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ON THE STAGES OF ANALYTICAL STUDIES IN THE CARPATHIANS AT BORDERLAND OF POLAND AND UKRAINE IN LAST TWENTY YEARS

ETAPY BADAŃ ANALITYCZNYCH W KARPATACH NA POGRANICZU POLSKO-UKRAIŃSKIM W OSTATNIM DWUDZIESTOLECIU

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Abstract. The area of the Outer Carpathians has been under a permanent research conducted in different aspects. Last twenty years of the analytical studies have been the most effective. Different types of analyses have been performed, the methology of which is presented in the paper, as well as exemplary results in different fields – geochemistry, mineralogy and petrology.

Key words: analytical methods, Carpathians, Poland, Ukraine.

Abstrakt. Obszar Karpat zewnętrznych od lat jest obiektem badań prowadzonych pod różnym kątem. Ostatnie dwudziestolecie jest najbardziej pod tym względem efektywne. Przeprowadzono analizy różnego typu, których metodykę zaprezentowano w pracy, jak też przykładowe wyniki analiz geochemicznych, mineralogicznych i petrologicznych.

Słowa kluczowe: metody badań analitycznych, Karpaty, Polska, Ukraina.

INTRODUCTION

For many years the area of the Outer Carpathians has been under a permanent research in different aspects. That has concerned a complex geological structure and rocks of different character and genesis as well as all sorts of minerals present. The mineralogical, petrological and geochemical analyses have been conducted mostly in reference to search for hydrocarbons.

The geological structure of the Carpathians as a whole and a Polish-Ukrainian borderland as a part, were widely discussed in such papers as e.g. Golonka and Picha (eds, 2006), Janočko *et al*. (2006), Oszczypko *et al*. (2006) and Ślączka *et al.* (2006). Newest carthographic elaborations are those at a scale of 1:200 000 showing the borderland of Poland and Ukraine (Jankowski *et al.*, 2004), of Ukraine and Romania (Jankowski *et al*., 2007), of Poland and Slovakia (Bezák *et al.*, 2008, 2011). Based on these geological and carthographical foundations, detailed petrographical, mineralogical and geochemical research was conducted (e.g. Naumko *et al*., 1999, 2009; Hurai *et al.*, 2002; Jarmołowicz-Szulc, 2009a-c; Jarmołowicz-Szulc *et al*., 2010; Jarmołowicz-Szulc and Jankowski, 2011; Jarmołowicz-Szulc *et al.*, 2011a).

The bibliography concerning whole Carpathians is very rich and numerous covering a time interval of about a century. That is why in the present paper, it will be limited to newest papers – mostly from the period of last twenty years. These papers contain elements from earlier studies, so such a limitation is significant and easy to understand.

The Oligocene–Miocene Menilite formation has been concerned a main maturity rock for oils in the depos-

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its of the Outer Carpathians and shows TOC over 20%. Last papers dealing with this formation are as follows: Kotlarczyk and Leśniak (1990), Bessereau *et al*. (1996), Malata (1996) and Kotarba and Koltun (2006). Hydrocarbon potential of this formation was characterized among others by: Koltun (1992), Kruge *et al*. (1996), Koltun *et al*. (1998) and Köster *et al*. (1998). Correlation between a source rock and oils based on geochemical analyses, in that for Polish Outer Carpathians, was studied by ten Haven *et al*. (1993), Curtis *et al.* (2004), Dziadzio and Matyasik (2006).

Papers dealing with the Ukrainian part of the Carpathians and the Menilite Formation of the marginal parts of the Polish and Ukrainian Carpathians were presented by Kotarba *et al*. (2005, 2007) and Kosakowski *et al*. (2008).

The aim of the present paper is to show analytical steps applied in the studies in the Western and Eastern Carpathians, mostly at the borderland of Poland and Ukraine.

