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## ORE MINERALIZATION OF THE MALÉ KARPATY MTS. (WESTERN CARPATHIANS)

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Abstract: The following types of ore mineralization are distinguished in the Malé Karpaty Mts.: I - metamorphosed, primarily exhalation-sedimentary pyrite; II - hydrothermal-molybdenum, polymetallic and antimony-gold; III - copper-barite and uranium in the Upper Paleozoic ; IV - sedimentary-manganese; V - gold placers. Pyrite and antimony-gold mineralization are the most frequently occurring ones and spatially as well as genetically related. The metals could have been mobilized from Paleozoic black schists, metavolcanites and metasediments by fluids released in the process of pre-intrusive regional metamorphism or during the intrusion of granitoids. Negative values of  $\delta^{34}$ S as well as the values of  $\delta^{18}$ O and  $\delta^{13}$ C and their distribution indicate intensive interaction of ore-bearing solutions with the surrounding rock environment. Homogenization temperatures of fluid inclusions in quartz (32° - 150 °C) confirm the succession on the formation of the distinguished Sb-Au mineralization parageneses. The formation of copper-barite mineralization is connected with Permian volcanism, and the origin of uranium mineralization with the circulation of groundwaters. Sedimentary Mn-mineralization occurs in Jurassic shales.

Key words: ore mineralization, metallogeny, Malé Karpaty Mts.

#### Introduction

The Malé Karpaty Mts. is one of the important ore districts of the Western Carpathians. The first written reports on the granting of mining rights and on gold panning in the region of Pezinok date from year 1339, and from the 16th to the end of the 19th century gold was mined. There is a note on the exploitation of the deposit Častá dated 1674 (Cambel 1959). The beginning of mining and treatment in Pernek and Pezinok are dated to around 1800. More intensive mining of Sb was renewed in the year 1940, and with short interruptions it continues till the present. Pyrite deposits were exploited in the 18th and 19th centuries for raw material used in the sulphuric-acid producing plant in Pezinok. At present, mining of gold-bearing arsenopyrite ore has started, on the deposit Kolársky vrch Hill, but the antimony mine has closed down. Geological survey continues above all on the Sb-Au-As mineralization at Pezinok - Trojárová.

#### **Geological setting**

The Malé Karpaty Mts. are the westernmost mountain range of the Inner Carpathians, linking the Carpathians with the Alps. They are core mountain ranges, which have attracted exceptional interest from geologists in the last years. Data on their geological structure are summarized on the geological map 1:50 000 (Mahel 1972). In more recent works of Mahel (1980, 1986), Plašienka et al. (1991), the autochthonous interpretation of Tatricum within the structure of the crystalline core of the Malé Karpaty Mts. has been abandoned and the considerable extent of Alpine thrusting has been pointed out.

Geological structure of the Malé Karpaty Mts. is characterized by several superposed nappes, consisting of pre-Alpine fundament, Mesozoic cover and higher nappes (Plašienka et al. 1991). Several volcano-sedimentary formations have been distinguished in the Tatric fundament. Camblel (1954) distinguished in the Lower Paleozoic of the Malé Karpaty Mts. the Harmónia Series and the underlying Pezinok-Pernek Series. Putiš (in Mahel et al. 1983), Plašienka et al. (1991) distinguished four lithologic units: the Pezinok Sequence (metamorphic mantle of the Bratislava granitoid Massif), Pernek and Harmónia Sequence (metamorphic mantle of the Modra granodiorite) and Dolany Sequence (Fig. 1). The sequences (with the exception of the Dolany Sequence) consist of two formations. The lower, predominantly pelitic-psammitic formation of flysch character (Silurian - Lower Devonian) gradually passes into the overlying volcano-sedimentary formation (Lower to Middle Devonian sensu Planderová & Pahr 1983), consisting of black schists, carbonates, basalts and their tuffs and sometimes also gabbros and gabbrodiorites. Volcanic rocks of the Pernek and Harmónia Sequences correspond to very slightly differentiated tholeitic basalts which were later metamorphosed (Grecula & Hovorka 1987). The above mentioned sequences differ from each other not only lithologically, but also by metamorphic zoning in relation to two main Variscan granitoid bodies: the Bratislava and Modra Massifs.

The sequence of Variscan tectono-metamorphic events was according to Putiš (1987) and Plašienka et al. (1991) the following:

1 - regional metamorphism and folding;

2 - periplutonic metamorphism concluded by the intrusion of the Bratislava granite;

3 - intrusion of the Modra granodiorite which occurred along the tectonic contact between the Pernek and Harmónia Sequence;

4 - late Hercynian tectonic displacement of the Pezinok unit towards the Pernek and Harmónia units causing steep metamorphic foliation with steep fold axes in the region between Pezinok and Pernek.

The age of the earliest metamorphism of the Pezinok-Pernek crystalline complex is according to Cambel et al.  $(1990) 380 \pm 20$ 

Ma. Isotopic data from the Bratislava and Modra Massifs cannot be used as evidence of a significant age discordancy between both massifs and their statistical analysis yielded ages of  $348 \pm 4$ Ma (Cambel et al. 1990).

