

EPITHERMAL TERTIARY Pb-Zn-Cu (Ag, Te) MINERALIZATION IN THE ROZTOKY VOLCANIC CENTRE, ČESKÉ STŘEDOHOŘÍ MTS., CZECH REPUBLIC

EDVÍN PIVEC¹, JAROMÍR ULRYCH¹, VLADIMÍR ŠREIN², JIŘÍ BENDL³,
PETR DOBEŠ⁴ and KAREL ŽÁK⁴

¹Institute of Geology, Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Praha 6, Czech Republic

²Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, V Holešovičkách 41, 182 09 Praha 8, Czech Republic

³Analytika, I.c., U Elektry 650, 198 00 Praha 9, Czech Republic

⁴Czech Geological Survey, Klárov 3, 118 00 Praha 1, Czech Republic

(Manuscript received May 20, 1997; accepted in revised form December 11, 1997)

Abstract: The abandoned Roztoky silver-base metal deposit represents a scarce example of Tertiary sulphide vein-type mineralization spatially and genetically associated with intraplate volcanic rocks of the Cenozoic West and Central European Volcanic Province. The deposit is situated in the Tertiary Roztoky Volcanic Centre (RVC) of the České středohoří Mts., within the Ohře (Eger) Rift. The main ore vein parallels an older bostonite dyke intersecting the monzodiorite body, however, both are intersected by a younger trachyte dike. This suggests that the origin of the mineralization is related to the development of the RVC. The $\delta^{13}\text{C}$ values of vein carbonates indicate the influence of deep-seated CO_2 but the O isotopic composition of hydrothermal fluids (calculated $\delta^{18}\text{O}_{\text{fluid}}$ values from -3 to -7 ‰ SMOW) shows the dominance of water with relatively shallow circulation. Sphalerite-galena sulphur isotopic geothermometry yielded temperatures between 200 and 250 °C and the presence of cubic hessite indicates temperatures above 155 °C. The calculated $\delta^{34}\text{S}_{\text{fluid}}$ values vary in the range -1.0 to -2.0 ‰. The presence of banded “colloform” sphalerite and chalcodony suggests lower temperatures. High lead isotope ratios of galena ($^{206}\text{Pb}/^{204}\text{Pb}$ about 19.03, $^{207}\text{Pb}/^{204}\text{Pb}$ about 15.67, $^{208}\text{Pb}/^{204}\text{Pb}$ about 39.17) can be a result of mobilization of lead either from Tertiary magmatic rocks, which show similar lead isotope ratios and were probably derived from a sublithospheric HIMU mantle source, or from upper-crustal rocks, e.g. local Upper Cretaceous sediments. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of the principal hydrothermal carbonates rhodochrosite (0.70524) and calcite-dolomite (0.70510) are higher than both the local primitive magma derivatives and even the developed rocks of the RVC and indicate an admixture of Sr derived from local crustal rocks. The volcanic rocks of the RVC were the dominant heat source during the formation of the ore deposit. The hydrothermal deposit was formed during relatively shallow hydrothermal circulation of low to medium salinity, low $-\delta^{18}\text{O}$ fluids supported by CO_2 influx of deep-seated origin.

Key words: Tertiary, Bohemian Massif, epithermal mineralization, stable isotopes, Sr isotopes, alkaline volcanics.

Introduction

There have been numerous publications over the last several decades concerning the post-Variscan mineralization related to the Alpine metallogenic epoch in the Bohemian Massif. The post-Variscan mineralization includes, according to Losert & Chrt (1962), Hanuš & Krs (1963), Losert (1964), Krs & Vondrová (1965), Legierski (1973), Čadek et al. (1975), Baumann (1977), Pivec et al. (1984), Vaněček et al. (1985), Thomas & Tischendorf (1987), Čadek & Malkovský (1988) and Žák et al. (1990), various types of fluorite, barite, uranium and sulphide (base-metal) mineralization. The Roztoky deposit represents a scarce example (together with Tertiary mineralization in Badenweiler and Wiesloch localities in Rhinegraben, Gehlen 1987) of the Tertiary sulphide vein-type mineralization spatially and genetically associated with volcanic and subvolcanic rocks in the whole Cenozoic West and Central European Volcanic Province. The Ohře (Eger) Rift zone, which hosts the Roztoky Volcanic Centre (RVC) and Roztoky deposit, also contains widespread fluorite and barite mineralization with fluorite deposition con-

tinuing even subrecently and recently from thermal springs (e.g. in Teplice and Děčín).

The $\text{Au}\pm\text{Ag}\pm\text{Te}\pm$ base metal deposits related to alkaline igneous rocks, known from numerous metallogenic provinces around the world, constitute one of important sources of precious and related metals. Well known examples of alkalic-type epithermal mineralization include Cripple Creek, Colorado; Colorado mineral belt; Montana alkalic province; Porgera, Mt. Kare, and Ladolam, Papua New Guinea etc. (Richards 1995). Within the Cenozoic West and Central European Volcanic Province the occurrence of a deposit of this type is quite exceptional. The purpose of this study is to summarize the essential facts concerning this poorly known deposit.

Geological setting of the Roztoky ore district

The Roztoky (Rongstock in German) village is better known from the petrologic literature as the type locality of the Tertiary monzodiorite (rongstockite after Tröger 1935) rather than the Pb-Zn-Cu (Ag, Te) deposit.

The RVC is the main volcanic centre of the České středohoří Mts. and represents the main strongly differentiated volcanic complex within the NE-SW trending Ohře Rift. Volcanic activity ranges from 42 to 10 Ma and frequently reveals a bimodal character (basanite-trachyte), cf. Wilson et al. (1994). Mantle derived alkali basaltic rocks display primitive $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in a range from 0.7032 to 0.7037 (Vokurka & Bendl 1992; Bendl et al. 1993; Wilson et al. 1994). A sublithospheric HIMU mantle plume could have been the source of the magma (Wilson et al. 1994).

