

Migration of palaeofluids in the contact zone between the Dukla and Silesian units, Western Carpathians — evidence from fluid inclusions and stable isotopes in quartz and calcite

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This study reconstructs the type and migration history of fluids within the Cretaceous–Paleogene rocks of the Silesian and Dukla units in the border area of the Polish and Ukrainian Carpathians. Quartz (the “Marmarosh diamonds”), calcite and organic matter fill fractures in the sedimentary rocks of the Tertiary accretionary prism of the Carpathian thrust units. The calcite and quartz contain numerous solid, liquid and gaseous inclusions. Generally two types of fluids are distinguished — aqueous and hydrocarbon. Homogenisation temperatures of hydrocarbons in quartz range from -128 to $+85^{\circ}\text{C}$. Hydrocarbon fluids contain light (methane) and heavier (oil) compounds. Aqueous inclusions generally display homogenisation temperatures between 110 and 230°C . The $\delta^{13}\text{C}_{\text{PBD}}$ values for calcite range from -3.5 to $+2.9\text{‰}$, while the $\delta^{18}\text{O}_{\text{SMOW}}$ range from 18.9 to 27.7‰ . The $\delta^{18}\text{O}_{\text{SMOW}}$ values for quartz range from 15.7 and 26.7‰ . Fluid inclusions indicate that maximum pressures and temperatures occur at the early development of the vein mineralization. They vary from 2.4 to 2.7 kbar in the Krosno (Silesian) Unit and from 1.7 to 1.9 kbar in the Dukla Unit at 190 – 230°C . The crystallisation of the “Marmarosh diamonds” in the NW part of the study area occurred at lower P–T conditions of 0.9 kbar and 110 – 175°C . Generally, the migrating fluids are represented by a mixture of the low salinity aqueous and the hydrocarbon-rich fluids.

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INTRODUCTION

Numerous publications on fluid inclusions in minerals in sedimentary basins discuss the temperature conditions in a sedimentary basin, the physical and chemical conditions of diagenesis and catagenesis, the dependence of hydrocarbon composition on temperature and pressure, and the P–T conditions of hydrocarbon fields: the hydrocarbon phase composition with depth, the chemical composition of hydrocarbons and the processes responsible for hydrocarbon expulsion from source rocks (Ahvledian and Gigashvili, 1975; Kityk and Petrichenko, 1976; Wieser, 1978; Kozłowski, 1982; Roedder, 1984; Cziczua *et al.*, 1985; Pagel *et al.*, 1986; McLimans, 1987; Bodnar, 1990; Goldstein and Reynolds, 1994; Kalyuzhnyi and Sachno, 1998; Hurai *et al.*, 2002). Within this context fluid inclusions were studied in samples from fault zones in sedimentary rocks in the Silesian and Dukla tectonic units, from the Tertiary accretionary prism of the Carpathians.

The main objective of this study is to characterise the fluids present during vein formation in the flysch in the Western Carpathians, especially regarding the “Marmarosh diamonds”. This quartz variety is particularly significant as an oil- and gas-inclusion-bearing mineral indicating hydrocarbon migration in the flysch sediments. The hydrocarbon-bearing and aqueous inclusions permit an estimation of pressures in addition to the temperatures of formation.

This paper represents a continuation of work by Dudok and Jarmołowicz-Szulc (2000), combining the results from two tectonic units — the Dukla and the Silesian (Krosno) units in their contact region, examined in an interregional (international) aspect.

It combines data from the Polish and Ukrainian segments of the Silesian and Dukla units, being, therefore, not only of local but also of international significance. Published work by other authors dealing with fluid inclusions in minerals in the Carpathians (Karwowski and Dorda, 1986; Vityk *et al.*, 1996; Świerczewska *et al.*, 2000; Dudok and Jarmołowicz-Szulc,

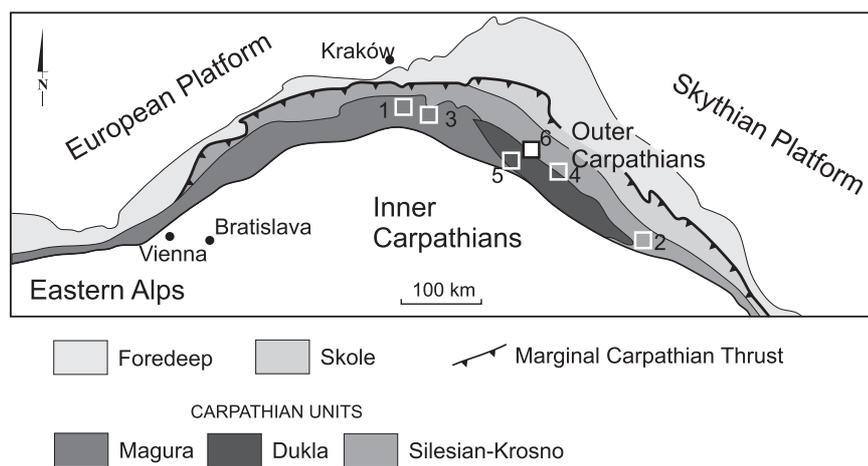


Fig. 1. Generalised geological map of the northern segment of the Carpathians (based on Hurai *et al.*, 2002, modified)

Squares point to the reference areas of studies on vein minerals in the Outer Carpathians (not to scale), after: 1 — Karwowski and Dorda (1986), 2 — Vityk *et al.* (1995, 1996), 3 — Świerczewska *et al.* (2000), 4 — Dudok and Jarmolowicz-Szulc (2000), 5 — Hurai *et al.* (2002), 6 — present study

2000; Hurai *et al.*, 2002) are mostly limited to sampling in one country and/or often within a single locality in the tectonic units (Fig. 1).

The potential application of this study may include mapping of oil and gas migration pathways to focus the direction of the exploration efforts based on the type of the prevailing inclusions in quartz. The characteristics of the preserved fluids have been determined by integrating field observations (minerals and mineralisation, some tectonic structures), microthermometry of fluid inclusions in vein minerals, stable isotope analyses of the components of these minerals and petrographic interpretations of the mineral paragenesis.

PREVIOUS STUDIES

The mineral associations filling the fractures, i.e. calcite and quartz are widespread in the Carpathians. They have been the subject of previous studies at different localities, as shown in Figure 1. In the Silesian and Dukla nappes, they were described by Dudok and Jarmolowicz-Szulc (1999). In the Magura Nappe, quartz-calcite associations in joints and small-scale faults were described by Świerczewska *et al.* (1999, 2000) and Tokarski *et al.* (1999).

Quartz, known as “Marmarosh diamonds”, has been reported from many localities of the Western Carpathians in Poland, Slovakia and Ukraine (Tokarski, 1905; Matkovskij, 1961; Vozniak *et al.*, 1973; Karwowski and Dorda, 1986; Hurai *et al.*, 1989, 2002).

Karwowski and Dorda (1986) reported the characteristics of the “Marmarosh diamonds” and described the perfect lustre and frequent transparency of the crystals of this quartz variety, features which cause a similarity of this mineral to real diamonds. They explained the origin by determining the conditions of crystallization, including the nature of the mineral forming fluids. Their studies focused in the tectonic window of Mszana Dolna where the Krosno Beds outcrop from below the layers of the Magura Nappe. These authors drew conclusions as to the complex character of the mineral-forming environment. They pointed to a wide range of pressures in fluid inclusions (from 5 to 99 MPa) and an upper temperature limit of crystallization of about 100°C. They suggested that the occur-

rence of the “Marmarosh diamonds” represented an indicator of hydrocarbon migration.

