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A FLUORESCENCE CONTRIBUTION TO THE RECOGNITION OF FLUIDS TRAPPED IN MINERALS IN THE CARPATHIAN OUTCROPS

ZNACZENIE FLUORESCENCJI W ROZPOZNANIU FLUIDÓW ZAMKNIĘTYCH W MINERAŁACH SKAŁ W ODKRYWKACH KARPACKICH

Katarzyna Jarmołowicz-Szulc[1]

Abstract. Based on the assumption that fluorescence studies are an important tool in search and characterization of hydrocarbons, samples of rocks, minerals and the organic matter were collected in the Western Carpathian area spreading from the Mszana Górna region in the west to the Bieszczady Mts. in the east, and continuously, towards SE outside the Polish frontier, in Ukraine and Slovakia. Analytical procedures comprised preparation, microscopic observation of the material (organic matter and minerals) from the point of view of inclusions and fluorescence followed by detailed luminescence studies. Those steps have been followed by the microthermometric determinations. The application of the fluid inclusion methods, which are one of the newest analytical tools in the last two decades have led to the characteristics of fluids trapped in the inclusions in the area. The fluorescence studies showed some diversity of hydrocarbons both in compositions and in distribution. The analyses were performed in double-sided polished thin sections prepared based on cold techniques. Fluorescence of inclusions in two minerals, quartz and calcite, was checked in those specific thin sections either in glued wafers, or loose (single) crystals. The fluid inclusion studies were accompanied later on by solid organic matter inclusion studies. Those point to the presence of the following minerals: quartz, dolomite, calcite, clay minerals, gypsum with anhydrite admixture, traces of pyrite and siderite, feldspars. General distribution of fluorescing and not fluorescing inclusions suggests the presence of light hydrocarbons (methane) in the west and south of the area, being enriched in higher hydrocarbons (oil) towards the east.

Key words: fluorescence, organic matter, fluid inclusions, quartz, the Carpathians.

Abstrakt. Badania fluorescencji podjęto w skałach, minerałach i bituminach w Karpatach Zachodnich w rejonie rozciągającym się od Mszany Górnej po Bieszczady i dalej – poza granicami Polski – na Ukrainie i Słowacji. Procedury analityczne obejmowały preparatykę, ocenę mikroskopową materiału (organika i minerały) z punktu widzenia występowania wrostków i fluorescencji inkluzji oraz zasadnicze badania świecenia. Po tych analizach wykonano oznaczenia mikrotermometryczne. Wszystkie badania przeprowadzono stosując nowe metody i nowoczesny sprzęt analityczny. W wyniku użycia metod badań inkluzji fluidalnych, będących jednym z najnowszych narzędzi analitycznych w ostatnim dwudziestoleciu, uzyskano charakterystykę fluidów zamkniętych w postaci inkluzji w minerałach. Badania fluorescencji wykazały zróżnicowanie wypełnień węglowodorowych. Analizy przeprowadzano w obustronnie polerowanych płytkach, przygotowanych na zimno. Badano dwa minerały – kwarc i kalcyt – zarówno w preparatach, jak i luźnych kryształach naturalnych (kwarc – diamenty marmaroskie). Badaniom inkluzji fluidalnych towarzyszyły analizy wrostków organicznych (np. badania czarnych agregatów występujących w odkrywkach w formie soczewek). W ich wyniku stwierdzono obecność następujących minerałów: kwarc, dolomit, kalcyt, minerały ilaste, mieszanina gipsu z anhydrytem, ślady pirytu i syderytu oraz skalenie. Ogólny rozkład fluorescencji wrostków w minerałach i inkluzji niewykazujących wzbudzenia sugeruje obecność lekkich węglowodorów (metan) w części zachodniej obszaru i na południu oraz wyraźne wzbogacanie w wyższe węglowodory (ropa naftowa) w kierunku wschodnim.

Słowa kluczowe: fluorescencja, bituminy, inkluzje fluidalne, kwarc, Karpaty.

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INTRODUCTION

The area of the Carpathians has been the study area for over a century for geologists. The studies on minerals in the Carpathians conducted for many years in different aspects represent one of multifold aspects. That mostly concerns the quartz and the calcite associated with bitumen in a very specific position. Previously, in 1905, Tokarski studied morphology of the Carpathian phenomenon called the Marmarosh diamonds. The research on the Marmarosh diamonds (MD) has been conducted in Ukraine and Poland in last few decades since the hydrocarbon inclusions have been concerned indicators of hydrocarbon migration and accumulation in the folded Carpathian formations (*e.g.*, Ripun, 1970; Wozhniak *et al.*, 1973; Bratus *et al.*, 1975; Kaliuzhnyj, 1982; Hurai *et al.*, 1989; Dudok, 1991; Vityk *et al.*, 1995, 1996; Kaliuzhnyj, Sachno, 1998). Mastella and Kojsar (1975) concerned MD as bound with the process of bituminization of the Podhale area. Early microthermometric studies proved methane and most probably nitrogen in some fluid inclusions in the quartz (*e.g.*, Kozłowski, 1982; Kozłowski *et al.*, 1996). The environment of formation of MD in the Mszana Dolna tectonic window in the Krosno beds, the Mszanka and Raba basins with tributaries, and the Dunajec basin was characterized by Karwowski and Dorda (1986). Detailed analysis was performed in the Bieszczady region in both Polish and Ukrainian sides (*e.g.*, Jarmołowicz-Szulc, 2000, 2001; Jarmołowicz-Szulc, Dudok, 2000, 2001).

According to these studies, the majority of hydrocarbon inclusions in the minerals in the Carpathians co-exist with the aqueous inclusions. These inclusions occur mostly in the quartz that displays a euhedral crystal habit (MD) and in the minerals of calcite-quartz-bitumen veins in the Carpathian units (Jarmołowicz-Szulc, Dudok, 2000, 2005; Jarmołowicz-Szulc, 2001; Dudok, Jarmołowicz-Szulc, 2005). In the Slovak side of the Western Carpathians Hurai *et al.* (2001, 2002) studied the origin of the methane in the quartz.

The stratigraphic, tectonic/structural and mineralogical studies have recently brought new study material and distinguishing of the mélange zones in the Carpathians (*e.g.*, Jankowski, 2015). First relations between these zones and mineralization were recorded (Jankowski, Jarmołowicz-Szulc, 2004; Jarmołowicz-Szulc *et al.*, 2005, 2008) being followed by multifold generated results (Jarmołowicz-Szulc, Jankowski, 2008, 2010; Jarmołowicz-Szulc, 2009; Jankowski, Jarmołowicz-Szulc, 2009; Jarmołowicz-Szulc *et al.*, 2012; Ciechanowska *et al.*, 2015; Matyasik *et al.*, 2015).

The present paper deals with that part of the studies on fluid inclusions (FIs) conducted in the area of the flysch Carpathians where the previous fluorescence studies of both of fluid inclusions and the organic matter are limited. The aim of the paper is to show the importance and advance of such studies in characterization of the fluids trapped in the inclusions and migrating in the Carpathian system.

GEOLOGICAL AND MINERALOGICAL SETTING

The study area in the Carpathians spreads from the Mszana Górna tectonic region to the Bieszczady Mts. is continued to the south and east. That is in detail shown in figures (Figs. 1, 2).

Traditionally, three tectonic units have been distinguished there (Jankowski, Jarmołowicz-Szulc, 2009). The section of the southermost Dukla unit comprises deposits from the Upper Cretaceous to Oligocene. The Inoceramus beds are the oldest layers in the sequence, being deposited from Upper Cretaceous to Palaeocene; their section has been completed by the so called Majdan beds of the Palaeocene age. In the Eocene part of the Dukla unit, there is a complex of variegated schists with sandstone interlayers either of the Przybyszów or Ciężkowice sandstone lithotypes. The hieroglyph beds, typically developed as thin sandstones and schists are the highest part of the Eocene deposits. At the Eocene–Oligocene boundary there is a distinct change in the sedimentation. The complex of the Mszanka sandstones appears, which has been recently ascribed to the lower part of the menilite beds. The complex of the menilite beds forms a Lower Oligocene part of the geological section. Black schists of hornstones and marls are interbedded with lenses of sandstones of different thickness (known as the Cergowa sandstones). The profile of the Dukla unit has been completed by the Krosno beds complex with thick schists at the top.

The fore-Dukla folds may be distinguished at the Dukla unit foreland, being generally ascribed to the Silesian unit. Their profile does not different from that of the Silesian unit. The Bystre slice is in this region a total tectonic phenomenon. The whole section of the Silesian unit developed from the Lower Cretaceous deposits to the Oligocene Krosno beds is present there. The Lower Cretaceous Cieszyn beds developed as the complex of dark schists, sandstones and marls or even limestones occur in the lowermost part. The Grodziskie beds, occur higher, being overlain by a twice folded, rather thick complex of the Lgota beds, completed by the Upper Cretaceous variegated schists. The complex of the Istebna sandstones and schists of the Upper Cretaceous/Palaeocene age and the Ciężkowice sandstones surrounded by the Eocene variegated schists lie higher in the profile. Similarly to the Dukla unit, the Upper Eocene is represented by the Hieroglyphic beds. The section has been completed by the menilite-Krosno series that is similar to other Carpathian tectonic units.