The RVC occurs at the intersection of the hypothetical central faults of the Ohře Rift, which is the main rift zone of the Bohemian Massif, and the Labe tectono-volcanic zone (Kopecký 1978). The RVC crops out in the deeply eroded Labe (Elbe) Valley. The central diatreme of the RVC is filled mainly by breccia of trachytic composition with carbonate-bearing groundmass. The carbonate component of this breccia was assumed to be of carbonatite origin by Kopecký (1978, 1987a). Younger trachytes and phonolites intrude into the breccia. Intrusive bodies of olivine nephelinite, basanites and phonolites in the vicinity outside the mentioned breccia, may belong to the RVC as well. The southwest part of the RVC is limited by a local fault intruded by breccia of lamprophyric composition.

The proper environs of the deposit consist of a hypabyssal body of monzodiorite situated at the southern margin of the RVC as a circular segment, about 200 m in diameter, bounded by the local fault in the W and by a block of contact metamorphosed marlstones of Late Cretaceous age towards the NE (Fig. 1). This monzodiorite segment probably represents part of an originally bigger elliptical body (Hibsch 1899). Stocks with elliptic shape of similar composition (essexites) and one of sodalite syenite occur scattered in the near vicinity.

More than 1,000 dykes forming a radiating system and rare cone-sheets extend up to 15 km from the centre of the RVC. The trachytic breccia of diatreme is probably younger than the older generation of lamprophyres but older than tinguaites (a textural variety of phonolite) and nepheline syenite porphyry dykes. The dyke system consists of lamprophyres and felsic derivatives-semilamprophyres and common rock dykes (Jelínek et al. 1989). Trachyte and bostonite dykes (in Fig. 1) belong to the dyke system mentioned above.

The Tertiary Pb-Zn-Cu (Ag, Te) bearing hydrothermal veins are located mostly within the monzodiorite segment and only partly in its marlstone envelope (Pivec et al. 1984), see Fig. 1. The host rock of the ore veins (i.e. monzodiorite) was dated by the K/Ar method (whole rock) at 29.5 Ma (H. Bellon, Orsay Univ. Paris, in Kopecký 1987b).

The ore deposit

The deposit is formed by three parallel mineralized veins (Pivec et al. 1984). The main vein parallels a 3 m thick bostonite dyke of NE-SW direction and dips steeply 70-75° to the NW. The main vein was mined in its southwestern part mainly in the 16th century and prospected in the northeastern part during the 1953 to 1956 period. The length of this vein is about 500 m (Fig. 1); its maximum thickness reaches 0.6 m. The hydrother-

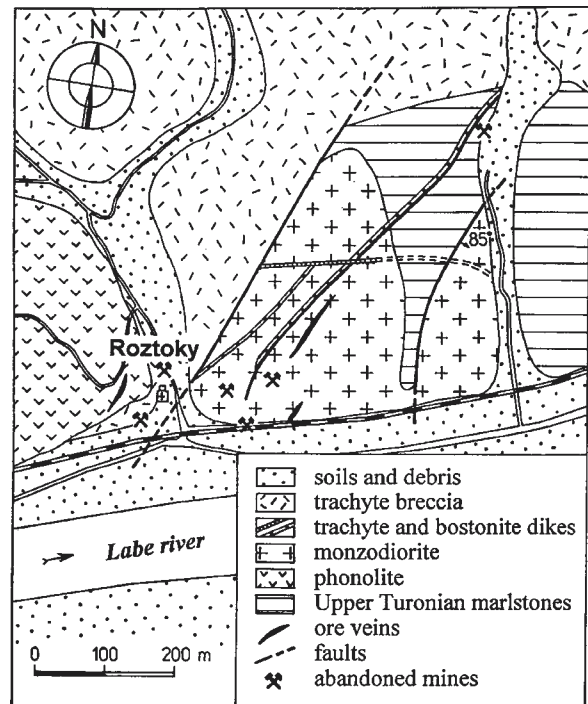


Fig. 1. Geological map of the Roztoky deposit. (Modified after Pivec et al. 1984). (Common symbol for railway in the lower part of Fig.)

mal filling is more widespread in sections where the vein occurs just at the contact between altered bostonite and monzodiorite. Where the vein parallels the bostonite dyke in the contact metamorphosed marlstones, replacements and impregnations from 2 to 10 cm thick are typically developed. Faults trending NW-SE, N-S and E-W disrupt the bostonite dyke and ore vein. Both the dyke and the vein are slightly displaced and younger trachyte dykes crosscut them. This fact proves that ore formation coincided with the development of the RVC.

In the vein filling, sphalerite prevails over galena. Pyrite, chalcocopyrite, tetrahedrite, and hessite are present in minor amounts. The gangue is composed of rhodochrosite, dolomite and calcite (from oldest to youngest). Quartz, chalcedony, and barite are present in minor amounts. The position of the main ore minerals in the paragenetic sequence is shown in Fig. 2.

The structure of the vein filling often indicates a cessation of mineralization due to tectonic movements. The breccia consists of fragments of pyritized contact-metamorphosed marlstone, bostonite, and monzodiorite. These fragments are usually coated by sphalerite and galena, and cemented by carbonate gangue. Transitions of breccia structure to cockarde structure were found. A special type of the breccia structure formed by sphalerite crystals (about 2 cm in diameter) "floating" in the host carbonate is characteristic for this locality. The presence of collomorphous aggregates ("Schalenblende") of sphalerite and a banded structure are local only.

Analytical methods

The ore minerals were analyzed using a JEOL XA 50 A electron microprobe, equipped with EDAX 711, operating at

Minerals	Stages				
	I.	II.	III.	IV.	V.
Pyrite	—				
Quartz	—				
Sphalerite		—			
Galena		—			
Tetrahedrite		—			
Hessite		—			
Barite		—			
Rhodochrosite			—		
Dolomite-calcite			—		
Chalcopyrite				—	
Chalcedony					—
Calcite					—

Fig. 2. The schematic succession of the hypogene vein minerals of the Roztoky deposit. (Modified after Pivec et al. 1984).

15 kV with a specimen current of 0.02 A. The standards used were pure metals (Sb, Ag, Te, Cu, Au) and synthetic PbSe, Ag₂Te, ZnS, and GaAs.

For the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurement on carbonates, the conventional reaction with 100 % H₃PO₄ (McCrea 1950) was used. Carbonates were, on the basis of their chemical composition, reacted at 25 °C (calcite) or 100 °C (rhodochrosite, dolomite) for 2 hours and corrections to measured $\delta^{18}\text{O}$ values were made depending upon the chemical composition of carbonates and the temperature of reaction. The reproducibility of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements on carbonates was ± 0.1 ‰.

