Original paper Fluorite-bearing vein mineralization from Bartoušov near Havlíčkův Brod: a complex fluid history related to post-Variscan uplift of the Moldanubian basement (Bohemian Massif, Czech Republic)

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A subvertical NW-SE trending fluorite-bearing vein at Bartoušov cut small body of two-mica granites hosted by high-grade metamorphic rocks of the Moldanubian Zone of the Bohemian Massif, in the northern part of the tectonic structure of the Jihlava Graben. The vein mineralization features open-space filling and multiple episodes of mineral precipitation. Early fine-grained quartz containing rare Nb- and W-enriched rutile is overgrown by crystals of late quartz and greenish to violet fluorite, followed by veinlets of dolomite-ankerite and calcite with pyrite and siderite. Quartz and fluorite crystallized from heterogeneous aquo-carbonic fluid with highly variable both bulk density and composition. Early CO₂-dominated aquo-carbonic fluids probably represent local retrograde-metamorphic fluids, whose variations in density likely reflect the pressure decrease during uplift of the basement during the Carboniferous. Late N₂-dominated low-density aquo-carbonic fluids were trapped at ~135-150 °C and ~60-100 bars. Raman analysis proved minor occurrence of CH₄, C₂H₆, H₅, and/or O₂ in the N₂-rich carbonic fluid. The composition of N₂-dominated carbonic fluid cannot be explained by the local basement sources only, but it could be derived from the now eroded immature Permo-Carboniferous sediments of the Jihlava Graben. In this concept, N₂, hydrocarbons, and possibly some H, could have been formed due to thermal alteration of immature organic matter, whereas O, and rest of H, were likely formed due to radiolysis of water within bodies of synsedimentary uranium ores present in this sedimentary basin. The infiltration of basinal fluids into basement was allowed due to an extensional tectonic regime. Paragenetically late carbonates originated from low- to moderate-salinity aqueous fluids derived from meteoric water and containing elevated amount of carbon from the oxidized organic matter.

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1. Introduction

Fluorite is rather uncommon mineral phase in hydrothermal veins hosted by the basement rocks of the Moldanubian Zone of the Bohemian Massif, including the typical Ag–Pb–Zn ore veins (e.g., Pelíšek 1951; Novák 2002). The most abundant mode of fluorite occurrence is minor to accessory phase in the Alpinetype veins, where it is typically associated with quartz, calcite, chlorite, epidote-group minerals and zeolites (Bernard et al. 1981; Litochleb et al. 1991; Mastíková 2009). Vein mineralizations, in which fluorite is a major constituent, are very rare. These include formerly mined fluorite-barite deposit Běstvina belonging to the Late Variscan-to-Mesozoic *fba* mineralization (*sensu* Bernard et al. 1981) and small fluorite deposits at Kožlí, Mutěnice and Topělec (Fig. 1a), which are believed to be representatives of a specific Variscan qf mineralization (*sensu* Bernard et al. 1981). None of these fluoritebearing mineralizations was subject of modern genetic investigation, except for the Běstvina deposit, which was included in a comprehensive fluid inclusion and Sr, S, O isotope study focused on barite mineralization in the Bohemian Massif (Žák et al. 1990).

A new locality of hydrothermal vein mineralization rich in fluorite was discovered by D. Holeczy and coworkers (Diamo Enterprise) in the Bartoušov sand pit in 2019. The mineralization was briefly described in the unpublished mapping report by Kropáč et al. (2019). In this paper we provide a detailed mineralogical characterization of the vein assemblage and supplement it by genetic interpretation based on fluid inclusion and stable isotope study that show a surprisingly complex fluid history.

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Fig. 1 Geological situation of the studied site: \mathbf{a} – Position of the Bartoušov site and other localities of vein fluorite mineralization in the Moldanubian Zone of the Bohemian Massif. CBP – Central Bohemian Plutonic Complex, CMP – Central Moldanubian Pluton. Fluorite localities: 1 - Kožli, 2 - Mutěnice, 3 - Topělec, 4 - Běstvina; \mathbf{b} – Local geology around the Bartoušov site (modified from electronic version of Geological map of the Czech Republic 1: 50 000; https://mapy.geology.cz/geocr50/).

2. Geological setting

The study area is formed by crystalline rocks of the Moldanubian Zone of the Bohemian Massif (Fig. 1a), representing deeply eroded root of the Variscan Orogen. Metasedimentary rocks, present in the area, belong to the Ostrong (Monotonous) Unit and were metamorphosed in the amphibolite facies. Lithologically, they are dominated by biotite and biotite-sillimanite paragneisses with minor intercalations of quartzite and amphibolite. Polyphase metamorphism was associated with a strong tectonic deformation or rocks. Rapid isothermal uplift of the Moldanubian domain during the Carboniferous led to extensive migmatitization and formation of large amounts of acidic magma giving rise to large granitoid plutons. Small granitoid bodies present in the study area (Fig. 1b) are considered to be extremities of the large composite Central Moldanubian Pluton (René and Dolníček 2023; Fig. 1a), which intruded in three successive phases within the 338-302 Ma period (Gerdes et al. 2003; Žák et al. 2011). Gravitational collapse of the Variscan Orogen led to normal faulting, intrusion of small dykes of lamprophyres and formation of NNE-SSW trending graben structures in the Moldanubian area (represented by the Jihlava Graben in the study area; Fig. 1a), which were filled out by Uppermost Carboniferous-to-Permian clastic sediments, in basal parts with coal seams (Pešek et al. 2001). Most of this sedimentary infill was, however, almost completely eroded in the Jihlava Graben during long-lasting post-Variscan uplift, leaving negligible relics only (Koutek 1940).

The late Variscan and post-Variscan tectonic activity led also to the formation and re-activation of faults, associated with circulation of fluids and formation of hydrothermal mineralization. The most prominent are polymetallic Ag-Zn-Pb ore veins belonging to the Havlíčkův Brod ore district. The mineralization of these k-pol veins sensu Bernard et al. (1981), composed especially of black Fe-rich sphalerite, galena, arsenopyrite, pyrite and pyrrhotite, hosted by quartz and/or siderite gangue, was formed at high temperatures (~200-~500 °C; Malý and Dolníček 2005; Mastíková 2011) soon after solidification of the granitic bodies. Another widely distributed type of hydrothermal mineralizations comprises Alpinetype veins, formed especially by quartz, calcite, minor fluorite, sulphides, chlorite, sometimes also scheelite, allanite and/or zeolites (Mastíková 2009). Other types of hydrothermal mineralization are much less frequent and include quartz-wolframite-scheelite veins, dolomite veins, palygorskite veins, and barren quartz veins (Pauliš and Kopecký 2007; Mastíková 2009).

The studied site is an active sand pit 0.5 km SW from Bartoušov, situated in a small body of two-mica granites hosted by migmatitized Moldanubian paragneisses (Fig. 1b). The pit is mined for sandy material from the weathered cup of granites for building purposes.

3. Methods

All studied samples were collected by the authors in the sand pit in 2019–2020. Polished sections and doubly polished plates were prepared by P. Sečkár, Comenius University, Bratislava. Prepared samples were inspected in transmitted/reflected light of the polarizing microscope Nikon Eclipse ME600 equipped with digital camera Nikon DXM1200F.

