava deposit.

The temperature estimates by various methods show some differences. Electron microprobe analyses gave the temperature of $425\text{ }^{\circ}\text{C}$, resp. $395\text{ }^{\circ}\text{C}$, and X-ray diffraction analyses gave the temperature of about $400\text{--}430\text{ }^{\circ}\text{C}$. Lower temperature has been estimated by fluid inclusion study of quartz – about $325\text{ }^{\circ}\text{C}$. On the basis of the low content of NaCl and high content of CO_2 in the gaseous phase we assume that the homogenization temperature varied in a wider range – $310\text{--}400\text{ }^{\circ}\text{C}$. The temperature estimated by arsenopyrite thermometer shows higher values than temperature estimated by fluid inclusions in quartz.

In the Lake George antimony deposit, according to Scratch et al. (1984), the formation of arsenopyrite in argillic alteration occurred above $360\text{ }^{\circ}\text{C}$, which corresponds to arsenic atomic % variation between 31.02 and 31.94.

The temperature of arsenopyrite formation varies slightly from the north to the south of the Dúbrava deposit. The slight extent of horizontal variation has been shown also by earlier mineralogical and geochemical studies (Chovan 1990). There is little difference in the temperature of formation between disseminated arsenopyrite and arsenopyrite from quartz veins. All types of arsenopyrite formed in the first period of sulphidic mineralization.

In the authors' opinion, at the time of arsenopyrite mineralization the temperature was high to moderate, as shown by the use of arsenopyrite geothermometer and fluid inclusion studies at the Dúbrava ore deposit. Younger periods of mineralization took place at medium to lower temperatures.

Conclusions

The temperature calculation based on arsenic atomic % in arsenopyrite, i.e. the arsenopyrite geothermometer, gave a temperature of about $425\text{ }^{\circ}\text{C}$, resp. $395\text{ }^{\circ}\text{C}$, while the fluid inclusion homogenization temperature in quartz from arsenopyrite-pyrite mineralization shows values of about $325\text{ }^{\circ}\text{C}$.

The temperature estimates indicate high temperature of formation of the quartz-arsenopyrite-pyrite paragenesis, which formed at the beginning of the sulphide mineralization deposition at the Dúbrava antimony deposit.

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References

- Barton P.B., 1969: Thermochemical study of the system Fe-As-S. *Geochim. Cosmochim. Acta* (London), 33, 841–847.
- Berglund S. & Ekström T.K., 1980: Arsenopyrite and sphalerite as T-P indicators in sulphide ores from Northern Sweden. *Mineral. Depos.* (Berlin), 15, 175–187.
- Chovan M., 1990: Mineralogical-paragenetical relations on the Dúbrava Sb deposit and their significance for metallogenesis of the N. Tatry Mts. *Acta geol. geogr. Univ. Comen., Geol.* (Bratislava), 45, 89–101.
- Clark L.A., 1960: The Fe-As-S system: Phase relations and application. *Econ. Geol.* (Lancaster), 55, Pt. I: 1345–1381, Pt. II: 1631–1652.
- Deb M. & Bhattacharya A.K., 1980: Geological setting and conditions of metamorphism of polymetallic Rajpura-Dariba, Rajasthan, India. In: *Proc. 5th Symp. IAGOD, Snowbird, Utah US.* Stuttgart, E. Schweizerbart'sche Verl., 1, 680–687.
- Either V.G., Campbell F.A., Both R.A. & Krouse H.R., 1976: Geological setting of the Sullivan ore body and estimates of temperature and pressure of metamorphism. *Econ. Geol.* (Lancaster), 71, 1570–1588.
- Kretschmar U., 1973: Phase relation involving arsenopyrite in the system Fe-As-S and their application. Unpubl. Ph. D. Thesis, Univ. Toronto, Canada.
- Kretschmar U. & Scott S.D., 1976: Phase relation involving arsenopyrite in the system Fe-As-S and their application. *Canad. Mineralogist* (Ottawa), 14, 363–386.
- Radvanec M. & Bartalský B., 1988: Vplyv metamorfózy na systém Fe-Zn-As-S v stratiformnej sulfidickej mineralizácii staršieho paleozoika gemerika. *Mineralia slov.* (Bratislava), 20, 307–322.

- Scratch R.B., Watson G.P., Kerrich R. & Hutchinson R.W., 1984: Fracture controlled antimony-quartz mineralization, Lake George Deposit, New Brunswick: Mineralogy, geochemistry, alteration and hydrothermal regimes. *Econ. Geol.* (Lancaster), 79, 1159–1186.
- Sundblad K., Zachrisson E., Smeds S.H., Berglund S. & Alinder C., 1984: Sphalerite geobarometry and arsenopyrite geothermometry applied to metamorphosed sulfides ores in the Swedish Caledonides. *Econ. Geol.* (Lancaster), 79, 1660–1668.