Preparation of SO₂ for $\delta^{34}\text{S}$ measurements on sulphides was done by combusting with CuO at 770 °C in a vacuum (Grinenko 1962). The reproducibility of $\delta^{34}\text{S}$ measurements on sulphides was ± 0.15 ‰. All stable isotope measurements were done using a Finnigan MAT 251 mass spectrometer.

Sr for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurement was isolated on quartz columns filled with Bio Rad cation exchange resin. Mass spectrometry was done by a Finnigan MAT 262 mass spectrometer. A double Re filament ionization technique was used. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were standardized to the value 0.1194 for $^{86}\text{Sr}/^{88}\text{Sr}$.

Fluid inclusions were studied utilizing doubly polished plates, 0.2–0.3 mm thick, by optical microthermometry on a Chaixmeca heating and freezing stage (Poty et al. 1976). The stage was calibrated for temperatures between –100 °C and 400 °C by Merck chemical standards, the melting point of distilled water, and phase transitions in natural pure CO₂ inclusions.

Results and discussion

Sulphide minerals of ore veins and their crystal chemistry

Pivec et al. (1984) did not detect the presence of silver minerals proper in spite of the deposit being known as a silver mine, even though they mentioned the content of 0.14 wt. % Ag in the galena. New microprobe data and reflected light microscopy studies have shown that (besides silver-bearing tetrahedrite with 3.3 wt. % of Ag), the main silver mineral is cubic hessite, which forms minute inclusions mainly in galena and, to a lesser extent, in sphalerite. The cubic form was identified on the basis of the isotropic behavior of hessite in

reflected light. Hessite has been known in the Bohemian Massif in the Variscan vein mesothermal Au-deposits only (Morávek 1992). The chemical composition of the studied ore minerals is presented in Table 1. Pivec et al. (1984) also reported contents of In (250–300 ppm), Ga (15 ppm) and Ge (2 ppm) in sphalerites.

The presence of color banded zones in colloform sphalerite together with the presence of chalcedony seems to indicate rather lower temperatures of deposition. However, the occurrence of cubic hessite indicates temperatures of deposition above 155 °C (Strunz 1982).

The geochemistry of hydrothermal carbonates

The chemical composition of carbonates from the main ore vein in Roztoky was studied by Pivec et al. (1984) and from sulfidic and barren veinlets by Kopecký et al. (1987). On the basis of the C and O isotope data of carbonates, Kopecký et al. (1987) suggest their low-temperature (late-stage C4) hydrothermal carbonatite origin (sensu Le Bas 1977) and connect them with a presumed hidden carbonatite intrusion, in the trachytic vent.

The prevailing pinkish to grey carbonate of the main ore vein is rhodochrosite with a dolomite admixture (MnO = 39.25 wt. %). The younger carbonate filling is represented by fine-grained calcite intergrown with dolomite (about 1:1). This second most frequent type of carbonate gangue in the vein, contains 9.05 wt % MgO and 43.20 wt. % CaO (bulk analysis). Pure manganian calcite (4.90 wt. % MnO) was found in small amounts only. The Σ REE (99.8–130.8 ppm) (Table 2) as well as mildly higher SrO (1,200–1,500 ppm) and BaO (2,150–8,800 ppm) (Ulrych et al. 1997), contents of the carbonates are too low for speculation about their carbonatite origin (cf. Kopecký 1987a). The higher contents of Sr and Ba in carbonates of hydrothermal veins should be interpreted cautiously because many carbonates from common ore-bearing veins with no carbonatite affinity show a similar composition to those at Roztoky. For example, the Sr content derived from altered aluminosilicates of the host rocks increases with the intensity of wall-rock alteration from old (100 ppm Sr) to young (2,000 ppm Sr) hydrothermal carbonates in ore veins of the Příbram ore district (Čílek et al. 1984). The REE contents of dolomite from an ultramafic lamprophyre dyke (polzenite, Ralsko Hill, northern Bohemia) — the highest Σ REE contents in carbonate (201 ppm) found until now in the Bohemian Massif (Ulrych et al. 1997 — are given in Table 2 for comparison). Pure calcite phases from sövite contain generally higher Σ REE, Sr and Ba contents — e.g. calcite from sövite, Kaiserstuhl: Σ REE 733 ppm; calcite from sövite, Alnö: Σ REE 751–1,751 ppm, Sr 750–1,900, Ba 7,000–14,500 ppm; dolomite from sövite, Fen: Σ REE 350 ppm, Sr 5,000–6,900 ppm, Ba 360–500 ppm (Möller et al. 1980). Contents of Σ REE in late magmatic carbonatite products are even much higher. An ankeritic carbonatite with Σ REE 11,570–13,078 ppm and ankeritic carbonatite with fluorite, barite and quartz with Σ REE 33,336–64,550 ppm were described from the Amba Dongar carbonatite, India, by Viladkar & Dulski (1986).

Carbonatites are commonly characterized by higher amounts of incompatible elements like Sr, Ba, REE, Zr, U, Th, Zr, Hf, Nb, Ta, P and F. High contents of these elements were not detected either in vein carbonates or in the trachytic breccia of the diatreme in Roztoky. The chemical composition of the carbonates thus does not support the idea of Kopecký (1987a) of their association with a hidden sövite intrusion in deeper sections of the RVC.

C and O isotopic composition of the hydrothermal carbonates

To corroborate the model of hidden carbonatite intrusion, seventeen carbonate samples representing seven genetically different types of carbonate occurrences in the RVC were analyzed for carbon and oxygen isotopes by Kopecký et al. (1987). From this sample set, only one analysis, a carbonatized monzodiorite xenolith from the „pseudotrachyte breccia“, plots within the field of primary igneous carbonatites (PIC) as defined by Taylor et al. (1967) and Deines & Gold (1973). All other samples possess higher $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (see Fig. 3), plotting in the field of “carbonatite associated carbonates”, which generally do not represent primary igneous carbonate.