Then, samples were coated by ~30 nm thick carbon layer in vacuum and studied by electron microprobe Cameca SX-100 in National Museum in Prague. The individual phases were identified by means of energy-dispersive (EDS) spectra and documented by back-scattered electron (BSE) imaging. Chemical composition of selected phases was studied quantitatively by means of spot wavelength-dispersive (WDS) analyses. Analyses of sulphides were conducted using acceleration voltage of 25 kV, beam current 20 nA and beam size 0.7 µm. The following standards, diffracting crystals and analytical lines were used: Ag (LPET, AgL α), albite (LTAP, NaK α), Au (LPET, Au $M\alpha$), Bi₂Se₂ (LPET, Bi $M\beta$), CdTe (LPET, CdLa), Co (LLIF, CoKa), CuFeS, (LLIF, CuKa; LPET, $SK\alpha$), FeS₂ (LLIF, FeK α), fluorapatite (LLIF, CaK α ; LTAP, $PK\alpha$), GaAs (LTAP, GaL α), Ge (LTAP, GeL α), HgTe (LLIF, HgLa), InAs (LPET, InLa), Mn (LLIF, MnK α), NaCl (LPET, ClK α), NiAs (LTAP, AsL β), Ni (LLIF, NiK α), PbS (LPET, PbM α), PbSe (LTAP, SeL β), PbTe (LPET, TeL α), sanidine (LPET, KK α), Sb₂S₂ (LPET, SbL α), Sn (LPET, SnL α), Tl(Br,I) (LLIF, TlL α), and ZnS (LLIF, $ZnK\alpha$). The peak counting times were 20 s and those for each background were 10 s. The collected data were converted to wt. % using the standard PAP correction matrix (Pouchou and Pichoir 1985) and corrected automatically for overlaps Cd-Ag and As-Sb.

Oxygen-bearing phases were measured at acceleration voltage of 15 kV, beam current of 20 nA (rutile) or 5 nA (carbonates) and beam size of 0.7 µm (rutile) or 4 µm (carbonates). In rutile the contents of Al, As, Ca, Cr, Fe, Mg, Mn, Mo, N, Na, Nb, P, Pb, S, Sc, Si, Sn, Ta, U, V, W, Y, and Zr were determined, whereas in *carbonates* Al, Ba, Ca, Co, Cu, Fe, Mg, Mn, Na, Ni, P, Pb, Si, Sr, and Zn were analysed. The following standards, diffracting crystals and analytical lines were used: albite (LTAP, NaK α), almandine (LTAP, AlK α ; LLIF, FeK α), antimonite (LPET, SbLa), fluorapatite (LTAP, PKa; LPET, CaK α), baryte (LLIF, BaL β), celestine (LPET, SK α ; LPET, SrL β), Co (LLIF, CoK α), Cr₂O₂ (LLIF, $CrK\alpha$), $CrTa_2O_6$ (LLIF, $TaL\alpha$), diopside (LTAP, MgK\alpha), chalcopyrite (LLIF, $CuK\alpha$), clinoclase (LTAP, AsL α), Nb (LPET, NbL α), Ni (LLIF, NiK α), rhodonite (LPET, MnK α), sanidine (LTAP, AlK α ; TAP, SiK α), scheelite (LLIF, WLa), ScVO₄ (LLIF, ScKa), Sn (LPET, SnLa), TiO_{2} (LPET, $TiK\alpha$), UO₂ (LPET, UM α), V (LLIF, VK α), vanadinite (LPET, Pb $M\alpha$), wollastonite (LPET, Ca $K\alpha$; TAP, SiK α), YVO₄ (LTAP, YL α), zincite (LLIF, ZnK α), zircon (LTAP, $ZrL\alpha$). The peak counting times were 20 s and those for each background were 10 s. The collected data were converted to wt. % using the standard PAP correction matrix (Pouchou and Pichoir 1985) and corrected automatically for overlaps V-Ti, Cr-V, P-Ca, Zr-Nb, Pb-Nb, Si-W, Zr-W, and P-W.

Raman analyses of minerals and fluid inclusions were performed using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope in National Museum in Prague. The Raman signal was excited by an unpolarised 532 nm Ar gas laser and detected by a CCD detector. The spectrometer was calibrated using software-driven procedure based on emission lines of neone (calibration of Raman shift), Raman bands of polystyrene (calibration of laser frequency) and standardized source of white light (calibration of intensity). The parameters of measurement were: $100 \times$ objective, 5 s exposure time, 200-300 exposures, 50 µm pinhole spectrograph aperture and 10 mW laser power. Spectral manipulations were performed using the Omnic 9 software (Thermo Scientific). The obtained mineral spectra were compared to the reference spectra included in the RRUFF database. The quantification of gaseous components in fluid inclusions was based on quantitative measurement of peak areas (Burke 2001) and calibration using natural fluid inclusions with known proportions of CH₄, N₂ and CO₂.

Fluid inclusions were investigated in standard doubly polished plates. Primary (P), pseudosecondary (PS) and secondary (S) inclusions were distinguished following the criteria given by Roedder (1984) and Shepherd et al. (1985). Petroleum in fluid inclusions was checked in ultraviolet (UV) light at 365 nm excitation wavelength. Microthermometric parameters were obtained using a Linkam THMSG 600 stage mounted on an Olympus BX-51 microscope in National Museum in Prague. The homogenization temperature (Th), freezing temperature (Tf), eutectic temperature (Te) and melting temperature of ice (Tm_{ine}) were measured in aqueous inclusions, and temperature of total homogenization (Th_{tot}), temperature of partial homogenization of carbonic phase (Th_{car}), melting temperature of solid CO₂ (Tm-CO₂) and melting temperature of clathrate (Tm_{cla}) were obtained for carbonic-rich inclusions. In order to avoid stretching of carbonic inclusions, all cryometric measurements preceded homogenization of aqueous inclusions. The stage was calibrated between -56.6 and 374.1 °C with chemical standards (naphtalene, sodium nitrate) and natural fluid inclusions with known temperatures of phase transitions. The reproducibility of measurements is within 0.1 °C for temperatures between -56.6 and 0 °C, within 0.3 °C at 80.6 °C, and within 1 °C for temperatures of 307 °C and 374.1 °C. Salinity of aqueous solutions was calculated in the system NaCl-H₂O according to Bodnar (1993). Chemical composition, densities and isochores of carbonic fluids were calculated from microthermometric and Raman compositional data using the software package Fluids (Bakker 2003) and calibrations by Duan et al. (1992, 1996).

