Pb – Zn – Cu mineralization in the historical Broumov – Tři Sekery mining district (Western Bohemia)

Pb – Zn – Cu mineralizace v historickém revíru Broumov – Tři Sekery (západní Čechy)

(8 figs, 1 tab.)

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A mineralogical and geochemical study has been carried out of the historical Pb-Zn-Cu Broumov – Tři Sekery mining district in the northern part of the Český les valley, in the vicinity of the boundary between the Moldanubian and Saxothuringian units.
Sulphide mineralization of NW-SE and NE-SW trending quartz veins was formed in three stages: 1) early alteration related stage: chlorite, tourmaline and quartz; 2) main stage: quartz, galena, sphalerite, chalcopyrite and pyrite; and 3) late fracture related stage : quartz, chalcopyrite and minor galena, sphalerite, pyrite, gersdorffite and unidentified Bi-Co-Ni-As minerals.

Formation temperatures of approx. 270–280 (±25) °C and 230–115 °C are suggested for the early and main stages, respectively. Fluid salinities vary from 10.8 to 16.9 and from 21.2 to 23.7 wt. % eq. NaCl for quartz and sphalerite of the main stage, respectively. The sulfur isotope composition of the main stage sulphides varies from –5.0 to +5.8 (‰ vs. CDT).

Barren banded quartz veins (quartz and amethyst), related to NNW-SSE trending tectonic zones, contain only one-phase liquid fluid inclusions. Consequently, their formation temperatures are interpreted lower than 50–60 °C.

Key words: ore mineralization; base-metals; fluid inclusions; chlorite thermometry; sulphur isotopes

Introduction

The studied “Broumov-Tři Sekery” area is located in the western part of the Bohemian Massif, close to the “triple” junction of the Moldanubian, Saxothuringian and Teplá-Barrandian Units. Geographically, it is situated in the northern part of the Český les highland, approximately 8 km to the SW of the Mariánské Lázně Spa.

Historically, four groups of vein-type ores were mined here (Fig. 1): Cu-Pb-Zn base-metal (Broumov-Tři Sekery area, Zadní Chodov area, Michalovy Hory); Ag-Bi-Co-Ni-U “five-element association” (Michalovy Hory); uranium mineralization (Zadní Chodov area, Vítkov area, Dyleň and Svatá Anna). Locally uneconomical Co-Ni-Ag (Svatá Anna) and sparse Au-occurences – vicinity of the Dyleň mt. and Oldřichov (Vítkov area; Šrein – Pivec 1988), where it is associated with selenide mineralization (Čech – Vavřín 1978). All these ores are dominated by quartz and carbonate gangue, and hosted by various types of brittle-fault zones.

Mining at the Tři Sekery area dates back to the 16th century (Bílek 1959), when supergene ores were mined in three main centers: Broumov (Berghausel, Antoni de Padua Zeche, Johann Baptist Zeche), Tři Sekery (Elias Zeche, Stephan Zeche) and Nový Metternich (Stock Zeche). The annual output of smelted copper varied from 5–8 tons during the mining boom in the 16th century to 1–1.2 tons in 1750, when the mines were closed. The city of Nürnberg in Germany was the main customer for the high quality copper (Bílek 1959).

Mining of the Pb-Zn-Cu ores at Broumov and Nový Metternich continued till the beginning of the 20th century. During the second half of the 20th century, only uranium deposits (Zadní Chodov and Dyleň) were exploited (1952–1991; Kolektiv 1984, Čech et al. 1996).

Regional Geology

The Broumov-Tři Sekery area is located in the Western part of the Bohemian Massif, near the boundary between the Moldanubian and Saxothuringian Zones, close to the Teplá-Barrandian Unit (Fig. 1). The E-W trending tectonic zone that represents tectonic boundary between the Moldanubian and Saxothuringian Units is referred to as the Erbendorf lineament (Siebel et al. 1997), or the Tirschenreuth-Mähring zone (Lapp 1995) in Germany and Czech Republic, respectively (Fiala – Vejnar 1993).

The Saxothuringian Unit is represented by Cambrian (Arzberg group) and Ordovician (Waldsassen group) siliciclastic rocks metamorphosed in the lower amphibolite facies (Behrman – Tanner 1997). The metamorphic gradient generally decreases to the N and NW. The most common rocks are banded biotite gneisses, mica schists and phylites. Banded quartzite (with disseminated magnetite) and graphite gneiss form intercalations in biotite gneisses.

In the southern part of the studied area, cordierite gneisses and biotite-cordierite gneisses of the Český les Moldanubian Monotonous Unit crop out. They are metamorphosed in the upper amphibolite facies.

