

ORIGIN OF SULFIDE-BEARING HYDROTHERMAL DEPOSITS HOSTED BY VARISCAN BASEMENT OF THE WESTERN CARPATHIANS IN LIGHT OF NEW FLUID INCLUSION, STABLE ISOTOPE AND GEOCHRONOLOGICAL DATA

V. HURAI¹, M. CHOVAN¹, J. KRÁL², J. LEXA² and W. PROCHASKA³

¹*Department of Mineralogy and Petrology, Comenius University, Mlynská dolina G, 842 15 Bratislava, Slovakia*

²*Geological Survey, Mlynská dolina I, 817 04 Bratislava, Slovakia*

³*Department of Geosciences, University of Leoben, A-8700 Leoben, Austria*

Abstract: Fluid inclusion and stable isotope data have discriminated among several contrasting types of hydrothermal mineralisations in the Variscan basement of the Western Carpathians. High temperature assemblages with scheelite, molybdenite and gold have been triggered by influx of low-saline CO₂-enriched aqueous fluids of magmatic or metamorphic origin. Mesothermal quartz-sulfidic assemblages have precipitated from NaCl-KCl aqueous solutions, representing mostly deeply circulating meteoric water. CaCl₂-bearing brines revealed in quartz-carbonate, carbonate-sulfide, baryte and hematite assemblages correspond to formation- or halite-fractionated marine water chemically modified and enriched in ¹⁸O during interaction with crustal rocks at low fluid/rock ratio.

Key words: fluid inclusions, stable isotopes, ore deposits, Variscan basement, Western Carpathians

The Central Western Carpathians are subdivided into the Tatricum, Veporicum, and Gemericum units separated by major mid-Cretaceous thrust-faults. The Tatric basement is composed of larger fragments with Variscan nappe structure, consisting of medium- to high-grade metamorphic rocks intruded by Variscan granitoid plutons. The Tatric unmetamorphosed sedimentary cover comprises characteristic lithological members dated from Upper Carboniferous to Middle Cretaceous. Mesozoic sedimentary nappes overthrust the Tatric basement/cover complexes. The Alpine low-to-medium grade metamorphism has influenced only several domains of the Central Western Carpathians (the Veporicum unit).

Hydrothermal ore mineralisations hosted by the Variscan basement can be divided into several major types: molybdenum, tungsten (scheelite), arsenopyrite-pyrite (\pm gold) and

quartz-gold, atimony with Cu, Pb, Sb sulphides, siderite with Cu, Sb sulphides, barite, galena – base-metal, hematite.

Microthermometry data from these deposits have permitted three principal types of ore-forming fluids to be distinguished:

- 1) Low-to-moderately saline aqueous solutions with high CO₂ contents,
- 2) medium saline aqueous containing NaCl and KCl as the main soluble compounds,
- 3) brines with significant CaCl₂ concentrations and total dissolved salt content ranging 15-35 wt. % NaCl eq.

Inclusions of the first group have been revealed in quartz from high *T* (~400°C) assemblages with scheelite, molybdenite, and Au-bearing arsenopyrite (e.g., the Dúbrava deposit). Similar fluids have been identified also in quartz associating with arsenopyrite, pyrite and gold at the Pezinok – Staré Mesto, Dúbrava, and Mlynná dolina deposits. The gold-bearing sulfidic assemblages, however, contain sometimes only aqueous fluid inclusions with 2-15 wt. % NaCl eq., resembling the second group of the inclusion fluids (e.g. the Nižná Boca deposit). Formation temperatures derived from arsenopyrite thermometry vary in the range between 320-480°C.

Aqueous fluids of the second group are typical of mesothermal assemblages with quartz, Fe-dolomite, chalcopyrite, tetrahedrite, sphalerite, zinckenite, berthierite and antimonite superimposed to the earlier high temperature assemblages. Typical total salt contents range between 10-20 wt. % NaCl eq.

