

# Origin and evolution of ore-forming fluids at Pezinok-Kolársky Vrch Sb deposit (Western Carpathians, Slovakia)

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**Abstract.** The article presents the main results of the Pb- isotope study of stibnites, S- isotope study of sulphide minerals, as well as the O- and C- isotopes study of carbonates and quartz from Pezinok – Kolársky Vrch deposit. Pb-isotope study in galenas from epigenetic deposits of Malé Karpaty Mts. shows the magmatic origin of lead in ore-forming fluids. Pb-isotope distribution in stibnites indicates upper crustal origin of lead. Model ages in stibnite are influenced by „J-effect.“ They vary from 220 to 230 Ma and from 110 to 130 Ma. In ores, the heavy sulphur <sup>34</sup>S was contaminated by light sulphur isotope <sup>32</sup>S. Distribution of carbon and oxygen isotopes in carbonates shows an increasing role of meteoric water in ore forming fluids during the hydrothermal process.

In quartz of the 1<sup>st</sup> stage of the epigenetic Sb-Au mineralization only data from secondary fluid inclusions were available. In the 2<sup>nd</sup> to 4<sup>th</sup> stages salinities of the ore-forming fluids are relatively higher: 2 – 25 wt % NaCl equiv. In the 4<sup>th</sup> stage the presence of Ca<sup>2+</sup> cations was detected in the solutions.

Thermal maturation of organic matter from ore-bearing black schists from Pezinok deposit indicates temperatures close to 400°C.

**Key words:** fluid inclusion, S-, O- and C- isotopes, organic matter reflectance

## Introduction

The Pezinok - Kolársky Vrch deposit is situated in the Malé Karpaty Mts. crystalline complex (Fig. 1, 2). It belongs to small Sb deposits. During the 1790 to 1811 period and later from 1914 to 1995 (with exception of years 1948/1949) 1 million tons of Sb-ores were exploited with average content 1.3 % Sb, 9-11 ppm Au and 20-40 ppm Ag. The stibnite-concentrate was very poor, it contained about 25 % Sb in average. Identified geological resources of antimony and gold are of the order of 5000 t and 5.5 t respectively.

Based on the C- and O- isotope study of carbonates, Andráš (1983) assumed an increasing role of the meteoric waters during the development of hydrothermal fluids (originally the fluids were nearly endogenous). The first temperature study of the 1<sup>st</sup> and 2<sup>nd</sup> stage was published by Andráš et al. (1998). Using fluid inclusion study and the arsenopyrite geothermometer he calculated the crystallization temperature of the 1<sup>st</sup> and 2<sup>nd</sup> stage: 425-450°C and 350-450°C respectively.

## Ore mineralization

According to Ilavský (1979), Pezinok-Kolársky Vrch deposit belongs to the group of Sb-FeS<sub>2</sub> ores of eugeo-synclinal formation in association with basic volcanism (Fig. 3).

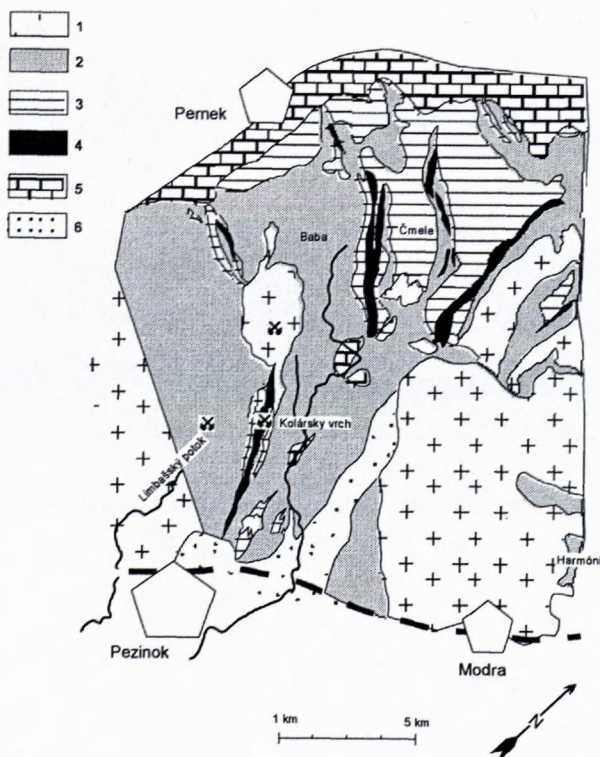


Fig. 1: Geological map showing the location of the Pezinok-Kolársky Vrch deposit (according to Cambel 1959 and Polák & Rak 1980 – modified) 1 – granitoid rocks, 2 – metamorphic rocks (phyllites, paragneisses), 3 – metabasalts, 4 – mineralized zones, 5 – carbonates, 6 – Tertiary and Quaternary sediments