The Variscan granitoids intruded both units through various tectonically weakened zones in three batches (Siebel et al. 1997): 340–325 Ma (redwitzite and quartz diorite of the Bor and Leuchtenberg massifs); 325–315 Ma (biotite granite, monzogranite and leucogranite

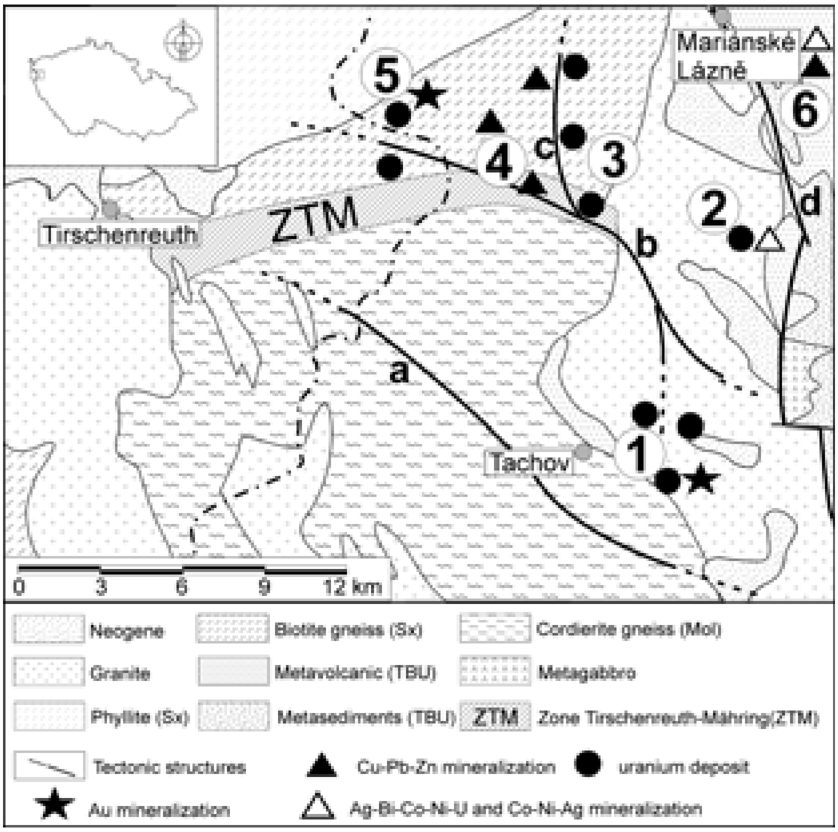

Fig. 1. Geological map of the northern part of the Český les area (modified after Romanidis 1974, Lapp 1995 and Siebel et al. 1997).
TBU – Proterozoic Teplá-Barrandien unit;
Mol – Moldanubian;
Sx – Saxothuringian;
a – Tachovský fault;
b – Centrální fault;
c – Zadní Chodov fault zone;
d – Mariánké Lázně fault;
1 – Vítkov ore district;
2 – Svatá Anna deposit;
3 – Zadní Chodov area;
4 – Broumov – Tři Sekery area;
5 – Dyleň area;
6 – Michalovy Hory deposit.

in the vicinity of Falkenberg, Flossenbürg and Rozvadov); and 325–305 Ma (syenogranite and two-mica monzogranite of the Smrčiny area).

The brittle and brittle-ductile tectonic structures were studied mostly in relation to the exploration of uranium deposits/mineralization (Romanidis 1976, Kolektiv 1984, Čech et al. 1996). The older (main) tectonic zones trending WNW-ESE to W-E [the Centrální (Central) and Tachovský faults] are only several meters wide, while the younger zones striking NNW-SSE to N-S (Zadní Chodov zone) are commonly more than 100 m wide and often brecciated. Amethyst quartz veins and graphite-bearing gneisses are typical for these zones. The base metal mineralization is usually related to NW-SE and NE-SW trending extension structures associated with the younger tectonic zones.

Geology of the studied deposits

Of the great number of small historical Cu-Pb-Zn base-metal mining sites, three main mining districts were studied: the Broumov, Tři Sekery and Nový Metternich (Fig. 2). Low-grade sulphide mineralization in quartz veins is hosted by: 1) brecciated zones (trending NNW-SSE to N-S, >1 m wide and >1km in length) dominated by barren poly-stage amethyst-gangue.; and 2) dilatational fracture zones (trending NW-SE and NE-SV) filled with <0.5 m thick banded quartz gangue. Carbonates are usually absent in both settings.

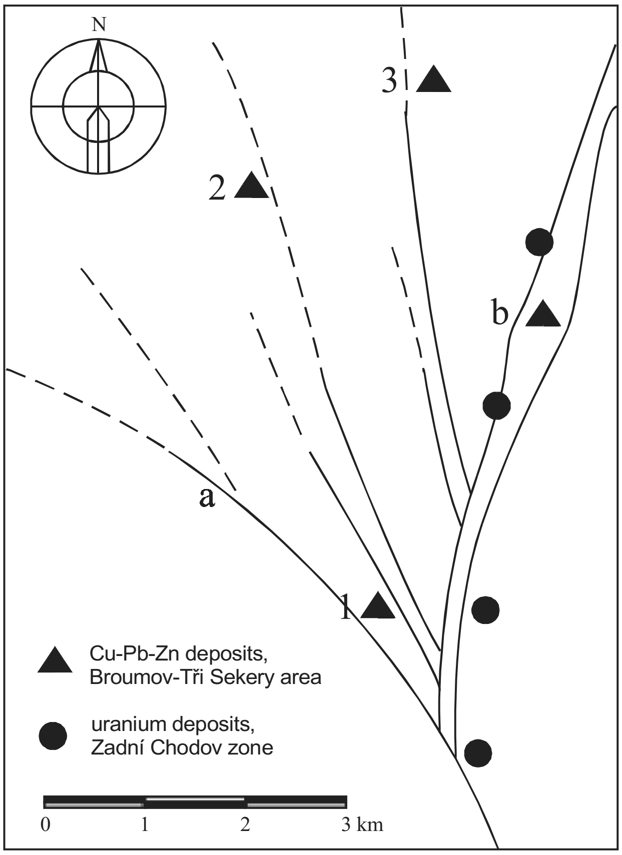

Fig. 2. Sketch of tectonic structures at the Broumov-Tři Sekery area: a – Centrální fault; b – Zadní Chodov fault zone; 1 – Broumov deposit; 2 – Tři Sekery deposit; 3 – Nový Metternich deposit.

