Hydrothermal veins linked with the Variscan structure of the Prague Synform (Barrandien, Czech Republic): resolving fluid-wall rock interaction

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Variscan syntectonic hydrothermal veins of the Prague Synform are important traces of small-scale fluid migration in Lower Palaeozoic sedimentary rocks — a process induced by late Variscan tectogenesis. Two main structural types of Variscan syntectonic calcite veins were recognised during fieldwork. Veins of Type I have an irregular or sigmoidal shape and are often arranged in en echelon arrays. A shearing regime during the formation of this type is deduced. Veins of a second structural type (Type II) have a more regular and straight shape relative to those of Type I and in some places form a dense network. The structural position of the Type II veins is related to structural elements of Variscan folds. Veins were formed due to interlayer-slip combined with fold-related fracturing that gave rise to the infilling of dilational structures. A tensional regime also permits growth of the fibrous veins. Two principal directions were distinguished within the Type II veins. The first one is NNW–SSE and the second one shows a perpendicular ENE–WSW orientation. These directions seem to be parallel and/or perpendicular to the nappe architecture of the Prague Synform. Variscan syntectonic veins crystallised in a relatively closed, rock-buffered system. Extraction of chemical components from surrounding rocks is indicated by a combined microprobe/cathodoluminescent study and by isotope geochemistry. The carbon isotope values of hydrothermal calcites reflect the carbon isotope composition of the host rocks. The $\delta^{13}C$ values of vein calcites and their host Silurian rocks are between –0.29 and –1.98‰ PDB. The same relationships were found between the veins and the host Devonian limestones (from 1.72 to 2.52‰ PDB). Samples close to the Silurian/Devonian boundary show transition values between 0.25 and +1.16‰ PDB. The Sr-isotopic signature supports a genetic link between the calcite veins and the host rocks. The $^{87}Sr/^{86}Sr$ ratio in calcites ranges between 0.708619 and 0.708738 and in wall rocks between 0.708755 and 0.709355. Aqueous and hydrocarbon-rich fluid systems have been found in fluid inclusions. Liquid hydrocarbons show mostly a light blue fluorescence suggesting the presence of higher hydrocarbons. They are more abundant in dark Silurian rocks, which are rich in organic matter. Lower salinities (0.5–8.9 eq. wt.% NaCl) and homogenization temperatures with a maximum around 140°C are typical for the aqueous (H_2O–NaCl) system. The oxygen isotopic composition of fluids ranges between –2.80 and +3.33‰ SMOW. This indicates that transformed formation waters interacted with the host rocks and/or deeply circulating isotopically depleted meteoric waters. Intersections with the isochore specify border trapping temperatures between 127 and 160°C and pressures from 300 to 1070 bars.

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INTRODUCTION

An increasing number of studies focused on syntectonic hydrothermal mineralization in sedimentary basins provide important evidence concerning the origin and migration pathways of palaeofluids during orogeny (Oliver, 1986; Muchez *et al*., 1995; Muchez *et al*., 2000; Schulz *et al*., 2002; Slobodník *et al*., 2006). Syntectonic hydrothermal veins are believed to be a product of mobilisation and crystallisation of hydrothermal solutions during deformation processes that affected the rock complexes (Ramsay and Huber, 1987). Consequently we can consider that

Variscan hydrothermal veins of the Prague Synform represent important traces of fluid migration induced by Variscan tectogenesis. The carbon, oxygen and strontium isotope composition of vein-filling calcite and quartz cements and their host rocks were successfully used for the study of fluid-rock interaction (e.g., Hilgers and Sindern, 2005; Lefticariu *et al*., 2005). The nature of syntectonic fluids can have or lack a genetic relation to the host rock (e.g., Gregory and Criss, 1986). If the solution composition is completely driven by exchange with the wall rock, precipitation takes place under rock-buffered conditions (Gray *et al*., 1991; Oliver and Bons, 2001).
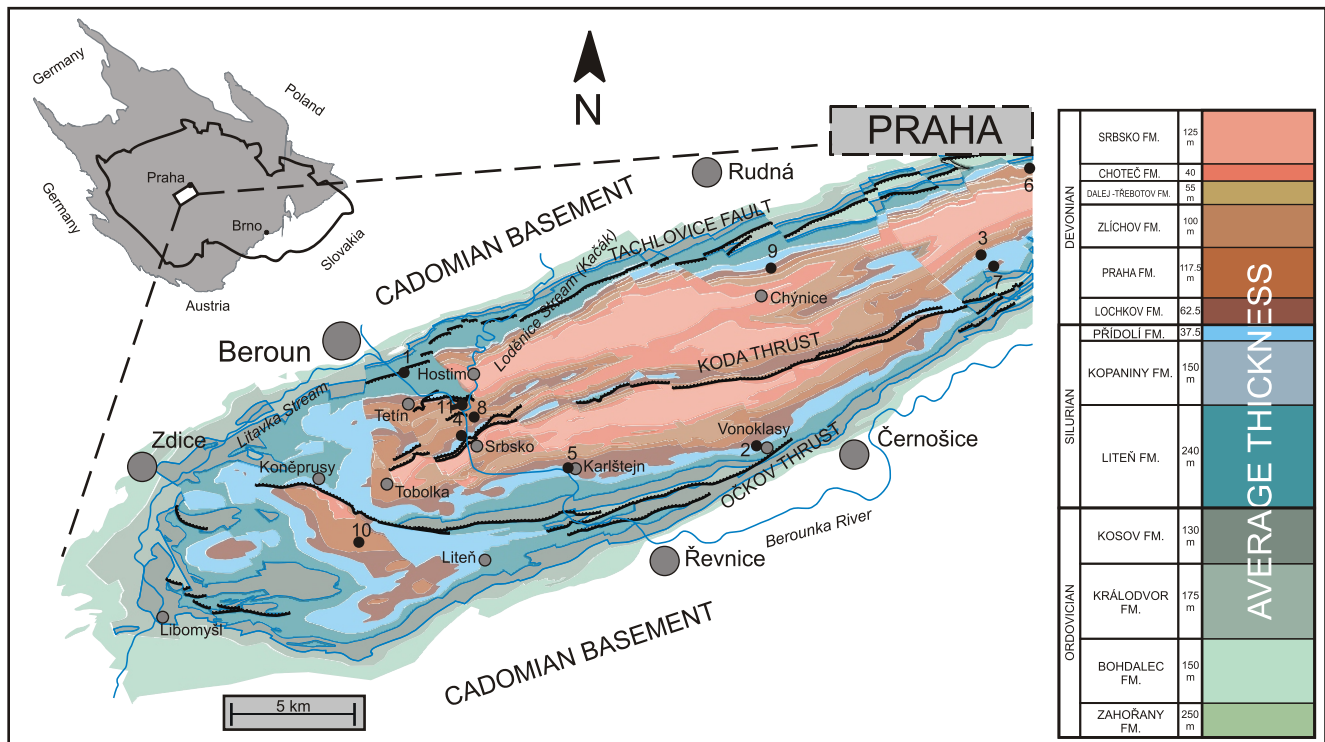
Fig. 1. Location of the area studied and simplified geological map of the Prague Synform (based on previous 1:50 000 mapping)

Sample localities: 1 — Lištice — abandoned quarry near the sewerage plant, SW of village, sigmoidal calcite veins from Lower Silurian basaltic tuff (Liteň Fm.); 2 — Vonoklasy — abandoned quarry near the water-station, W of village, fibrous calcite veins from fine bioclastic limestones and black shales (Přídolí Fm.); 3 — Velká Chuchle — Žákův Quarry, WNW of village, syntectonic veins within bioclastic limestones and shales (upper Přídolí/lower Lochkov Fm.); 4 — Srbsko — Berounka River, outcrops along the right bank, NW of village, syntectonic veins within bioclastic limestones (upper Přídolí/lower Lochkov Fm.); 5 — Buďany Rock at Karlštejn, international parastratotype of the Silurian/Devonian boundary along the left bank of the Berounka River, calcite veins parallel with and perpendicular to bedding planes of finely laminated platy limestones (upper Přídolí/lower Lochkov Fm.); 6 — Barrande's Rock in Prague, syntectonic veins within dark grey finely bioclastic limestones (lowermost Lochkov Fm.); 7 — Velká Chuchle — outcrops on the Homolka Hill, sigmoidal calcite veins from bioclastic platy limestones (Lochkov Fm.); 8 — Srbsko — "Na Chlumu" Quarry, N of village, irregular calcite veins and younger narrow reddish calcite veins from biodetritic limestones (Praha Fm.); 9 — Chýnice — Mramorka Quarry, NNE of village, sigmoidal calcite vein arranged into en echelon arrays within the micritic limestones termed the "Zbuzany Marble" (Praha Fm.); 10 — Koněprusy — Homolák Quarry, SE of village, syntectonic veins within reef limestones (Praha Fm.); 11 — Hostim — Alkazar Quarry, SSW of village, irregular calcite veins within massive bioclastic limestones (Praha Fm.). Abbreviated stratigraphic scheme (Upper Ordovician–Middle Devonian) adapted from Chlupáč (1993). Numbers on the map correspond to sample localities described above

The principal aim of this study is to determine the composition and possible origin of mineralizing solutions in the Prague Synform. Attention is given to the types of veins that make it possible to distinguish Variscan syntectonic veins and fluid flow from other events. The characteristics of the preserved fluids have been determined by a combination of field observations, petrographic investigation and microthermometric study of fluid inclusions together with microprobe/cathodoluminescent study and stable/radiogenic isotope analyses of the hydrothermal mineralization.