For determination of isotopic composition of C, O and S, approximately 100 mg of pure mineral phase was separated by handpicking and grounded in an agate mortar. Pyrite was mixed with V2O5, placed in tin capsules and combusted at 1000 °C in a Carlo Erba NC 1500 elemental analyzer. The produced SO₂ was concentrated in a gas chromatograph column (Porapak QS) and introduced into the Thermo Finnigan Mat 251 continuous flow isotope-ratio mass spectrometer (CF-IRMS) through a Thermo-Finnigan ConFlo II interface, which injects SO, reference gas and helium for sample dilution. The conversion of carbonates to CO₂ was made by reaction with 100% orthophosphoric acid (McCrea 1950) in vacuum at 25 °C. The measurement of C and O isotopic compositions of the resultant CO₂ gas was performed using Delta V Advantage mass spectrometer (dual inlet methodology) in laboratories of the Czech Geological Survey in Prague. Results of all isotope analyses are conventionally expressed in δ notation as per mil (‰) deviation from commonly used standards (V-PDB, V-SMOW, V-CDT). Uncertainty is better than ± 0.05 , ± 0.1 and ± 0.2 ‰ for δ^{13} C, δ^{18} O and δ^{34} S values, respectively. The dolomite δ^{18} O values were corrected for fractionation during sample preparation by a value of -0.84 ‰ (Friedman and O'Neil 1977). The isotopic composition of equilibrium fluids was calculated using the equations published by Northrop and Clayton (1966; dolomite-water), O'Neil et al. (1969; calcite-water), and Ohmoto and Rye (1979; pyrite– H_2S). As HCO₂⁻ is predominating carbon species in near-neutral low-temperature fluids (Matsuhisa et al. 1985) and no fractionation factors are published for system carbonate-HCO₃, we have subtracted published equations carbonate-CO2 and CO2-HCO3. In the latter case, fractionation factors by Ohmoto and Rye (1979; CO₂-HCO₂), Ohmoto and Goldhaber (1997; dolomite-CO₂) and Chacko et al. (1991; calcite–CO₂) were used.



Fig. 2 A typical sample of fluorite mineralization from Bartoušov. Crystals of violet fluorite together with white quartz incompletely filling a fracture in altered greenish granite.

4. Results

4.1. Mineralogy

Fluorite mineralization was recorded in unweathered granite in the east wall of the pit. The steep (dip $70-95^{\circ}$) morphologically complex hydrothermal vein (in places rather stockwork composed of several veinlets up to 1 cm thick) trends NW-SE and cuts hydrothermally altered granite. Breccia of host rocks, cemented by quartz, fluorite and carbonates, was found in places too. Hydrothermal alterations of wall rock adjacent to vein, highlighted by change of rock colour to grey-green (Fig. 2), include weak silicification, minor carbonatization, widespread argillitization and sericitization of feldspars and chloritization of biotite. Exceptionally, sporadic scheelite was found in altered granite (Kropáč et al. 2019). Hydrothermal minerals incompletely fill out the vein leaving abundant drusy cavities up to several cm in size, lined by fluorite, quartz or pyrite crystals (Fig. 2).

A detailed mineralogical study of hydrothermal vein revealed the presence of quartz, rutile, fluorite, pyrite, calcite, siderite, and carbonates of the dolomite-ankerite series.

Quartz is the oldest phase. Macroscopically, older portions of quartz are fine-grained, white-grey, and overgrow silicified fragments of host rock (Figs. 2, 3a–d). The younger portions of quartz, continuously evolving from the earlier one, form palisade drusy coatings, with crystal sizes increasing up to 1 mm in the youngest parts (Fig. 3d). Quartz crystals are sometimes zoned due to a variable abundance of fluid inclusions in neighbouring well-defined growth zones.

Rutile is rarely enclosed in the earlier fine-grained portion of quartz. It forms euhedral isometric to columnar crystals and xenomorphic grains up to 80 µm in size, those sometimes cluster in larger porous aggregates (Fig. 3c). Raman spectra show main peaks at ~612, 446, 238 and 684 cm⁻¹ (ordered according to decreasing intensity) and two weak peaks at ~370 and 147 cm⁻¹, which confirms rutile according to the RRUFF database. In BSE image, rutile is distinctly zoned, with sharp brighter cores and darker rims (Fig. 3c). Cores are rich in W (≤0.022 *apfu*), Fe ($\leq 0.031 apfu$), less in Nb ($\leq 0.003 apfu$) and Sn $(\leq 0.001 apfu)$. Chemical composition of rutile is different from that from pegmatites from the neighbouring Pohled quarry, which contains similarly elevated Nb and Zr, but lacks W and Sn (Fig. 4a; Dolníček et al. 2020). It is also similar to rutile from Alpine-type veins from the Pohled quarry, which is also enriched in W and Fe (Fig. 4a).

Fluorite is a major component of the vein, overgrowing quartz and predating carbonates. It usually forms isolated violet or green grains up to 0.5 cm in size, those sometimes concentrate into larger accumulations. In drusy cavities, there often occur transparent crystals (octahedrons or cubes) up to 1 cm in size, usually with slightly etched crystal faces (Fig. 2). In thin section, fluorite is often zoned (colourless core with violet margin; Fig. 3a) and distinctly corroded by carbonates from grain margins and along cracks (Fig. 3b).

Carbonates of the dolomite-ankerite series are younger than quartz and fluorite (Fig. 3b, d, e) and older than calcite (Fig. 3b, e). Macroscopically pink aggregates of dolomite-ankerite grow over fluorite or replace it along cracks. Dolomite-ankerite forms individual zoned crystals, veinlets, or fills up small cavities in the vein. In some cases, skeletal relics intensely replaced by calcite were observed (Fig. 3e). In transmitted light, dolomite-ankerite is mostly poorly transparent due to a huge amount of minute fluid inclusions (Fig. 3a). In BSE images, it is oscillatory zoned, with a general evolution from darker core to brighter rim (Fig. 3d). Younger brighter parts of grains tend to have, in addition, patchy fabric in some cases. The youngest portions adjacent to drusy cavities show again detailed zonation with contrasting well defined thin zones. Spot WDS analyses revealed wide variations in chemical composition, which range from pure dolomite to almost pure ankerite, although dolomite composition clearly prevails volumetrically (Fig. 4b). The amount of kutnohorite component does not exceed 10.3 mol. % and its content tends to be elevated in ankerites. The content of Ca ranges 0.92-1.12 apfu; slight excess of Ca, found in most analyses, is however common in carbonates of dolomite series. In anionic part of the formula, minor contents of sulphur and/or phosphorus (both not exceeding 0.003 *apfu*) were recorded in some analyses.

White coarse-grained calcite is undoubtedly one of the youngest minerals of the vein. It forms veinlets in fluorite and replaces fluorite and carbonates of the dolomite-ankerite series (Fig. 3b, e). No zonation is observed in BSE images. Calcite contains slightly elevated siderite (0.5–1.3 mol. %) and rhodochrosite (0.2–0.8 mol. %) admixtures but lacks magnesite component.

Siderite was found together with pyrite in a single aggregate enclosed in dolomite-ankerite (Fig. 3f). In BSE image, siderite shows weak irregular zonation especially due to variations in magnesite and siderite endmembers $(\text{Sid}_{79-91}\text{Mag}_{4-19}\text{Cal}_{1-8}\text{Rdc}_{0-1})$. The composition is mostly similar to those from other vein mineralizations in the wider area (Fig. 4c).