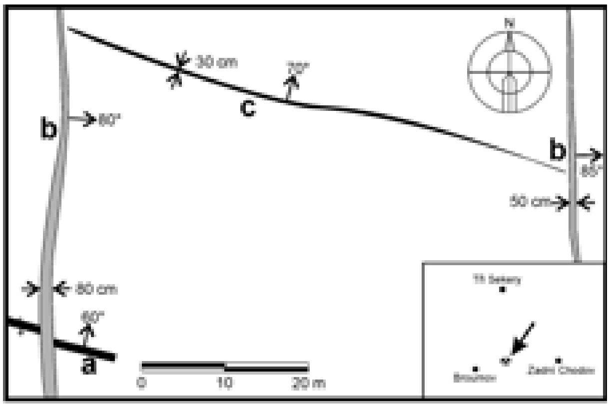

Fig. 3. Geology and tectonics of the Antoni de Padua adit (Broumov district): a – reverse fault; b – breccia zone with barren quartz gangue; c – quartz-sulphide vein filling a dilatational zone

The Broumov district is located near the Tirschenreuth-Mähring zone, where the Moldanubian cordierite gneisses intimately alternate with the Saxothuringian banded biotite gneisses. The samples used in this study come from the dumps and from the Antoni de Padua adit (Fig. 3). The NW-SE striking, only about 10 cm thick reverse fault is displaced here by a younger more than 1 m wide NNW-SSE trending zone filled by brecciated and altered rocks and by minor quartz veins. The width of the quartz veins varies from 1 cm to 30 cm; sulphides are represented by galena, sphalerite, chalcopyrite and pyrite. The mineralized NW-SE trending structures probably represent extensional feather joints related to the evolution of the NNW-SSE trending zone.

The Tři Sekery district is hosted by Saxothuringian layered biotite gneisses, and by Variscan granite and diorite bodies. The tectonic style is similar to that of the Broumov occurrence. Quartz veins, striking NW-SE carry disseminated chalcopyrite and pyrite. The maximum vein thickness is 1 m. The studied samples come only from abandoned dumps.

The Nový Metternich district is hosted by Saxothuringian rocks only (banded biotite gneisses, quartzite gneisses and graphite gneisses). Two types of quartz veins were found here in shallow trenches (Fig. 4). The amethyst-dominated, sulphide-free vein (up to 80 cm wide) strikes NNW-SSE to N-S and was most probably already recognized during uranium exploration (Janda 1967). The sulphide-beraring quartz veins (quartz-2) are related to the NNE-SSW to NE-SW trending tectonic zones that probably represent feather structures of the main NNE-SSE faults. Veins in the northern part of the district are richer in galena and sphalerite, while those in southern part are rich in chalcopyrite (galena and sphalerite are minor minerals here).

