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Paleofluid temperatures and pressures in Tertiary accretionary prism of the Western Carpathians

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Abstract. Formation of euhedral quartz („Marmarosh Diamonds“) in mineralized joints of the Tertiary collisonal belt of the Western Carpathians can be correlated with a folding-superimposed, regional collapse-related flow of hot fluids. The essentally aqueous fluids have been enriched by methane and locally also by petroleum.

Temperatures of quartz crystallisation derived from microthermometry data on coexisting, immiscible methane- and water-dominated fluid inclusions increase from 140-205°C in the unfolded Central Carpathian Paleogene Basin (CCPB), through 160-210°C in the Magura nappe, to 190-220°C in the Dukla nappe. The temperature increase has been accompanied by a fluid pressure increase from 0.5-1.5 kbar in the *CCPB*, through 0.7-2 kbar in the Magura nappe, to as much as 3.7 kbar in the Dukla nappe.

A concept of cyclically changing lithostatic and hydrostatic fluid regimes in fractured rocks could account for the unusual pressure fluctuations observed during the quartz precipitation. Estimated fluid pressures correspond to overburden of 5-5.9 km in the *CCPB* (Spišská Magura Mts.), 7.5-7.9 km in the Magura Nappe, and > 8 km in the Dukla nappe.

Keywords: fluid inclusions, methane, flysch sediments, joints, temperature, pressure, Carpathians

Introduction

Mineralized joints in folded Upper Cretaceous-Oligocene flysch of the Outer Carpathians contain transparent quartz crystals with typical bi-pyramidal habitus. Typical localities have been known mainly from bitumen-rich beds in the ukrainian and the east-slovakian segments of the Outer Flysch Belt (***OFB***), but some occur also in the polish part (Zepharovich 1859; Tóth, 1882; Tokarski, 1905; Laskiewicz, 1960). Large quartz crystals, up to 5 cm in size, have been revealed in fissures from unfolded Paleogene flysch basin of the Central Western Carpathians – ***CCPB*** (Zepharovich 1859; Tóth 1882; Mastella & Koisar, 1975). The euhedral quartz is generally the latest mineral of the fissures, but it partly overlaps precipitation interval for the earlier drusy calcite. The calcite-quartz age relationship is the same in the *OFB* and the *CCPB*. Similar relationship has been reported also in the Rahiv nappe from the ukrainian segment of the *OFB* (Vityk et al., 1995, 1996).

Primary, methane-dominated fluid inclusions are characteristic of the euhedral quartz from the Carpathian region (e.g. Kozlowski, 1982; Zacicha et al., 1984; Karwowski & Dorda, 1986; Kalyuzhniy, 1993; Vityk et al., 1994, 1995, 1996; Hurai et al., 1995; Świerczewska et al. 1997, 1998; Dudok & Jarmolowicz-Szulc, 1999) and also from other segments of the Alpine-Himalayan orogenic belt (see reviews in Mullis, 1987, Vityk et al., 1996). Similar methane-bearing euhedral quartzes have been described from low-grade accretionary wedges of south-western Japan (Sakaguchi, 1999, Lewis et al., 2000), Kodiak formation in Alaska (Vrolijk et al., 1985, 1988), and Central and Northern Appalachians (Kisch & van den Kerkhof, 1991, Evans 1995, Evans & Battles, 1999, O´Reilly & Parnell, 1999).

The paper is aimed to elucidate instantaneous *PT* conditions in the Tertiary accretionary complex of the Western Carpathians recorded by the quartz-hosted fluid inclusions trapping coexisting immiscible CH_4- and H_2O-rich phases.

Origin of mineralized joints

Origin of joints and their mineralization has been studied in terms of structural evolution only in the Magura nappe. During Tertiary times, the nappe has experienced three development stages: 1) NW-verging synsedimentary folding and thrusting, 2) NE-verging thrusting accompanied by strike-slip faulting, 3) regional collapse (Decker et al., 1997, Tokarski & Świerczewska, 1998, Tokarski et al., 1999).

The cross-fold joints comprise T-joints, striking subperpendicular (80-90°) to fold axes, and two sets of D-joints, striking under high angle (66-80°) to fold axes. The fold-parallel joints comprise two longitudinal sets of joints (L, L´), striking under small angle to fold axes. The cross-fold joints are normal to bedding, which is indicative of their formation prior to folding, most likely during sedimentation of the host strata. The fold-parallel joints postdate the cross-fold ones. Folding incidental to the first stage has led to transformation of some D-joints into minor cross-fold strike-slip faults of two conjugate sets. Some of the T-joints have been also transformed into tension gashes. After completion of the regional folding in the first stage, the maximum stress axis s1 has rotated 90° clockwise. The 1st stage-related T-joints have re-activated as strike-slip faults, whereas some D-joints have been transformed into tension gashes. Close to completion of the 2nd stage-related rotation, the longitudinal L and L′ joints have re-activated as small-scale faults. Regional collapse of the 3rd stage has been marked by normal faulting, resulting in re-activation of the pre-existing joints and strike-slip faults as small-scale normal faults (Tokarski et al., 1999).