Pyrite forms usually rather sporadic coatings on crystals of earlier phases (quartz, fluorite, carbonates) composed of small cubic crystals. Exceptionally rich pyrite samples were also found, which are formed by pentagondodecahedrons reaching up to 2.5 cm in size. No zonality can be observed in both reflected light and BSE images. The WDS analyses confirmed pure composition without any admixture.



Fig. 3 Mineral assemblage and textures of the studied mineralization. \mathbf{a} – Altered rock fragments (R) cemented by zoned palisade quartz (Qtz) overgrown by fluorite (Fl) and dolomite-ankerite (Do). Thin section, transmitted polarized light. \mathbf{b} – Quartz crystals (Qtz) overgrown by fluorite (Fl), which is strongly replaced by carbonates (Do – dolomite-ankerite, Cal – calcite). BSE image. \mathbf{c} – Zoned rutile (Rt) enclosed in early fine-grained quartz (Qtz). BSE image. \mathbf{d} – Strongly zoned dolomite-ankerite (Do) overgrowing euhedral crystals of quartz (Qtz). BSE image. \mathbf{e} – Corroded relics of zoned dolomite-ankerite (Do) enclosed in calcite (Cal). Fl – fluorite. BSE image. \mathbf{f} – An aggregate of siderite (Sid) and pyrite (Py) filling a cavity in dolomite-ankerite (Do). BSE image.

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Fig. 4 Variations in chemical composition of some minerals from Bartoušov. \mathbf{a} – Rutile in the W–Nb plot; comparative data for pegmatites are from Dolníček et al. (2020), those for Alpine-type veins are unpublished data of the authors. \mathbf{b} – Carbonates of the dolomite-ankerite series from three samples from Bartoušov in the classification scheme by Trdlička and Hoffman (1975). \mathbf{c} – Siderite in the classification scheme by Trdlička and Hoffman (1975). \mathbf{c} – Siderite in the classification scheme by Trdlička and Hoffman (1975); comparative data from neighbouring hydrothermal vein mineralizations (Pohled, Mírovka, Koječín) are unpublished data of the authors. Note that Koječín samples are Mn-rich.



4.2. Fluid inclusions

Fluid inclusions were studied by means of petrography, microthermometry, and Raman analysis in three hand specimens covering the whole paragenetic sequence of the vein. Fluid inclusions suitably sized for optical microthermometry occur in quartz, fluorite, dolomite–ankerite and calcite hosts.

4.2.1. Quartz and fluorite

Primary and pseudosecondary fluid inclusions are abundant in quartz and fluorite (Fig. 5a-g). Quartz-hosted primary inclusions occur on growth zones with elongation perpendicular to direction of growth zones (Fig. 5c). Their morphology is irregular, oval, isometric, oblong or negative-crystal shaped with sizes up to 15 µm. Pseudosecondary fluid inclusions, hosted by intra-granular trails, predominate in fluorite (Fig. 5d-f). They have similar morphology, but slightly larger sizes (up to 52 µm). Primary and pseudosecondary inclusions are usually characterised by highly variable phase compositions due to variable proportions of aqueous solution and carbonic phase (5-90 vol. % of carbonic phase), even within individual trails (Fig. 5d-f). Less frequent are groups showing very stable phase compositions of individual inclusions (Fig. 5a, f); such trails composed of carbonic inclusions with low amount of water often occur in fluorite. The carbonic phase is mostly monophase vapour (V), less frequently two-phase liquid+vapour (L+V) at room temperature. Micro-Raman analysis showed mostly CO₂-N₂-CH₄ compositions of homogeneous carbonic phase with broad variations in contents of CO₂ and N₂, and less variable subordinate amounts of CH_4 (0–97 mol. % of CO_2 , 2–86 mol. % of N_2 , 2–23 mol. % of CH_4). Although N_2 - and CO₂-dominated compositions clearly predominate, a few 'intermediate' compositions were also recorded, altogether defining a distinct linear general trend in a CO₂-N₂-CH₄ plot (Fig. 6). Inclusions with CO₂-rich compositions occurring especially within growth zones and short trails seem to be older than inclusions with N₂-rich compositions occurring more frequently along longer intra-granular trails. In fluorite both types mainly occur along sub-parallel intra-granular trails precluding the determination of their relative timing (Fig. 5d). Raman analysis also yielded the presence of small amounts of H₂ (peaks at ~587, ~815, ~1035, and ~4156 cm⁻¹), and/ or C_2H_{ϵ} (peak at ~2954 cm⁻¹) in a few N₂-rich inclusions. Water-rich inclusions coexisting on trails with aquocarbonic inclusions (both N₂- and CO₂-rich) are always two-phase (L+V) with variable degree of filling (vapour phase occupies 5-30 vol. %). They have the same morphology and size as the carbonic inclusions (Fig. 5d-e). In vapour bubbles of some of them the presence of CO₂-

 N_2 -CH₄ gases was proved by Raman analysis (Fig. 6), however, such evidence is scarce because the analysis is often hampered due to bubble movement. Nevertheless, the mutual proportions of gases are mostly fully comparable to those of carbonic phase in aqueous–carbonic inclusions (Fig. 6). Bubbles of two aqueous inclusions in fluorite yielded Raman spectra showing quite high peaks of H₂ together with peak of molecular O₂ (at ~1555 cm⁻¹, Fig. 7) and trace amount of N₂. In addition, bubbles in few water-rich inclusions yielded only high fluorescence during Raman measurements, however, the presence of liquid hydrocarbons was not confirmed in an UVfluorescence microscope in any inclusion from the vein.

Primary and pseudosecondary water-rich inclusions yielded wide intervals of temperatures of total homogenisation, ranging 96–319 °C in quartz and 137–266 °C in fluorite (Tab. 1, Fig. 8a). However, some of them did not homogenise even at 350 °C. In fluorite, no significant differences were recorded in minimum Th values of aqueous inclusions associated with gas-rich inclusions with contrasting compositions (144–153 °C and 137–142 °C for CO_2 - and N_2 -dominated gas-rich inclusions, respectively). Aqueous solution in water-rich inclusions froze between –45 and –30 °C. The initial melting was observed only once at –33 °C. The final melting of ice occurred in largely very similar temperature intervals in water-rich inclusions (–2.3 to –2.9 °C and –0.1 to –2.6 °C, respectively).

Carbonic-aqueous inclusions yield wide spread of microthermometric data, reflecting contrasting chemical compositions of carbonic phase. All three modes of partial homogenization of carbonic phase were observed in the CO_2 -rich inclusions: to vapour, to liquid and critical, at temperatures –16.0 to 27.9, 16.7 to 27.8 and 16.9 to 27.0 °C, respectively (Tab. 2). However, vapour and critical homogenizations were observed in fluorite only. Individual groups/trails of inclusions show mostly homogeneous chemical composition of non-aqueous phase and

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Fig. 5 Appearance of fluid inclusions from Bartoušov. a - The fracture-hosted N₂-dominated fluid inclusions in quartz. b - A sequence of photographs illustrating phase transitions in a pseudosecondary N₂-dominated (Vcar) fluid inclusion with minor aqueous solution (Laq) hosted by quartz. c - Growth zoning in quartz, with growth zones poor and rich in primary fluid inclusions. Note that trails of inclusions are oriented perpendicularly to the course of growth zones. d - A complex fracture-hosted trail in fluorite containing water-dominated (with small bubbles), N2-dominated (with negative Thear values), and CO2-dominated (with positive Th_{car} values) inclusions. e - A fracture-hosted trail in fluorite containing co-existing water-dominated (with small bubbles) and CO_2 -dominated (with large bubbles) fluid inclusions. f - A fracture--hosted trails in fluorite containing water- and CO2-rich fluid inclusions. g - Pseudosecondary-to-secondary aqueous fluid inclusions in fluorite showing stable phase proportions. h - A group of aqueous PS/S fluid inclusions in calcite with uniform degree of fill. i - Primary aqueous fluid inclusions in dolomite-ankerite.