Vityk *et al.* (1995, 1996) studied fluid inclusions in quartz from the nappes in the Ukrainian part of the Carpathians. They observed explosion features in many of the early inclusions caused by tectonic uplift of the enclosing strata during the Miocene. They described characteristic textural features and patterns of homogenization temperatures within different nappes, i.e. Marmarosh, Rachiv, Porculec and Charnogora. Their suggestion was that the various nappes experienced significantly different burial — uplift histories. These authors suggested that the Krosno zone was the most deeply buried part of the Ukrainian Carpathians.

Świerczewska *et al.* (1999, 2000) described quartz mineralisation in the Magura Nappe within the Krynica–Bystrica and Racá–Siary areas. These studies concern quartz overgrowths on detrital grains and quartz-calcite associations filling joints and small-scale faults. The authors distinguished different types of the quartz and tried to correlate the drusy quartz selected with the Ukrainian “Marmarosh diamonds” (compare: Tokarski, 1905; Vityk *et al.*, 1995, 1996). Based on fluid inclusion studies, they obtained temperatures from 200–220°C in the Dukla Nappe to 160–210°C in the Magura Nappe. They reported a fluid pressure decrease from 2.1–3.7 kbar in the Dukla to 0.75–2 kbar in the Magura nappes.

In a previous paper (Dudok and Jarmolowicz-Szulc, 2000), we described hydrocarbon inclusions in the quartz (the “Marmarosh diamonds”) from the deposits of the Krosno and Dukla units in the Ukrainian Carpathians. The inclusions were studied chromatographically, microthermometrically and in ultraviolet light. The sequence of inclusions observed ranges from methane through light hydrocarbon complex inclusions with a variety of bitumens to gas-liquid inclusions with two different hydrocarbon phases. P–T paths for the Dukla and Krosno zones were reconstructed based on fluid inclusion data in this part of the Ukrainian segment of the Carpathians.

A later paper by Hurai *et al.* (2002) characterized quartz crystals from mineralised joints of the Carpathians in the Dukla and Magura nappes in the Slovakian part of the Outer Carpathians. Localities at Velky Lipnik and Dara were investigated. The authors identified methane-bearing inclusions and obtained trapping conditions for the fluids between 130

and 205°C and from 0.5 to 2.7 kbar. Based on the fluid-inclusion-derived crystallization data that are inconsistent with the vitrinite reflectance results, they drew conclusions on the tectonic context of methane generation and tried to generalise their effects to the whole Carpathian basin using data obtained from drusy quartz reported by Świerczewska *et al.* (1999, 2000).

Elongated, prismatic quartz crystals often occur in deposits of different age (e.g. Eocene and Oligocene) of the Krosno Zone while isometric and pseudo-hexagonal crystals are found in the upper formations of the Dukla Unit (Dudok, 1991). Apart from these mineral forms, other minerals such as dolomite, anhydrite and pyrite are present in the quartz-calcite veinlets (Szakall, 2002). Organic matter in the calcite-quartz veins covers calcite crystal faces and fills the central parts of the veinlets. The organic matter in the veins has been studied by Dudok *et al.* (2002). In Ukraine, Dudok *et al.* (1989) studied in detail bitumens in the Chernohora and Krosno zones. They observed lesser amounts of bitumens in the Cretaceous rocks than in the Oligocene rocks. Several types of bitumens can be distinguished, such as anthraxolite, elkerite, asphaltite and paraffine.

Ore minerals are sometimes noted in the same localities as the “Marmarosh diamonds” and calcite. They include the Rabe area (the Bieszczady Mts., Poland; Wieser, 1978; Ślącza, 1980) and the Chernohoriv area (the Dukla Unit, Ukraine; Didenko, 1985). Ore mineralisation comprises realgar, orpiment, antimonite, cinnabar, metacinnabarite and native mercury. The nature of this mineralisation and its relationship to the quartz occurrences remain unclear.

GEOLOGICAL AND MINERALOGICAL SETTING

The arc of the Outer Carpathians (Fig. 1) is mostly built of folded Cretaceous–Neogene sediments, including stacked thrust sheets: the Magura Unit, the Dukla Unit, the Silesian (called the Krosno Unit in the Ukrainian territory) and the Skole (Skiba) Unit (e.g. Oszczytko *et al.*, 1989). The Borislav-Pokuttia Unit has been recently concerned the main unit, too (Jankowski *et al.*, 2004). In front of the Skole and Borislav-Pokuttia units occur more or less folded and thrust foredeep deposits of Miocene age.

The study area lies in the Western Carpathians, on both sides of the Polish-Ukrainian border (Fig. 2). It extends from

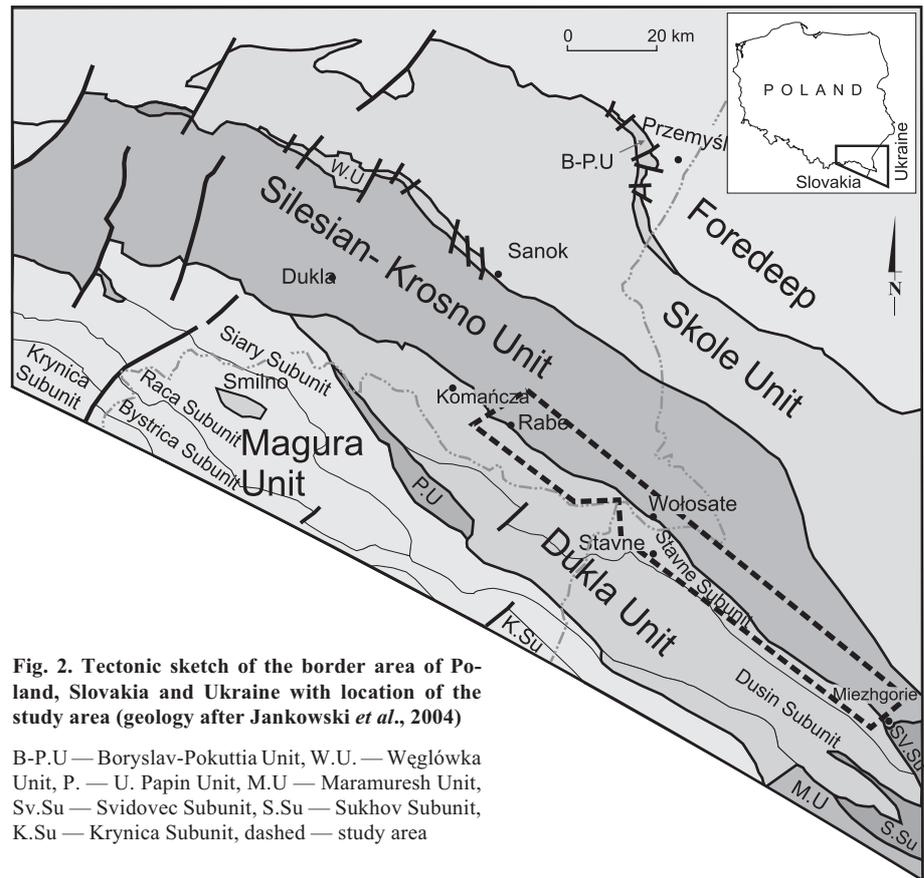


Fig. 2. Tectonic sketch of the border area of Poland, Slovakia and Ukraine with location of the study area (geology after Jankowski *et al.*, 2004)

B-P.U — Borislav-Pokuttia Unit, W.U. — Węglówka Unit, P. — U. Papin Unit, M.U — Maramuresh Unit, Sv.Su — Svidovec Subunit, S.Su — Sukhov Subunit, K.Su — Krynica Subunit, dashed — study area

north-west to south-east from Komańcza through Wołosate, in Poland, and Stavne to Miezhgorie (Soymy), in the Ukrainian segment.