Numerous hydrothermal carbonates from various hydrothermal ore veins of the Bohemian Massif, which clearly do not have any carbonatite affinity, plot in the same field, some even within the PIC field (e.g. some hydrothermal carbonates of the West Bohemian uranium deposits, some carbonates of polymetallic veins in the Jihlava ore district, etc.). This coincidence can be easily explained by the fact that the isotopic composition of a carbonate plots in the $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ space as a result of the influence of three independent factors: (i) the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the hydrothermal fluid; (ii) temperature of deposition; and (iii) the nature of the carbon species in the fluid. When an independent temperature estimate can be obtained most uncertainties are eliminated since the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ characteristics of hydrothermal fluids can be calculated. Only in the cases where an independent thermometry indicates magmatic temperatures and the calculated fluid composition plots within and/or close to the PIC, can a carbonatite affinity be assumed.

The temperature of deposition of hydrothermal carbonates of the studied Roztoky sulphide deposit probably did not exceed 280 °C, because carbonate deposition postdates sulphide deposition, for which sphalerite-galena sulphur isotopic thermometers indicate temperature in the range of 200 to 250 °C (see below). Fluid inclusion homogenization temperatures exhibit a similar range (220 to 285 °C).

New carbon and oxygen isotopic determinations on carbonates from the main vein of the Roztoky sulphide deposit have shown similar $\delta^{13}\text{C}$ but lower $\delta^{18}\text{O}$ values when compared with data for sulphide-bearing veinlets reported by Kopecký et al. (1987; see Fig. 3). If a temperature of deposition between 200 and 280 °C for the carbonates of the main vein is accepted, $\delta^{13}\text{C}_{\text{fluid}}$ values from ca. -3.0 to -5.0 ‰ and $\delta^{18}\text{O}_{\text{fluid}}$ values from ca. -3 to -7 ‰ (SMOW) can be calculated.

Table 1: Composition of ore minerals from the Roztoky deposit (in wt. %).

	sphalerite			galena	tetra- hedrite	hessite	
	rim	trans.zo	core			average	range
n of anal.	2	2	2	1	6	10	
Zn	65.41	65.25	65.81	-	6.22	0.00	0.00
Au	-	-	-	-	-	0.05	0.02-0.10
Fe	1.19	0.38	0.21	-	1.23	0.36	0.00-0.06
Bi	-	-	-	0.16	0.15	0.13	0.03-0.21
Cd	0.99	1.75	1.30	-	-	-	-
Sb	-	-	-	0.10	23.81	0.08	0.03-0.17
Mn	0.10	0.10	0.20	-	-	-	-
Ag	-	-	-	-	3.30	62.95	62.60-63.51
Cu	0.02	0.04	0.05	0.01	36.96	0.04	0.00-0.10
Pb	-	-	-	86.34	0.08	0.07	0.01-0.12
As	0.06	0.06	0.08	-	3.15	0.00	0.00
Te	-	-	-	0.12	0.02	37.13	36.77-37.36
S	32.92	32.80	32.85	13.28	25.16	0.11	0.22-0.34
Se	-	-	-	-	-	0.27	0.22-0.34
Σ	100.69	100.38	100.50	100.01	100.08	100.93	
Number of ions per formula unit							
Zn	0.971	0.975	0.981	-	1.574	-	
Au	-	-	-	-	-	0.001	
Fe	0.021	0.007	0.004	-	0.364	0.022	
Bi	-	-	-	0.002	0.012	0.002	
Cd	0.009	0.015	0.011	-	-	-	
Sb	-	-	-	0.002	3.235	0.002	
Mn	0.002	0.002	0.004	-	-	-	
Ag	-	-	-	-	0.506	1.966	
Cu	0.000	0.001	0.001	0.000	9.622	0.002	
Pb	-	-	-	1.000	0.006	0.001	
As	0.001	0.001	0.001	-	0.696	-	
Te	-	-	-	0.002	0.003	0.980	
S	0.997	1.000	0.999	0.994	12.982	0.012	
Se	-	-	-	-	-	0.012	
Σ	2.000	2.000	2.000	2.000	29.000	3.000	

This carbon isotopic composition of hydrothermal fluids is within the range accepted for deep-seated carbon (-5 ± 2 ‰; Ohmoto 1986) near its upper limit. Since the carbon isotopic composition in the same range can also be produced by mixing of different sources, adjacent contact-metamorphosed Upper Cretaceous marlstones, representing the dominant carbon reservoir in the host-rocks, were also analysed. Samples collected in a 1100 m long profile perpendicular to the contact of monzodiorite segment show $\delta^{13}\text{C}$ values in the range from +1.48 to -4.86 ‰ and $\delta^{18}\text{O}$ values in the range from +15.7 to +2.8 ‰ (SMOW), see Fig. 3 in Chaloupková (1986). Carbonate phases from contact metamorphic pyroxene and albite-epidote hornfels close to the contact show the lowest $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, while the more distant, less influenced Upper Cretaceous host rocks plot near the upper limit of the above mentioned

Table 2: REE contents of carbonates from Roztoky ore veins, and in ultramafic lamprophyre (polzenite), Ralsko Hill (in ppm). 1 — rhodochrosite, main ore vein, Roztoky; 2 — dolomite-calcite, main ore vein, Roztoky; 3 — dolomite, polzenite dike, Ralsko Hill, northern Bohemia (Analyst: P. Povondra, Charles University, Prague).

	1	2	3
La	25.2	34.3	54.7
Ce	39.9	51.9	86.4
Pr	4.3	5.6	8.7
Nd	16.7	21.0	35.7
Sm	3.7	4.7	4.8
Eu	2.4	3.0	1.6
Ga	3.7	4.8	4.4
Dy	2.3	3.0	2.0
Ho	0.4	0.6	0.5
Er	0.7	1.1	<0.8
Yb	0.4	0.7	0.2
Lu	0.1	0.1	<0.1
Y	10.7	16.9	8.3
ΣREE+Y	110.5	147.7	207.3

range. Mass balance calculation shows that the dominant portion of the carbonate-carbon which was released from the host rock sedimentary sequence as a result of decarbonation and hydrothermal mobilization had $\delta^{13}\text{C}$ values in the range from +2 to -2 ‰ while the hydrothermal fluid which formed the gangue of sulphidic veins ranged from -3 to -5 ‰. This shows that important proportion of CO_2 in the hydrothermal fluids was derived from another, probably deep-seated source.

