

Pb-Zn-Ag vein mineralization of the central part of the Českomoravská vrchovina Upland (Czech Republic): S, C, and O stable isotope study

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Abstract. The central part of the Českomoravská vrchovina Upland (Czech Republic) is characterized by the presence of base-metal vein mineralizations of various origins. Three groups of mineralizations were distinguished based on sulfur isotope analyses of sulfides and barite (329 analyses in total), and the carbon and oxygen isotope analyses of carbonates (124 analyses in total). 1) High-temperature mineralizations (ca 400–500 °C) show source sulfur values between +3 and +5 ‰ CDT, and are derived from metamorphic or granitic rocks of the Moldanubicum. $\delta^{18}\text{O}$ values of carbonates are high; $\delta^{13}\text{C}$ values are low, indicating the involvement of originally organic carbon in the hydrothermal process. 2) Mesothermal mineralizations (ca 200–350 °C) show source sulfur values that are either markedly positive (up to +10 ‰ CDT) or within the range of ca –3 to +3 ‰ CDT. The $\delta^{18}\text{O}$ values of water in the hydrothermal fluid were usually higher than 5 ‰ SMOW, with water of low $\delta^{18}\text{O}$ values being sometimes involved in the final stages of the mineralization processes (meteoric or marine waters). The values of $\delta^{13}\text{C}$ correspond to homogenized carbon of the Earth's crust, locally affected by carbon from marbles/limestones. 3) Low-temperature mineralization (< 130 °C) shows markedly negative sulfane fluid values, whereas the sulfate values range from +11 to +14 ‰ CDT. In its $\delta^{13}\text{C}$ values, the carbon of the fluids corresponds to homogenized crustal values (with local influence of carbon from limestones and oxidized organic matter). The water of the hydrothermal fluid shows values around 0 ‰ SMOW, thus indicating a prevalence of (i) marine water, (ii) meteoric water, or (iii) a mixture of waters of various origins in the hydrothermal system. The first and the third mineralization types can be considered as distinct genetic categories (minerogenetic type): high-temperature mineralizations are genetically associated with Variscan magmatic and metamorphic processes, while the low-temperature mineralizations are genetically associated with hypersaline brines of a still controversial but possibly marine origin. The mesothermal type most probably includes mineralizations genetically linked with a variety of geological processes.

Key words: polymetallic mineralization, stable isotopes, Českomoravská vrchovina Upland

Introduction

The Českomoravská vrchovina Upland is constrained by the western exocontact of the Moldanubian pluton in the west, the rim of the Boskovice Graben in the east, and by sediments of the Bohemian Cretaceous Basin in the north. The metallic ores deposits of the central part of this unit are typical of numerous occurrences of Pb-Zn-Ag vein mineralization. Most of the sites have been mined or at least explored using mining techniques as early as the Middle Ages, and the last prospecting and mining took place there in the mid-20th century. Some deposits constitute historically significant ore districts with numerous sites (e.g., Jihlava Ore District, Havlíčkův Brod Ore District), while others are completely isolated. The deposits are hosted by various regional-geological units.

The metallogenic characteristics of these sites are not unified and have been the subject of controversy (e.g., Bernard 1991, Češková 1978). Most of the sites have not been subjected to modern methods of study, or else the relevant data are unpublished or scattered in a number of incomplete scientific reports. Only one deposit has so far been investigated using modern analytical methods: the Rožná uranium deposit (with vein-sulfide, stratiform barite-hyalophane etc. type mineralizations, e.g., Hladíková et al. 1995, Kříbek et al. 1996). This deposit is therefore not discussed here.

The present article is intended to summarize all available data on the S, C, and O stable isotope geochemistry of

these deposits, and to supplement it with new analytical data. The material thus gathered was used for establishing some genetic conditions of the origin of the Pb-Zn-Ag vein mineralization in this part of the Bohemian Massif. The present study is also a contribution to the discussion on metallogenic subdivision of the Bohemian Massif and on the metallogenic typology of this mineralization type.

Characteristics of the studied sites

The site locations are shown in Fig. 1. Their general economic-geological characteristics are given below (Table 1). Combined characteristics are given for historically or geographically delimited ore districts consisting of two or more deposits. Mineralogical and economic-geological studies are referred only if published in the recent past.

Methods

Sulfur, carbon, and oxygen isotope analyses were carried out on a Finnigan MAT 251 mass spectrometer in the laboratories of the Czech Geological Survey (analysts K. Žák, J. Hladíková). The samples were prepared for measurement using standard methods: sulfides were oxidized by CuO to SO₂ at 800 °C (Griněnko 1962); SO₂ from barite was liberated by heating with a mixture of V₂O₅ and SiO₂ at

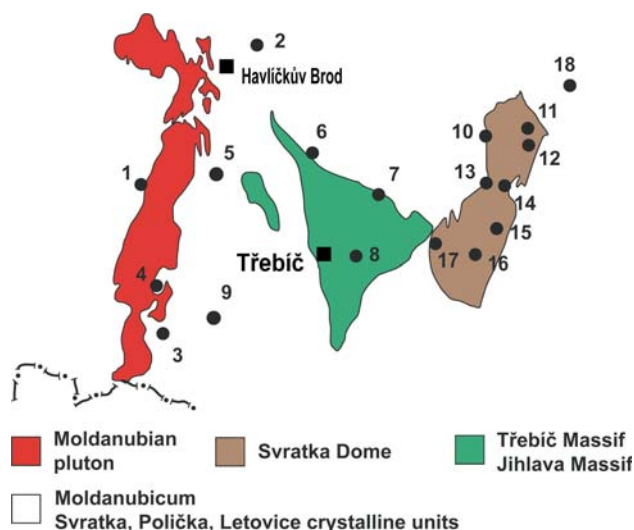


Figure 1. Position of the studied sites in a schematic geological map.

1050 °C; carbonates were decomposed by 100% H_3PO_4 (McCrea 1950). The measured values were related to conventional standards: CDT ($\delta^{34}\text{S}$), PDB ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$ of carbonates), and SMOW ($\delta^{18}\text{O}$ of water). Measurement precision was $\pm 0.2\text{‰}$ for $\delta^{34}\text{S}$ in sulfides; $\pm 0.3\text{‰}$ for $\delta^{34}\text{S}$ in barite; $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ in carbonates; $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ in carbonates. The $\delta^{34}\text{S}$ values of the source sulfur and isotope thermometry was determined using the equation of Ohmoto and Rye (1979). $\delta^{18}\text{O}$ values of hydrothermal fluids were estimated from those of carbonates, in accordance with O'Neil et al. (1969).