CaCl₂-bearing fluids of the third group have been revealed in quartz-carbonate, carbonate-sulfide, baryte and hematite assemblages. These fluids have played particularly important role during formation of siderite-ankerite veins, superimposed quartz-Fe-dolomite-sulfide assemblages and baryte. The CaCl₂-rich fluids of the third group are typical also of the chalcopyrite-galena and hematite assemblages of the Jasenie-Soviansko deposit (the Nízke Tatry Mts.). Range of salinities in these fluids varies typically between 15-35 wt. %. Thus, the inclusions frequently contain a small halite cube along with a halite-saturated brine and a vapour bubble at room temperature. Another typical feature of the brine inclusions of the third group is their high density manifested by the bubble disappearance prior to halite dissolution upon heating. Less saline inclusions of the third group usually contain small amount (up to 2 mole %) of carbon dioxide. The CaCl₂/(CaCl₂+NaCl) weight ratio fluctuates within the range of 0.1-0.6. Formation *PT* conditions derived from microthermometry data have been estimated at 170-230°C and 1-2 kbar in the Gemericum unit (Hurai et al., 2002), and 250-290°C and 2-2.5 kbar in the tatricum unit (Chovan et al., 2000).

Application of infrared microscopy has permitted direct observation of primary fluid inclusions trapped in stibnite (Chovan et al., 1999). Eutectic temperatures ($>-30^{\circ}\text{C}$) indicate simple NaCl-KCl solutions devoid of divalent cations. Microthermometry data are separated into two groups. The first group (10-15 wt. % NaCl eq., $\sim 1.05 \text{ g/cm}^3$) consistent with the fluid inclusion data from associated quartz pertains probably to primary stibnite growing from the typical aqueous fluids of the second group. Another group, however, reveals a lower salinity (0-5 wt. % NaCl eq.) and less dense ($0.95\text{-}1.0 \text{ g/cm}^3$) aqueous fluid, which has been probably trapped during stibnite recrystallisation.

Combined stable isotope and microthermometry data have discriminated among the three defined types of the ore-forming fluids (Fig. 1). The high- T assemblages containing CO_2 -rich aqueous fluid inclusions must be linked with ^{18}O -enriched water of magmatic/hydrothermal origin. In contrast, mesothermal quartz-Fe-dolomite-sulfidic assemblages with stibnite, chalcopyrite, sphalerite, berthierite, and zinckenite have precipitated from hydrothermal fluids containing isotopically lighter water of meteoric origin.

Contrasting with those two groups are the fluids observed in the siderite/ankerite veins and associated quartz-sulfidic assemblages (chalcopyrite, tetrahedrite). These mineralisations have crystallised at relatively low temperatures ($170\text{-}290^{\circ}\text{C}$) from isotopically heavier aqueous fluids ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = 2.5\text{-}9.3 \text{ ‰ SMOW}$) and high Br concentration (Fig. 2). Low relative chlorinity rules out formation of the brines by dissolution of evaporites. The high Br and ^{18}O concentrations accompanied by increased Ca^{2+} and Li^+ contents are believed to reflect intense interaction of deeply circulating formation waters or evaporated marine waters with medium grade metamorphic rocks at low fluid/rock ratios.

Carbon dioxide equilibrated with the siderite-forming aqueous fluids exhibits depleted $\delta^{13}\text{C}$ values ranging between -5 and -13 ‰ PDB . These values are interpreted to reflect a mixture of CO_2 coming from dissolved matrix carbonates in the surrounding rocks, and that liberated during thermal decarboxylation of organic acids, mainly acetates, which normally occur in formation waters. High densities of the siderite-forming fluids must be attributed to high fluid pressures (1-2 kbar) and deep circulation (at least 4 km) of evaporated marine water isotopically enriched and chemically modified by water-rock interaction.

Progressively increasing fluid pressures and temperatures during crystallisation of vein and drusy siderite in the Gemicum unit could be attributed to a compressional regime and crustal thickening triggered by Jurassic subduction or to a continental collision during Middle Cretaceous times. In contrast, the high temperature assemblages (scheelite, molybdenite, arsenopyrite, gold, pyrite), and most likely also substantial part of the stibnite are linked with

Variscan magmatic and/or metamorphic processes. The Alpine rejuvenization in the Variscan basement, however, has played more important role than previously assumed.

