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Hydrothermal mineralisation of the Tatric Superunit (Western Carpathians, Slovakia): I. A review of mineralogical, thermometry and isotope data

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Abstract: The Tatric Superunit of the Western Carpathians hosts many ore deposits and occurrences. Inspection of innumerable surface and underground outcrops, drill cores, and hand specimens in the past allowed to distinguish these mineralisation stages, ordered from the oldest to the youngest ones: molybdenite, scheelite, arsenopyrite–pyrite–gold, stibnite–sphalerite–Pb–Sb-sulfosalts, dolomite–baryte–tetrahedrite, siderite–ankerite, quartz–tourmaline, quartz–Cu-sulfide, galena–sphalerite, baryte, and hematite stages. This work gives a detailed account of the mineralogy, fluids, depth of formation, and stable isotope signatures of these stages, based on the extensive published and unpublished literature. The early molybdenite, scheelite, and arsenopyrite–pyrite–gold stages contain fluid inclusions with low-salinity (0–10 wt. % NaCl eq.), CO_2-rich aqueous fluids. The homogenisation temperatures (TH) are 300–350 °C, in agreement with the results of arsenopyrite and chlorite geothermometry. Estimated formation depth is down to 12 km and stable isotopes ($\delta^{18}O$, δD) suggest a metamorphic source of the fluids and the genetic association with orogenic gold deposits. The voluminous stibnite–sphalerite–Pb–Sb-sulfosalts stage originated from aqueous fluids (with NaCl–KCl, below halite saturation), with traces or without CO_2, and TH of 105–170 °C. This stage was concluded with precipitation of senarmontite, kermesite or other oxygen-bearing ores, suggesting increase of oxygen fugacity in the terminal phases of ore precipitation, and perhaps an influx of meteoric water. The rich assemblages of Sb minerals at the deposits in the Malé Karpaty Mts. allows to trace the evolution of the hydrothermal systems in the fO_2–fS_2–T space. The calculated $\delta^{18}O_{fluid}$ values for the siderite–ankerite stage may correspond to marine or formation waters influenced by the isotopic exchange with high-grade metamorphic rocks. The siderite–ankerite, galena–sphalerite and dolomite–baryte–tetrahedrite stages are related to NaCl–$CaCl_2$ fluids, often supersatured with respect to halite at room temperature. Some fluid inclusions showed higher TH (230–290 °C), confirmed also by myrmekitic breakdown of meneghinite. Later fluids with TH of 120–170 °C were recorded at many localities of these stages.

Keywords: Mineralisation stages, sulfosalts, fluid inclusions, stable isotopes.

Introduction

Central Western Carpathians (CWC) host innumerable hydrothermal, metasomatic, and volcano-exhalative ore mineralisations, mined from prehistoric times until 1990s. CWC are a central segment of the Alpine–Carpathian mobile belt between stable North European Platform and drifting continental fragments correlated with Apulia and Adria (Plašienka et al. 1997). Variscan basement of CWC is divided into the Tatric, Veporic, and Gemeric Superunits, all of them with Alpine sedimentary cover in autochthonous or allochthonous position (Fig. 1). Age and fluid sources for the hydrothermal mineralisations in the Tatric Superunit are not constrained so well in spite of extensive mineralogical and geochemical investigations. The large amount of information summarised by Chovan et al. (1995a, 1996, 1998b) from Nízke Tatry Mts. (Fig. 2a) resulted in a provisional genetic model outlined in an unpublished report (Chovan et al. 2006). Similarly, the knowledge on Sb–Au ores of the Malé Karpaty Mts. (Fig. 2b) amassed over the second half of the 20th century has been summarised by Chovan et al. (1992). Compared to these two regions, information on metallic ore deposits from other parts of the Tatric Superunit is inconsistent. Geological cross-sections, profiles and documentation pertaining to the period before 1989 have been published by Chovan et al. (1994a, 1996) and Grecula et al. (1996). Owing to additional analytical data obtained in this area after 2006, there is a need to summarize the scattered data and to develop a new model of hydrothermal ore generation.

This paper aims to summarize information gained from mineralogical, fluid inclusion microthermometric, and stable isotope data on ores and associated gangue minerals from hydrothermal mineralisations of the Tatric Superunit. Only in a few cases, additional information is brought for comparison for similar ores from the Veporic Superunit from localities adjacent to the Tatric basement. The accompanying paper (Majzlan et al. 2020) presents new geochronological data for the ore mineralisations of the Tatric Superunit. Both papers distinguish mineralisation stages, as defined by Chovan et al.

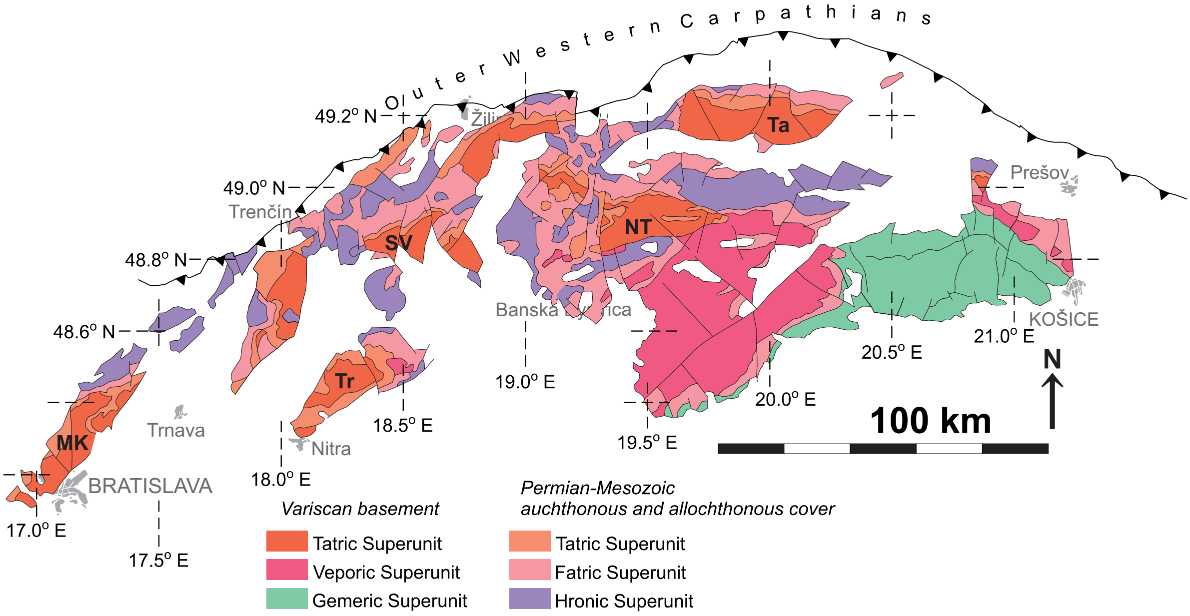


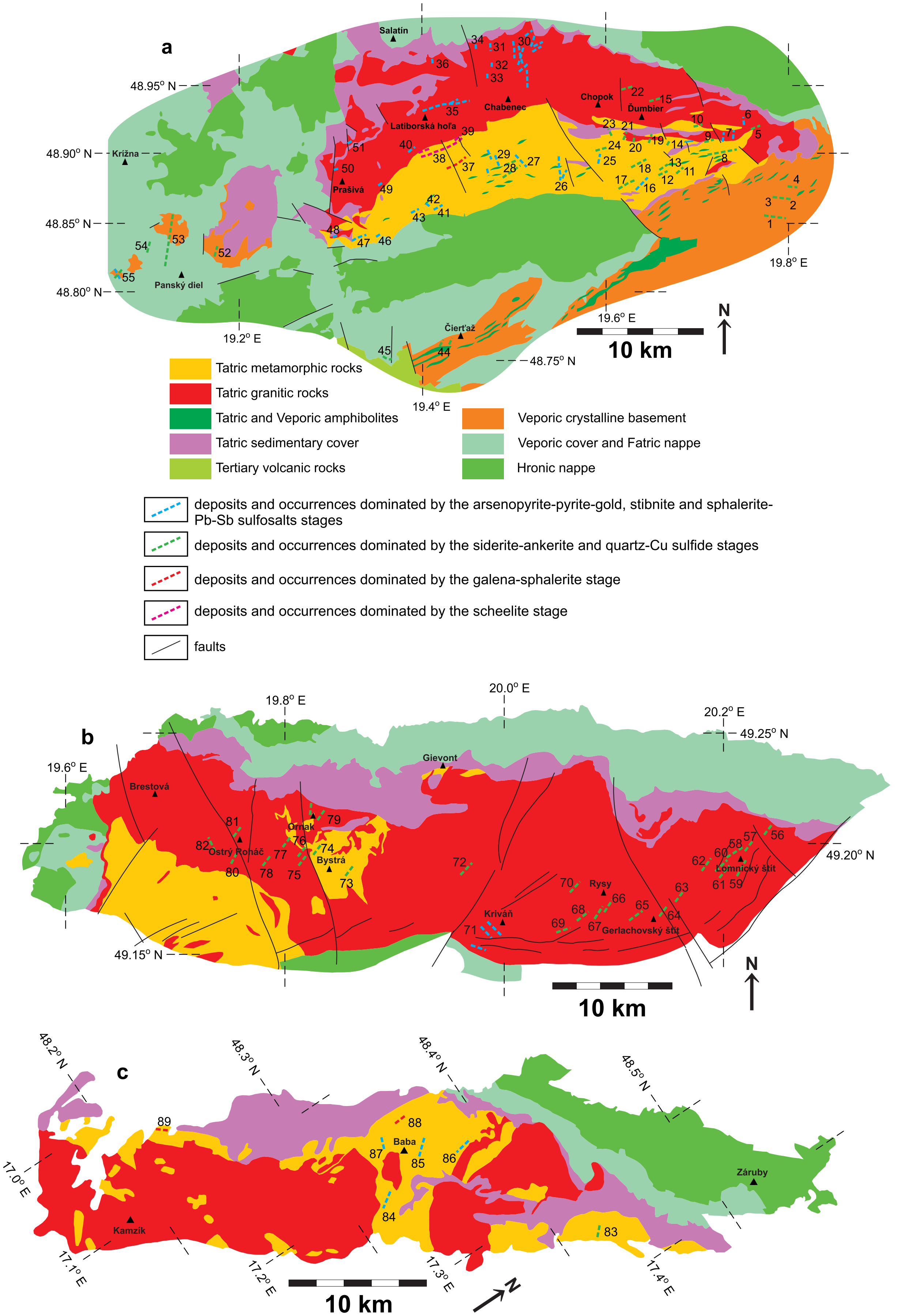
Fig. 1. A geological sketch of the superunits (marked in italics) of the Central Western Carpathians (simplified after Lexa et al. 2000) and parts of their sedimentary cover, with the position of larger cities in Slovakia. The Tatric Superunit is split into the Variscan cores (igneous and metamorphic rocks, red) and autochthonous cover (unmetamorphosed sediments, orange). The Variscan cores of mountain ranges mentioned in this paper are labelled as follows: Ta — Tatry Mts., NT — Nízke Tatry Mts., SV — Strážovské vrchy Mts., Tr — Tríbeč Mts., MK — Malé Karpaty Mts. Detailed geological maps of Nízke Tatry, Tatry, and Malé Karpaty Mts. with the ore deposits and occurrences are shown in Fig. 2a–c.

(1994a, p. 8), primarily on the basis of their mineral content. This work compiles and recaps mineralogy, fluid inclusion and stable isotope data for each stage, and the accompanying paper assigns an age or an age range to these stages.

Brief geological setting

The earliest geochronologic record in the Tatric and Veporic basement rocks is preserved in cores of zircon crystals that carry the evidence of the Cadomian or earlier magmatic activity (e.g., Kohút et al. 2008; Putiš et al. 2008). These authors also reviewed other studies that point to the presence of pre-Cambrian or Early Paleozoic rocks in CWC. However, the majority of the CWC basement complexes were created during the Variscan orogenic cycle. In a tectono-stratigraphic sense, one of the lowermost segments of the CWC basement corresponds to the metamorphosed leptyno-amphibolite complex (LAC, Hovorka & Méres 1993), whose diagnostic feature is tonalitic and leuco-tonalitic layers alternating with gabbroic and gabbrodioritic cumulate layers. Other rare rock types involved in the LAC are garnet–clinopyroxene amphibolite (thought to represent relics of eclogites and granulites), antigorite serpentinite, garnet–kyanite orthogneiss, and paragneiss.

Fig. 2. Geological maps, ore deposits and occurrences in: **a** — Nízke Tatry Mts. (geological map simplified after Biely et al. 1992); **b** — Tatry Mts. (geological map simplified after Nemčok et al. 1994); **c** — Malé Karpaty Mts. (geological map simplified after Ivan & Méres 2006 and Polák et al. 2011). Locations of ore mineralisations after Chovan et al. (1996), Pršek & Chovan (2001), Bakos (2003), Ozdín (2003), Bakos & Chovan (2006), and Chovan (unpublished data).
Localities in the Nízke Tatry Mts.: 1: Bacúch-Biela Skala, 2: Bacúch-Jánov Grúň, 3: Bacúch-Krškova dolina, 4: Bacúch-Sokolova dolina, 5: Vyšná Boca-Fišiarka, 6: Nižná Boca, 7: Vyšná Boca-Chopec, 8: Vyšná Boca-Kliesňava, 9: Stará Boca-Pod Ištván, 10: Bruchatý Grúnik, 11: Jarabá-Trojička, 12: Jarabá-Koleso, 13: Jarabá-Malý Gápeľ, 14: Králička-Mária, 15: Ludárova hoľa, 16: Mlynná dolina-Valachovo, 17: Mlynná dolina-Hviezda, 18: Mlynná dolina-Fe, 19: Mlynná dolina-Kačské, 20: Raktár, 21: Zadné Komôrky, 22: Demänovka, 23: Trangoška, 24: Standiarka, 25: Bystrianka, 26: Lom, 27: Dve Vody, 28: Dve Vody-Ždiar, 29: Lomnistá-Studená dolina, 30: Dúbrava, 31: Kľačianka, 32: Krámec, 33: Veľké Oružné, 34: Rišianka, 35: Magurka, 36: Malé Železné, 37: Soviansko, 38: Kyslá, 39: Jasenie-Špíglová dolina, 40: Husárka, 41: Jasenie-Suchá dolina, 42: Jasenie-Suchý potok, 43: Seče, 44: Svätodušná, Kolba, 45: Podlipa, 46: Javorinka, 47: Medzibrod, 48: Hiadeľ, 49: Ramžené, 50: Korytnica, 51: Liptovská Lúžna-Banské, 52: Baláže, 53: Špania Dolina, Piesky, Richtárová, 54: Polkanová, 55: Harmanec.
Localities in the Tatry Mts.: 56: Biele plesá, 57: Medená kotlina, 58: Baranie Sedlo, 59: Murárikova rokľa, 60: Sedielko, 61: Priečne sedlo, 62: Javorová škára, 63: sedlo Prielom, 64: Svišťovky, Široká, 65: Zlomisková štrbina, 66: Dračia hlava-Vysoká, 67: Popradský hrebeň, 68: Mengusovská dolina, 69: Predná bašta-Satan, 70: Mengusovské sedlo, 71: Kriváň, 72: Krajný Holý vrch, 73: Kamenistá dolina, 74: Klin-Gáborovo sedlo, 75: Račkove plesá, 76: Račkovo sedlo, 77: Končistá-Hrubý vrch, 78: Jamnícka dolina, 79: Ornak, 80: Žiarske sedlo, 81: Jamnícke sedlo-hrebeň Volovca, 82: hrebeň Plačlivého-Smutné sedlo.
Localities in the Malé Karpaty Mts.: 83: Častá, 84: Kolársky vrch, 85: Trojárová, 86: Kuchyňa, 87: Turecký vrch, 88: Pod Babou, 89: Marianka.


a
Salatín
Chabenec
Chopok
Ďumbier
Latiborská hoľa
Prašivá
Krížna
Panský diel
Čierťaž
48.95° N
48.90° N
48.85° N
48.80° N
48.75° N
19.2° E
19.4° E
19.6° E
19.8° E
10 km
N
Tatric metamorphic rocks
Tatric granitic rocks
Tatric and Veporic amphibolites
Tatric sedimentary cover
Tertiary volcanic rocks
Veporic crystalline basement
Veporic cover and Fatric nappe
Hronic nappe
deposits and occurrences dominated by the arsenopyrite-pyrite-gold, stibnite and sphalerite-Pb-Sb sulfosalts stages
deposits and occurrences dominated by the siderite-ankerite and quartz-Cu sulfide stages
deposits and occurrences dominated by the galena-sphalerite stage
deposits and occurrences dominated by the scheelite stage
faults
b
Brestová
Giewont
Ostrý Roháč
Osobitá
Bystrá
Kriváň
Rysy
Gerlachovský štít
Lomnický štít
19.6° E
19.8° E
20.0° E
20.2° E
49.25° N
49.20° N
49.15° N
10 km
N
c
Baba
Kamzík
Záruby
48.2° N
48.3° N
48.4° N
48.5° N
17.0° E
17.1° E
17.2° E
17.3° E
17.4° E
10 km
N

U–Pb dating returned a Cambrian–Ordovician (508–450 Ma) age of the layered amphibolites in the Tatric and Veporic Superunits (Putiš et al. 2008). Janák et al. (1993) determined peak metamorphic conditions at 700–750 °C and 1.0–1.4 GPa and interpreted these rocks as recrystallised members of the lower continental crust.

The Variscan orogeny generated also voluminous igneous rocks, mostly of granitoid composition. The Devonian S-type granites (380–400 Ma, Petrík & Kohút 1997; Putiš et al. 2003) were deformed to orthogneisses in a ductile regime during the peak igneous–metamorphic Variscan activity at ≈340 Ma. The Early Carboniferous crustal thickening produced abundant peraluminous, water-unsaturated, syn-collisional S-type granites (350–330 Ma) in reducing conditions. A Late Carboniferous thermal event is responsible for the generation and emplacement of metaluminous I-type granites (310–300 Ma) in oxidizing conditions with slightly higher water content but still water-unsaturated (Petrík & Kohút 1997). The emplacement of the granitic rocks coincidental with high-grade metamorphism resulted in the generation of large migmatite complexes (e.g., in Nízke Tatry Mts.). Small granite bodies, such as the Králička granite, may have been produced by *in situ* melting of surrounding metamorphic rocks (Dupej & Siegl 1984). Permian rifting generated large granite bodies in the Gemeric Superunit (e.g., Broska & Kubiš 2018) and dykes of basalts and lamprophyres in the Tatric Superunit (e.g., Pelech et al. 2017; Spišiak et al. 2018).

Beside the Gemeric Superunit, low-grade metamorphic rocks also occasionally occur in the Variscan basement of the Tatric Superunit. They are relatively abundant in the Malé Karpaty Mts. (e.g., Ivan & Méres 2006). Their intrusive contact with Variscan granites has been known for a long time. The low-grade basement comprises metabasic rocks, phyllites, and black shales, locally with disseminated pyrite grading into small pyrite-rich bodies. A large fraction of the metabasic rocks corresponds to an incomplete metamorphosed ophiolite suite. Most of the metapelitic rocks together with the associated sparse metabasalts and black shales represent a rift basin infilling (Ivan & Méres 2006), although Putiš et al. (2004) interpreted the entire sequence as a suture zone with a complicated Variscan nappe structure. Rocks of similar affinity were also found as small bodies, albeit with a higher metamorphic overprint, in the Strážovské vrchy Mts. (Ivan & Méres 2015). Low-grade metamorphic rocks, black shales for instance, also occur in the Nízke Tatry Mts. near the Medzibrod village, but their origin, either sedimentary–metamorphic (Molák 1998) or retrograde metamorphic (Pitoňák & Spišiak 1989) was not conclusively resolved. Phyllites of Klinisko are another enigmatic body whose origin remains unclear (e.g., Michálek 1998). These low-grade metamorphic rocks are of a scientific interest as possible sources of metals. In some cases, the contact between the high- and low-grade metamorphic rocks is penetrated by ore veins. Hence, these rocks could provide constraints on the timing and genesis of the ore mineralisations.

Magmatic cooling of the Variscan rocks is documented by ^{40}Ar/^{39}Ar ages of biotite (e.g., Janák 1994). Exhumation is evidenced by fragments of these rocks in the Triassic clastic sediments, and by the direct sedimentation of the siliciclastic sediments onto the granitic rocks. A detailed analysis of the metamorphic, exhumation and cooling history of the Variscan basement of the Západné Tatry Mts. was published by Moussallam et al. (2012). It remains to be clarified to what extent these data apply to other Tatric segments within the CWC.

