Cassiterite-wolframite mineralization at Jermanice in the Krkonose-Jizera pluton (Czech Republic) – mineral chemistry, fluid inclusions, and stable isotopes

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Wolframite-bearing quartz veins occur at Jermanice (Czech Republic) in the Saxothuringian Zone of the Bohemian Massif, which is the largest exposure of the Variscan collisional orogen (Fig. 1a). The mineralization is situated near the intrusive contact of the Tanvald type two-mica alkali-feldspar granite of the Krkonose-Jizera batholith (318–314 Ma, Machowiak and Armstrong 2007) penetrating the chlorite-sericite phyllites with minor bodies of metavolcanics of Lower Paleozoic age (Fig. 1b).

The mineralized veins form a parallel swarm striking NNW-SSE, which crosscut the E-W oriented subhorizontal metamorphic foliation of phyllites. The veins are from a few to 25 cm thick and 50–200 m long. The veins are formed by massive milky and vuggy quartz aggregates with abundant cavities, and with minor disseminated tourmaline or with irregularly distributed wolframite crystals, up to 10 cm large. The surrounding phyllites have undergone pervasive tourmalinization.

Black coarse-grained prismatic wolframite crystals contain 59–79 mol% ferberite and 20–31 mol % hübnerite. Scheelite (with 0.1 mass% Bi_2O_3) was found along cracks in wolframite or as individual grains in quartz gangue. Cassiterite (with up to 0.7 mass% TiO_2), anhedral rutile (up to 11 mass% WO_3, 2.3 mass% FeO, and 1.85 mass% SnO_2), apatite (with 4.9 mass% F), rare stolzite ($PbWO_4$), bismutine and ilmenite are also present in the wolframite-bearing veins. Tourmaline forms grains up to 5 cm in rock matrix as well as single euhedral grains in veins. The composition is nearly elbaite with minor schorl component.

Small quartz - tourmaline ± wolframite foliation-parallel veins are composed of white or milky quartz with minor tourmaline. The primary H_2O–CO_2 inclusions in quartz had variable liquid to vapour ratio, φ(liq) = L/L+V, CO_2–only inclusions were also observed. $T_m(CO_2)$ were measured between –57.5 and –58.4 °C, temperatures of melting of CO_2 clathrate between 7.2 and 8.4 °C, corresponding to salinity 3.3 to 5.8 eq mass% NaCl. CO_2 homogenized partly to vapour phase at 24.9 to 30.0 °C, partly to liquid phase at 12.4 to 30.0 °C, thus the CO_2 density ranged between 0.243 and 0.845 g/cm^3. Temperature of total homogenization was not measured due to variable φ(liq). Aqueous inclusions with φ(liq) of ~0.9 were also found in these veins. They yielded temperatures of homogenization between 154 and 186 °C, and salinity of 3.1–4.3 eq mass% NaCl.
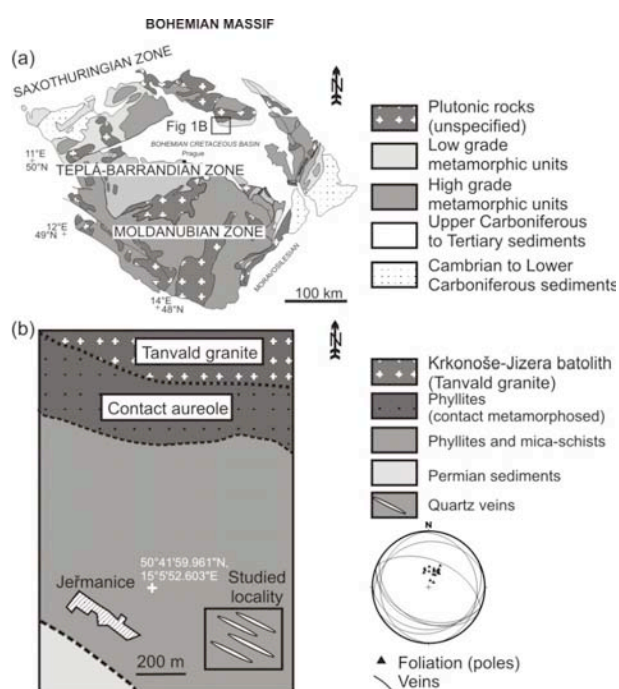