METHODS OF APPLIED STUDIES

A hitherto conducted research and analytical procedures in the area of the Polish – Ukrainian Carpathians comprised many stages. They were conducted in the fields of tectonics and carthography, mineralogy, petrology and geochemistry. First of all, that concerns field works and sampling (e.g. Dudok and Jarmołowicz-Szulc, 2000; Jankowski *et al*., 2004; Jankowski *et al*., 2007). Further – preparation and macroscopic and microscopic evaluation of the material from the point of view of minerals, organic matter and inclusions; detailed microscopic determinations and auxiliary studies (e.g. Jarmołowicz-Szulc and Dudok, 2005). The microscopic analyses in detail correspond to the following steps (as in short is shown by Jankowski and Jarmołowicz-Szulc, 2009): standard analysis of thin sections and mineral pieces, cathodoluminescence studies, fluorescence studies, microthermometry.

Fluid inclusion analysis was performed on double-sided polished thin sections prepared based on the cold techniques (Roedder, 1984)..

General description and standard petrological studies comprised observations in the polarization microscope (Nikon Optiphot). The character of the rocks in tectonic units was determined in samples further analysed.

The cathodoluminescence analysis was conducted by use of CCL 8200 mk 3 (Cambridge Image Technology Ltd.) mounted on Nikon Optiphot microscope. The analysis was photographically registered. The cathodoluminescence studies were the auxiliary analyses (Zirkennagel, 1978). Generally, these observations have been limited in the fluid inclusion studies (Jarmołowicz-Szulc, 2001). From one side – the image of the mineral in cathodoluminescence gives an important piece of information on the position and relation of the mineral in the rock. From that point of view – cathodoluminescence analysis should be performed prior to microthermometry. However, the electron beam falling down the sample and causing luminescence heats the sample, changing the original p-T conditions of the inclusions. That excludes a possibility of cathodolumninescence observations before the microthermometric determinations. As a solution – CL studies were conducted in sections twin to those studied microthermometrically. They were mostly performed in carbonates aiming at their sequence.

Fluorescence studies were conducted under the quartz lamp in uV Nikon device with filters (uV- 365 nm, blue – 480 nm). Samples were analysed in two directions aiming at rock, mineral and fluid inclusion diagnosis. One direction of observations aimed at fluorescence of fluid inclusions being based on the assumption that microfluorescent features of petroleum, strongly dependent on the aromatic character of hydrocarbons, are the evidence of the organic composition (Lumb, 1978; Burruss *et al.,* 1991). The observations of luminescence were conducted consequently in one magnitude (eye-piece 15 x Nikon, objective 10 x Nikon).

The second direction of fluorescence studies was the analysis of rocks and the organic matter in samples studied subsequently under the microscope aiming at determinations of the dispersed organic matter.

Microthermometric studies of fluid inclusions were conducted using Fluid Inc. System mounted on the Leitz Orthoplan microscope. The system was calibrated against international standards (Reynolds, 1993). Fluid inclusions were analyzed in the freezing and heating moods in the range of temperatures from –196 to +250°C. The homogenization of hydrocarbon inclusions was conducted prior to the homogenization of the aqueous inclusions. Homogenization temperatures were measured prior to freezing to avoid a potential change in the inclusion volume (Roedder, 1984). Characteristic values were measured in the heating after freezing in that *freezing point depression* (Bodnar, 1990). The analytical results were calculated using computer programs (earlier: FLINCOR – Brown, 1989, recently FLUIDS – Bakker, 2003) for AQFI and methane systems. That resulted in fluid density, character and composition (Pagel *et al*., 1986). Where possible, a method of crossing isochors was used to estimate trapping temperature and pressure of HCFI and AQFI pairs (Jarmołowicz-Szulc *et al.*, 2011b).

Paralelly to microscopic analyses, isotopic studies of light isotopes (oxygen, carbon) were performed. Rules for the calculations are those of O'Neil (1979).