The late Paleozoic occurs in the Choč Nappe it is represented by the Ipoltica Group consisting of the Upper Carboniferous Nižná Boca Formation and the Permian Malužiná Formation, represented by clastic rocks accompanied by basic volcanism (Vozárová & Vozár 1988).



Fig. 1. Metallogenic map of the Malé Karpaty Mts.

Legend: PEZ - Pezinok, PER - Pernek, DOL - Doľany, HAR - Harmónia sequences. 1 - Tertiary and Quarternary; 2 - Mesozoic (Triassic, Jurassic, Cretaceous), limestones, dolomites, shales, qurtzites; 3 - Upper Paleozoic (Upper Carboniferous - Permian), volcano-sedimentary beds; 4 - granites of the Bratislava Massif; 5 - granodiorites of the Modra Massif; 6 - metamorphosed Paleozoic volcano-sedimentary complexes; 7 - Variscan tectonics; 8 - Alpine tectonics; 9 - Alpine overthrust faults; 10 - nappe planes; 11 - faults; 12 - geological boundaries.

*Mineralization types*: 13 - large deposits of pyrite and stibnite-gold ores, a - operating, b - closed; 14 - manganese mineralization; 15 - barite and copper mineralization in the Permian; 16 - uranium mineralization in the Permian; 17 - pyrite mineralization; 18 - stibnite mineralization, sometimes with gold; 19 - gold-quartz mineralization; 20 - polymetallic and copper mineralization; 21 - gold placers.

Compiled from geological map of the Malé Karpaty Mts. (Mahel et al. 1972), tectonic sketch (Putiš 1987; Plašienka et al. 1991), metallogenic maps (Cambel 1959; Polák & Rak 1980), as well as materials of the Uranium Survey (1983).

Alpine development of the Malé Karpaty Mts., according to Plašienka et al. (1991) is as follows: Mesozoic sedimentation of all units took place in three sedimentation cycles (Triassic, Jurassic - Lower Cretaceous and Upper Cretaceous). During the Middle Cretaceous, significant space reduction occurred as well as nappe thrusting and folding. A basin formed during the Upper Cretaceous in the eastern part, spread westwards during the Paleogene. Fault tectonics during the Neogene caused the horst structure of the territory.

#### Ore mineralization

A number of geologists have studied the problem of ore mineralization. In the period after World War II, mineralogical-geochemical and metallogenetic problems were dealt with above all in the works of Cambel and others (1959, 1959a, 1967, 1977, 1979, 1990 etc.), the problems of deposits were studied above all by Polák et al. (1957, 1970, 1971, 1979, 1980, 1986 etc.), Žákovský (1962) and many other authors.

The following types of ore mineralization have been so far identified in the Malé Karpaty Mts. (Fig. 1):

I - Metamorphosed, primarily exhalation-sedimentary pyrite mineralization.

II - Hydrothermal mineralization: 1 - molybdenum in granitoids; 2 - copper-polymetallic with silver - a) Cu-Pb, Ag, (Ni), b) Pb-Zn, c) Pb-Ag; 3 - antimony-gold -a) gold-sulphidic, b) gold quartz, c) stibnite.

III - Mineralization in the Upper Paleozoic: I - mineralization in cavities and fissures of Permian basalts and andesites - a) copper, b) barite; 2 - uranium mineralization in Permian volcano-sedimentary rocks - a) U-REE, b) U-Cu.

IV - Sedimentary mineralization. Manganese mineralization in Jurassic shales.

V - Gold placers.

Metamorphosed pyrite mineralization and hydrothermal mineralization is spatially related mostly to metamorphic rocks of the Pernek Sequence, less of the Harmónia and Pezinok Sequence, in the region between Pezinok, Pernek and Častá. From the viewpoint of ore deposit occurrence, 4 or 5 productive zones can be distinguished (Cambel 1959; Polák & Rak 1980), corresponding to the location of black schists and the related pyrite and stibnite mineralization (Fig. 2).

# I. Metamorphosed, primarily exhalation-sedimentary pyrite mineralization

This very frequent mineralization type is, as far as deposit accumulations are concerned, associated with thick beds of black schists and phyllites, occurring in zones of actinolite schists and amphibolites (Fig. 3). The most extensive pyrite exploitation took place at the Pezinok and Pernek deposits. Further important ore accumulation are marked on Fig. 2.

All occurrences lie in the so-called productive zones and they form several ore belts. The general direction of all the deposits is NW - SE (Žákovský 1962; Cambel & Jarkovský 1967; Polák 1971) (Fig. 2). The mineralization is monotonous, consisting mostly of pyrite, pyrrhotite (predominantly hexagonal, less monoclinal; Kantor & Ďurkovičová 1973), less of chalcopyrite, sphalerite, magnetite, markasite, uraninite and pentlandite (?) are rare (Cambel et al. 1977). Besides these, a varied assemblage of accompanying nonmetalliferous minerals is found in the ores - quartz, carbonates, amphiboles, pyroxenes etc. Smaller occur-



Fig. 2. Schematic geological map of the Pezinok-Pernek deposit crystalline complex with marked deposits and occurrences of raw materials (adjusted after Polák & Rak 1980; Cambel 1959).