The Central Carpathian Depression, which contacts with the fore-Dukla folds, is filled in with the Krosno beds, strongly deformed and with a complicated geometry of the thrusts (Fig. 1).

The main mélange zone, very distinct in the Bieszczady Mts. and the Beskid Niski areas, stretches from the territory of Ukraine through the Bieszczady region, outcropped at several sites (Figs. 2, 3). At the Polish side of the Bieszczady Mts., the mélange outcrops are seen west of Ustrzyki Górne

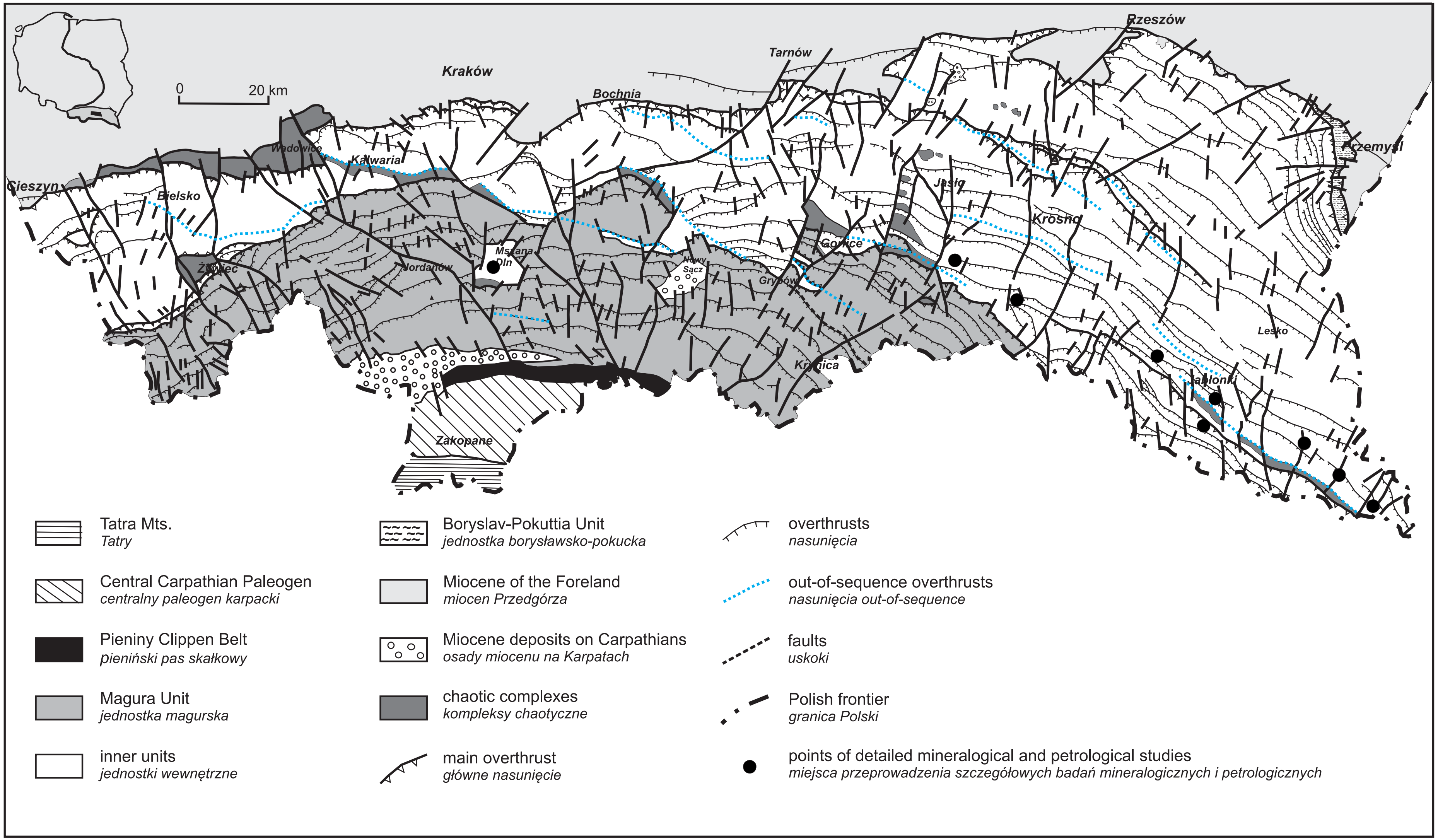

Fig. 1. Tectonic sketch map of the Carpathians (after Jarmołowicz-Szulc, Jankowski, 2011)

Szkic tektoniczny Karpat (wg Jarmołowicz-Szulc, Jankowskiego, 2011)

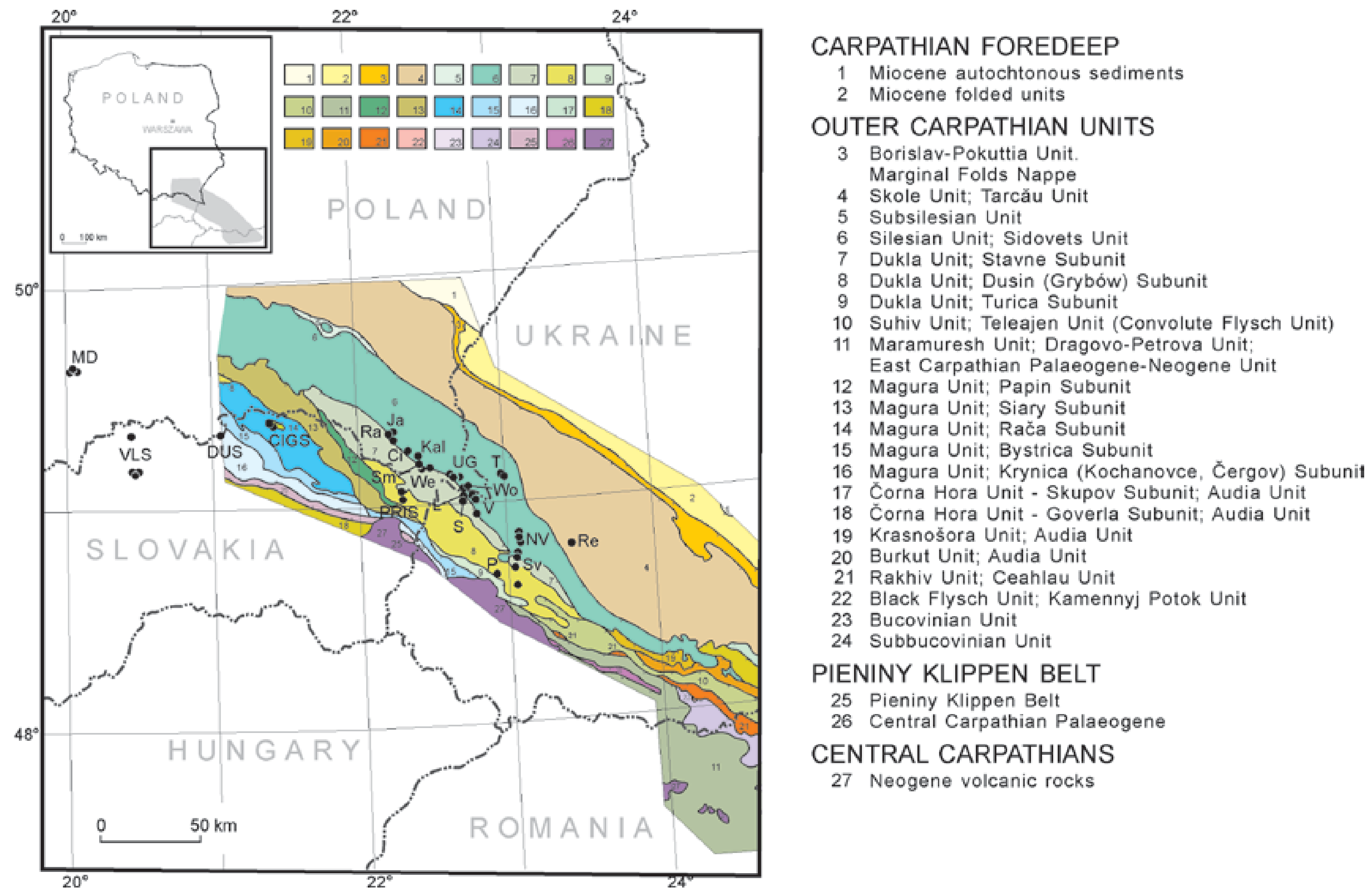

Fig. 2. Detailed geology and outline of sampling in the adjacent area of Poland, Ukraine and Slovakia (after Jarmołowicz-Szulc *et al.*, 2012, modified)

Explanation of abbreviations: MD – Mszana Dolna ; VLS – Velky Lipnik ; DUS – Duszatyn ; CiGS – Cigla ; Ra – Rabe; Ja – Jabłonki; UG – Ustrzyki Górne; Wo – Wołosate; V – Volovec ; NV – Nizhnyje Vorota; Re - Repinka; Sv – Svalava; P – Pavlovka; S – Stavne; We –Wetlina; Sm – Smerek; PRIS – Prislop; Ci – Cisna; T – Turka. Underlined are places referred in photographs on Figures 4–8