Fig. 6 Chemical composition (mol. %) of non-aqueous phase of fluid inclusions hosted by quartz and fluorite from Bartoušov projected in a CH_4 - CO_2 - N_2 plot. Data from Pb–Zn ore veins of the Blanice Graben (Ulmanová 2018) are visualised for comparison.

uniform or exceptionally moderately variable Th_{car} values in individual fluid inclusions, ranging within 2–27 °C (Fig. 5d, 8b). Therefore, most trails follow the definition of fluid inclusion assemblages (*FIA*s) sensu Goldstein and Reynolds (1994). The solid CO₂ melted between -60.5 and -57.5 °C, clathrate disappeared between 9.1 and 10.8 °C and melting of ice was never observed. In most N₂-rich inclusions hosted by quartz a small amount of solid CO₂ froze out at temperatures around -110 °C (Fig. 5b). Deeper cooling of N₂-rich inclusions led to condensation of a liquid phase, which did not freeze out even at the lowest temperature limit of the apparatus (-196 °C). On reheating, the liquid carbonic phase in N₂-rich inclusions evaporated at temperatures between -143 and -134 °C, followed by sublimation of solid CO₂ in N₂-rich quartz-hosted fluid inclusions (at -100.1 to -77.2 °C). Clathrate melted between 2.3 and 5.7 °C and melting of ice was not visible. A carbonic inclusion with N₂:CO₂ ratio close to 1:1 showed partial homogenization of carbonic phase at -28.7 °C to vapour, melting of solid CO₂ at -60.6 °C, and clathrate melting at 8.2 °C. The total homogenization of aqueous-carbonic inclusions was observed to vapour between 149 and 324 °C, however, some inclusions decrepitated during heating prior reaching the homogeneous state.

Pseudosecondary to secondary aqueous inclusions occurring on separate trails in fluorite (Fig. 5g) do not contain Raman-detectable amounts of volatile gases. They have variable morphology, including oblong, oval and three-dimensional or planar, irregular and isometric shapes with sizes varying from 5 to 52 μ m. These pseudosecondary to secondary inclusions are mostly characterized by stable phase proportions at room temperature, with vapour bubble taking approximately 5–10 vol. %; only exceptionally are monophase (L-only). Based on crosscutting evidence and refilling phenomena it is evident that trails of these inclusions are younger than trails bearing above characterized cogenetic carbonic and aqueous inclusions. These inclusions had homogenization



temperatures between 86 and 195 °C, eutectic temperatures between -38 and -37 °C and ice-melting temperatures between -7.9 and 0.0 °C (Tab. 1).

4.2.2. Carbonates

Only monophase (L) or twophase (L+V) aqueous inclusions occur in carbonate of the dolomite series. Primary inclusions are uniformly distributed in dolomite crystals or occur along growth zones. They are three-dimensional, mainly regular, often negative-crystal shaped, sometimes oblong or ir-

Fig. 7 Raman spectrum of vapour bubble of a fluorite-hosted aqueous fluid inclusion containing high amount of H_2 and O_2 . The unlabelled peaks belong to host fluorite.

Sample	Mineral	Genesis	System	Phase comp.	Th	Tf	Te	Tm _{ice}	Tm _{cla}	Salinity
BAR-1b	Quartz	Р	H ₂ O-CO ₂ >N ₂ -CH ₄	L+V, L	96-319 (23)	-43/-33		-2.1/-0.6 (21)		1.1-3.6
		PS	H2O-CO2>N2-CH4	L+V	101-198 (3)	-45/-36		-1.2/-0.3 (2)	9.8 (1)	0.5 - 2.1
		PS	H ₂ O	L+V	97-186 (8)	-45/-36		-3.9/-3.4 (7)		5.6-6.3
		PS	H2O-N2>CO2-CH4	L+V	105-273 (12)	-40/-30		-2.6/-0.1 (19)		0.2-4.3
	Fluorite	PS/S	H ₂ O	L+V, L	86-152 (89)	-43/-40	-38/-37	-7.9/-0.0 (83)		0.0-11.6
		PS	H2O-CO2>N2-CH4	L+V	142-156 (30)	-44	-33	-3.2/-1.2 (32)		2.1 - 5.3
		PS	H2O-N2>CO2-CH4	L+V	137-142 (8)	-43		-1.7/-1.4 (7)		2.4-2.9
	Dolomite	Р	H ₂ O	L+V, L	63–137 (14)	-45/-30	-36	-4.2/0.0 (25)		0.0-6.7
BAR-3	Dolomite	Р	H ₂ O	L+V, L	62–115 (11)	-48/-40		-4.8/0.0 (9)		0.0-7.6
	Calcite	PS/S	H ₂ O	L+V, L	118–134 (10)	-40/-36		-0.3/-0.2 (6)		0.2 - 0.5
BAR-4	Calcite	PS/S	H ₂ O	L+V, L	53-205 (72)	-58/-35	-34	-8.5/-0.2 (59)		0.4-12.3

Tab. 1 Microthermometric data of aqueous fluid inclusions from Bartoušov. Temperature parameters in °C, salinity in wt. % NaCl eq. Numbers in parentheses refer to number of measurements.

regular with sizes from 10 to 50 μ m (Fig. 5i). Two-phase inclusions have almost constant degree of fill (up to 5 vol. %). Secondary inclusions occurring on intergranular trails were mostly monophase (L). Only two two-phase L+V secondary inclusions reaching up to 40 μ m were found. Their morphology was planar and irregular. The gaseous phase occupies 5 vol. %. Fluid inclusions in dolomitic carbonate homogenize at temperatures 62–137 °C and freeze out between -48 and -30 °C. The initial melting was observed around -36 °C. The last melting of ice occurred at temperatures between -4.8 and 0.0 °C (Fig. 8a, Tab. 1).

Fluid inclusions in calcite are mostly two-phase (L+V), less often monophase (L) occurring on both intergranular and intragranular trails. Their morphology is both planar and three-dimensional, mostly irregular or oblong, less often isometric, regular or close to negative-crystal shape. Their size varies from 5 to 53 µm. In two-phase L+V inclusions the vapour phase occupies 5 to 10 vol. % (Fig. 5h). The homogenization temperatures range between 53 and 161 °C. Inclusions freeze out at temperatures between -58 and -35 °C and the eutectic temperature was measured at -34 °C. Last ice melted between -8.5 and -0.2 °C, the latter representing the lowermost value of the whole dataset collected from the Bartoušov site (Tab. 1, Fig. 8a). No hydrohalite or clathrate melting was observed, similarly to dolomitic carbonate.