Legend: 1 - metamorphic rocks of the central deposit area; 2 - Mesozoic; 3 - granites of the Bratislava Massif; 4 - granodiorites of the Modra Massif; 5 - Quarternary; 6 - productive zones with black schists and stibnite-gold and pyrite mineralization; 7 - deposits of Sb, Au, and Fe ores (1 - Pezinok-Kolársky vrch Hill, 2 - Pernek); 8 - occurrences of Sb, Au ores (3 - Trojárová, 4 - Kuchyňa); 9 - gold occurrence (Staré Mesto); 10 - occurrences of pyrite ores; 11 - occurrences of polymetallic and copper ores; 12 - gold placers; 13 - molybdenite in granite.

rences of this mineralization type are also known to exist in graphitic rocks of the Harmónia Sequence, in the surroundings of the Dolinkovský vrch Hill (Cambel 1959). The principal mass of the mineralization is genetically associated with basic volcanism of early Paleozoic age, while the resulting character of mineralization was affected by contact and regional metamorphism, causing mobilization and redistribution of sulphides (Cambel 1959; Polák 1971; Cambel et al. 1977 and others).

#### II. Hydrothermal mineralization

1 - Molybdenum - the occurrence of molybdenite in quartz veins has been described in a fragment of alterated granite found near Kuchyňa (Holický & Hrnčár 1978). Molybdenite flakes and scheelite in heavy-mineral concentrates from the region of Kolársky vrch Hill have been mentioned by Kantor (1974). The first occurrence of primary molybdenite in situ was found on the locality Trojárová (Augustín-Čmele) (Hanas et al. 1989), in a





Fig. 4. Intensively folded graphitic schist - fine-grained pyrite is accumulated mostly in darker zones. Loc. Trojárová.



Fig. 3. Geological profile across the Sb and Fe deposit Pernek (adjusted after Žákovský 1962).

Legend: 1 - amphibolites; 2 - actinolite schists; 3 - graphitic schists; 4 - pyrite mineralization; 5 - stibnite mineralization.

drill core of greisenitized leucocratic granite of the Bratislava Massif, at a depth of 270 *m*. This is a confirmation of the presence of high-temperature mineralization in the Malé Karpaty Mts. (Chovan et al. 1990).

2 - Copper-polymetallic with silver:

*a* - Gold (?) and silver were mined at the Častá deposit in the 17th century, and later, at the end of the 19th century, copper and sulphur (pyrite). Ore veins lie in the graphitic phyllites of the Harmónia Formation. They are lenticular, occurring between beds, having a direction of NW - SE and inclination of  $50^{\circ}$  to S. The mineralization formed in four stages: 1 - quartz-sulphidic; 2 - carbonate; 3 - pyrite; 4 - polymetallic with Cu and Ni minerals. In the lower parts, the veins are richer in Ni and Ag. Besides common pyrite, the most abundant ore mineral is chalcopyrite, while galena, sphalerite and tetrahedrite with increased Ag contents are frequent (Cambel 1953, 1959). Ni-Co mineralization is represented by gersdorffite, cobaltite, korynite and ullmanite.

b-SE of Pernek, in the area Pod Babou, there are occurrences of Pb-Zn mineralization. The quartz veins lie in a zone between gneisses and schists, they are maximally 50 m long and up to 30 cm thick, with a north - west direction. The sulphides are in them dispersed or they occur in the form of nests and veinlets. Sphalerite prevails over galena. The mineralization formed in three stages: quartz-arsenopyrite, sphalerite-galena and barite (carbonate) (Cambel 1959).

*c* - Near the eastern margin of the village Pernek, there are occurrences of Ag-Pb mineralization. The quartz-carbonate veins lie in a zone of actinolite schists with graphitic phyllite beds. According to archival reports, the most important ore mineral is Ag-bearing galena, pyrargyrite (?) and pyrite. The Ag content was found to be as high as 400 g/t and Au 7.3 g/t (Cambel 1959). Small occurrences of Ag-Pb-Zn mineralization with gold (?) have been mentioned in old reports to occur in the area of Modra (Cambel 1959).

3 - Antimony-gold (Sb, Au, As):



Fig. 5. Bands and clusters of pyrite (py) and pyrrhotite (po) in graphitic schist. Loc. Trojárová.

This mineralization type is the most frequently occurring one in the Malé Karpaty Mts. and at the present it is also the most important one. All deposits and occurrences are located in the so-called productive zones of the Pernek crystalline complex.

*a* - Gold-arsenopyrite, sulphidic mineralization occurs on the structures of younger antimony mineralization. It also extends to the area of ancient mining W of Pezinok, where it is spatially overlapping with the superposed gold-quartz mineralization. The mineralization is spatially associated with black quartz lenses in black schists, or it occurs in the surrounding hydrothermaly altered rocks of the schist formation, in which it forms small impregnations (Fig. 6). It crystallized from solutions with a relatively low arsenic content and high sulphur (Andráš et al. 1988).

In the area of Pezinok gold-bearing sulphidic mineralization is represented by arsenopyrite and pyrite with submicroscopic gold. According to Andráš (1988) the gold contents are highest in fine-crystalline idiomorphic arsenopyrite (in average 120 *ppm*) with increased antimony content (Dadák 1983). Gold contents in gold-bearing pyrite vary about 55 *ppm* (Andráš 1987).