The calculated oxygen isotopic composition of hydrothermal water is extremely low, indicating the dominance of low- $\delta^{18}\text{O}$ water (with respect to its low to medium salinity probably groundwater from Cretaceous sediments) in the

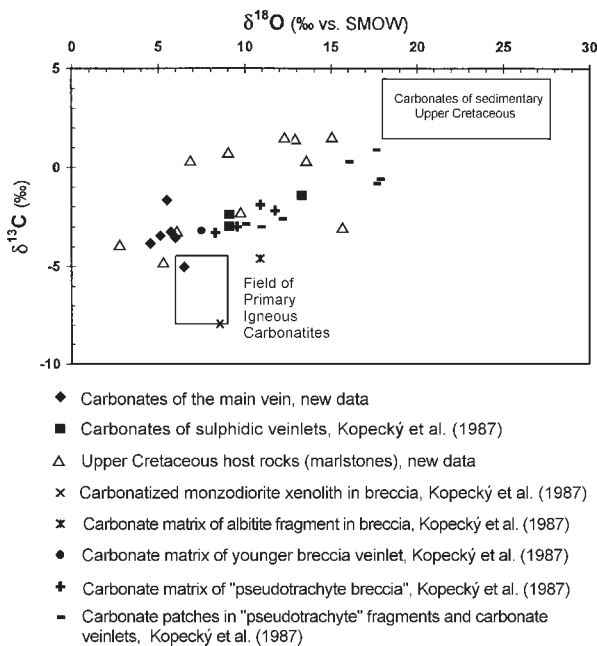


Fig. 3. $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ plot for various carbonates from the Roztoky volcanic center. The field of Primary Igneous Carbonatites (PIC) is after Taylor et al. (1967) and Deines & Gold (1973) and the field for normal Upper Cretaceous sedimentary rocks after Hladíková et al. (1979).

hydrothermal fluid. Hydrothermal circulation also decreases the original „sedimentary“ $\delta^{18}\text{O}$ signature of the Upper Cretaceous host marlstones in the whole contact aureole up to a distance of several hundred meters from the monzodiorite intrusion. This significant shift in the $\delta^{18}\text{O}$ of host rocks locally down to +2.8 ‰ (SMOW) cannot be explained by decarbonation reactions and requires extensive water/rock interactions under high water/rock ratios.

Carbon and oxygen isotope study therefore shows that the volcanic activity and especially the intrusion of the monzodiorite body into a shallow crustal level at Roztoky caused extensive circulation of heated low to medium salinity low- $\delta^{18}\text{O}$ fluids which formed the sulphidic veins and altered the host rocks. An important proportion of the carbonate carbon of the hydrothermal fluids forming the sulphidic veins had a $\delta^{13}\text{C}$ composition in the deep-seated range and was not derived from the Upper Cretaceous sediments.

S isotopic composition of the sulphides

Sulphur isotopic compositions of both galena and sphalerite from the main vein show narrow ranges of $\delta^{34}\text{S}$ values: from -4.4 to -3.1 ‰ for galena (5 samples) and from -2.5 to -1.4 ‰ for sphalerite (5 samples). Deposition of these sulphides in the main vein is usually not contemporaneous. This, together with the frequent presence of spherical structures formed by the different colored zones of sphalerite, makes the application of sphalerite-galena sulphur isotope thermometry problematic. In such case the sphalerite-galena sulphur isotope thermometry can yield reliable data only in environments, where the $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values had minimum variability during the period in which the minerals were precipitated. Two pairs with the most intimate textural relationships between sphalerite and galena yielded sphalerite-galena sulphur isotopic temperatures of 218 and 226 °C (± 25 °C) (using the equation of Ohmoto & Rye 1979).

Assuming H_2S -dominated fluids during sulphide deposition, $\delta^{34}\text{S}_{\text{fluid}}$ values in the range -1.0 to -2.0 ‰ can be calculated. No exact conclusion concerning the sulphur source can be made, because no accurate information concerning the sulphur isotopic composition of the RVC rock and adjacent country rocks is available. The isotopic composition of this source sulphur of hydrothermal fluids is slightly shifted from the range typical for “average uncontaminated mantle” (ca. -0.5 to +0.5 ‰; Ohmoto 1986).

Pb isotopic composition of the galena

The Pb isotopic composition of the galena from the Roztoky deposit was reported by Legierski (1973). Vaněček et al. (1985), based on small but systematic differences in lead isotope ratios of some localities studied by both Legierski and Doe & Zartman (1979), introduced correction factors to the data of Legierski (1973) to align both data sets. Pb isotope ratios reported in this paper are those of Vaněček et al. (1985).

The lead isotopic ratios of galena from the Roztoky deposit are high ($^{206}\text{Pb}/^{204}\text{Pb}$ about 19.03, $^{207}\text{Pb}/^{204}\text{Pb}$ about 15.67, $^{208}\text{Pb}/^{204}\text{Pb}$ about 39.17).

Lead with this isotopic composition can be derived directly from alkaline basic to intermediate magmatic rocks of the RVC. Wilson et al. (1994) reported $^{206}\text{Pb}/^{204}\text{Pb}$ isotope ratios of primitive Tertiary mafic volcanic rocks of the České středohoří Mts. area in the range from 19.4 to 20.0 and suggested that the source of magmas is a sublithospheric HIMU mantle plume. With respect to the well-known regional enrichment of Upper Paleozoic and Upper Cretaceous sedimentary rocks of this region in U and Th (Lepka 1980), the lead could have been derived from this upper crustal source as well.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the hydrothermal carbonates

For the rhodochrosite of the main vein of the Roztoky deposit, a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.705237 ± 0.000009 (2σ) and for the calcite with dolomite admixture from the same vein, a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.705104 ± 0.000010 (2σ) were obtained. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of primitive basaltic volcanic rocks of the Czech part of the Cenozoic Central European Volcanic Province, which can be used as an estimate of the mantle array in this region, range from 0.7031 to 0.7037 (Vokurka & Bendl 1992; Bendl et al. 1993; Wilson et al. 1994). The rocks of the RVC yielded slightly higher and wider initial $^{87}\text{Sr}/^{86}\text{Sr}$ range (0.7037 to 0.7045; Ulrych et al. in prep) indicating probable minor contamination by crustal material.