A Permian rifting event followed the main phase of the Variscan orogeny at around 260–280 Ma (Plašienka et al. 1999; Finger et al. 2003). During most of the Mesozoic, the CWC experienced extensive sedimentation of carbonate and siliciclastic rocks. Thick packets of these sediments were thrusted over the Variscan basement and the autochthonous sedimentary cover during the Alpine shortening in the Late Cretaceous orogenesis (Plašienka 2018) accompanied by a metamorphic reworking. The degree of Alpine metamorphic overprint of the Tatric basement is still a matter of discussion. Some authors concluded that the overprint was very weak (e.g., Plašienka 2003), others argued for a stronger reworking (e.g., Anczkiewicz et al. 2015). The metamorphic reworking of the Veporic Superunit dated to ≈140 Ma and 105–110 Ma (Maluski et al. 1993) was undoubtedly stronger. Exhumation of the Variscan segments began earlier in the inner parts of CWC, e.g. in the Veporic Superunit (Plašienka et al. 1999; Janák et al. 2001; Vojtko et al. 2017), and propagated toward the former plate boundary, being the youngest in the Tatry and Považský Inovec Mts. (Anczkiewicz et al. 2015). The comprehensive tectonic model of Plašienka (2018) summarizes most of the existing data and recognizes a set of episodic tectonic events which shaped the today's complicated geological structure of CWC.

Stages of hydrothermal mineralisation

Mineralogical research since the late 1940s until today provided a wealth of information that can be used to distinguish mineral stages of hydrothermal mineralisations in the Tatric Superunit. The definition of a stage is adopted from Chovan et al. (1994a, p. 8) and further expanded and compared to other terms in the supplementary electronic information. The primary criterion for the distinction of the stages is their mineral content. The stages differ only little from those proposed by Slavkay & Chovan (1996), who labelled them according to the most abundant ore minerals. Gangue minerals are most commonly quartz and carbonates, but they are usually not specified in the stage name. The only exceptions are two stages with dominant Cu sulfides, which were named 'quartz–Cu-sulfide' and 'dolomite–baryte–tetrahedrite' to clearly distinguish them from each other. The 'quartz–tourmaline' stage does not contain ore minerals; it is commonly referred to in the Slovak literature as the 'Alpine-type veins'. The term 'quartz–tourmaline' was given preference in order to maintain compatibility with the stage names proposed for the Gemeric Superunit (Rojkovič 1985; Hurai et al. 2008). The mineralisation stages arranged consecutively from the presumably oldest to the youngest ones, are listed as follows:

- molybdenite,
- scheelite,
- arsenopyrite–pyrite–gold,
- stibnite–sphalerite–Pb–Sb-sulfosalts,
- dolomite–baryte–tetrahedrite,
- siderite–ankerite,
- quartz–tourmaline,
- quartz–Cu-sulfide,
- galena–sphalerite,
- baryte,
- hematite.

The relative timing of the listed stages is based on the macroscopic (outcrop scale, hand specimens, Fig. 3) and microscopic evidence. Although details on temporal relationships of minerals within the individual stages may be a subject of discussion, general features of the relative timing presented here seem to be recognised and corroborated in a number of studies.

The relative timing of stages is exemplified by mineral precipitation sequences established for large, mineralogically variable deposits in the studied region (Figs. 4–7). The Sb–Au deposit of Dúbrava, the best-studied deposit among those considered hereafter, contains prominent examples of molybdenite, scheelite, arsenopyrite–pyrite–gold, stibnite–sphalerite–Pb–Sb-sulfosalts, dolomite–baryte–tetrahedrite,

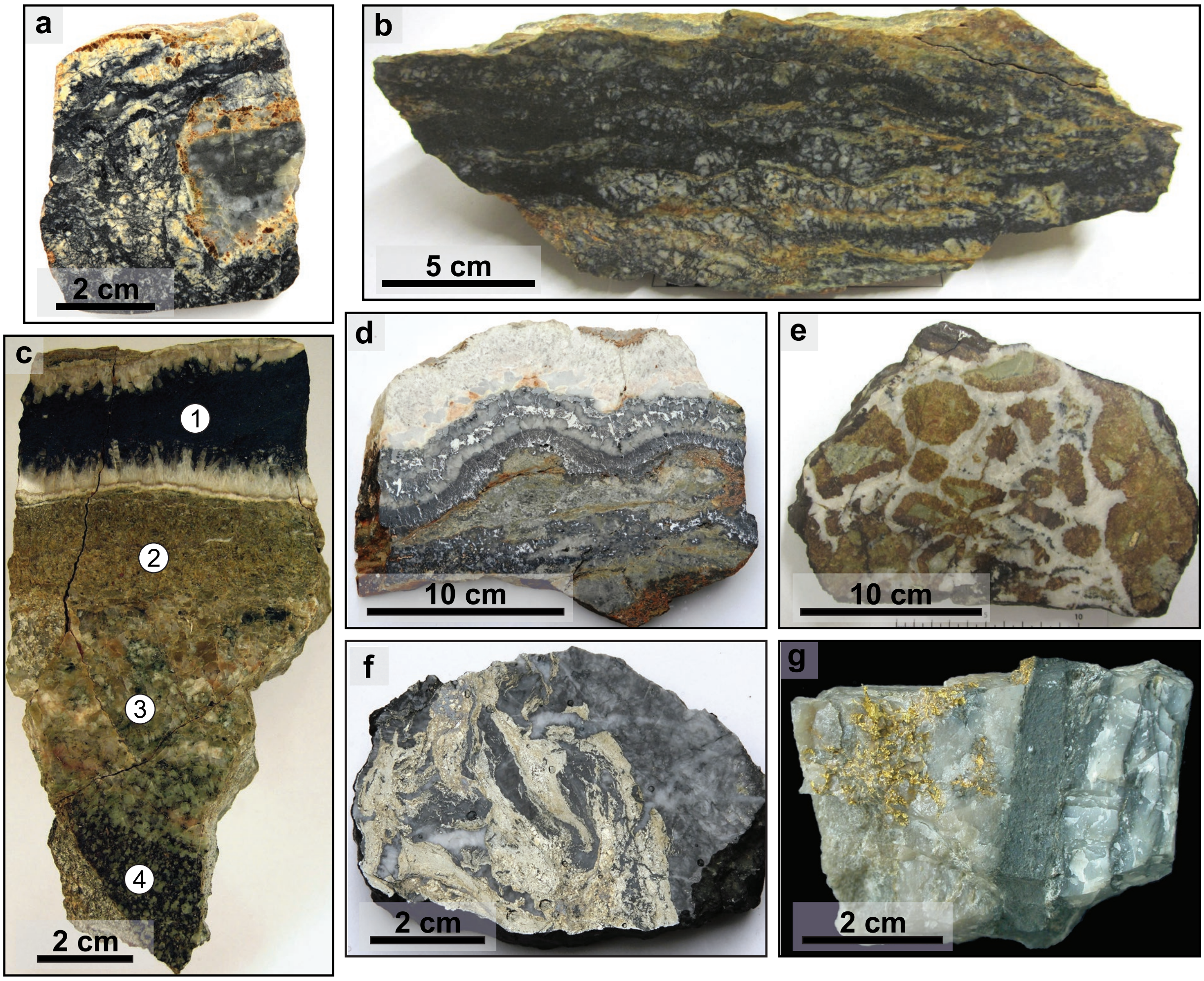


Fig. 3. Typical textures of ore mineralisations in the Tatric Superunit. **a** — Fragments of arsenopyrite-pyrite-gold stage enclosed in a mass of carbonates and Pb–Sb sulfosalts. Dve Vody. **b** — Shear zone impregnated by rich stibnite-quartz mineralisation (stibnite–sphalerite–Pb–Sb-sulfosalts stage). Husárka. **c** — Stibnite-quartz vein (1, stibnite–sphalerite–Pb–Sb-sulfosalts stage) with the illite–carbonate (2), muscovite (3), and chlorite (4) alteration zones. Dúbrava. **d** — Banded texture typical for the galena–quartz and barite mineralisation at Soviansko (galena–sphalerite stage). The mineralisation forms veins and veinlets that penetrate and incorporate fragments of strongly altered country rocks. **e** — Brecciated texture of siderite–sulfide ore. Strongly altered fragments of country rocks (greenish) are wrapped by siderite (brown, siderite–ankerite stage) and cemented by quartz with thin tetrahedrite veinlets (quartz–Cu-sulfide stage). The tetrahedrite veinlets, barely visible in the image, fill the central parts of the quartz matrix between the siderite fragments. Kliesňová dolina. **f** — Massive arsenopyrite and pyrite with invisible gold in quartz and carbonate. Pezinok. **g** — Rich aggregate of gold in milky quartz (arsenopyrite–pyrite–gold stage) rimmed by stibnite associated with greyish quartz (stibnite–sphalerite–Pb–Sb-sulfosalts stage). Magurka.

and baryte stages (Fig. 4). The timing of the individual stages was determined by cross-cutting relationships (Chovan 1990; Chovan et al. 1994a, 1995a; Michálek & Chovan 1998, Fig. 3a, b, g). The relative timing of superimposed siderite–ankerite, quartz–tourmaline, and quartz–Cu-sulfide stages was determined at the deposits and occurrences in the vicinity of the Vyšná Boca village (Figs. 3e, 5). The temporal position of galena–sphalerite stage was determined in the Pb–Zn deposit of Soviansko (Figs. 3d, 6). In both cases, the quartz–tourmaline stage serves as a marker that divides the earlier carbonates from the later sulfide mineralisations, in accordance with the observations in large siderite–polymetallic deposits of the Gemeric Superunit (e.g., Hurai et al. 2008). The stibnite–sphalerite–Pb–Sb-sulfosalts stage of the deposits hosted by low-grade metamorphic rocks was studied in detail at the Pezinok deposit (Figs. 3f, 7), where it differs in terms of the mineral composition from that hosted in high-grade metamorphic and igneous rocks of the Tatric Superunit.

Tourmaline-rich rocks of the Mlynná dolina Valley (Tatric Superunit) were opened by small underground workings (Majzlan & Chovan 1997), but the target metals/minerals of the historical mining were not identified.

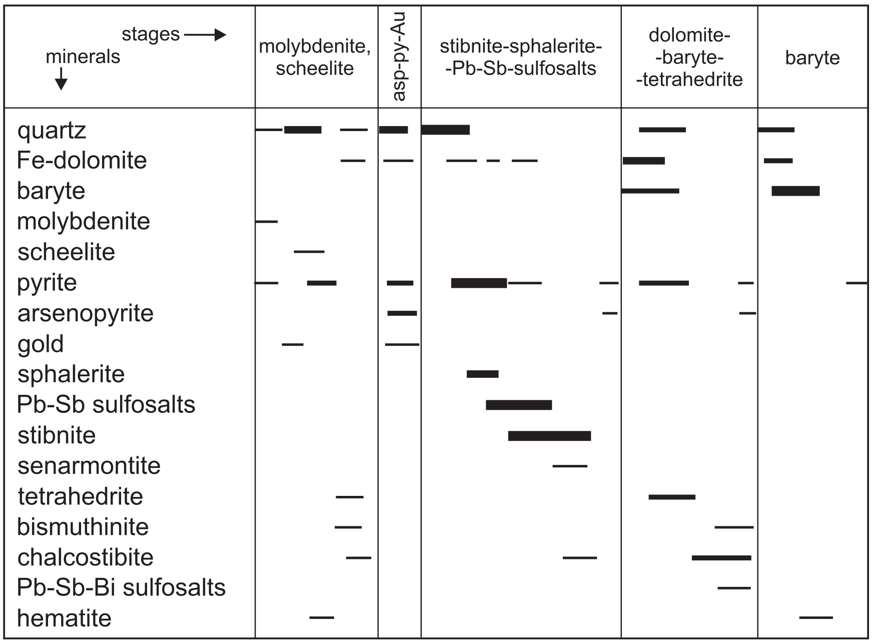
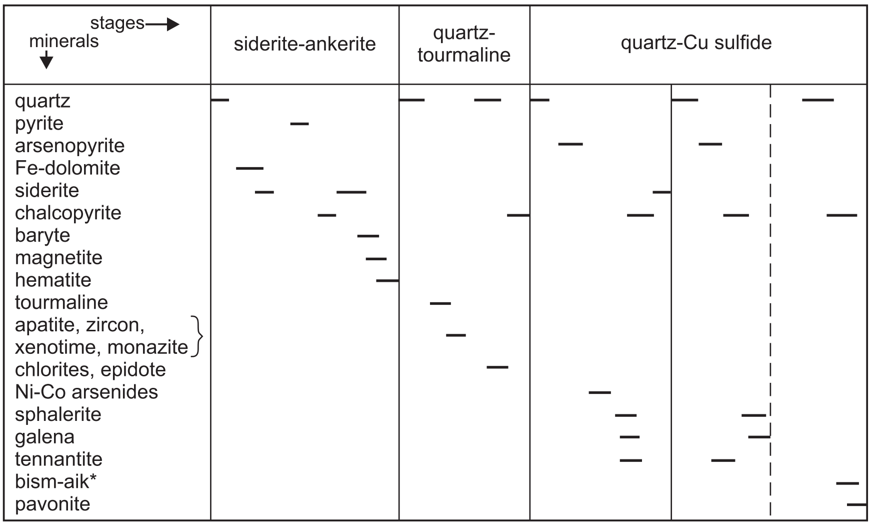


Fig. 4. Precipitation sequence of minerals at Dúbrava simplified after Chovan et al. (1990).



* members of bismuthinite-aikinite series

Fig. 5. Precipitation sequence of minerals at Vyšná Boca simplified after Ozdín (2003).

Textures and styles of hydrothermal alterations

Ore textures are particularly well-known from the Dúbrava deposit. Unless otherwise specified, the following text refers mostly to this deposit. The shortened descriptions are modified after Chovan (1979) and Chovan et al. (1994a).

Quartz–sulfide veins are the prevailing form of the ore mineralisation. Less abundant are disseminated and veinlet-type ores, occurring in tectonically deformed zones nearby the veins. Symmetric, as well as asymmetric textures are the most frequent (Fig. 3b, c, g). The massive texture is characteristic of monomineral stibnite or zinkenite ores. Less frequent are cockade and brecciated textures, whereas drusy textures are sporadic.

The molybdenite and scheelite stages occur as simple, massive quartz veinlets or lenses. The arsenopyrite–pyrite–gold stage precipitated along margins of the main quartz–sulfidic veins, thus forming banded textures, or it occurs in the form of impregnations in hydrothermally altered granitic rocks. Fine-grained pyrite arranged into bands is either intersected by later mineralisations or crushed and cemented by stibnite or tetrahedrite.

The stibnite–sphalerite–Pb–Sb-sulfosalts stage shows symmetrically banded textures composed of quartz margins and stibnite- or zinkenite-rich centres (Fig. 3c). Frequent combed textures originated by the crystallisation of euhedral grains in open spaces and subsequent interstitial

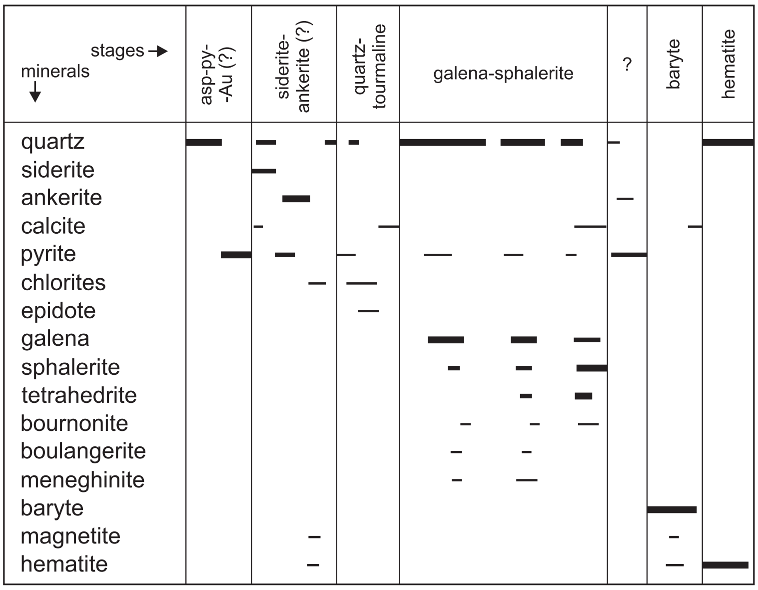


Fig. 6. Precipitation sequence of minerals at Soviansko simplified after Luptáková (2007).

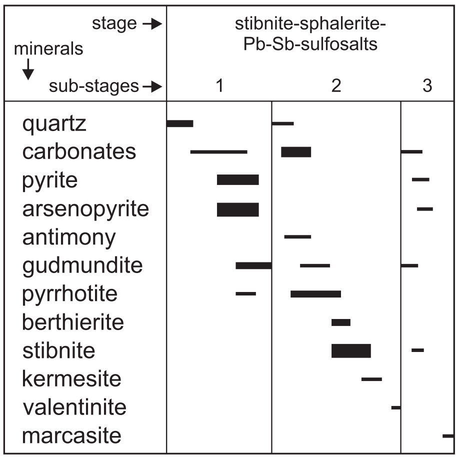


Fig. 7. Precipitation sequence of minerals at Pezinok simplified after Bukovina (2006) and Chovan et al. (2006). The sequence shows the division of the minerals into three precipitation sub-stages; all of them belong to the stibnite–sphalerite–Pb–Sb-sulfosalts stage.

cementation. There are also massive stibnite lenses, up to several meters in diameter, or accumulations of coarse-columnar stibnite. Rare cockade textures are important for the understanding of relative timing of the stages. Fragments of altered rocks with disseminated pyrite and arsenopyrite are surrounded by quartz and cemented by stibnite. Similar to the Dúbrava deposit, fragments of the arsenopyrite–pyrite–gold stage are submerged in a matrix of quartz, sheet silicates, carbonates, and Sb minerals at Dve Vody (Fig. 3a, Majzlan et al. 2002).

The youngest baryte stage is represented by quartz–dolomite–baryte veins with banded texture. Less frequent are cockade and brecciated textures with dolomite and quartz accompanied by Ag-bearing tetrahedrite and Sb–Cu–Pb sulfides cemented by or embedded in breccia fragments of altered rocks. An increased amount of Bi results in precipitation of Bi-chalcostibite, Pb–Sb–Bi sulfosalts and intermediate members of the stibnite-bismuthinite solid solution. Intergrowths of these minerals typically create diffusion zoning and graphic textures and metasomatically replace tetrahedrite.

Brecciated textures are very common for the siderite–ankerite and quartz–Cu-sulfide stages (Fig. 3e, Pršek & Chovan 2001; Ozdín 2003). The Fe carbonates cement and overgrow fragments of strongly altered rocks. Younger quartz, with or without sulfides, penetrates hydrothermal breccias. Combed textures made of intergrowths of coarse-grained siderite and quartz are also common. Siderite and baryte associated sometimes with quartz or hematite may form banded textures.

Hydrothermal alterations were studied in detail at Dúbrava (Orvošová et al. 1998), Pezinok (Moravanský & Lipka 2004) and Soviansko deposits (Luptáková 2007). In other localities, style and mineralogy of the alterations are similar. In most of the other papers, the description of the alterations was limited to macroscopic or microscopic observations or a statement that alterations could not be studied because of intense tectono-thermal reworking or mylonitisation.

Most commonly, high-grade Variscan metamorphic rocks or Variscan granites are the hosts of ore mineralisations. In a few instances, however, the host rocks may also be represented by metabasic rocks, low-grade metamorphites or Permian siliciclastic rocks. The Variscan basement may have undergone a pervasive alteration possibly associated with the Alpine metamorphic overprint. This alteration affected especially rock-forming plagioclase, giving rise to a strong saussuritisation around hydrothermal veins (Petrík et al. 1994).

The hydrothermal alterations are spatially closely associated with veins or stockworks, forming several tens of centimetres thick haloes (Fig. 3c). The distal zones are characteristic by the presence of IIb-polytype trioctahedral chlorite that has not been obliterated by later alterations (Luptáková 2007). The proximal, innermost alteration zone in acidic magmatic rocks and gneisses contains predominantly quartz (both rock-forming and newly-formed), illite, pyrite, and carbonates. In some places, the proximal illite and distal chlorite zones are separated by a thin muscovite zone, with larger crystals of sheet silicates and still discernible rock-forming minerals. In metabasic rocks, the proximal zone is dominated by carbonates, and a transitional chlorite–carbonate zone occurs between the distal and proximal alteration zones.