GEOLOGICAL SETTING

The Barrandien is situated in the central part of the Bohemian Massif, within the easternmost part of the Variscan Fold Belt in central Europe. Regionally viewed, it represents a terrain bound by the Variscan Central Bohemian Pluton in the SE and diverse metamorphic units in the SW and NW. To the NE, the Barrandian Proterozoic and Palaeozoic continue as the basement of the Bohemian Cretaceous Basin (Chlupáč et al.,

1998). The Barrandian sequence consists of three units marked by unconformities: the Late Proterozoic and the Lower Palaeozoic (Cambrian unit, Ordovician to Devonian unit). While the Cadomian processes formed the Proterozoic and Cambrian unit, the Ordovician to Devonian unit was folded and fractured during the Variscan Orogeny. All these parts are covered by postorogenic Upper Carboniferous and Cretaceous deposits (Chlupáč, 1993). The youngest part of the Barrandian Palaeozoic consists of Ordovician to Middle Devonian sedimentary and effusive volcanic rocks more than 3500 m thick (Fig. 1). The rocks form a large synform or synclinorium (Máška and Zoubek, 1961) sometimes called the Prague Basin (Havlíček, 1981). The Ordovician rocks of the Prague Synform unconformably overlie the Cadomian basement. In the central section, clayey, sandy and pyroclastic rocks dominate. Sedimentary iron ores and lenses of carbonates are common in marginal segments (Chlupáč et al., 1998). Marine sedimentation persisted without any substantial break from the beginning of the Silurian to the later part of the Mid Devonian. Two typical facies were distinguished within the Silurian successions: black and grey graptolitic shales formed in basinal depressions and

bioclastic to micritic limestones developed on volcanic elevations (Bouček, 1934). With the exception of the latest flysch-like Srbsko Formation, the Devonian strata are characterised by carbonate development. An accessible facies, common fossils with a high correlative value and instructive exposures support the assertion that the Siluro-Devonian development of the area studied is typical of the Lower Palaeozoic of the region. The base of the Přídolí Series as well as those of several stages (Lochkovian, Pragian, Zlichovian and Dalejan) were established here for the first time, the Silurian/Devonian and Lochkovian/Pragian boundaries have their internationally accepted boundary stratotypes here, and there is also the parastratotype of the Lower/Middle Devonian boundary (Chlupáč et al., 1998).

The shape and fabric of the Prague Synform was long considered to be the result of synsedimentary rifting parallel to the prolongation of the basin (e.g., Havlíček, 1982). Melichar and Hladil (1999) and Melichar (2004) recently suggested a nappe structure for the Prague Synform on the basis: (I) the duplication of stratigraphic sequences along bedding-parallel thrusts, (II) flat-and-ramp geometry of the thrusts, (III) uniform top-to-the south-southeast movement on detachment thrusts and (IV) tectonic juxtaposition of different facies. The thrusting age with respect to lithology is presumed to be Frasnian, whereas the post-sedimentary synformal structure was formed during the Lower Carboniferous (Melichar, 2004).

According to the results of sedimentological studies in the central part of the Prague Synform, about 2–3 km of Lower Palaeozoic strata were removed as a result of post-Devonian erosion (Suchý et al., 1996; Franců et al., 1998). Devonian and Silurian rocks typically experienced diagenetic burial to the depth of the oil window (Suchý et al., 1996), whereas the underlying Ordovician rocks were partly affected by anchimetamorphism with temperatures above 200°C (Franců et al., 1998). Models of the thermal history of the Barrandian Lower Palaeozoic based on apatite fission track analysis were published by Glasmacher et al. (2002), Suchy et al. (2002) and Filip and Suchý (2004).

PREVIOUS RESEARCH

Not many papers have been focussed on a detailed studies of the syntectonic fluid systems associated with Variscan structures of the Prague Synform. Moreover, strictly distinguishing between diagenetic, syntectonic and post-tectonic mineralizing phases is still often unclear.

The first investigation of the possible origin of the mineralization solutions was carried out for the widespread undeformed N–S trending huge calcite veins by Žák et al. (1987) and Cílek et al. (1994). Suchý and Zeman (1998) and Zeman et al. (2000) connected the subvertical N–S striking Barrandian calcite veins to a major fracture zone, 10–20 km wide, that cuts across the Bohemian Massif. Veins postdating the Variscan deformation precipitated at 55–115°C from fluids with a complex chloride system of variable salinity (up to 23 eq. wt.% NaCl) that originated in a distant reservoir.

Suchý et al. (1996) reported occurrences of epigenetic dolomites within the upper part of the Přídolí Formation (Přídolí Series). The dolomites were formed during deeper burial through recrystallization by hot basinal fluids. The formation of xenotopic dolomite was followed by coarse-grained saddle dolomite cement, petroleum-bearing quartz crystals, and minor sulphides.

Based on previous studies, Suchy et al. (2000) described three successive generations of calcite cements precipitated in post-Devonian fractures that cut across Lower Palaeozoic limestones of the Prague Synform. The two oldest generations (Stage 1 and 2) are represented by differently tectonically deformed calcites. Fluid inclusion data indicate that precipitation of these calcites occurred at conditions of up to 70°C from H_2O–NaCl solutions with variable salinity (0–12.4 eq. wt.% NaCl), which contained an admixture of liquid petroleum hydrocarbons. Some Stage 2 calcites contain also highly saline inclusions of a complex chloride system. The lower range of the calculated $\delta^{18}O$ values of the ambient fluids (–3.5‰ to +2.7‰ SMOW) indicates precipitation of calcite cements from deeply circulating meteoric waters. The presence of petroleum hydrocarbon inclusions in some samples may reflect partial mixing with deeper basinal fluids. The youngest generation of vein calcite cements (Stage 3) differs from Stages 1 and 2 calcites in its stable isotope and cathodoluminescence characteristics.

Suchy et al. (2002) described three vein generations associated with burial, tectonic movement and uplift that were recognised within the Silurian and Devonian limestones and shales in Kosov Quarry at Beroun. The first vein generation is composed of "beef" (fibrous) calcites that were formed during deeper burial of the strata, at ~ 65°C. Structural observations and fluid inclusion analysis of these cements indicate that the "beef" calcites likely precipitated in an overpressured system from hydrocarbon-rich aqueous fluids, derived from adjacent shales. Subsequent generation of E–W striking veins occurred under deep burial conditions, at temperatures of up to 80–110°C. The youngest generation of N–S-striking veins probably represents a regional, uplift-related fracture set that developed after the Cenomanian.

Volk et al. (2000, 2002) characterise petroleum inclusions in vein, fossil and vug cements. Petroleum inclusion samples have been classified into five groups based on the relative distribution of n-alkanes. They provided specific constraints for petroleum migration processes in the Prague Synform. The resulting data not only show pristine live oils, gases, residual and precipitated bitumens and a broad variation of mixtures of the groups above, but also show that gas migration and fractionation processes played a major role in the Prague Synform.

METHODS

Hydrothermal veins were sampled at large exposures (e.g., quarries) in several parts of the Prague Synform (Fig. 1). The sample set represents different stratigraphic levels and lithologies.

Formal names of formations used in this work were taken from Chlupáč (1993; Fig. 1). With reference to the International Stratigraphic Chart (Gradstein et al., 2004) the Silurian studied formations belong to the Llandovery and Wenlock Se-

ries (Liteň Fm.) and the Pridoli Series (Přídolí Fm.) whereas the Devonian formations correspond to the Lochkovian (Lochkov Fm.) and Pragian stages (Praha Fm.). Hydrothermal veins were carefully sampled only at localities where structural/genetic relations between the different vein types and the folded strata are clearly visible. Silurian samples dominantly came from bituminous carbonates and black shales of the Přídolí (Požáry) Formation, whereas Devonian samples were taken especially from the facially variable carbonates of the Praha Formation.