According to modern structural concepts (Fig. 2, after Jankowski *et al.*, 2004), there are two main tectonic units in the study area: the Silesian (Krosno) and Dukla units. According to Polish geologists the Silesian Unit (nappe) can be divided into two parts — the Central Carpathian Depression (Subunit) and the Fore-Dukla Subunit (Ślącza and Żytko, 1978; Oszczytko, 1989; Rubinkiewicz, 2000). The Fore-Dukla has not been distinguished at the Ukrainian side.

The Dukla and Silesian units are parallel to each other and extend from NW to SE (Figs. 1 and 2).

The Silesian Unit is built up of tectonically deformed Cretaceous–Oligocene flysch deposits, arranged in a southwards-dipping thrust system (Ślącza and Żytko, 1978; Ślącza, 1980; Mastella and Cipko, 1988; Oszczytko *et al.*, 1989; Mastella and Szykaruk, 1998; Jankowski and Ślącza, in press). Numerous backthrusts are recognised in the Silesian Unit (Kuśmerek, 1979; Jankowski and Ślącza, in press)

The Dukla Unit (nappe) also composes a thrust system, usually verging to the north-east (Mastella and Zuchiewicz, 2000).

In the Carpathians, several fracture systems are distinguished (Mastella and Zuchiewicz, 2000; Rubinkiewicz, 2000). According to Ripun (1970) and Dudok (1991), fractures which display an orientation of 190–210° and 70–90° are filled with vein minerals such as calcite and quartz, as well as with organic matter (Dudok *et al.*, 1997). The thickness of the veins varies from a fraction of millimetre to decimetres. The veins are filled with calcite displaying composite textures. Some carbonate veins are ac-

accompanied by widespread veinlets of calcite-quartz associations. The latter fill veins, e.g. in the rocks in the Silesian and Dukla units (*cf.* Dudok and Jarmołowicz-Szulc, 1999). In the Magura Nappe, the quartz-calcite associations occur in joints and small-scale faults (Świerczewska *et al.*, 1999; Tokarski *et al.*, 1999). Calcite usually has a primary character. It is white or milky-white, locally honey-yellow in colour. The individual crystals are twinned and occur in form of rhombohedra. In the Krosno Unit (Dudok, 1991) the calcite is covered with a thin film of hard bitumens. The “Marmarosh diamonds” quartz occurs in many localities of the Western Carpathians in Poland, Slovakia and Ukraine (Tokarski, 1905; Matkovskij, 1961; Karwowski and Dorda, 1986; Hurai *et al.*, 1989). Apart from the minerals mentioned above, dolomite, anhydrite and pyrite are present in the quartz-calcite veinlets.

ANALYTICAL PROCEDURES

Sixty-three samples of calcite, quartz and anthraxolite from 13 localities (see [Appendix](#)) were taken for mineralogical analysis, more than half of them being analysed as indicated below. Sections for fluid inclusion studies in quartz were prepared using two preparation techniques (Jarmołowicz-Szulc, 2000, 2001). Double-sided polished thin sections, 0.1–0.2 mm thick, were obtained by low-temperature mounting of crystals in the ring and successive polishing which uncovered the crystal interior. In addition, whole unpolished crystals were glued to the thin glass plates and arranged in fractions. General microscopic observations were conducted applying a polarisation microscope both in transmitted and reflected (UV) light. These comprised a microscopic analysis of fluid inclusions (*Leitz Orthoplan*), fluorescence studies and microphotography (*Nikon* microscope and UV device), cold cathodoluminescence studies (CCL 8200 mK3) and microthermometric analyses. The latter included heating and freezing using a *Fluid Inc. System*, mounted on a *Leitz Orthoplan* microscope. The studies were conducted at the Petrological Department of the Polish Geological Institute in Warsaw and at the Institute of Geology and Geochemistry of the Combustible Minerals of the National Ukrainian Academy of Sciences in Lviv, Ukraine.

The *Fluid Inc. System* was calibrated against melting temperatures of pure chemicals and phase transitions in synthetic fluid inclusions (Synflinc standards, Reynolds, 1993). The uncertainty limits are 0.2°C below –100°C, 0.1°C between –100°C and +100°C, and 0.2°C above 100°C. Fluid inclusions in quartz were studied microthermometrically by partly heating after freezing. This allowed characterization of the behaviour of the methane-bearing inclusions. It also enabled the measurement of the homogenisation temperatures of inclusions which homogenised at negative temperatures, and determinations of the eutectic and ice melting temperatures of the aqueous inclusions (Roedder, 1984). Thermometric studies in the heating mode led to a determination of temperatures of quartz crystallization, since it has been assumed that the homogenisation temperature of the primary aqueous inclusions represents a minimum temperature of fluid trapping during mineral precipitation (Roedder, 1984).

The estimation of the pressure and temperature conditions of the formation of the “Marmarosh diamonds” is based on the crossing isochore technique using coexisting methane and aqueous inclusions, following the method introduced by Kalyuzhnyj (1982). Isochores for pure methane were calculated with the Flnacor program (Brown, 1982).

Fluorescence of the organic matter was induced by ultraviolet reflected light in the plates prepared for the fluid inclusion microthermometry studies. The long-wavelength light (368 nm) was provided by the 100 W mercury lamp and a set of filters.

The isotope studies were conducted by means of two methods — a point analysis in quartz and classical determinations in calcite. Secondary *Ion Mass-Spectrometry* (SIMS) isotope analysis of the oxygen in quartz was performed at the Arizona State University in Tempe (AZ, USA) according to the procedure of Hervig *et al.* (1992) and Williams *et al.* (1997). Each quartz grain point selected was scanned from 49 to 94 times. The determinations were performed against the Arkansas quartz standard, the characteristics of which, calibrated against international standards, has been given in Hervig *et al.* (1992), together with the measurement precision. Three grains of quartz (the “Marmarosh diamonds”) have been studied, both in automatic and manual modes.

Analyses of the isotope composition of oxygen and carbon in calcite were conducted in the Isotope Laboratory of the Maria Curie-Skłodowska University at Lublin. The method has been described by Durakiewicz and Hałas (1994) and Durakiewicz (1996). Gaseous carbon dioxide is released from carbonates during reaction with phosphoric acid. Isotope measurements of carbon and oxygen were made in the modified mass spectrometer *MI 1305*. The precision of these measurements is ±0.08‰ (one sigma). Measurements were conducted in reference to international standards (Durakiewicz, 1996).

The gas composition of the hydrocarbon inclusions in the “Marmarosh diamonds” was determined using the chromatograph “*Chrom 5*” and mass spectrometer *MX-1304* in Lviv. The analytical studies were performed based on the assumption that the maximum temperatures of the formation of the “Marmarosh diamonds” have not exceeded 230–240°C. Three intervals of short heating in a helium atmosphere were applied (Dudok and Shanina, 2000). Gas components were released gradually, during crystal destruction at room conditions. With this technique, it was possible to measure nitrogen, carbon dioxide and hydrocarbons up to octane. This method was used for the first time on the vein minerals in the Carpathian oil-bearing province (Dudok and Jarmołowicz-Szulc, 2000). The accuracy of the determinations is: CH₄ – 2 × 10^{–9} g; C₂H₄ – 7 × 10^{–9} g; C₂H₆, C₃H₆ – 5 × 10^{–9} g; C₂H₈ – 4 × 10^{–9} g; C₄H₁₀, i-C₄H₁₀ – 3 × 10^{–10} g; C₅H₁₂ – 4 × 10^{–10} g; C₆H₁₂ – 2 × 10^{–10} g; C₆H₁₄, C₇H₁₆, C₈H₁₈ – 2 × 10^{–11} g.