Most of the data presented here are original, with some being adopted from earlier published studies. In contrast, most isotope data for minerals from the Jihlava Ore District (site 5) come from an unpublished study by Vosáhlo (1988). Some data on the Havlíčkův Brod Ore District (site 2) come from a published source (Bernard and Žák 1992) and an unpublished database by Žák (Czech Geological Survey, Praha). The data sources are not specified in the text below.

Results

The results of isotope analyses of sulfur in sulfides and barite are summarized in Fig. 2 (329 analyses in total). The results of the isotope analyses of C and O in the carbonates are summarized in Fig. 3 (124 analyses in total).

Discussion

Sulfur isotopes in sulfides and barite

Isotopic relations among minerals

The data and their distribution permit the characterization of some properties of the hydrothermal fluids (or, more exactly, the degree of variability of these properties), which control the establishment of $\delta^{34}\text{S}$ values of the mine-

rals formed (sulfides and possibly barite). These properties include the $\delta^{34}\text{S}$ value of source sulfur in the hydrothermal fluid, temperature, pH, Eh and sulfur activity in the fluid.

It can be stated that:

- Data dispersal is relatively small for most sites. This evinces minor variability of the above parameters.
- Site 14 in the Tišnov area and site 16 in Maršov are exceptional. Here, the variability in the $\delta^{34}\text{S}$ values in sulfides is probably due to major local Eh differences in the hydrothermal fluid. A prominent dispersal in $\delta^{34}\text{S}$ values was also observed at site 3 in the Dačice-Slavonice area. This can also be explained by the low Eh stability in the fluid. Another less likely possibility is that the sulfides analyzed may belong to different mineralization stages, characterized by different temperatures of mineral crystallization, and different $\delta^{34}\text{S}$ values of sulfane in the fluid. This possibility cannot be excluded due to the poorly known succession of relations at the site.
- Prominent outliers in the $\delta^{34}\text{S}$ values of pyrite were observed in some cases (e.g., site 6 Měřín, site 3 Dačice-Slavonice area). This can be explained by the fact that, in most cases, pyrite is formed throughout the existence of the hydrothermal fluid, and its isotope composition reflects changes in fluid properties. For example, pyrite with value $\delta^{34}\text{S} = -15.7\text{‰}$ from the site 6 Měřín was formed only in the final stage of mineralization, during which an increase in oxygen fugacity can be presumed. Another possible explanation is a different mechanism of pyrite (and chalcopyrite) formation: their precipitation from sulfane-containing fluids requires an oxidation mechanism, contrary to that of simple sulfides (Ohmoto 1986).
- $\delta^{34}\text{S}$ values of individual minerals at most of the studied sites indicate the establishment of isotopic equilibrium (with a few exceptions – mostly in pyrite). $\delta^{34}\text{S}$ values can be therefore used for thermometric calculations (see below). The absence of isotope equilibrium among sulfur-containing minerals is evident only at site 3 Dačice-Slavonice, site 14 Tišnov, and site 16 Maršov: the application of isotope thermometry on the deposits at those sites is therefore problematic or impossible.

Sulfur isotope thermometers

Sphalerite-galena pairs were preferably used for the purpose of isotope thermometry. These minerals are common at sulfidic deposits and show sufficiently contrasting fractionation with respect to sulfane. Thermometry pairs with pyrite do not generally yield geologically realistic temperatures (see explanation above).

Sulfide-barite isotope pairs from the studied sites did not yield geologically realistic temperatures. This may be explained as follows:

- Barite was formed at a different stage of fluid development than were the sulfides (sphalerite, galena), thus precluding the establishment of isotopic equilibrium. This explanation can be suggested (based on succession relations) for site 5 Jihlava, mineralizations 5.2,

Table 1. Characteristics of the studied sites

Locality – Ore district	Site examples	Sites studied	Regional-geological unit	Host rock of the deposit	Ore minerals			Gangue minerals		Relative size of the deposit (occurrence)	Principal mineralogical and economic-geological studies
					major	minor	accessory	major	minor		
1. Pelhřimov Ore District	Pavlov, Branišov, Vyskytná, Proseč, Rohozná, Těšenov, Zadní Pole	Nemojov	Moldanubicum	granite (Moldanubian pluton), paragneiss	pyrite, Fe-sphalerite	arsenopyrite, galena, pyrrhotite	chalcopyrite, tetrahedrite, freibergite, acanthite	quartz	siderite, ankerite, dolomite	minor deposits mined in the past	Litochleb (2001)
2. Havlíčkův Brod Ore District	Česká Bělá, Stříbrné Hory, Utín, Mírovka, Dlouhá Ves, Bartoušov, Pohled, Svatý Kříž	Česká Bělá, Stříbrné Hory, Utín, Dlouhá Ves, Bartoušov, Pohled	Moldanubicum	paragneiss, granite (Moldanubian pluton), granite porphyry	pyrite, pyrrhotite, Fe-sphalerite	galena, arsenopyrite	tetrahedrite, pyrrargyrite, marcasite, chalcopyrite, cassiterite, argentite, stannite	quartz	Fe-Mg-Mn carbonate	large deposits mined from the Middle Ages to 20 th century	Pokorný (1964), Holub and Tenčík (1973), Doběš and Malý (2001)
3. Dačice-Slavonice area	Vlastkovec, Radlice, Horní Radčkov, Valtínov, Český Rudolec, Markvarec	Vlastkovec, Radlice, Horní Radčkov	Moldanubicum	Granite (Moldanubian pluton), paragneiss	pyrite, sphalerite, galena	chalcopyrite	argentite, chalcocite, covellite, silver, naumannite	quartz		minor deposits mined in the past	no studies
4. Dobrá Voda			Moldanubicum	paragneiss, granite (Moldanubian pluton)	pyrite, Fe-sphalerite, galena	arsenopyrite, chalcopyrite, pyrrhotite	tetrahedrite	quartz	siderite	minor deposits mined in the past	Stýblo (1972)
5. Jihlava Ore District											
Pluskal and Vosáhlo (1998) distinguish six types of mineralization in the Jihlava Ore District:											
5.1. black sphalerite ± Fe-sulphide ± carbonates	Kamenná, Jihlava-Rudný, Jihlava-Pfaffenhof, Jezdovice	Kamenná, Hybálec, Ježná, Hosov, Popice, Jezdovice	Moldanubicum	paragneiss, granite (Moldanubian pluton), durbachite (Jihlava Massif)	pyrite, sphalerite, galena	chalcopyrite, arsenopyrite, pyrrhotite	tetrahedrite, argentite, pyrrargyrite	quartz	carbonates Fe-Mg-Mn type, dolomite – ankerite	large deposits mined from the Middle Ages	Pluskal and Vosáhlo (1998), Vosáhlo (1988)
5.2. dark brown sphalerite ± barite ± carbonates	Malý Beranov, Kosov, Sasov	Malý Beranov, Kosov, Sasov	Moldanubicum	paragneiss, granite (Moldanubian pluton), durbachite (Jihlava Massif)	sphalerite, galena	chalcopyrite	tetrahedrite, silver, argentite, pyrrargyrite	quartz, barite	dolomite – ankerite, calcite	large deposits mined from the Middle Ages	Pluskal and Vosáhlo (1998), Vosáhlo (1988)