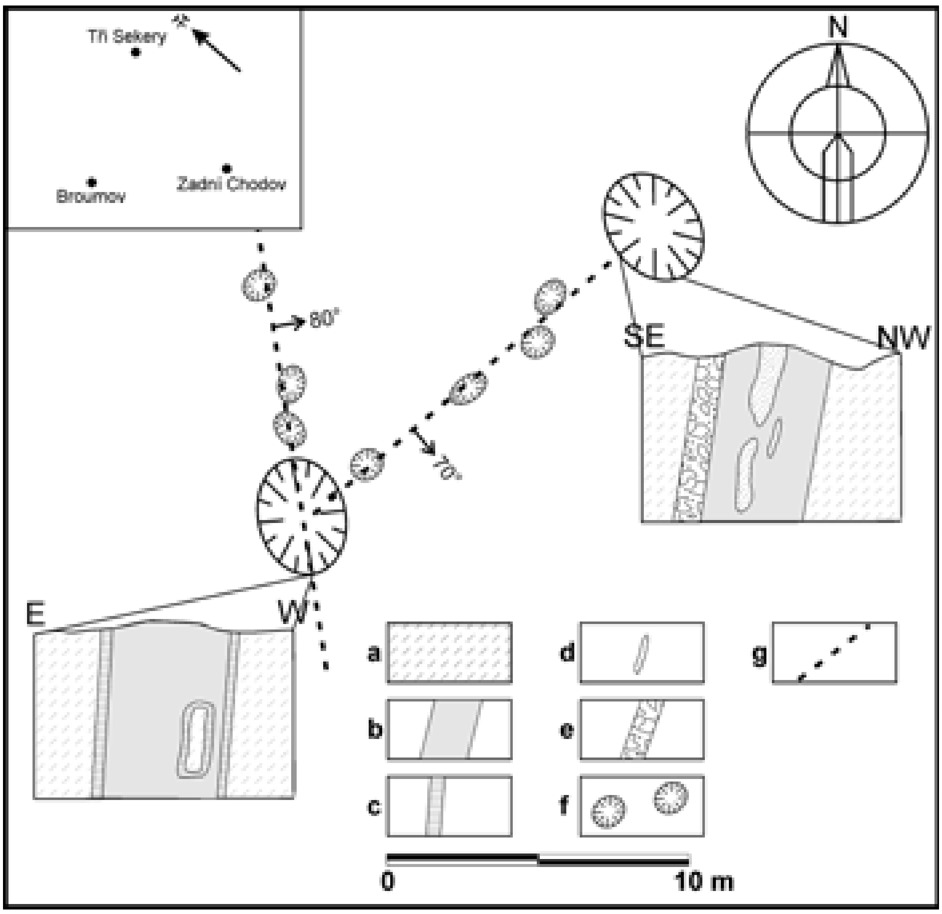

Fig. 4. Old mine workings at the southern part of the Nový Metternich district – topography and outcrops sections. a – quartzite gneiss; b – massive quartz; c – amethyst; d – sulphide mineralization; e – breccia fault zone; f – old workings; g – quartz veins.

Mineralization of breccia zones

The amethyst-dominated gangue of the NNW-SSE trending fault zones commonly exhibits breccia texture. Up to three quartz types can be distinguished: white massive quartz (oldest) with illite-filled cavities, dark violet-colored quartz (amethyst), and white-milky quartz (youngest). They all most probably represent products of one, more-or-less-continuous, crystallization sequence, rather than three separate mineralization stages. The relatively low-degree of deformation of the amethyst gangue suggests that it may be younger than the quartz-sulphide veins from the dilatational zones.

Mineralization of dilatational zones

Three mineralization stages can be distinguished in the banded quartz gangue (Fig. 5a): the early stage represents up to several mm thick alteration rims consisting of chlorite-sericite, anhedral quartz-1 and euhedral black tourmaline.

The main stage is characterized by subhedral quartz-2 aggregates and by the first generation of sulphides: Broumov (galena-1, sphalerite-1), Tři Sekery (chalcopyrite-1, pyrite-1, Fig. 5c), Nový Metternich (galena-1, sphalerite-1, pyrite-1, chalcocite-1). Sphalerite-1 is mostly replaced by galena-1 along cleavages (Fig. 5b). Sulphides are generally stoichiometric, only 3–5 wt. % of Fe was identified in the sphalerite-1 of the Broumov occurrence.

Minerals of the late stage fill cavities and fractures in minerals of the previous stages. Two quartz populations (subhedral quartz-3a and euhedral quartz-3b) were found. The second generation of sulphides usually replaces/penetrates quartz (quartz-2). At Broumov galena-2, sphalerite-2 and chalcopyrite-2 were identified. The latter contains sparse Bi-Co-Ni-As inclusions, among which native bismuth and gersdorffite predominate (Fig. 5d). At Tři Sekery quartz-3a with carbonate perimorphoses was found only. Similarly only quartz-3 and pyrite-2 were observed at Nový Metternich.