The chemical studies of the bitumens from the vein filling were performed in the Mining and Metallurgy Academy by a group under the leadership of M. Kotarba (Kotarba *et al.*, 2000). The studies comprised pyrolytic analysis of the elementary composition and of the composition of the stable carbon isotopes in the organic matter. The method has been described in detail by Kotarba *et al.* (2000) and Dudok *et al.* (2002).

RESULTS

Table 2

ISOTOPES

All $\delta^{13}\text{C}_{\text{PDB}}$ values measured for calcite lie in the interval between -3.5 and $+2.9\%$ (Table 1). The results for the western part of the area investigated (Polish section) fall into the narrower interval from -3.0 to -0.3% . The general range of calcite oxygen values for the whole region studied is between 18.9% and 27.7% . The values obtained for the calcite samples in the Polish area are from 20.6 to 23.1% . The results of the isotope analyses of carbon ($\delta^{13}\text{C}_{\text{PDB}}$) for anthraxolite are shown in Table 2. The $\delta^{13}\text{C}_{\text{PDB}}$ values lie within the interval from -26.3 to -24.3% . The results of the isotope point analysis (SIMS) in three quartz samples are shown in Figure 3 with one example illustrated in detail in Figure 4. The point analyses show $\delta^{18}\text{O}_{\text{SMOW}}$ values in a wide interval between 15.7 and 26.7% .

INCLUSIONS IN THE “MARMAROSH DIAMONDS”

The results of the gas composition analyses in the inclusions from the Polish part of the study area are given in Table 1

Table 1

Oxygen and carbon isotopic determinations in calcite

Sample	Location	$\delta^{13}\text{C}_{\text{PDB}}$ [‰]	$\delta^{18}\text{O}_{\text{SMOW}}$ [‰]
PD4	Rabe	-0.8	21.9
D9	Solinka	-2.0	21.4
W 13	Wołosate	-1.5	20.6
PS 2	Wołosate	-1.3	21.9
PS 1	Solinka	-3.0	21.2
U1	Stavne	-0.7	21.4
U7/1	Miezhgorie	-3.1	22.2
U7/2	Miezhgorie	-3.5	20.3
U8	Ripinne	-1.2	19.9
U17	Ripinne	-1.3	20.7
U33	Soymy	-1.6	19.6
U34	Soymy	+2.9	18.9
708	Miezhgorie	-0.9	22.7
723	Veca	+1.1	27.7
729	Lazy	-2.3	19.7
754	Turka	-0.7	23.4
757	Turka	-0.6	25.4
767	Stavne	-1.0	22.7
794	Ripinne	-0.9	22.6
796	Ripinne	-1.0	22.5

Location points named after the settlements; larger ones are shown in Figure 2; sampling localities described in Appendix

 $\delta^{13}\text{C}_{\text{PDB}}$ isotope determinations of anthraxolite from the Carpathian Silesian–Krosno and Dukla units

Sample	Location	$^{13}\text{C}_{\text{PDB}}$ [‰]
702 K	Soymy	-26.3
704 K	Soymy	-25.0
713 D	Ploske	-25.4
722 K	Veca	-25.2
723 K	Veca	-25.1
727 K	Lazy	-25.1
755 K	Turka	-24.3
757 K	Turka	-24.9
762 D	Stavne	-26.2
764 D	Stavne	-24.8
796 K	Ripinne	-25.9

Location points named after the settlements; D — Dukla Unit, K — (Silesian)–Krosno Unit

ble 3. Comparative data for the samples from the Ukrainian territory have been already published by Dudok and Jarmołowicz-Szulc (2000).

Fluid inclusions in the “Marmarosh diamonds” range between 1 to 1000 mm in size and display various shapes. They are of primary and secondary origin. The primary inclusions occur along growth zones of the host quartz crystal. They have either a negative crystal form or the shape of a vacuole elongated along the c axis. The walls of the vacuoles are sometimes covered as a distinct film with a brown organic matter. In ultraviolet light these inclusions either do not show luminescence or display a fluorescence in dull bluish colours. The brown organic matter does not show fluorescence. Inclusions of shape varying from negative crystals to irregular are situated at the top of the quartz crystals and close to their surface. In ultraviolet light they exhibit fluorescence in white or yellow. Occasionally the inclusions showing a white fluorescence contain a separate phase in the form of a drop which in some cases may appear elongated. These minute accumulations do not show fluorescence (Dudok and Jarmołowicz-Szulc, 2000).

The gas-liquid inclusions, which contain two different hydrocarbon phases, are the latest in the general sequence of the primary inclusions. They are characteristic of the central and northwestern parts of the area studied. They display different colours in ultraviolet light. The large internal part of the vacuole has a blue fluorescence, while the exterior part fluoresces in yellow. Based on the fluorescence data, the density of these fluids corresponds to about 38 and 40° API (Bodnar, 1990; Jarmołowicz-Szulc, 1998). In regions with ore mineralisation, an additional type of primary inclusion corresponds to light hydrocarbons with a non-fluorescing bubble of carbon dioxide. Secondary gas-liquid and liquid-gas inclusions are present in

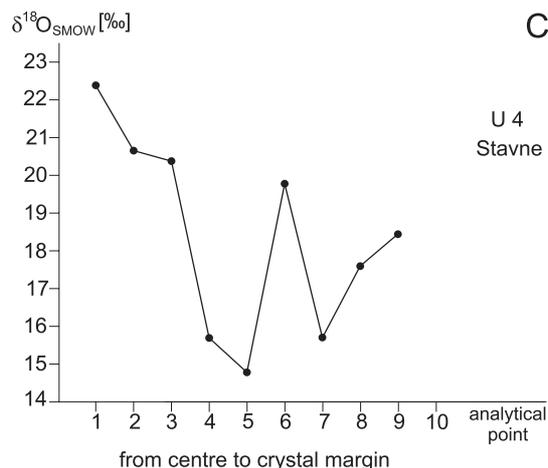
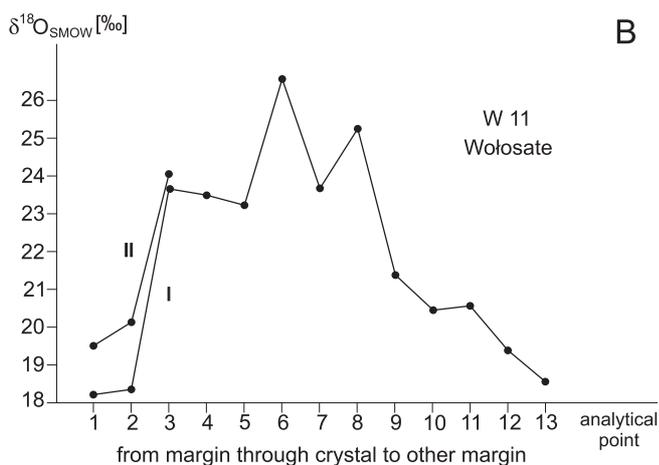
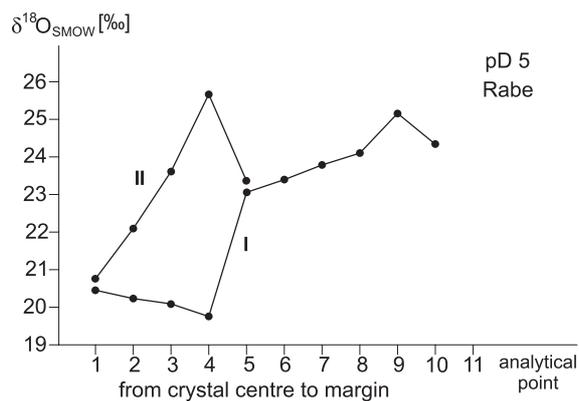