References:

- Chovan M., Luptáková J., Huraiová M. (2000) Mineralogy of the Pb-ore occurrence at Jasenie – Soviansko. Unpublished manuscript, Archive PFUK, Bratislava, 1-73.
- Chovan M., Lüders V., Hurai V. (1999) Fluid inclusions and C,O-isotope constraints on the origin of granodiorite-hosted Sb-As-Au-W deposit at Dúbrava (Nízke Tatry Nts., Western Carpathians). *Terra Nostra* 99/6, 71-72
- Hurai V., Harčová E., Huraiová M., Ozdín D., Prochaska W., Wiegerová A. (2002) Origin of siderite veins in the Western Carpathians I. *P-T-X- $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$* relations in ore-forming fluids of the Rudňany deposit. *Ore Geology Reviews* (in print)

Fig. 1. Temperature and oxygen isotope composition of water for selected ore assemblages of the tatricum, veporicum and gemicum units recalculated from isotope composition of gangue minerals (quartz, carbonate) and from fluid inclusion data.

Fig. 2. Na-Cl-Br plot of leachate analyses of fluid inclusions trapped in siderite and quartz from siderite veins in the Gemicum and Tatricum units. Crosses – metasomatic siderite deposits at Erzberg and Schendleck (Eastern Alps), squares – vein siderite, quartz-sulfide and quartz-tourmaline assemblages from the Gemicum unit, shaded circles – vein siderite, quartz-chalcopyrite and quartz-tourmaline assemblages from the Tatricum and Veporicum units.

Fig.1.

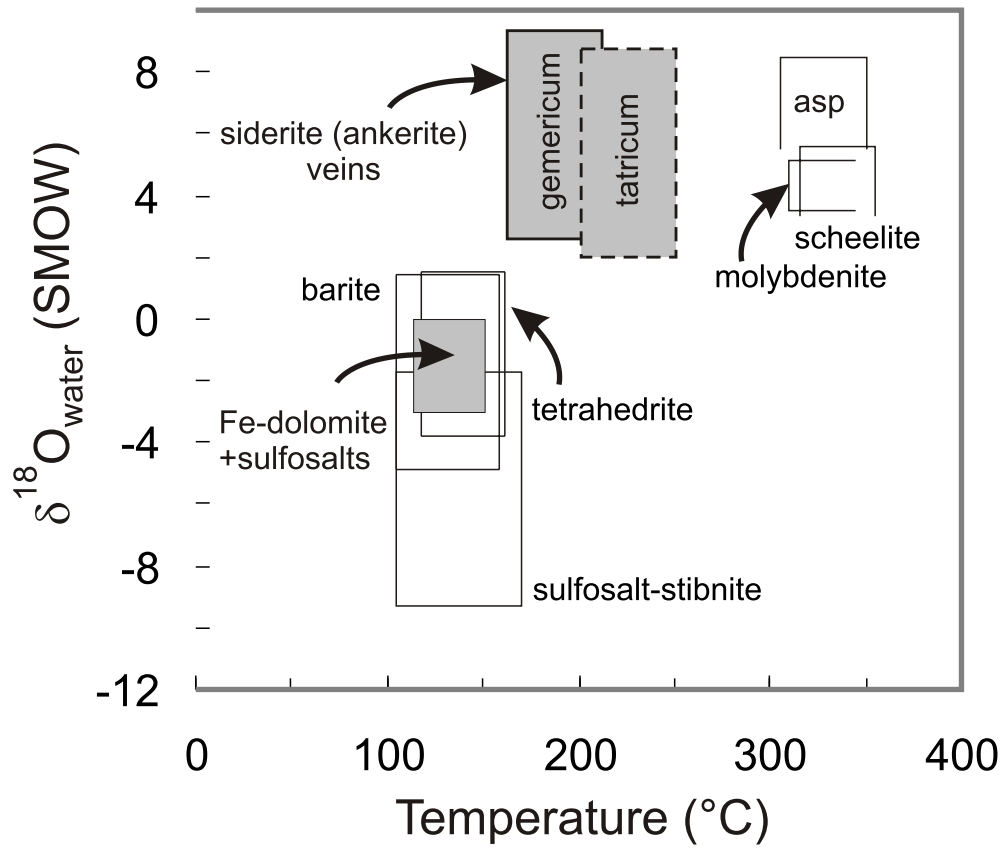


Fig.2.