Analysis of content of saturated hydrocarbons was performed aiming at composition of the organic matter in the mélange zones and at comparison of those described in the other formations. These determinations were done both in the Institute of Oil and Gas in Cracow and in PGI-NRI in Warsaw. Determinations were performed by use of GS/MSD Hewlett Packard. Contents of n-alkanes and isoprenoids were

determined using the external detector and the biomarker qualitative analysis performed. Bitumens from the lenses in the mélange zones and samples of rocks and minerals were analysed (Rock-Eval; Espitalié *et al.*, 1985) according to the well-known procedures (e.g. Dudok *et al*., 2002; Kotarba *et al*., 2005; Dziadzio and Matyasik, 2006; Kosakowski *et al*., 2008; Matyasik *et al*., 2010).

The pyrolitic analysis was conducted by use of Vinci Technologies Rock-Eval 6 in the Institute of Oil and Gas in Cracow. Extracts were treated with n-pentane aiming at removal of the asphaltenes. Fractions dissolving in n-hexane were later fractionated in the chromatographic column prior to GC-MS analysis. The quadrupole Fisons spectrometre equipped with the Quadrex capillary with helium as a gas medium was used. Analyses occurred in the whole scan system, from50 do 550 amu (e.g. Matyasik *et al*., 2010).

XRD determinations were performed by powder metod 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, in the reflected white and blue with use of polarization mikroscope Axioskop (Zeiss), equipped with an electronically steered microfotometer MPM 200. The reflectivity measurements of the organic master were performer in immersion (reflectivity index n = 1.515 at room conditions), in the monochromatic light of a wave length of 546 nm, against a glass standard of reflectance of 1.00%. The diameter of the measurement blend was equal to 0.16 mm.

SEM were performed by use of two electron scanning microscopes: JSM – 35, JEOL and 1430, LEO, combined with EDS ISIS. Uncovered thin sections were analyzed being covered with a coal film.

EXAMPLES OF ANALYTICAL RESULTS

Multifold studies that have been conducted in the period of last two decades have led to numerous petrological, mineralogical and geochemical data. The examples of these data will be shown in the present paper aiming at detailed presentation of the analytical stages (Fig. 1A–D).

PETROLOGICAL RESULTS

It is clear due to the analysis of rock samples, that sandstones and claystones are major types of the rocks. The sandstones are quartz arenites with structures changing from random to directional (Fig. 1E). Detrital components of sandstones are: mono- and polycrystalline quartz, feldspars, lithoclasts (clasts od sedimentary, magmatic and metamorphic rocks). Cements are constituted of: carbonates (occasionally coarse, or nest forms), clay minerals, fine crystalline silica.

The claystones – siltstones and mudstones are mostly built of illite, calcite, quartz, iron oxides and hydroxides. The rock structure is more evident because of linear arrangement of oxides, hydroxides and, occasionally, mica flakes. Organic matter is either dispersed or linearly arranged (Fig. 1F).

MINERALOGICAL RESULTS

As it results from the macroscopic observations (Dudok, 1991; Świerczewska *et al.,* 2000; Jankowski and Jarmołowicz-Szulc, 2009) and microscopic studies (Jarmołowicz-Szulc and Dudok, 2005; Jarmołowicz-Szulc *et al*., 2010), the Carpathian flysch has been cut by different fractures and fissures, filled with minerals and bitumens (Fig. 2). These minerals are mostly quartz and carbonates (e.g. calcite, Fig. 2A). There are at least two generations of calcite in veins in the units of Polish and Ukrainian Carpathians (Dudok and Jarmołowicz-Szulc, 2000; Świerczewska *et al*., 2000; Jarmołowicz-Szulc and Dudok, 2005) and in the tectonic mélange zones (Jarmołowicz-Szulc and Jankowski, 2008; Jankowski and Jarmołowicz-Szulc, 2009; Jarmołowicz-Szulc *et al*., 2010).

In their composition they comprise: from 47 to 49% CaO, 0.1–0.2% TiO_2 and from 0.01 to 0.5% Mn in the Dukla and Silesian units (Jarmołowicz-Szulc, 2001).