Szczegółowa budowa geologiczna i zarys opróbowania na przyległych do siebie obszarach Polski, Ukrainy i Słowacji (wg Jarmołowicz-Szulc i in., 2012, zmienione)

Objaśnienie skrótów: MD – Mszana Dolna; VLS – Velky Lipnik; DUS – Duszatyn; CiGS – Cigla; Ra – Rabe; Ja – Jabłonki; UG – Ustrzyki Górne; Wo – Wołosate; V – Volovec; NV – Nizhnyje Vorota; Re – Repinka; Sv – Svalava; P – Pavlovka; S – Stavne; We – Wetlina; Sm – Smerek; PRIS – Prislop; Ci – Cisna; T – Turka. Podkreślono miejsca prezentowane w na figurach 4–8

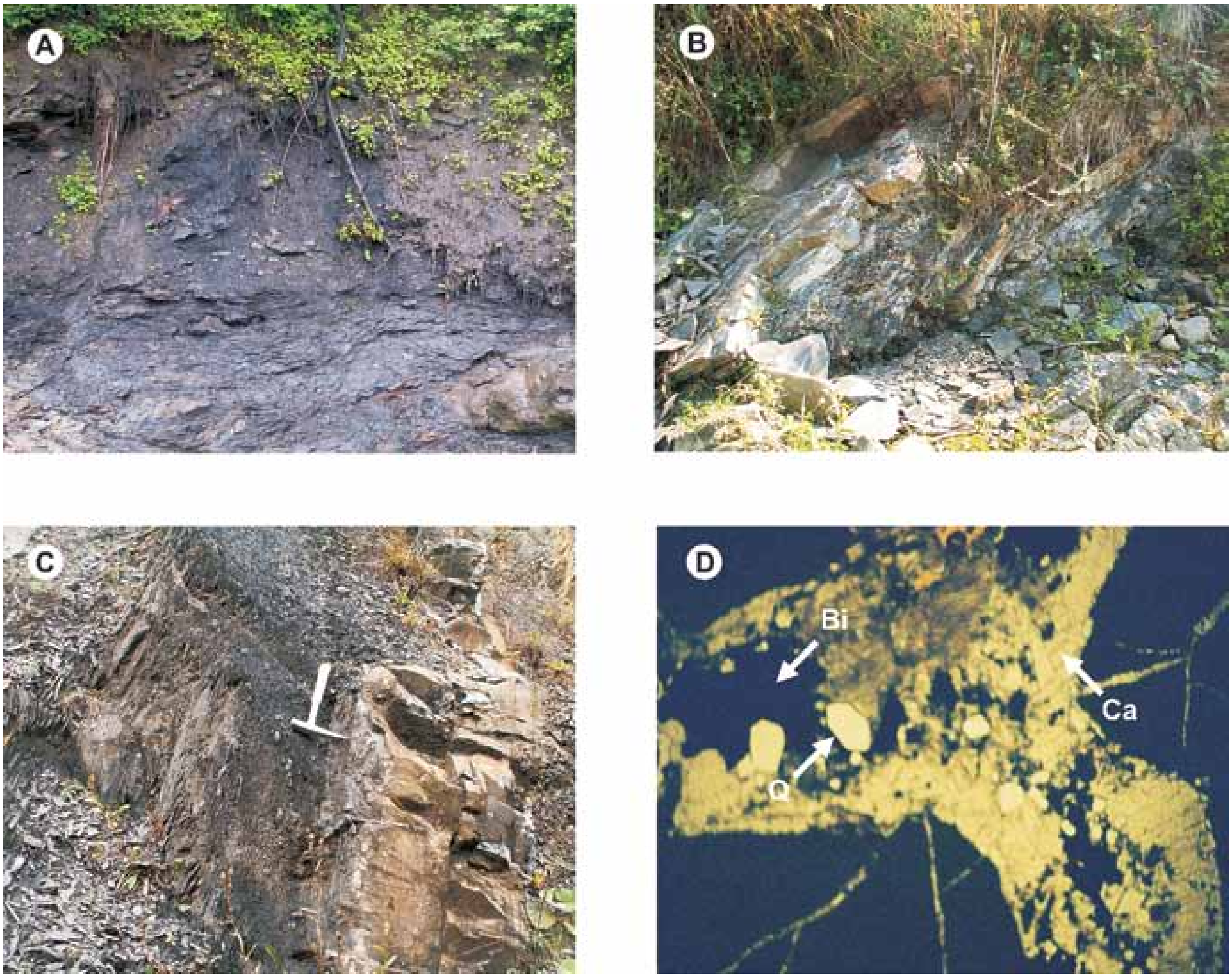

Fig. 3. Carpathian outcrops and tectonic mélange zones in Jabłonki, Stavne and Prislop localities and the character of vein mineralization

A – the tectonic mélange in the Jabłonki vicinity (Poland); **B** – the Stavne outcrop at the stream bank (Ukraine); **C** – the outcrop at Prislop (Slovakia); **D** – vein filled by quartz (Q), black bitumen (Bi) and carbonate (Ca); sample Ja/05; the Jabłonki region

Karpackie odkrywki i strefy melanżu tektonicznego w lokalizacjach Jabłonki, Stavne i Prislop oraz charakter mineralizacji żyłowej

A – melanż tektoniczny w okolicy Jabłonek (Polska); **B** – odkrywka w brzegu potoku w Stavne (Ukraina); **C** – odkrywka w rejonie Prislop (Słowacja); **D** – żyłka wypełniona kwarcem (Q), czarnymi bituminami (Bi) i węglanami (Ca); próbka Ja/05; rejon Jabłonek

(in the Bystry stream). They occur in the upper run of the Wetlinka stream (Wetlina) as well as in Smerek. The most spectacular beautiful mélange outcrops in the Bieszczady area are present in the Jabłonki region (the Jabłonki stream), in Kalnica as well. A potential prolongation of this mélange zone westwards is under further consideration (Jankowski, 2015). A strong mineralization of this zone is, however, restricted only to the Bieszczady area and is manifested in the accumulation of quartz and carbonates in a certain genetic sequence. The accumulations in the caverns and fissures gradually filled are extremely distinct. The observations in the Beskid Niski Mts. and in the northern part of the Polish Carpathians point to band – like zones of the tectonic mélange, which, however, do not display mineralization as strong as in the Bieszczady region (Jarmołowicz-Szulc, Jankowski, 2010).

As it is seen in Figure 1, sampling took place in the widespread area from the Mszana Górna tectonic window to the Bieszczady Mts. region in Poland, whereas the sampling points outside Polish territory are presented in Figure 2. Some outcrops are shown in Figure 3A–C. Main sampling in the mélange zone took place in the vicinity of Jabłonki–Rabe and Cisna in the Bieszczady Mts. (Jarmołowicz-Szulc, Jankowski, 2008, 2010). In black, schistous rocks of the mélange, where larger and smaller blocks (“block-in-matrix”), clasts and lenses occur (Fig. 3A). Fragments of clasts vary in size, from some tens of centimeters to some meters. The clasts are fractured. The fractures are filled with mineralization (*e.g.*, Fig. 3D) which represents the object of the petrological, mineralogical and geochemical studies (*cf.* Jarmołowicz-Szulc, Jankowski, 2010; Jarmołowicz-Szulc *et al.*, 2012; Jarmołowicz-Szulc, 2016).

METHODOLOGY

SAMPLING AND ANALYTICAL METHODS

Mineralogical, petrologic and geochemical studies were conducted on samples of rocks, minerals and the organic matter taken from the selected tectonic mélange zones, tectonic windows and other areas **(**Fig. 1). Sampling was also performed in adjacent area to the Bieszczady Mts. region in Ukraine and Slovakia (Fig. 2). Details of sampling may be also followed in some papers (Jarmołowicz-Szulc, Dudok, 2005; Jarmołowicz-Szulc, Jankowski, 2010; Jarmołowicz-Szulc *et al.*, 2012). Presentation of sampling sites is also displayed in Figure 3, as already mentioned above.

Analytical procedures were mostly performed in the Polish Geological Institute – National Research Institute, Warsaw. All works including sampling, sample preparation, microscopic observation, inclusion petrography, determination of inclusions, organic matter and host minerals, fluorescence studies and microthermometry have been completed at PGI Department of Regional Geology. The microthermometric and bitumen analyses in detail are described by Jankowski, Jarmołowicz-Szulc (2004, 2009), Jarmołowicz-Szulc (2009) and Jarmołowicz-Szulc *et al.* (2012). The present paper describes the fluorescence studies in details below.

DETAILED DESCRIPTION OF METHODS AND EQUIPMENT

The research comprised general description of minerals and standard petrologic studies that were conducted using Nikon-Optiphot polarization microscope either on the thin sections or double-sided polished thin sections.

Fluorescence studies were conducted under the quartz lamp in UV Nikon device with filters (UV – 365 nm, blue – 480 nm). Samples were analyzed in two directions aiming at rock, mineral and fluid inclusion diagnosis. The observations of luminescence were conducted consequently at standard magnitude (eye-piece 15×, objective 10×), which ensures always the same conditions during evaluation of fluorescence colors. Recently, a fluorescence device has been added to the digital camera that transfers an image onto the computer monitor and enables a digital record instead of analogue picture.