*b* - Gold-quartz mineralization consits of thin quartz veins with visible gold associated with the body of two-mica granodiorite with abundant pegmatite veins, near to the surface, W of Pezinok (Staré Mesto) (Fig. 8). The metal contents of the ores ex-



Fig. 6. Gold-bearing arsenopyrite (asp) and pyrite (py) in quartz (black). Reflected light, 1 nicol. Loc. Pezinok.



Fig. 7. Gold grain (Au) with sphalerite inclusion (sp) in quartz (black). Reflected light, 1 nicol. Loc. Staré Mesto.



Fig. 8. Geological profile across the area between the Sb-Au-As deposit Pezinok (Kolársky vrch Hill) and gold-quartz mineralization in the Staré Mesto (adjusted after Polák & Hanas 1981).

Legend: 1 - metamorphic rocks of the central deposit area; 2 - two-mica granites; 3 - gneisses; 4 - biotite-quartz phyllites; 5 - ore zones; 6 - main thrust planes.

ploited in the past have been mentioned to vary between 3 - 70 ppm Au (in row gold amalgam there was 10 - 16 % Ag) (Cambel 1959). Gold-bearing white quartz veinlets, several cm thick, enclose sphalerite grains and visible electrum (Andráš et al. 1990). Electrum in quartz forms individual grains of irregular shape. Frequently it penetrates by thin veinlets along the boundaries of quartz grains, or it fills interstitial spaces in quartz. Among large gold grains, elongated shapes are predominant, smaller ones are usually isometric. The dimensions of individual gold grains vary from 0.1 to 1.0 mm. The grains contain abundant sphalerite inclusions (Fig. 7). The content of Ag in electrum is 25 - 30 wt.% (Andráš et al. 1990).

Gold is paragenetically accompanied by galena, Ag-tetrahedrite, polybasite, chalcopyrite, sphalerite and pyrite and by a not precisely identified carbonate. The dimensions of silver minerals are in order of hundreths of *mm*.

The study of the relations of sulphidic and precious-metal minerals of the gold-quartz mineralization indicates that it is one paragenetic mineral association. The position of sulphidic minerals, especially of pyrite and sphalerite, as well as their intergrowths on the margin of a quartz veinlet indicate that they precipitated together with quartz at the beginning of the formation of the gold-quartz mineralization. Preciuos-metal minerals - polybasite, Ag-tetrahedrite, and especially electrum - which, in a similar way to the carbonate, crystallized on the boundaries of quartz grains, or they fill interstitial spaces between them, concluded the process of formation of mineralization (Andráš et al. 1990).

c - Antimony mineralization. Three large and several small occurrences of Sb mineralization are known to exist in the Malé Karpaty Mts. All have similar geological and deposit positions are as well as development of mineralization. The deposit Pezinok-Kolársky vrch Hill lies among crystalline schists (amphibolites, actinolite schists, gneisses, phyllites) intersected by vein bodies of granitoids. It is associated with a large fault zone of low-scale folded and petrographically variable black schist and phyllites. The mineralized zone of NW- SE direction, with an inclination of 60 - 90 ° to NE or SW, has folded, anticlinal structure (Cambel 1959). The mineralization is irregularly developed in the form of short carbonate-sulphidic veinlets, nests and incrustations. The fault zone is up 50 -70 m thick, with signs of mineralization occurring in a lenght of up to 1 km. The thickness of mineralization varies from 10 to 40 m, it is 300 - 500 m long and it is reaching to a depth of 60 - 100 m (Cambel 1959; Polák & Rak 1980 and others).

Below the deposit there is a subhorizontal ore body folded together with the surrounding biotite gneisses. Pastor (1972) assumed that stibnite formed as a result of metasomatic substitution of marly layers.

Mineral parageneses have been studied by Cambel (1959). On the basis of his results as well as his own studies, Andráš (1983) distinguished four mineralization stages during which the hydrothermal Sb-Au-As mineralization formed:

1 - quartz-arsenopyrite, with gold associated with arsenopyrite and pyrite;

2 - quartz-pyrite-arsenopyrite±löllingite, tetrahedrite, chalcopyrite;

quartz-carbonate-stibnite±gudmundite, pyrrhotite,
pyrite, sphalerite, Pb-Sb sulphosalts, berthierite;

4 - stibnite-kermesite ± antimony, valentinite, schafarzikite.

The principal ore mineral of the Sb-mineralization is stibuite, in some zones there is an increases content of berthierite, or sometimes of gudmundite and primary kermesite. The following homogenization temperatures of gas-liquid inclusions have been determined in quartz of the above mentioned four stages: stage 1:300-320 °C; stage 2:210-255 °C; stage 3:180-220 °C; stage 4:150-200 °C (Fig. 8).