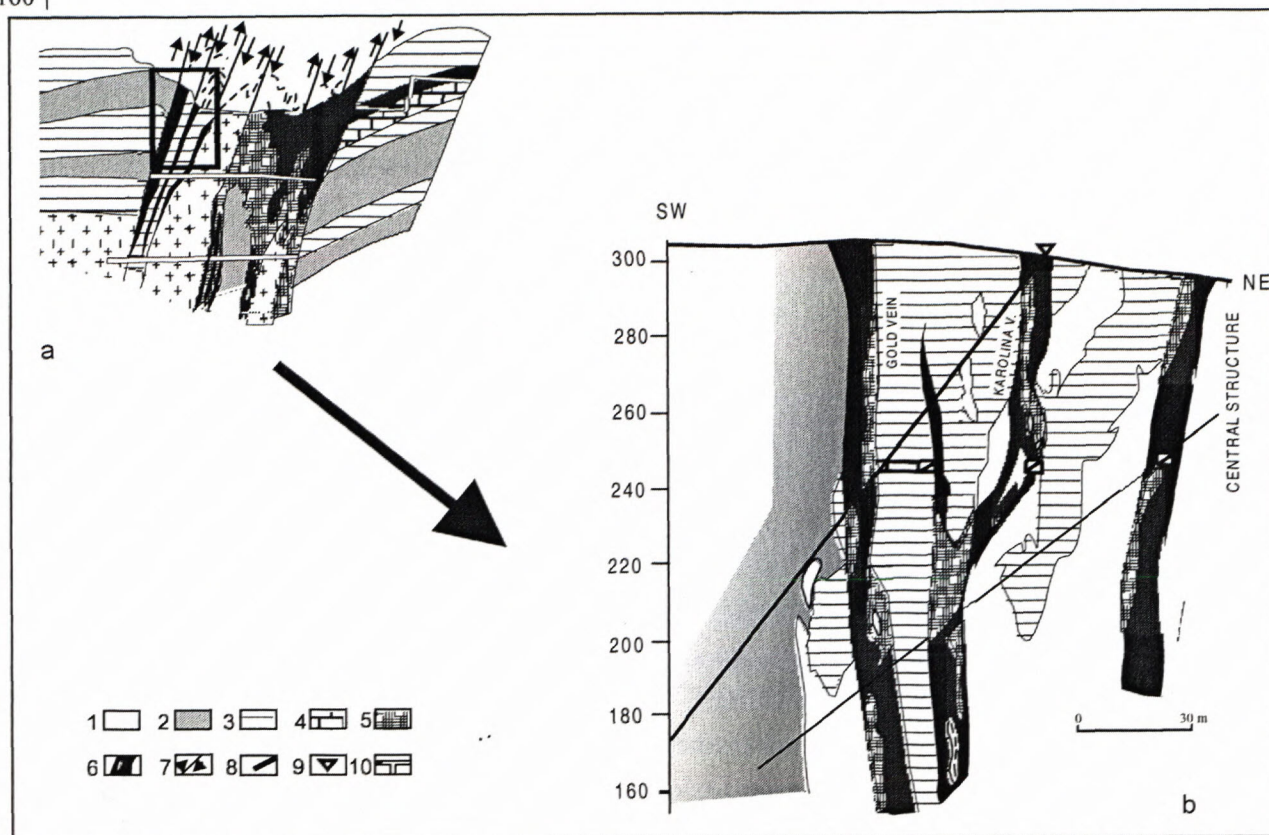


Fig. 2: Geological cross section of the central zone of the Pezinok-Kolársky Vrch Sb deposit (according to Ilavský 1979 and Mikula 1994). 1 – granitoid rocks, 2 – amphibolites, 3 – metamorphic rocks (phyllites, paragneisses), 4 – carbonates, 5 – black schists with syngenetic pyrite-pyrhotite mineralization, 6 – epithermal mineralization with quartz lenses, 7 – fault zones, 8 – bores, 10 – adits

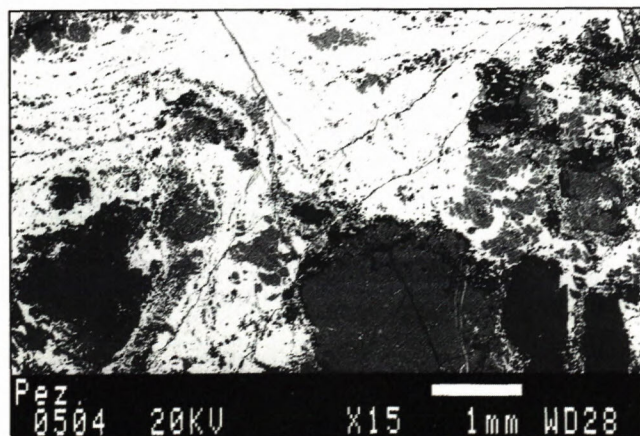


Fig. 3: Fine-grained metamorphosed, primarily exhalation-sedimentary pyrite (white) -pyrhotite (grey) ore in black schist.

MINERALS	STAGES AND ASSEMBLAGES			
	QUARTZ ARSENOPYRITE	QUARTZ PYRITE ARSENOPYRITE	STIBNITE CARBONATE QUARTZ	STIBNITE KERMESITE
	I	II	III	IV
QUARTZ	■	■	■	■
PYRITE	■	■		
ARSENOPYRITE	■	■		
ANKERITE		■	■	
SIDERITE		■	■	
TETRAHEDRITE		■		
CHALKOPYRITE		■		
LÖLLINGITE		■		
GUDMUNDITE			■	
PYRRHORITE			■	
SPHALERITE			■	
GLAUKODOTE			■	
JAMESONITE			■	
BOULANGERITE			■	
BERTHIERITE			■	
DOLOMITE			■	
STIBNITE			■	■
CALCITE				■
GARAVELLITE				■
BISMUTH				■
HOROBETSUITE				■
ANTIMONY				■
KERMESITE				■
VALENTINITE				■

Fig. 4: Succession scheme of Sb mineralization at the Pezinok-Kolársky Vrch deposit (according to Cambel 1959 and András 1983 – modified).



The Pezinok – Kolársky Vrch deposit is situated in about 3500 m long tectonic fault of NW-SE direction. At the surface the mineralized structure is 25-70 m thick and about 430 m long (Mrákava, 1987). Two types of ore mineralization can be distinguished: 1 – metamorphosed, primarily exhalation-sedimentary pyrite mineralization genetically related to Devonian basic volcano-sedimentary cycle which was subsequently metamorphosed (Cambel 1956; Polák 1956) and 2 – hydrothermal Sb (Au-As) mineralization of epigenetic character which is located mostly in beds of tectonically deformed black shales. Metals could have been mobilised from the black shales by the circulation of fluids released during regional and periplutonic metamorphism, caused by granitoid rock intrusion (Cambel & Khun 1983; Chovan et al. 1992).

The main ore mineral is stibnite. There is a higher amount of berthierite and gudmundite in some zones. About 20 000 t of antimony was exploited by a 50x300 m open pit and several underground galleries (Uher et al. 2000). Identified resources of antimony are 5000 t of ores and 5.5 t of gold. According to various authors, the average gold content in ore varies from 3.04 to 4.20 ppm, silver content from 3.20 to 9.10 ppm and stibnite content is 0.10 %. Sb-flotation concentrate (data from 1990) contained 9-11 ppm of gold, 20-40 ppm of silver. 0.40 ppm of gold was lost in the waste (Mikula 1992).

Cambel (1959) described three mineralization stages of Sb epigenetic mineralization. and Andráš (1983) described the oldest gold-bearing arsenopyrite-pyrite stage and completed the succession scheme (Fig. 4):

- 1 – gold-bearing quartz-arsenopyrite-pyrite (Fig. 5),
- 2 – quartz-pyrite-arsenopyrite  $\pm$  löllingite, tetrahedrite, chalcopyrite (Figs. 6, 7),
- 3 – quartz-carbonate-stibnite  $\pm$  gudmundite, pyrrhotite, pyrite, sphalerite, Pb-Sb sulphosalts, berthierite (Figs. 8 – 10)
- 4 – stibnite-kermesite  $\pm$  antimony, valentinite, bismuth, Bi-Sb sulphosalts (Figs. 11 – 13).

Sb mineralization is spatially associated with exhalation-sedimentary metamorphosed pyrite and pyrrhotite mineralization. Patterns of its remobilization are observed in the form of stibnite films on surfaces of alpine faults in granitoids and gneisses (Chovan et al. 1990).

## Methods

Pb isotope analyses in stibnite were performed in laboratories of Vereinigung der kooperativen Forschungsinstitute der Österreichischen Wirtschaft, Arsenal in Vienna (analysed by M. Kralik). Distribution of sulphur isotopes in gold-bearing sulphides of the 1<sup>st</sup> stage of epigenetic mineralization was analysed in BRGM Orléans, France (analysed by A. M. Fouillac). Isotope analyses of oxygen and carbon in carbonates were performed in laboratories of the Czech Geological Survey in Prague (analysed by V. Šmejkal) and isotope analyses of oxygen in quartz in laboratory of the Geological Survey of Slovak Republic in Bratislava (analysed by A. Hašková).