Microthermometric studies of hydrocarbon fluid inclusions (HCFI) that followed the fluorescence diagnosis, were conducted either using manually controlled Fluid Inc. System mounted on the Leitz Orthoplan microscope or automatically controlled Linkam stage mounted on Nikon-Optiphot microscope. The temperature measurements were checked with international standards (Reynolds, 1991). The analytical results were calculated using computer programs (Flincor – Brown, 1989) for aqueous and methane systems to obtain fluid density, character/type and composition. A method of crossing isochors was used to estimate trapping temperature and pressure of HCFI and AQFI pairs (see additional details in Jarmołowicz-Szulc *et al.*, 2008, 2010, 2012).

The analysis of content of saturated hydrocarbons was performed aiming at composition of the organic matter in the samples. This part of the study was done both in the Institute of Oil and Gas in Cracow and in the chemical laboratory of Polish Geological Institute in Warsaw by use of GS/MSD Hewlett-Packard. Bitumen samples from the lenses in the mélange zones and samples of rocks and minerals were analysed (Rock-Eval) that is shown in bibliography (*e.g.*, Kotarba *et al.*, 2000; Dudok *et al.*, 2002; Dudok, Jarmołowicz-Szulc, 2005; Jarmołowicz-Szulc *et al.*, 2012)

The pyrolitic analysis was conducted by use of Vinci Technologies Rock-Eval 6. XRD determinations were performed by powder method with a use Philipps X' Pert PW 3020 in respect to the international standards (JCPDS). The reflectance of the organic matter was determined both in the double-sided polished sections (approximate data) and in the polished slabs.

RESULTS

Microscopic observations of fluid and bitumen inclusions have led to their characterization.

Hydrocarbon and aqueous inclusions were mostly distinguished due to fluorescence studies being further confirmed by microthermometry. A fluorescence characteristics of fluid inclusions is shown in the Table 1 with references to the Figures 4–8.

Generally, two types of hydrocarbons have been distinguished in FI in the UV excitation in the host minerals (which are quartz and calcite grains). These are oil and methane inclusions. The oil inclusions exhibit a distinct fluorescence in white-blue colors since the fluid contains heavy aromatic hydrocarbons that can/make luminesce (Lumb, 1978). According to the Jarmołowicz-Szulc (2016, 2017), the character of the fluid may be estimated for its maturity (high mature) and American Petroleum Institute gravity (°API – around 41). Some inclusions displayed a yellow to red-orange fluorescence that points to another composition of heavier hydrocarbon mixtures, lower maturity and heavier oil composition. The fluorescing inclusions are two-phased in character. One phase inclusions either do not fluoresce or display a faint dull blue fluorescence. In the first approximation they are methane. Their exact content, however, must be and has been confirmed both by microthermometric studies and some Raman analyses (*e.g.*, Jarmołowicz-Szulc *et al.*, 2012). The fluorescence phenomenon of hydrocarbon inclusions in the Carpathians is presented in photomicrographic plates (Figs. 4–8) which correspond to the localities pointed out in Figures 1 and 2.

Table 1

Fluid diagnosis based on the fluorescence character of inclusions

Diagnoza fluidów w inkluzjach w oparciu o charakter fluorescencji

Region	Mineral	Type of inclusions	Co-occurring organic matter	Fluorescence (UV)	Type of fluid*	Remarks	Ref.
Mszana Dolna	quartz	one phase	black bitumen	dull blue	methane**	characteristic shape of FI	Fig. 4
Mszana Dolna	quartz	two phase	–	no luminescence	brine	–	Fig. 4
Cisna	carbonate	two phase	–	blue-white	oil	small inclusions in clouds	Fig. 5
Jabłonki	quartz	one phase	black bitumen	no fluorescence to dull blue	methane	very stretched FI	Fig. 5
Wołosate	quartz	one phase	–	dull blue to no	methane	very stretched FI	Fig. 6
Rabe	quartz	one phase	–	dull blue to no	methane	–	Fig. 5
Rabe	quartz	two phase	black bitumen	blue-white	oil	brown colour of fluid in polarized light	Fig. 5
Jabłonki	carbonate	two phase	–	blue-white	oil	–	Fig. 6
Stavne	quartz	two phase	black bitumen	blue-white	oil	huge inclusions and bubbles	Fig. 7
Nizhnyje Vorota	quartz	one phase	–	no fluorescence	methane	–	Fig. 7
Pavlovka	quartz	two phase	black bitumen	blue-white	oil	–	Fig. 7
Prislop – Dara	quartz	one phase	–	no fluorescence	methane	very stretched FI	Fig. 8
Prislop – Dara	quartz	two phase	–	no fluorescence	brine	–	

*Detailed composition of the fluid demands further studies – microthermometry and Raman
**The term “methane” may correspond to the mixture of methane, carbon dioxide and nitrogen in different mutual proportions

*Określenie dokładnego składu fluidu wymaga dalszych badań – mikrotermometrycznych i ramanowskich
**Określenie „metan” może odnosić się do mieszaniny metanu, dwutlenku węgla i azotu w różnych wzajemnych proporcjach

The organic matter closed in the minerals showed no fluorescence either in the UV or in blue light.

Due to the fluid inclusion studies, conducted under the microscope in thin sections (calcite) and either in glued wafers or loose crystals (quartz – the “Marmarosh diamonds”), also mixed inclusions may be characterized in minerals.

Based on the fluorescence character and types of the filling of inclusions in the minerals that are present in the veins, the following assemblages of inclusions can be distinguished: primary liquid-gas inclusions filled with brine of low salinity (no fluorescence); primary single phase inclusions filled with methane (no or dull-blue fluorescence); primary two phase hydrocarbon inclusions (white-blue fluorescence); secondary liquid-gas brine inclusions.

DISCUSSION

As it has been proved from the present and past fluorescence and microthermometry studies, hydrocarbons are trapped as fluid inclusions mostly in the Marmarosh diamonds wide-spread in the Carpathians, whereas two-phase brine or gas inclusions are more frequent in calcite (Figs. 4–8). The fluid inclusion petrography chapter should show it.

The fluorescence studies either in UV or in blue lights lead to the conclusions on the differentiation of the inclusions in the host minerals. The adequate luminescence is the first criterion in selection of the aqueous (brine) and hydrocarbon fluids (Jarmołowicz-Szulc, 1999, 2001, 2016). In its

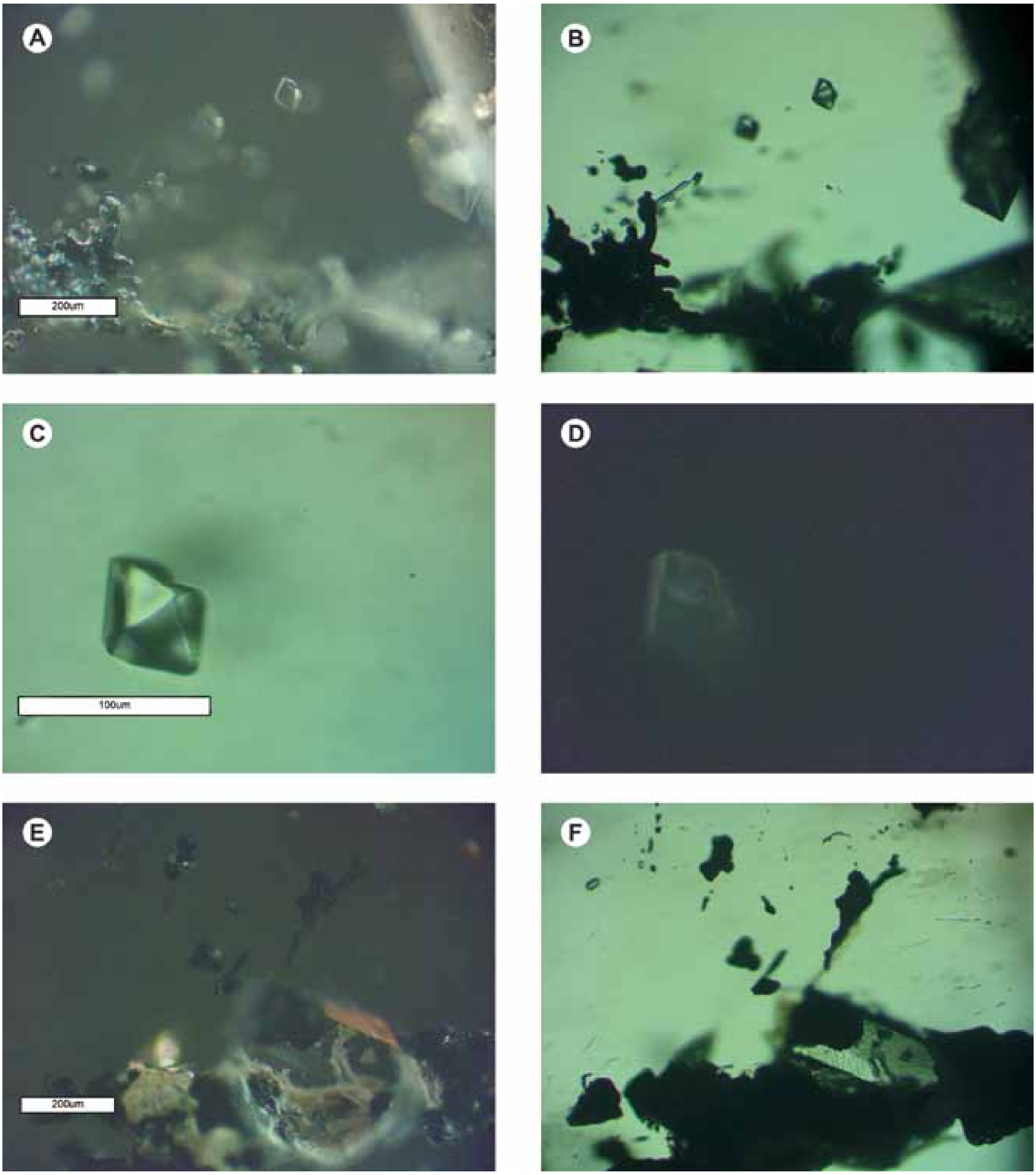

Fig. 4. Hydrocarbon fluid inclusions in the Mszana Dolna tectonic window (Poland)