Quartz mineralization has formed during several stages. Euhedral quartz armouring detrital quartz grains exposed in open fissures can be correlated with diagenesis and synsedimentary folding (Świerczewska et al., 1999). Fibrous and columnar calcites have crystallized during strike-parallel extension in horizontally positioned host strata. The calcite is rarely accompanied by fibrous quartz, particularly in small-scale faults. Crystallization of the columnar calcite in some joints has taken place during and/or after the 2nd stage-related folding due to cross-fold extension. Blocky calcite has precipitated during fold-parallel extension after completion of the folding. This is valid also for relatively frequent blocky quartz. Drusy quartz represents the last phase of the composite calcite-quartz veins, precipitating during extensional tectonic regime and open-space fluid circulation.

In the *CCPB*, calcite-filled veins are ubiquitous, but quartz is present only in the Spišská Magura Mts. Calcite infillings correspond to blocky and drusy types. Fibrous and columnar types have not been observed. Euhedral quartz growing onto blocky calcite is the latest mineral phase of the composite veins. In simple joints, the euhedral quartz and calcite grow directly on rockwalls.

Subvertical quartz-bearing joints in the CCPB form conjugate E-W- and SE-SW-trending rhomboidal sets interpreted provisionally as accomodation structures created due to shearing in the adjacent Pieniny Klippen Belt. In contrast, mostly N-S-(NNE-SSW)-trending subvertical (75-90°) mineralized veins in the southern part of the CCPB are believed to be coeval with shear fractures of strike-slip origin, originating during inversion (uplift) of the CCPB. These veins only very rarely contain blocky quartz with methane-gasoline inclusions trapped at temperatures around 80°C (Hurai et al., 1995).

Fluid inclusions

According to phase composition at room temperature, primary CH_4-bearing inclusions can be subdivided into three groups:

I. Monophase inclusions composed of methane-rich liquid.

II. Monophase inclusions with light brown to greenish-brown methane-saturated petroleum, in places with dark brown and black opaque asphaltite blebs attached to inclusion walls.

III. Two-phase aqueous inclusions with vapour bubble.

IV. Composite, two- and three-phase inclusions, consisting of liquid methane-petroleum, liquid methane-water, or liquid methane-petroleum-water assemblages. The inclusions sometimes contain transparent-to-brown, highly birefringent, radially concentric aggregates of parafinic hydrocarbons. These inclusions, usually with inconsistent phase ratios record a heterogeneous entrapment of methane-petroleum-water, methane-petroleum or methane-water mixtures.

Formation PT conditions and fluid inclusion bathymetry

Coexistence of immiscible methane- and water-dominated liquids trapped as group IV inclusions provides unique opportunity for obtaining crystallisation *PT* conditions of quartz directly from microthermometry data. In a group of coeval inclusions, minimum homogenization temperature of the aqueous inclusions has been considered as approaching the actual trapping temperature, and the corresponding fluid pressure has been bracketted by intersection of the temperature with isochores for most and least dense coexisting methane inclusions. Densities of the methane-bearing inclusions have been derived from equation of state for saturation curve of pure methane for H1-type inclusions (Setzman & Wagner, 1991) or from the phase diagrams by Thiéry et al. (1994) for the H2- and S2-types, CH_4-CO_2 inclusions. Isochore has been recalculated from density and composition using equation of state for multicomponent gaseous system (Holloway, 1981).

Crystallisation temperatures of the quartz are relatively broad in the CCPB (140-205°C), and the Magura nappe (160-210°C) in contrast with the narrow range estimated for the Dukla nappe (190-220°C), which might result from a still limited set of data. Large pressure differences have been observed among selected localities in the Dukla unit. Fluid pressures between 2.2-3.7 kbar are limited to one locality (Szczawa), while the two other sites have yielded values between 1.6-2.1 kbar, with one estimate at 1.1 kbar. The inclusion fluid pressures between 2.2-3.7 kbar may be thus interpreted either as real, resulting from extreme local fluid overpressure, possibly exceeding the lithostatic load, or fictious, resulting from local influx of nitrogen into the CH_4-bearing fluid.

