

SUPERDENSE CO₂ INCLUSIONS IN CRETACEOUS QUARTZ-STIBNITE VEINS OF THE GEMERIC UNIT, WESTERN CARPATHIANS, SLOVAKIA

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Variscan basement of the Gemic unit of the Western Carpathians contains more than 1 000 hydrothermal veins (GRECULA *et al.*, 1995), which have been for centuries one of the most important resources of iron and base metals, particularly copper, quicksilver and antimony. The majority of these veins has been exploited since prehistoric times. Siderite and quartz-sulphide veins are arranged parallel to the regional metamorphic cleavage of the low-grade Palaeozoic basement, and/or within mylonite shear zones. Origin of the siderite and stibnite veins has been widely discussed for many years. Detailed fluid inclusion and mineralogical studies have been recently carried out with the aim to elucidate more exactly the origin and age of the ore-forming fluids of the Gemic unit.

CO₂ inclusions with density up to 1,197 kg.m⁻³ occur in quartz-stibnite veins in the southern part of the Gemic unit. It is the first known occurrence of the superdense CO₂ in hydrothermal veins and low-grade crustal environments. Inclusions with high density of CO₂ ($D > 1,100$ kg.m⁻³) were described from high-pressure/high-temperature low crust and upper mantle environments. Archean garnet granulites from the South Indian craton contain CO₂ inclusions with highest density (1,174 kg.m⁻³) recorded in crustal rocks up to present (SANTOSH & TSUNOGAE, 2003). Higher densities, up to 1,210 kg.m⁻³, were described only from upper mantle pyroxenites from Salt Lake Crater, Hawaii (FREZZOTTI *et al.*, 1992). Inclusions of pure superdense CO₂ homogenize by melting of CO₂-solid in CO₂-liquid at temperatures greater than -56.6°C, and metastable total homogenization by CO₂-vapour disappearance can be seen at $T < -56.6$ °C.

In the Gemic hydrothermal veins superdense CO₂ inclusions are often accompanied by monophasic CO₂ inclusions with variable density and also by two-phase aqueous and three-phase CO₂-rich aqueous inclusions with high salinity (23–32 wt% NaCl eq.). Variable phase ratios in the inclusions indicate entrapment of a heterogeneous fluid, consisting of CO₂-rich and aqueous phases. Raman microanalysis of the monophasic CO₂ inclusions corroborated CO₂ as dominant gas species accompanied by small amounts of nitrogen (<7.3 mol%) and methane (<2.5 mol%). Trapping PT conditions have been derived from coeval monophasic CO₂ and two-phase aqueous inclusions. The superdense CO₂ phase exsolved from an aqueous bulk fluid at temperatures of 183–237 °C and pressures between 1.6 and 3.5 kbar, possibly up

to 4.5 kbar. The wide range of fluid pressures indicates a periodical opening of the vein system due to a crack-seal mechanism, when fluid pressure varies between hydrostatic and lithostatic pressures. The calculated fluid pressures are equivalent to depths between 15 and 18 km.

Low thermal gradients (12–13 °C.km⁻¹) and the CO₂-CH₄-N₂ fluid composition rule out a genetic link of the hydrothermal veins with the subjacent Permian granites and indicate an external, either metamorphogenic (oxidation of siderite, dedolomitization) or lower crustal/mantle, source of the ore-forming fluids. According to microprobe dating of hydrothermal monazite from the quartz-tourmaline assemblage, the quartz-stibnite veins formed during early Cretaceous (~120 Ma) thrusting of the Gemic unit over the adjacent Veporic unit, and rejuvenation of the veins occurred during late Cretaceous (~76 Ma) transpressional shearing. The 15- to 18-km depth of burial estimated from the fluid inclusion trapping PT parameters indicates an 8- to 11-km thick Upper Palaeozoic–Jurassic accretionary complex overlying the Gemic basement and its Permo-Triassic autochthonous cover.

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