North of the Kolársky vrch Hill deposit (in the second productive zone) (Fig. 2) lies the Trojárová deposit (Fig. 9), which is at present being subjected to geological survey. On the basis of geochemical-geophysical prospection, a zone of Sb-Au-As ore accumulation has been found with the help of a drilling survey. The zone has NW - SE direction. with an inclination of about  $50^{\circ}$  to NE, and a lenght of 1200 m (Hanas et al. 1989). The immediate surroundings of the black schist beds in which the pyrite and sulphidic Sb-Au-As mineralization is located of actinolite schists. They, together with amphibolites, form a complex of metatuffs and metabasites, below which lies two-mica granitoids and staurolite-biotite paragneisses of the Bratislava Massif (Vilinovič in Chovan et al. 1990) (Fig. 9). The following mineral parageneses have been distinguished at the locality Trojárová (Chovan et al. 1990): 1 - pyrite-pyrrhotite (exhalation-sedimentary, metamorphosed); 2 - molybdenite in muscovite leucogranite; 3 - quartz-arsenopyrite-pyrite with gold; 4 - quartz--arsenopyrite; 5 - carbonate-pyrite-gudmundite; 6 - carbonatepyrrhotite with gudmundite, chalcopyrite, tetrahedrite and berthierite; 7 - carbonate-stibnite, sometimes with kermesite, berthierite and antimony; 8 - calcite with markasite. Antimony mineralization (parageneses 5 - 7) occurs in carbonate (ankerite-dolomite) veinlets, in which Sb-minerals form nests, small aggregates, impregnations and veinlets (Figs. 10, 11, 12, 13).

A presence of low amount of graphite in black schists at Kolársky vrch Hill as well as at the locality Trojárová has been confirmed with the help of X-ray study of separated graphite. The average value of the lattice parameter calculated for graphite of the deposit Trojárová is  $c = 6.735 \times 10^{-10} m$ . Microcrystalline graphite forms tiny fragments with a size exceeding 1  $\mu m$  and crystal with maximal dimensions of 100 x 170  $\mu m$ .

An antimony ore deposit was exploited in the past NE of Pernek. It occurs in a complex of amphibolitic rocks with layers of actinolite schists and graphitic schists, near an older pyrite mineralization (Fig. 3). Sb-mineralization forms lenses, nests, stockworks of quartz-carbonate veins in the black schists, as well as incrustations (Cambel 1960). The mineralization has a stratabound character, lying in a black-schist bed. Higher up, veins with stibnite cut through schists and sporadically also through the older pyrite mineralization. They formed as a result of mo-



Fig. 9. Geological profile across the deposit crystalline complex at Pezinok-Trojárová (Hanas et al. 1989). Legend: 1 - graphitic schists; 2 - actinolite schists; 3 - amphibolites; 4 - granitoids (Bratislava Massif); 5 - biotite gneiss; 6 - thrust tectonics; 7 -Sb-Au mineralization, locally with pyrite accumulations; 8 - prospection drill-hole; 9 - molybdenite.



Fig. 10. Cross-section of a drill-core from the locality Trojárová. Hydrothermally altered schist with pyrite impregnation (py) is penetrated by carbonate veinlet (carb) with pyrite and gudmundite (py + gd). The youngest is the carbonate veinlet (carb) with stibnite (stib).



Fig. 12. Stibnite (stib) ingrown into hypidiomorphic gudmundite crystals (gd). Reflected light. Loc. Trojárová.



Fig. 11. Hypidiomorphic crystals of gudmundite (gd) surrounded by berthierite (ber). Reflected light. Loc. Trojárová.

bilization of antimony from the underlying black schists (Polák & Rak 1980). This indicates the epigenetic character of Sbmineralization.

Another important occurrence of Sb ores is near Kuchyňa (Fig. 2). It lies in a lens of black schists of N - S direction, with an inclination of  $60 - 80^{\circ}$  to NE. The deposit itself is formed by a lenticular body with impregnation and stockwork mineralization. Besides stibnite, berthierite and gudmundite as well as Pb—Sb sulphosalts are also found here in considerable quantities (Cambel 1960).

#### III. Mineralization in Permian rocks

The Permian of the Choč Nappe extends in the Malé Karpaty Mts. in the territory between Smolenice and Sološnica, in a belt of NE - SW direction, 1.5 - 2.5 km wide. It is represented by the Malužiná Formation of the Ipoltica Group (Vozárová & Vozár 1988). It consists of conglomerates, sandstones, shales, andesites, basalts and their volcanoclastics (Fig. 14).

1 - Cu mineralization in basic volcanics is found in cavities and



Fig. 13. Grains of gudmundite (gd) and pyrrhotite (po) in crystalline schist and carbonate vein filling. Remobilized stibnite (stib) penetrates as well into the rock and older sulphides along cracks. Reflected light. Loc. Trojárová.

cracks of basalts and andesites. Sulphidic minerals form up to several *cm* large aggregates accompanied by carbonate amygdales and veinlets. Varček & Regásek (1962) reported the occurrence of chalcopyrite, covellite, bornite, chalcopyrite, pyrite and tetrahedrite in the form of impregnations in the volcanics as well as in barite veins. Beside these minerals, we also identified digenite, galena, sphalerite, arsenopyrite and tennantite (Fig. 15). Primary magmatic ore minerals are magnetite and ilmenite and their alteration products are hematite, rutile and leucoxene. In weathered samples there is abundant malachite and goethite. From trace element analyses, it follows that basalts are locally enriched by Pb (1000 ppm), Cu (3000 ppm), Ba (up to 345 ppm), Sr (up to 260 ppm), Ag (up to 100 ppm), Cd (40 - 50 ppm) and Zr (up to 2020 ppm).