Pyrolytic analyses of black shales were performed at the Czech Geological Survey in Brno using device Rock-Eval (analysed by Juraj Franců).

The reflectance of organic matter was measured in standard condition on rock polished sections using Leitz Orthoplan microscope with microphotometer MPV 2. Conditions: as a standard a glass-prism  $R_0=7.39\%$  was used, measuring field  $2\times 2\mu\text{m}$ , 50x lens, immersion oil, wavelength of light 545 nm, analysator in position of  $45^\circ$ . Maximum ( $R_{\text{max}}$ ) and minimum ( $R_{\text{min}}$ ) values of reflectance were measured on phytoclasts in 4 positions of microscope table.

Fluid inclusion studies were performed with THM 600 Linkam (Geological Institute, Slovak Academy of Sciences) and THMSG 600 Linkam (Faculty of Natural Sciences, Comenius University) freezing-heating stages calibrated using natural fluid inclusions with pure  $\text{CO}_2$  and inorganic compounds with known temperatures of phase transitions. Uncertainty of the final melting and homogenization temperatures is within  $\pm 0.2^\circ\text{C}$ .

## Isotope study

Distribution of Pb-isotopes in galena indicates magmatic origin of fluids (Černýšev et al. 1984) in postorogenic phase of the Variscan cycle. The present study shows the relatively inhomogeneous Pb-isotope distribution in stibnites (Tab. 1), which corresponds with average values of upper crustal Pb origin (Fig. 14). Application of Stacey-Kramer classification (1975) enables to distinguish two fields of model ages: the first one ranges from 220 to 230 Ma and the second one, probably corresponding with ore remobilization, about 110-130 Ma. Low model ages are consequence of the „J-effect“, caused by contamination by radiogenic lead during the ore remobilization in metamorphic process.

Tab. 1 Pb-isotope distribution in stibnites from Pezinok-Kolársky Vrch deposit

Sample	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
1	18.638	15.702	38.542
2	18.553	15.677	38.442
3	18.626	15.698	38.534
4	18.747	15.702	38.533

Analysed in Vereinigung der kooperativen Forschungsinstitute der Österreichischen Wirtschaft laboratories, Arsenal, Vienna (analysed by Dr. M. Kralik)

According to Kantor (1974) and Andráš et al. (1998) (tab. 2), the  $\delta^{34}\text{S}_{\text{(CDT)}}$  isotope distribution varies in the range from 2.0 to  $-21.5\%$  (Fig. 15). The increase of light  $^{32}\text{S}$  isotope content in syndepositional pyrite-pyrrhotite ores is a consequence of the influence of bacterias. Sb-Fe-minerals (gudmundite and berthierite) crystallized from solutions, which penetrated through these ores. They show the same high content of  $^{32}\text{S}$ . The  $^{32}\text{S}/^{34}\text{S}$  ratio in stibnite is close to that of the troilite standard, resp. to the hypogene plutogenic sulphur (Kantor 1974). Existence of more sulphur sources and intensive contamination of hypogenous sulphur by light  $^{32}\text{S}$  isotope was proved.

Carbon and oxygen isotope distribution in carbonates associated with Sb (Au) mineralization of four hydro-



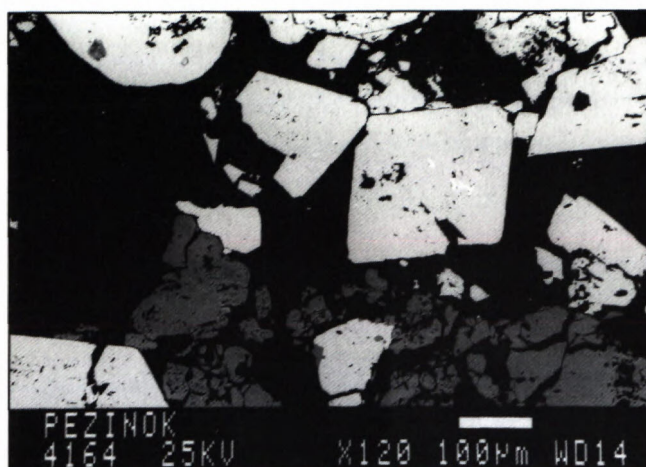


Fig. 5: Euhedral gold-bearing arsenopyrite (white) and pyrite (grey) in quartz (black) of the 1<sup>st</sup> stage

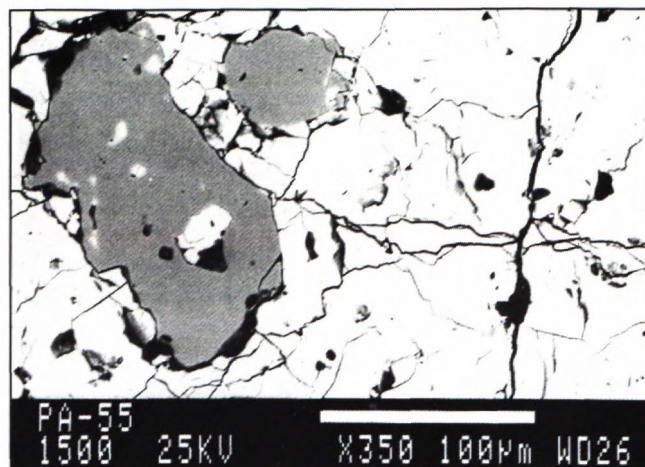


Fig. 6: Brecciated massive arsenopyrite (white) and pyrite (grey) mineralization of the 2<sup>nd</sup> stage.

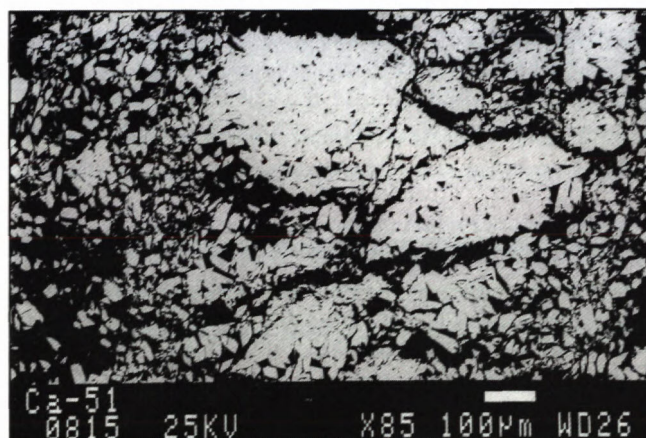


Fig. 7: Relic texture of original pyrite aggregate replaced by euhedral löllingite crystals – 2<sup>nd</sup> stage.