Fig. 3. Distribution of SIMS point oxygen isotope determinations in crystals of the “Marmarosh diamonds” in three samples

I, II — different crystals; for a location of microsampled points in pD 5 see [Figure 4](#)

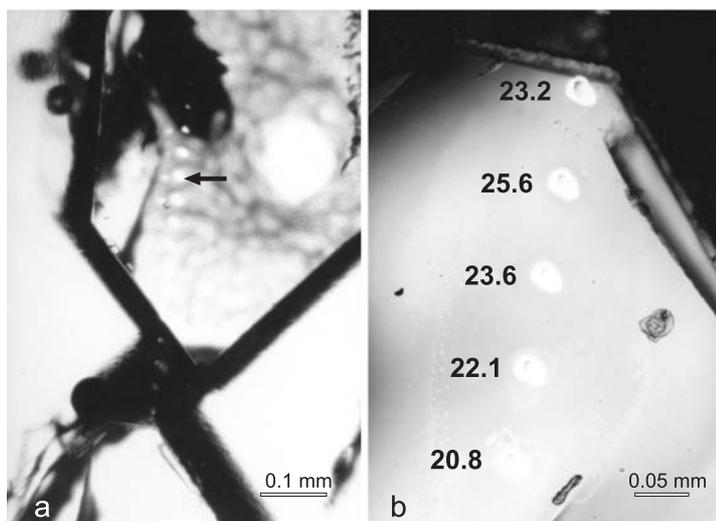


Fig. 4. Analytical points in quartz crystals of sample pD 5

a — general view of two crystal fragments analysed; arrow points to a line of analytical craters; b — analytical points (craters) in crystal II (lower in Fig. 4 a) with $\delta^{18}\text{O}$ values in ‰

healed fissures in the crystals. In ultraviolet light, they display fluorescence colours changing from white-bluish to yellow.

According to the phase nomenclature of Dudok *et al.* (1997) for fluid inclusions, the liquid phase occurs as: an aqueous solution with a low concentration of salt (L); a liquid hydrocarbon phase (L_1); a condensed mixture of hydrocarbons from meth-

ane to butane under pressure (L_2), being gas at room temperature; and liquid CO_2 (L_3). The solid phase is represented by different bitumens (B).

Summarising the characteristic features of the primary hydrocarbon fluid inclusions at room temperature, the following groups can be distinguished:

- group 1: methane-rich inclusions (L_2 ; $L_1 + L_2 + G$);
- group 2: methane-oil inclusions ($L_2 + L_1$, $L_2 + L_1 + G$, $L_2 + L_1 + B$);
- group 3: oil-methane inclusions ($L_1 + L_2$, $L_1 + L_2 + G$, $L_1 + L_3 + G$);
- group 4: oil inclusions (L_1 , $L_1 + B$, $L_1 + L_3$).

They are accompanied by two phase aqueous inclusions (with a vapour bubble). [Table 4](#) shows a summary of the inclusions and their characteristic features.

The inclusions ascribed to group 1 are characteristic of the “Marmarosh diamonds” in the entire Carpathian region; group 4 prevails in the Bieszczady Mts. from Komańcza in the west to the Stavne region in the east, while groups 2 and 3 tend to be abundant further eastwards as far as Volovec.

Anthraxolite and, less frequently, calcite and quartz, form solid inclusions trapped in the quartz. Anthraxolite occasionally creates a platform for liquid inclusions or it forms distinct zones parallel to the crystal faces. Fine anthraxolite is occasionally present on the calcite crystals, which, in turn, form solid inclusions in the “Marmarosh diamonds”. Euhedral calcite and

Table 3

Gas composition in inclusions in the “Marmarosh diamonds” [%]

Sample number and location	CH ₄	N ₂	CO ₂	Heavier hydrocarbons
pD 1/5 Rabe	87.4	5.2	7.4	–
pD 3/18 Rabe	92.6	2.1	5.3	traces
pD 3/24 Rabe	93.5	–	–	6.5
pD 5/9 Rabe	97.7	–	–	2.3
pD 5/17 Rabe	92.8	4.1	2.2	0.9
pD 6/5 Rabe	89.5	0.8	6.4	3.3
pD 6/22 Rabe	97.6	2.3	–	traces
W 13/10 Wołosate	87.4	4.4	8.2	–
W 13/11 Wołosate	90.0	3.2	6.6	0.4
UD 15/3 Ustrzyki Górne	91.6	–	–	9.4
UD 15/16 Ustrzyki Górne	84.0	–	–	16.0
pD 21/7 Smerek	99.2	–	0.8	–
pD 21/9 Smerek	99.4	0.2	5.4	traces

Analyses conducted using mass spectrometer *MX-1304* in Lviv with the financial support of the grant No 5.45.0000.99.2; numbers of samples after Jarmołowicz-Szulc and Dudok (2000); location points correspond to the names of settlements; comparative data for the Ukrainian samples are presented in Dudok and Jarmołowicz-Szulc (2000); pD 5/17, pD 5/9 — different crystals from the sample pD 5; n.d. — not determined

quartz occur as solid inclusions in the exterior parts of the crystals of the “Marmarosh diamonds”.

MICROTHERMOMETRY AND PHASE TRANSITIONS OF THE FLUID INCLUSIONS

On freezing down to -196°C (liquid nitrogen temperature), one-phase inclusions developed a vapour bubble. Heating after the freezing resulted in an initial melting of the frozen content at -182.6°C , i.e. close to the triple point of pure methane at -182.5°C (Kleinrahm and Wagner, 1986), followed by a complete disappearance of the bubble between -128 to -82°C . The inclusions of the type L_2 (G_2) in Bieszczady homogenised between -89 to -85°C , while those from the quartz sampled more to the east between -128 and -82°C . The critical temperature of pure methane is -82.6°C (Kleinrahm and Wagner, 1986), therefore the inclusions which show homogenisation at lower temperatures must have an admixture of higher hydrocarbon compounds.

The complex methane — oil inclusions, which show a blue fluorescence, developed a bubble in the methane part during freezing. Homogenisation occurred either to gas or to liquid. First homogenisation at -68°C was to gas (methane

with an admixture of higher hydrocarbon compounds). Final homogenisation occurred between $+43$ and $+56^{\circ}\text{C}$ (either to liquid or to gas).