For the marine Cretaceous sedimentary rocks of this region which represent, besides the rocks of RVC, another important reservoir of Sr, no $^{87}\text{Sr}/^{86}\text{Sr}$ determinations exist. The average ratio for Turonian marine carbonate sediments can be estimated at close to 0.7074 (Burke et al. 1982).

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained for hydrothermal carbonates indicate that the Sr content of hydrothermal fluids was most probably a mixture of Sr derived from the rocks of the RVC and of Sr originating from local crustal rocks, probably Upper Cretaceous sediments. Direct "carbonatite" origin of studied hydrothermal carbonates is less probable.

Fluid inclusion study

Fluid inclusions were studied in sphalerite and rhodochrosite.

Sphalerite contains a large number of inclusions but the majority are unsuitable for microthermometry due to their opaque nature. The measured inclusions are 5 to 20 μm in size, H_2O -rich, two phase, with vapour phase between 5 and 20 vol. %. Two generations of inclusions have been distinguished. Probably pseudosecondary inclusions have homogenization temperatures (Th) in the range of 221 to 285 $^\circ\text{C}$ (see Fig. 4) and melting temperatures of ice (Tm) -1.4 to -7.0 $^\circ\text{C}$, i.e. salinity of the fluid is 2.4 to 10.4 wt. % NaCl equiv. (Bodnar 1993). An exceptional distinct group of inclusions shows lower Tm of ice, from -12.6 to -15.4 $^\circ\text{C}$, corresponding to salinity from 16.5 to 18.9 wt. % NaCl equiv. The homogenization temperature of abundant secondary inclusions are between 151 and 212 $^\circ\text{C}$ and their salinity ranges from 1.4 to 4.6 wt. % NaCl equiv. (Tm = -0.8 to -2.8 $^\circ\text{C}$). The eutectic tem-

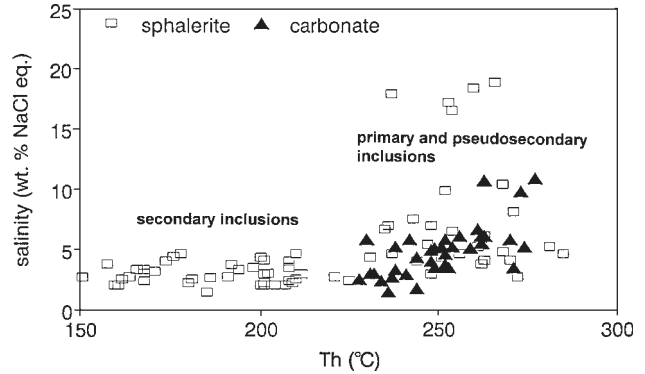


Fig. 4. Homogenization temperatures versus salinity of fluid inclusions in sphalerite and carbonate from the main ore vein of the Roztoky deposit.

peratures of the inclusions in sphalerite were not observed due to the dark colour of the mineral.

Abundant large, 10 to 40 mm, two-phase inclusions with vapour phase to vol. 30 % have been found in carbonate. They occur mainly in isolated groups and are considered to be primary. They are also water-rich, Th are in the range between 228 and 277 $^\circ\text{C}$ and salinity from 1.5 to 10.9 wt. % NaCl equiv. (Tm = -0.9 to -7.4 $^\circ\text{C}$). The eutectic temperatures have values between -22.0 and 29.2 $^\circ\text{C}$, and indicate that NaCl is the dominant salt of the solution.

If we take into account that the deposit was formed under hydrostatic pressure conditions in a depth not exceeding 800 m, then the pressure correction between the Th and temperature of trapping is less than 10 $^\circ\text{C}$ (Potter 1977) and the Th of the primary and pseudosecondary inclusions are close to temperatures of the formation of the minerals.

In the diagram Th (homogenization temperature) versus salinity (Fig. 4) three fields of fluid inclusion data can be distinguished. Secondary inclusions in sphalerite have distinctly lower Th and salinity. The majority of the data of sphalerite and carbonate lie in the same field and indicate that the hydrothermal fluid responsible for the formation of sphalerite and carbonate was low-saline at a temperature below 300 $^\circ\text{C}$. The inclusions with salinity of about 17 wt. % NaCl equiv. form a separate cluster of data and seem to be uncommon.

Conclusions

The geological position of the base metal deposit and its close spatial affinity to the rock suite show that the ore veins represent an integral part of the RVC. This conclusion is supported by the young trachyte vein cutting both the bostonite dyke and the parallel ore vein (Pivec et al. 1984).

The revision of the chemical composition of ore minerals in the Roztoky deposit demonstrates that the silver-bearing minerals are cubic hessite forming inclusions mainly in galena and the minor silver-bearing tetrahedrite.

According to Kopecký (1987a), ore-bearing carbonate vein material represents products of the residual solutions derived from a hypothetical carbonatite intrusion. There are, however, no unambiguous proofs for this interpretation. From the pa-

parameters of the hydrothermal fluids studied, only the C isotopic composition lies in the range typical for deep-seated carbon. The very low $\delta^{18}\text{O}$ values of the hydrothermal fluids (-3 to -7 ‰ vs. SMOW) indicate the dominance of meteoric water in the ore fluid. The radiogenic lead isotope ratios of the galena prove the upper crustal origin of the lead, outside the rocks of the RVC. Similarly, the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of the hydrothermal carbonates which are slightly higher than those of the RVC and higher than the local mantle range indicate an admixture of Sr derived from crustal rocks.

The low REE, Sr and Ba contents of both the carbonates of ore veins and trachytic breccia of diatreme do not indicate their carbonatite origin. The simple ore vein character (no cone-sheets — Kopecký 1987a), dominance of sulfidic minerals and composition of sulphidic and carbonate minerals in the ore veins, their textural (colloform) and structural (cockarde) arrangement, lack of any silicate and scarcity of barite and fluorite practically exclude a carbonatite affinity for the Roztoky sulphidic ore veins.

The temperature of deposition probably reached a maximum of 200–280 °C during the main ore stage (presence of cubic modification of hessite, data of sphalerite-galena sulphur isotopic thermometer, fluid inclusion homogenization temperatures) with a decrease in the younger stages.