Mineralogy

Molybdenite stage

In the Dúbrava deposit, molybdenite occurs in hydrothermal quartz veins together with pyrite and rutile (Chovan et al. 1990). Rare molybdenite was found also in quartz veinlets with scheelite in the Dúbrava–Rakytová adit (Chovan, unpublished). Molybdenite in the Malé Železné occurrence is hosted by pegmatite and quartz veins (Michalenko 1959, 1960; Majzlan et al. 1998), where it is accompanied only by granitic rock-forming minerals. Molybdenite in quartz veinlets with ferberite and other minerals was also reported from Kyslá (Molák 1990 in Bláha & Bartoň 1991). Large molybdenite crystals, up to 2 cm in diameter, were found in a borehole intersecting muscovite granite near Pezinok (Chovan et al. 1992). Molybdenite crystals have been found scattered in a quartz vein hosted in granite near Kuchyňa (Holický & Hrnčár 1978) and in pegmatites in the vicinity of Modra (Majzlan, unpublished).

Scheelite stage

Mineralogical studies on scheelite ores from Kyslá deposit targeted by intensive exploration in the 1980s were compiled by Bláha & Bartoň (1991). Grey quartz is the main gangue mineral that hosts scheelite associated with rare pyrite and arsenopyrite. Crystallisation of scheelite was accompanied by the formation of abundant biotite, especially in amphibolite host rocks. Scheelite also replaces earlier ferberite. Somewhat younger sulfide assemblage, still closely associated with the scheelite ores, comprises chalcopyrite, pyrite, tetrahedrite, and arsenopyrite. Gold, tetradymite, tellurobismuthite, and bismuthinite are rare but typical minerals (Beňka & Suchý 1983; Bláha & Bartoň 1991) accompanied by joséite and another mineral probably related to pilsenite described with the discredited mineral name wehrlite (Boriskin et al. 1990; Kuznecov et al. 1990).

At the Dúbrava deposit, this stage consists of abundant quartz with minor scheelite, pyrite, and muscovite (Čillík et al. 1979; Chovan et al. 1990). Scheelite appears especially within quartz vein segments that penetrate migmatite bodies. Additional uncommon minerals include Bi–Te–S phases, such as tetradymite, bismuthinite, native bismuth, joséite-A, and unnamed phases corresponding to Bi_2S_2Te and Bi_3S_4 (Chovan & Michálek 1988; Ozdín et al. 2009).

Arsenopyrite–pyrite–gold stage

This historically important stage is rather simple in terms of mineralogy. Quartz is the host of pyrite and arsenopyrite, the latter projecting mostly between the FeAsS and $FeAs_{0.9}S_{1.1}$ compositions (Fig. 8). Gold occurs as macro- and microscopic particles (e.g., Fig. 3g, Magurka deposit, Chovan et al. 1995b) of high fineness (800–950) (Fig. 9), nanoinclusions in sulfides (Pezinok deposit, Majzlan et al. 2010), or chemically bound “invisible” gold revealed using the ^{197}Au Mössbauer spectroscopy in the Pezinok deposit (Andráš et al. 1995). Carbonates (ankerite, calcite) are occasionally abundant gangue minerals, especially in the Pezinok deposit, where arsenopyrite and pyrite are accompanied by smaller amounts of löllingite, gudmundite, and pyrrhotite (Chovan et al. 2002). Gudmundite was also provisionally identified at the Medzibrod and Sopotnická dolina occurrences in Nízke Tatry Mts. (Lalinská 2003) as a member of the arsenopyrite–pyrite–gold stage. Rare sulfosalts observed in the gold ores are likely constituents of later stages.

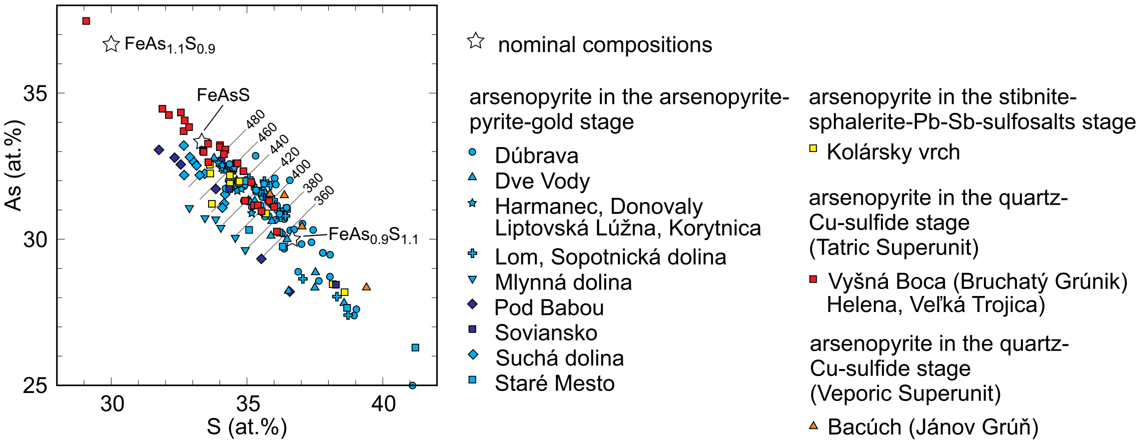


Fig. 8. Chemical composition of arsenopyrite from the localities in the Tatric and Veporic Superunits. Large stars show nominal compositions of arsenopyrite, with the formula attached. Thin diagonal lines marked with numbers indicate the temperature of arsenopyrite crystallisation in the assemblage arsenopyrite+pyrite+liquid after Kretschmar & Scott (1976). Compositions with high Sb concentrations (Bruchatý Grúnik, Ozdín 2003) were omitted. Analyses from: Dúbrava (Sachan & Chovan 1991; Chovan et al. 1994b), Soviansko and Pod Babou (Luptáková 2007), Dve Vody (Majzlan et al. 2002), Lom, Sopotnická dolina (Lalinská 2003), Mlynná dolina (Majzlan 1996), Harmanec, Liptovská Lúžna, Korytnica, Donovaly (Stankovič 1998; Bakos et al. 2004), Bruchatý Grúnik, Helena, Veľká Trojica (Ozdín 2003), Jánov Grúň (Pršek 1999), Suchá dolina (Čík 2010), Kolársky vrch (Andráš et al. 1993), Staré Mesto (Bakoš et al. 2002).

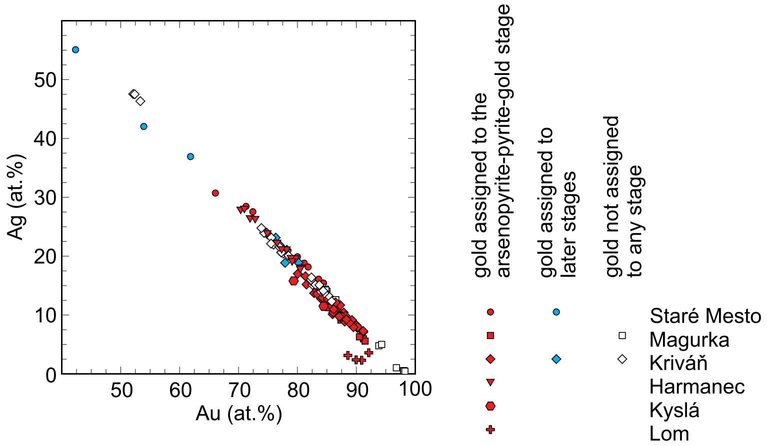


Fig. 9. Chemical composition of (Au, Ag) alloys from the arsenopyrite–pyrite–gold and stibnite–sphalerite–Pb–Sb-sulfosalts stages in the Tatric Superunit. Analyses from: Magurka (Bakoš 1998), Staré Mesto (Bakoš et al. 2002), Harmanec (Bakos et al. 2004), Kriváň (Bakos & Chovan 2006), Kyslá (Bláha & Bartoň 1991), Lom (Lalinská 2003).

Stibnite–sphalerite–Pb–Sb-sulfosalts stage

The stibnite–sphalerite–Pb–Sb-sulfosalts stage is dominated by stibnite that was economically the most important mineral during modern mining since the advent of flotation processing (Fig. 3b,c,g). Stibnite was accompanied by abundant quartz and carbonates of the dolomite–ankerite series (Fig. 10). Altered rocks in the immediate vicinity of the dolomite–ankerite veinlets may contain minute grains of siderite and magnesite. Other associated ore and gangue minerals may vary from one deposit to another. There are, however, substantial differences between ore minerals of these stages hosted in high-grade metamorphic and magmatic rocks of Nízke Tatry and Tatry Mts., or in low-grade metamorphic rocks within the deposits of Malé Karpaty Mts. and the Medzibrod deposit of Nízke Tatry Mts.

In the deposits hosted in high-grade metamorphic and magmatic rocks, pyrite is a common sulfide associated either with stibnite or with sphalerite and a number of Pb–Sb sulfosalts (Figs. 3a, 11). There are different types and likely also generations of pyrite distinguished according to their textural appearance, minor elements, microhardness, and electric conductivity (Ďurža & Chovan 1983). Sphalerite and sulfosalts are regarded as older or younger than stibnite; the opinions vary based on variably interpreted microscopic observations. Unequivocal macroscopic observations of vein crossing or replacement have never been observed. Sphalerite hosts only small amounts of elements that substitute for Zn (Fig. 12). Native antimony (older than stibnite) is very rare (Chovan et al. 1985).

Two assemblages of Pb–Sb sulfosalts were defined in these deposits. The first one is associated with stibnite, and comprises sulfosalts with Sb that are more abundant than those with Pb. The most common mineral of this group is zinkenite associated with much less common scainiite, jamesonite, robinsonite, fülöppite, and plagionite. The second assemblage is dominated by boulangerite accompanied by less abundant semseyite, heteromorphite, robinsonite, and some other unspecified very rare sulfosalts. This assemblage may also be accompanied by galena.

Pb–Sb sulfosalts occur in the following deposits and occurrences: Dúbrava (Chovan et al. 1998a), Magurka (Chovan et al. 1995b), Malé Železné (Majzlan et al. 1998; Hovorič 2008), Dve Vody (Majzlan et al. 2002), Lom (Lalinská et al. 2004), Rišianka, Kľačianka, Krámec, and Veľké Oružné (Majzlan et al. 1998; Bakos et al. 2000; Hovorič 2008), Hiadeľ (Majzlan et al. 2015), Lomnistá, Husárka, Suchá dolina, Riavka (Čík 2010), Kriváň (Bakos & Chovan 2006), and Kyslá (Bláha & Bartoň 1991). Sulfosalts predominate over stibnite in some occurrences (e.g., Malé Železné). Pb–Sb sulfosalts may be infrequently accompanied by Cu–Sb sulfides, such as bournonite, tetrahedrite, or chalcostibite (e.g., Malé Železné and Kľačianka, Hovorič 2008). Rare sulfosalt species include launayite from Dúbrava (Adamus et al. 1993), andorite from Dúbrava (Ozdín & Sejkora 2009), dadsonite, scainiite, chovanite, pellouxite, geocronite, and rouxelite from Dúbrava, Malé Železné, Magurka, and Kľačianka (Orlandi et al. 2005; Hovorič 2008; Topa et al. 2012). At some deposits and occurrences, berthierite and jamesonite occur in small amounts, for example at Lom (Lalinská et al. 2004), and Dve Vody-Mistrík (Majzlan et al. 2002). Berthierite is more abundant than stibnite at Suchá dolina (Čík 2010). Stibnite rarely includes microscopic grains of gold (Mlynná dolina, Majzlan et al. 2001). Stibian ‘mustard gold’ with a presumed composition Au_2Sb was reported from Kriváň (Makovicky et al. 2007). At Nižná Boca, zinkenite associates with stibnite, but boulangerite accompanies bournonite and galena (Smirnov et al. 2006). Galena was occasionally reported as a part of the Pb–Sb sulfosalt assemblage, particularly where Pb-rich members (e.g., boulangerite) were abundant. It is therefore likely that the galena–sphalerite ores at Magurka (František adit,

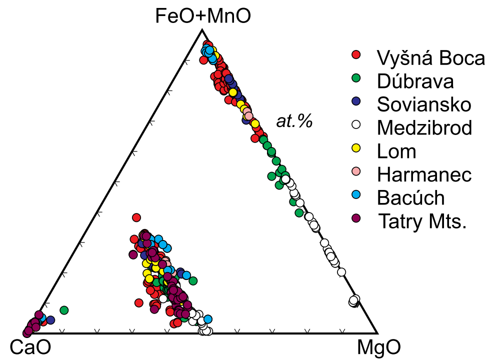


Fig. 10. Chemical composition of hydrothermal carbonates from the localities in the Tatric and Veporic Superunits. Analyses from: Vyšná Boca (Ozdín 2003), Dúbrava (Majzlan, unpublished data), Soviansko (Luptáková 2007), Medzibrod, Lom (Lalinská 2003), Harmanec (Bakos et al. 2004), Bacúch (Pršek 1999), Tatry Mts. (Bakos 2003).

Chovan et al. 1995b) belong to this, rather than to the galena–sphalerite stage.

The ultimate deposition of Sb-rich dadsonite, scainiite, and chovanite is interpreted as to reflect an increased chlorine- and oxygen activity in the ore-bearing fluids. In some cases, late primary precipitation products include even oxides instead of sulfides, as exemplified by lenses of senarmontite at Dúbrava (Chovan et al. 1990), valentinite at Suchá dolina (Čík 2010), or unidentified primary Sb-oxide at Malé Železné (Hovorič 2008).

In the deposits hosted in low-grade metamorphic rocks, the dominant stibnite is accompanied by berthierite, gudmundite, native antimony, pyrite or pyrrhotite (Chovan et al. 1994a). Sulfosalts are largely missing and sphalerite is rare. In Malé Karpaty Mts., the deposition of Sb minerals was terminated by abundant kermesite, valentinite (Bukovina 2006), and rare schafarzikite (Sejkora et al. 2007). Considering that these ores are spatially associated (strata-bound) with reducing black shales, the abundance of antimony oxides is puzzling. Rare chapmanite from the Pezinok deposit is considered to be of secondary origin (Polák 1983, 1988), although such an interpretation could be questioned. Chapmanite is a Sb^{3+}-containing phyllosilicate and its samples are well-crystallised. Both the presence of reduced Sb and the crystallinity speak against the notion of secondary origin.

Quartz and carbonates are typical gangue minerals of this stage. At Medzibrod, these carbonates are unusually Mg-rich (Lalinská 2003) compared to carbonates from this stage in other deposits (Fig. 10). Siderite and ankerite with Mg-rich rims were interpreted by Korikovsky & Molák (1995) as primary constituents of weakly metamorphosed siderite–ankerite–muscovite metasandstones and phyllites, found at a number of sites on the southern slopes of the Nízke Tatry Mts. In addition to the carbonates and sheet silicates, these rocks were reported to contain pyrite, arsenopyrite and iron oxides. Given that the ore bodies at Medzibrod deposit are concordant (perhaps strata-bound) (Michálek 1988), it could be argued that the carbonates analyzed by Lalinská (2003) are not hydrothermal but metamorphic or are at least derived from the Mg-rich metamorphic carbonates in this area.

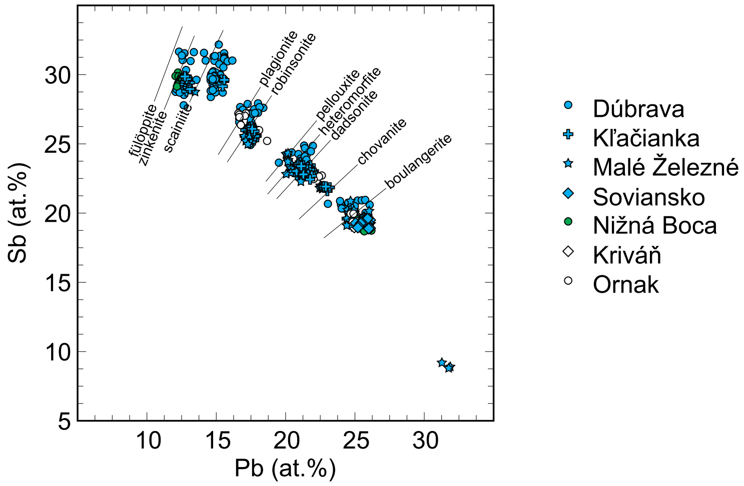


Fig. 11. Chemical composition of Pb–Sb sulfosalts from the localities in the Tatric and Veporic Superunits. Analyses from: Dúbrava (Chovan et al. 1998a; Pršek, unpublished data), Kľačianka and Malé Železné (Hovorič 2008; Pršek, unpublished data), Soviansko, Nižná Boca, Kriváň, Ornak (Pršek, unpublished data). Centres of the diagonal line segments show the nominal composition of the Pb–Sb sulfosalts.

Dolomite–baryte–tetrahedrite stage

This stage typically contains Fe-dolomite, quartz, sulfides and sometimes also baryte. It occurs not only in the Tatric basement of

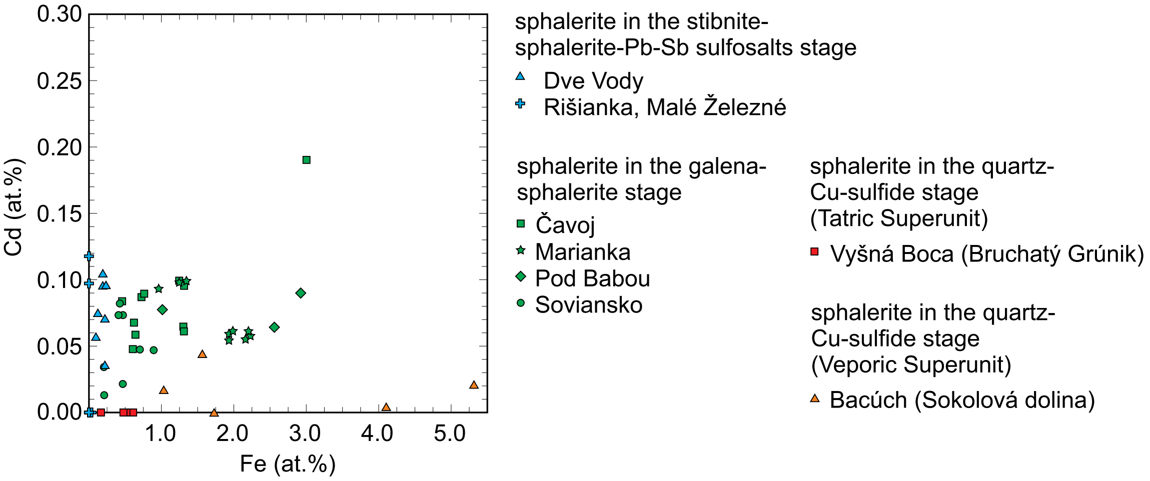


Fig. 12. Chemical composition of sphalerite from the localities in the Tatric and Veporic Superunits. Analyses from: Marianka (Kubač et al. 2014), Pod Babou and Soviansko (Luptáková 2007), Rišianka and Malé Železné (Majzlan et al. 1998), Dve Vody (Majzlan et al. 2002), Čavoj (Mikuš et al. 2003), Bruchatý Grúnik (Ozdín 2003), Sokolova dolina (Pršek 1999).

Nízke Tatry Mts. (e.g., Dúbrava, Chovan et al. 1990), but also in Tatry, Malé Karpaty, and Strážovské vrchy Mts.

Sulfides of this stage are most commonly represented by tetrahedrite. Chemical composition of tetrahedrite (Fig. 13), typical for this stage, is discussed below (see *Sulfosalts as indicators of ore stages*).

Chalcostibite with metacrystals of pyrite is a common companion of tetrahedrite in this stage. Bi-minerals are represented here by the stibnite–bismuthinite solid solution, Bi-zinkenite, Bi-jamesonite, and tintinaite, especially at the Dúbrava deposit (Chovan et al. 1995a, 1998a) and in the vicinity of the Magurka deposit (Majzlan et al. 1998; Bakos et al. 2000).

Gold, if present, is usually of lower fineness than the gold from the arsenopyrite–pyrite–gold stage. Such gold was found at the Magurka deposit (Chovan et al. 1995b). Gold in similar association of minerals, but of much higher fineness, was reported from Medzibrod (Mikuš et al. 2018). Here, the authors consider also supergene origin of this gold.