Despite the position in the Carpathian units, the calcite displays similar isotopic composition that lies in the interval from 19.5 to 23.5‰ (SMOW) (Table 1). That has been evidently proved by Jarmołowicz-Szulc (2009a, b) and in the wider context by Jarmołowicz-Szulc *et al.* (2011b).

Carbonates present in the rocks/veins correspond to calcite, Mn-calcite and dolomite, Mn-dolomite, ankerite (Jarmołowicz-Szulc, 2009a, c). Minerals as: quartz, dolomite, calcite, clay minerals, feldspars, gypsum with admixture of anhydrite, some pyrite and siderite are present in black organic aggregates in the veins.

Quartz in steep fissures in sandstones and claystones (Fig. 2B), less frequently in clay shales (Lazrienko *et al.*, 1963; Dudok *et al*., 1997) occurs in the association with calcite and black bitumens (Fig. 2C). The youngest quartz generation, known as the "Marmarosh diamonds", displays a specific crystal habit and composition. The $\delta^{18}O$ isotopic content of this quartz is in average +22.3‰ (SMOW) and points to the isotopic content of paleofluid in the range between 5 and 10‰ (Jarmołowicz-Szulc, 2001).

Both petrological and mineralogical studies have proved an occurrence of different fluid inclusions in the calcite and the quartz. The spectrum of fluids trapped in inclusions is wide. It changes from non-fluorescing aqueous fluids (brines) through fluorescing hydrocarbons to non fluorescing/dull blue methane and carbon dioxide dioxide (Fig. 2D–F).

GEOCHEMICAL RESULTS FOR BITUMENS

Geochemical studies (Rock-Eval analyses, content and composition of bitumens, stable isotopes of carbon, elemen-