Analytical techniques were focused on hydrothermal phases and wall rocks. Thin sections of veins were studied by conventional optical and cathodoluminescence (CL) microscopy. The CL study was carried out using a hot cathode *HC2-LM* (Simon Neuser, Bochum) with an accelerating voltage of 14 kV and beam density of 10 $\mu A/mm^2$. CL microscopy, with respect to CL-theory (e.g., Frank *et al*., 1982; Machel, 2000), was applied to distinguish vein generations and the possibly zonal nature of the hydrothermal carbonates.

Mineral analyses were performed with the *CAMECA SX100* electron microprobe employing the *PAP* correction program at the Laboratory of Electron Microscopy and Microanalysis, a joint facility of Masaryk University and the Czech Geological Survey in Brno. The microprobe was operated at 15 keV acceleration voltage, 10 nA beam current, 10 μm beam diameter and with 10 to 40 seconds counting time. The following standards and lines were used for the carbonates analyzed: Ca K_α, Fe K_α (andradite), K K_α, Al K_α (sanidine), Mg K_α ($MgAl_2O_4$), S K_α (barite), P K_α (apatite), Mn K_α (rhodonite) and Sr L_α ($SrSO_4$). Of the nine elements measured in carbonates, only Ca, Fe, Mg, Mn, Sr were found to be above their respective detection limits, which were 350 to 700 ppm (based on the counting statistics).

Double-polished thin sections was prepared for microthermometry of fluid inclusions and fluorescence microscopy. The epi-fluorescence microscope *Olympus BX60* were equipped with filter blocks B-2A (Exc.: 450–490 nm, mirr.: 500 nm, barr.: 515 nm) and UV-2A (Exc.: 330–380 nm, mirr.: 400 nm, barr.: 420 nm). Microthermometric analyses were obtained by using a *Linkam THMSG 600* heating and freezing stage mounted on the *Olympus* microscope with ×50 and ×100 long working distance objectives. Thermometric measurements were calibrated against phase transitions in synthetic fluid inclusions. The eutectic temperature (T_e) and melting temperature (T_m) were used for estimation of the ionic nature and salt concentration of the aqueous phase. The salinity of the fluid was calculated according to Borisenko (1977) and Bodnar (1993). The homogenization temperature (T_h) corresponds to the minimum fluid-trapping temperatures (Roedder, 1984). Isochores were calculated using the *FLUIDS* computer package programs (Bakker, 2003) based on the equation of Zhang and Frantz (1987). The vapour phases of several inclusions were checked by *Raman* microspectrometry performed with an *ISA JOBIN YVON LABRAM* apparatus at Montanuniversität Leoben.

The carbon and oxygen isotopic composition of the calcites and their carbonate host rocks were performed using a *Finnigan MAT 251* mass spectrometer at the Czech Geological Survey in Prague. The carbon and oxygen were liberated by reaction with 100% orthophosphoric acid under high vacuum (McCrea, 1950). The results are reported in per mil deviation from the international standards (PDB, SMOW). The precision of both carbon and oxygen isotope analyses was better than 0.1‰. Isotopic composition $\delta^{18}O$ (‰ SMOW) of parent fluids were calculated for calcite–H_2O system according to the equation published by Zheng (1999).

The strontium isotope analyses of a few calcite veins and their carbonate host rocks were processed at the Czech Geological Survey in Prague. Strontium was separated by the Sr-Spec ion exchanger (Eichrom; Pin *et al*., 1994) and determined on a *Finnigan MAT 262* thermal ionization mass spectrometer in dynamic mode. The $^{87}Sr/^{86}Sr$ standard NBS987 provided a value of 0.710247 to which all measurements were corrected. The standard deviation (1σ) was ±0.000013.

RESULTS

STRUCTURAL AND PETROGRAPHIC CHARACTERISTICS

Abundant Variscan syntectonic hydrothermal veins in the area studied occur within the Silurian and Devonian shales and limestones. Calcite is a dominant mineral phase in the veins. Examination under the microscope reveals several features of deformation such as the plastic deformation of calcite twins or less commonly, dynamic recrystallization along grain boundaries. Calcites are usually medium to fine grained with a gray to milky colour. Only a few Variscan calcites (e.g., from Mramorka Quarry) are rose-coloured.

Two main structural types of syntectonic vein were recognised during our field study. Both structural types post-date folded diagenetic veins and are crosscut by straight veins that are not visibly genetically related in deformed strata. Veins of Type I are not very long, have an irregular or sigmoidal shape and are often arranged in en echelon arrays (Fig. 2A–D). The length of veins is usually 10–50 cm. The thickness is highly variable but generally does not exceed 10 cm. Selvage-like microstructures formed by an insoluble residuum are often developed in the host rocks. The subsequent shearing regime during the formation of this type caused the plastic deformation of calcite cement. It was very difficult to measure vein direction in many localities. En echelon arranged sigmoidal veins usually have an oblique orientation to bedding planes.

The second structural type of syntectonic vein (Type II) shows a genetic relationship to the fold geometry of the host rocks. These veins have a more regular and straight shape relative to the Type I veins. The length of veins is variable, but does not exceed 1 m. They are usually thinner than the Type I veins and in some places form a dense network. Veins are usually perpendicular or parallel to the bedding planes and were formed due to interlayer-slip accompanied by fold-related fracturing that gave rise to infilling dilational structures (Fig. 2E, F). The structural position of the Type II veins is related to structural elements of the Variscan folds. A tensional regime permitted the growth of the fibrous veins (Fig. 3). The calcite fibres were oriented perpendicular to the main stress (Fig. 4). Generally two principal vein directions were distinguished within this structural type. The first one is NNW–SSE
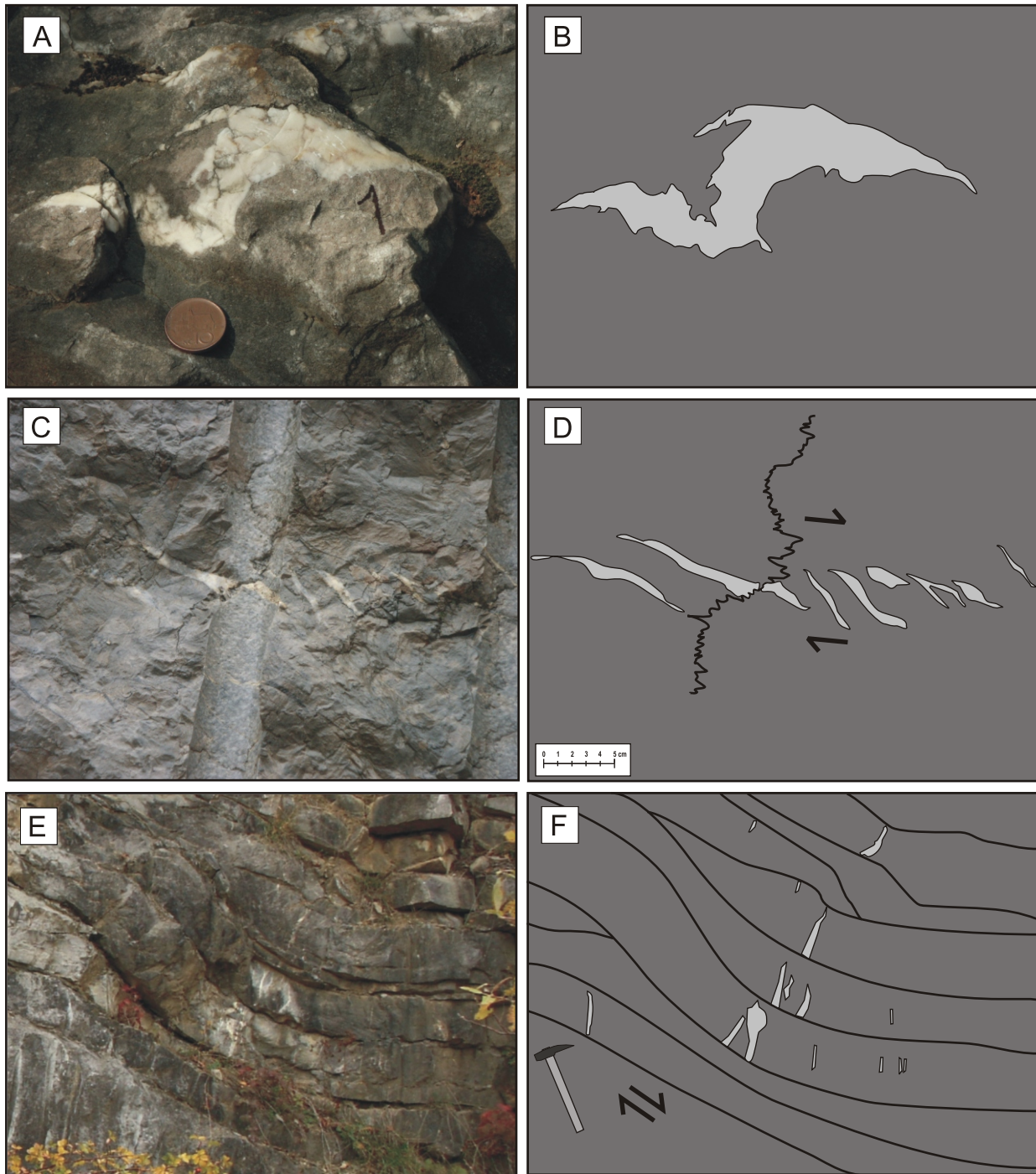
Fig. 2. Main structural types of the syntectonic calcite veins studied

A, **B** — irregular vein from Srbsko, "Na Chlumu" Quarry; **C**, **D** — sigmoidal veins arranged into en echelon arrays from Chýnice, Mramorka Quarry; **E**, **F** — veins infilling dilational structures in Chýnice, Mramorka Quarry

and the second one seems to be in a perpendicular ENE–WSW orientation (Fig. 5).