The assignment of unusually Hg-rich tetrahedrite from Husárka (Čík 2010) to a specific stage is problematic. This tetrahedrite type occurs together with stibnite, chalcopyrite, chalcostibite, and very rare cinnabar in a quartz–carbonate–baryte gangue. The mineral is rare, found only in a single sample. The Hg-enrichment has been known so far from only few

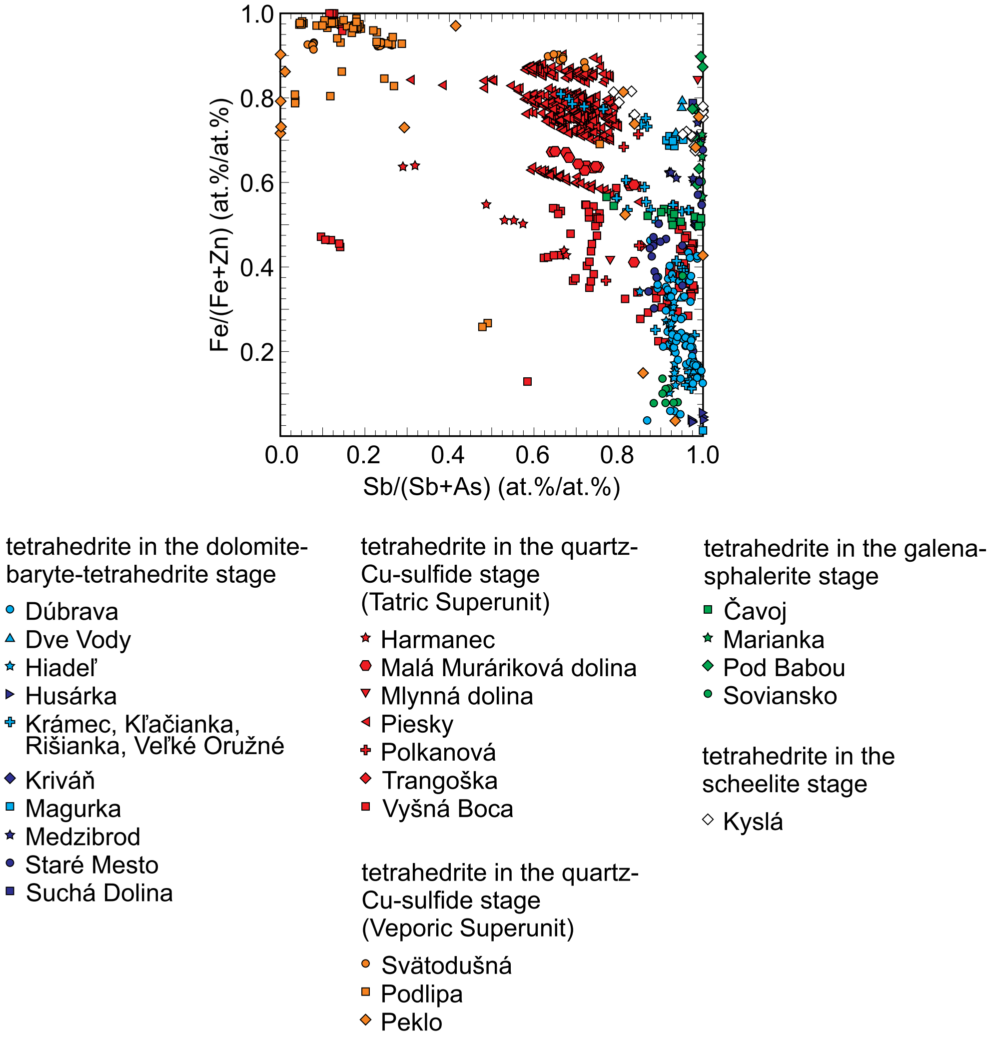


Fig. 13. Chemical composition of the members of tetrahedrite–tennantite solid solution from the localities in the Tatric and Veporic Superunits. Analyses from: Kriváň (Bakos & Chovan 2006; Pršek 2008), Harmanec (Bakos et al. 2004), Dúbrava (Chovan et al. 1998a; Pršek 2008), Piesky (Sejkora et al. 2013; Borčinová Radková et al. 2017; Majzlan et al. 2018), Ľubietová-Svätodušná (Borčinová Radková et al. 2017), Ľubietová-Podlipa (Luptáková et al. 2016), Ľubietová-Peklo (Ferenc et al. 2019), Magurka (Jancsy 1993; Póč 1993; Chovan et al. 1995b), Vyšná Boca and Jarabá (Ozdín & Chovan 1999; Pršek 2008), Veľké Oružné, Krámec, Kľačianka, Rišianka (Chovan et al. 1997; Bakoš 1998; Hovorič 2008; Pršek 2008), Husárka, Suchá Dolina (Čík 2010), Medzibrod (Lalinská 2003), Soviansko, Pod Babou (Luptáková 2007), Dve Vody (Majzlan et al. 2002), Čavoj (Mikuš et al. 2003; Pršek 2008), Staré Mesto (Andráš et al. 1990; Bakoš et al. 2002; Pršek 2008), Hiadeľ (Majzlan et al. 2015), Polkanová (Michňová & Ozdín 2010), Kyslá (Bláha & Bartoň 1991), Mlynná dolina (Majzlan & Chovan 1997), Trangoška (Hak & Losert 1962). Note that the data used are not necessarily always included in these publications. The sites studied and the methods, however, are documented there. Some data were retrieved either from supplementary information files or obtained from the authors of the cited papers upon request.

other localities in Nízke Tatry Mts., such as Rišianka, Ďurková-Magurka, Veľké Oružné, with inclusions of rouxelite – an Hg-bearing sulfosalt (Hovorič 2008). Hg-rich tetrahedrite also occurs together with cinnabar in alluvial sediments. Hak (1966) concluded that Hg is a common trace element associated with tetrahedrite, zinkenite, and especially sphalerite.

Siderite–ankerite stage

The siderite–ankerite stage contains mostly members of the siderite–magnesite series, to a lesser extent the ankerite–dolomite series (Fig. 10). This behaviour pertains to the Tatric (e.g., Nízke Tatry, Ozdín 2003; Michňová & Ozdín 2010; Strážovské vrchy, Mikuš et al. 2003) and the Veporic Superunits (e.g., Tríbeč, Ozdín 2008; Nízke Tatry, Pršek & Chovan 2001). Carbonates are generally inhomogeneous, with significant compositional variations within and between the crystals. Siderite from hydrothermal veins of Nízke Tatry Mts. contains 72–90 mol. % $FeCO_3$. Ozdín (2003) postulated that older siderite is enriched in Mg, whereas the younger generation is enriched in Fe and Mn. Dolomite is much less common but may locally prevail (e.g., Jánov Grúň, Pršek & Chovan 2001), whereas ankerite is sporadic. Ozdín & Chovan (1999) noted that "vein carbonates hosted by metamorphic rocks belong mostly to the siderite, less to the ankerite–dolomite series". The opposite is true for the veins hosted in granitoid rocks, implying a host-rock control over the composition of vein carbonates. The same can be concluded from the compositional data from Tatry Mts, where the carbonates are represented by dolomite-ankerite series (Bakos 2003). Here, however, we have to emphasize that this author reported that the main carbonate mass is younger than the quartz with Cu sulfides, unlike elsewhere.

Sulfides, if present, are most commonly associated with fine-grained siderite. They are represented by pyrite, less frequently by chalcopyrite, tetrahedrite, or sulfosalts. Ozdín (2003) labelled only pyrite and chalcopyrite as the sulfides coeval with siderite ores in his general crystallisation scheme for the Tatric occurrences. Hematite, magnetite, and baryte are additional minerals that accompany siderite and were formed within this stage.

The affiliation of ankerite–dolomite with minor siderite and calcite at the Soviansko deposit is rather questionable (Luptáková 2007, Fig. 6). Their position in the precipitation sequence proposed in earlier (Pouba & Vejnar 1955; Lisý & Sobolič 1959) and recent works (Luptáková 2007) combined with the predominance of carbonates and minor quartz and pyrite are features reminiscent of the siderite–ankerite stage.

Quartz–tourmaline stage

This stage is dominated by quartz with minor albite, schorl, hydroxyapatite, zircon, rutile, chamosite, tourmaline, and muscovite. Monazite and xenotime are the main REE carriers (Ozdín 2003). This stage does not contain ore minerals. However, it is an important marker dividing the earlier siderite–ankerite from later sulfidic stages.

Quartz–Cu-sulfide stage

Quartz with Cu-sulfides, predominantly tetrahedrite (Fig. 3e), is found at many occurrences in the Tatric and Veporic Superunits. Carbonates of the dolomite–ankerite series may be a minor component of this stage (Fig. 10).

The quartz–Cu-sulfide stage is a typical and common companion of the siderite–ankerite stage developed prominently in the Tatric basement (e.g., Vyšná Boca), Veporic basement (e.g., Bacúch) or Permian siliciclastic sediments (e.g., Špania Dolina) of Nízke Tatry Mts., but also in Tríbeč and Strážovské vrchy Mts., belonging to the Veporic and Tatric Superunits, respectively. Many small occurrences are also scattered in Tatry Mts. (Bakos 2003), the northernmost Variscan segments of CWC.

Quartz, tetrahedrite, chalcopyrite, and pyrite are the most common minerals of this stage. Chemical composition of tetrahedrite (Fig. 13) typical for this stage is discussed below (see section *Sulfosalts as indicators of ore stages*).

Ni–Co minerals are usually found in small amounts in the quartz–Cu-sulfide stage at Ľubietová-Kolba (Láznička 1966), Čavoj (Mikuš et al. 2003), Vyšná Boca (Ozdín 2003), and Jedľové Kostolany (Ozdín 2008). They are represented by gersdorffite, carrolite, cobaltite, krutovite, and skutterudite. They are usually considered to slightly predate the more voluminous Cu-sulfides and sulfosalts. The relationship of the Ni-arsenide mineralisation at Čierna Lehota (Mikuš et al. 2013), represented mostly by pararammelsbergite, with the quartz–Cu-sulfide stage is unclear.

Sulfosalts are also commonly present as microscopic inclusions in other sulfides, occasionally as exsolutions and macroscopic crystals intergrown with other phases. Members of the bismuthinite–aikinite series (Fig. 14) are the most abundant sulfosalts in this stage. Their crystallisation seems to commence with Cu-rich members followed by Cu-free members, i.e., bismuthinite. They occur together with less frequent members of the lillianite series (lillianite, gustavite, schirmerite, heyrovskýite), pavonite series (pavonite, benjaminite), kobellite–tintinaite series, izoklakeite–giessenite series, nuffieldite, galenobismutite, and matildite. These sulfosalts were described from Bacúch (Pršek & Chovan 2001; Pršek 2004), Bruchatý grúnik (Pršek & Ozdín 2004; Pršek et al. 2006), Paurovská (Ozdín & Chovan 1999), Kolba (Pršek & Mikuš 2006), and Zingoty (Pršek & Ozdín 2004).

A variegated assemblage of sulfosalts, including members of the aikinite–bismuthinite series with eclarite, cosalite, and other sulfosalts, was described from Hviezda (Majzlan 1996; Majzlan & Chovan 1997; Pršek & Ozdín 2004; Pršek et al. 2006, 2008). In this assemblage, however, the Bi-sulfosalts are unusually enriched in Sb in comparison to other occurrences within the quartz–Cu-sulfide stage. A different assemblage of sulfosalts represented by andorite, ramdohrite, gustavite, lillianite, and heyrovskýite was found at Chyžné (Bálintová et al.

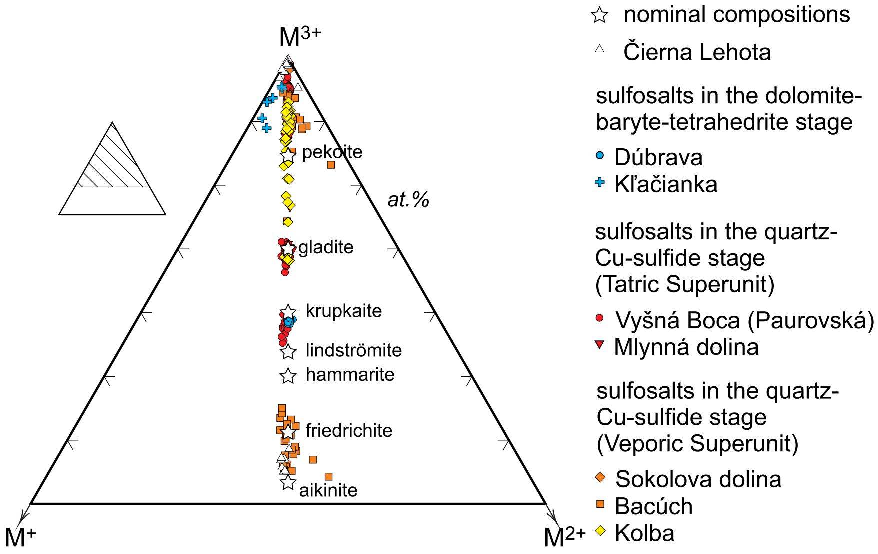


Fig. 14. Chemical composition of members of the aikinite–bismuthinite series from the localities in the Tatric and Veporic Superunits. Analyses from Pršek (2008). Electron microprobe analyses were recalculated to sums of mono-, di- and trivalent cations (M^+, M^{2+}, M^{3+}, respectively).

2006), whereas kupčíkite was reported from Podlipa (Luptáková et al. 2016). Hodrušite is the most common sulfosalt of the unusual Ni–As–Bi mineralisation at Čierna Lehota, where it is associated with rare kupčíkite, matildite, cuprobismutite, and minerals of the aikinite–bismuthinite series (Pršek et al. 2005).

Pršek (2008) summarised most of the knowledge on sulfosalts at these localities complemented with new analyses. He also commented on the similarity or disparity of sulfosalts from the Tatric, Veporic, and Gemeric Superunits. The quartz–Cu-sulfide stage described here resembles in many aspects the quartz–Cu-sulfide ores from the southwestern part of the Veporic Superunit (Ferenc 2008) with abundant chalcopyrite, tetrahedrite, Bi-sulfides, and Bi-rich sulfosalts.

Galena–sphalerite stage

The main gangue mineral is quartz accompanied by galena, sphalerite, and a suite of less common minerals (Fig. 3d). Galena was earlier reported as a silver-bearing variety (e.g., Cambel 1959) but newer analytical work showed that the galena is essentially silver-free. Inclusions of Ag-tetrahedrite are silver carriers in galena from Soviansko (Luptáková 2007) and Dve Vody (Majzlan et al. 2002). Galena devoid of Ag was found even if intergrown with stephanite or Ag-tetrahedrite.

Sphalerite abundance varies from subordinate (Dve Vody) to major (Soviansko) and it contains negligible Fe (Fig. 12). Analyses from Soviansko yielded up to 1 wt. % Fe, contrasting with 3.4 wt. % Fe in sphalerite from the Pod Babou occurrence (Luptáková 2007; Luptáková et al. 2009), and as much as 6.2 wt. % Fe in Marianka (Kubač et al. 2014).

Sulfosalts in this stage are commonly Pb-rich, usually represented by boulangerite or bournonite (Majzlan et al. 2002; Luptáková & Pršek 2004; Luptáková 2007; Luptáková et al. 2009; Kubač et al. 2014). Meneghinite and myrmekitic intergrowths of bournonite and galena interpreted as a breakdown product of meneghinite were reported from Soviansko (Luptáková 2007) and Marianka (Kubač et al. 2014).

Baryte stage

Baryte veins at the Dúbrava deposit contain minor Fe-dolomite, siderite, calcite, strontianite, hematite, pyrite (Chovan 1979; Chovan & Michálek 1981; Chovan 1990), and rare witherite (Števko et al. 2013). Similarly, baryte at the Soviansko deposit is accompanied by small amounts of calcite, hematite, and magnetite (Luptáková 2007). Baryte–quartz veins near Nižné Matejkovo in Veľká Fatra Mts. contain only accessory sulfides (Turan 1962). A baryte vein at Trangoška contains tetrahedrite and galena (Zoubek 1937; Turan 1961; Hak & Losert 1962). Despite the greater abundance of sulfides at Trangoška in comparison to other occurrences that belong to the baryte stage, the mineral assemblage of the Trangoška vein is more reminiscent of the baryte than the dolomite–baryte–tetrahedrite stage. The veins at Trangoška and Nižné Matejkovo extend from the Variscan basement to Early Triassic sandstones, thus attesting their relative ages.

Hematite stage

This stage is well-developed in mineralogically simple veinlets of quartz and hematite hosted in Lower Triassic sandstones or Variscan basement rocks. They were described from the vicinity of Magurka near Kapustisko, Latiborská hoľa, and Mestská hora (Chovan et al. 1995b; Bakos et al. 2000), Soviansko (Luptáková 2007), Kumštové sedlo (Ozdín & Chovan 1999), and the Zach ore field near Nižná Boca village (Smirnov 2000). Hematite veinlets were also found in Považský Inovec Mts. hosted in quartz porphyries or Permian conglomerates (Hovorka 1960; Polák 1971).

Hematite–magnetite ores from Mlynná dolina (Majzlan et al. 2001) and Lom occurrences (Lalinská et al. 2004) are of uncertain affiliations. In Mlynná dolina, they are located in the Tatric Superunit near the tectonic contact called the Čertovica fault with the Veporic Superunit, and they may be correlated with hematite–magnetite ores from Bacúch in the Veporic Superunit (Pršek et al. 2010). It is possible that the Mlynná dolina ores are actually hosted by the Veporic Superunit rocks thrusted over the Čertovica fault onto the Tatric Superunit.

Sulfosalts as indicators of ore stages

The stages defined above are characterised by typical assemblages of sulfosalts (Table 1). Although the information could be extracted from the text above, this section specifically addresses the sulfosalts that are distinctive for each stage. Some of the stages do not contain sulfosalts, namely the molybdenite, arsenopyrite–pyrite–gold, siderite–ankerite, quartz–tourmaline, baryte, and hematite stages. They are not listed in Table 1.

Scheelite stage is characterised by the presence of Bi-tellurides with small amounts of Bi-sulfosalts. Bismuthinite, the only identified sulfosalt, is accompanied mainly by tetradymite, in lesser amounts by joséite-A and -B (Dúbrava), and other Bi–Sb–Te–S phases (Kyslá).

There are sulfosalts spatially associated with the ores of the arsenopyrite–pyrite–gold stage. The textural evidence, however, suggest that these sulfosalts are younger and belong genetically to one of the later stages.

Stibnite–sphalerite–Pb–Sb-sulfosalts stage (Fig. 11) forms the principal components of ore deposits in the Tatric Superunit. A total of three main assemblages can be distinguished: i) Sb-dominated Pb–Sb sulfosalts with stibnite, ii) Pb-dominated sulfosalts with or without galena, and iii) berthierite, gudmundite, and jamesonite accompanied by stibnite.

The first assemblage is by far the most abundant. It was found essentially at all deposits and occurrences in Nízke Tatry Mts. (e.g., Dúbrava, Dve Vody) and it is the main carrier of antimony there. The main minerals are stibnite and Cu,Ag-bearing zinkenite. Robinsonite, jamesonite, and scainiite may be present in lesser amounts together with rarer sulfosalts.

The second assemblage is less frequent. It was found especially at Malé Železné, Kľačianka and Nižná Boca occurrences. The principal sulfosalt is boulangerite, accompanied with minor semseyite and heteromorphite, and a suite of rare mineral species involving dadsonite, rouxelite, geocronite, and chovanite. Robinsonite occurs in both sulfosalt assemblages.

The assemblage of Fe–Sb sulfides is typical for deposits and occurrences hosted in black shales overprinted by low-grade Variscan metamorphism. These include Pezinok, Pernek, Kuchyňa, Medzibrod, and Suchá dolina. Pb–Sb sulfosalts are typically missing here.

Dolomite–baryte–tetrahedrite stage carries tetrahedrite with Bi-bearing sulfosalts. Tetrahedrite from the dolomite–baryte–tetrahedrite stage is typical of high Sb/(Sb+As) ratio (Fig. 13). Tetrahedrite from this stage covers almost the entire range of Fe/(Fe+Zn) ratios and Zn-rich compositions are conspicuously common. The Bi-sulfosalts include members of chalcostibite–emplectite solid solution, Bi-bearing bournonite, Bi-bearing jamesonite and Bi-bearing zinkenite. Other sulfosalts that may occasionally occur include tintinaite and members of the bismuthinite–aikinite series (bismuthinite–stibnite solid solution, gladite, pekoite and Sb-dominant krupkaite).

Quartz–Cu-sulfide stage is the second principal sulfosalt carrier after the stibnite–sphalerite–Pb–Sb-sulfosalts stage. Tetrahedrite from the quartz–Cu-sulfide stage shows Sb/(Sb+As) ratios less than 0.8, with an exception of a few analyses from Vyšná Boca and Polkanová. This tetrahedrite is usually Fe-rich, with Fe/(Fe+Zn) ratios mostly above 0.4. Hence, there is a clear-cut chemical difference between tetrahedrite from the quartz–Cu-sulfide and from the preceding dolomite–baryte–tetrahedrite stages. Among the samples thought to be representative of the dolomite–baryte–tetrahedrite stage, only those from Kľačianka overlap partially with the analyses from the quartz–Cu-sulfide stage (Fig. 13). It is interesting, however, that Hovorič (2008) identified two tetrahedrite generations in Kľačianka. Only the later generation associated with Cu–Bi sulfosalts of the aikinite–bismuthinite series is chemically comparable to the tetrahedrite from the quartz–Cu-sulfide stage. The two tetrahedrite generations at this locality were also confirmed by Bakos et al. (2000).