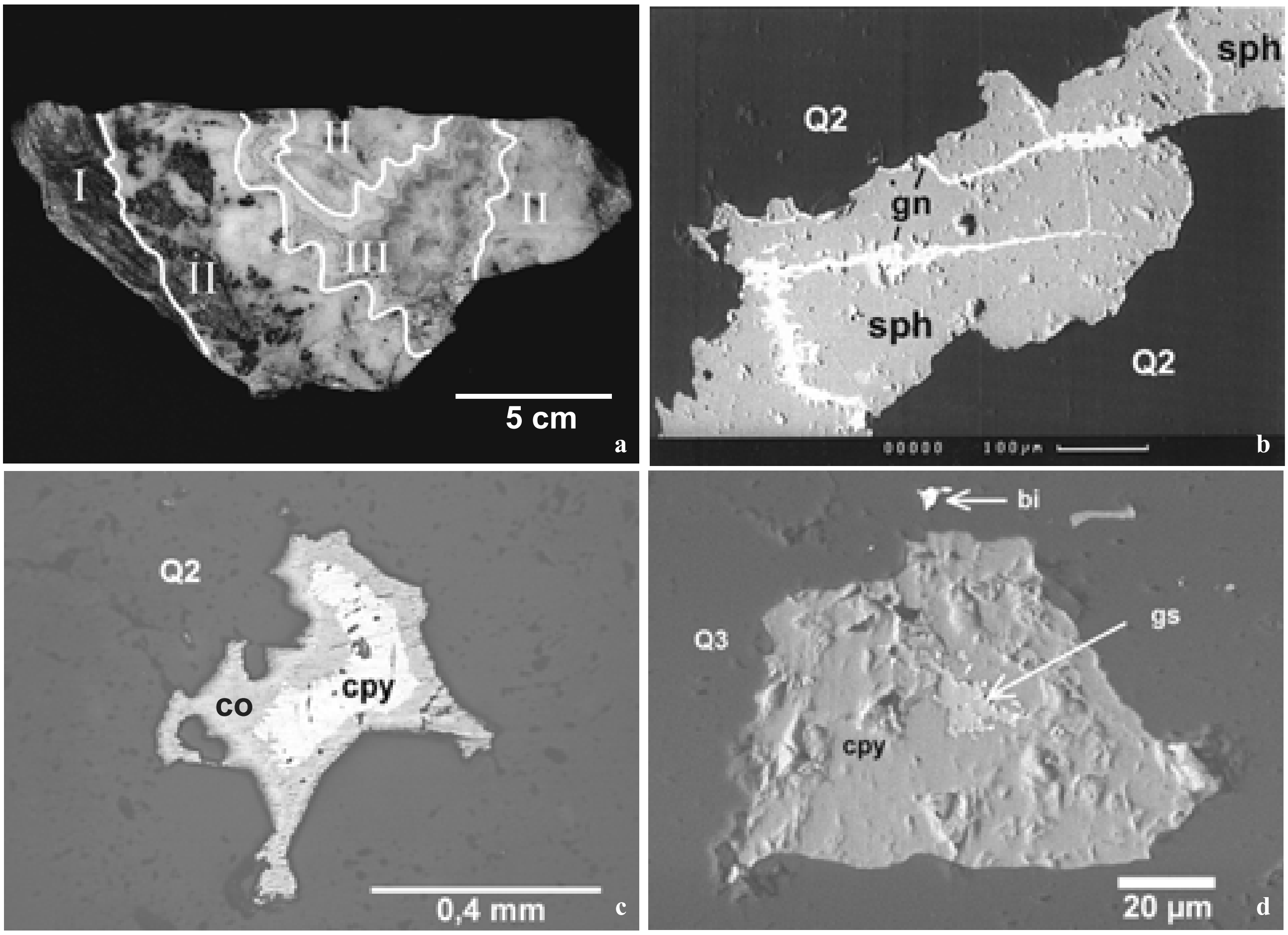

Fig. 5. Gangue and ore textures: a – banded texture of quartz gangue from the Broumov district with distinguished mineralization stages: early (I), main (II), and late (III); b – sphalerite (sph) replaced by galena (gn), BSE photo, Nový Metternich district; c – chalcopyrite grain (cpy) with covellite margin (co) in quartz-2 (Q2), reflected light photo, Tři Sekery ditrict; d – quartz-3 (Q3) with bismuth (bi), chalcopyrite (cpy) and gersdorffite (gs), BSE photo, Broumov district.

Chlorite thermometry

Chlorite- and pyrite-bearing alteration rims associated with early stage formation of the quartz veins at the Tři Sekery were used for the chlorite thermometry. The studied chlorites correspond to tri-trioctahedral chlorites (after Wiewiora – Weiss 1990) of the clinochlore-chamosite series. The average temperature of chlorite formation, based on Cathelineau – Nieva (1985), Cathelineau (1988), Jowet (1991), Zhang – Frantz (1995) calibrations, is 270–280±25 °C (Tab. 1).

Fluid inclusions

Despite the fact that the studied samples contained numerous fluid inclusions, microthermometry was successful for only two samples from the Nový Metternich occurence. The fluid inclusions in the other samples/localities were too small for microscopic studies.

Sample of the NE-SE trending quartz vein (Fig. 4; quartz-2, main mineralization stage) with minor sulphides (sphalerite-1, galena-1) contained clearly visible growth zones marked by numerous fluid inclusions (Fig. 6a). Both one-phase liquid and minor two-phase liquid-rich primary aqueous inclusions (up to 20 µm in size) were found in the quartz-2. The inclusions in sphalerite-1 are mostly two-phase liquid-rich (Fig. 6c); however, discrimination between those of primary and secondary origin is not possible. The first melting (eutectic) temperatures (–49 to –51.2 °C) indicate the presence of complex salt systems in all the studied fluid inclusions. Two intervals of ice melting in quartz-2 and in sphalerite-1 (–7.2 to –13.0 °C and –18.3 to –22.8 °C) were recorded, indicating salinities: 10.8–16.9 and 21.2–23.7 wt. % eq. NaCl (Bodnar 1993). Two fluid inclusions with ice melting –32.6 and –36.3 were found in quartz-2. These inclusions are either $CaCl_2$-rich or contain some LiCl. The homogenization temperatures of two-phase liquid-rich inclusions in sphalerite-1 vary from 148 to 115 °C (Fig 7).