2 - Barite veins in řmelaphyresť of the Choč Nappe have been described by Čechovič (1948) W and SW of Smolenice. Veins of NW - SE direction, 15 - 80 cm thick, with a maximal lenght of 100 m are found here. According to the results of prospection works, the veins have no industrial importance. The filling of the veins consists of white barite with rare copper minerals men-



Fig. 14. Geological map of the Upper Paleozoic of the Malé Karpaty Mts. (adapted after Vozárová & Vozár 1988). a - Neogene; b - Mesozoic; c, d - Permian, c - andesites, basalts and volcanoclastics; d - conglomerates, sandstones and shales; e - Carboniferous. . Locations: 1 - 2 - Cu-mineralization; 1 - Sološnica; 3 - Lošonec, 3 - 4 - barite veins; 3 - Jahodník; 4 - Zabité; 5 - 11 - U-mineralization; 5 - U-REE, Zabité; 6 - 8 - U-Cu-mineralization in sediments; 6 - Kolovrátok; 7 - Chrásť; 8 - Kolárová; 9 - 11 - increased U-contents in volcanics; 9 - Vápenná; 11 - Jahodné.

tioned above. We found also carbonates, goethite, rutile and leucoxene. Chemical analysis of barite has shown the following composition (Bartalský in Slávik et al. 1967):  $BaSO_4 - 95.87$  %;  $SrSO_4 - 0.61$  %;  $SiO_2 - 1$  %;  $MgSO_4 - 0.26$  %;  $Al_2O_3 + Fe_2O_3 - 1.08$  %. In rocks with abundant barite we also determined increased contents of Pb (1000 ppm), Cu (3000 ppm) and slightly increased Sr (200 ppm).

3 - Uranium mineralization occurs especialy in the basement of Permian basalts and andesites, in a horizon of sandstones and conglomerates 1.4 km wide and 20 - 30 m thick (Uranium Survey 1983). Its boundary with the underlying beds is tectonic, extending along an E - W fault with an inclination of  $50 - 60^{\circ}$  to north. The ore-bearing horizon is of strata-bound character. The predominant rocks are grey-green conglomerates and arkose sandstones.

Ore minerals occurring in sandstones and conglomerates at localities marked on Fig. 14 are dispersed as impregnation grains or thin veinlets. They are represented by pyrite (Fig. 16), chalcopyrite, rutile-leucoxene, uraninite, galena, tennantite, chalcopyrite, löllingite, torbernite and goethite. The contents of U, Pb, Cu, Zr, Co, Y, Ba and Sr in mineralized rocks are mostly increased from 100 to 1000 *ppm*. The contents of  $C_{org}$  reach the values of 6500 *ppm* and they are far less than the values found in the Permian of the Choč Nappe at Kozie Chrbty (Rojkovič 1975). Sandstones with increased radioactivity sometimes also contain monazite, xenotime and apatite, which is confirmed by high contents of P<sub>2</sub>O<sub>5</sub> (2 *wt.* %), Ce (360 *ppm*), La (120 *ppm*), Nd (150 *ppm*) and U (30 *ppm*) in the rock.

Slightly increased U contents (mostly up to 100 ppm) can be

observed in basalts and their tuffs (Fig. 14) with occurrences of barite and Cu-mineralization (Uranium Survey 1982).

#### **IV.** Sedimentary mineralization

Manganese mineralization occurs in marly Mariatal shales of the Upper Lias in the mantle series of the Malé Karpaty Mts., in a zone between Stupava and Pernek (Fig. 1). Mn-ores with Mn contents of 20 - 30 % and Fe contents of 15 - 20 % are found in the shales as beds and lenses with a thickness of 1 - 8 m and they are their normal stratigraphic member. The concentration of Mn and Fe is a result of biochemical processes, the source having been continental (Polák 1957). The basic component of the primary Mn-ore is manganite, manganocalcite and pyrolusite, which forms also in hypergene zone. Prospection for Mn -ores was done at the end of the 19th century, at the beginning of the 20th century and in the fifties. Low quantities and unfavourable distribution of the ores caused the prospection and exploitation to be stopped, however, the extent of the mineralization as well as the possibilities of the use of this raw material have not been investigated sufficiently (Polák et al. 1983).

#### V. Gold placers

They were exploited in the 14th and 15th centuries north of Pezinok (Staré Mesto) (Fig. 2). Gold in placers came from primary gold-quartz veins. Gold-bearing delluvial and alluvial sediments reached into a depth of approx. 80 *cm* (Cambel 1959), and they probably yielded only a few *kg* of gold (Polák 1970).



Fig. 15. Chalcocite (cc) intergrown with bornite (bo) and enclosing pyrite (py). Their margins are surrounded by galena (gn). Reflected light. Loc. Lošonec.



Fig. 16. Goethite (goe) substituting pyrite (py) and forming pseudomorphs after it. Associated with pyrite are tennantite (tn) and löllingite (lö). SEM. Loc. Kolovrátok.