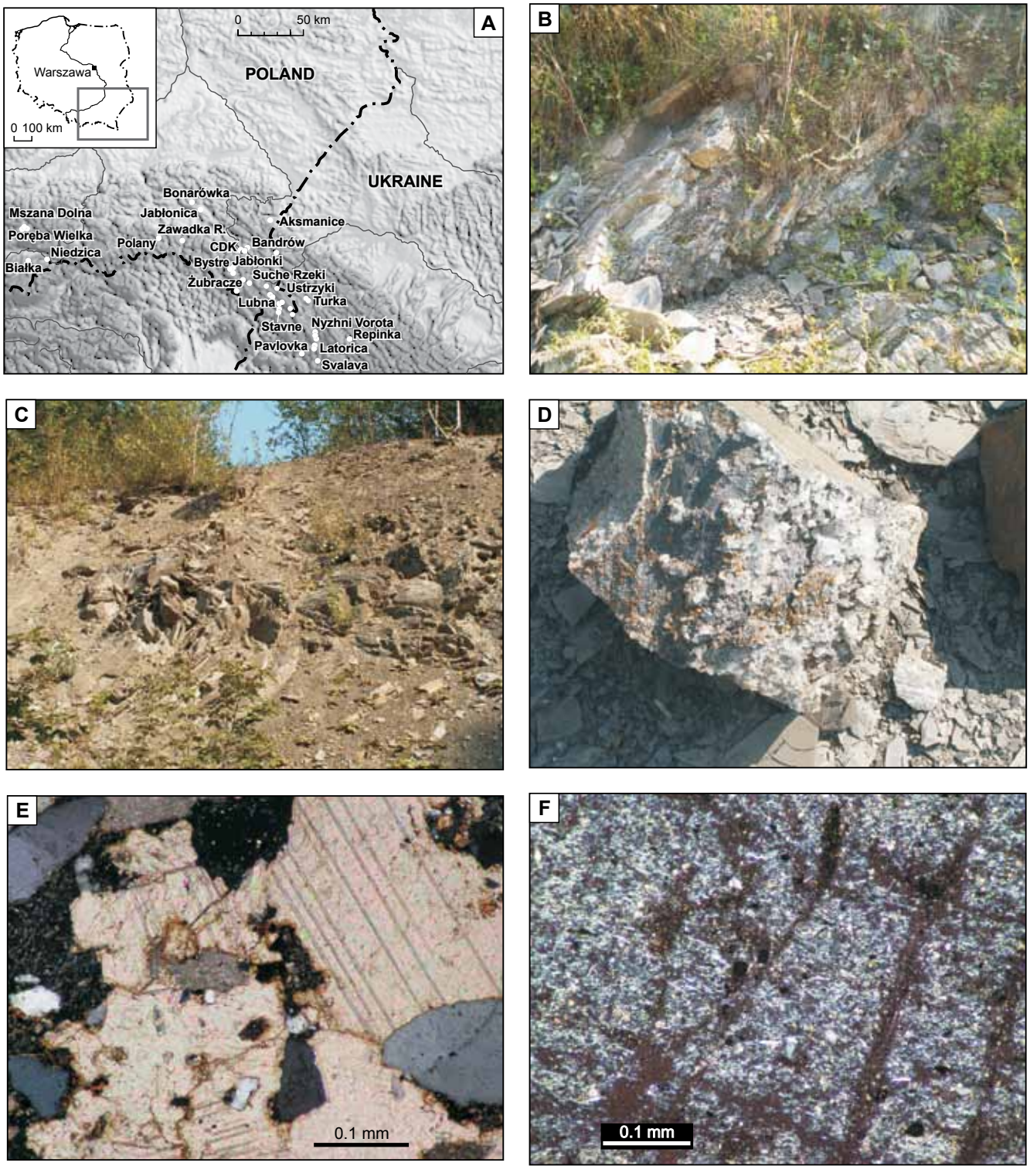

Fig. 1. From sampling to microscopic studies of rocks

A – localization of samples at the Polish-Ukrainian borderland in the Carpathians (compiled from Jarmołowicz-Szulc, Jankowski, 2011 and Jarmołowicz-Szulc *et al*., 2011a); **B** – sampling in the Ukrainian field area in the Stavne region, Ukraine; **C** – zone of occurrence of the Marmarosh diamonds, Latoritsa, Ukraine; **D** – calcite mineralization in macro scale, Svalava, Ukraine; **E** – quartz arenites of random structure, Zawadka Rymanowska, Poland, photomicrograph, transparent light, crossed nicols; F – claystones, Bonarówka, Poland, photomicrograph, transparent light, crossed nicols

Od opróbowania do badań mikroskopowych skał

A – miejsca opróbowania na pograniczu polsko-ukraińskim w Karpatach (kompilacja na podstawie Jarmołowicz-Szulc, Jankowski, 2011 oraz Jarmołowicz-Szulc i in., 2011a); **B** – odsłonięcie w regionie Stavne, Ukraina; C – strefa występowania diamentów marmaroskich, Latorica, Ukraina; **D** – mineralizacja kalcytowa w skali makroskopowej, Svalava, Ukraina; **E** – arenity kwarcowe o strukturze bezładnej, Zawadka Rymanowska, Polska, mikrofotografia, światło przechodzące, nikole skrzyżowane; **F** – iłowiec, Bonarówka, Polska, mikrofotografia, światło przechodzące, nikole skrzyżowane