Table 1: Sulfosalt assemblages typical for hydrothermal stages defined in this work.

Stage	Selected localities	Diagnostic elements and typical associated sulfosalts/sulfides
scheelite	Kyslá, Dúbrava	Bi–Te: bismuthinite, tetradymite, tellurobismuthite, joséite
stibnite–sphalerite–Pb–Sb-sulfosalts	Dúbrava, Dve Vody, Lom	Sb–Pb: zinkenite, robinsonite, jamesonite
	Malé Železné, Kľačianka	Pb–Sb: boulangerite, bournonite, heteromorphite, robinsonite
	Pezinok, Medzibrod, Suchá dolina	Fe–Sb: berthierite, jamesonite, gudmundite
dolomite–baryte–tetrahedrite	Dúbrava, Magurka, Rišianka	Cu–Sb–Pb–Bi: chalcostibite–emplectite solid solution, bournonite, jamesonite, zinkenite, tintinaite, bismuthinite–aikinite series
	Staré Mesto, Kriváň	Pb–Sb±Cu: bournonite, boulangerite, Ag: polybasite
quartz–Cu-sulfide	Hviezda, Paurovská, Bacúch	Cu–Pb–Bi: aikinite, friedrichite, lindströmite, krupkaite Pb–Bi±Ag: cosalite, galenobismutite, pavonite, heyrovskýite, gustavite, vikingite, lillianite
	Mlynná dolina, Veľká Trojica	Pb–Bi±Cu: nuffieldite, Sb-cosalite, Sb-galenobismutite, Sb-krupkaite, kobellite
	Bruchatý grúnik	Ag–Pb–Bi: nuffieldite, vikingite, heyrovskýite
galena–sphalerite	Soviansko, Čavoj, Marianka, Pod Babou	Cu–Pb–Sb: bournonite, boulangerite, meneghinite Ag: pyrargyrite, polybasite, stephanite
mineralisation not assigned to any stage	Čierna Lehota	Cu–Ag–Bi: hodrušite, cuprobismuthite, matildite, aikinite, bismuthinite

Three main sulfosalt assemblages were distinguished in this stage. The first one is the most abundant, occurring essentially in each occurrence, where this stage is present, prominently at Hviezda, Paurovská, and Bacúch. Ag-free, Fe-dominant tetrahedrite, and chalcopyrite associated with bismuthinite–aikinite derivatives (Fig. 14) with a higher (Cu+Pb)/Bi ratio, i.e. aikinite, friedrichite, lindströmite and krupkaite, are typical constituents. Other Bi-sulfosalts, such as kobellite, eclarite, nuffieldite, and cosalite, may also occur.

The second assemblage consists of members of the bismuthinite–aikinite series (Fig. 14) with lower (Cu+Pb)/Bi ratio, sometimes also associated with pavonite or galenobismuthite. Typical sulfosalts are bismuthinite, gladite, and pekoite, less commonly krupkaite (Hviezda, Paurovská, Bacúch).

The third, youngest assemblage contains Ag–Bi-rich galena associated with Pb–Bi–Ag sulfosalts of the lillianite homologous series. Vikingite, heyrovskýite, gustavite, lillianite, and cosalite are the main sulfosalt minerals, sometimes accompanied by nuffieldite and Ag-tetrahedrite (Bacúch, Bruchatý grúnik). All three assemblages belong to the quartz–Cu-sulfide stage; however, only two of them usually occur in individual occurrences.

Galena–sphalerite stage is mineralogically relatively heterogeneous in terms of sulfosalts. Tetrahedrite exhibits high Sb/(As+Sb) ratio and high Ag concentrations, with Ag/(Ag+Cu) ratios up to 0.5. For instance, the ores at the Soviansko deposit contain Bi-free bournonite and tetrahedrite, in lesser amounts also boulangerite and meneghinite. At other occurrences (Pod Babou, Čavoj, Marianka), small amounts of pyrargyrite, polybasite, and stephanite were described. Galena is always silver-free and the entire Ag content is bound in minerals of the tetrahedrite group, which contain 2–11, locally up to 31 wt. % Ag.

The distinctive **Ni–Bi mineralisation at Čierna Lehota** contains sulfosalts that are not encountered in other hydrothermal deposits or occurrences of the Tatric Superunit. The most common sulfosalt is hodrušite intergrown with kupčíkite and rare paděraite. Typical are also Bi sulfosalts of the cuprobismuthite homologous series associated with Bi–Fe tennantite. The other sulfosalts are bismuthinite and aikinite, both Sb-free. Cuprobismuthite was sometimes identified in association with Cu-bearing matildite and bismuthinite.

T-X conditions inferred from fluid inclusions and geothermometers

Molybdenite, scheelite, and arsenopyrite–pyrite–gold stages

Quartz from the early mineralisation stages hosts fluid inclusions corresponding to two compositional types. The first one is a CO_2-rich aqueous fluid, heterogeneous at the time of trapping. The second one is an aqueous fluid devoid of CO_2, most likely homogeneous at the time of trapping. Fluid inclusions of both types may be found together in one sample, they appear to be primary, but their time relationship is unclear. CO_2-rich aqueous fluids were detected at Dúbrava (Chovan et al. 1995a), Mlynná dolina (Majzlan et al. 2001), Staré Mesto (Bakoš et al. 2002), Kriváň-Banský žľab (Bakos & Chovan 2006), and Kyslá (Kantor & Eliáš 1983).

Salinity of the aqueous phase of the CO_2-rich aqueous fluids varied mostly between 3 and 15 wt. % NaCl eq. (Fig. 15a). Solid CO_2 melted near the triple point of pure CO_2 (−56.6 °C), thus indicating essentially pure CO_2 without admixture of other gases. Most of these inclusions decrepitated before reaching the total homogenisation. Those that persisted homogenised between 280 and 380 °C.

The conclusive assignment of the CO_2-rich fluids to the molybdenite, scheelite, and arsenopyrite-pyrite-gold stages is not as clear as the mineralogical differences among the individual stages. Quartz associated with stibnite and gold in Mlynná dolina contained abundant CO_2-rich aqueous inclusions (Majzlan et al. 2001). The authors assumed that these inclusions predated the formation of massive stibnite and belonged actually to earlier stages which also occur in this area. This assumption is supported by the infrared microscopic observations of only two-phase aqueous inclusions without visible CO_2 in the stibnite (Majzlan, unpublished data).

On the other hand, not all quartz assigned to the arsenopyrite–pyrite–gold stage contains CO_2-rich aqueous inclusions. For instance, quartz with gold from Nižná Boca contained only CO_2-free aqueous inclusions (Smirnov 2000; Smirnov et al. 2006). Quartz with arsenopyrite and pyrite from Kolársky vrch contained similar aqueous inclusions, but they were interpreted as secondary in origin (Andráš et al. 2002).

A gradual transition between CO_2-rich and CO_2-free aqueous inclusions was observed in the salinity *versus* homogenisation temperature diagram only for the molybdenite and scheelite stage at Dúbrava (Chovan et al. 1995a). The lack thereof in the arsenopyrite–pyrite–gold stage could be an evidence of two independent, chemically distinct mineralising fluids, or a bias caused by statistically insufficient number of measurements.

Homogenisation temperatures of fluid inclusions are consistent with independent geothermometers. Arsenopyrite thermometry indicated an average temperature of ≈425 °C for the Dúbrava deposit (Sachan & Chovan 1991) and similar temperatures, between 330 and 445 °C, have been calculated for other occurrences of the arsenopyrite–pyrite–gold stage in Nízke Tatry Mts. (Chovan et al. 2006, their table 7.2.1 and Fig. 8, this work). Temperatures of 300–410 °C were derived from the arsenopyrite composition for the Kolársky vrch and Trojárová deposits of Malé Karpaty Mts. (Chovan et al. 1994a; Andráš et al. 1999a). Chlorite (IIb-polytype trioctahedral) from alteration zones assigned to the early high-temperature crystallisation at Dúbrava yielded temperatures of 280–360 °C (Orvošová et al. 1998). In Pezinok deposit, chlorite from the distal alteration zone provided temperatures of 280–414 °C (Moravanský et al. 2001; Moravanský & Lipka 2004). Bláha & Bartoň (1991) estimated crystallisation temperatures of scheelite at the Kyslá deposit to around 470 °C, using the equilibrium oxygen isotope fractionation between coexisting quartz and scheelite. Using feldspar thermometry, Kohút (2006) estimated the temperature of hydrothermal homogenisation in the subsolidus state from the granitic rocks in the Nízke Tatry Mts. to 260–360 °C, but the direct assignment of these temperatures to the early, high-temperature stages, is questionable.

Stibnite–sphalerite–Pb–Sb-sulfosalts stage

Fluid inclusions in quartz associated with stibnite, sphalerite, and sulfosalts at the Dúbrava deposit contain aqueous fluids without CO_2 and other gas compounds (Chovan et al. 1995a). Homogenisation temperatures for quartz associated with stibnite were 105–160 °C and salinities varied between 15 and 23 wt. % NaCl eq. (Fig. 15a). Similar inclusions, albeit with a small amount of CO_2, were described from Kriváň, where homogenisation temperatures and salinities were 148–250 °C and 10–18 wt. % NaCl eq., respectively (Bakos & Chovan 2006). Homogenisation temperatures of aqueous inclusions clustered at 140 °C and salinities fluctuated between 8 and 25 wt. % NaCl eq. in quartz associated with stibnite from the Kolársky vrch deposit (Andráš et al. 1999b). Fluid inclusions in quartz associated with stibnite in Lomnistá and Suchá dolina homogenised at much higher temperatures, mainly between 200 and 320 °C (Čík 2010). Salinity was similar to that in the previous cases, i.e. between 11 and 22 wt. % NaCl eq. The genetic interpretation of the significant deviation in the homogenisation temperatures from other deposits remains unclear.

Observation and measurements of fluid inclusions in stibnite using infrared light showed that fluid inclusions trapped in quartz may not represent the ore-forming fluid (Chovan et al. 2010). Fluid inclusions in stibnite from Dúbrava, Malé Železné and Kolársky vrch showed homogenisation temperatures of 100–170 °C comparable to those determined in quartz (Fig. S2). However, salinities were much lower, between zero and 16 wt. % NaCl eq., clustering distinctly below 7 wt. % NaCl eq. This behaviour may be interpreted as reflecting an influx of a low-salinity fluid that triggered the precipitation of stibnite and associated ore minerals. Alternatively, fluids trapped in quartz and stibnite could be completely independent from each other, in terms of their origin and the time of formation. Some inclusions in the quartz that hosts sphalerite and Pb–Sb sulfosalts at Malé Železné also contained fluids of low salinity (Treichel 2016). These inclusions, however, were identified as secondary from the textural evidence. Hence, their assignment to a mineral assemblage or a geological event is ambiguous.

The fraction of smectite interlayers in illite/smectite from the proximal alteration zone is generally very low. Hence, the relatively high alteration temperatures were estimated based on the illite crystallinity: 180–200 °C at Dúbrava (Orvošová et al. 1998) and 185–245 °C in Pezinok (Moravanský & Lipka 2004). Feldspar thermometry on granitic rocks in the Nízke Tatry Mts. (Kohút 2006) detected a cluster of temperatures between 160–270 °C, interpreted as secondary, post-magmatic alteration of the granitic rocks. These low-temperature alteration features could be perhaps related to the stibnite–

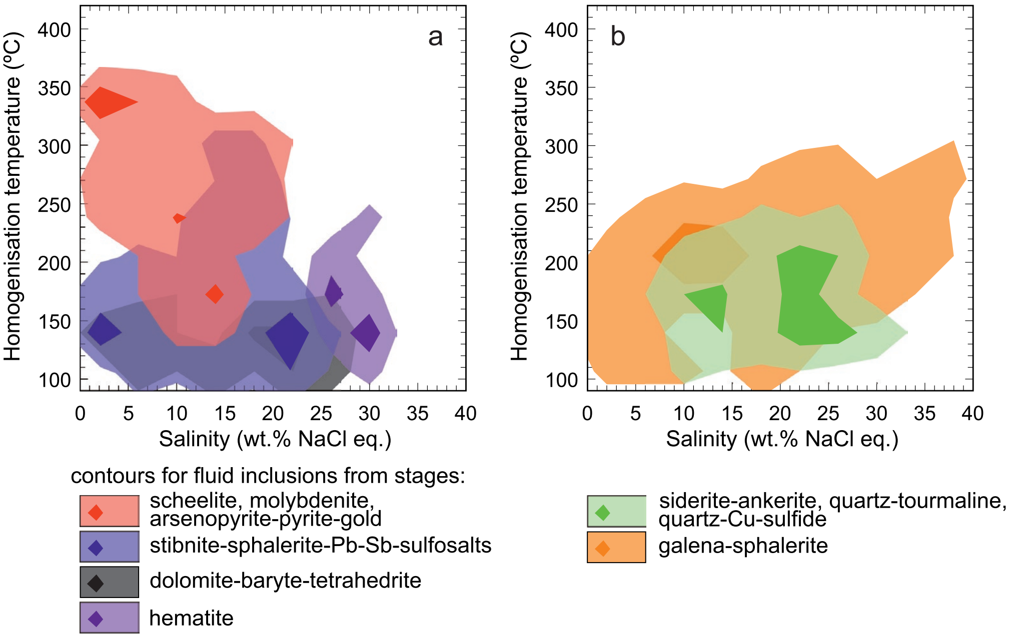


Fig. 15. Contour plots of fluids inclusion data distribution in the homogenisation temperature–salinity space, for various hydrothermal stages. Contours calculated for areas with low density of data points are shown by colors with lower saturation, for areas with high data density by colors with high saturation. Data from Chovan et al. (1995a), Smirnov (2000), Majzlan et al. (2001), Pršek & Chovan (2001), Bakos (2003), Ozdín (2003), Bakos & Chovan (2006), Bukovina (2006), Luptáková (2007), Michňová et al. (2008), Chovan et al. (2010, data in poster, not in abstract), Čík (2010), Kubač et al. (2014), Treichel (2016). Diagrams with individual data points and all contours are plotted in Supplementary Figs. S1–S6.

sphalerite–Pb–Sb-sulfosalts stage. The calculation of chemical gains and losses have shown that altered rocks were enriched in K, H_2O, CO_2, Sb, and S, and depleted in Ca, Na, Mg, and Fe^{3+} (Orvošová et al. 1998).

The variable mineral assemblages of the Sb-deposits hosted in black shales, exemplified by the Kolársky Vrch and Trojárová deposits, allow for semiquantitative estimates of sulfur and oxygen fugacities during the ore deposition. The first sub-stage of the ore formation in Pezinok (Fig. 7) commenced with the precipitation of arsenopyrite and pyrite (Chovan et al. 2002; Bukovina 2006), showing high crystallisation temperatures (Andráš et al. 1999a) and increased sulfur fugacities (Fig. 16, box 1). The transition to gudmundite and pyrrhotite at the end of the first sub-stage requires significant drop in both parameters (Fig. 16, box 2) that could perhaps be assigned to the desulfurisation of hydrothermal fluids triggered by reactions with the host rocks. Simple temperature drop, while retaining the high sulfur fugacity, would result in the precipitation of stibnite and pyrite, i.e. minerals not encountered in the first sub-stage.

The second sub-stage (Fig. 7) commenced with the precipitation of pyrrhotite, native antimony, and gudmundite. Microscopic observations, however, did not provide any clear clues to the precipitation sequence. They could only establish that the early minerals were replaced by later berthierite and finally by stibnite. Comparison of these observations with the phase diagram in Fig. 16 indicates that the earliest pyrrhotite+native antimony assemblage crystallised at the highest temperature (>280 °C). Temperature decrease led to the precipitation of pyrrhotite+gudmundite, followed by pyrrhotite+berthierite and pyrite+berthierite (all three possible within box 4 in Fig. 16). The final lowest temperature assemblage corresponds to stibnite+pyrite (box 5 in Fig. 16). Fig. 16 indicates that the mineral precipitation was principally controlled by the temperature decrease, whereas variations in the sulfur fugacity need not be large. This suggests that the ore-forming fluids were not buffered by host rocks.

The same sequence of minerals from the second sub-stage can also be discerned using a T-fO_2 plot (Fig. 17), showing that native antimony precipitated at the highest temperatures. As temperature decreases, the stability fields of gudmundite (circle 2), berthierite (3), and stibnite (4) were intersected. The mineral precipitation terminated by the formation of abundant primary kermesite (5) and valentinite–senarmonite (6). This path also documents the dominant role of temperature decrease in a mineralising fluid not buffered by host rocks, i.e. controlled by the adiabatic cooling. A significant increase in the oxygen fugacity is not necessary, but may aid in the final precipitation of primary Sb-sulfoxides and Sb-oxides.

Dolomite–baryte–tetrahedrite stage

Aqueous fluid inclusions in quartz belonging to this stage yielded homogenisation temperatures of 108–157 °C and salinities mostly between 1 and 14 wt. % NaCl eq. (Fig. 15a). All these data pertain to samples from the Dúbrava deposit (Chovan et al. 1995a). Fluid inclusion data corresponding to this stage are unavailable from other occurrences.

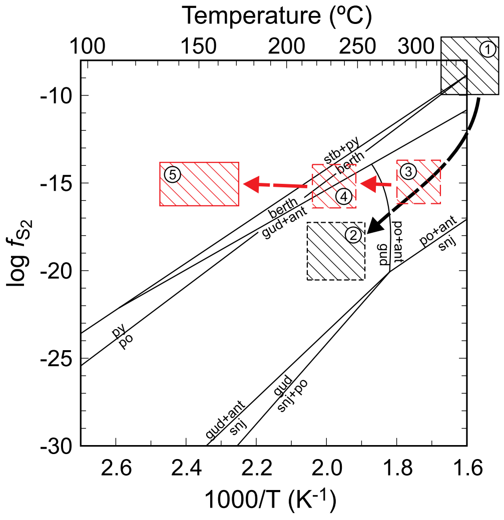


Fig. 16. A temperature–sulfur fugacity phase diagram for the system Fe–Sb–S (simplified after Williams-Jones & Normand 1997), with T–f_{S2} conditions assumed for different stages of mineralisation at the Sb deposit Pezinok. Mineral abbreviations: py=pyrite, po=pyrrhotite, stb=stibnite, berth=berthierite, gud=gudmundite, ant=antimony, snj=seinäjokite. Evolution of the fluids in the first sub-stage (cf. Fig. 7) is shown by black boxes, that for the second sub-stage by red boxes. Boxes with solid outlines are those for which temperature is known from geothermometers or fluid inclusions; for those with dashed outlines, temperature is assumed (cf. Chovan et al. 2006).

Siderite–ankerite, quartz–tourmaline, and quartz–Cu-sulfide stages

Only sparse fluid inclusion data are available from these stages (Fig. 15b). Pršek & Chovan (2001) reported on measurements of fluid inclusions in ankerite and quartz from Bacúch in the Veporic Superunit. Ankerite was interpreted here as a part of the quartz–Cu-sulfide stage. Aqueous inclusions in ankerite exhibited the highest homogenisation temperatures (173–246 °C) and salinities (17–24 wt. % NaCl eq.), whereas those in the associated quartz homogenised at lower temperatures (98–201 °C) and had variable, though generally lower salinities (9–24 wt. % NaCl eq.). In all cases, the fluids corresponded to the NaCl–KCl–H_2O system devoid of CO_2. Two inclusions in quartz associated with chalcopyrite and tetrahedrite from Hviezda yielded homogenisation temperatures of 157 and 187 °C, and salinities of 17.9 and 22 wt. % NaCl eq. (Majzlan et al. 2001).