The presented data, especially the low $\delta^{18}\text{O}$ values of the hydrothermal fluids, indicate that the Roztoky sulphide deposit is a result of circulation in an upper crustal hydrothermal system in which the rocks of the RVC acted dominantly as a heat source driving (with the support of influx of deep-seated CO_2 , cf. Pačes 1974) the movement of pore waters from local Cretaceous sedimentary rocks.

Most parameters of the Roztoky deposit agree with features of epithermal deposits defined by Pirajno (1992). It is formed at low temperature from dominantly meteoric hydrothermal fluids having moderate to low salinity (in the early stages of mineralization higher than 5 wt.% NaCl equivalent which is supposed by Pirajno l.c. as maximum). The deposit is volcanically hosted and clearly related to volcano-plutonic activity. The present authors suggest processes analogous to those proposed by Richards et al. (1991) for the Porgera gold deposit, where it is supposed that the metals in the epithermal system were derived largely from leaching of earlier disseminated ores at depth. The presence of fine-grained chalcedonic quartz, calcite and other carbonates, quartz pseudomorphs and hydrothermal breccias are common features. The element association with the ore elements such as Au, Ag, As, Sb, Te, Pb, Zn and Cu corresponds to epithermal deposits. Ore textures including open-space filling, crustification, colloform banding and comb structures are present.

Acknowledgement: The research was partly funded by the Grant Agency of the Czech Academy of Sciences, Grant No. A 3111601. The authors would like to thank J. G. Strnad for review of the earlier draft of the manuscript. Special thanks go to T. Armbrustmacher and M. Novák, who improved the English considerably and to J. Hedenquist for many helpful comments.

References

- Baumann L., 1977: Zur Frage varistischer und postvaristischer Mineralization in sächsischen Erzgebirge. *Freiberg. Forsch. - H.*, C209, 15–28.
- Bendl J., Vokurka K. & Sundvoll B., 1993: Strontium and neodymium isotope study of Bohemian Basalts. *Mineral. Petrol.*, 48, 35–45.
- Bodnar R.J., 1993: Revised equation and table for determining the freezing point depression of H_2O -NaCl solutions. *Geochim. Cosmochim. Acta*, 57, 683–684.
- Burke W.H., Denison R.E., Hetherington E.A., Koepnick R.B., Nelson N.F. & Otto J.B., 1982: Variation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout Phanerozoic time. *Geology*, 10, 516–519.
- Cílek V., Prokeš S., Škubal M., Hladíková J., Šmejkal V. & Žák K., 1984: Geochemistry of hydrothermal carbonates of the Příbram uranium deposit. In: S. Polák & J. Litochleb (Eds.): Vlastivedný sborník Podbrdská. *Okresní archiv a muzeum, Příbram*, 26, 79–102 (in Czech).
- Čadek J., Syka J., Vavřín I. & Veselý T., 1975: The conditions of metal accumulation in sediments. *Unpublished Report, Geological Survey, Prague* (in Czech).
- Čadek J. & Malkovský M., 1988: Fluorite in the vicinity of Teplice-Spa in Bohemia — a new type of fluorite deposit. In: E. Zachrisson (Ed.): 7th IAGOD symposium Proceedings, *Lulea Sweden.*, Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 253–257.
- Deines P. & Gold D.P., 1973: The isotopic composition of carbonatite and kimberlite carbonate and their bearing on the isotopic composition of deep-seated carbon. *Geochim. Cosmochim. Acta*, 37, 1709–1733.
- Doe B.R. & Zartman R., 1979: Plumbotectonics I. The Phanerozoic. In: H. Barnes (Ed.): *Geochemistry of hydrothermal ore deposits*. J. Wiley, New York, 2–70.
- Gehlen von K., 1987: Formation of Pb-Zn-F-Ba mineralizations in SW Germany: A status report. *Fortschr. Miner.*, 65, 87–113.
- Grinenko V.A., 1962: Preparation of sulphur dioxide for sulphur isotope analysis. *Zhur. Neorgan. Chim.*, 7, 2478–2483 (in Russian).
- Hanuš V. & Krs M., 1963: Paleomagnetic verification of Neoidic age of hydrothermal mineralization in Krušné hory Mts. and Slavkovský les. *Věst. Ústř. Úst. Geol.*, 38, 119–122 (in Czech).
- Hibsch J.E., 1899: Der Doleritstock und das Vorkommen von Blei- und Silbererzen bei Rongstock im böhmischen Mittelgebirge. *Verh. K.-kön. geol. Reichsanst.*, 11, 204–210.
- Hladíková J., Čadek J., Šmejkal V. & Vavřín I., 1979: Isotopic study of oxygen and carbon in carbonates of the Bohemian Cretaceous Basin. *Sbor. Geol. Věd, Ř. LG*, 20, 37–48 (in Czech).
- Chaloupková M., 1986: Geochemistry of the contact of the Roztoky volcanic body. *M.Sc. Thesis, Charles University, Praha*, 1–90 (in Czech).
- Jelínek E., Souček J., Tvrđý J. & Ulrych J., 1989: Geochemistry and petrology of alkaline dyke of the Roztoky volcanic centre, České středohoří Mountains, ČSSR. *Chem. Erde*, 49, 201–217.
- Kopecký L., 1978: Neoidic taphrogenic evolution and young alkaline volcanism of the Bohemian Massif. *Sbor. Geol. Věd, Ř. G*, 31, 91–104.
- Kopecký L., 1987a: The Roztoky pseudotrachyte caldera in the České středohoří Mts., Czechoslovakia. In: L. Kopecký (Ed): *Proceeding on carbonatites and alkaline rocks*. Geol. Survey, Prague, 119–156.
- Kopecký L., 1987b: Young volcanism of the Bohemian Massif. Part 1. *Geol. Hydrometalurg. Uranu*, 11, 30–67 (in Czech).
- Kopecký L., Šmejkal V. & Hladíková J., 1987: Isotopic composition and origin of carbonates in alkaline-metasomatic and cognate rocks of the Bohemian Massif, Czechoslovakia. In: Kopecký L. (Ed.): *Proceeding on carbonatites and alkaline rocks*. 177–196.
- Krs M. & Vondrová N., 1965: Paleomagnetic of the Neoidic miner-