For comparative study we also sampled a sigmoidal calcite vein from Lower Silurian basaltic tuff from the Lištice Quarry (Fig. 6). These volcano-sedimentary rocks are called "frogstone" because of their greenish colour. Under the microscope we can see irregular altered fragments of glassy basalt with calcite cement (around 40 vol.%). Typically, amygdales filled by chlorite and relicts of albitised plagioclase laths in a variolitic groundmass are present. Calcites from the vein show plastic deformation of the narrow calcite twins.

CATHODOLUMINESCENT AND MICROPROBE CHARACTERISTICS

Syntectonic veins of both structural types show analogous cathodoluminescent features. Typically, the calcites are of similar luminescent colour (dull red/brown tones) with barely distinguish-
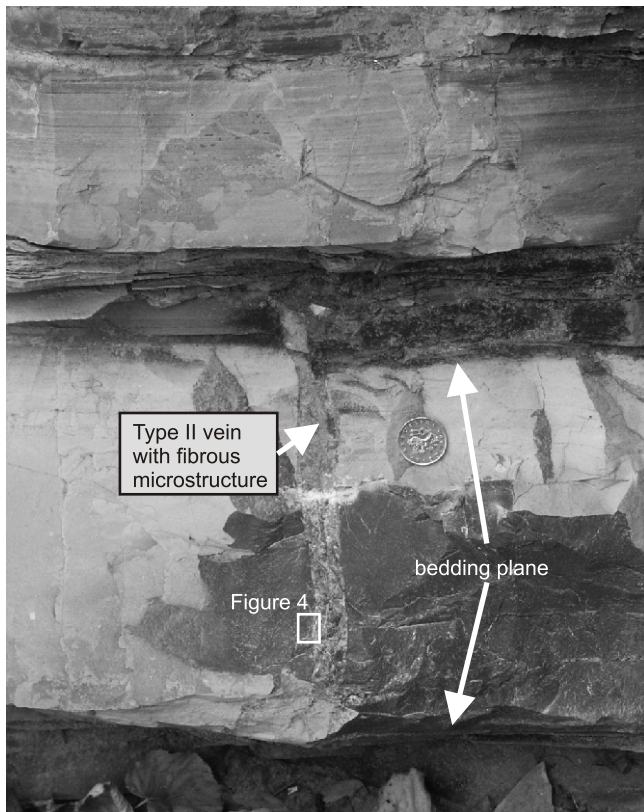
Fig. 3. Position of fibrous calcite vein within bituminous limestone from abandoned quarry at Vonoklasy
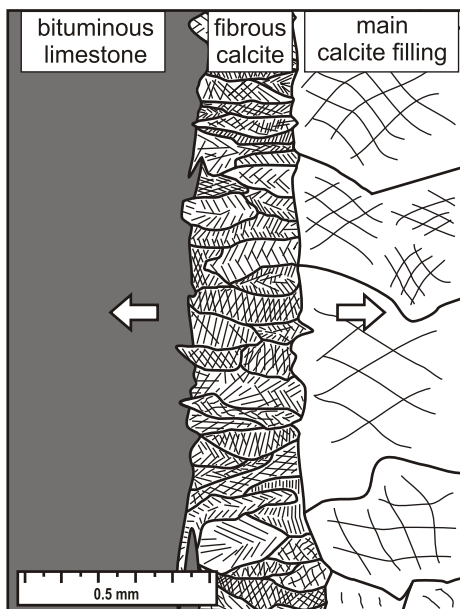

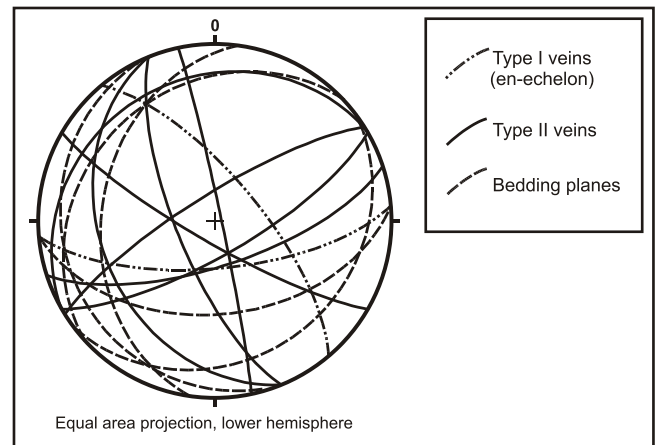Fig. 4. Orientation of calcite fibres in thin section

Fig. 5. Principal directions of Variscan syntectonic hydrothermal veins in the Prague Synform

Fig. 6. Example of sigmoidal calcite vein from Lower Silurian basaltic tuff (Lištice Quarry)

able transitions between CL-generations (Fig. 7A). The calcites show similar colour and intensity in cathodoluminescence as their host limestones. Equivalent luminescence characteristics are indicative of narrow fluid-rock interaction, which produced rock-buffered fluids during formation of syntectonic calcite veins. The low intensity of luminescence and different genetic model of the syntectonic veins is clearly visible in comparison with post-Variscan veins from the studied area. These latter veins, characterised by an intensely zoned luminescence pattern (bright red and non-luminescent zones), were formed by multiple flow events of a fluid-buffered system (Fig. 7B).