The two-phase oil, containing inclusions showing fluorescence from white-bluish to yellow, totally homogenised in the interval from 62 to 82°C [$L_1 + L_2$, $L_1 + G$, $L_1 + (L_2 + L_3)$]. Decrepitation occurred at about 90°C . In this group, inclusions of the composed L_1 type (two liquid hydrocarbon phases in one vacuole) have a specific fluorescence, i.e. yellow at the walls, blue in the interior. The oil-containing inclusions created a condensed phase (rosette needle forms) at about -30°C in the oil part of the inclusion during the freezing run. At about -60°C , a bubble developed in the non-fluorescing part. During the subsequent heating, first melting occurred at temperatures from -120 to -75°C (methane component), being followed by bubble-in-bubble homogenisation around -55.8°C (-56.6°C is the critical point of CO_2 — Kalyuzhnyi, 1982). Rosettes started to disappear from -5°C , their final melting being at $+12^{\circ}\text{C}$.

One group of one-phase inclusions ($L_3 + G$; $L_3 + L_2$, $L_2 + L_3$) which do not show fluorescence, become solid when cooled to -100°C . Melting occurs around -56.6°C , or at lower temperatures. The major component of these inclusions is CO_2 . The lower temperatures indicate the presence of another gaseous component, e.g. methane or nitrogen. Homogenisation is between 23 and 31°C .

Slightly or non-fluorescent aqueous inclusions are totally frozen at -70°C . When heated, these inclusions show a first melting (eutectic) at about -21°C ($\text{NaCl-H}_2\text{O}$ system; e.g. Vozniak *et al.* 1973), ice melting from -2 to -3°C (salinity of about 3–4 wt % NaCl eq., Bodnar, 1992), CH_4 clathrate melting between $+3$ and $+15^{\circ}\text{C}$ and homogenisation to liquid between 110 and 230°C .

Homogenisation data for hydrocarbon fluid inclusions in the “Marmarosh diamonds” within the Dukla and Silesian units (Polish and Ukrainian segments) are shown in Figure 5. The earliest group of fluid inclusions — one-phase at room temperature as well as one-phase liquid and one-phase solid inclusions — displays the lowest homogenisation temperatures. The coexisting, aqueous inclusions homogenise between $+190$ to $+230^{\circ}\text{C}$. Later formed, higher hydrocarbon inclusions containing bitumens and carbon dioxide show two types of homogenisation temperatures, both in the negative and positive range. Primary aqueous inclusions, which coexist with the higher hydrocarbons, homogenise between $+110$ and $+175^{\circ}\text{C}$. The latest primary oil inclusions homogenise at temperatures between 62 and 82°C .

In the inclusions studied, the molar volumes of individual components have not been determined as the Raman spectrometry was not available. The estimation of the crystallisation conditions of the “Marmarosh diamonds” is, however, possible due to the co-occurrence of the aqueous and hydrocarbon inclusions and the application of the homogenisation temperatures of the hydrocarbon inclusions and the co-occurring aqueous inclusions (Vozniak *et al.*, 1973; Vityk *et al.*, 1996; Dudok and Jarmołowicz-Szulc, 2000; Hurai *et al.*, 2002).

Table 4

Characteristics of fluid inclusions in the "Marmarosh diamonds"

Inclusion type	Fluorescence colour	Homogenisation temperature [°C]	Composition
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Polish part of the Carpathians (Bieszczady)

L ₂ L ₂ (G ₂) G ₂	white-bluish to blue	from -89 to -85	methane (CH ₄) with admixtures
L ₁ + G ₂ L ₂ (G ₂) + B L + L ₁ + G L ₁ + G + B L ₁ + B	white-bluish to blue	from 43 to 56 (→L; →G)	light liquid hydrocarbons + bitumens
G + L L ₂ + L L ₂ + L + (G)	blue	-68 (→G)	complex inclusions
L ₁ + L ₂ L ₁ + G ₂ L ₁ + (L ₂ + L ₃)	white-bluish to yellow	from 62 to 82 (decr. + 91)	heavier liquid hydrocarbons (oil)
G + L L + G	no fluorescence or bluish	from 130 to 230	aqueous inclusions
L ₃ + G L ₃ + L ₂ L ₂ + L ₃	no fluorescence or bluish	from 23 to 31	carbon dioxide

Ukrainian part of the Carpathians

L ₂ (G ₂)	white-bluish to blue	from -128 to -82 -88 to -82	methane (CH ₄) with admixtures
L ₁ L ₂ (G ₂) + B L + L ₁ + G L ₃ + G L ₁ + G + B L ₁ + B	white-bluish to blue	from 43 to 56 (→L; →G)	light liquid hydrocarbons + bitumens
L ₁ + L ₂	white-bluish to yellow or orange	from +62 to +82	heavier liquid hydrocarbons (oil)
G + L L + G	no fluorescence or bluish	190-230	aqueous inclusions

Explanations (partly according to the nomenclature of Dudok *et al.*, 1997; Kalyuzhnyi and Sachno, 1998; modified by Jarmolowicz-Szulc, 2000): L₁ — light oil (liquid hydrocarbon phase); L₂ — liquid CH₄; G₂ — gaseous CH₄; L₃ — CO₂; L — water; B — bitumens (anthracolite, paraffine, asphaltite); G — gas phase (aqueous vapour/gas CO₂); L₂(G₂) — liquid or gas in supercritical state; →G — homogenisation to gas; →L — homogenisation to liquid; decr. — decrepitation

INTERPRETATION AND DISCUSSION

The oxygen and carbon isotope data for calcite show a scatter of values, similarly to the results given by Dudok and Vovnyuk (2000), but most of them group together. This may

suggest at least two stages of calcite formation. In the joints in the Magura Nappe, Świerczewska *et al.* (2000) distinguished four types of calcite. The calcite studied in the present area is an early, primary calcite (calcite-I, Dudok, 1996). This type of the calcite was followed by the crystallisation of the "Marmarosh diamonds". The δ¹³C_{PDB} data of this calcite (-3.5 to +2.9‰), correspond to the results obtained for the sedimentary rocks in the Carpathian flysch by Ripun (1970), which range from -3.8 to -1.7‰ and have been interpreted as suggesting that the light isotope anomalies have been caused by hydrocarbon migration.

Results of the isotope measurements in quartz (Figs. 3 and 4) for the studied crystals from one Ukrainian and two Polish samples show that the δ¹⁸O_{SMOW} values described by point analyses lie in a wide interval between 15.7 and 26.7‰. Changes within the grains are notable, with no general trend, however. These changes may either reflect temperature or composition variation during the crystallisation process. No zoning in the studied quartz crystals has been observed in the cold CL studies, that could suggest compositional differences. According to the information of Hurai (2003, pers. comm.), this type of quartz contains little Al, thus cold CL images may not reflect changes. The reason for the scatter in oxygen values requires more detailed studies, as for instance, on aqueous fluid inclusions in different zones in the grains. The scatter is too large to calculate average values and interpret them further. Some trends can be, however, observed. Although scattered, the results of the δ¹⁸O analyses in quartz crystals from three regions in the area studied (Rabe, Wolosate and Stavne) point to a general decrease from NW towards SE. This could suggest an increase in crystallisation temperatures of quartz towards the SE. Higher temperatures may have been pointed out in the Dukla Unit.

Also, previous published results show that the isotope data for quartz are generally dispersed (Dudok and Vovnyuk, 2000). These δ¹⁸O_{SMOW} values range from 21.3 to 27.0‰, the lowest value recorded corresponding to the south-easternmost part of the area studied. Again, it is difficult to interpret such data and it can be suggested that quartz from SE regions may have been formed at a higher temperature range than that in the NW part. The distribution

of T_h values of aqueous inclusions seems to have the same pattern, thus supporting these suggestions (see below).