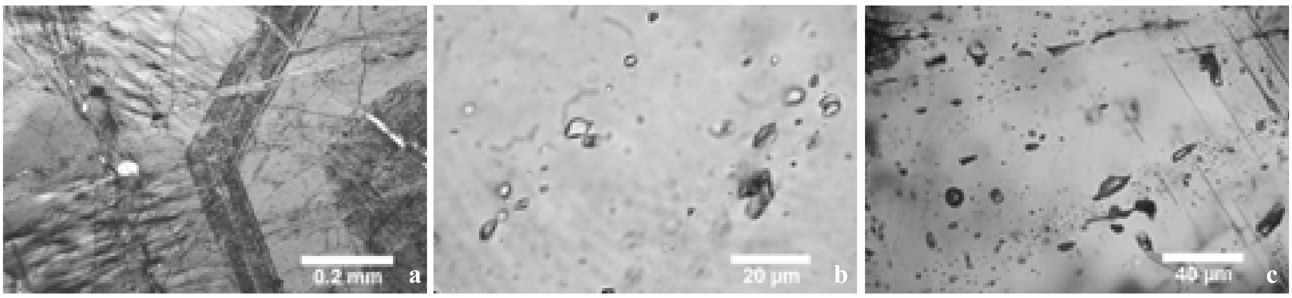

Fig. 6. Fluid inclusions from the Nový Metternich district: a – growth zones in quartz-2 marked by primary fluid inclusions; b – one-phase liquid fluid inclusions in amethyst; c – two-phases liquid-rich fluid inclusions in sphalerite.

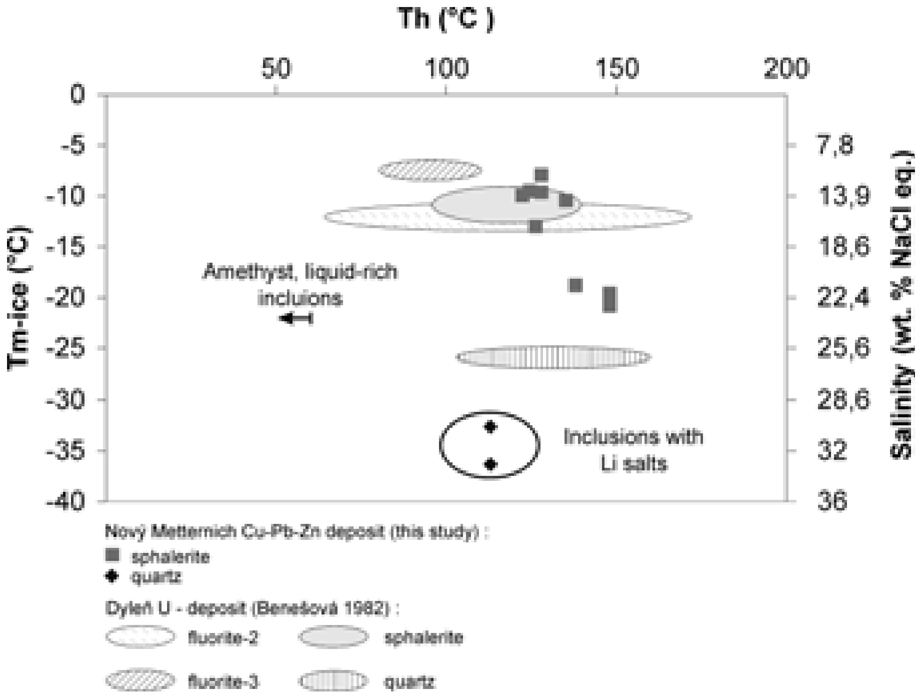

Fig. 7. Summary of microthermometric characteristics of fluid inclusions from the Nový Metternich district. For comparison, data from the U-deposit Dyleň (Benešová 1982) are also included.

The other sample represented the NNW-SSE trending quartz vein from the breccia zone of the Nový Metternich. Fluid inclusions were studied in euhedral amethyst crystals (up to 2 cm long) with numerous repetitive growth zones. Only one-phase liquid fluid inclusions were found in the growth zones (Fig. 6b), thus indicating amethyst formation at temperatures below approx. 50–60 °C. The brownish color of frozen inclusions and first melting temperatures of about –51 °C indicate the presence of $CaCl_2$. Ice melting temperatures (–23 °C, 5 inclusions) suggest salinities about 21.9 wt % eq. NaCl (Fig. 8).

Sulfur isotopes

Main sulphides from each of the studied districts were analyzed for sulfur isotopes: chalcopyrite (Tři Sekery), pyrite (Broumov, Nový Metternich, Tři Sekery), galena and sphalerite (Broumov, Nový Metternich).

The sulfur isotope composition of the entire sample-suite ranges from –5.0 to +5.8 δ^{34}S (‰ vs. CDT). Most of the data are clustered around –5.0 ‰ (Nový Metternich and Broumov), and 0.0 ‰ (Broumov and Tři Sekery; Fig. 8). Only galena and sphalerite of the Broumov (main stage) were suitable for isotope thermometry, yielding a temperature of 230±25 °C (after Ohmoto – Rye 1979; $\Delta_{sp\text{-}gn} = 0.74/T^2 \times 10^6$).

Discussion

Two types of quartz gangue were identified in the studied area: banded quartz-sulphide veins hosted by dilatational NW-SE (Broumov, Tři Sekery) and NE-SW (Nový Metternich) tectonic zones, and amethyst-dominated gangue hosted by N-S trending brecciated zones. Of the former ones, only the NW-SE trending zones were mentioned by earlier authors (Vejnar 1962 and Kucharczyk et al. 1962).