The chemical composition of the dull luminescent syntectonic calcites is relatively uniform. Backscattered electron images indicate narrow variations within the calcite composition (Fig. 7C). Typically low Mg contents are relatively higher in the calcites from the outer part of the calcite veins as well as in the calcites from the wall rock (Table 1). Stylolite seams have often developed between the host rock and the syntectonic vein (Fig. 7C). Euhedral crystals of dolomite are dominant within these 200–600 μm wide seams (Fig. 7D). Dolomites have slightly elevated Fe contents (up to 4.4% ankerite component). The highest Sr content (up to 3230 ppm) was found in the fibrous calcite veins (Table 1). The Mn content is below the detection limit in both the calcites from the syntectonic veins and in the calcites from the host rock. In contrast, the Mn contents in the post-Variscan calcite samples (Srbsko, "Na Chlumu" Quarry) are as high as 8570 ppm.
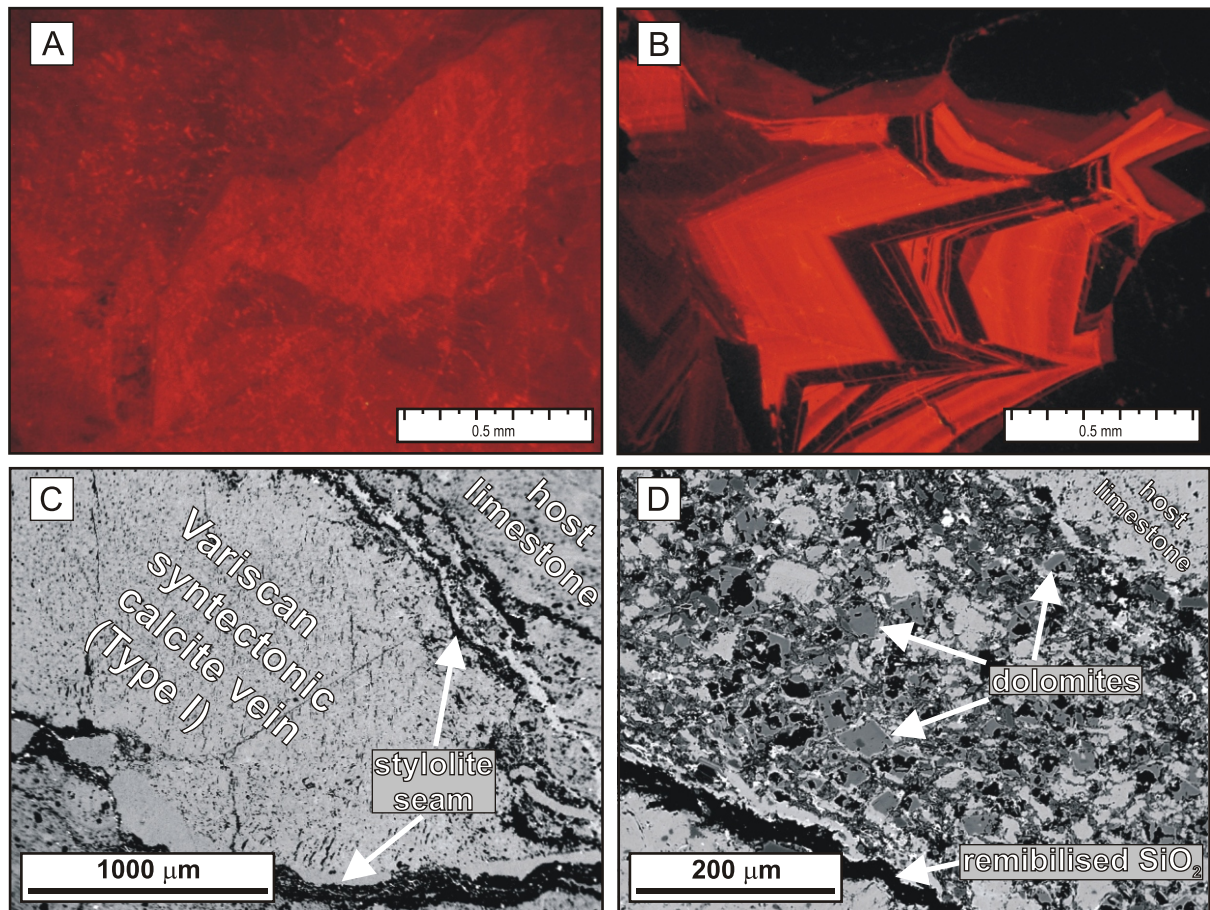
Fig. 7. Compositional features of vein carbonates

A — typical dull luminescence of Variscan syntectonic calcites, Budňany Rock at Karlštejn; **B** — intensely zoned luminescence pattern of post-Variscan calcites, Srbsko, "Na Chlumu" Quarry; **C** — backscattered electron image of Variscan syntectonic vein rimmed by stylolite seam, Chýnice, Mramorka Quarry; **D** — backscattered electron image showing euhedral crystals of dolomite within a stylolite seam, Chýnice, Mramorka Quarry

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Representative microprobe analyses of the carbonates studied

Sample	CaO [wt.%]	FeO [wt.%]	MgO [wt.%]	MnO [wt.%]	SrO [wt.%]	Total	Type of analysed carbonate
MR 4	56.434	0.202	0.102	BDL	BDL	56.786	Variscan — Type I, vein centre
MR 4	55.269	0.33	0.417	BDL	0.126	56.217	Variscan — Type I, vein rim
MR 4	55.401	0.264	0.422	BDL	0.115	56.25	Variscan — Type I, near stylolite seam
MR 4	32.467	1.462	18.031	BDL	BDL	52.257	Variscan — Type I, dolimte from stylolite seam
MR 4	32.966	1.872	18.054	BDL	BDL	53.096	Variscan — Type I, dolimte from stylolite seam
MR 4	55.489	0.153	0.411	BDL	BDL	56.171	calcite from the host rock
MR 4	55.333	0.18	0.553	BDL	BDL	56.187	calcite from the host rock
VV 2	54.447	0.379	0.319	BDL	0.225	55.43	Variscan — Type II, vein centre
VV 2	55.299	0.138	0.338	BDL	0.197	56.055	Variscan — Type II, vein rim, fibrous calcite
VV 2	54.681	0.182	0.451	BDL	0.4	55.777	Variscan — Type II, vein rim, fibrous calcite
SCH3	53.851	0.293	0.137	1.063	BDL	55.413	post-Variscan
SCH3	55.962	0.199	0.115	0.076	BDL	56.432	post-Variscan
SCH3	56.008	0.108	0.1	1.107	BDL	57.402	post-Variscan
SCH3	55.506	BDL	0.478	BDL	BDL	56.103	calcite from the host rock

BDL — values below the detection limit; sample localities: MR — Chýnice, Mramorka Quarry; VV — Vonoklasy; SCH — Srbsko, "Na Chlumu" Quarry

ISOTOPE GEOCHEMISTRY

Carbon isotope values of Variscan calcites reflect the carbon isotope composition of the host rocks (Fig. 8). Samples from the Silurian rocks have typically slightly negative $\delta^{13}C$ values whereas samples from the Devonian rocks display positive $\delta^{13}C$ values, with an overlap field close to the Silurian/Devonian boundary (Table 2). The vein calcites and their host Silurian rocks provided $\delta^{13}C$ values between –0.29 and –1.74‰ PDB. Syntectonic calcite from Lower Silurian basaltic tuff has a value of –1.98‰ PDB. The same relationships in positive values are seen between the veins and host Devonian limestones. Carbon isotope values are between 1.72 and 2.52‰ PDB. Samples close to the Silurian/Devonian boundary (upper Přídolí/lower Lochkov Fm.) show transition isotope ratios of inorganic carbon between 0.25 and +1.16‰ PDB.

Oxygen isotope values show a large scatter in composition with overlap values for syntectonic calcites from the Silurian localities (from +16.44 to +23.44‰ SMOW) and the Devonian localities (from +14.99 to +26.66‰ SMOW). Values of the wall rocks are between +24.65 and +25.93‰ SMOW in the Silurian rocks, but tend to be slightly higher in the Devonian rocks (+27.12 and +29.09‰ SMOW).

The $^{87}Sr/^{86}Sr$ ratio is 0.708619 for a calcite vein within the Silurian bioclastic limestone (Přídolí Fm.; Přidolí Series) and 0.708755 in the wall rock (Table 2). The $^{87}Sr/^{86}Sr$ ratios of vein calcite and the host Devonian micritic limestone (Praha Fm.; Pragian Stage) correspond to 0.708738 and 0.709355, respectively.
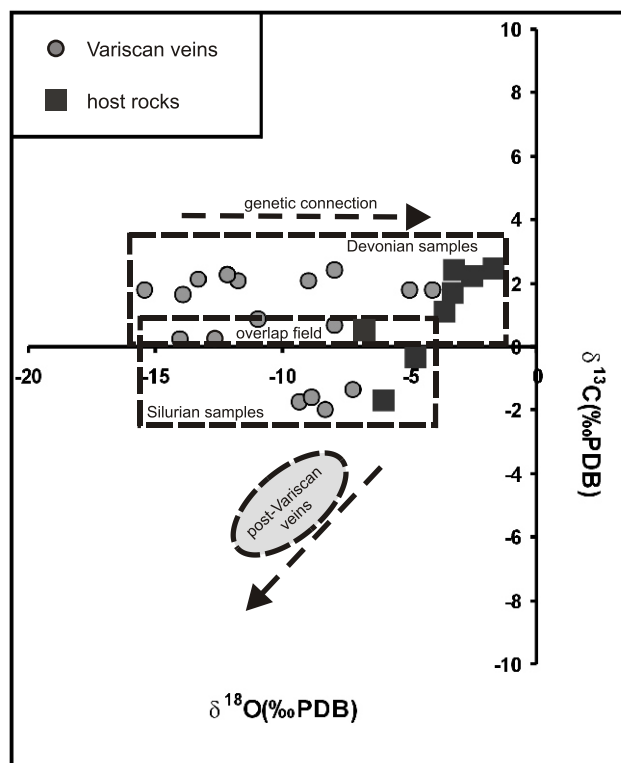

Fig. 8. Carbon and oxygen isotope values of calcite veins and their host rocks in the Prague Synform. Field for post-Variscan veins based on unpublished data of the first author