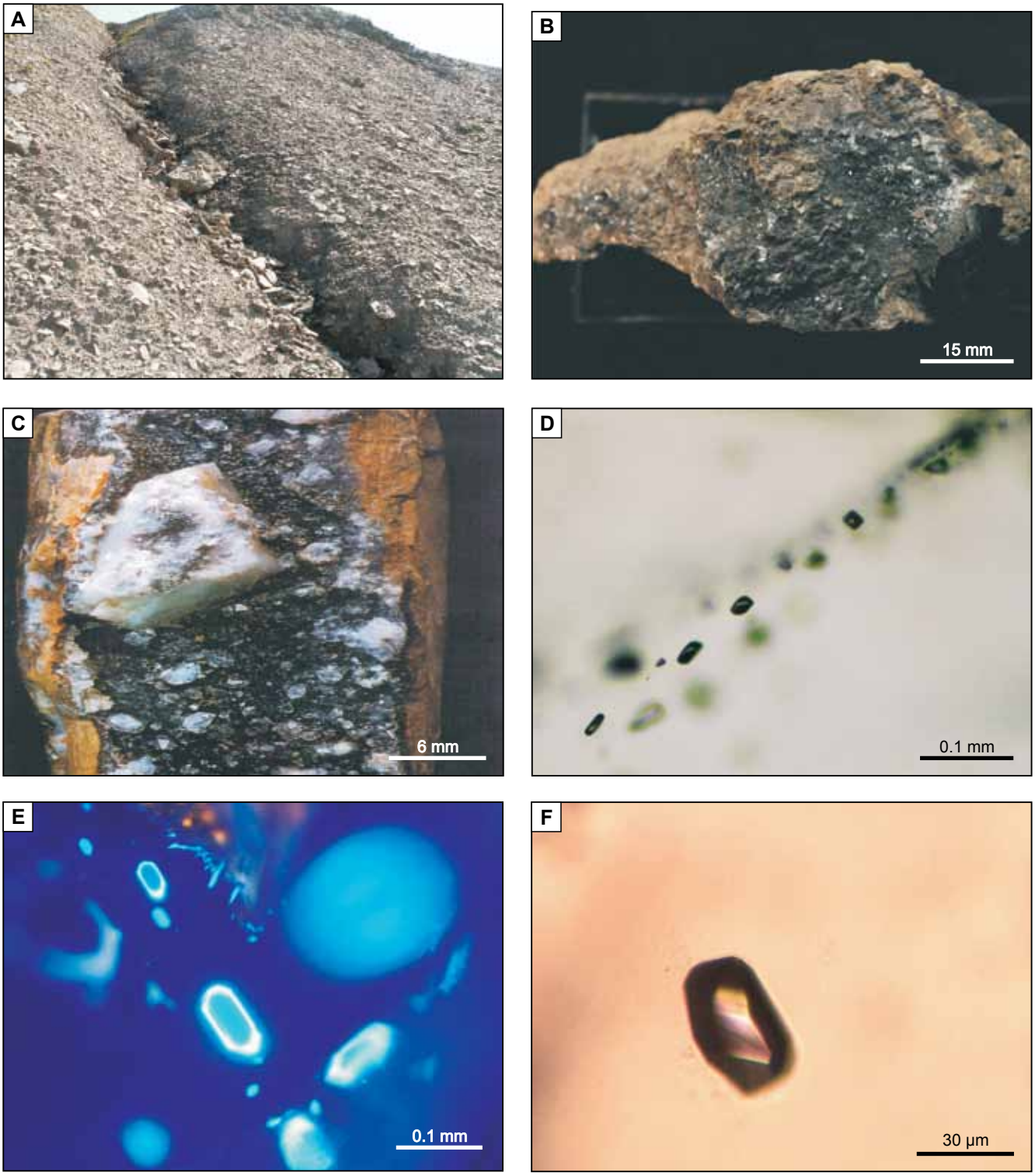

Fig. 2. From sampling to microscopic studies of minerals and bitumens

A – sampling in the field (carbonate veins, Nyzhni Vorota region, Ukraine); **B** – sampling of bitumens (Stavne region, Ukraine; **C** – quartz – calcite – bitumen association; **D** – fluid inclusions in quartz – non- fluorescing brine inclusions; **E** – fluid inclusions in quartz – two phase oil inclusions; fluorescence in ultraviolet light; **F** – fluid inclusions in quartz – non-fluorescing carbon dioxide inlusion