A – fluid and solid hydrocarbon inclusions in the Marmarosh diamond quartz; in fluorescence mode; no luminescence exhibited; reflected light, ultraviolet; **B** – inclusions from photo A; polarized light; 1 nicol; **C** – one phase fluid inclusion in the Marmarosh diamond quartz filled in with methane; characteristic habit of the inclusion; polarized light; 1 nicol; **D** – total no fluorescence of the inclusion from photo C; reflected light, ultraviolet; **E** – fluid and solid hydrocarbon inclusions in the Marmarosh diamond quartz; different luminescence; reflected light, ultraviolet; **F** – inclusions from photo E; polarized light; 1 nicol

Węglowodorowe inkluzje fluidalne w oknie tektonicznym Mszany Dolnej (Polska)

A – fluidalne i stałe inkluzje węglowodorowe w diamencie marmaroskim; we fluorescencji; brak świecenia; światło odbite; nadfiolet; **B** – inkluzje z fot. A; światło spolaryzowane; 1 nikol; **C** – jednofazowa inkluzja fluidalna w diamencie marmaroskim; charakterystyczny kształt inkluzji; światło spolaryzowane; 1 nikol; **D** – całkowity brak wzbudzenia dla inkluzji z fot. C; światło odbite, nadfiolet; **E** – węglowodorowe inkluzje fluidalne i wrostki stałe w kwarcu typu diament marmaroski; zróżnicowanie fluorescencji; światło odbite, nadfiolet; **F** – wrostki z fot. E; światło spolaryzowane; 1 nikol

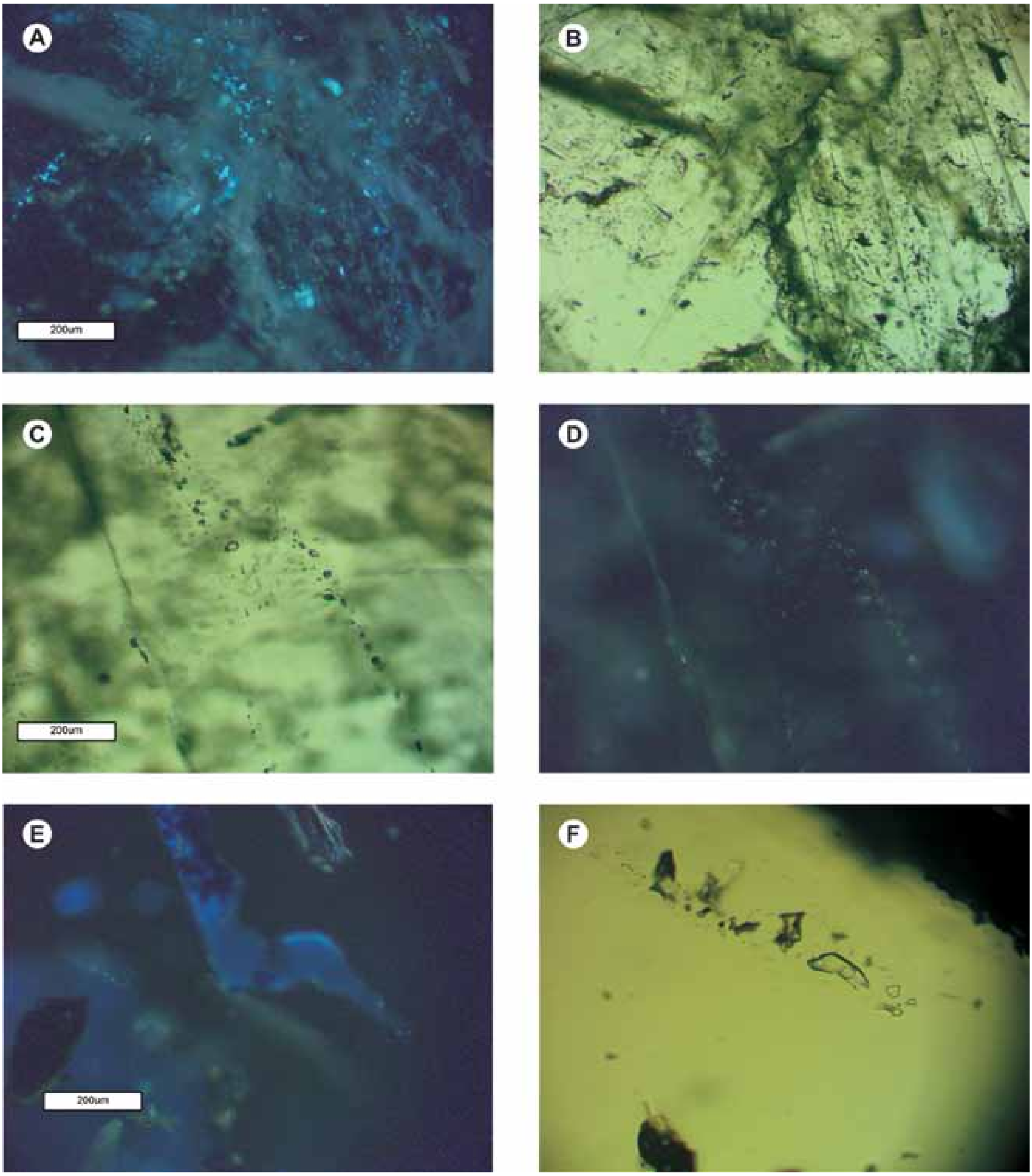

Fig. 5. Hydrocarbon fluid inclusions in the Carpathian minerals in Cisna, Jabłonki and Wołosate localities (Poland)

A – different fluorescence of fluid inclusions in carbonates and quartz; some associations show blue-white fluorescence colors; the Cisna region; reflected light, ultraviolet; **B** – Same image as in photo A; polarized light; 1 nicol; **C** – one phase fluid inclusions in the Marmarosh diamond quartz filled in by methane; the Jabłonki region, Jabłonki; polarized light; 1 nicol; **D** – no fluorescence of the inclusion from photo C; reflected light, ultraviolet; **E** – group of fluid inclusions in the Marmarosh diamond quartz filled in by methane; no fluorescence of the inclusions; the Jabłonki region, Wołosate; reflected light, ultraviolet; **F** – inclusions from photo E; polarized light; 1 nicol

Węglowodorowe inkluzje fluidalne w minerałach Karpat w miejscowościach Cisna, Jabłonki i Wołosate (Polska)

A – zróżnicowane świecenie inkluzji w kalcycie i kwarcu; niektóre grupy inkluzji wykazują niebiesko-białą fluorescencję; rejon Cisnego; światło odbite, nadfiolet; **B** – obraz jak na fot. A; światło spolaryzowane;1 nikol; **C** – jednofazowe inkluzje w diamencie marmaroskim wypełnione metanem; rejon Jabłonek, Jabłonki; światło spolaryzowane;1 nikol; **D** – brak fluorescencji inkluzji z fot. C; światło odbite, nadfiolet; **E** – grupa inkluzji w diamencie marmaroskim wypełnionych metanem; brak fluorescencji; rejon Jabłonek, Wołosate; światło odbite, nadfiolet; **F** – inkluzje z fot. E; światło spolaryzowane; 1 nikol