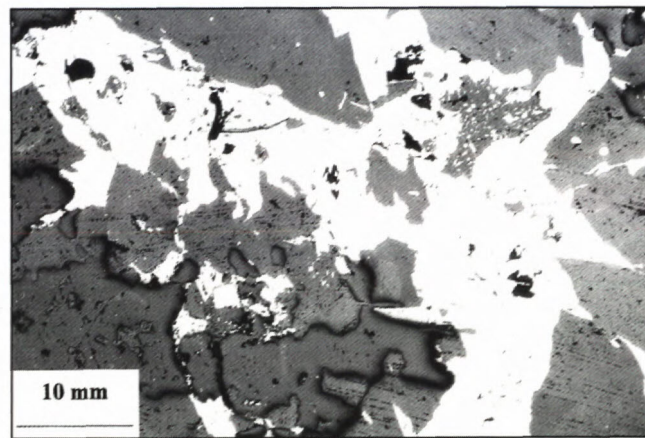


Fig. 8: Aggregate of stibnite (white) in quartz (grey), // nicols – 3<sup>rd</sup> mineralization stage.

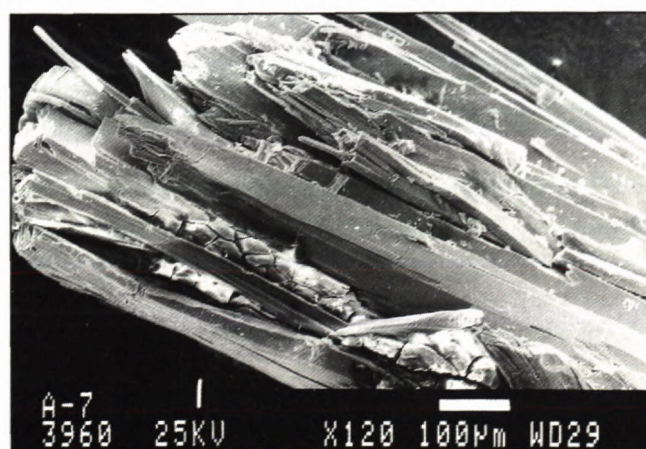


Fig. 9: Morphology of rare stibnite needles (3<sup>rd</sup> stage).

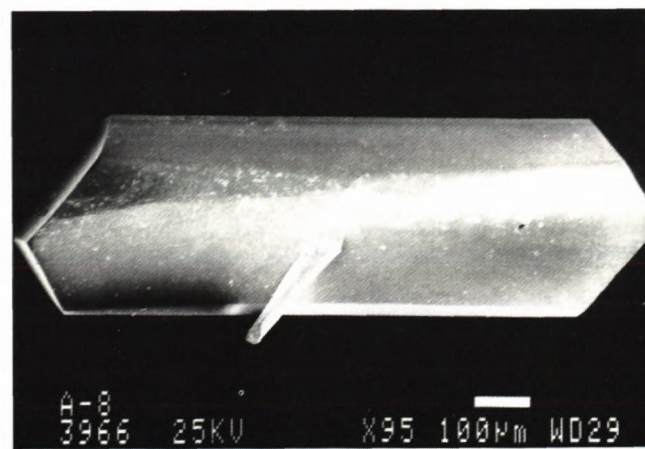


Fig. 10: Morphology of euhedral gudmundite crystal from the 3<sup>rd</sup> mineralization stage.



thermal stages is considerable inhomogeneous (Tab. 3, Fig. 16) and varie in the following ranges:  $\delta^{13}\text{C}_{\text{PDB}}$  = from -13.2 to 9.1 ‰ and  $\delta^{18}\text{O}_{\text{PDB}}$  = from -17.5 to -13.6 ‰ ( $\delta^{18}\text{O}_{\text{SMOW}}$  = -13.89 up to -20.54 ‰).  $\delta^{18}\text{O}_{\text{PDB}}$  isotope distribution in quartz (from -10.01 to -16.46) indicates meteoric origin of fluids. In carbonates it is possible to observe a moderate shift of  $^{18}\text{O}$  values to the field of metamorphogenous and endogenous origin of oxygen in direction: calcite-dolomite-ankerite/siderite. Comparison of O-isotope data with those of  $^{12}\text{C}/^{13}\text{C}$  ratio gives an evidence about the increasing role of meteoric fluids predominantly in the final stages of crystallization.

Tab.2  $\delta^{34}\text{S}_{(\text{CDT})}$  isotope data in gold-bearing arsenopyrites and pyrites of the 1<sup>st</sup> mineralization stage from the Pezinok-Kolársky Vrch deposit

Sample	Mineral	$\delta^{34}\text{S}_{(\text{CDT})}$
RB-201	arsenopyrite	-0.5
RB-201	pyrite	-14.4
RB-206	arsenopyrite	+1.3
RB-214	pyrite	-11.9
RB-214	arsenopyrite	-1.6
RB-217	pyrite	-3.0
RB-217	arsenopyrite	0.0
RB-223	pyrite	-14.0

Analysed in BRGM, Orléans, France (Dr. A. M. Fouillac)

Tab. 3 Distribution of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  (‰ PDB) isotopes in vein carbonates and in quartz from Sb mineralization from the Pezinok-Kolársky Vrch deposit

a) carbonates

Sample	Mineralization		‰ PDB $\delta^{13}\text{C}$	‰ PDB $\delta^{18}\text{O}$
	Mineral	stage		
RB - 77	ankerite	2	-13.10	-17.54
RB - 12	ankerite	2	-10.83	-16.11
RB - 13	ankerite	2	-10.75	-16.22
RB - 47	ankerite	2	-10.20	-13.60
PA - 14	siderite/dolomite	3	-10.50	-16.34
RB - 48	siderite/dolomite	3	-9.80	-15.10
RB - 47	calcite	4	-9.00	-14.97
RB - 79	calcite	4	-10.10	-14.55

b) quartz

Sample	Mineralization		‰ PDB $\delta^{18}\text{O}$
	Mineral	stage	
RB-204	black quartz	1	-13.52
P-20	black quartz	2	-15.36
RB-109	grey quartz	2	-16.05
RB-205	grey quartz	2	-12.98
RB- 10	black quartz	3	-14.12
RB-108	grey quartz	3	-13.80
RB-216	milky quartz	4	-16.46

Department of Isotopic Geology of the Geological Survey of Slovak Republic, Bratislava (A. Hašková)

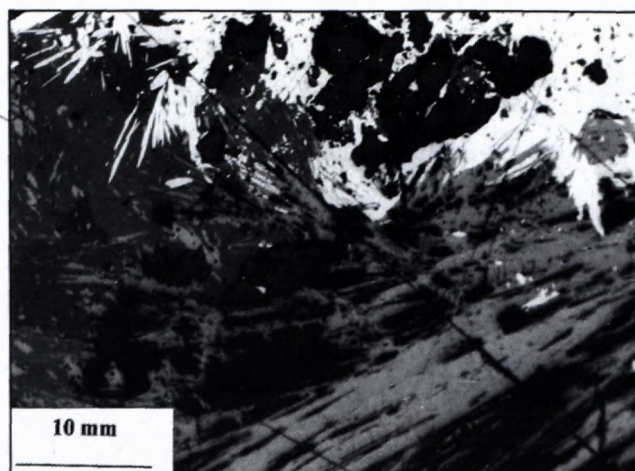


Fig. 11: Typical mineral assemblage of the 4<sup>th</sup> stage: euhedral crystals of stibnite (white), long needles of valentinite (light grey) and kermesite (dark grey) in quartz (black).