Bakos (2003) inspected a number of small occurrences of the quartz–Cu-sulfide stage in Tatry Mts. with the aim to decipher their mineralogy and to determine the fluid composition. Only a few samples contained measurable fluid inclusions, which homogenised at similar temperatures clustered mostly between 130 and 160 °C. The salinities varied substantially, from 14 wt. % NaCl eq. to those significantly surpassing

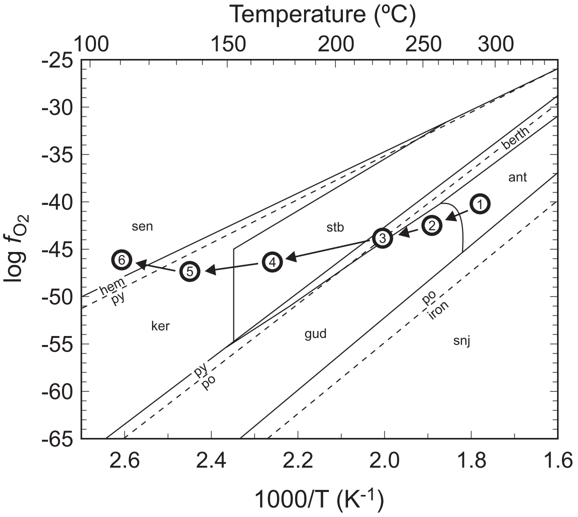


Fig. 17. A temperature–oxygen fugacity phase diagram for the system Fe–Sb–S (simplified after Williams-Jones & Normand 1997), with T–f_{O2} conditions assumed for different mineral assemblages of the second sub-stage of mineralisation at the Sb deposit Pezinok (cf. Fig. 7). Mineral abbreviations: py=pyrite, po=pyrrhotite, stb=stibnite, berth=berthierite, gud=gudmundite, ant=antimony, snj=seinäjokite, ker=kermesite, hem=hematite, sen=senarmontite.

the halite saturation at room temperature (>26 wt. % NaCl). Measurements of halite and ice dissolution temperatures yielded $CaCl_2$/(NaCl+$CaCl_2$) ratios of 0.14–0.26 and 0.44–0.55. The existence of two inclusion groups characterised by the different $CaCl_2$/(NaCl+$CaCl_2$) ratios may be either real or fictitious, the latter resulting from a low number of measurements.

Fluid inclusions in the quartz–tourmaline stage of the Tatric Superunit were studied only in a single sample from Koleso (Ozdín 2003). These fluid inclusions trapped in quartz associated with chamosite homogenised at 180–210 °C, whereas salinities ranged between 20 and 25 wt. % NaCl eq. Eutectic temperatures indicated the H_2O–NaCl–$CaCl_2$ system. The author mentioned also CO_2 gas in the aqueous inclusions, but did not provide any supporting information (temperatures of phase transitions, Raman spectra). The chlorite thermometer applied to the chamosite yielded temperatures of 364±11 °C. A similar datum, 361±15 °C, was reported for chamosite from Predsvätodušná (Ozdín 2001).

Michňová et al. (2008) measured fluid inclusions in tourmaline from quartz veinlets of Podlipa associated with albite, rutile, pyrite, and monazite. Total homogenisation temperatures of the tourmaline-hosted aqueous inclusions varied between 122 and 227 °C, and salinities covered the range from 3.4 to 14.4 wt. % NaCl eq.

Galena–sphalerite stage

Fluid inclusion studies revealed fluids with different temperatures and salinities despite very similar mineralogical content (Fig. 15b). In the Soviansko deposit with the largest proportional representation of this stage, Luptáková (2007) found primary aqueous inclusions in sphalerite, and quartz that homogenised at 230–280 °C and 290 °C, respectively. These temperatures are somewhat lower than the 330–380 °C range estimated from the chemical composition of chlorite–chamosite that occurs directly inside the veins. This could indicate a larger pressure correction in this deposit, although such high temperatures have not been encountered in any other occurrence of the galena–sphalerite stage. Salinities of aqueous inclusions from the Soviansko deposit corresponded to 19–39 wt. % NaCl eq. and the fluids were enriched in $CaCl_2$. The $CaCl_2$/(NaCl+$CaCl_2$) ratios were between 0.08 and 0.35, most frequently around 0.2. Pseudosecondary inclusions exhibited lower homogenisation temperatures and salinities, being thus indicative of progressive cooling and fluid mixing. Fluid inclusions in later sphalerite generation yielded homogenisation temperatures of 120–170 °C, i.e. much lower than those in the early sphalerite. Temperatures of ≈200 °C were also confirmed by measurements of illite crystallinity at Soviansko (Luptáková 2007) in the zones most proximal to the ore veins. Detailed crystallographic analyses showed that the abundance of the $2M_1$ illite polytype slightly increases and that of the $1M_d$ polytype slightly decreases toward the veins within the illite zone (Luptáková 2007). The least abundant $1M_t$ polytype remains constant across the studied profiles.

Increased crystallisation temperatures of ores at the Soviansko deposit are corroborated by the presence of meneghinite that is stable presumably above 300 °C (Pruseth et al. 1995). Myrmekitic intergrowths of galena and bournonite at this deposit (Luptáková 2007) and at Marianka in Malé Karpaty Mts. (Kubač et al. 2014) were interpreted as breakdown products of meneghinite.

Fluid inclusions in quartz from the galena–sphalerite stage homogenised mostly between 180 and 230 °C in the Dve Vody deposit (Luptáková 2007). A few inclusions in sphalerite gave slightly lower homogenisation temperatures, between 150 and 170 °C. Salinity showed two maxima at 8–12 and 14–16 wt. % NaCl eq. Fluid inclusions with a higher salinity (23–25 wt. % NaCl eq.) were interpreted as pseudosecondary or secondary.

Aqueous fluid inclusions homogenised mostly between 110 and 160 °C at Brestová in Mlynná dolina, where salinities of 16–22 wt. % NaCl eq. were determined (Majzlan et al. 2001). At Marianka, homogenisation temperatures and salinities clustered at 100–150 °C and 0.1–19.1 wt. % NaCl eq., respectively (Kubač et al. 2014).

Baryte stage

A few measurements of fluid inclusions in baryte from Dúbrava (Chovan et al. 1995a) and Soviansko (Luptáková 2007) showed homogenisation temperatures of 100–157 °C (Fig. 15a) and increased salinities, between 15 and 25 wt. % NaCl eq., with both NaCl and $CaCl_2$ as the major electrolytes dissolved in water.

Hematite stage

There is only a limited set of data available for this stage from the Soviansko deposit (Luptáková 2007). Fluid inclusions corresponded to the H_2O–NaCl–$CaCl_2$ system. Homogenisation temperatures and salinities clustered at 110–230 °C and 26–31 wt. % NaCl eq., respectively (Fig. 15a).

Pressures and burial depths

Depth of formation can be of interest when considering the contribution of near-surface, especially meteoric fluids. Only fragmental data with relatively large uncertainties are available for some deposits. The available data are summarised in Table 2.

Smirnov (2000) estimated the formation depth of 11.8 km for the arsenopyrite–pyrite–gold stage of Nižná Boca from isochores of primary aqueous inclusions trapped in a homogeneous state combined with independent temperature estimates from the arsenopyrite thermometer.

Depths could also be estimated from densities of the spatially associated CO_2-rich and CO_2-free fluid inclusions, assuming that these inclusions are also genetically related. The minimum homogenisation temperatures of CO_2-rich fluids trapped in a heterogeneous state indicate true formation temperatures. On the other hand, the homogenisation temperature of homogeneously trapped CO_2-free fluids indicates a minimum formation temperature. From the temperature difference, pressures and depths can be calculated using isochores of the homogeneously trapped fluids. Using the microthermometric data from the Dúbrava deposit, the estimated formation depth of the arsenopyrite–pyrite–gold stage corresponded to 4–7 km, assuming the lithostatic load and the average density of crustal rocks ($2.7\ g\cdot cm^{-3}$).

Formation depths of the gold-bearing quartz veins at Kriváň were estimated at 5–8 km (Bakos & Chovan 2006). Majzlan et al. (2001) calculated the formation pressure of 150–350 MPa for CO_2-rich fluids from Mlynná dolina; these pressures correspond to burial depths of 6–13 km, assuming a lithostatic load. As mentioned above, the genetic correlation of these fluids to ore minerals (stibnite and gold) is equivocal. Chovan et al. (1995a) argued that the formation pressure of fluid inclusions with CO_2-rich fluids should be at least 200 MPa (corresponding to a depth of ≈7.5 km), based on the high density of the CO_2-rich phase.

Bláha & Bartoň (1991) calculated the pressure of 200 MPa for the scheelite mineralisation at Kyslá, corresponding to a depth of 7.5 km assuming the lithostatic load. They used for the calculation the difference between the homogenisation temperature of aqueous fluid inclusions (260 °C) and the estimated true formation temperature (470 °C) calculated from the equilibrium oxygen isotope fractionation between scheelite and quartz.

Pršek & Chovan (2001) estimated the formation depth of 4–7 km for quartz and ankerite, both likely being a part of the quartz–Cu-sulfide stage at Bacúch. Luptáková (2007) inferred the depth of ≈8 km from the halite dissolution temperature and vapor-unsaturated liquidus for the brine with 40 wt. % NaCl trapped in minerals of the galena–sphalerite stage from the Soviansko deposit. This calculation pertains to the high-temperature sphalerite. She also estimated the formation depth of the late hematite–quartz veinlets to <4 km.

Stable isotopes

Oxygen, carbon, hydrogen

Water in the fluid precipitating the early, high-temperature scheelite, molybdenite, and arsenopyrite–pyrite–gold stages at Dúbrava (Chovan et al. 1995a) and Kyslá deposits (Bláha & Bartoň 1991) was assigned increased $\delta^{18}O$ values (Fig. 18, boxes 1–4). Bláha & Bartoň (1991) also determined δD_{SMOW} values in fluid inclusions in quartz (−38 ‰) and arsenopyrite (−11 ‰) from the scheelite stage. All these values were attributed to metamorphic or magmatic waters (see also Hurai et al. 2002b).

In contrast, fluids precipitating quartz and dolomite associated with stibnite, Pb–Sb sulfosalts, tetrahedrite, and baryte at Dúbrava and Soviansko were depleted in ^{18}O (Fig. 18, boxes 8–12), what was interpreted as a contribution of seawater and/or meteoric water components. The $\delta^{13}C$ values of dolomite from the Dúbrava (Chovan et al. 2006) and Pezinok deposits (Andráš et al. 1999b) pointed to CO_2 produced by the thermal degradation of organic matter, with a contribution of isotopically heavier carbon, perhaps of magmatic origin. The calculated $\delta^{13}C$ values for CO_2 in the fluids varied mostly between −13 and −15 ‰.

Isotopic composition of carbonates from the siderite–ankerite stage deviates much from that of the dolomite associated with stibnite and Pb–Sb sulfosalts. The calculated equilibrium $\delta^{18}O_{fluid}$ values are much heavier (Fig. 18, box 5) and they may correspond to marine or formation waters influenced by the isotopic exchange with high-grade metamorphic rocks (Hurai et al. 2002b). Similar or even heavier $\delta^{18}O$ values were also determined for carbonates of the galena–sphalerite stage from Soviansko and Pod Babou (Fig. 18, boxes 6 and 7). The $\delta^{13}C$ values of the fluid, calculated from the isotopic composition of carbonates and temperature determined from crush-leach analyses (171–293 °C), varied between −7 to −8 ‰. These values may correspond to a mixture of carbon from a deep source, carbonate rocks and organic matter (Chovan et al. 2006). Systematic differences in the isotopic composition of the siderite–magnesite and ankerite–dolomite carbonates indicate higher crystallisation temperature for ankerite–dolomite, assuming unchanged isotopic composition of the fluid.

Sulfur

Sulfur isotopes in the mineralisations considered here were determined by Kantor & Eliáš (1983), Sachan & Kantor

Table 2: Summary of physical, chemical, and isotopic properties of fluids assigned to the individual stages defined in this work, together with assumed fluid source, examples of deposits and occurrences, and age of the stages.

Stage	**Examples**	**Fluids and their main components**	**Th, salinities (°C, wt.% NaCl eq.)** [a]	**Other temperature data (°C)** [a]	**Estim. form. depth (km)** [b]	**Age** [c]	**Isotopic composition of the fluid (‰)**	**Fluid source**
molybdenite	Malé Železné, Dúbrava	aqueous–carbonic, heter., H_2O–CO_2–NaCl	280–380, 3–15			late Variscan (Carboniferous)	$\delta^{18}O$ +3 to +5	Variscan magmatism
scheelite	Kyslá, Dúbrava	aqueous–carbonic, heter., H_2O–CO_2–NaCl	280–380, 3–15	470 (isotopic equilibrium quartz–scheelite)	8	Variscan	$\delta^{18}O$ +3 to +8; $\delta^{34}S$ −0.5 to 1.0, δD −38 and −11	
arsenopyrite–pyrite–gold	Dúbrava, Magurka, Dve Vody, Kriváň, Nižná Boca	aqueous–carbonic, heter., H_2O–CO_2–NaCl	280–380, 3–15	280–360 (chlorite thermometry); 330–445 (arsenopyrite thermometry)	estimates scattered, 4–13	late Variscan (Carboniferous)	$\delta^{34}S$ −2 to −10; $\delta^{18}O$ +5 to +8	Variscan metamorphism
		aqueous, hom., H_2O–NaCl	150–250, 5–20					
stibnite–sphalerite–Pb–Sb-sulfosalts	Dúbrava, Pezinok, Magurka, Medzibrod, Lom, Rišianka	aqueous, hom. (in stibnite), H_2O–NaCl	100–170, 0–16			late Variscan (Carboniferous)	$\delta^{13}C$ −13 to −15 %; $\delta^{34}S$ +5 to +8 (Dúbrava); $\delta^{18}O$ −10 to 0	Variscan metamorphism, with contribution of sea water or meteoric fluids
		aqueous, hom. (in quartz), H_2O–NaCl	120–200, 8–25	180–200 (illite crystallinity)				
dolomite–baryte–tetrahedrite	Dúbrava, Magurka	aqueous, hom., H_2O–NaCl–$CaCl_2$	100–160, 1–14			Alpine (Cretaceous)	$\delta^{18}O$ −5 to +1	modified basinal brines
siderite–ankerite	Vyšná Boca, Bacúch			170–300 (Na/K ratio in leachates)			$\delta^{18}O$ +2 to +9	formation waters modified by interaction with high-grade metamorphic rocks
quartz–tourmaline	Vyšná Boca	aqueous, hom., H_2O–NaCl–$CaCl_2$	180–210, 20–25	300–370 (chlorite thermometry)		Alpine (Cretaceous)		
quartz–Cu-sulfide	Vyšná Boca, Špania Dolina	aqueous, hom., H_2O–NaCl–$CaCl_2$	120–220, 10–26		4–7		$\delta^{34}S$ +6 to +10	formation waters modified by interaction with high-grade metamorphic rocks
galena–sphalerite	Sovиansko, Pod Babou	aqueous, hom., H_2O–NaCl–$CaCl_2$	250–300, 19–39	300–380 (chlorite thermometry), >300 (stability of meneghinite)	8	Alpine	$\delta^{13}C$ −7 to −8 %	
		aqueous, hom., H_2O–NaCl–$CaCl_2$	120–200, 0–25	200 (illite crystallinity)				
baryte	Dúbrava, Nižné Matejkovo, Trangoška	aqueous, hom., H_2O–$CaCl_2$	100–160, 15–25			Alpine	$\delta^{18}O$ −2 to +3	
hematite	Magurka, Soviansko, Nižná Boca	aqueous, hom., H_2O–$CaCl_2$	110–230, 26–31		<4	Alpine		

[a] typical temperatures, without outliers
[b] estimated formation depth
[c] see Majzlan et al. (2020)

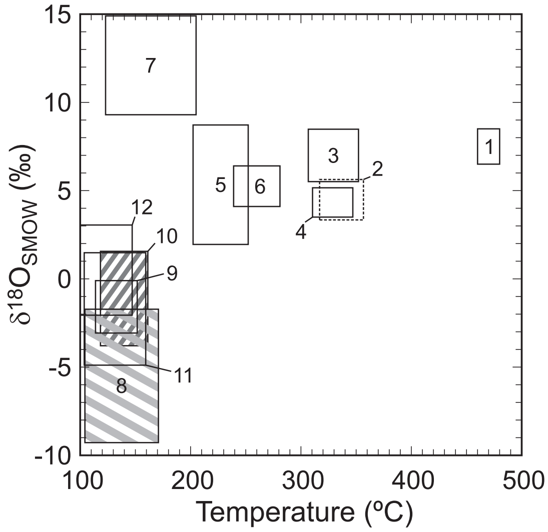


Fig. 18. Temperature and isotope composition ($\delta^{18}O$) of hydrothermal fluids for different stages in the Tatric Superunit. 1 — scheelite stage, Kyslá; 2 — scheelite stage, Dúbrava; 3 — arsenopyrite–pyrite–gold stage, Dúbrava; 4 — molybdenite stage, Dúbrava; 5 — siderite–ankerite stage, Tatric Superunit; 6 — carbonates in siderite–ankerite (?) stage, Soviansko; 7 — calcite in galena–sphalerite (?) stage, Pod Babou; 8, 9 — stibnite–sphalerite–Pb–Sb-sulfosalts stage, Dúbrava (data from quartz and Fe-dolomite, respectively); 10, 11 — dolomite–baryte–tetrahedrite stage, Dúbrava (data for tetrahedrite- and baryte-dominated samples, respectively); 12 — baryte stage, Soviansko. Data from Bláha & Bartoň (1991), Hurai et al. (2002b), Luptáková (2007).

(1990), Bláha (1994), Ferenčíková & Repčok (1995), Chovan et al. (1998b), Luptáková (2007), Luptáková et al. (2016) and interpreted by Chovan et al. (2006). These interpretations are adopted and reiterated hereafter.

The calculated $\delta^{34}S$ for the parental fluid that formed pyrite ranged from −0.5 to 1 ‰ (scheelite stage, Dúbrava, Nízke Tatry Mts.), 3.9 ‰ (arsenopyrite–pyrite–gold stage, Dúbrava), and from −2 to −10 ‰ (early arsenopyrite, see Fig. 7, Pezinok, Malé Karpaty Mts.). The data from Dúbrava can be interpreted as indicative of sulfur derived from a deep magmatic source. At Pezinok, a mixture of the deep-sourced sulfur with isotopically light sedimentary sulfur can be discerned. This interpretation is in accord with the known spatial relationship of the hydrothermal ores with syngenetic volcano-sedimentary mineralisations.

The $\delta^{34}S$ values for the ore-forming fluids parental to the stibnite–sphalerite–Pb–Sb-sulfosalts stage correspond to 5–8 ‰ in the Dúbrava and to the range from −3 to 2 ‰ in the Pezinok deposit. Analysed stibnite and sphalerite yielded similar results. Similar values of $\delta^{34}S$ were reported for some stibnite deposits in the Bohemian Massif (Němec & Zachariáš 2018) and explained by the inherited isotopic composition from the local Neoproterozoic and early Paleozoic rocks with disseminated sulfides (Zachariáš et al. 2014). If magmatic source of sulfur was assumed, the enrichment in ^{34}S could be explained by the presence or predominance of sulfate ions, perhaps compatible with the presumably oxidising fluids near the end of mineral-forming processes, as indicated by mineralogical investigations. The sulfur isotope ratios in ores of Malé Karpaty Mts. are consistently depleted in ^{34}S compared to Nízke Tatry Mts., for the reasons explained above.

Isotopic composition of chalcopyrite and tennantite from the quartz–Cu-sulfide stage (Podlipa) is 6.7 to 9.8 ‰ (Luptáková et al. 2016). These $\delta^{34}S$ values may be very close to those for H_2S in the fluid and could be interpreted as sulfur from a deep metamorphic source.

Radiogenic lead isotopes

Lead isotopes from the ore deposits of the Tatric and Veporic Superunits were reported by Kantor & Rybár (1964), Chernyshev et al. (1984) and Andráš et al. (2010), and their results are presented in a $\Delta\beta$-$\Delta\gamma$ plot (Fig. 19). All data from Chernyshev et al. (1984) and Andráš et al. (2010) fall in the field of the crustal lead related to magmatism. The data from the Tatric Superunit are clearly split into two groups. One group is represented by Pezinok, Pernek, and Kuchyňa deposits hosted in black shales and amphibolites. Although all these data fall into the field of magmatic crustal lead, they are slightly shifted toward the submarine hydrothermal field. Hence, lead isotopes in these deposits are influenced by those from the spatially associated syngenetic, stratiform pyrite mineralisation (Chovan et al. 1994a).

Remaining deposits of the Tatric Superunit project in the central part of the field for crustal magmatic lead. This group includes Nízke Tatry, Tatry, Strážovské vrchy, and Malé Karpaty Mts. Some samples from Pezinok hosted in high-grade metamorphic or granitoid rocks also fall in this group. These occurrences are not located far away from those hosted in black shales and amphibolites, but their Pb-isotope signature deviates markedly. These results point to a strong local influence of the host rocks on the elemental budget of ore-forming fluids. Even though the zones of strong alterations are restricted to narrow haloes around the veins, the cryptic fluid-rock interaction must have played an important role in large volumes of country rocks.