- alization on the Geschieber vein in Jáchymov. *Věst. Ústř. Úst. Geol.*, 40, 167–173 (in Czech).
- Le Bas M.J., 1977: Carbonatite-nephelinite volcanism. *J. Wiley Intersci. Pub.*, London, 1–347.
- Legierski J., 1973: Model ages and isotopic composition of ore leads of the Bohemian Massif. *Čas. Mineral. Geol.*, 18, 1–23.
- Lepka F., 1980: Review of the average contents of U and Th in sedimentary and magmatic rocks of the Bohemian Massif. *Geol. Hydrometalurg. Uranu*, 4, 3–52 (in Czech).
- Losert J., 1964: Tertiary and Quaternary volcanic metallogenetic zones of central Europe, their character and deposits in Czechoslovakia. *XXII. Intern. Geol. Congres, V. Genetic problems of ores*, 405–417.
- Losert J. & Chrt J., 1962: Neoidic platform metallogenetic province of the Bohemian Massif. *Věst. Ústř. Úst. Geol.*, 37, 210–214 (in Czech).
- McCrea J.M., 1950: On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.*, 18, 849–857.
- Morávek P., 1992: Gold in the Bohemian Massif. *Czech Geol. Survey*, Praha, 1–248 (in Czech).
- Möller P., Morteani G. & Schley F., 1980: Discussion of REE distribution patterns of carbonatites and alkalic rocks. *Lithos*, 13, 171–179.
- Ohmoto H., 1986: Stable isotope geochemistry of ore deposits. In: J.W. Valley, H.P. Taylor Jr. & J.R. O'Neil (Eds): *Stable isotopes in high temperature geological processes. Reviews in Mineralogy*, 16, 491–560.
- Ohmoto H. & Rye R.O., 1979: Isotopes of sulfur and carbon. In: Barnes H.L. (Ed.): *Geochemistry of hydrothermal ore deposits*. 2nd ed. *J. Wiley*, New York, 509–567.
- Pačes T., 1974: Springs of carbon dioxide in northwestern Bohemia. *Field-trip guide, Internat. Symposium on Water-Rock-Interaction. Academia*, Prague.
- Pirajno F., 1992: *Hydrothermal Mineral Deposits. Springer Verlag*, Berlin Heidelberg, 1–709.
- Pivec E., Chrt J., Kašpar P. & Ulrych J., 1984: Neoidic polymetallic mineralization in Roztoky nad Labem. *Studie ČSAV, Academia*, Praha, 10, 1–64 (in Czech).
- Potter R.W.II., 1977: Pressure corrections for fluid-inclusion homogenization temperatures based on the volumetric properties of the system NaCl-H₂O. *U.S. Geol. Survey J. Res.*, 5, 603–607.
- Poty B., Leroy J. & Jachimowicz L., 1976: Un nouvel appareil pour la mesure des temperatures sous le microscope: L'installation de microthermometrie Chaixmeca. *Bull. Soc. Franc. Minéral. Cristallogr.*, 99, 182–186.
- Richards J.P., 1995: Epithermal Gold Deposits. Shortcourse 23. *Miner. Assoc. Canada*, 1–400.
- Richard J.P., McCulloch M.T., Chappel B.E. & Kerrich R., 1991: Sources of metals in the Porgera gold deposit, Papua New Guinea: Evidence from alteration isotope, and noble metal geochemistry. *Geochim. Cosmochim. Acta*, 55, 565–580.
- Strunz H., 1982: *Mineralogische Tabellen. 8. Aufl. Geest & Portig K.-G.*, Leipzig, 1–621.
- Taylor H.P., Jr., Frenchen J. & Degens E.T., 1967: Oxygen and carbon isotope studies of carbonatites from the Laacher district West Germany, and Alnö district, Sweden. *Geochim. Cosmochim. Acta*, 31, 407–430.
- Thomas R. & Tischendorf G., 1987: Evolution of Variscan magmatic-metallogenetic processes in the Erzgebirge according to thermometric investigation. *Z. Geol. Wiss.*, 15, 25–42.
- Tröger W.E., 1935: *Spezielle Petrographie der Eruptivgesteine. Ein Nomenklatur-kompodium. Verlag. Deutsch. Mineral Gesell.*, Bonn, 1–360.
- Ulrych J., Pivec E., Fiala J. & Lang M., 1983: Petrology of the alkaline subvolcanic rocks from the Roztoky area České středohoří Mts. *Rozpr. Čs. Akad. Věd, Ř. Mat. Přír. Věd.*, 1–84.
- Ulrych J., Pivec E., Rutšek J., Höhendorf A., Balogh K. & Bendl J., (in prep.): Rhyolite dike differentiates in the Roztoky intrusive centre, České středohoří Mts.: Primary or secondary.
- Ulrych J., Pivec E., Povondra P. & Bendl J., 1997: Geochemical and isotope characteristic of representative carbonates in young alkaline volcanites from northern Bohemia. *J. Czech Geol. Soc.*, 42, 26–32.
- Vaněček M., Patočka F., Pošmourný K. & Rajlich P., 1985: The use of isotopic composition of ore lead in metallogenic analysis of the Bohemian Massif. *Rozpr. Čs. Akad. Věd, Ř. Mat. Přír. Věd*, 95, 1–114.
- Viladkar S.G. & Dulski P., 1986: Rare earth element abundances in carbonatites, alkaline rocks and fenites of the Amba Dongar complex, Gujarat, India. *Neu. Jb. Mineral. Mh.*, 37–48.
- Vokurka K. & Bendl J., 1992: Sr isotope geochemistry of Cenozoic basalts from Bohemia and Moravia. *Chem. Erde*, 52, 179–187.
- Wilson M., Rosenbaum J.R. & Ulrych J., 1994: Cenozoic magmatism of the Ohře rift, Czech Republic: Geochemical and mantle dynamics. *Abstr. Internat. Volcanolog. Congress IAVCEI*, Ankara 1994, 1.
- Žák K., Čadek J., Dobeš P., Šmejkal V., Reichmann F., Vokurka K. & Sandstat J.S., 1990: Vein barite mineralization of the Bohemian Massif: sulfur, oxygen and strontium isotope and fluid inclusion characteristics and their genetic implications. *Proceedings of the symposium on barite and barite deposits. Geological Survey*, Prague, 35–49.