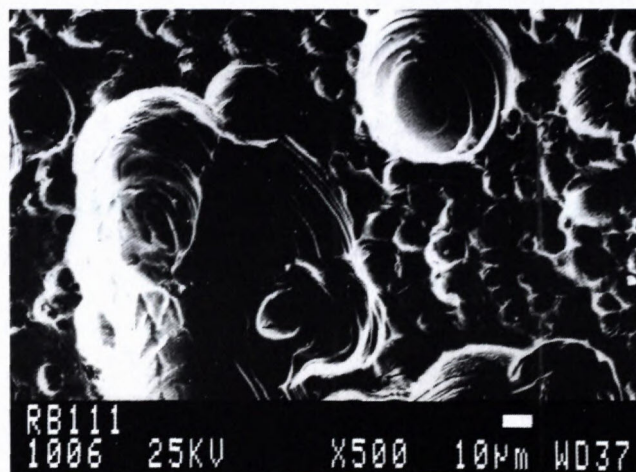


Fig. 12: Sulphuric acid-etched surface of native antimony aggregate (4<sup>th</sup> stage).

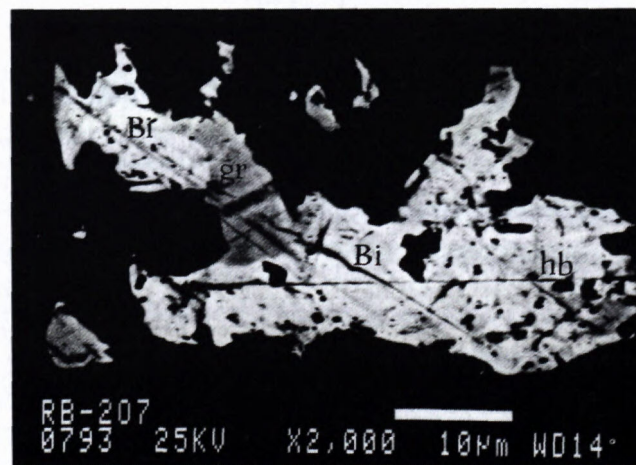


Fig. 13: Intimate intergrowths of Bi-minerals (4<sup>th</sup> stage): native bismuth (Bi), horobetsuite (hb) and garavellite (gr).



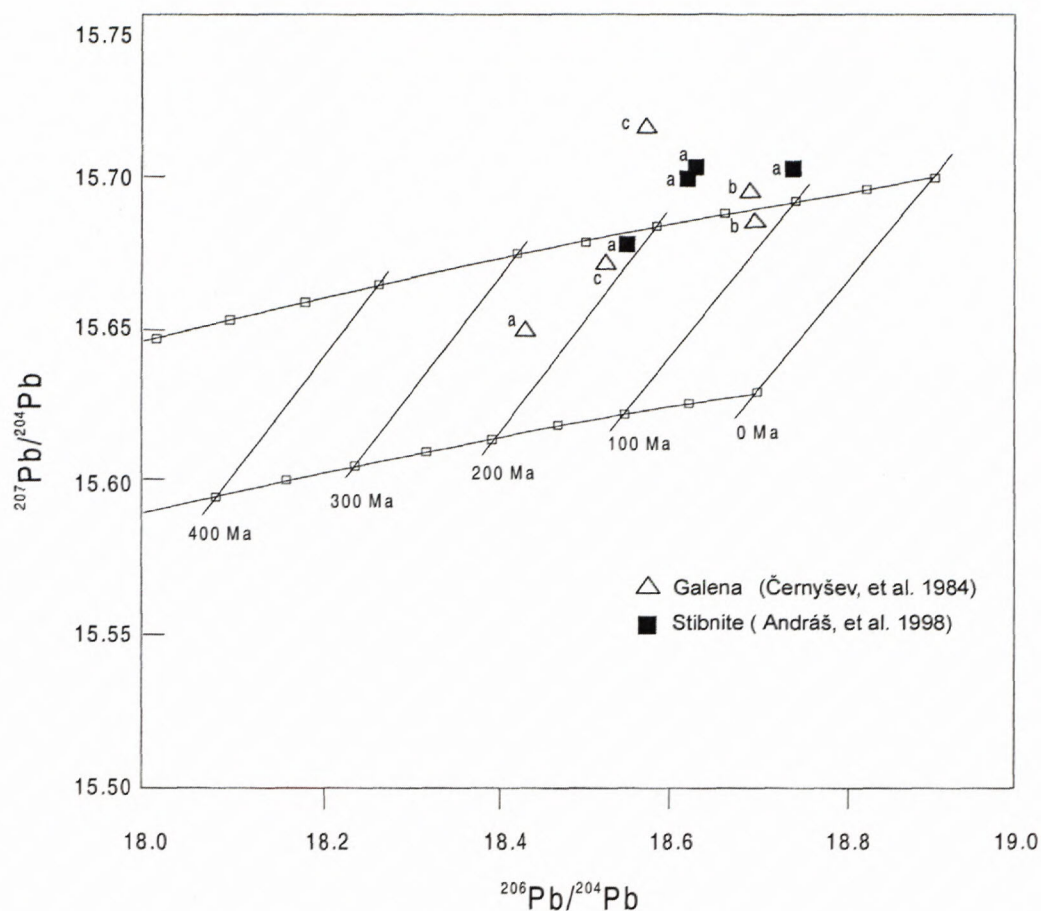


Fig. 14: Evolution diagram of Pb-isotopes in galenas and stibnites from the Pezinok-Kolársky Vrch deposit (according to Stacey-Kramer 1975). 1 – 4: analyse numbers in tab. 1; galena is from the following occurrences: a – Pezinok, — Pod Babou, c – Častá