Table 2

Carbon, oxygen and strontium isotope composition of Variscan syntectonic vein calcites and their wall rocks

| Sample	Type	Locality	$\delta^{13}C$ [‰ PDB]	$\delta^{18}O$ [‰ PDB]	$\delta^{18}O$ [‰ SMOW]	$^{87}Sr/^{86}Sr$
LT1	calcite vein	Lištice	–1.98	–8.32	22.34	
VV2	calcite vein	Vonoklasy	–1.74	–9.32	21.30	0.708619
VV2r	limestone	Vonoklasy	–1.63	–6.08	24.65	0.708755
VV3	calcite vein	Vonoklasy	–1.61	–8.88	21.75	
VV1r	limestone	Vonoklasy	–0.29	–4.83	25.93	
VCZ1	calcite vein	Velká Chuchle — Žákův Quarry	–1.36	–7.25	23.44	
SB	calcite vein	Srbsko — Berounka river	0.25	–14.03	16.44	
KB	calcite vein	Budňany Rock at Karlštejn	0.87	–10.96	19.61	
BS 1	calcite vein	Barrande's Rock in Prague	0.18	–12.66	17.86	
BS 1r	limestone	Barrande's Rock in Prague	0.68	–8.56	22.08	
VC1	calcite vein	Velká Chuchle	0.66	–7.96	22.71	
VC1r	limestone	Velká Chuchle	1.16	–3.68	27.12	
SCH4r	limestone	Srbsko — "Na Chlumu" Quarry	1.72	–3.35	27.46	
SCH1	calcite vein	Srbsko — "Na Chlumu" Quarry	1.77	–4.12	26.66	
SCH5	calcite vein	Srbsko — "Na Chlumu" Quarry	1.78	–15.44	14.99	
SCH4	calcite vein	Srbsko — "Na Chlumu" Quarry	1.81	–5.00	25.76	
MR4	calcite vein	Chýnice — Mramorka Quarry	1.63	–13.92	16.56	0.708738
MR4r	limestone	Chýnice — Mramorka Quarry	2.25	–2.62	28.21	0.709355
MR3	calcite vein	Chýnice — Mramorka Quarry	2.06	–8.95	21.69	
MR2	calcite vein	Chýnice — Mramorka Quarry	2.12	–13.29	17.21	
MR1	calcite vein	Chýnice — Mramorka Quarry	2.25	–12.17	18.37	
HO1	calcite vein	Koněprusy — Homolák Quarry	2.08	–11.74	18.81	
HO3	calcite vein	Koněprusy — Homolák Quarry	2.29	–12.18	18.35	
HO1r	limestone	Koněprusy — Homolák Quarry	2.45	–3.30	27.51	
AK1	calcite vein	Hostim — Alkazar Quarry	2.41	–7.98	22.69	
AK1r	limestone	Hostim — Alkazar Quarry	2.52	–1.76	29.09	
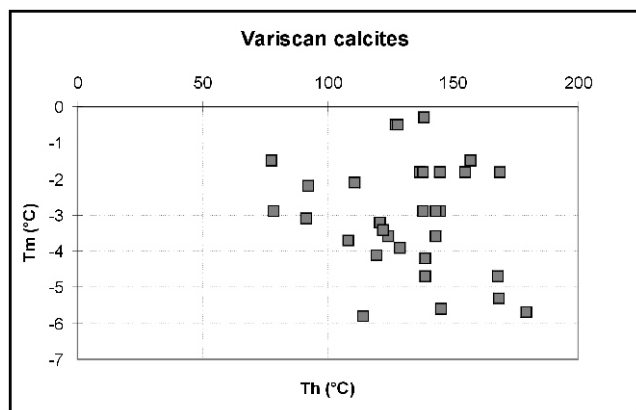
Fig. 9. Plot of the homogenization temperatures (T$_h$) *versus* melting temperatures (T$_m$) of ice in fluid inclusions in syntectonic Variscan calcites of the Prague Synform

The isotopic composition of two samples from undeformed calcite veins (Srbsko, "Na Chlumu" Quarry) indicates distinct isotopic sources for the post-Variscan type of veins genetically associated with, for example, subsurface brines (Fig. 8). Carbon isotope ratios of calcites are from –4.36 to –4.44‰ PDB, whereas the host limestone has a more positive value of +1.72‰ PDB. The oxygen isotope composition is between +21.21 and +22.59‰ SMOW for veins and +27.46‰ SMOW for the surrounding rock. The $^{87}Sr/^{86}Sr$ ratio in post-Variscan calcite corresponds to 0.709232 and is higher than the ratio in the wall rock ($^{87}Sr/^{86}Sr$ = 0.708610).

MICROTHERMOMETRY OF THE FLUID INCLUSIONS

Aqueous and hydrocarbon-rich fluid systems have been found in the fluid inclusions. Generally, sizes of inclusions are fairly small (3–15 mm). Most of the inclusions are one-phase but two-phase fluid inclusions are also present. The homogenization temperature of primary and/or pseudo-secondary aqueous fluid inclusions ranges between 77–179°C with most frequent values around 140°C (Fig. 9). Melting temperatures of ice are between –0.3 and –5.8°C and after recalculation correspond to salinities between 0.5 to 8.9 eq. wt.% NaCl. Eutectic temperatures were difficult to observe, but if measurable they are around –21°C, which indicates a H$_2$O–NaCl fluid system (Borisenko, 1977).

Liquid hydrocarbon-rich inclusions are easily visible with the application of fluorescence microscopy. The most common light bluish to blue fluorescence suggests the presence of higher liquid hydrocarbons (Stasiuk and Snowdon, 1997). Fluid inclusions with liquid hydrocarbons are more frequent in syntectonic calcites from Silurian black shales and bituminous limestones, which are rich in organic matter. The presence of methane in the vapour phase of inclusions (sample from Barrande's Rock in Prague) has been shown by Raman microspectrometry (Halavínová, unpubl.).

P–T CONDITIONS DURING VEIN FORMATION

The average value of homogenization temperatures has been used for the calculation of the isochore. Two thermobaric
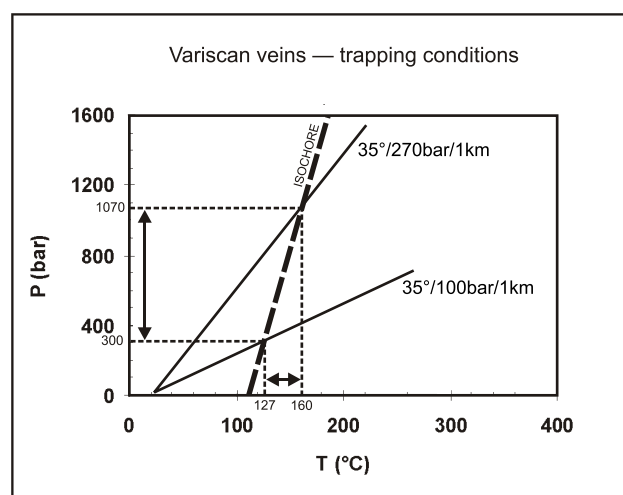

Fig. 10. Pressure-temperature conditions for the precipitation of the Variscan syntectonic calcite veins

gradients (for lithostatic and hydrostatic pressure and a thermal gradient of 35°C/km, see Suchy *et al*., 2002) were applied to determine P–T conditions (Fig. 10). The pressure may have changed during development of the Type I and Type II veins. We assume that the thermobaric gradients represent border trapping conditions for Variscan hydrothermal veins in the area studied. It is likely that precipitation of the extensional hydrothermal veins (Type II) took place during conditions close to the hydrostatic gradient. Intersections with the isochore specify trapping temperatures between 127 and 160°C and pressures ranging from 300 to 1070 bars. The P–T conditions obtained correspond to a depth of 1–4 km.

DISSCUSION

Based on this study, we can distinguish two completely different genetic groups of hydrothermal veins associated with the post-diagenetic development of the Prague Synform: Variscan syntectonic veins and post-Variscan veins (Figs. 8 and 11). Variscan syntectonic veins characterized in this paper are represented by at least two main structural types (Type I and Type II). Both Type I and Type II veins show genetic association with deformation and structural development of their host rocks (Fig. 11). With respect to the age of formation of the Prague Synform they could be considered as late Variscan. Deformation of the Palaeozoic rocks initiated fluid migration through the rock sequences. Variscan syntectonic veins seem to be parallel to or perpendicular with the nappe architecture of the Prague Synform. This may provide another supporting argument for the tectonic concept of the Prague Synform proposed by Melichar and Hladil (1999) or Melichar (2004).