#### Discussion

The geological setting as well as the texture of ores indicate syngenetic formation and synsedimentary and metamorphic deformation, as well as recrystallization of pyrite ores. The values of  $\delta^{34}$ S = -8 to -20% (Kantor 1974) and -11 to -27% (Cambel et al. 1980) obtained from pyrites of stratiform ores are characterized by increased content of light sulphur, which can be explained by the influence of bacterial reduction of sulphates from mineralized solutions in the environment of marine sediments. Similar values of  $\delta^{34}$ S (-15.9%) from pyrite of primary disseminated ores and pyrite of amphibolites (-13.9%) indicate a relationship of ore-bearing fluids to Paleozoic (Devonian) volcanism (Cambel et al. 1981a). A possible genetic relation between granitoids and pyrite mineralization is, besides other facts, contradicted by different values of  $\delta^{34}$ S (-2.6%) of pyrite from granodiorites (Cambel et al. 1980).

The ores as well as rocks were recrystallized during regional periplutonic metamorphism in the greenschist and amphibolite facies. In the ores formed above all hexagonal pyrrhotite and younger generation of pyrite (Kantor & Ďurkovičová 1973), in which the presence of the heavy <sup>34</sup>S isotope has been determined. This is probably connected with an increased grade of

metamorphism and mobilization of fluids from an endogenic source (Kantor & Ďurkovičová 1973; Cambel et al. 1980).

Gold-quartz mineralization (Staré Mesto) and antimony mineralization (Kolársky vrch Hill) were have long been considered to be two independent mineralizations. Polák (1986) pointed out the conspicious spatial closeness of both mineralizations as well as the parallel strike and dip of the main ore structure (Fig. 8).

The genetic relatedness of gold-quartz and stibnite mineralization is indicated by:

 the correlation of the contents of Sb, As, Au and other metals, especially in black schists and hydrothermally altered rocks (Cambel & Khun 1979);

 the enrichment of gudmundite by gold (Háber & Mlynárová 1984);

- the occurrence of gold in Sb-ores and concentrates;

- the gold-bearing capacity of stibnite and deposit accumulations of stibnite in gold-quartz veins (Cotta & Fellenberg 1862);

- the presence of gold on stibnite deposits which does not correlate with arsenic.

The paragenesis of gold-quartz mineralization represented by electrum, polybasite and Ag-tetrahedrite indicates its formation in medium- to low temperature conditions, in medium to nearsurface depths (Boyle 1979). It is probable that mineral parageneses of antimony-gold mineralization formed in the sequence (from the oldest): gold-sulphidic, gold-quartz, stibnite.

Antimony-gold, hydrothermal mineralization is spatially related to the stratiform pyrite exhalation-sedimentary, metamorphosed mineralization. Both mineralizations occur in black schists, however, they are separated. At the deposit Pernek (Polák & Rak 1980) as well as at the locality Trojárová (Figs. 3, 9) (Hanas et al. 1989; Chovan et al. 1990), a similar lithologic sequence has been determined: two-mica granitoids and paragneisses of the Bratislava Massif - zone of tectonic schists - amphibolites - actinolite schists - black schists with Sb-Au-As mineralization - actinolite schists and other above-lying rocks. The existence of a tectonic-schist zone is consistent with the theory of Putiš (1987) assuming an overthrust of the metabasite and metatuff complex on paragneisses.

The younger Sb-mineralization usually occurs conformly with the above-lying pyrite ores. Younger remobilization is indicated by the presence of stibnite in cracks of granitoids and gneisses as well as the penetration of younger stibnite veinlets into older Sb-sulphidic and pyrite mineralization (Polák & Rak 1980; Chovan et al. 1990 and others).

Antimony mineralization is spatially related to black-schist beds, however, it is of epigenetic character. At the locality Trojárová, a correlation of Sb and  $C_{org}$  has not been observed. Increased correlation with  $C_{anorg}$  corresponds to the association of Sb-mineralization with carbonate veinlets and it lowers the importance of impregnation Sb-mineralization in black schists (Chovan et al. 1990). Sericitization, carbonatization, silicification and chloritization of surrounding rocks was caused by circulating hydrothermal fluids (Andráš 1983).

It has been assumed that metals were molized by penetrating fluids not only from black schists, but also from the synsedimentary sulphidic mineralization and sedimentary-volcanic rocks.

These rocks have primarily increased contents of ore elements (Polák 1974; Cambel & Khun 1979, 1983; Cambel et al. 1981, 1981a). It has been found that the contents of V, Cu, Ni, Sb as well as Cr, Zn, Hg and U are increased in black schists of productive zones, in comparison with similar rocks from other locations in the Malé Karpaty Mts. (Cambel 1983). More recently, increased Mo contents have been determined in productive black schists from Trojárová (Oružinský et al. 1990). Increased Sb and Cu contents have also been found in phyllites and amphibolites; in higher-metamorphic rocks - gneisses and granitoids - are Sb contents low. The highest contents of Ni have been determined in amphibolites (Cambel 1983).