Fig. 1. (a) Bohemian Massif, (b) Geological sketch map of cassiterite-woframite mineralization

Quartz-wolframite veins crosscut the metamorphic foliation and host the wolframite ± cassiterite mineralization. Primary H_2O–CO_2 and aqueous fluid inclusions were found in euhedral quartz crystals in cavities up to 6 cm large. The aqueous-carbonic inclusions (10 to 60 μm in diameter) preferentially occur near the crystal base, show negative crystal shapes, and rather consistent liquid to vapour ratios (0.6–0.7). Temperature of melting of solid CO_2 was measured between –57.3 and –58.2 °C. These temperatures indicate only a minimal admixture of CH_4 or N_2 in gaseous phase. Temperatures of melting of CO_2 clathrate were measured between 8.0 and 9.6 °C, corresponding to low salinity of aqueous solution from 0.8 to 4.2 eq mass% NaCl. CO_2 homogenized to vapour phase, $T_h(CO_2)$ to vapour between 8.2 and 28.2 °C correspond to the density of CO_2 in the range from 0.126 to 0.292 g/cm^3. Temperatures of total homogenization fall within a narrow range between 318 and 357 °C.

Negative crystal shape of inclusions, consistent $\varphi(liq)$, and the narrow range of $T_h(CO_2)$ indicates that the inclusions were trapped at homogeneous environment (Bodnar et al. 1985), thus total T_h can be assumed to represent the minimum temperatures of trapping of inclusions. The pressure, corresponding to T_h, reached 40 to 70 MPa.

Primary H_2O inclusions can also be found at the central and peripheral part of crystals. The inclusions had relatively consistent $\varphi(liq)$ from 0.7 to 0.9, and yielded T_h from 218 to 266 °C and salinity from 4.0 to 5.6 eq mass% NaCl.

Late-stage quartz overgrowths occur on the euhedral crystals described above. They host primary aqueous fluid inclusions of oval shape (up to 60 m), with liquid to vapour ratio = 0.8–0.9. Temperatures of homogenization vary from 172 to 240 °C, the salinity of aqueous solution is between 1.1 and 7.3 eq mass% NaCl.

Oxygen stable isotopes were analyzed in vein quartz, tourmaline, and wolframite. Quartz has $\delta^{18}O_{SMOW}$ = 11.0–11.6 ‰, tourmaline gives $\delta^{18}O_{SMOW}$ = 9.3 ‰, whereas wolframite is depleted in ^{18}O, with $\delta^{18}O_{SMOW}$ = 1.0–1.6 ‰. Despite the weak alteration of wolframite to scheelite along microfractures, the quartz-wolframite thermometer of Zheng et al. (1994) yields temperatures of 240–280 °C. This temperature range is in a good agreement with the fluid inclusion features in the early quartz-tourmaline ± wolframite veins (variable $\varphi(liq)$ of inclusions and CO_2 density indicate a probable immiscibility of vapour and aqueous phase under 300 °C). The temperatures corresponding to isotopic equilibrium of quartz-tourmaline pairs are as high as 600 °C. The discrepancy in calculated temperatures has not been solved and it remains ahead for the further study.

The genesis of wolframite-bearing veins is in general connected with the pluton emplacement and thus the tungsten mineralization could be found in the pluton or host rocks (eg. Rios et al. 2003, Neiva 2008). We suppose that time constrain of quartz vein occurrence could be related with the emplacement of the Krkonose – Jizera batolith in 314 Ma (Machowiak and Armstrong 2007). Pressure build-up caused by pluton intrusion led to hydraulic fracturing of the phyllites and circulation of the solutions through the open spaces in phyllite. The cavities were filled with quartz-tourmaline and quartz-wolframite veins under estimated pressures at least 40–70 MPa and temperatures 240–360 °C. With decreasing temperature wolframite was precipitated from cooling Fe-W-bearing fluid originated from the Krkonose-Jizera batolith.

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