Microstructures preserved in the veins studied provide important indications regarding the mechanism of their origin. Dilational veins show a fibrous microstructure (Fig. 4) which is typical for crack-seal origin (Ramsay, 1980). Developed selvage-like microstructures (Fig. 7C, D) support the key role of diffusion as a mass transport mechanism from the surrounding rock (Oliver and Bons, 2001).
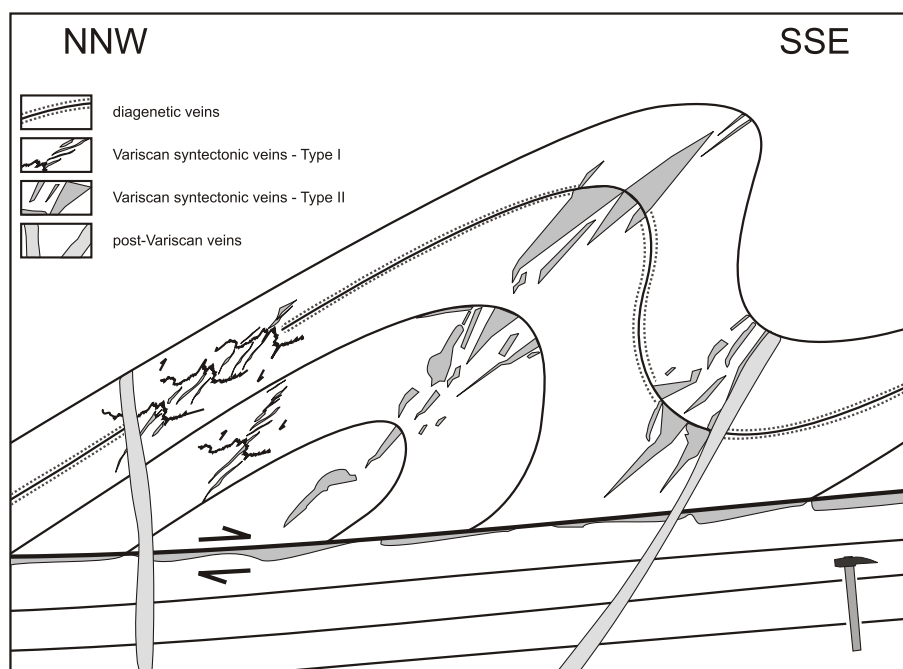
**Fig. 11. Schematic sketch showing spatial position of observed vein generations
in the Prague Synform and their relation to Variscan fold structures**

The mineral and isotope compositions indicate small-scale migration under rock-buffered conditions during formation of the syntectonic veins. Extraction of some chemical components from host rocks is also shown by CL study. Carbon isotope values of Variscan calcites clearly reflect the carbon isotope composition of the wall rocks (Fig. 8; Table 2). This fact may suggest that carbon from the veins was derived from the surrounding rocks. A gradual shift in $\delta^{13}C$ from negative to positive values was observed in Přidolí and Lochkovian limestones by Hladíková et al. (1997). This shift is inferred to have been related to a combination of higher productivity, increased deposition of organic matter and shallowing of the basin.

Oxygen isotope values show a large scatter in composition what can indicate various interactions and/or sources of aqueous fluids. $\delta^{18}O$ isotope values together with results of microthermometric study were used for calculation of isotopic composition of parent aqueous solutions. Fractionation equations for the calcite–H_2O system (Zheng, 1999) give values between –2.80 and +3.33‰ SMOW. This indicates that transformed formation waters interacted with the host rocks and/or deeply circulating meteoric waters. Strontium isotope ratios support a direct genetic link between the Variscan syntectonic calcite veins and their surrounding rocks. Our results point to precipitation in a relatively closed system. This may indicate a relatively restricted volume of fluids connected with a rock-buffered system (e.g., Richards et al., 2002). Similar limitation during fluid flow in terrains with thrust faults was described by Kirschner and Kennedy (2001).

Across the entire Prague Synform we can also find undeformed veins without geochemical (Fig. 7B; Table 1) or isotopic connection (Fig. 8) to surrounding rocks. This type could be considered as a post-Variscan with respect to widespread analogues in different sedimentary successions of Variscan Europe (e.g., Muchez et al., 1995; Jochum, 2000; Heijlen et al., 2003).

Based on previous research the late Variscan hydrothermal veins belong to Stage 1 and partly to Stage 2 according the distinguishing factors presented by Suchy et al. (2000). Calcites with highly saline inclusions of Stage 2 and calcites with intensely zoned luminescence patterns of Stage 3 demonstrate characteristic features typical of post-Variscan hydrothermal veins.

Our data also support previous studies (e.g., Suchý et al., 1996) that Variscan veins crystallised during P–T conditions of the oil window.

CONCLUSIONS

Variscan syntectonic hydrothermal veins in the area studied occur in Lower Palaeozoic sedimentary rocks. Two main structural types of Variscan syntectonic veins are described.

Veins of Type I are not very long, have an irregular or sigmoidal shape and are often arranged in en echelon arrays. Veins of Type II have a more regular and straight shape relative to Type I and show common orientations parallel to and perpendicular with the nappe architecture of the Prague Synform. Plastically deformed calcite crystals are the dominant mineral phase. The veins crystallised in a predominantly closed, rock-buffered system. Extraction of chemical components from surrounding rocks is documented through mineral and isotope geochemistry. The $\delta^{13}C$ values of Variscan syntectonic calcites reflect the carbon isotope composition of the host rocks (Fig. 8). The veins were predominantly formed from relatively low-salinity aqueous systems. The oxygen isotope composition

of parent aqueous solutions is indicative for transformed formation waters that interacted with the host rocks and/or deeply circulating meteoric waters. The strontium isotope signature supports a close genetic link between the calcites and their host rocks. Fluid inclusions with liquid hydrocarbons are frequent in syntectonic calcites from Silurian black shales and bituminous limestones, which are rich in organic matter. Variscan syntectonic veins crystallised at P–T conditions of the oil window. Intersections with the isochore specify trapping temperatures between 127 and 160°C and pressures of 300 and 1070 bars. Folded strata of the Prague Synform are also crosscut by undeformed hydrothermal veins without direct geochemical and isotopic connection to surrounding rocks. This type is considered as post-Variscan.

REFERENCES

BAKKER R. J. (2003) — Package FLUIDS 1. Computer programs for analysis of fluid inclusion data and for modelling bulk fluid properties. Chem. Geol., **194** (1–3): 3–23.

BODNAR R. J. (1993) — Revised equation and table for determining the freezing point depression of H_2O–NaCl solutions. Geochim. Cosmochim. Acta, **57**: 683–684.

BORISENKO A. S. (1977) — Study of salt composition of fluid inclusions in minerals using cryometric technique. Geol. Geofiz., **8**: 16–27.

BOUČEK B. (1934) — Bemerkungen zur Stratigraphie des böhmischen Gotlandien und seinen Faziesverhältnissen. Zbl. Geol. Paläont., Abt. B: 477–494.

CHLUPÁČ I. (1993) — Geology of the Barrandian. A field trip guide. Senckenberg-Buch 69.Verlag Waldemar Kramer, Frankfurt am Main.

CHLUPÁČ I., HAVLÍČEK V., KŘÍŽ J., KUKAL Z. and ŠTORCH P. (1998) — Palaeozoic of the Barrandian (Cambrian to Devonian). Czech Geol. Surv. Praha.

CÍLEK V., DOBEŠ P. and ŽÁK K. (1994) — Formation conditions of calcite veins in the quarry "V Kozle (Hostim I, Alkazar)" in the Bohemian Karst. J. Czech Geol. Soc., **39** (4): 313–318.

FILIP J. and SUCHÝ V. (2004) — Thermal and tectonic history of the Barrandian Lower Paleozoic, Czech Republic: Is there a fission-track evidence for Carboniferous-Permian overburden and pre-Westphalian alpinotype thrusting? (Critical comments on the paper by Ulrich A. Glasmacher, Ulrich Mann and Günther A. Wagner). Bull. Geosc., **79** (2): 107–112.

FRANCŮ E., MANN U., SUCHÝ V. and VOLK H. (1998) — Model of burial and thermal history of the Tobolka-1 borehole profile in the Prague basin. Acta Univ. Carol., Geol., **42**: 248–249.

FRANK J. R., CARPENTER A. B. and OGLESBY T. W. (1982) — Cathodoluminescence and composition of calcite cement in the Taum Sauk Limestone (Upper Cambrian), Southeast Missouri. J. Sediment. Res., **52** (2): 631–638.

GLASMACHER U. A., MANN U. and WAGNER G. A. (2002) — Thermotectonic evolution of the Barrandian, Czech Republic, as revealed by apatite fission-track analysis. Tectonophysics, **359**: 381–402.

GRADSTEIN F. M., OGG J. G., SMITH A. G., BLEEKER W. and LOURENS L. J. (2004) — A new geologic time scale, with special reference to Precambrian and Neogene. Episodes, **27**: 83–100.

GRAY D. R., GREGORY R. T. and DURNEY D. W. (1991) — Rock-buffered fluid-rock interaction in deformed quartz-rich turbidite sequences, Eastern Australia. J. Geophys. Res., **96**: 19681–19704.

GREGORY R. T. and CRISS R. E. (1986) — Isotopic exchange in open and closed systems. Rev. Mineral. Geoch., **16** (1): 91–127.