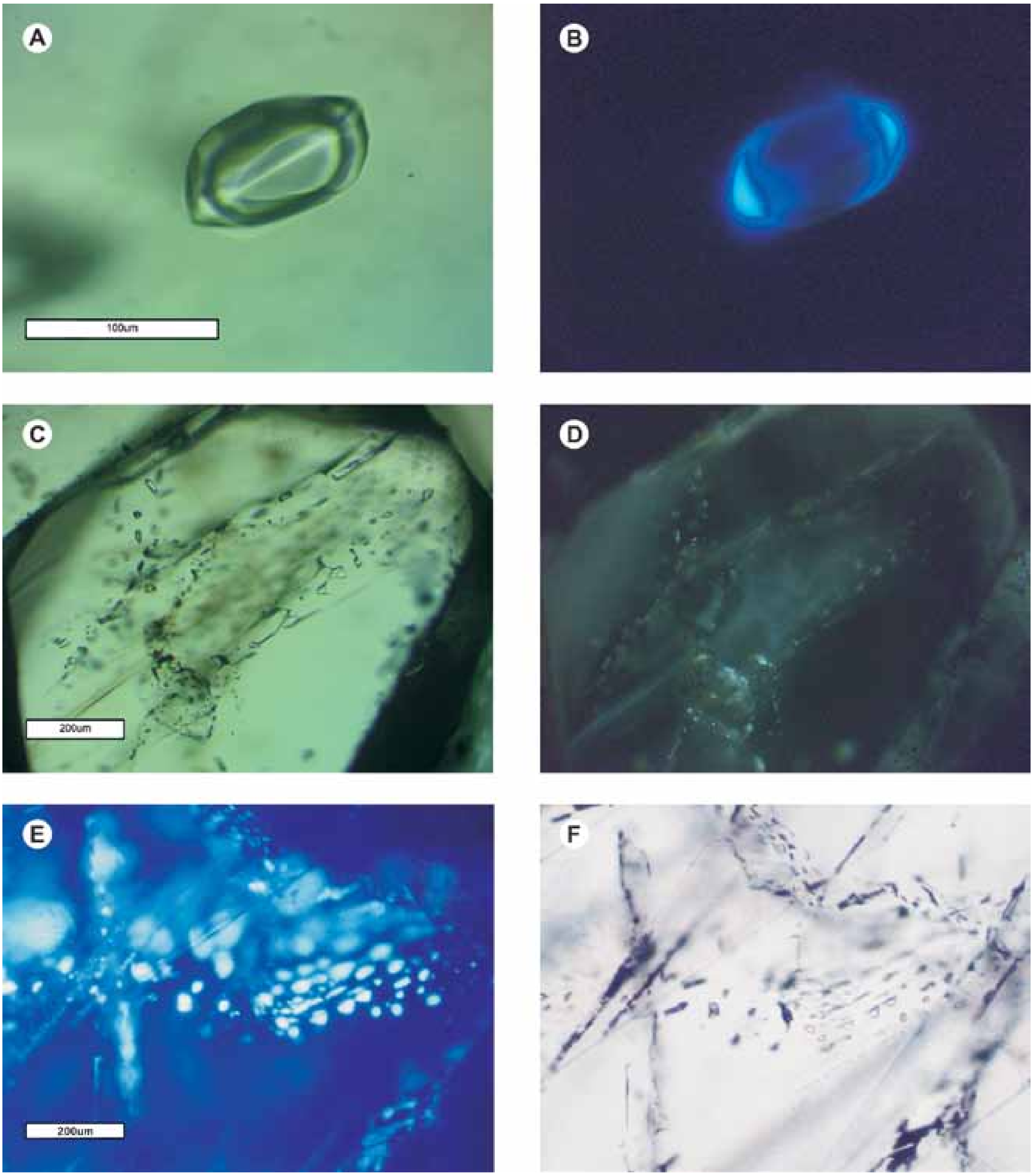

Fig. 6. Hydrocarbon fluid inclusions in the Carpathian minerals in Rabe, Wołosate and Jabłonki localities (Poland)

A – two phase fluid inclusion in the Marmarosh diamond quartz; the Rabe region; polarized light; 1 nicol; **B** – bluish-white fluorescence of the inclusion from photo A; huge not fluorescing bubble contains methane; reflected light, ultraviolet; **C** – different fluid inclusions in the quartz crystal; the Wołosate locality; polarized light; 1 nicol; **D** – differentiated fluorescence of inclusions; same image as in photo C; most inclusions do not fluoresce; some associations show blue-white fluorescence colors; reflected light, ultraviolet; **E** – diversity of fluid inclusion associations in calcite; an intensive white-blue fluorescence of small two phase inclusions and dull blue of one phase inclusions; the Jabłonki vicinity; sample Ja 3/03; reflected light, ultraviolet; **F** – inclusions from photo E; polarized light; 1 nicol

Węglowodorowe inkluzje fluidalne w minerałach Karpat w miejscowościach Rabe, Wołosate i Jabłonki (Polska)

A – dwufazowe inkluzje w diamencie marmaroskim; rejon Rabego; światło spolaryzowane; 1 nikol; **B** – niebiesko-biała fluorescencja inkluzji z fot. A; duży nieświecący pęcherz wypełniony jest metanem; światło odbite, nadfiolet; **C** – różne asocjacje inkluzji w krysztale kwarcu; Wołosate; światło spolaryzowane; 1 nikol; **D** – zróżnicowana fluorescencja inkluzji; obraz jak na fot. C; większość inkluzji nie wykazuje wzbudzenia; niektóre asocjacje charakteryzuje niebiesko-białe świecenie; światło odbite, nadfiolet; **E** – różne asocjacje inkluzji w kalcycie; wyraźna fluorescencja małych dwufazowych inkluzji w barwach biało-niebieskich i niebieskawa – inkluzji jednofazowych; rejon Jabłonek; próbka Ja 3/03; światło odbite; nadfiolet; **F** – inkluzje z fot. E; światło spolaryzowane; 1 nikol

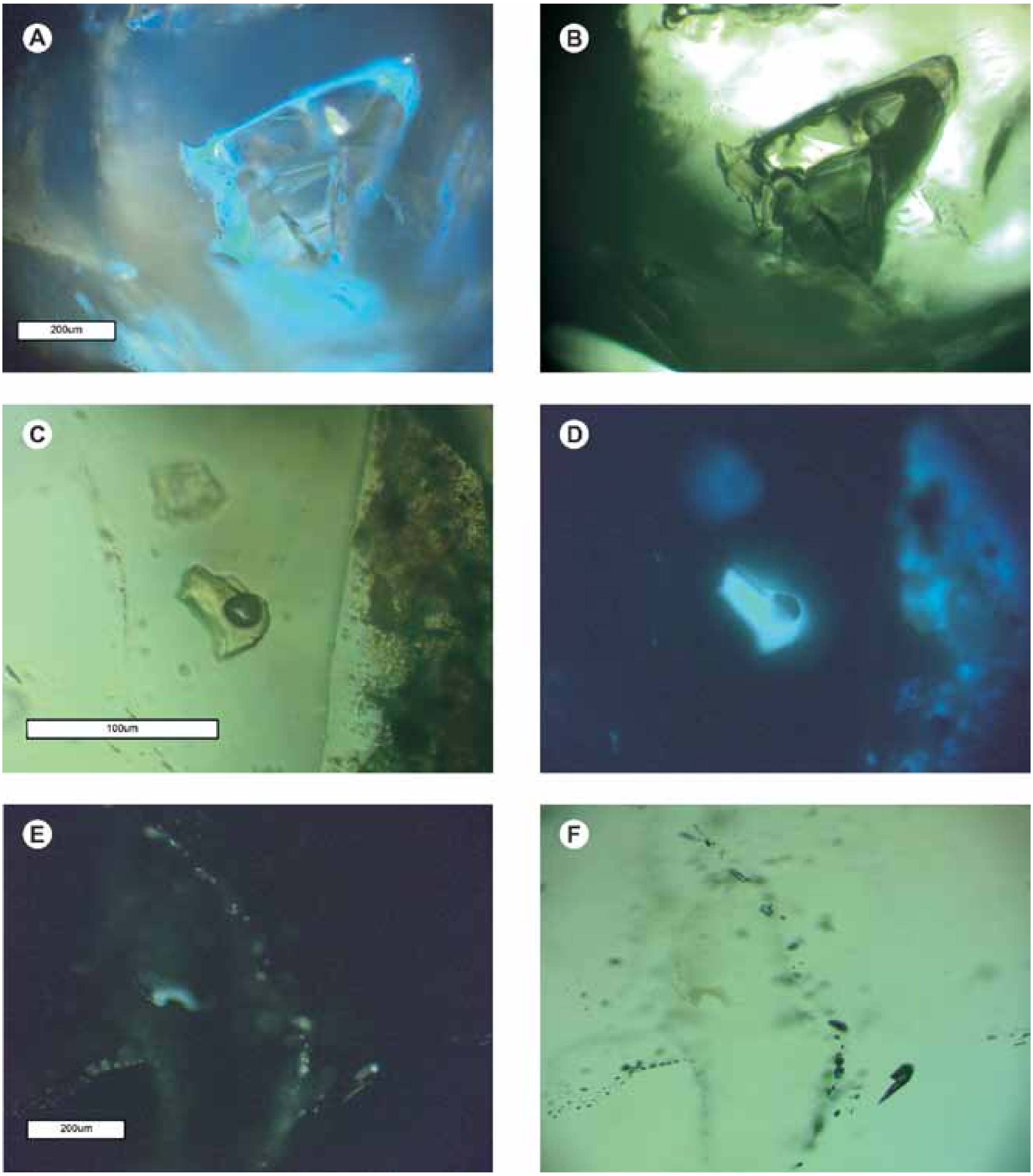

Fig. 7. Hydrocarbon fluid inclusions in the Stavne, Nizhnyje Vorota and Pavlovka localities (Ukraine)