4.3. Stable isotopes

The isotopic composition of C, O, and S was determined in carbonates and pyrite from four samples (Tab. 3). Two pyrite separates yielded different δ^{34} S values as high as -0.7 and +11.6 ‰ V-CDT. Two samples of dolomiteseries carbonate gave identical both δ^{13} C and δ^{18} O values equal to -6.1 and -15.6 ‰ V-PDB, respectively. One calcite sample had δ^{13} C = -10.2 ‰ V-PDB and δ^{18} O = -17.8 ‰ V-PDB.

5. Discussion

5.1. Composition of fluid inclusions and P–T conditions

Prior to interpretation of fluid inclusion study results, some evaluation of reliability of collected data is necessary. This approach is required due to highly variable both phase composition and microthermometric data, which could be potentially altered by superimposed processes, including leakage, stretching, or necking-down of fluid inclusions, especially in soft and perfectly cleavable mineral as fluorite is (Bodnar and Bethke 1984). The microthermometric data collected from carbonic-aqueous inclusions show very good correlation ($R^2 = 0.94$;

Tab. 2 Microthermometric data of carbonic-rich fluid inclusions from Bartoušov. Temperature parameters in $^{\circ}$ C, numbers in parentheses refer to number of measurements. F – degree of fill.

Sample	Mineral	Genesis	System	Phase comp.	F	Th-tot	Th _{car} (mode)	Tm-CO ₂	Tm _{cla}
BAR-1b	Quartz	P/PS	H ₂ O-CO ₂ >N ₂ -CH ₄	$L_1 + L_2 + V$	0.4-0.7	324 (1)	26.1–29.2 (L) (4)	-56.9/-56.7 (3)	9.1-10.8 (3)
		PS	$N_2 > CO_2 - CH_4 \pm H_2O$	V, L+V	0.0 - 0.5		-143.0/-134.6 (V) (15)	-100.1/-77.2 (6)	2.3-3.0 (5)
	Fluorite	PS	$CO_2 > N_2 - CH_4 \pm H_2O$	$L_1 + V, L_2 + V,$ V, L_1 + L_2 + V	0.0–0.4	149-266 (9)	-16.0/27.9 (V) (66)	-60.5/-57.3 (66)	9.4–10.3 (10)
		PS	$CO_2 > N_2 - CH_4 \pm H_2O$	L	0.0		16.7–17.0 (L) (3)	-59.3 (3)	
		PS	$CO_2 > N_2 - CH_4 \pm H_2O$	V	0.0		16.9–27.0 (C) (2)	-59.3/-57.5 (2)	
		PS	N ₂ >CO ₂ -CH ₄ ±H ₂ O	V, L+V	0.0-0.3		-141.1/-136.4 (V) (7)		2.3-5.7 (3)
		PS	$N_2 - CO_2 - CH_4 \pm H_2O$	V	0.0		-28.7 (V) (1)	-60.6 (1)	



Tange of temperatures estimated from nata metaster staal.										
C	$\delta^{13}C$	$\delta^{18}O$	$\delta^{18}O$	$\delta^{34}S$	T (0C)	$\delta^{13}C_{\text{fluid}}$	$\delta^{18}O_{\text{fluid}}$	$\delta^{34}S_{fluid}$		
Sample	(‰ V-PDB)) (‰ V-PDB)	(% V-SMOW)	(‰ V-CDT)	Temperature (°C)	(‰ V-PDB)	(% V-SMOW)	(‰ V-CDT)		
Dolomite BAR-1b	-6.1	-15.7	14.8		63-137	-8.3/-9.1	-2.2/-11.5			
Dolomite BAR-3	-6.1	-15.6	14.9		62-115	-8.2/-9.2	-4.4/-11.6			
Calcite BAR-3	-10.2	-17.8	12.6		118-134	-12.2/-12.1	-2.2/-0.6			
Pyrite BAR-5				11.6	118-134			9.0/9.2		
Pyrite BAR-6				-0.7	118-134			-3.3/-3.1		

Tab. 3 The C, O, and S isotope composition of carbonates and pyrite and isotope characteristics of their parental fluids calculated for the given range of temperatures estimated from fluid inclusion study.

Fig. 8b) between Tm-CO₂ (as a measure of composition) and Th_{car} (as a measure of density). Excellent correlation exists between Raman-derived composition and Th_{car} ($R^2 = 1.00$; Fig. 8c), implying for good preservation of the studied fluid inclusions with respect to stretching and/or leakage. This is also supported by mostly small variability in Th_{car} and composition of carbonic phase in individual fluid inclusions hosted by individual *FIAs*. No petrographic evidence of significant involvement of necking-down was observed, although this is not always unequivocal. However, highly variable phase proportions were observed also in solitary fluid inclusions, where necking certainly cannot take place. In summary, our observations suggest for generally good preservation of the studied inclusions and reliability of collected data.

Therefore, the wide ranges in phase composition, densities, and chemical composition of primary and pseudosecondary water-carbonic fluid inclusions hosted by quartz and fluorite seem to be the primary feature of the studied fluid inclusions. Such nature is indicative for trapping of a heterogeneous fluid mixture, composed of an aqueous solution and a vapour mixture. In such a situation, the trapping P–T conditions can be derived directly from the microthermometric data. The minimum ascertained homogenization temperature of the aqueous inclusions reflects the true trapping temperature, while the trapping pressure is located at the isochore of associated non-aqueous inclusion (e.g., Hurai et al. 2002).

In Table 4, there are listed bulk compositions and bulk densities of representative carbonic fluids. Calculation of these parameters necessary for construction of isochores was based on a combination of microthermometric data and Raman-derived compositional data for carbonic phase. Because there is some mutual solubility of aqueous and carbonic fluids at elevated temperatures and pressures, we have arbitrarily corrected the amount of water in carbonic phase according to experimental data by Tabasinejad et al. (2011), even in inclusions where no water phase was observed, as low amounts of aqueous solution coating walls of carbonic inclusions are invisible in light microscope due to optical reasons (Diamond 1994). The salt content of low-density carbonic fluids was neglected, as it is necessarily very low owing to poor solubility of electrolytes in non-aqueous fluids (Bowers and Helgeson 1983). The salinity of water-rich inclusions associated with carbonic ones is low and ranges between 0.2 and 4.8 wt. % NaCl eq.

The calculated isochores for contrasting types of carbonic fluids differing in densities and composition are visualised in Fig. 9. The trapping P-T conditions derived by intersection of isochores of carbonic fluids and minimum homogenization temperatures of associated aqueous fluids (e.g., Hurai et al. 2002) for two well documented FIAs involving low-density (to vapour homogenizing) carbonic fluids hosted by both quartz and fluorite range ~135-155 °C and ~60-120 bars. To liquid homogenizing CO₂-dominated inclusions were trapped at higher pressures (above 200 bars), but the precise location of PT conditions is not possible due to absence of co-existing water-rich inclusions. The pressures 60-120 bars are equal to depths ~600-1200 m at hydrostatic conditions. Pressure and temperature decreased from CO₂-dominated towards N₂-dominated carbonic fluids (Fig. 9). This implies for change of composition of carbonic phase during fluid evolution, also supported by the existence of intermediate compositions (Fig. 6).