Homogenisation temperatures obtained from fluid inclusions show a distinct variation corresponding to the complex character of the inclusions trapped in the quartz (Fig. 5). The primary hydrocarbon inclusions generally homogenise at very low temperatures in the range from -128 to -82°C. The mini-

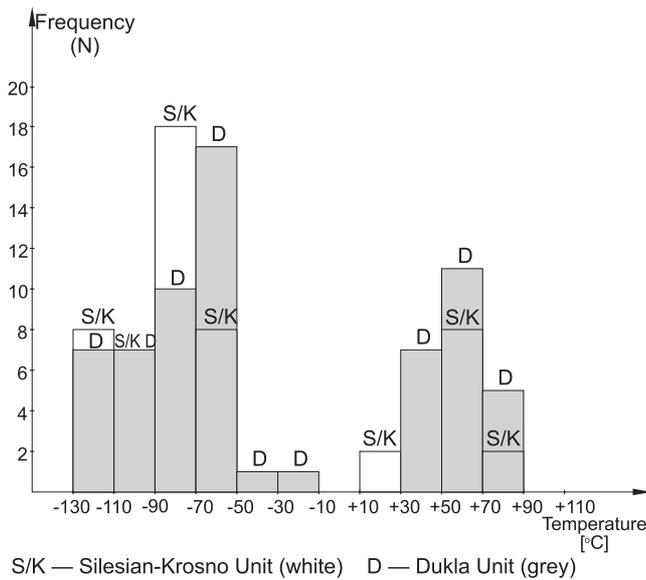


Fig. 5. Histogram of homogenization temperatures of hydrocarbon inclusions in quartz from the Dukla and Silesian-Krosno units in the area studied

imum values occur in the areas located in the Krosno Zone in Ukraine in the southeastern part of the region studied (Dudok and Jarmołowicz-Szulc, 1999). They correspond to the data published by Vityk *et al.* (1996). The temperature results obtained in the NW part of the present study area are higher, and lie in a narrower interval between -89 and -82°C . The low temperatures point to the presence of methane with admixtures of nitrogen and/or carbon dioxide (compare to e.g. Vityk *et al.*, 1996). This suggestion is also supported by the gas composition data, discussed below.

The aqueous inclusions, co-existing with the individual associations of the hydrocarbon inclusions, homogenise in general between 110 and 230°C . The fluids have salinities of about 3–4 weight % eq. NaCl. These salinity values are higher than the data given by Hurai *et al.* (2002) in the Slovak segment of the Dukla Unit, but correspond to the upper salinity range for the Magura Nappe.

Densities for methane obtained using the Kalyuzhnyi (1982) method and Brown's (1982) program correspond on average to about 0.267 g/cm^3 , with a maximum of 0.367 g/cm^3 at. The lower pressure values calculated, characteristic of the "Marmarosh diamonds" formation in the NW part of the area, are about 0.9–0.8 kbar.

The results of the gas analysis in the inclusions indicate the predominance of hydrocarbons, predominantly methane, in the fluid inclusions trapped in quartz. Carbon dioxide and nitrogen are minor components. The CO_2 content lies in the interval of 5 to 22% for the inclusions from Ukraine (Dudok and Jarmołowicz-Szulc, 1999) and between 1 and 8% for the inclusions from the Polish segment. The presence of CO_2 -rich fluid inclusions in quartz in the SE of the Bieszczady region occasionally overlaps with the occurrences of some Fe-ore evidence in the area studied. This could reflect areas of multi-stage hydrothermal activity. Ore-bearing fluids may have used the same pathways as the earlier quartz-forming ones, but the precise relationship has not been studied. The presence of nitrogen is

characteristic of the thrust plane between the Dukla Unit and the Silesian Nappe. The nitrogen content varies between 0.2 and 5.2%, with the highest recorded values in the part of the Silesian Unit near Rabe. Some gas inclusions are rich in higher hydrocarbons. Their maximum content is observed in the Ustrzyki Górne area, where it varies from 9.4 to 16% (with reference to total hydrocarbon content). Hydrocarbon accumulations are present to the west of the region discussed. For example oil showings are observed west of Komańcza.

There exists a correlation between the chromatographically determined composition of inclusions and the composition obtained from fluorescence and cryometrical studies. Mixed inclusions from methane to pentane show a fluorescence in dull bluish to blue colours while the light oil inclusions in both units display fluorescence in colours from white-blue to yellow. Their composition in the hydrocarbon part corresponds to the heavy methane homologues (from 25.89 to 86.06% — Dudok and Jarmołowicz-Szulc, 2000).

Anthraxolite in the veins formed later than calcite and is contemporaneous with, or later than, the "Marmarosh diamonds". According to field observations and stable isotope and geochemical data, anthraxolite displays considerable complexity (Kotarba *et al.*, 2000; Dudok and Vovnyuk, 2000). It occurs as individual, irregular accumulations in fluid inclusions, fills free space in the calcite-quartz veins and forms individual veinlets. $\delta^{13}\text{C}_{\text{PDB}}$ in anthraxolite is between -27.2 and -24.3% . Comparison of the $\delta^{13}\text{C}_{\text{PDB}}$ values of the vein anthraxolites from the Silesian and Dukla units (Dudok *et al.*, 2002) combined with the data from the Fore-Carpathian oils (Gabinet *et al.*, 1990), organic matter from the hydrocarbon reservoir rocks (Gabinet and Gabinet, 1990) and bitumens of hydrothermal origin (Bratus *et al.*, 1975) suggests that the origin of the organic matter is due to the migration of mixed hydrocarbons. The vitrinite reflectance (R_v) values for the Dukla and Silesian units are between 0.5 and 1.35% (Kotarba *et al.*, 2000), which is close to the single value of 0.81% obtained by Swadowska (1999, pers. comm.). This points to oil-producing kerogen of type I and II. Similar vitrinite reflectance values were obtained by Hurai *et al.* (2002) in the Dara vicinity. Maximum Rock-Eval temperatures are within the oil window in the area studied, while gas conditions occur in the southeastern part of the region (Kotarba *et al.*, 2000).

The highest temperatures and pressures of mineral formation in the area studied correspond to 190 – 230°C and 2.4–2.7 kbar in the Krosno (Silesian) Unit and 1.7–1.9 kbar in the Dukla Zone. These results are in agreement with the data of Vityk *et al.* (1996) for the Cretaceous–Paleogene accretionary orogenic belt of the Carpathians which revealed temperatures between 190 and 230°C and pressures between 0.5 and 2.7 kbar. The values are partly similar to those obtained by Hurai *et al.* (2002), for the Dukla Unit (Dara region), where the temperatures and pressures obtained for seven inclusions range from 195 to 203°C and from 1.5 to 2.1 kbar, respectively. They are, however, lower than the graphically presented pressure limits for the Dukla Nappe between 2.0 and 3.7 kbar (figure 7 in Hurai *et al.*, 2002 after Świerczewska *et al.*, 1999). The maximum values reported in the present paper are characteristic of the southeastern and central parts of the study area. The crystallisation of the "Marmarosh diamonds" in the northwest-

ern part occurred under lower pressure and temperature conditions (0.8–1.0 kbar and 110–175°C).

Methane-bearing crystals postdate calcite in the Silesian and Dukla tectonic units of the Polish and Ukrainian segments of the Carpathian flysch. The same relationship has been recorded both in the Rahiv Nappe (continuation of the Ukrainian segment towards the south-east) by Vityk *et al.* (1995) and in the Magura and Dukla units in the Slovak segment (Huraj *et al.*, 2002).