Table 1, continued

Locality – Ore district	Site examples	Sites studied	Regional-geological unit	Host rock of the deposit	Ore minerals			Gangue minerals		Relative size of the deposit (occurrence)	Principal mineralogical and economic-geological studies
					major	minor	accessory	major	minor		
5.5. quartz ± pyrite	Ježena, Hlávkov, Jezdovice, Vilanec	it was not studied in this article	Moldanubicum	paragneiss, granite (Moldanubian pluton), durbachite (Jihlava Massif)	pyrite			quartz			Pluskal and Vosáhl (1998), Vosáhl (1988)
5.6. psilomelane ± chalcedony	Malý Beranov, Kosov	it was not studied in this article	Moldanubicum	paragneiss, granite (Moldanubian pluton), durbachite (Jihlava Massif)	psilomelane			quartz, chalcedony			Pluskal and Vosáhl (1998), Vosáhl (1988)
6. Měšin	Měšin	Měšin	Moldanubicum	paragneiss, durbachite (Třebíč Massif)	sphalerite, galena	pyrite, chalcocopyrite	pyrargyrite, tetrahedrite	quartz	barite	minor deposits mined in the past	Malý (2003)
7. Velké Meziříčí	Velké Meziříčí	Velké Meziříčí	Moldanubicum	durbachite (Třebíč Massif)	galena	sphalerite, pyrite, chalcocopyrite	tetrahedrite, ullmanite	calcite, ankerite	siderite	mineralogical occurrence	no studies
8. Ptáčov	Ptáčov	Ptáčov	Moldanubicum	durbachite (Třebíč Massif)	chalcocopyrite, galena			calcite, dolomite – ankerite		mineralogical occurrence	no studies
9. Jemnice	Jemnice	Jemnice	Moldanubicum	paragneiss, granulite	sphalerite, galena	chalcocopyrite, pyrite	tetrahedrite – freibergite, polybasite	quartz	calcite, dolomite – ankerite	minor deposits mined in the past	Houzar and Pošmurný (1991), Zimák and Šendová (1999)
10. Štěpánov nad Svratkou Ore District Malý and Dobeš (2001) distinguish two types of mineralization in the Štěpánov Ore District											
10.1. Pb-Zn(-Sb) type	Horní Čepí, Švařec, Koroužné	Švařec, Koroužné	Moravicum – Svratka Dome, Olešnická Group	paragneiss, micaschist, marble, quartzite	galena, sphalerite	chalcocopyrite	pyrite, antimonite, bournonite, tetrahedrite, freibergite, boulangerite, pyrargyrite	quartz	calcite, dolomite – ankerite	intermediate deposits mined in the past	Mál (1965), Malý and Dobeš (2001), Houzar and Malý (2002)
10.2. Cu-Pb(-Zn) type	Borovec	Borovec	Moravicum – Svratka Dome, Olešnická Group	paragneiss, micaschist, marble, quartzite	galena, chalcocopyrite	sphalerite	pyrite, tetrahedrite	quartz, barite	calcite	intermediate deposits mined in the past	Mál (1965), Malý and Dobeš (2001), Houzar and Malý (2002)

Table 1, continued

Locality – Ore district	Site examples	Sites studied	Regional-geo-logical unit	Host rock of the deposit	Ore minerals			Gangue minerals		Relative size of the deposit (occurrence)	Principal mineralogical and economic-geological studies
					major	minor	accessory	major	minor		
11. Rozseč nad Kunštátem	Rozseč nad Kunštátem	Rozseč nad Kunštátem	Moravicum – Svratka Dome, Olešnická Group	micascist, marble, paragneiss	sphalerite, galena	tetrahedrite, bournonite	chalcopryrite, pyrite, marcasite, arsenopyrite, boulangerite	quartz, dolomite – ankerite	calcite	minor deposits mined in the past	Šouba and Mál (1961), Málý (1999)
12. Štěchov-Lačnov	Štěchov-Lačnov	Štěchov-Lačnov	Moravicum – Svratka Dome, Olešnická Group	marble, micascist	sphalerite, galena	pyrite		ankerite – dolomite		minor deposits mined in the past	Málý (1999)
13. Horní Loučky	Horní Loučky	Horní Loučky	Moravicum – Svratka Dome, Olešnická Group	paragneiss, marble, micascist	sphalerite, galena	pyrite	arsenopyrite, marcasite	quartz	dolomite – ankerite, calcite	mineralogical occurrence	Hrazdil et al. (2003)
14. Tišnov area	Dřínová, Květnice, Dolní Loučky, Štěpánovice	Dřínová, Květnice, Dolní Loučky, Štěpánovice	Moravicum – Svratka Dome, (para-)autochthon unit	limestone, metagranitoid, quartzite	chalcopryrite, galena	pyrite	sphalerite, tetrahedrite, bravoite, gersdorffite	barite, calcite	quartz, fluorite	minor deposits mined in the past (barite)	Mál (1960), Dolníček (1999), Dolníček (2001), Dolníček and Málý (2003), Dolníček (2004)
15. Heroltice	Heroltice	Heroltice	Moravicum – Svratka Dome, (para-)autochthon unit	limestone	galena, sphalerite	chalcopryrite	tetrahedrite, hessite	quartz	dolomite – ankerite, calcite	minor deposits mined in the past	Češková and Orel (1971), Málý (2004)
16. Maršov-Javůrek area	Maršov	Maršov	Moravicum – Svratka Dome, Bílý potok Group	micascist, quartzite, limestone	chalcopryrite, galena	sphalerite, tetrahedrite, pyrite		quartz, barite	fluorite	minor deposits mined in the past	Mál (1963), Málý and Dobeš (2002)
17. Jasenice	Jasenice	Jasenice	Moravicum – Svratka Dome, Olešnická Group	marble, paragneiss, micascist	sphalerite, galena	tetrahedrite, chalcopryrite, pyrite, marcasite		quartz	barite, calcite, dolomite – ankerite	minor deposits mined in the past	Málý (2000)
18. Letovice	Letovice	Letovice	Letovice Crystalline Unit	serpentinite, amphibolite	galena, magnetite	chalcocite, chalcopryrite, covellite, sphalerite, bornite, pyrite, marcasite		dolomite		mineralogical occurrence	no studies