In contrast, pseudosecondary to secondary aqueous fluid inclusions hosted by fluorite seem to represent gases-absent fluid system, similar to those observed in fluid inclusions hosted by calcite and dolomite. All these inclusions were likely trapped from a homogeneous fluid. In such case, the obtained homogenization temperatures represent minimum possible trapping temperatures and exact P-T conditions can be specified only if independent estimates of pressure or temperature are available (e.g., Roedder 1984; Shepherd et al. 1985). Unfortunately, these are not available in our case. Nevertheless, pressure during the preceding fluid event (involving low-density carbonic fluids) did not exceed 120 bars and if it did not increase substantially (which is not probable during the post-Variscan epoch characterized by overall erosion and uplift), the influence of such a low pressure can be neglected. Therefore, in such case homogenization temperatures of aqueous fluid inclusions (53-165°C) will

 $[\]Leftrightarrow$

Fig. 8 Results of microthermometric and Raman studies of fluid inclusions from Bartoušov. **a** – The Th–Tm_{ice} plot for aqueous fluid inclusions. **b** – The Th_{car} Tm-CO₂ plot for carbonic-rich fluid inclusions. **c** – The Th_{car}-XCO₂ plot for carbonic-rich fluid inclusions. The XCO₂ parameter is based on Raman analysis of the carbonic phase. Symbols (L) and (V) refer to mode of partial homogenization of carbonic phase.

Tab. 4 Microthermometric data, calculated bulk compositions, and densities of representative carbonic fluids used for P–T calculations. Amount of water in carbonic phase was corrected according to experimental data by Tabasinejad et al. (2011).

Trail	Mineral	Th _{car}	Tm-CO ₂	$X(H_2O)$	X(CO ₂)	$X(CH_4)$	$X(N_2)$	D (g/cc)
1	Quartz	-139.0 (V)	_	0.06	0.00	0.17	0.77	0.057
1	Quartz	-134.5 (V)	-77.2	0.06	0.05	0.16	0.73	0.057
2	Fluorite	16.7 (L)	-59.3	0.06	0.78	0.02	0.14	0.363
2	Fluorite	16.9 (C)	-59.3	0.06	0.78	0.02	0.14	0.152
3	Fluorite	26.0 (C)	-57.5	0.04	0.88	0.01	0.08	0.185
3	Fluorite	21.0 (V)	-57.9	0.04	0.85	0.01	0.09	0.163
4	Fluorite	11.2 (V)	-59.6	0.05	0.77	0.03	0.15	0.131
4	Fluorite	-12.9 (V)	-60.5	0.04	0.51	0.08	0.38	0.103
5	Fluorite	-136.4 (V)	_	0.06	0.00	0.20	0.74	0.056
5	Fluorite	-138.2 (V)	_	0.07	0.00	0.20	0.73	0.050

be close to the true trapping temperatures. Salinity of the fluids largely overlaps with those of older aqueous inclusions associated with carbonic inclusions, except for few higher values reaching up to 12.3 wt. % NaCl eq. (Fig. 8a).

5.2. Sources of the fluid phase

Participation of several fluid endmembers during formation of the studied mineralization is suggested from available data. The H_2O-CO_2 fluids with small admixtures of CH_4 and/or N_2 widely participated during the Late Variscan uplift of the Moldanubian Zone, as indicated from numerous studies on metamorphic rocks, pegmatites, ore deposits, and Alpine-type veins (Ackerman et al. 2007; Halavínová and Přichystal 2008; Zachariáš et al. 2009; Cempírek et al. 2010; Fuksová 2014; Fišerová and Dolníček 2014; Ulmanová 2018). Decrease of pressure during fluid evolution is evidenced by both decrease of density of carbonic phase and, in many cases, heterogenization of the fluid. Similar evolution is suggested



By contrast, the N₂-dominated carbonic fluids are very rare in the Moldanubian domain. They are reported from late (usually secondary) fluid inclusions in various rocks and in Roudný Au deposit and are characterized by low density (Zachariáš et al. 2009; Fuksová 2014). The origin of such late N₂ fluids in

the crystalline basement is an intriguing question. One possibility is an intraformational source, due to oxidation of NH₄ cation which is substituting potassium in rock-forming micas and feldspars (e.g., Andersen et al. 1995; Bebout 1997; Wang et al. 2018). This possibility, however, suffers from the fact, that the primary source of such basement-hosted ammonium was original sedimentary protolith, whose NH4 content was subject of significant degradation already during the prograde phases of metamorphism (cf. Bottrell et al. 1988; Bebout and Fogel 1992; Bebout 1997) culminating by anatexis leading to its low, if any, residual contents available for retrograde alteration. In the absence of increase of redox potential, in situ process of N₂ generation is allowed also by the decreasing activity of water in the fluid phase (Andersen et al. 1995). Significant consumption of water due to hydration of rocks should be evidenced by increased salinity of co-existing aqueous solutions, but no significant differences are observed in salinity of aqueous inclusions associated with CO₂- and N₂-dominated inclusions at Bartoušov. These constraints would therefore favour a



second explanation involving an external source of N_2 -rich fluids. The N-rich source can be seen in unmetamorphosed sediments rich in organic matter, which are fertile sources of N_2 -rich fluids (e.g., Kroos et al.

Fig. 9 Interpreted P–T conditions of trapping of the studied fluid inclusions. Isochores are visualised for representative carbonic fluids characterized in Table 4. The P–T fields were constructed for two trails yielding enough data from coexisting aqueous and low-density carbonic-rich fluid inclusions. Black arrow indicates the probable evolution of P–T conditions; the uncertainty of location of P–T conditions during early stage of mineralization is marked by dashed curves.

1995; Littke et al. 1995; Lüders et al. 2005; Mingram et al. 2005).

Probable influence of thermally immature organic matter during evolution of fluids associated with mineralization from Bartoušov is further indicated also by the presence of ethane recorded in some fluid inclusions. Higher hydrocarbons are very sensitive to elevated temperatures, being above ~130 °C cracked to methane (Allen and Allen 1990). This implies for a local source of higher hydrocarbons and short distance of their migration in the relatively hot basement. The admixtures of C₂-C₇ hydrocarbons, reported in some late CH₄-rich fluid inclusions in rock or vein samples from the Moldanubian (Fuksová 2014; unpublished data of Z. Dolníček) may be the result of such pronounced thermal cracking of oil. Inorganic synthesis of these higher hydrocarbons (Potter et al. 2004; Graser et al. 2008; Nivin 2009) is not likely due to the absence of H₂ and CO (Z. Dolníček, unpublished gas-chromatographic data).