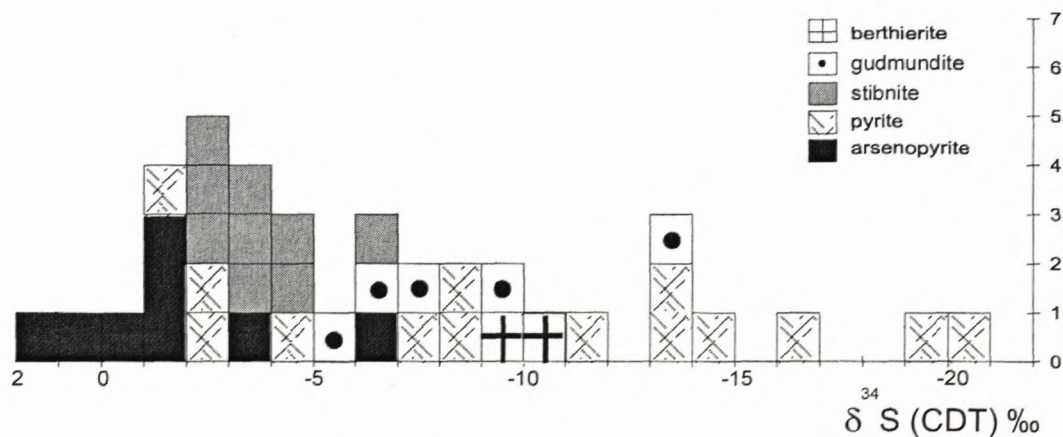


Fig. 15:  $\delta^{34}\text{S}$  isotope data in sulphides from hydrothermal mineralization (Kantor 1974 and Andráš et al. 1998)

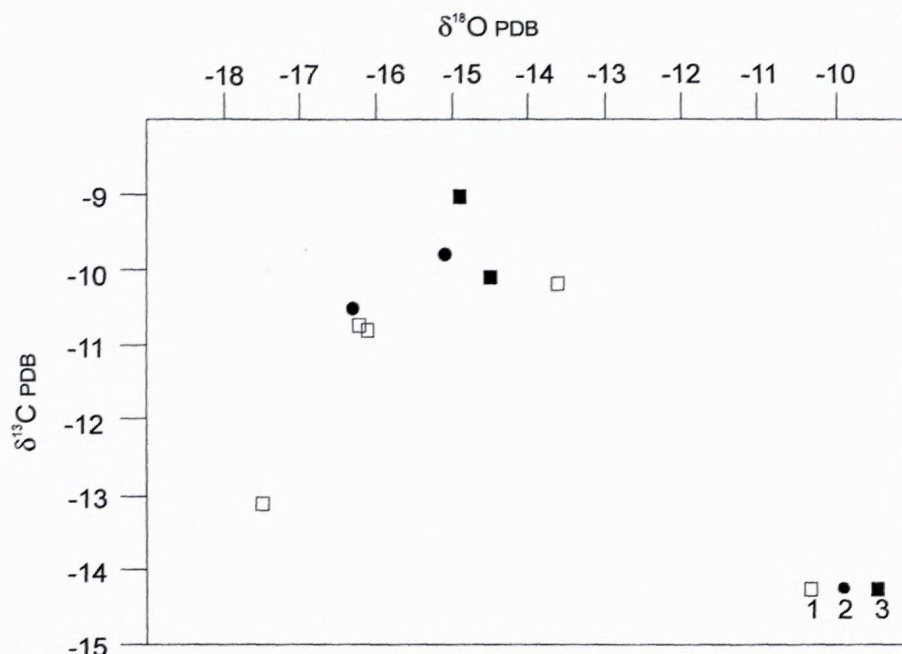
### Thermometric study

Syndepositional exhalation-volcanogenic ores were recrystallized during the regional-periplutonic metamorphism in greenschist and amphibolite facies. According to Cambel et al. (1990) the temperature of this metamorphism varies in the range 350 – 600 °C and the

pressure is about 3.5 – 5.5 kbar. Graphite geothermometer gives the temperature about 450 °C and pressure 3 (up 3.5) kbar (Andráš & Horváth 1985). Such temperature and pressure enable mobilization of metallic elements. Different character of fluids, varying temperature and changes of pressure caused the final variability of the mineralization.



Fig. 16:  $\delta^{13}\text{C}/\delta^{18}\text{O}_{\text{PDB}} \text{‰}$  plot of isotope distribution in carbonates in association with Sb mineralization: 1 – ankerite, 2 – siderite/dolomite, 3 – calcite.



Contents of organic carbon ( $C_{\text{org}}$  in tab. 4) show that the black shales are, sensu Hunt (1972) classification, „rich“ (RB-102 and 24/482-3), and „very rich“ (RB-101, RB-104, 43/329) in organic carbon. The contents of the distillable and pyrolytic hydrocarbons are low. This fact indicates a high degree of graphitization (maturation) of the organic matter. Parameter  $S_3$  - pyrolytic  $\text{CO}_2$  (mg/g of sample) indicates oxidation of the organic matter.

Tab. 4 Pyrolytic analyses of mineralized black schists

Sample	$S_3$	TC	$C_{\text{org}}$
RB-101	0.36	4.62	3.5
RB-102	0.56	0.71	0.5
RB-104	0.12	2.60	1.5
24/482-3	0.38	0.50	
43/329		3.98	2.0

$S_3$  =  $\text{CO}_2$ -pyrolytic

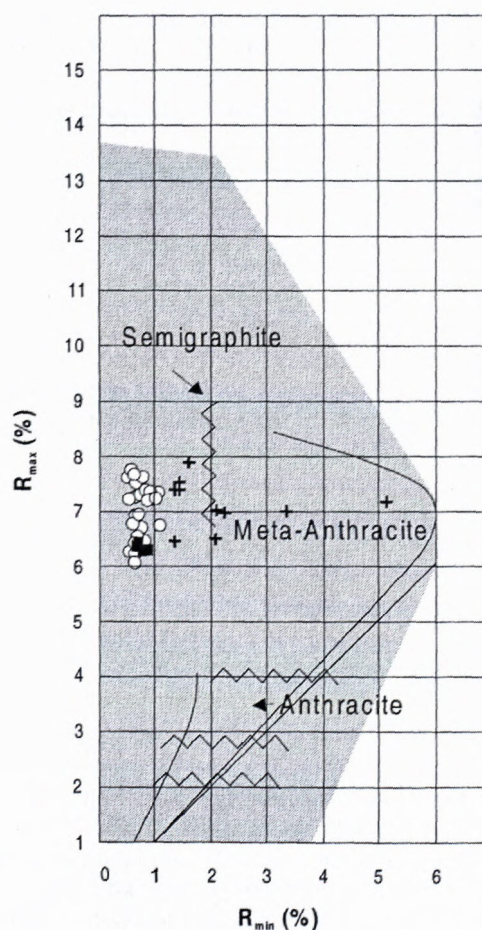
TC – total-carbon

$C_{\text{org}}$  – organic carbon

Two main types of organic matter were distinguished in samples of ore-bearing black schists from Pezínok deposit:

1. Flocky organic matter of the size 2 – 5  $\mu\text{m}$ , parallel with the rock foliation. Thermal overwork of the organic substance destroyed original textures. Small size and strong thermal reworking of particles do not permit distinguish original textures of organic particles and to state terrestrial or marine origin of the organic matter.