A – hydrocarbon fluid inclusion in the Marmarosh diamond quartz in fluorescence; the Stavne region; the fluid displays white-blue fluorescence, the bubble is black; reflected light, ultraviolet; **B** – the two phase inclusion from photo A; polarized light; 1 nicol; **C** – hydrocarbon fluid inclusion in the Marmarosh diamond quartz; the filling displays a yellow color; the Pavlovka vicinity; polarized light; 1 nicol; **D** – bluish-white fluorescence of the two phase inclusion from photo C; the inclusion is filled with a mature oil; reflected light; ultraviolet; **E** – total no fluorescence of the group of inclusions in the Marmarosh diamond quartz; the Nizhnyje Vorota locality; reflected light; ultraviolet; **F** – same group of fluid inclusions as in photo E filled in with methane (one phase); no characteristic habit of the inclusions; polarized light; 1 nicol

Węglowodorowe inkluzje fluidalne w minerałach Karpat w miejscowościach Stavne, Nizhnyje Vorota i Pavlovka (Ukraina)

A – fluidalna inkluzja węglowodorowa w diamencie marmaroskim we fluorescencji; rejon Stavne; fluid wykazuje niebieskawo-białe świecenie, pęcherzyk jest ciemny; światło odbite; nadfiolet; **B** – inkluzja z fot. A; światło spolaryzowane; 1 nikol; **C** – węglowodorowa dwufazowa inkluzja fluidalna w kwarcu typu diament marmaroski; widoczne żółtawe wypełnienie wnętrza inkluzji; Pawłówka; światło spolaryzowane; 1 nikol; **D** – niebiesko-biała fluorescencja wrostka z fot. C; wypełnienie inkluzji to ropa; światło odbite; nadfiolet; **E** – całkowity brak świecenia dla grupy inkluzji fluidalnych w diamencie marmaroskim; rejon Nizhnyje Vorota; światło odbite; nadfiolet; **F** – ta sama grupy inkluzji, jak na fot. E; brak charakterystycznych kształtów inkluzji; światło spolaryzowane; 1 nikol

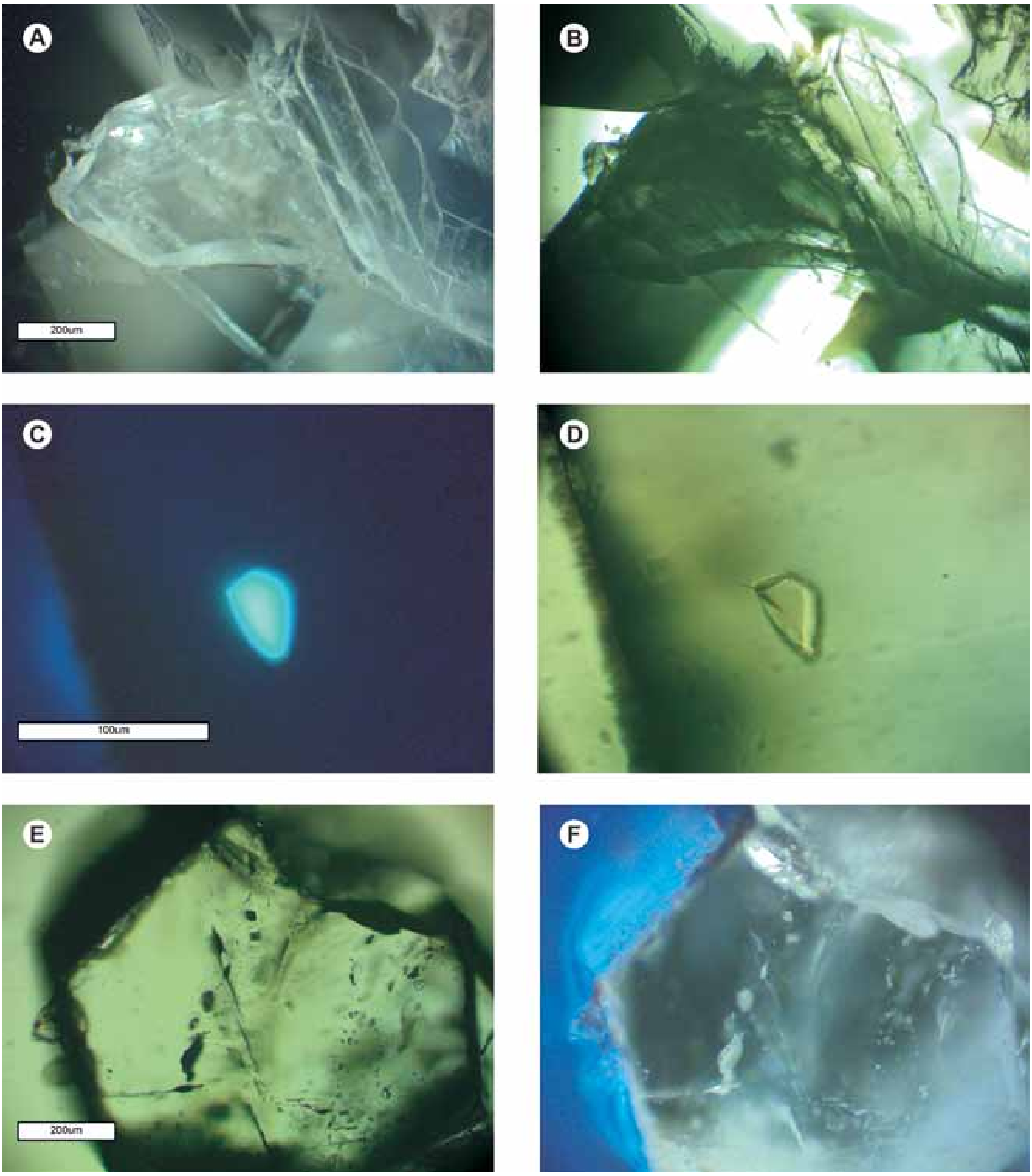

Fig. 8. Hydrocarbon fluid inclusions in the Lubna and Ploske (Ukraine) and Dara–Prislop (Slovakia) regions

A – fluorescing accumulations of hydrocarbon inclusions in the Marmarosh diamond quartz; the Lubna locality (Ukraine); reflected light; ultraviolet; **B** – inclusions from photo A in transparent mode; polarized light; 1 nicol; **C** – one phase fluid inclusion in the Marmarosh diamond quartz filled in with methane with blue fluorescence; the Ploske locality (Ukraine); reflected light; ultraviolet; **D** – same inclusion as in photo C; the inclusion shows some stress features and must have a slight admixture of higher hydrocarbons; polarized light; 1 nicol; **E** – fluid and solid hydrocarbon inclusions in the Marmarosh diamond quartz; the Dara–Prislop region (Slovakia); polarized light; 1 nicol; **F** – no luminescence of the inclusions from photo E; reflected light; ultraviolet

Węglowodorowe inkluzje fluidalne w minerałach Karpat w miejscowościach Łubna i Płoskie (Ukraina) oraz rejonie Dara–Prislop (Słowacja)

A – fluidalne i stałe inkluzje węglowodorowe w diamencie marmaroskim; rejon Łubnej (Ukraina); światło spolaryzowane; 1 nikol; **B** – inkluzje z fot. A we fluorescencji; brak świecenia; światło odbite, nadfiolet; **C** – jednofazowa inkluzja fluidalna w diamencie marmaroskim; charakterystyczny kształt inkluzji; rejon Płoskie (Ukraina); światło spolaryzowane; 1 nikol; **D** – całkowity brak wzbudzenia dla inkluzji z fot. C; światło odbite, nadfiolet; **E** – węglowodorowe inkluzje fluidalne i wrostki stałe w kwarcu typu diament marmaroski; rejon Dara–Prislop (Słowacja); światło spolaryzowane; 1 nikol; **F** – zróżnicowanie fluorescencji wrostków z fot. E; światło odbite; nadfiolet turn, the color of fluorescence in UV maybe indicative to the hydrocarbon content and character in the inclusion (methane, oil, oil maturity, oil density) (Jarmołowicz-Szulc, 2016, 2017). The white luminescence is characteristic for very mature, light oils of density between 45 and 41 as expressed in American Petroleum Institute gravity. Yellow or red colors are characteristic for more dense and low mature oils.

Photomicrographs showing different fluorescence colors for different hydrocarbon types are a useful summary of the study results (Figs. 4–8). White-bluish fluorescence points to the presence of light oil, trapped in the inclusions in the quartz (MD), high mature and of parraphine type. Yellow fluorescence corresponds to another roil generation – heavier, less mature, of naftene character. Lack of fluorescence or a dull blue luminescence points to the methane filling (with or without other gases). The presence of differentiated fluid inclusions in the quartz is the proof for the migration of hydrocarbon fluids different in their character in the geological time of the Carpathian region.