The older data of Kantor & Rybár (1964) agree generally with the recent results, albeit showing a larger scatter. Model ages reported by Chernyshev et al. (1984) and Andráš et al. (2010) are difficult to put into the geological context. In some cases, the Variscan age has been assigned to veins which penetrate Triassic sediments, thus making these ages doubtful. In addition, the total range of the model ages is very large (>200 Ma) even for similar deposits. Hence, we refrain from interpreting the geological significance of these ages.

Discussion and conclusions

The physical and chemical properties of the fluids typical for the mineralisation stages are summarised in Table 2. This table also lists the calculated isotopic compositions of

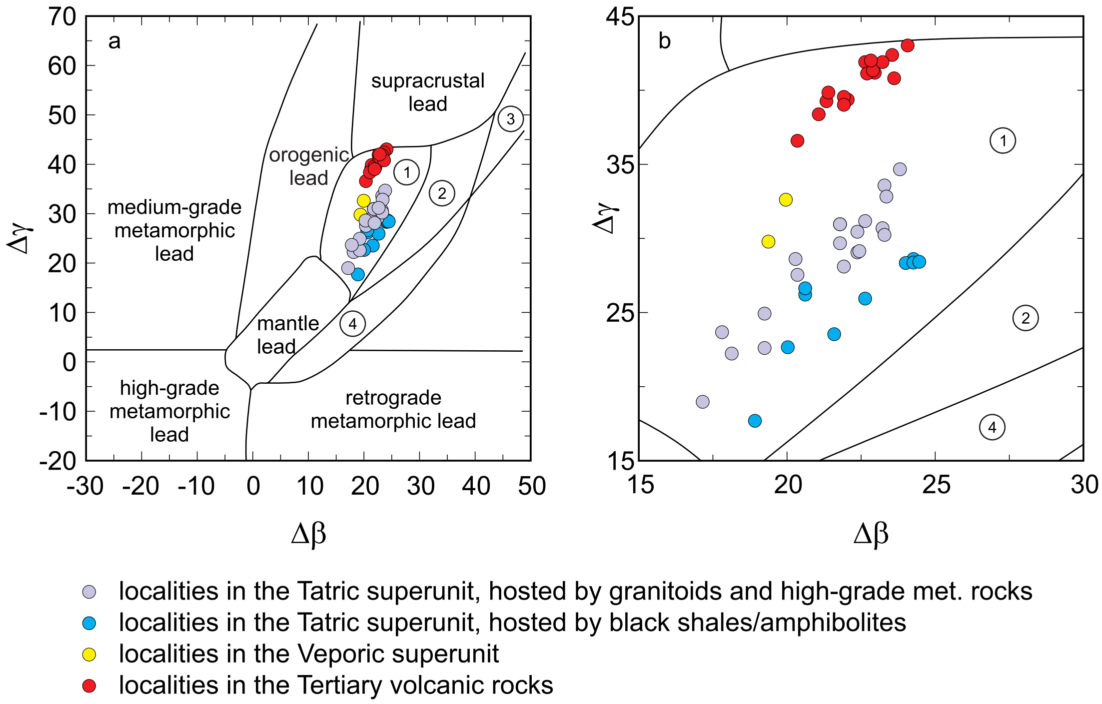


Fig. 19. A Δβ–Δγ plot (see Tan et al. 2015 for the definition of Δβ and Δγ) (**a** — the entire plot; **b** — detail populated by the data) for the ore deposits and occurrences from the Western Carpathians, with projections of the data from Chernyshev et al. (1984) and Andráš et al. (2010). Data for mineralisations in the Tertiary volcanic rocks in the Western Carpathians are also shown for comparison. The fields of different types of lead are from Zhu (1998 in Tan et al. 2015) and are either marked by their name or by a number (1 — crustal lead related to magmatism; 2 — crustal lead related to sedimentation; 3 — ancient shale lead; 4 — hydrothermal submarine lead).

the fluids, presumed source of the fluids and the age of the invididual stages.

The scheelite, molybdenite, and arsenopyrite–pyrite–gold stages are associated with low-salinity (0–10 wt. % NaCl eq.), CO_2-rich aqueous fluids, with typical temperatures between 300–350 °C. The spatially associated CO_2-free aqueous inclusions exhibit lower homogenisation temperatures and higher salinities, up to 20 wt. % NaCl eq. Isotopic composition of the fluids ($\delta^{18}O$, δD) suggests magmatic or metamorphic source. Such an interpretation agrees with relatively large estimated depths of formation, down to 12 km. The estimated negligible ore-forming potential of granitic rocks (Kohút 2006), together with the chemical and stable isotope compositions of the ore-forming fluids, point to their metamorphogenic origin. The estimated age of 330–320 Ma (Majzlan et al. 2020) and the comparison to similar deposits in the Bohemian Massif (Němec & Zachariáš 2018) and elsewhere in the European Variscides (Romer & Kroner 2018) suggest the affiliation with shear-zone hosted Au mineralisations generated in the late stages of the formation of Variscan terranes. Romer & Kroner (2018) linked the European Variscan Au deposits, in general, to the Cambrian and Ordovician sediments accumulated in the pre-Variscan times on a stable continental crust. Such sediments or a record thereof, however, are missing in the Western Carpathians.

The stibnite–sphalerite–Pb–Sb-sulfosalts stage is related to lower temperature fluids dominated by NaCl and KCl. The fluids contain traces of CO_2. Homogenisation temperatures cluster roughly between 105 and 170 °C. Salinities vary widely but they did not reach the halite saturation limit. Fluid inclusions in stibnite and some populations in quartz show low salinities discrepant with those in the fluid inclusions in the spatially associated quartz. More abundant berthierite or even its predominance over stibnite at some localities points to a decreased sulfur fugacity of the ore-forming fluid. Such localities are concentrated in metamorphic rocks of the Tatric Superunit. The depletion in sulfur could be assigned to the interaction of the ore fluids with the host metamorphic rocks which are locally richer in Fe than the granitoid rocks. Fluid-rock interactions resulted in the precipitation of pyrite and the depletion in sulfur of the remnant fluids. Berthierite is usually missing in the ore occurrences hosted in granites. Variscan age of these stages (Majzlan et al. 2020) and relatively low temperatures suggest that minerals of this age could have been precipitated from the same fluid as the earlier arsenopyrite–pyrite–gold stage, after simple fluid cooling. This view is also in line with the conclusions of Romer & Kroner (2018) that the Variscan mineralised shear zones were active under a wide range of conditions, from high-pressure and high-temperature (0.5–1.0 GPa, 700 °C) to low-pressure and low-temperature (< 0.1 GPa, 200–300 °C).

Precipitation of mineral phases that require elevated oxygen fugacity (e.g., senarmontite, kermesite) was observed at numerous deposits in the Nízke Tatry and Malé Karpaty Mts. Even though this phenomenon could be interpreted as reflecting the mixing with an oxidised, low-temperature, perhaps meteoric fluids, the precipitation of Sb-oxides could follow the precipitation of stibnite even at constant $\log fO_2$ (Fig. 17), provided that the fluids still contained excessive dissolved Sb. On the other hand, the precipitation of Cl-bearing sulfosalts (e.g., dadsonite) favours the elevated chlorine activity in the late ore-forming fluids, thus speaking against the dilution with meteoric waters.

Isotope data together with dilution trends revealed in salinity–homogenisation temperature plots (Chovan et al. 1995a) were taken as an evidence for the influx of meteoric fluids during the stibnite–sphalerite–Pb–Sb-sulfosalts stage. Chovan et al. (1995a) postulated "*epithermal origin*" of the ores with stibnite and Pb–Sb sulfosalts. The participation of meteoric fluids in the deep crust is a matter of a long debate; it was favoured, for instance, by Bouchot et al. (2000) and Stober et al. (2016), and opposed by Bierlein et al. (2006). Isotopic evidence for influx of meteoric waters, provided especially by carbonates and quartz (Fig. 18) could be accepted or challenged because of pronounced heterogeneity of the carbonates and their repeated mobilisation (cf. Majzlan et al. 2020).

Parental fluids of the galena–sphalerite and dolomite–baryte–tetrahedrite stages are characterised mostly by lower homogenisation temperatures and higher salinities, often exceeding the halite saturation limit. Fluid inclusions from these stages show also commonly higher $CaCl_2/(CaCl_2+NaCl)$ ratios, 0.08–0.35, compared to those from the earlier stages. Significantly higher homogenisation temperatures recorded at Soviansko agree with the occurrence of meneghinite and its breakdown products believed to represent high-temperature (>300 °C) phases. In other deposits and occurrences, e.g., Marianka, however, the presence of presumably high-temperature meneghinite contradicts the low homogenisation temperatures of fluid inclusions in quartz. In general, fluid inclusions in the galena–sphalerite stage paint an inconsistent picture as the fluid temperatures and chemical compositions vary widely. It is likely that different fluid types were able to remobilize lead and zinc and to generate mineralogically similar ores. Isotopic data suggest that these fluids were modified basinal brines (Chovan et al. 2006), circulating and depositing their metal load in early Cretaceous times (Majzlan et al. 2020).

There are only a few microthermometric and isotopic data on the fluids of the siderite–ankerite, quartz–tourmaline, and quartz–Cu-sulfide stages in the Tatric Superunit. The isotopic data for siderite and ankerite ($\delta^{18}O$, $\delta^{13}C$) did not constrain the source of CO_2 or H_2O (Chovan et al. 2006). The fluids responsible for the quartz–Cu-sulfide stage are interpreted as basinal brines, strongly modified by dehydration reactions and cation exchange with crustal rocks at elevated temperatures. More research is needed to adopt more abundant information gained from the Veporic and Gemeric Superunits (e.g., Hurai 1983; Hurai et al. 2002a, 2008) also for the Tatric Superunit.

In summary, the hydrothermal mineralisations described here seem to have formed from three principal types of fluids with specific chemical compositions and physical properties (Hurai et al. 2002b; Chovan et al. 2006). Similar properties, however, do not imply that such fluids have been generated and circulated in the same or similar tectonic settings and at the same time. For this reason, we refrain from the grouping of mineralisations according to the corresponding fluid types. Further distinction of the mineralisations and their assignment to the tectonothermal events during the evolution of the Western Carpathians (Plašienka 2018) requires more analytical results.

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Supplement

Definitions of terms

This work is aimed to classify, compare, and group hydrothermal ore mineralisations in the Tatric Superunit. In order to reach that goal, some of the terms need to be exactly defined in order to avoid some misinterpretations.

A **mineralisation stage** or a **stage** (see also Chovan et al. 1994, p. 8) is understood as a single step in the process of formation of hydrothermal ores. The stages are separated from each other by inter-mineralisation tectonics, cross-cutting relationships, brecciated textures, etc. The mineral and chemical content of a stage is similar among different deposits and occurrences. Deviations, if detected, are minor. In their previous classification, Slavkay & Chovan (1996) used the term "mineralisation" in this context. Here, we opt for the term "stage" to emphasize both the temporal and material (mineral and chemical) similarities among all occurrences of one stage. Some of the previous studies summarized here used the term period in the same context.

A **sub-stage** is a section of a stage separated from other sub-stages of the same stage by intra-mineralisation tectonics. Sub-stages usually also differ among each other by their mineral content. This term is only sparsely used in this work.

An **assemblage** is a set of minerals that occur together in one stage or sub-stage. This set need not include all minerals of this stage or sub-stage. One stage or sub-stage may contain several assemblages. An assemblage, as discussed hereafter, need not have originated under conditions of a thermodynamic equilibrium.

Localities studied

All localities mentioned in this paper are in the area of today's Slovakia, with the exception of Ornak in Poland. Names of the localities evolved historically and through the use in recent research projects and publications. Some localities are named after proximal administration units (villages, towns). Others are named after small settlements (e.g., Magurka), valleys and streams (e.g., Mlynná dolina, Kľačianka) or hills (e.g., Kriváň). In some cases, each occurrence in a cluster is given a unique name (Rišianka, Kľačianka, Krámec) even though other clusters of a similar size are described as a single deposit (e.g., Dúbrava). Some deposits are usually called by the name of the adjoining village and the local name (e.g., Jasenie-Kyslá), especially if those local names are commonly used throughout the Slovak territory. In order to maintain consistency, the deposits and occurrences are referred to in this work only by their local name, without identification of the appropriate administration unit (town, village). In that way, lengthy names (e.g., Partizánska Ľupča-Malé Železné) can be avoided. Individual localities within a cluster, adits, and veins are specified with the reference to the deposit name (e.g., Dve Vody-Mistrík). An exception is in the captions to Fig. 2, where some localities, shown in the maps but not mentioned in the text, are listed together with their administration units. All names of the localities studied, with notes and corresponding administration units, are listed in the Supporting electronic information below.

List of the localities and local names mentioned in the text of this publication

Bacúch — village in central Slovakia (Brezno county, Banská Bystrica region). There are these localities in the territory of Bacúch, mentioned in this paper: →Jánov Grúň, →Sokolová dolina. A sketch of the localities around Bacúch can be found in Pršek & Chovan (2001, their fig. 1).

Brestová — small occurrence of Pb–Zn ores in →Mlynná dolina, administrative part of Brezno.

Brezno — city in central Slovakia (Brezno county, Banská Bystrica region).

Bruchatý Grúnik — small occurrence of siderite–sulfide mineralisation, administrative part of →Vyšná Boca. A detailed map with localisation of this occurrence can be found in Ozdín (2003, his fig. 2, page 22).

Brusno — village in central Slovakia (Banská Bystrica county, Banská Bystrica region). Small occurrences in →Sopotnická dolina belong administratively to this village.

Čavoj — village in central Slovakia (Prievidza county, Trenčín region). A detailed sketch of the adits and dumps can be found in Mikuš et al. (2003, their fig. 1).

Chopec — small occurrence of quartz-gold ores, administrative part of →Vyšná Boca. A detailed map with localisation of this occurrence can be found in Ozdín (2003, his fig. 2, page 22).

Chvojnica — village in central Slovakia (Prievidza county, Trenčín region).

Chyžné — village in eastern Slovakia (Revúca county, Banská Bystrica region). Small occurrence of Sb mineralisation. GPS coordinates of one of the adits: 48°41.384' N, 20°12.803' E.

Čierna Lehota — village in central Slovakia (Bánovce nad Bebravou county, Trenčín region). A detailed sketch of the adits and dumps can be found in Mikuš et al. (2013, their fig. 1).

Dolná Lehota — village in central Slovakia (Brezno county, Banská Bystrica region). There are these deposits and localities in the territory of Dolná Lehota, mentioned in this paper: →Dve Vody, →Lom, →Riavka.

Donovaly — village in central Slovakia (Banská Bystrica county, Banská Bystrica region).

Dúbrava — village in central Slovakia (Liptovský Mikuláš county, Žilina region). This large Sb—Au deposit was mined until 1992. Several veins were opened with a number of adits. The data presented in this paper refer to the entire deposit as there are no major differences among the individual veins.

Dve Vody — moderately large Sb–Au deposit that belongs to the administrative territory of the village of →Dolná Lehota. The main ore field is located in the Štelerová dolina valley. The adits Horná Vyšná, Vyšná Spodná, Hrable, and →Mistrík are located outside of the main ore field. GPS coordinates of the Mistrík adit: 48°53.462' N, 19°31.596' E. Approximate GPS coordinates of the middle of the main ore field: 48°53.887' N, 19°30.581' E. Sketch of the dumps can be found in Majzlan et al. (2002, their fig. 3).

Ďurková — local name in the vicinity of the →Magurka settlement, administrative part of Partizánska Ľupča.

Harmanec — village in central Slovakia (Banská Bystrica county, Banská Bystrica region). Small occurrence of quartz–gold and siderite–sulfide mineralisation. A sketch of the old mines and their dumps can be found in Bakos et al. (2004).

Helena — small occurrence of siderite–sulfide mineralisation, administrative part of →Vyšná Boca. A detailed map with localisation of this occurrence can be found in Ozdín (2003, his fig. 2, page 22).

Heľpa — village in central Slovakia (Brezno county, Banská Bystrica region). Small occurrence of metamorphosed pyrite–pyrrhotite ores.

Hiadeľ — village in central Slovakia (Banská Bystrica county, Banská Bystrica region). Small occurrence with weak Sb mineralisation. GPS coordinates of the dump: 48°50.033' N, 19°18.805' E.

Hviezda — small occurrence quartz–chalcopyrite ores in →Mlynná dolina. It is probably located in the administrative territories of Brezno but very close to the administrative area of the village of Bystrá.

Husárka — small occurrence of Sb mineralisation, administrative part of →Jasenie. GPS coordinates of one of the dumps: 48°53.917' N, 19°23.467' E. Coordinates from Čík (2010).

Jánov Grúň — small occurrence of siderite–sulfide ores, administrative part of →Bacúch. A sketch of the localities around Bacúch can be found in Pršek and Chovan (2001, their fig. 1).

Jarabá — village in central Slovakia (Brezno county, Banská Bystrica region). There are these localities in the territory of Jarabá, mentioned in this paper: →Kumštová dolina.

Jasenie — village in central Slovakia (Brezno county, Banská Bystrica region). There are these localities in the territory of Jasenie, mentioned in this paper: →Husárka, →Soviansko, →Kyslá, →Lomnistá.

Kapustisko — local name in the vicinity of the →Magurka settlement, administrative part of Partizánska Ľupča.

Kľačianka — small occurrence of Sb ores, near →Magurka, administrative part of Partizánska Ľupča. A detailed sketch of the localities in the vicinity of Magurka can be found in Bakos et al. (2000, their fig. 1).

Kliesňová dolina — valley in Nízke Tatry Mts, administrative part of →Vyšná Boca. Occurrence of siderite-sulfide mineralisation. GPS coordinates of one of the dumps (where the sample shown in Fig. 1e in this paper was collected): 48°54.882' N, 19°44.078' E.

Klinisko — area around the occurrence →Malé Železné.

Kolársky vrch — large Sb deposit in the administrative part of the city of →Pezinok.

Kolba — small occurrence of Ni-Co ores, administrative part of →Ľubietová.

Koleso — small occurrence of siderite-sulfide mineralisation, administrative part of →Brezno. A detailed map with localisation of this occurrence can be found in Ozdín (2003, his fig. 2, page 22).

Korytnica — part of Liptovská osada, village in central Slovakia (Ružomberok county, Žilina region). Minute ore occurrence.

Kyslá — deposit of W (scheelite) ores, targeted by exploration in the 1970s and 1980s but never opened for commercial exploitation. Administrative part of →Jasenie.

Krámec — small occurrence of Sb ores, near →Magurka, administrative part of Partizánska Ľupča. A detailed sketch of the localities in the vicinity of Magurka can be found in Bakos et al. (2000, their fig. 1). GPS coordinates of the dumps: 48°57.976'N, 19°28.148'E; 48°57.997'N, 19°28.154'E.

Kriváň — peak in the →Vysoké Tatry Mts.

Kumštová dolina — small occurrence of siderite–sulfide ores, administrative part of →Jarabá. A detailed map with localisation of this occurrence can be found in Ozdín (2003, his fig. 2, page 22).

Kumštové sedlo — mountain pass in Nízke Tatry Mts., administrative part of →Vyšná Boca.

Latiborská hoľa — local name in the vicinity of the →Magurka settlement, administrative part of Partizánska Ľupča. A detailed sketch of the localities in the vicinity of Magurka can be found in Bakos et al. (2000, their fig. 1).

Liptovská Lúžna — village in central Slovakia (Ružomberok county, Žilina region). Minute occurrence of Sb ores, marked in the geological map of Biely et al. (1992).

Lom — small occurrence of Sb–Au mineralisation, administrative part of →Dolná Lehota. GPS coordinates of the lower adit: 48°53.045' N, 19°33.029' E; upper adit: 48°53.081' N, 19°33.059' E.

Lomnistá — small occurrence of Sb–Au ores, administrative part of →Jasenie. GPS coordinates of the dump of the Dolná Anton adit: 48°53.900' N, 19°28.883' E; of the dump of the Horná Anton adit: 48°53.883' N, 19°28.967' E; dump of the Emília adit: 48°54.100' N, 19°28.417' E; dump of the Gregor adit: 48°54.150' N, 19°28.350' E; dump of the Jozef adit: 48°54.140' N, 19°28.300' E. All coordinates from Čík (2010).

Ľubietová — village in central Slovakia (Banská Bystrica county, Banská Bystrica region). There are the following localities in the territory of Ľubietová, mentioned in this paper: →Podlipa, →Svätodušná, →Predsvätodušná, →Kolba.