2. Organic matter of high level of maturation in stylolithes and in calcite and quartz veinlets. Individual particles have predominantly size about 2 – 5  $\mu\text{m}$ , rarely 7  $\mu\text{m}$ . This second type of organic substance represents pyrobitumen. The bitumen was probably generated in the past - during the diagenetic stage from organic matter stored in sediments and later temperature-overworked during the metamorphosis of the rock complex.



- Pezínok - Kolársky vrch - Budúcnosť mine, organic particles reflectance
- Pezínok Augustín mine, organic particles reflectance
- + Pezínok - Trojárová mine, solid bitumen reflectance

Fig. 17 Reflectances of organoclasts from ore-bearing black schists from Pezínok deposit



Tab. 5 Characteristics of ore forming fluids

Stage	Salinity (wt. % NaCl equiv.)	Chemical composition of fluids	Homogenization temperature (°C)	Crystallization temperature(°C)	Eutectic temperature (°C)	Density of fluids g/cm <sup>3</sup>
1	6-11	secondary inclusions	180-275	425-450*	-45 to -55	
2-3	7-20	NaCl-KCl-H <sub>2</sub> O	145-200	350-450**	< -45	0.98-0.93
4	8-25	CaCl <sub>2</sub> -H <sub>2</sub> O (±NaCl)	82-198		-57 to -48	0.99-1.16

\* sensu Dubaj (in Andráš et al. 1998)

\*\* only for the 2. stage sensu Dubaj (in Andráš et al. 1998)

Increasing temperature caused irreversible changes in molecular structure of the organic matter which correspond to the increasing light reflectance of the organic matter. The maximum reflectance ( $R_{\max}$ ) of organic particles, as well as of solid bitumen, varies in the range 6.0 – 7.8 %. Organic matter in black shales from Pezinok deposit has reached the meta-anthracite up to semigraphite stages (Fig. 17).

By using average  $R_{\max}$  values of organic particles ( $R_{\max} = 6.95$  %) and solid bitumen ( $R_{\max} = 7.14$  %) in Barker & Pawlewicz (1986) and Baker & Bone (1995) equations for calculation of maximum temperature of metamorphism, we have obtained temperature close 400 °C.

#### Fluid inclusion study

Fluid inclusions were studied in relation to mineral assemblages in doubly polished wafers (thickness of 0.2 – 0.5 mm) of quartz and carbonates. Fluid inclusions had almost regular shape and occurred in small clusters or planes and trails. Studied fluid inclusions were of a very small size <10  $\mu$ m, which made measurements more difficult, particularly at low temperatures. Another frequently encountered problem was non-transparency of the host mineral. The following phase changes have been recorded: eutectic or first melting temperature ( $T_e$ ), to determine salt-water system; final melting temperature of ice ( $T_{mi}$ ), to calculate salinity; total homogenization temperature ( $T_h$ ), to calculate the density of fluids and estimate the formation temperature.

Phase changes at low temperatures were studied before those upon heating because of the risk of decrepitation.

After heating of completely frozen inclusions (to – 100°C) the first appearance of liquid phase was observed in the temperature range from –56.7 to –42.7 °C. This indicates the presence of chlorides of bivalent cations such as Ca<sup>2+</sup> or Mg<sup>2+</sup> in the fluids (Borisenko 1977).

In some cases it was not possible to observe melting of ice, however, as an indirect evidence of ice melting the last sudden movement of vapour bubble was considered (Roedder 1984).

All inclusions homogenised to liquid. Some of them decrepitated before homogenisation ( $T_h = 80 - 402$ °C), nevertheless massive decrepitation (if measured) occurred at temperatures around 400°C. In a few cases some solid phases have been observed.

#### 1<sup>st</sup> stage

In quartz of the 1<sup>st</sup> stage of the epigenetic Sb-Au mineralization only data from secondary fluid inclusions were available. Homogenization temperatures of inclusions varied from 180 to 275 °C (Fig. 18a).

Salinity of the solutions is 6-11 wt. % NaCl equiv., eutectic temperature ranges from –45 to –55 °C (Tab. 5).

Using the data obtained by independent geobarometer and the tables of Hurl (1988) it is possible to ascertain the real temperature of the quartz crystallization. According to Andráš et al. (1998), the crystallization temperatures in the gold-bearing arsenopyrite-pyrite 1. stage are equal with range from 425 to 450 °C.

#### 2<sup>nd</sup> and 3<sup>rd</sup> stage

Quartz of 2<sup>nd</sup> and 3<sup>rd</sup> stage contained two-phase (liquid-vapour) aqueous inclusions, with occasionally observed solid phases (daughter crystals), represented by halite and ore minerals. Eutectic (first melting) temperatures below –45 °C suggest the presence of CaCl<sub>2</sub> in H<sub>2</sub>O-NaCl solution. Homogenization temperatures range from 145 to 200 °C (Fig. 18b). Decrepitation temperature peak is around 400°C. Salinities are in the range of 7 – 25 wt.% NaCl equiv.

The temperature calculation corresponding with the highest possible ore forming pressure of 3 kbar (Andráš & Horváth 1985), using the pressure-temperature curves (Hurl 1988), gives the quartz crystallization temperature 350 – 390 °C.

The arsenopyrite thermometers of Kretschmar & Scott (1976) and Sundblad et al. (1984), used on massive arsenopyrite of 2<sup>nd</sup> stage, give temperatures 350 – 410 °C and 350 – 450 °C, respectively (Andráš et al. 1998).