As for their genesis, the primary inclusions with hydrocarbons in the Carpathian minerals may be divided into three phase groups: solid, liquid and gas (*e.g.*, Hurai *et al.*, 2001, 2002; Jarmołowicz-Szulc, Dudok, 2005; Jarmołowicz-Szulc *et al.*, 2012). Homogeneous inclusions are those solid ones which contain different types of bitumen; liquid ones, which occur mostly in the outer growth parts of crystals and contain either one or two immiscible fluids; gas inclusions contain methane with admixture of higher hydrocarbons. Heterogenic inclusions display the following compositions: gas + liquid hydrocarbon + brine; gas + liquid hydrocarbon + brine + solid bitumen; liquid hydrocarbons + solid bitumen. The hydrocarbon fluid inclusions either display an evident fluorescence (petroleum fluid) or no luminescence at all. Solid bitumen occasionally observed in the quartz in such amounts that it causes macroscopically almost black color of the host mineral do not exhibit any special fluorescence (*e.g.*, Fig. 4E, F). Such black, usually long prismatic, crystals were observed in the Mszana Dolna region, in very rare cases in the Bieszczady area and, in some places in Ukraine.

Small, primary aqueous inclusions and secondary hydrocarbon inclusions (in fissures cutting cleavage planes) are observed in calcite. These last ones display fluorescence in blue-white colors, which proves a presence of higher hydrocarbons, namely petroleum.

An occurrence of the carbonate-quartz mineralization with bitumen that fills fissures and cavers, and nests and occurs in form of veinlets, brushes and nests is the characteristic feature of the mélange zones (Jankowski, Jarmołowicz--Szulc, 2004; 2009; Jarmołowicz-Szulc *et al.*, 2005, 2010, 2012; Jarmołowicz-Szulc, Jankowski, 2008, 2010, 2011). The mutual relationship of the components might be distinguished both in the macroscopic and microscopic scales. Small veinlets prove the occurrence of the earlier crystalline quartz prior to the white calcite (calcite II). The organic matter (bitumen) described previously as *e.g.*, asphaltite (Karwowski, Dorda, 1986), or anthraxolite (Dudok *et al.*, 2002), or pyrobitumen (Marynowski, in Jarmołowicz-Szulc *et al.*, 2012) fills in general the central part of the fissures. The quartz crystallizes as fine crystals on the fissure walls and distinct authigenic, transparent crystals within the bitumen and/or carbonates. Detailed characteristics of the selected mélange zones has been already continuously presented by Jarmołowicz-Szulc (2008), Leśniak *et al.*, (2009), Jarmołowicz-Szulc, Jankowski (2011) and (partly) – Jarmołowicz-Szulc *et al.* (2012) being followed by Matyasik *et al.* (2015).

Based on the fluorescence distribution pattern, it can be seen that the distinct mélange zones as in Jabłonki locality, are really special places. That is the area where, apart from the gas, some oil is present in the system. Please, refer your microscopic/petrographic pictures.

The pyrolitic Rock-Eval analysis of twelve samples from the Jabłonki region (Jarmołowicz-Szulc, Jankowski, 2010) showed a variable total organic carbon (TOC) in the interval from 0.77 to 35.80% TOC, whereas the average values of the studied samples lie between 0.77 and 4.44%. Samples display high degree of thermal evolution, which corresponds to the end of generation processes (the end of the oil window). In the composition of the extractable organic matter, the saturated hydrocarbons constitute a majority of 61.3%, that points to adsorption of the generated or migrating oil (*op. cit.*). These data are compatible to the fluorescence conclusions.

Microthermometric data reported in earlier published papers (Jankowski, Jarmołowicz-Szulc, 2004; Jarmołowicz-Szulc *et al.*, 2005, 2012) also confirm the fluorescence results. They point to the following assemblages of inclusions: primary liquid-gas inclusions filled with brine of low salinity and homogenization temperatures from +150 to +184°C; primary single phase inclusions filled with methane and homogenization temperatures from –75 to –90°C; decrepitation of these inclusions occurs between +85 and +95°C; primary liquid-gas and gas-liquid hydrocarbon inclusions showing white-blue fluorescence; secondary liquid-gas brine inclusions.

On the base of earlier mineralogical studies and fluid inclusion analysis in the tectonic mélange zones, it may be finally concluded that the areas studied, in that – the mélange in the Jabłonki region – are the hydrocarbon migration paths. Hydrocarbons were generated from the terrigenic organic matter, which corresponds to the menilite schists, studied many times in the Silesian unit (Jarmołowicz-Szulc *et al.*, 2005). Jarmołowicz-Szulc (2015) and Jankowski (2015) concerned all the mélange zones as the migration paths for mineralization fluids as well as the mineral waters.

CONCLUSIONS

The mineralogical and petrologic studies on fluid and solid inclusion fluorescence conducted for many years in the Carpathian area encourage to draw general conclusions on fluid circulation and formation of host minerals and bitumen.

Strong vein formation following tectonic events and the accompanying mineralization of the mélange zones is the Carpathian phenomenon, being best observed in the surface outcrops in the Bieszczady region. The organic matter occurs in the association with quartz and calcite as vein and cavern filling as well as the material dispersed in the rocks.

Different types of fluids must have migrated through the sedimentary rocks of the flysch Carpathians, evidently using tectonic zone paths what at results in the vein mineralization and solid bitumen occurrence. The solid bitumen differ in their degree of thermal alteration that points to their inhomogeneous genesis. In their turn, the Carpathian oils are relatively uniform in their character, displaying only minor variability (see: Jarmołowicz-Szulc *et al.*, 2012).

Being proved by UV luminescence and well reflected both in inclusions in the quartz and bitumen accumulations, a brine and hydrocarbon migration occurred. The specific traps in the host rocks must have contained accumulations of early oils, that were further influenced by migrating brines. Hydrocarbon and brine migration occurred repeatedly through the tectonic discontinuities, in that the evident mélange zones.

Heavy liquid hydrocarbons dominated at the final stage of the mineral formation (minimum temperatures and minimum pressures). In some regions (the Stavne and Rabe villages) migration of hydrocarbon and the carbon dioxide-bearing fluids occurred (possibly due to a local oxidation processes). As it was discussed homogenization temperatures of the heavy hydrocarbon inclusions slightly decrease from the Ukrainian segment (*e.g.*, Stavne) toward NW in the Polish sector (*e.g.*, Rabe). The relative maturity of oils in quartz that may be also estimated using the UV fluorescence method decreases from Wetlina (the mélange zone in the Silesian unit) to Mszana Dolna (the tectonic window of the Dukla unit within the Magura nappe) in NW and to Stavne (the Dukla unit, the Stavne subunit) in SE.

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STRESZCZENIE

Badania fluorescencji podjęto w skałach, minerałach i bituminach w Karpatach Zachodnich w rejonie rozciągającym się od Mszany Górnej po Bieszczady i dalej – poza granicami Polski – na Ukrainie i Słowacji (fig. 1–3). Procedury analityczne obejmowały preparatykę, prace wstępne: ocenę mikroskopową materiału (organika i minerały) oraz wybór próbek do badań wrostków i fluorescencji inkluzji, oraz zasadnicze badania mikroskopowe wzbudzenia luminescencji fluidów w świetle lampy kwarcowej (zakres UV). Po tych analizach wykonywano oznaczenia mikrotermometryczne, których celem jest określenie temperatur charakterystycznych dla poszczególnych minerałów i estymacja składu wypełnień inkluzji. Analizy przeprowadzano w obustronnie polerowanych płytkach, przygotowanych na zimno. Badano

dwa minerały – kwarc i kalcyt – zarówno w preparatach, jak i luźnych kryształach naturalnych (kwarc – tzw. diamenty marmaroskie).Wszystkie badania przeprowadzono głównie w Państwowym Instytucie Geologicznym – Państwowym Instytucie Badawczym z zastosowaniem nowych metod i nowoczesnego sprzętu analitycznego. W wyniku przeprowadzonych badań inkluzji fluidalnych, stanowiących jedno z najnowszych narzędzi analitycznych w ostatnim dwudziestoleciu, uzyskano charakterystykę fluidów zamkniętych w postaci inkluzji w minerałach. Badania fluorescencji wykazały zróżnicowanie wypełnień węglowodorowych (fig. 4–8, tab. 1). W dwufazowych inkluzjach stwierdzono obecność fluidów o charakterze solankowym („wodnych") i ciężkich węglowodorów. W inkluzjach jednofazowych zaobserwowano obecność lekkich węglowodorów, potwierdzoną mikrotermometrycznie (metan, temperatury homogenizacji od ok. –90 do ok. –110°C. Badaniom inkluzji fluidalnych towarzyszyły analizy wrostków organicznych (np. badania czarnych agregatów występujących w odkrywkach w formie soczewek). W wyniku badań rentgenowskich w czarnych agregatach w melanżu tektonicznym okolic Jabłonek (Bieszczady, Polska) stwierdzono obecność następujących minerałów: kwarc, dolomit, kalcyt, minerały ilaste, mieszanina gipsu z anhydrytem, ślady pirytu i syderytu oraz skalenie. Wrostki organiczne – o dużej obfitości – charakterystyczne są dla kryształów kwarcu w okolicy Mszany Dolnej (Polska) i Pawłówki (Ukraina). Ich ilość powoduje ciemne makroskopowo zabarwienie kryształów.

Podsumowując, ogólny rozkład fluorescencji wrostków w minerałach i rozprzestrzenienie inkluzji niewykazujących wzbudzenia sugerują obecność lekkich węglowodorów (metan) w części zachodniej obszaru i na południu oraz wyraźne wzbogacanie w wyższe węglowodory (ropa naftowa) w kierunku wschodnim.