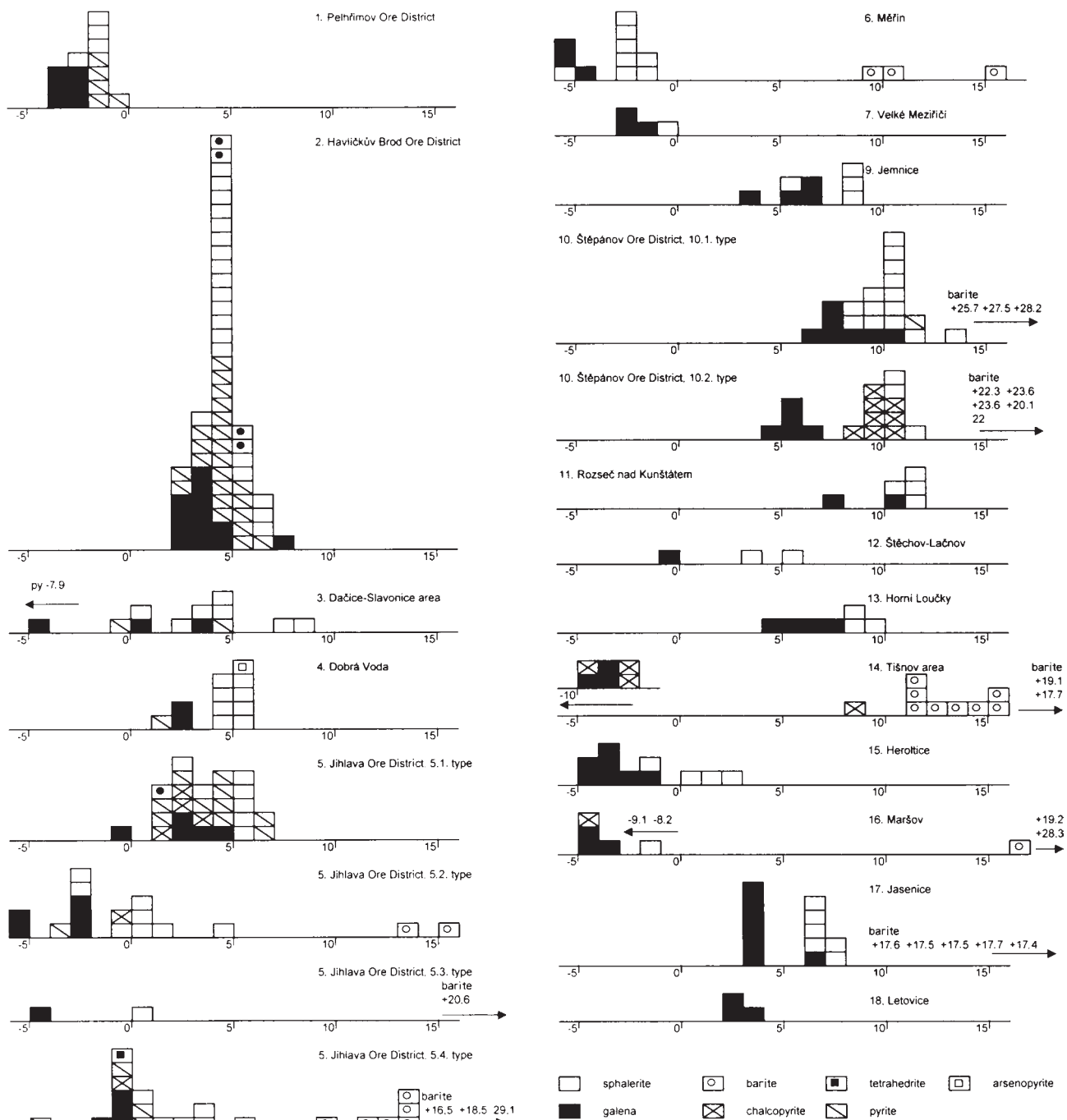


Figure 2. Isotope analyses of sulfur in sulfides and barite ($\delta^{34}\text{S}$ ‰, CDT).

5.3, 5.4, site 6 Měříň, site 10.1 Štěpánov Ore District, mineralization Pb-Zn(-Sb), and for site 17 Jasenice.

- The slow rate of isotope exchange reactions between sulfane and sulfate in the fluid at low temperatures (Ohmoto and Lasaga 1982), in which no isotopic equilibrium was established. This was probably the cause for sulfide-barite pair failure at all studied sites where barite is present.

Table 2 summarizes the geologically realistic temperatures of isotopic equilibria. These temperatures were calculated from average $\delta^{34}\text{S}$ values of sulfides at the given sites (outliers in $\delta^{34}\text{S}$ values were not included in the mean value

calculation). Where a thermometric pair was available from a single hand specimen, the results are listed (including the minerals used) – temperatures thus obtained can be considered more realistic.

Based on the results of sulfur isotope thermometry, the studied sites can be subdivided into three groups:

1. High-temperature ore occurrences and deposits (ca 350 to 450 °C). This group includes site 1, the Pelhřimov Ore District; site 2, the Havlíčkův Brod Ore District; site 4, Dobrá Voda; and site 5, Jihlava, mineralization 5.1. Temperatures markedly exceeding 500 °C were sometimes obtained by isotope thermometry: such values