Three mineralization stages were recorded in the veins of dilatational zones. The temperature of the early stage was constrained by chlorite thermometry to 270–280 °C, and that of the main stage was constrained by sulfur isotope thermometry (230 °C) and by fluid inclusions in sphalerite-1 (148–110 °C). Large differences between temperatures inferred for sphalerite from sulfur isotopes compared to that from the fluid inclusions may reflect either trapping of fluid inclusions at higher pressures (about 1.2 kbar), or isotope disequilibrium between analyzed galena and sphalerite.

In contrast to relatively higher temperatures suggested for veins from dilatational settings, the presence of only one-phase liquid fluid inclusions in the amethyst-dominated gangue of N-S trending brecciated zones indicates their formation below 50–60 °C, and consequently implies younger age of the amethyst-dominated gangue.

The thermal evolution of veins hosted by dilatational structures is similar to that inferred for the Zadní Chodov and Dyleň uranium deposits, where alteration zones composed of chlorite, sericite, albite, minor Ti oxides, epidote and quartz were probably formed between 300 and 400 °C (Fiala 1984). Galena and sphalerite of the next mineralization stage equilibrated isotopically at about 250 °C (Hladíková et al. 1997; Zadní Chodov deposit).

The sulfur isotope composition of the main sulphides from the Broumov-Tři Sekery area ranges from –5.0 to +5.8 δ^{34}S (‰ vs. CDT). As the individual occurrences differ slightly in the isotope composition of sulphides, derivation of their sulfur from the surrounding rocks is more likely, rather than introduction from a deeper homogeneous source, or derivation from rocks of the Teplá-Barrandien unit (as suggested by Šmejkal et al. 1974), with sulphide isotopic composition ranging from –34 to +4 δ^{34}S (‰ vs. CDT).

Fluid inclusion study of sparse samples from Nový Metternich resulted in recognition of three types of aqueous fluids, differing mutually in their salinity and temperature: 1) 10.8–16.9 wt. % eq. NaCl, Th 122.3–128 °C; 2) 21.2–23.7 wt. % eq. NaCl, Th 135.2–155 °C and 3) ~ 21.9 wt. % eq. NaCl, Th < 50–60 °C.

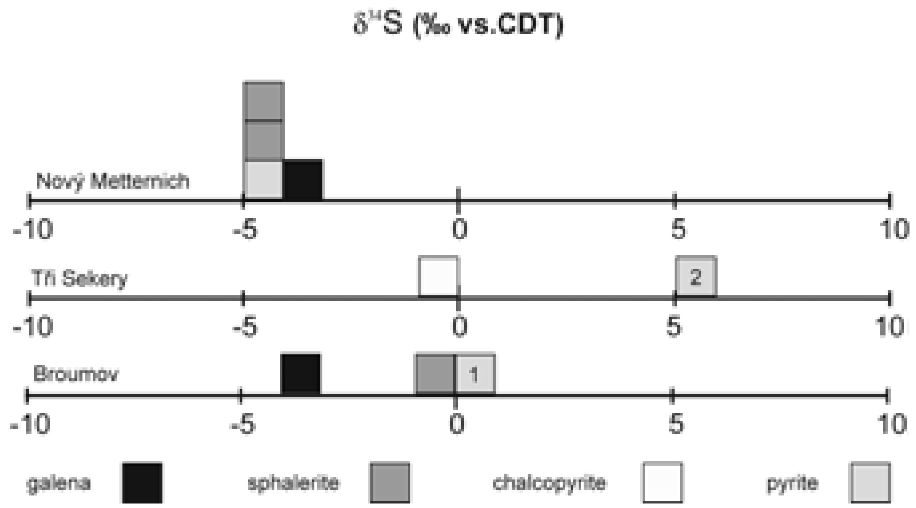

Fig. 8. Sulfur isotope composition of vein- and rock-forming sulphides. Disseminated rock-forming sulphides are labeled by numbers: 1 – pyrite in quartzite gneiss; 2 – pyrite in diorite.

Table 1. Microprobe analyses of chlorites of the oldest (i.e. first) mineralization stage at the "Tři Sekery" district. The structural formulae were recalculated on the basis of 14 oxygen atoms. The individual thermometers (T_1–T_5) used for the temperature estimation (in °C), average (AVG) and standard deviation (SD) data, (n.d. = not detected) are indicated at the bottom.

	#1	#2	#3
SiO_2	28.51	28.08	28.40
TiO_2	n.d.	n.d.	n.d.
Al_2O_3	20.35	19.92	20.74
Cr_2O_3	n.d.	n.d.	n.d.
FeO_{tot}	19.70	19.55	19.98
MnO	n.d.	n.d.	n.d.
MgO	18.91	18.95	19.05
CaO	n.d.	n.d.	n.d.
Na_2O	n.d.	n.d.	n.d.
K_2O	n.d.	n.d.	n.d.
TOTAL	87.47	86.50	88.17
Si^{IV}	2.900	2.891	2.869
Al^{IV}	1.100	1.109	1.131
T site	4.000	4.000	4.000
Al^{VI}	1.339	1.309	1.339
Fe^{2+}	1.676	1.683	1.688
Mg^{2+}	2.867	2.908	2.869
O site	5.881	5.900	5.896
Total	9.881	9.900	9.896
T_1	249	251	255
T_2	251	253	258
T_3	267	270	269
T_4	292	295	302
T_5	294	296	304
AVG±SD	271±22	273±22	277±24