HAVLÍČEK V. (1981) — Development of a linear sedimentary depression exemplified by the Prague basin (Ordovician–Middle Devonian;

Barrandian area–central Bohemia). Sbor. Geol. Věd, Geol., Praha, **35**: 7–48.

HAVLÍČEK V. (1982) — Ordovician in Bohemia: Development of the Prague Basin and its benthic communities. Sbor. geol. Věd, Geol., Praha, **37**: 103–136.

HEIJLEN W., MUCHEZ PH., BANKS D. A., SCHNIDER J., KUCHA H. and KEPPENS E. (2003) — Carbonate-hosted Zn-Pb deposits in Upper Silesia, Poland: origin and evolution of mineralizing fluids and constraints on genetic models. Econ. Geol., **98**: 911–932.

HILGERS C. and SINDERN S. (2005) — Textural and isotopic evidence on the fluid source and transport mechanism of antitaxial fibrous microstructures from the Alps and the Appalachians. Geofluids, **5** (4): 239–250.

HLADÍKOVÁ J., HLADIL J. and KŘÍBEK B. (1997) — Carbon and oxygen isotope record across the Pridoli to Givetian stage boundaries in the Barrandian basin (Czech Republic). Palaeogeogr., Palaeoclimat. Palaeoecol., **132**: 225–241.

JOCHUM J. (2000) — Variscan and post-Variscan lead-zinc mineralization, Rhenish Massif, Germany: evidence for sulfide precipitation via thermochemical sulfate reduction. Miner. Depos., **35**: 451–464.

KIRSCHNER D. L. and KENNEDY L. A. (2001) — Limited syntectonic fluid flow in carbonate-hosted thrust faults of the Front Ranges, Canadian Rockies, inferred from stable isotope data and structures. J. Geophys. Res., **106** (B5): 8827–8840.

LEFTICARIU L., PERRY E. C., FISCHER M. P. and BANNER J. L. (2005) — Evolution of fluid compartmentalization in a detachment fold complex. Geology, **33** (1): 69–72.

MACHEL H. G. (2000) — Application of cathodoluminescence to carbonate diagenesis. In: Cathodoluminiscence in Geosciences (eds. M. Pagel, V. Barbin, P. Blanc and D. Ohnenstetter): 160–166. Springer Verlag, Berlin.

MÁŠKA M. and ZOUBEK V. (1961) — Teplá-Barrandian area. In: Tectonic development of Czechoslovakia (eds. T. Buday, O. Kodym, M. Mahel´, M. Máška, A. Matějka, J. Svoboda and V. Zoubek): 43–73 (in Czech). Ústř. Úst. Geol., Praha.

MCCREA J. M. (1950) — On the isotopic chemistry of carbonates and a paleotemperature scale. J. Chem. Phys., **18**: 849–857.

MELICHAR R. (2004) — Tectonics of the Prague Synform: a hundred years of scientific discussion. Krystalinikum, **30**: 167–187.

MELICHAR R. and HLADIL J. (1999) — Restored and new evidence for early Variscan nappe structures in Central Bohemia. Terra Nostra, Freiberg, **99** (1): 147–148.

MUCHEZ PH., SINTUBIN M. and SWENNEN R. (2000) — Origin and migration pattern of palaeofluids during orogeny: discussion on the Variscides of Belgium and northern France. J. Geochem. Explor., **69–70**: 47–51.

MUCHEZ PH., SLOBODNIK M., VIAENE W. A. and KEPPENS E. (1995) — Geochemical constraints on the origin and migration of palaeofluids at the northern margin of the Variscan foreland, southern Belgium. Sediment. Geol., **96**: 191–200.

OLIVER J. (1986) — Fluids expelled tectonically from orogenic belts; their role in hydrocarbon migration and other geologic phenomena. Geology, **14** (2): 99–102.

OLIVER N. H. S. and BONS P. D. (2001) — Mechanisms of fluid flow and fluid–rock interaction in fossil metamorphic hydrothermal systems inferred from vein-wallrock patterns, geometry and microstructure. Geofluids, **1** (2): 137–162.

PIN C., BRIOT D., BASSIN C. and POITRASSON F. (1994) — Concomitant separation of strontium and samarium-neodymium for isotopic analysis in silicate samples, based on specific extraction chromatography. Ann. Chim. Acta., **298**: 209–217.

RAMSAY J. G. (1980) — The crack-seal mechanism of rock deformation. Nature, **284**: 135–139.

RAMSAY J. G. and HUBER M. I. (1987) — The Techniques of Modern Structural Geology, **2**: Folds and Fractures. Strain Analysis. Acad. Press, London.

RICHARDS I. J., CONNELLY J. B., GREGORY R. T. and GRAY D. R. (2002) — The importance of diffusion, advection, and host-rock lithology on vein formation: A stable isotope study from the Paleozoic Ouachita orogenic belt, Arkansas and Oklahoma. Geol. Soc. Am., **114**: 1343–1355.

ROEDDER E. (1984) — Fluid inclusions. Mineral. Soc. Am., Rev. Mineral., **12**: 1–644.

SCHULZ B., AUDREN C. and TRIBOULET C. (2002) — Oxygen isotope record of fluid-rock-SiO_2 interaction during Variscan progressive deformation and quartz veining in the meta-volcanosediments of Belle-Ile (Southern Brittany). J. Struct. Geol., **24**: 1281–1297.

SLOBODNÍK M., MUCHEZ PH., KRÁL J. and KEPPENS E. (2006) — Variscan veins: record of fluid circulation and Variscan tectonothermal events in Upper Palaeozoic limestones of the Moravian Karst, Czech Republic. Geol. Mag., **143** (4): 491–508.

STASIUK L. D. and SNOWDON L. R. (1997) — Fluorescence micro-spectrometry of synthetic and natural hydrocarbon fluid inclusions: crude oil chemistry, density and application to petroleum migration. Appl. Geochem., **12**: 229–241.

SUCHY V., DOBES P., FILIP J., STEJSKAL M. and ZEMAN A. (2002) — Conditions for veining in the Barrandian Basin (Lower Palaeozoic), Czech Republic: evidence from fluid inclusion and apatite fission track analysis. Tectonophysics, **348**: 25–50.

SUCHY V., HEIJLEN W., SYKOROVA I., MUCHEZ P., DOBES P., HLADIKOVA J., JACKOVA I., SAFANDA J.and ZEMAN A. (2000) — Geochemical study of calcite veins in the Silurian and Devonian of Barrandian Basin (Czech Republic): evidence for widespread post-Variscan fluid flow in the central part of the Bohemian Massif. Sediment. Geol., **131**: 201–219.

SUCHÝ V., ROZKOŠNÝ I., ŽÁK K. and FRANCŮ J. (1996) — Epigenetic dolomitization of the Přídolí formation (Upper Silurian), the Barrandian basin, Czech Republic: implications for burial history of Lower Paleozoic strata. Geol. Rundsch., **85**: 264–277.

SUCHÝ V. and ZEMAN A. (1998) — Episodic post-Variscan fluid flows and hydrothermal karstification in the Bohemian Massif, Czech Republic: A preliminary note. Abstr. 15th Intern. Sediment. Congress, Alicante: 747–748.

VOLK H., HORSFIELD B., MANN U. and SUCHÝ V. (2002) — Variability of petroleum inclusions in vein, fossil and vug cements — a geochemical study in the Barrandian Basin (Lower Palaeozoic, Czech Republic). Org. Geochem., **33**: 1319–1341.

VOLK H., MANN U., BURDE O., HORSFIELD B. and SUCHÝ V. (2000) — Petroleum inclusions and residual oils: constraints for deciphering petroleum migration. J. Geochem. Explor., **71**: 307–311.

ZEMAN A., SUCHY V., STEJSKAL M., JANKU J., CERMAK J. and TUREK K. (2000) — Migration of fluids controlled by equidistant fracture systems: an example from Central Europe (Czech Republic, Slovakia and Austria). J. Geochem. Explor., **69–70**: 499–504.

ZHANG Y. G. and FRANTZ J. D. (1987) — Determination of the homogenization temperatures and densities of supercritical fluids in the system NaCl–KCl–CaCl_2–H_2O using synthetic fluid inclusions. Chem. Geol., **64**: 335–350.

ZHENG Y. F. (1999) — Oxygen isotope fractionation in carbonate and sulfate minerals. Geochem. J., **33** (2): 109–126.

ŽÁK K., HLADÍKOVÁ J., LYSENKO V. and SLAČÍK J. (1987) — Carbon and oxygen isotopic composition of cave sinters, vein calcites and sedimentary carbonates from the Bohemian Karst (in Czech). Český kras, Beroun, **13**: 5–28.