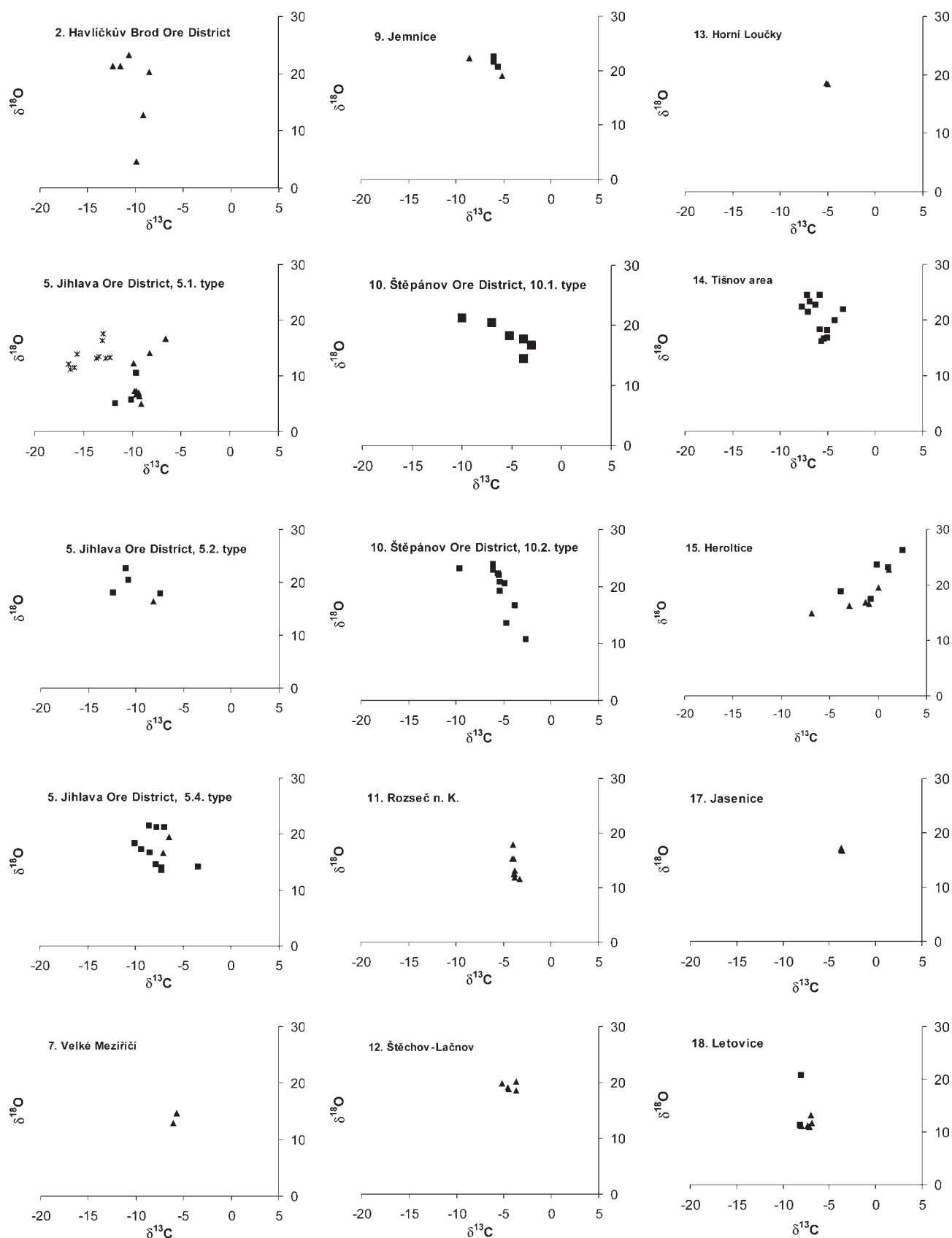


Figure 3. Isotope analyses of carbon and oxygen in carbonates ($\delta^{13}\text{C}$ ‰, PDB, $\delta^{18}\text{O}$ ‰ SMOW). ▲ – dolomite-ankerite-kutnohorite, ■ – calcite, * – siderite.

Table 2. Sulfur isotope thermometers

Locality		Temperature from one hand-specimen		Temperature from average $\delta^{34}\text{S}$ data	
		t (°C)	minerals	t (°C)	minerals
1. Pelhřimov Ore District	Nemojov	449	sf–ga	279	sf–ga
		463	py–ga	483	py–ga
		653	py–ga		
		411	py–ga		
2. Havlíčkův Brod Ore District	Česká Bělá	382	py–sf		
	Stříbrné Hory	542	sf–ga	382	sf–ga
	Utín	581	sf–ga	507	sf–ga
		529	py–ga	593	sf–py
				529	py–ga
	Pohled	593	py–sf		
	Dlouhá Ves			593	sf–py
	Bartoušov	441	sf–ga	581	sf–ga
		653	py–ga		
3. Dačice-Slavonice area		non-realistic temperature			
4. Dobrá Voda		402	sf–ga	317	sf–ga
5. Jihlava Ore District	5.1. black sphalerite $\pm$ sulphide $\pm$ carbonates	370–410	according Pluskal and Vosáhlo (1998)	507	sf–ga
	5.2. dark brown sphalerite $\pm$ barite $\pm$ carbonates	280–340	according Pluskal and Vosáhlo (1998)	184	sf–ga
	5.3. dark brown sphalerite + barite + fluorite	250	according Pluskal and Vosáhlo (1998)	171	sf–ga
	5.4. light brown sphalerite $\pm$ barite $\pm$ carbonates	230–260	according Pluskal and Vosáhlo (1998)	109	sf–ga
6. Měřín		257	sf–ga	303	sf–ga
7. Velké Meziříčí				364	sf–ga
8. Ptáčov	no data				
9. Jemnice				267	sf–ga
10. Štěpánov Ore District	10.1. Pb-Zn(-Sb)	247	sf–ga	303	sf–ga
				174	sf–py
				255	py–ga
	10.2. Cu-Pb(-Zn)			95	sf–ga
				96	sf–chp
				94	ch–ga
11. Rozseč nad Kunštátem		220	sf–ga	303	sf–ga
12. Štěchov-Lačnov				121	sf–ga
13. Horní Loučky				257	sf–ga
14. Tišnov area		non-realistic temperature			
15. Heroltice		205	sf–ga	165	sf–ga
16. Maršov-Javůrek area				113	sf–ga
17. Jasenice				197	sf–ga
18. Letovice	no data				

were considered irrelevant (this was especially the case of thermometric pairs with pyrite – see explanation above).

2. Mesothermal ore occurrences and deposits (ca 200–250 °C). This group includes site 5, Jihlava Ore District, mineralizations 5.3 and 5.4; site 6, Měřín; site 9, Jemnice; site 10, Štěpánov Ore District, mineralization

10.1. site 11, Rozseč nad Kunštátem; site 12, Štěchov-Lačnov; site 13, Horní Loučky; site 15, Heroltice; and site 17, Jasenice.

Where homogenization temperatures of fluid inclusions are available, they are consistent with the results obtained from isotope thermometry (Malý and Dobeš 2001, Malý 2003, Hrazdil et al. 2003).

3. Low-temperature ore occurrences and deposits (below ca 130 °C). This group includes site 10, Štěpánov Ore District, mineralization 10.2; site 14, Tišnov area; and site 16, Maršov. The results of isotope thermometry clearly show that the mineralization 10.2 of the Štěpánov Ore District occurred at low temperatures. No exact data could be obtained for site 14 Tišnov and site 16 Maršov. These conclusions are supported by the results of fluid inclusion studies (Malý and Dobeš 2002, Dolníček 1999).

Formation temperatures of ca 350 °C were indicated for site 5 Jihlava Ore District, mineralization 5.2, and site 7 Velké Meziříčí by isotope thermometry. With respect to the small amount of analytical data, however, these values should be considered preliminary.