Presence of molecular H₂ and O₂ found in substantial quantities in a few N2-bearing inclusions (Fig. 7) is rather surprising in the given geological situation. To date, by Raman microanalysis detectable concentrations of these gases were only reported in fluid inclusions from uranium ores, where they are invariably explained in terms of radiolysis of inclusion water (Dubessy et al. 1988; Savary and Pagel 1997; Derome et al. 2003). Since no uranium mineralization occurs in the proximity of the studied site, an external source of these gases must be taken into account. It is noteworthy that rich concentrations of uranium (reaching up to economic grade) bound to unmetamorphosed organic matter were recorded in uppermost part of the polymetallic Ag-Pb-Zn vein deposit Staré Hory in the Jihlava ore district (J. Vosáhlo, pers. comm.), situated ca. 20 km to SSW in the Jihlava Graben. Possible explanation may thus be related to the occurrence of uranium mineralization in now eroded sedimentary cover of the Moldanubian (Kříbek et al. 2009) combined with focused transport of radiolytic gases into the basement rocks.

Sources of mineral forming components for the late portion of the studied mineralization can be constrained from available stable isotope data. The δ^{18} O values of the parental fluids, calculated for carbonates using homogenization temperatures of fluid inclusions obtained in the same samples (Tab. 3), range between -0.6 and -11.6 %V-SMOW, which are values typical for meteoric water (Sheppard 1986). The fluid δ^{13} C values ranging between -8.2 and -12.2 % V-PDB most likely represent a mixture of carbon from the oxidized organic matter (δ^{13} C = $\leq \sim -20 \%$ V-PDB; Hoefs 1997) with either carbon of the 'homogenized Earth's crust' or 'deep' carbon from the lower crust or upper mantle (both with δ^{13} C = -5 to -8 %V-PDB). The δ^{34} S values of H₂S, from which pyrite precipitated, was probably very variable (-3 and +9 ‰ V-CDT in two samples, respectively). However, it is not surprising considering the late paragenetic position of this pyrite: the end of hydrothermal activity could be possibly associated with changes of physicochemical parameters (pH, Eh), to which S isotopes are very sensitive (Hoefs 1997).

Isotope and fluid inclusion characteristics of carbonate-precipitating fluids is similar to those of dolomites and late vein calcites from the neighbouring Pohled quarry (cf. Mastíková 2011). Indeed, this implies a distinct fluid source and regional fluid flow.

5.3. Genetic model

The available data allow construction of the following scenario of the studied mineralization origin (Fig. 10). The initial opening of fracture, in which the studied mineralization formed, was associated with Late Variscan uplift of the Moldanubian domain. First mineral phase, which crystallized in the vein, was early quartz and W-rich rutile which began to precipitate from late-metamorphic aqueous-carbonic CO2-rich fluids (Fig. 10, Stage 1). The normal faulting associated with post-orogenic extension of the Variscan Orogen gave rise to the Jihlava Graben, which was filled by Upper Carboniferous-to-Lower Permian clastic sediments, in places with coal seams and/or to organic matter sorbed uranium mineralization. High thermal flow characterizing basement rocks during this period allowed for rapid maturation of these sediments (reaching up to anthracite stage; Franců et al. 1998; Pešek et al. 2001) releasing volatile components (CO₂, CH₄ and other hydrocarbons, NH₄ and/or N₂) into fluid phase. Similarly, local accumulations of sediment-hosted uranium ores might have produced the H₂-O₂ bearing fluid phase. The subsequent downward infiltration of pore fluids from sediments into the basement was allowed due to extensional tectonic regime characterized by activity of normal faults (Fig. 10, Stage 2). In such situation, downward fluid movement can be reinforced by the mechanism of suction pump (Sibson 1987). Heating of sedimentary fluid after infiltration into hot basement rocks allowed for conversion of NH4 to N2 and cracking of higher hydrocarbons to methane. Sediment-derived fluids mixed with local late-metamorphic fluids (cf. intermediate compositions of carbonic phase in Fig. 6) but in certain episodes they became the dominating component in the studied vein system. During this stage, hydrothermal alteration of host granites was probably the reason why fluids became enriched in fluorine and began to precipitate fluorite. Final stage of evolution of the hydrothermal system was characterized by precipitation of carbonates (Fig. 10, Stage 3). During this



Stage 1: Early quartz: Late metamorphic fluids

Stage 2: Late quartz and fluorite: Late metamorphic fluids and waters from Piedmont basins Evaporation



Stage 3: Carbonates: Waters from Piedmont basins



stage, activity of surface-derived aqueous fluids without detectable admixture of gases is evidenced from fluid inclusion and stable isotope data.

Infiltration of sedimentary fluids into crystalline basement is frequently reported to explain the origin of numerous types of hydrothermal mineralizations (e.g., Hoffman et al. 1988; Polya et al. 2000; Gleeson et al. 2001; Boiron et al. 2002; Dutkiewicz et al. 2004; Schubert et al. 2007). In the Bohemian massif, the participation of fluids derived from overlying freshwater Permo–Carboniferous Piedmont Basins was interpreted for the formation of vein/shear zone uranium (Žák and Dobeš 1991; Kříbek et al. 2009; Dolníček et al. 2014), vein Ag–Pb–Zn (Žák and Dobeš 1991; Dolníček et al. 2023), and vein barite deposits (Žák et al. 1990).

6. Conclusions

The fluorite-rich vein mineralization in Bartoušov is hosted by steep NW-SE trending vein/stockwork developed in a small body of Variscan granite enclosed in gneisses of the Ostrong Group of the Moldanubian Zone in the Bohemian Massif. Fluorite is accompanied by quartz, Nb and W-enriched rutile, siderite, dolomite-ankerite, calcite and pyrite. Fluid inclusion and stable isotope studies were realized in order to assess the origin of this mineralization. Quartz and fluorite contain primary and pseudosecondary fluid inclusions with highly variable proportions of a low-salinity aqueous solution and a carbonic phase, whose composition range from CO₂- to N₂-dominated. Methane, ethane, H₂, and surprisingly also O2 were found in some cases, too. Late low-density CO2and N₂-dominated aquo-carbonic fluids were trapped from a heterogeneous fluid at temperatures ~135-155 °C and pressures ~60-120 bars. Late carbonates crystallized from low- to moderate-salinity low-temperature aqueous fluids, whose water was meteoric in origin and HCO,⁻ contained significant proportion of carbon from oxidized organic matter. We interpret the origin of the studied mineralization in the context of post-Variscan uplift of the Moldanubian basement and associated formation of the tectonic structure of the Jihlava Graben, now deeply eroded, but originally filled up by Carboniferous-Permian freshwater sediments. The early CO₂-rich aquo-carbonic fluids probably represent local basementderived retrograde-metamorphic fluids, whose decrease in density probably reflects the post-orogenic uplift of the area. Younger low-density N2-dominated CH4-, C2H6-, H2-, O2-bearing aquo-carbonic fluid could be sourced from immature sediments of the Jihlava Graben due to thermal alteration of organic matter (N_2 , hydrocarbons, possibly part of H_2) and synsedimentary uranium ores (H_2 , O_2). As such, the studied mineralization illustrates the dynamics of ancient fluid movement at the interface of basement and its sedimentary cover in a tectonically active orogenic area.

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Fig. 10 A sketch illustrating the interpreted genetic scenario of formation of fluorite vein mineralization in Bartoušov. Arrows refer to directions of fluid flow.

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