Recent nitrogen emanations have been recorded in deep boreholes from crystalline basement granodiorites and gneisses beneath the CCPB (Harča, 1987). The admixture of nitrogen would significantly depress homogenization temperature of the CH_4-N_2 inclusion in comparison with pure CH_4 inclusion of equivalent density, thus leading to overestimation of the density and corresponding pressure expressed in terms of pure CH_4 or CH_4-CO_2 systems.

Considering average density of 2.54 g/cm^3 of flysch sediments in the OFB (M. Nemčok, pers. comm.) and a

lithostatic load, minimum depth of burial during quartz crystallisation in the CCPB, the Magura nappe and the Dukla nappe should correspond to 2.0-5.9 km, 2.8-7.9 1.
km, and 6.3-14.6 km, respectively. Pressure of 1.9 kbar, corresponding to depth of 7.5 km, has been inferred by Dudok & Jarmolowicz-Szulc (1999) for the Dukla nappe, using the same method. 2.

Extreme inclusion fluid pressure fluctuations are observed between some adjacent growth zones inside the 3.
quartz crystals. The density differentials are often reversal, i.e. increasing towards the rim. In the CCPB, some joints contain quartz crystals with large inclusions entirely undisturbed by re-equilibration, while the inclusions from neighbouring joints are intensively re-equilibrated. This points to an inhomogenous thermal and pressure field, which might be attributed to influx of deep-seated hot fluids rather than to a passive cooling of an extinct hydrothermal system. 4.

Large and abrupt pressure changes can be expected in recurrent high- and low-permeability sedimentary layers of extensional basins due to interaction between fracture and associated compartment pore pressures (Holbrook, 1999). Pore pressure compartment is a layer of high permeability rock mated by low-permeability one, which retards escape of the pore fluid to the subsurface. Compartment pore pressure in excess of the minimum fracture propagation pressure (min. P_f) will open vertical fractures in the compartment-sealing caprock. With fluid release, pressure within the compartment will fall to hydrostatic until fracture seals due to precipitation of newly formed minerals. Increasing compartment pore pressure will reopen the associated fractures if the min. P_f is reached. The min. P_f cannot exceed lithostatic load at depths shallower than approximately 5 km (Barker, 1990, Holbrook, 1999). Driving mechanism for such a cyclic fracture reopening could be a pore fluid volume increase due to thermal cracking of petroleum and kerogen accompanied by its conversion to methane-rich gas. By this mechanism, lithostatic gradient can be reached in a petroleum reservoir under hydrostatic regime, if only 1 vol. % of the petroleum is converted to methane (Barker,1990).

In the *CCPB*, nitrogen content determined in fluid inclusions by micro-Raman spectrometry is negligible (Dubessy, unpubl. data). Thus, the inclusion fluid pressure fluctuations between 0.5-1.5 kbar in the *CCPB* are realistic, or slightly underestimated due to presence of C_2-C_5 gases along with methane and CO_2. The concept of a lithostatic fluid regime applied to the inclusion fluid pressure data results in the overburden of 2-5.9 km. In contrast, the concept of an overpressurised compartment with min. $P_f = P_{lit.}$ and cyclically changing hydrostatic and lithostatic fluid regimes results in a relatively constant depth of 5-5.9 km during formation of quartz in the *CCPB*.

Considering recurrent litho- and hydrostatic regimes in the *OFB*, the minimum overburden between 7.5-7.9 km for the Magura nappe and >8 km for the Dukla nappe can be ascertained. Presence of nitrogen and a potential existence of fluid overpressures exceeding the lithostatic load, however, may shift the estimated values to lower depths.

Conclusions

Formation of euhedral quartz in mineralized joints of the Tertiary collisonal belt of the Western Carpathians can be correlated with a regional collapse-related hot fluid flow superimposed to folding.

Migration of the hot fluids has been accompanied by ubiquitous methane and local occurrence of petroleum.

Temperatures of quartz crystallisation derived from microthermometry data on coexisting methane- and water-dominated fluid inclusions increase from 140-205°C in the unfolded Central Carpathian Paleogene Basin, through 160-210°C in the Magura nappe, to 190-220°C in the Dukla nappe. Similarly, a pressure increase from 0.5-1.5 kbar in the *CCPB*, through 0.7-2 kbar in the Magura nappe, to as much as 3.7 kbar in the Dukla nappe has been recorded.

A model of cyclically changing lithostatic and hydrostatic fluid regimes in fractured rocks has been employed to account for pressure fluctuations observed during the quartz crystallisation. Estimated pressures correspond to overburden of 5-5.9 km in the *CCPB* (Spišská Magura Mts.), 7.5-7.9 km in the Magura Nappe, and > 8 km in the Dukla nappe.

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