Isotopic composition of source sulfur and its origin

Determination of the $\delta^{34}\text{S}$ value for sulfur of the hydrothermal fluid (the so-called source sulfur) is generally problematic, as it is generally impossible to determine the oxidized vs. reduced sulfur ratio in the fluid. The presence of pyrrhotite (stable), temperatures below 500 °C, and fluid pH values less than 6 seem to suggest the dominance of H_2S as a sulfur carrier in the fluid (isotopic composition of sulfides then corresponds to source sulfur). The simultaneous formation of pyrite and hematite is thought to indicate the prevalence of sulfate in the fluid, in which case the $\delta^{34}\text{S}$ values of sulfides may widely differ from those of the source sulfur.

The assumed formation conditions for the deposits studied, and the inferred $\delta^{34}\text{S}$ values of source sulfur, are summarized in Table 3.

In principle, the sulfur sources of hydrothermal fluids at the studied sites include the following:

1. Deep-seated sulfur with $\delta^{34}\text{S}$ values around 0 ‰.

This source of sulfur can be assumed only for site 7 (Velké Meziříčí) and site 15 (Heroltice). At the latter site, however, this interpretation is contrary to the following considerations: lead at this site is derived from upper crustal rocks (Vaněček et al. 1985); the source of carbon for hydrothermal fluids was strongly affected by the host limestone; and the salinity of the hydrothermal fluid is merely ca 6 wt.% NaCl equiv. (Malý 2004). The effect of fluids derived from a deep-seated source was therefore probably weak at this site, and the source of sulfur in the ambient rocks should be considered.

2. Sulfur derived from rocks in which the ore mineralization occurred.

Bernard and Žák (1992) reported 28 isotope analyses of accessory (stratiform) sulfides (pyrite, pyrrhotite) from rocks in the surroundings of the Moldanubian pluton. The values of $\delta^{34}\text{S}$ encompass a wide range from ca -15 ‰ CDT to +6 ‰ CDT; a prominent peak is, however, observed in the interval of ca 0 to +5 ‰ CDT. Sulfur of this isotopic composition could have posed a direct source for hydrothermal fluids at site 2 Havlíčkův Brod Ore District, site 4 Dobrá Voda, and site 5 Jihlava Ore District, mineralizations 5.1 and 5.3.

Six analyses of rock sulfur have been performed from different rocks and different regional-geological units of

the Svratka Dome of the Moravicum (Dolníček 2004, Malý – unpublished data). The $\delta^{34}\text{S}$ values range from +1.1 to +14.7 ‰ CDT, with most data concentrated in the interval of ca +5 to +10 ‰ CDT. Sulfur of this isotope composition could have posed a direct source for hydrothermal fluids at site 10 Štěpánov Ore District, site 11 Rozseč nad Kunštátem, site 12 Štěchov-Lačnov, site 13 Horní Loučky, and site 17 Jasenice.

Without the knowledge of $\delta^{34}\text{S}$ values of the rock types in the ambience of a specific ore occurrence, reference to the ambient rocks as a source of the sulfur is somewhat speculative. This category includes ore occurrences in the Moldanubicum with negative $\delta^{34}\text{S}$ values of source sulfur (i.e. site 1 Pelhřimov Ore District; site 5 Jihlava Ore District, mineralizations 5.2 and 5.4; site 6 Měřín) and sites with markedly positive $\delta^{34}\text{S}$ values of source sulfur (site 9 Jemnice, site 18 Letovice).

3. Permian-Triassic marine sulfate.

This source is believed to be responsible for the formation of barite-dominating Upper Permian–Lower Triassic (Dolníček et al. 2003) mineralizations in the Svratka Dome (Maršov and Tišnov sites). Barite $\delta^{34}\text{S}$ values are higher than those of the host rocks, precluding sulfur sources in the mobilized sulfur (i.e. oxidized to sulfate) derived from the host rocks because no significant isotopic fractionation occurs during pyrite oxidation (Bottrell et al. 2001). Nevertheless, we cannot exclude host rocks as a direct source of sulfur. Theoretically, the superimposed bacterial reduction of mobilized host rock sulfur may explain the observed $\delta^{34}\text{S}$ values, although temperatures above ~80 °C terminate the bacterial activity. Alternatively, most barite sulfur isotope data fall within the range reported for Permian-Triassic marine sulfate (Claypool et al. 1980). A marine evaporitic origin of the parent fluids may also be supported by other methods (high Br/Cl ratios in fluid inclusion leachates, oxygen isotope composition of the parent fluid; Dolníček 2004).

The values of $\delta^{34}\text{S}$ can be expected to vary depending on the host lithology at the sites where sulfur is believed to come from the ambient rocks. This trend is readily apparent: mineralizations hosted in metamorphic rocks (of the Olešnice Group of the Svratka Dome Moravicum) show positive $\delta^{34}\text{S}$ values (usually highly positive values) in all cases; mineralization 15 Heroltice (autochthonous part of the Svratka Dome of the Moravicum) is located in different rocks (limestones) and shows $\delta^{34}\text{S}$ values of around 0 ‰. Mineralizations hosted by Moldanubian metamorphic rocks show $\delta^{34}\text{S}$ values in the range of ca -3 to +3 ‰.

The idea of local material sources is also supported by lead isotope geochemistry (Table 4): mineralizations hosted by the same regional-geological (or lithological) unit have practically identical lead isotope compositions. No correlation is visible between the lead isotope composition and other properties of the mineralizations (formation temperature, $\delta^{34}\text{S}$ values, presumed mineralization ages). This is well documented by mineralizations in the Moravicum: lead at all of the studied sites (meso- and epithermal) is markedly enriched in radiogenic isotopes compared to other sites.