An influence of granitoid rock intrusion on the formation of ore mineralization can be allowed for in the case of the Modra Massif (Type I, Cambel & Vilinovič 1987), which caused contact metamorphism of the Harmónia and Pernek Sequences (Putiš 1987). The Bratislava granitoid Massif (Type S, Cambel & Vilinovič 1987) is in a tectonic position to the deposit crystalline complex, however, it caused its relatively extensive periplutonic metamorphism and its influence on the formation of ore mineralization can be assumed as well. The isotopic composition of lead (Chernyshev et al. 1984) indicates a magmatic source of solutions and their origin in the post-orogenic stage of the Variscan cycle (240 - 270 Ma).

Sulphides from the Sb deposit Kolársky vrch Hill have negative  $\delta^{34}$ S values varying in the range -1.0 to -13.5‰ (Fig. 17). Biogenic sulphur had an important role, affecting especially Sb minerals with Fe content (gudmundite, berthierite). It can be assumed that Sb and partly also S were transported from a deeplying source, while during the penetration of endogenic fluids, assimilation with pre-granitic synsedimentary pyrite mineralization took place (Kantor 1974). The study of the isotopic composition of carbon and oxygen in carbonates formed in paragenesis with Sb-mineralization yielded negative values of  $\delta^{13}$ C (-11.8 to -9.7‰) and  $\delta^{18}$ O (-17.5 to -13.6‰) (Fig. 18) (Andráš 1983). This data as well as the large dispersion of values indicates strong



Fig. 17. Histograms of  $\delta^{34}$ S values (Kantor 1974).

Upper part: Pezinok, stibnite deposit; lower part: Pezinok-Turecký vrch Hill, pyrite mineralization.

Legend: 1 - pyrite; 2 - arsenopyrite; 3 - berthierite; 4 - berthierite + stibnite; 6 - gudmundite; 7 - pyrite (Turecký vrch Hill); 8 - pyrite (Pezinok, Sb-adit); 9 - pyrite from other locations.



Fig. 18. Relationship of  $\delta^{18}$ O and  $\delta^{13}$ C values from the deposit Pezinok-Kolársky vrch Hill (after Andráš 1983). 1 - ankerite; 2 - dolomite; 3 - calcite.

contamination of fluids by the surrounding rocks, a possibility of genetic relation of the carbonate to organic matter (Cambel et al. 1980) and an important role of meteoric water. The resulting isotopic composition of oxygen and carbon is a result of mixing of meteoric and endogenic solutions, as well as exchange reaction between solutions and rocks through which they migrated (Andráš 1983).

Using geothermometry and geobarometry in the study of crystalline schists, various authors determined temperatures in the range of T 350 - 600 °C and pressure P 3.5 - 5.5 kbar (Cambel et al. 1990a). Graphite thermometers applied to black schists yielded the following values: T 450 °C and P 3.5 kbar (Andráš & Horváth 1985). The above mentioned temperature and pressure conditions existing during metamorphism were sufficient for the mobilization of ore components. The varying character of fluids, different P-T conditions and lithologic environments allowed the formation of various types of ore mineralizations. There remains the question, whether deposit-forming fluids were released during the process of regional or periplutonic metamorphism, or as the result of granitoid intrusions. In younger, post-Paleozoic formations, accumulations of Sb-mineralization have not been found.

The Permian basic volcanism of the Choč Nappe is accompanied by unimportant copper mineralization and barite veins characteristic of the Choč Permian in the whole Western Carpathians. According to Ilavský (1980), these mineralizations are the products of Permian volcanism.

Uranium mineralization in the Permian of the Choč Nappe is in the Malé Karpaty Mts. less abundant than other occurrences in the Western Carpathians (Nízke Tatry Mts., Kozie Chrbty Hills), which are richer in carbonified plant remnants. Stratiform concentration is the result of U transportation by ground waters and its absorption in places where Ti-oxids and Fe, Mn-oxids and hydroxids accumulated, probably on the boundary of the Permian and Triassic. Less important mobilization and accumulation of uranium was caused by residual solutions of Permian basic volcanism in association with barite and Cu-mineralization. The accumulation of monazite, xenotim and apatite is represented by a small Permian placer.

#### Conclusions

The primary exhalation-sedimentary, pyrite mineralization is genetically related to the Paleozoic (Devonian) basic volcanosedimentary cycle and it was subsequently metamorphosed.

Hydrothermal Sb-mineralization has an epigenetic character and it is most frequently located in beds of tectonically deformed black schists, which provided a favourable environment for the penetration of fluids and crystallization of ore minerals. The increased contents of some elements in productive zones of black schists could be genetically related to Devonian basic volcanism. Ore elements could have been molized by the circulation of fluids released during regional and periplutonic metamorphism of granitoid rock intrusion. However, it can not be excluded that hydrothermal fluids containing Sb, Au, or further elements genetically related to Variscan granitoid intrusions or other abyssal rocks, even though evidence of such ore-bearing bodies is missing. The increased of ore elements in productive zones of black schists can be explained also in this way. The question concerning the source of metals and origin of fluids can not be answered very clearly in the present state of knowledge.

Permian basic volcanism caused the formation of copperbarite mineralization. Stratiform uranium mineralization was produced by ground waters on the boundary of the permian and Triassic.

The youngest one is the Jurassic sedimentary manganese mineralization and Quarternary delluvial and alluvial gold placers.

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