Ľupčianka — stream flowing through the →Magurka settlement down to →Partizánska Ľupča. Locally rich placers for gold.

Magurka — settlement in Nízke Tatry Mts., administrative part of Partizánska Ľupča. Large Sb–Au deposit, mined until

1923. There are the following localities in the vicinity of Magurka, mentioned in this paper: →Ďurková, →Kapustisko, →Kľačianka, →Latiborská hoľa, →Krámec, →Ľupčianka, →Mestská hora, →Rišianka, →Ritterstein. GPS coordinates of the dump of Kilián adit: 48°56.234’ N, 19°25.686’ E; dump of Adolf adit: 48°56.189’ N, 19°25.717’ E; dump of Pillersdorf adit: 48°56.029’ N, 19°25.128’ E. A detailed sketch of the adits and the assumed strike of the ore veins can be found in Chovan et al. (1995, their fig. 1).

Malá studená dolina — valley in →Vysoké Tatry Mts.

Malé Železné — small occurrence of Sb ores, administrative part of →Partizánska Ľupča. GPS coordinates of the lower dump: 48°58.040’ N, 19°24.268’ E.

Marianka — village in western Slovakia (Malacky county, Bratislava region). Minute occurrence of Pb- Zn mineralisation was found in a local quarry, with GPS coordinates 48°14.890’ N, 17°4.705’ E. Coordinates from Kubač et al. (2014).

Medzibrod — village in central Slovakia (Banská Bystrica county, Banská Bystrica region). A deposit of Sb. A sketch of the localities can be found in Lalinská & Chovan (2006).

Mestská hora — local name in the vicinity of the →Magurka settlement, administrative part of Partizánska Ľupča. A detailed sketch of the localities in the vicinity of Magurka can be found in Bakos et al. (2000, their fig. 1).

Mistrík — adit in the vicinity of the →Dve Vody deposit.

Mlynná dolina — valley in Nízke Tatry Mts, most of which belongs to the administrative area of →Brezno. There are these occurrences in Mlynná dolina, mentioned in this paper: →Brestová, →Hviezda, →Zingoty. A detailed map with all occurrences in Mlynná dolina can be found in Majzlan and Chovan (1997, their fig. 1).

Murárikova rokľa — side valley in →Malá studená dolina.

Nižná Boca — village in central Slovakia (Liptovský Mikuláš county, Žilina region).

Nižné Matejkovo — occurrence of baryte–sulfide mineralisation, administrative part of →Ružomberok.

Ornak — peak in the →Vysoké Tatry Mts., in Poland.

Partizánska Ľupča — village in central Slovakia (Liptovský Mikuláš county, Žilina region). There are the following localities in the territory of Partizánska Ľupča, mentioned in this paper: →Magurka, →Malé Železné, →Kapustisko, →Latiborská hoľa, →Mestská hora, →Ďurková, →Rišianka.

Paurovská — small occurrence of siderite–sulfide mineralisation, administrative part of →Vyšná Boca. A detailed map with localisation of this occurrence can be found in Ozdín (2003, his fig. 2, page 22).

Pernek — village in western Slovakia (Malacky county, Bratislava region). The occurrences of Sb mineralisation near Pernek are usually known under the name ‘Pernek’. A small occurrence of Pb–Zn ores in the administrative area of Pernek is known as ‘→Pod Babou’.

Pezinok — town in western Slovakia (Pezinok county, Bratislava region). The large Sb deposit in the administrative area of Pezinok is called →Kolársky vrch. Arsenopyrite–pyrite mineralisation targeted by intensive exploration in the 1980’s was located at →Trojárová. A small occurrence of quartz–gold ores, known under the names →Staré Mesto, Slnečné údolie, or Limbach, falls also in the administrative area of Pezinok.

Piesky — ore field of the →Špania Dolina district, administrative part of Špania Dolina. GPS coordinates of one of the old dumps: 48 49.072’ N, 19 7.890’ E.

Pod Babou — a small occurrence of Pb–Zn ores, administrative part of →Pernek.

Podlipa – deposit of secondary Cu ores, administrative part of →Ľubietová.

Polkanová — part of the village of Staré Hory (Banská Bystrica county, Banská Bystrica region). Small occurrence of copper ores.

Predsvätodušná — small occurrence of secondary Cu ores, administrative part of →Ľubietová.

Riavka — small occurrence of Sb mineralisation, administrative part of →Dolná Lehota.

Rišianka — small occurrence of Sb ores, near →Magurka, administrative part of →Partizánska Ľupča. A detailed sketch of the localities in the vicinity of Magurka can be found in Bakos et al. (2000, their fig. 1). GPS coordinates of the dump #4 (as numbered in Daniel et al. 1984): 48°58.118’N, 19°27.585’E; dump #1: 48°58.153’N, 19°27.601’E; dump #3: 48°58.168’N, 19°27.569’E; dump #2: 48°58.195’N, 19°27.563’E.

Ritterstein — one of the adits and dumps of the →Magurka deposit.

Ružomberok — city in central Slovakia (Ružomberok county, Žilina region). The occurrence →Nižné Matejkovo belongs administratively to this city.

Sokolová dolina — small occurrence of siderite–sulfide ores, administrative part of →Bacúch. A sketch of the localities around Bacúch can be found in Pršek & Chovan (2001, their fig. 1).

Sopotnická dolina — valley in Nízke Tatry Mts., administrative part of →Brusno. There are small occurrences of gold–stibnite ores in this valley.

Soviansko — moderately large Pb–Zn deposit, administrative part of →Jasenie. In older publications, the deposit was also called Sova. GPS coordinates: dump of the Emil adit: 48°53.566‘ N, 19°26.471‘ E. Dump of adit G: 48°53.570’ N, 19°26.582’ E. Dump of adit A: 48°53.581’ N, 19°26.609’ E. Dump of adit P: 48°53.595’ N, 19°26.753’ E. Dump of adit R: 48°53.653’ N, 19°26.795’ E. Dump of adit S: 48°53.706’ N, 19°26.857’ E. All coordinates from Luptáková (2007).

Špania Dolina — village in central Slovakia (Banská Bystrica county, Banská Bystrica region). Deposit of copper ores. The locality →Piesky belongs to the Špania Dolina ore district.

Staré Mesto — a small occurrence of quartz–gold ores, administrative part of →Pezinok.

Striebornica – small surficial mining area that belongs to the →Magurka deposit.

Suchá dolina — valley in Nízke Tatry Mts., small occurrence of Sb ores, administrative part of →Jasenie. Coordinates of the dumps: 48°51.483’ N, 19°25.417’ E; 48°51.517’ N, 19°25.400’ E; 48°51.517’ N, 19°25.233’ E. All coordinates from Čík (2010).

Svätodušná — small occurrence of secondary Cu ores, administrative part of →Ľubietová.

Trangoška — small occurrence of barite with tetrahedrite, administrative part of →Horná Lehota.

Trojárová — deposit of arsenopyrite–pyrite ores, targeted by exploration in the 1980’s, administrative area of →Pezinok.

Veľká Trojica — small occurrence of siderite–sulfide ores, administrative part of Jarabá.

Veľké Oružné — small occurrence of Sb ores, near →Magurka, administrative part of Partizánska Ľupča. A detailed sketch of the localities in the vicinity of Magurka can be found in Bakos et al. (2000, their fig. 1).

Vyšná Boca — village in central Slovakia (Liptovský Mikuláš county, Žilina region). There are the following localities in the territory of Vyšná Boca, mentioned in this paper: →Bruchatý Grúnik, →Chopec, →Helena, →Kliesňová dolina, →Paurovská.

Vysoké Tatry — mountain range in the northern part of central Slovakia.

Zach — ore field near the village of →Nižná Boca.

Zingoty — small occurrence of siderite–sulfide ores in the →Mlynná dolina, administrative part of Brezno.

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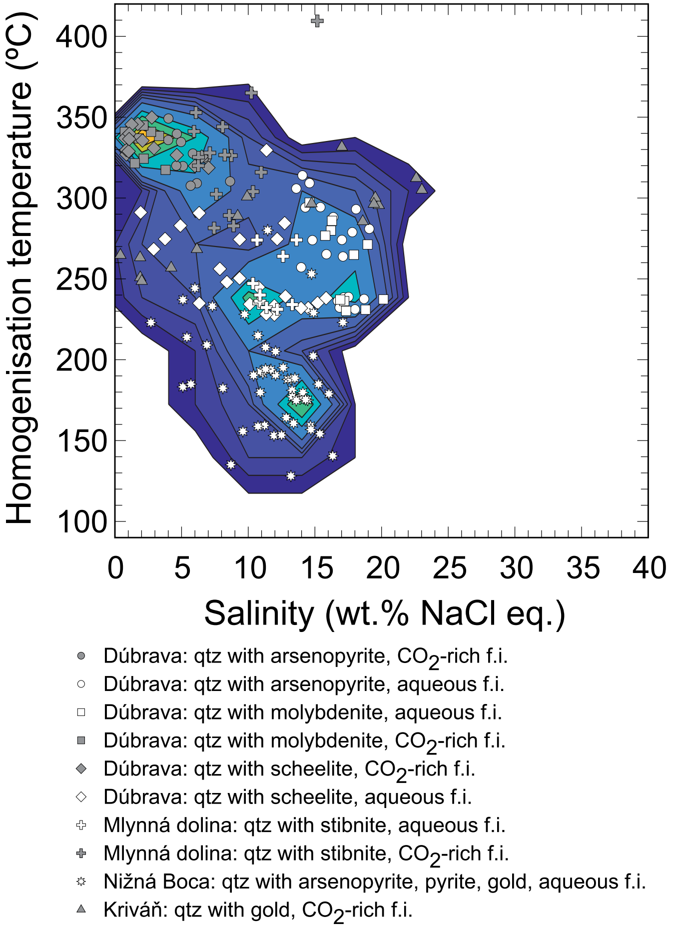

Fig. S1. Salinities and homogenisation temperatures of fluid inclusions related to the scheelite, molybdenite, and arsenopyrite–pyrite–gold stages. Data from: Dúbrava (Chovan et al. 1995a), Mlynná dolina (Majzlan et al. 2001), Nižná Boca (Smirnov 2000), Vysoké Tatry (Bakos & Chovan 2006). qtz=quartz, f.i.=fluid inclusions.

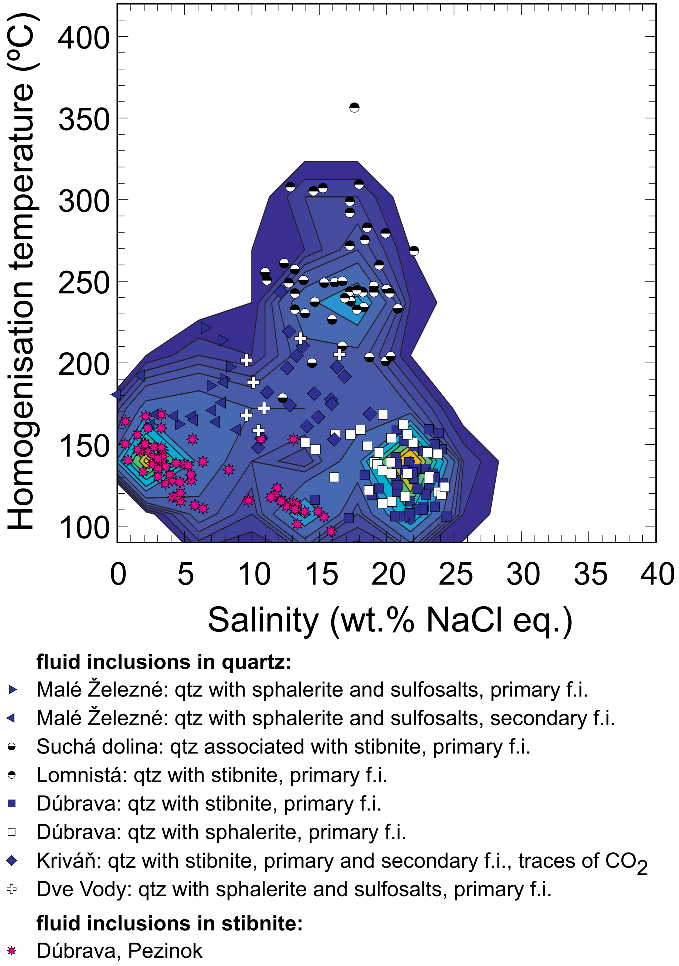

Fig. S2. Salinities and homogenisation temperatures of fluid inclusions related to the stibnite and sphalerite–sulfosalt stages. All measured inclusions were two-phase, aqueous. Data from: Malé Železné (Treichel 2016), Suchá dolina, Lomnistá (Čík 2010), Dúbrava (inclusions in quartz: Chovan et al. 1995a), Dúbrava (inclusions in stibnite: Chovan et al. 2010), Pezinok (inclusions in stibnite: Bukovina 2006, Chovan et al. 2010), Kriváň (Bakos and Chovan 2006), Dve Vody (Luptákova 2007).

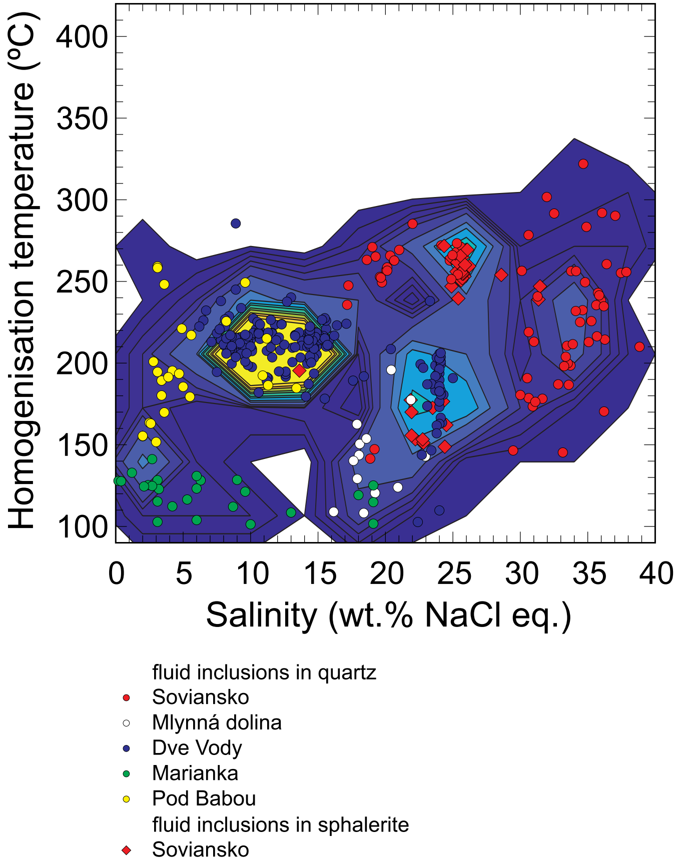

Fig. S3. Salinities and homogenisation temperatures of fluid inclusions related to the galena–sphalerite stage. All measured inclusions were two-phase, aqueous. Data from: Soviansko, Dve Vody, Pod Babou (Luptáková 2007), Mlynná dolina (Majzlan et al. 2001), Marianka (Kubač et al. 2014).

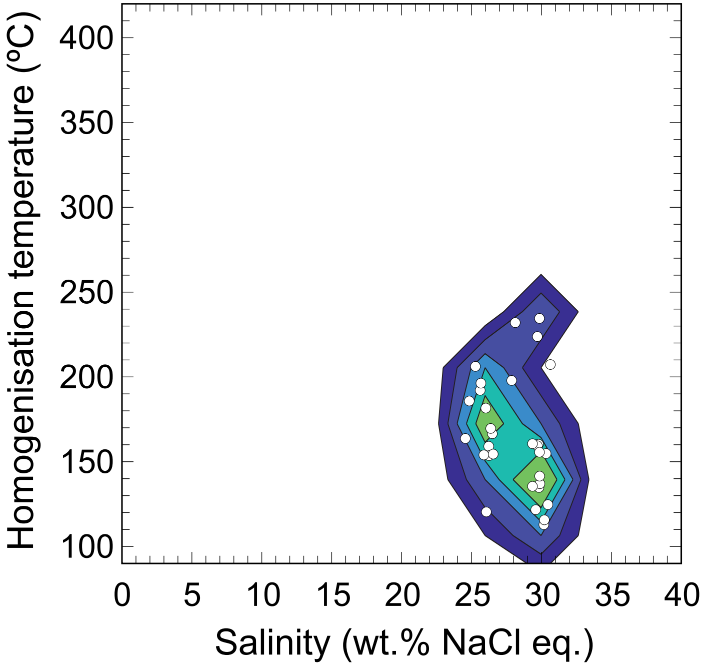

Fig. S4. Salinities and homogenisation temperatures of fluid inclusions related to the hematite stages. All measured inclusions were two-phase, aqueous. Data from fluid inclusions in quartz from Soviansko (Luptáková 2007).

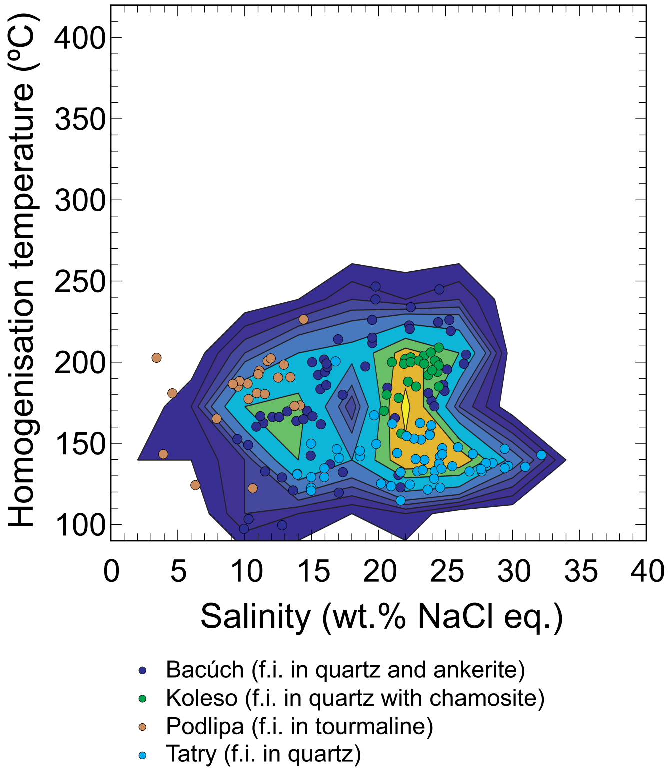

Fig. S5. Salinities and homogenisation temperatures of fluid inclusions related to the siderite–ankerite, quartz–tourmaline, and quartz–Cu-sulfide stage. All measured inclusions were two-phase, aqueous. Data from: Bacúch (Pršek & Chovan 2001), Koleso (Ozdín 2003), Podlipa (Michňová et al. 2008), Tatry (Bakos 2003).

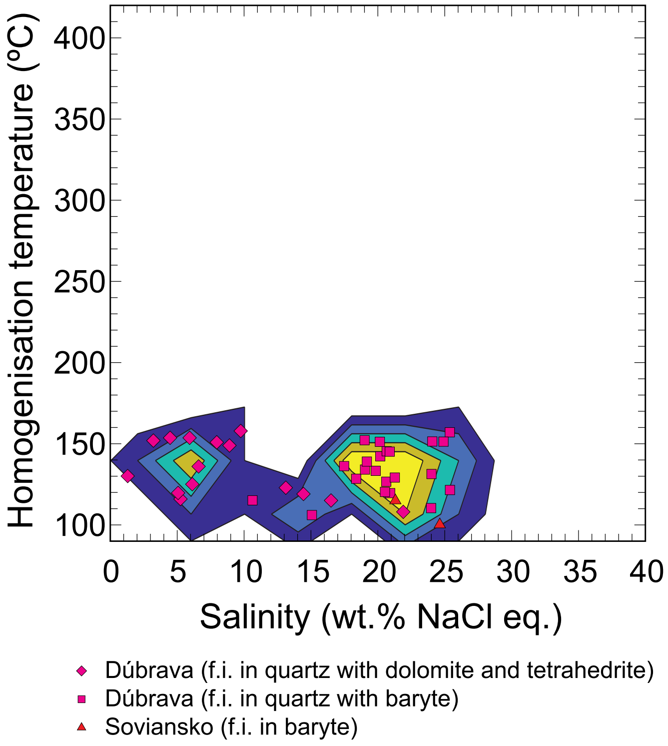

Fig. S6. Salinities and homogenisation temperatures of fluid inclusions related to the dolomite–baryte–tetrahedrite stage. All measured inclusions were two-phase, aqueous. Data from: Dúbrava (Chovan et al. 1995a), Soviansko (Luptáková 2007).