Table 3. $\delta^{34}\text{S}$ value of source sulfur (‰, CDT)

Locality		t (°C)	$\text{H}_2\text{S}/\text{SO}_4^{2-}$ ratio	$\delta^{34}\text{S}_{\text{SS}}$
1. Pelhřimov Ore District	Nemojov	400–500	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	–1 to –2
2. Havlíčkův Brod Ore District	Česká Bělá	400–450	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+3 to +5
	Stříbrné Hory	450–500	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+3 to +5
	Utín	450–550	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+4 to +5
	Pohled	about 500	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+4 to +5
	Dlouhá Ves	450–550	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+3 to +4
	Bartoušov	450–550	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+4 to +5
3. Dačice-Slavonice area		160–200*	probably extremely variable Eh	?
4. Dobrá Voda		400–450	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+4 to +5
5. Jihlava Ore District	5.1. black sphalerite $\pm$ sulphide $\pm$ carbonates	350–450	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+3 to +5
	5.2. dark brown sphalerite $\pm$ barite $\pm$ carbonates	250–350	variable $\text{H}_2\text{S} > \text{SO}_4^{2-}$	0 to –3
	5.3. dark brown sphalerite + barite + fluorite	about 250	variable $\text{H}_2\text{S} > \text{SO}_4^{2-}$	+1 to +3
	5.4. light brown sphalerite $\pm$ barite $\pm$ carbonates	about 250	variable $\text{H}_2\text{S} > \text{SO}_4^{2-}$	0 to –3
6. Měřín		about 250	variable $\text{H}_2\text{S} > \text{SO}_4^{2-}$	–3 to –4
7. Velké Meziříčí		350 ?	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	about 0
8. Ptáčov	no data			
9. Jemnice		about 250	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+7 to +8
10. Štěpánov Ore District	10.1. Pb-Zn(-Sb)	about 250	variable $\text{H}_2\text{S} > \text{SO}_4^{2-}$	+8 to +10
	10.2. Cu-Pb(-Zn)	100–150	variable $\text{H}_2\text{S} > \text{SO}_4^{2-}$	+9 to +10 (main mineralization stage)
11. Rozseč nad Kunštátem		200–250	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+10 to +12
12. Štěchov-Lačnov		200–250 ?	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+2 to +4
13. Horní Loučky		about 250	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+8 to +9
14. Tišnov area		80–120**	variable $\text{H}_2\text{S} > \text{SO}_4^{2-}$ $\text{SO}_4^{2-} > \text{H}_2\text{S}$	–8 sulfane, +11 to +14 sulphate
15. Heroltice		200–250	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+1 to –1
16. Maršov-Javůrek area		up to 130	variable $\text{H}_2\text{S} > \text{SO}_4^{2-}$ $\text{SO}_4^{2-} > \text{H}_2\text{S}$	–1 to –6 sulfane
17. Jasenice		200–250	variable $\text{H}_2\text{S} > \text{SO}_4^{2-}$	+6 to +7
18. Letovice		200–250*	$\text{H}_2\text{S} > \text{SO}_4^{2-}$	+5 to +6

* according Th of fluid inclusion (Dobeš, Malý – unpublished data)

** according Th of fluid inclusion (Dolníček 1999)

Carbon isotopes in carbonates

In common hydrothermal fluids, H_2CO_3 and HCO_3^- are the main carriers of oxidized carbon to be considered in isotope studies of carbonates. At temperatures above 100 °C, the main carrier of carbon is H_2CO_3 (Ohmoto 1986).

If temperatures used in the study of isotope geochemistry of sulfur are considered for the origin of carbonates (see above), the sites studied here can be divided into three groups based on the calculated $\delta^{13}\text{C}$ values of fluids:

1. At a majority of the sites, the values of source $\delta^{13}\text{C}$ fall within the range typical of the homogenized carbon of Earth crust, or deep-seated carbon (ca –5 to –8 ‰ CDT).
2. Some sites falling within this range show a trend towards more negative $\delta^{13}\text{C}$ values of source carbon.

Such a trend can be interpreted as showing the more prominent involvement of organic carbon in the hydrothermal process. This applies to site 2 Havlíčkův Brod Ore District and site 5 Jihlava Ore District, mineralization 5.1 and 5.2.

3. In contrast, some sites show a shift towards more positive $\delta^{13}\text{C}$ values of source carbon: site 12 (Štěchov-Lačnov), site 15 (Heroltice), site 17 (Jasenice), and to a lesser degree also site 14 (Tišnov area). This trend can be interpreted as the involvement of carbon from the marbles and limestones that hosted the hydrothermal mineralization process. Alternatively, the decrease of crystallization temperature also increases the $\delta^{13}\text{C}$ values of younger carbonates (site 14, Tišnov area).

Table 4. Isotope composition of sulfur and lead (data for lead after Vaněček et al. 1985)

Locality		Pb isotope ratios			
		$\delta^{34}\text{S}_{\text{SS}}\text{‰}$, CDT	206/204	207/204	208/204
1. Pelhřim Ore District		−1 to −2	18.16	15.59	38.36
2. Havlíčkův Brod Ore District	Stříbrné Hory	+3 to +5	18.12	15.59	38.12
	Bartoušov	+4 to +5	18.14	15.61	38.25
3. Dačice-Slavonice area		?	18.11	15.65	38.29
5. Jihlava Ore District	5.1. black sphalerite ± sulphide ± carbonates	+3 to +5	18.17	15.59	38.18
	5.2. dark brown sphalerite ± barite ± carbonates	0 to −3	18.22	15.65	38.34
	5.3. dark brown sphalerite + barite + fluorite	+1 to +3	18.11	15.52	38.25
	5.4. light brown sphalerite ± barite ± carbonates	0 to −3	18.15	15.59	38.21
10. Štěpánov Ore District	10.1. Pb-Zn(-Sb)	+8 to +10	18.81	15.64	38.57
			18.76	15.68	38.70
			18.74	15.59	38.42
	10.2. Cu-Pb(-Zn)	+9 to +10	18.99	15.76	38.66
11. Rozseč nad Kunštátem		+10 to +12	18.82	15.77	38.61
12. Štěchov-Lačnov		+2 to +4	18.35	15.58	38.34
			19.02	15.82	38.80
14. Tišnov area*	Květnice	−8 (H ₂ S)	18.55	15.64	38.29
15. Heroltice		+1 to −1	18.78	15.60	38.37
16. Maršov-Javůrek area		−1 to −6 (H ₂ S)	18.78	15.76	38.66
			18.90	15.82	38.91
			18.69	15.64	38.60

* Dolníček and Slobodník – unpublished data

Oxygen isotopes in carbonates

Provided that the temperatures used in the study of isotope geochemistry of sulfur, and the temperatures obtained from the study of Th from fluid inclusions in carbonates (see above), are considered for the origin of carbonates, approximate $\delta^{18}\text{O}$ values for the water of the hydrothermal fluids can be determined. These values allow the division of the studied sites into two groups:

1. Most sites show high $\delta^{18}\text{O}$ values for the water of the hydrothermal fluid, from ca +4 to +10 (even higher values can be presumed in some cases). These values are typical for fluids subjected to isotopic equilibration with the host rock at high temperatures.
2. At some sites, the number of analyzed samples, and the knowledge of their paragenetic position, permitted a more detailed isotope study. It revealed that water with lower $\delta^{18}\text{O}$ values was involved in the hydrothermal process during final stages of mineralization. This was the case at site 5 (Jihlava, mineralization 5.1), site 10 (Štěpánov Ore District, mineralization 10.2), and site 11 (Rozseč nad Kunštátem). Such a trend can be explained by the involvement of water of a different type in the system (probably water of meteoritic or marine origin).