The areas where oil occurs in the inclusions in quartz in the Silesian and Dukla units may be most prospective for the search for oil and gas. This concept was discussed by Jarmolowicz-Szulc and Dudok (2000). Such a suggestion may be supported by the results of the gas chromatography and Rock-Eval studies of the organic matter (Kotarba *et al.*, 2000; Dudok *et al.*, 2002) which prove oil window conditions in the NW and gas conditions in the SE of the studied area.

CONCLUSIONS

The vein mineralization and fluid migration may be connected with tectonic deformation and the formation of thrusts in the Carpathians.

Migration of aqueous chloride-sulphate-hydrocarbonate fluids in the Carpathian area studied occurred at the early stage of vein formation during crystallisation of early calcite (calcite-I, compare Dudok, 1991). The crystallisation temperature of this type of calcite was rather high, i.e. between 220 and 235°C.

Quartz crystallization followed that of calcite resulting in formation of the “Marmarosh diamonds” due to pH decrease (Dudok, 1991). The migrating aqueous — hydrocarbon fluids contained predominantly methane with an average density of about 0.267 g/cm³ (as is inferred from primary inclusions of type L₂ trapped in the quartz). The beginning of the mineral formation corresponds to the maximum temperatures and pressures (190–230°C and 2.4–2.7 kbar obtained in the Krosno (Silesian) Unit and 1.7–1.9 kbar in the Dukla Unit).

The successive stage of mineralization development was characterized by a decrease in temperature to 135–180°C and in pressure to 0.6–0.8 kbar and was recorded by crystallization of quartz with fluid inclusions of L₁ and L₁ + B types. Conden-

sation of amorphous forms of organic matter (sometimes rounded in shape) of a composition close to paraffin probably also took place. At present these accumulations occasionally show a tendency towards structuralisation (Dudok and Jarmolowicz-Szulc, 2000).

The fluids migrating through the sedimentary rocks rich in the organic matter may have extracted some hydrocarbon components. In some areas, the hypothetical hydrocarbon accumulations might have been unsealed, which led to hydrocarbon leakage. Different hydrocarbon phases might have differentiated resulting from natural hydrocarbon separation, similar to that occurring in industrial processes. Consequently, heavy hydrocarbons dominated at the final stage of mineral formation (minimum temperatures and minimum pressures). In some regions (around the villages of Soymy, Stavne and Rabe) migration of hydrocarbons and the carbon dioxide-bearing fluids occurred. Homogenisation temperatures of the inclusions range from +68°C (Soymy), through +58 and +56°C (Stavne) to +56°C till +41°C (Rabe). This migration must have been followed by the ore-bearing fluids which obviously used the same paths.

Hydrocarbon migration occurred repeatedly through the veins. A petroleum film is present along the crystal growth planes, on the surfaces of the veins and on the crystals. These processes are particularly characteristic of the NW part of the study area (from Stavne towards the NW). In that part of the region (the Dukla Unit), oil fields are known to be present e.g. at Wetlina and Dwernik (Karnkowski, 1993).

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APPENDIX

SAMPLING LOCALITIES

SILESIA-KROSNO UNIT

Samples pD1, pD3 in the Bystre area

Location: Outcrops on the bank of the Rabski Potok under the bridge. The fault zone.

Description: Intercalations of quartz and anthraxolite in the complex of the menilite schists and sandstones.

Samples pD4, pD5, pD6, Ra 4 in the Rabe–Bystre area

Location: An outcrop about 5 km along the road towards the Rabe settlement. At the mouth of the right hand side tributary.

Description: Grey sandstones with fissures. Co-occurrence of calcite, anthraxolite, quartz.

Samples W10–W13 in the Wołosate area

Location: An outcrop at the right bank of the Wołosaty Stream, about 2 km from the settlement.

Description: Lithology — sandstones with limestones and black argillites, tectonically deformed “Marmarosh diamonds” co-occurring with athraxolite.

Samples 708, U7/1, U7/2 in the Mezhgorie area

Location: An outcrop about 5.5 km from the stream mouth.

Description: Interlayers of strongly deformed sandstones with siltstones of the Krosno type. Quartz and anthraxolite in the fissures.

Samples 722, 723 from near the village of Volovec (region between Stavne and Mezhgorie)

Location: An outcrop about 6 km from the village, down the Vecha Stream. Left bank.

Description: Sandstones and argillites intercalated with marls of the Krosno type. Subvertical fissures cut the layers. The thickness of the vein fillings range from a few to about 10 cm. Filling material: calcite, quartz, anthraxolite.

Samples 704, U17, U8 in the Ripinka area (region between Stavne and Mezhgorie)

Location: An outcrop situated about 1.5 km from the mouth of the Rika River into the Ripinka, at the left riverbank.

Description: Massive grey sandstones with fissures filled with transparent, well-crystallized quartz. Crystals of the “Marmarosh diamonds” up to 0.8 cm in size.

Samples 725, 729 in the village of Lazy (region between Stavne and Mezhgorie)

Location: An outcrop in the village of Lazy in the Lazy Stream at a distance of about 1.2 km.

Description: Repeating interlayers of grey sandstones with argillites. Subvertical veinlets in the sandstones filled with quartz and anthraxolite.

Samples 794, 796 in the Ripinne area (region between Stavne and Mezhgorie)

Location: Left riverbank, at a distance of about 5 km from the village of Ripinne.

Description: Rhythmic interlayering of grey sandstones (thickness from 10 to 20 cm) and siltstones (thickness from 5 to 10 cm) with siderite lenses (to 20 cm). Numerous fractures. Quartz and calcite are the predominant vein minerals. Abundant athraxolite. The thickness of fissures ranges from a few millimetres to 2 cm.

Samples U10, U12 in the Abramka village (east of Stavne)

Location: An outcrop in the village of Abramka and northwards along the road towards another settlement.

Description: Strongly tectonized schists and sandstones. Fissures filled with quartz and calcite.

DUKLA UNIT

Samples D7, D8, D9, PS1 in the Solinka area (south-east of Komańcza)

Location: The outcrop under the bridge over the river.

Description: The menilite schists in the Solinka River valley. Anthraxolite co-occurring with calcite; pyrite veinlets in silicites.

Samples 712 in the Svalava area (region between Stavne and Mezhgorie)

Location: An outcrop situated on the right side of the Volovec–Svalava road in the rocks of the Dukla Unit, about one km from the contact with the Krosno Unit.

Description: Intercalations of dark grey sandstones with black argillites. Intense tectonic deformation of the rocks. Subvertical fissures filled with calcite, quartz, anthraxolite and pyrite.

Sample 713 in the Ploske area (region between Stavne and Mezhgorie)

Location: An outcrop in the village of Ploske, about 5.5 km from the crossroads towards the settlement of Rodnikovka, on the right bank of the river.

Description: Intercalations of argillites and marls with sandstones with siderite lenses. Small layers of bitumens with separate crystals of honey-yellow quartz crystals and calcite. Dipping azimuth of 200–220°, dip angle of 25–30°.

Samples 762, 764, 767, U1, U3 in the Stavne village area

Location: Outcrops in the village of Stavne on the right bank of the Uzh River, about 0.6 km from the church, along the river.

Description: Late Cretaceous sequence. Rhythmic interlayering of grey sandstones (thickness up to 15 cm) and siltstones (thickness up to 5 cm). Strong tectonic deformation. Numerous fissures. Quartz and calcite are the predominant vein minerals. Abundant anthraxolite.