#### 4<sup>th</sup> stage

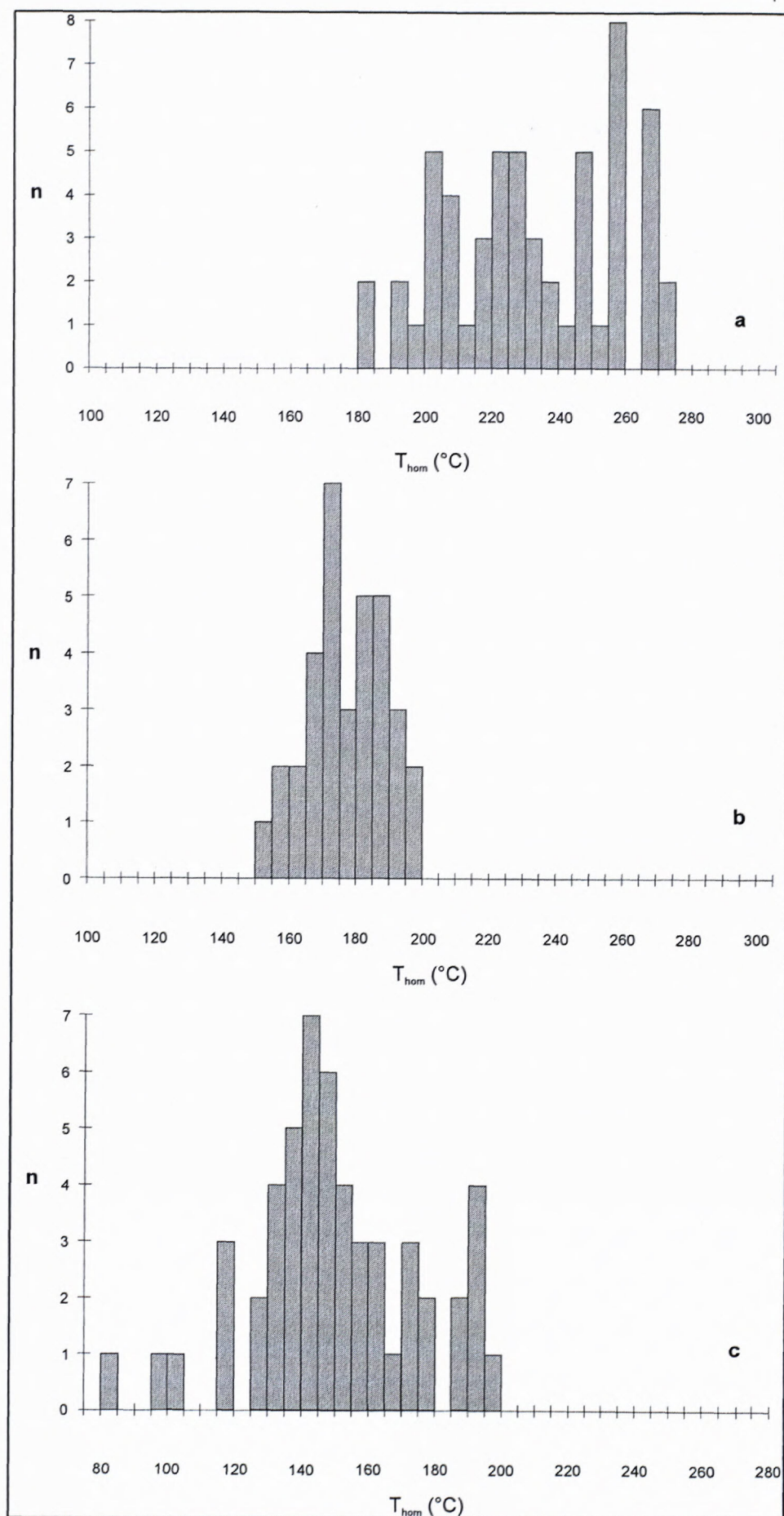
Milky quartz of 4<sup>th</sup> stage contained two-phase (L + V) aqueous inclusions, with the average size of about 6  $\mu$ m. The vapour bubble occupies less than 10 vol. % of the total volume.

Eutectic temperature varies between –56.7 and –42.7 °C, corresponding to the CaCl<sub>2</sub>+NaCl+H<sub>2</sub>O system. Final melting of ice was observed in a wide temperature range, from –30.4 up to –5.1 °C. Homogenisation to liquid occurred in the range of +82 to +199 °C (Fig. 18c) with the



Fig. 18: Histogram of homogenization temperatures in fluid inclusions from quartz from Sb epigenetic mineralization:

a) 1<sup>st</sup> stage, b) 2<sup>nd</sup> and 3<sup>rd</sup> stage, c) 4<sup>th</sup> stage.





main interval between 130 and 160 °C. Salinities were calculated from ice melting temperatures using equation of state (EOS) of Oakes et al. (1990) and vary between 8 – 25 wt. %  $\text{CaCl}_2$  equiv. Densities were calculated from the homogenisation temperatures using EOS of Zhang and Frantz (1987) and range from 0.99 to 1.66  $\text{g/cm}^3$ .

## Conclusions

Lead in stibnites is of upper crustal origin. The young model ages (220-230 and 110-130 Ma) are the consequence of the „J-effect“, caused by the younger metamorphogenous processes and rejuvenation of Sb (-Au) ores. Isotope distribution shows at least two sources of sulphur. Biogenic sulphur had an important role predominantly in metamorphosed, primarily exhalation-sedimentary pyrite mineralization and in Sb hydrothermal minerals with Fe content (gudmundite, berthierite). Sulphur isotopes in gold-bearing sulphide mineralization are differentiated: the light biogenic sulphur is incorporated into pyrite while the sulphur from deep lying source is incorporated into arsenopyrite. Ore fluids mainly of 3<sup>rd</sup> and 4<sup>th</sup> stage are probably meteoric in origin but they incorporated predominantly magmatic sulphur, which could have been juvenile or derived from older plutonic rocks.

Distribution of carbon and oxygen isotopes in carbonates and oxygen isotopes in quartz from Sb mineralization is inhomogeneous. The values show a relatively wide range and indicate predominantly meteoric origin of fluids.

It is possible to distinguish two types of fluid inclusions. In direction from the oldest 1<sup>st</sup> gold-bearing sulphide stage to pyrite-arsenopyrite, carbonate-stibnite and stibnite-kermesite mineralizations of 2<sup>nd</sup> – 4<sup>th</sup> stages, the evolution of fluids is as follows:

Generally, the first type of inclusions is typical for secondary inclusions in the oldest quartz coexisting with gold-bearing arsenopyrite-pyrite. The salinity of these fluids is low: 6-11 wt %  $\text{NaCl}$  equiv. Temperatures of the eutectic point vary from -45 to -55°C and the fluid density is 0.88  $\text{g/cm}^3$ . The estimated pressure is about 3 kbar. These fluids were of endogenous-metamorphogenous (or magmatic) origin.

The second type is represented by aqueous, moderately saline,  $\text{NaCl} \pm \text{CaCl}_2$  bearing inclusions. They are typical for stibnite-sulphosalts mineralization of 2<sup>nd</sup> and 3<sup>rd</sup> stages. Homogenization temperatures range between 145-200 °C (Tab. 5). The salinity of the fluids is ranging from 7 to 25 mol %  $\text{NaCl}$  equiv. The temperature of crystallization changes according to way of calculations used. An increasing role of meteoric water and their intensive mixing with endogenous fluids during its penetration into the wall rock and during metamorphic process is suggested.

The salinity of  $\text{CaCl}_2$ - $\text{NaCl}$ - $\text{H}_2\text{O}$  solutions of the 4<sup>th</sup> stage ranges from 8 to 25 wt. %  $\text{CaCl}_2$  equiv. The homogenization temperatures are low: 82-199°C (Tab. 5). The importance of meteoric water is equal or more significant as in the case of the fluids of the 2<sup>nd</sup> and 3<sup>rd</sup> stage.

Thermal maturation of organic matter from ore-bearing black schists from Pezinok deposit is in meta-anthracite and semigraphite stages and indicates temperatures close to 400°C.

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