At site 14 (Tišnov area), $\delta^{18}\text{O}$ values of water in hydrothermal fluids focus around 0 ‰ (± 3 ‰) SMOW. This in-

dicates a prevalence of (i) marine water, (ii) meteoric water (with possible O-exchange with the rock environment at relatively low temperatures), or (iii) a mixture of waters of different origins in the hydrothermal system. The proportion of meteoritic water was increasing during the final stages of mineralization: −5 to −1 ‰ SMOW (Dolníček 2004).

Conclusion

Based on our interpretation of the obtained isotope data, the studied sites can be divided into three types:

1. High-temperature mineralization (ca 400–500 °C, depending on isotope thermometer) with source sulfur having $\delta^{34}\text{S}$ values mostly between +3 and +5 ‰ (with the exception of site 1 Pelhřimov Ore District). As suggested by mineralogical, isotopic, and geochemical data, the hydrothermal fluids were characterized by a marked dominance of sulfane over sulfate (more reducing environment). Analytical data indicate (at some sites) an increase in oxygen fugacity in the final stages of the mineralization process. The source of sulfur is believed to have been the metamorphic rocks, or possibly the granitic rocks, of the Moldanubicum. The values of $\delta^{18}\text{O}$ in carbonates of the main mineralization stage are high (due to high-temperature isotope exchange reactions with oxygenated host-rock miner-

als); the low $\delta^{13}\text{C}$ values indicate the involvement of carbon of organic origin in the hydrothermal process.

This group includes the following sites:

1. Pelhřimov Ore District
2. Havlíčkův Brod Ore District
4. Dobrá Voda
5. Jihlava Ore District, mineralization 5.1

This type of mineralization fits the characteristics of the Kutná Hora type Lower Permian Fe-Zn-Pb-Ag vein mineralization in the sense of Bernard and Žák (1992), as well as the mineralization of the “kb+eb Erzformation” type (Baumann 1958) or “k-pol” type (Bernard 1991). Bernard and Žák (1992) suggest that this mineralization has temporal and genetic relationships to middle Variscan metamorphism and magmatism.

2. Mesothermal mineralization (200–350 °C, based on isotope thermometry). The values of $\delta^{34}\text{S}_{\text{SS}}$ are either markedly positive (max. +8 to +10 ‰ CDT) or lie within the range of ca –3 to +3 ‰ CDT. The sulfur source can be expected in rocks surrounding the ore occurrences (this fact has been confirmed at some sites and is presumed at others). Hydrothermal fluids were more oxidative than those of the preceding mineralization type; their oxidative character usually became even more distinct during the final stages of mineral formation. Waters of hydrothermal fluids generally show $\delta^{18}\text{O}$ values higher than 5 ‰ SMOW (due to isotope exchange reactions with oxygenated host-rock minerals). The involvement of water with low $\delta^{18}\text{O}$ values in the final stages of the mineralization process was documented in some cases (probably meteoritic or marine water). The values of $\delta^{13}\text{C}$ correspond either to homogenized carbon of the Earth’s crust or its mixture with carbon from marbles/limestones (at sites where ores are hosted by these lithologies).

This group includes the following sites:

3. Dačice-Slavonice area
5. Jihlava Ore District, mineralizations 5.2, 5.3 and 5.4
6. Měříň
7. Velké Meziříčí
8. Ptáčov
9. Jemnice
10. Štěpánov Ore District, mineralization 10.1
11. Rozseč nad Kunštátem
12. Štěchov-Lačnov
13. Horní Loučky
17. Jasenice
18. Letovice

In some parameters, the mineralizations correspond to, for example, the “Lower Permian Pb-Zn-Cu-Ag veins: Ratibořské Hory type” in the sense of Bernard and Žák (1992) or to the “pol” mineralizations *sensu* Bernard (1991). It is, however, very probable that mineralizations of this group were in fact formed due to different processes and are of different ages. The establishment of this group cannot therefore be considered as genetic.

While the genesis of some sites is fairly constrained, that of others remains uncertain. Mineralization in the Svratka Dome of the Moravicum (site 10 Štěpánov Ore

District, site 11 Rozseč nad Kunštátem, site 12 Štěchov-Lačnov, site 13 Horní Loučky, and site 17 Jasenice) are traditionally genetically linked to the final stages of Variscan metamorphism (Malý and Dobeš 2001). Mineralization in the Třebíč Massif and its envelope (site 6 Měříň, site 7 Velké Meziříčí, and site 8 Ptáčov) is probably genetically linked with local tectonic structures such as the Třebíč and Sázava Faults (cf. Chmelař 1986).

3. Low-temperature mineralization (below 130 °C). The $\delta^{34}\text{S}$ values of sulfane in the hydrothermal fluid were markedly negative, while those of sulfate range from ca +11 to +14 ‰ CDT. Sulfane was introduced from an external source by migrating fluids or was formed in lower-temperature areas of the hydrothermal system by the process of bacterial sulfate reduction. The sulfate sulfur may have been sourced from the host rocks or from the sulfate of the marine water (the stable isotope signature of which may be locally modified by other processes and sources). Carbon in the fluids has $\delta^{13}\text{C}$ values most commonly in the range of –6 to –11 ‰ PDB, which indicates the prevalence of “deep-seated” or homogenized crustal carbon (with limited effects of carbon from the host limestone, and local effects of carbon from oxidized organic matter from the ambient metasediments or possibly hydrocarbons of the hydrothermal fluid). Water of the hydrothermal fluid most commonly shows values around 0 ‰ SMOW. This may indicate a prevalence of marine water in the hydrothermal system. Although this interpretation is not the only possible one, it may be further supported by independent results (Br/Cl in fluid inclusion leachates; Dolníček 2004). Significant changes in redox conditions occurred in the course of the mineralization process.

This group includes the following sites:

14. Tišnov area
16. Maršov

In its parameters, the mineralization perfectly corresponds to the “fba” association *sensu* Bernard (1991). Its genesis can be linked with hypersaline fluids of primarily marine origin. The age of the mineralization has been established as the Late Permian to Early Triassic at site 14 (Tišnov area; Dolníček et al. 2003).

A distinct position is occupied by the mineralization at site 10 Štěpánov Ore District, mineralization 10.2. It is clearly a low-temperature occurrence, but fully corresponds to the mineralizations of group 2 in other aspects.

The definitions of group 1 (high-temperature) and group 3 (low-temperature) are quite certain: their features are characteristic enough to make them distinct genetic types.

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