Thennometers used:
T_1: Zhang – Frantz (1995): A^{IV}, Fe/Mg
T_2: Cathelineau – Nieva (1985): Al^{IV}
T_3: Cathelineau – Nieva (1985): Al^{VI}
T_4: Cathelineau (1988): Al^{VI}
T_5: lovett (1991): A^{IV}, Fe/Mg

Similar fluid compositions were reported by Benešová (1982) at the Dyleň U-deposit (Fig. 8): fluorite-1 (14–17 wt. % eq. NaCl, Th 235–370 °C); fluorite-2 (14–17 wt. % eq. NaCl, Th 60–172 °C); fluorite-3 (9.5 wt. % eq. NaCl, Th 85–118 °C); quartz (24 wt. % eq. NaCl, Th 100–164 °C); sphalerite (13.5–16.5 wt. % eq. NaCl, Th 90–130 °C).

For the first time, we are also reporting the presence of Bi-Co-Ni-As mineral inclusions in sulphides from the studied area (hosted by chalcopyrite-1 from the dilatational zones of the Broumov district). This may reflect interaction of the late mineralizing fluids with the Saxothuringian rocks/unit, where such element association is widespread.

Conclusions

The entire area of the base metal and uranium deposits in this Western Bohemian region seems to have a nearly uniform temperature fluid evolution. The first, hydrothermal alteration stage, occurred at ~ 250–300 °C. The main sulphide stage fluid had temperature of ~ 110–160 °C and was followed by barren quartz vein at temperature < 100 °C.

Two types of hydrothermal quartz veins were studied in the historical mining district of the Broumov-Tři Sekery area. The first one represents barren quartz gangue associated with NNW-SSE to N-S tectonic zones within graphite-bearing gneisses. Three quartz types form the gangue: massive quartz (oldest), amethyst, and milky quartz (youngest). The amethyst-bearing zone is volumetrically the largest. Only one-phase liquid fluid inclusions were found in it, thus indicating amethyst formation at temperatures below 50–60 °C.

The second type of quartz veins is associated with NW-SE and NE-SW dilatational zones that form complementary structures to the main NNW-SSE fault zones. These veins bear Cu-Pb-Zn base metal mineralization and were mined historically. Three mineralization stages were distinguished: early, main and late. Minerals of the early stage (quartz-1, tourmaline, chlorite) form narrow alteration rims of the veins. Chlorite thermometry suggests chlorite crystallization at 270–280 °C (± 25 °C).

The main stage is represented by quartz-2, galena-1, sphalerite-1, pyrite-1 and chalcopyrite-1. The isotope composition of sulphides varies from –5.0 to +5.8 $\delta^{34}S$ (‰ vs. CDT); isotope thermometry between galena-1 and sphalerite-1 from the Nový Metternich indicates a temperature of 230±25 °C. Two-phase liquid-rich fluid inclusions in sphalerite-1 homogenize to the liquid between 148 and 115 °C. The fluid salinities in quartz and sphalerite lie in two ranges, 10.8–16.9 and 21.2–23.7 wt. % NaCl eq.

Minerals of the late mineralization stage (quartz-3 and minor chalcopyrite-1, pyrite-2, galena-2 and sphalerite-2) fill fractures and cavities in earlier minerals. The late chalcopyrite from the Broumov district contains sparse Bi-Co-Ni-As inclusions (namely gersdorffite and native bismuth). These minerals are characteristic for epigenetic mineralization of the Saxothuringian unit and have not yet been described in this district.

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Pb – Zn – Cu mineralizace v historickém revíru Broumov – Tři Sekery (západní Čechy)

V historickém Pb-Zn-Cu revíru Broumov – Tři Sekery, který se nachází v severní části Českého lesa, byl proveden mineralogický a geochemický výzkum. Revír se nachází v blízkosti hranice mezi moldanubikem a saxothuringikem.

Sulfidická mineralizace je vázána na křemenné žíly směru SZ-JV a SV-JZ. Výzkumem byly zjištěny tři hlavní stádia mineralizace: 1) křemen-silikátové: chlorit, turmalín, křemen; 2) křemen-sulfidické: křemen, galenit sfalerit, chalkopyrit a pyrit; 3) nejmladší křemenné: křemen, chalkopyrit a méně častý galenit, sfalerit, pyrit, gersdorffit a další neidentifikované Bi-Co-Ni-As minerály.

Nejstarší křemen-silikátové stádium vzniklo za teplot 270–280 (±25) °C a mladší hlavní křemen-sulfidické stádium mineralizace vzniklo za teplot a 230–115 °C. V hlavním křemen-sulfidickém stádiu mají fluidní inkluze v křemeni a ve sfaleritu salinity v rozmezí 10,8–16,9 a 21,2–23,7 hm. % NaCl ekv. Izotopické složení sulfidů ze stejného stádia se pohybuje v rozmezí –5,0 až +5,8 (‰ vs. CDT).

Paralelně s tektonickými strukturami směru SSZ-JJV byly zjištěny páskované křemen – ametystové žíly bez sulfidické mineralizace. Křemen obsahuje pouze jednofázové fluidní inkluze, které byly pravděpodobně zachyceny za teplot nižších než 50–60 °C.