Od opróbowania po badania mikroskopowe minerałów i bituminów

A – opróbowanie w terenie – żyły węglanowe, region Nyzhni Vorota, Ukraina; **B** – opróbowanie bitumów, region Stavne, Ukraina; **C** – asocjacja kwarc – kalcyt – bituminy; **D** – inkluzje fluidalne w kwarcu – nieświecące inkluzje solankowe; **E** – inkluzje fluidalne w kwarcu – dwufazowe inkluzje ropy; fluorescencja w nadfiolecie; **F** – inkluzje fluidalne w kwarcu – nieświecące inkluzje dwutlenku węgla

Table 1

Isotopic determinations in calcite (oxygen and carbon) and in quartz (oxygen)

Oznaczenia izotopowe w kalcycie (tlen i węgiel) oraz w kwarcu (tlen)

Part of Carpathians	δ^{13}CPDB [‰]	δ^{18}OSMOW [‰]	References
			CALCITE
Poland	(–3.0) – (–0.8)	(+20.6) – (+21.9)	Jarmołowicz-Szulc, Dudok, 2005
	(–3.5) – (+1.1)	(+19.7) – (+27.7)	Jarmołowicz-Szulc, 2009b
Ukraine	(–1.4) – (+0.5)	(+20.6) – (+28.6)	
Poland, Ukraine, Slovakia	(–6.25) – (+1.54)	(+17.1) – (+25.2)	CALCITE Jarmołowicz-Szulc *et al.,* 2011a
Poland, Ukraine		(+23.2) – (+27.4)	QUARTZ Jarmołowicz-Szulc, Dudok, 2005; Jarmołowicz-Szulc *et al.,* 2011a

tary analysis of kerogen etc.) have been performed in samples of menilitic shales of the Skole (Skiba) and Boryslav-Pokuttya units (Kotarba *et al.*, 2007; Kosakowski *et al*., 2008), in the filling of fissures in the mélange zones (Jarmołowicz-Szulc, 2009a-c; Jankowski and Jarmołowicz-Szulc, 2009) and in mineral associations and bitumens filling fractures in different Carpathian units as the Dukla, Silesia (Krosno), Boryslav-Pokuttya, Węglówka and Magura units (Dudok *et al.*, 2002; Matyasik *et al.*, 2010; Jarmołowicz-Szulc and Jankowski, 2011). They have resulted in numerous data on content, genetical types and maturity of dispersed organic matter (Table 2).

The deposits are rich in organic carbon; their TOC is from 2–8 wt. %, exceeding locally 10 wt.% (Skole, Boryslav-Pokuttya, Kosakowski *et al*., 2008). Oil productive II kerogen dominates, with a varying component of type III kerogen. The menilitic shales in the Boryslav-Pokuttya unit have higher hydrocarbon potential than those in the Skole (Skiba) unit. The alteration degree is variable. They are immature in the outcrops, while in "oil window" when covered by the Skole thrust, contrary to the rocks of the Skole unit.

According to the isotopic results of determinations of bitumens, values obtained in the Ukrainain and Polish parts of the Carpathians are similar (Table 3).

Table 2

Characteristic features of organic matter in different Carpathian units based on geochemical analyses

Charakterystyka materii organicznej w różnych jednostkach karpackich na podstawie analiz geochemicznych

Unit	Analyzed material	TOC [weight %]	Type of kerogen	Maturity	References
Dukla	Menilitic rocks, oil, gas	0.4–5.4	II & II/III	Immature & mature	Kotarba *et al.*, 2007
Krosno (Silesian)		0.4–20.2 (Pl)	II & II/III	Immature & mature	
Skiba (Skole)		1.0–7.8 (UA) 1.7–12.6 (Pl)	I & II/III II & II/III	Immature & low mature	
Boryslav-Pokuttya		2.5–16.9 (UA) 1.0–12.5	II II & II/III	Immature Immature & low mature	
Boryslav-Pokuttya Skole	Menilitic schists	2–8	II & III	Immature/ mature Immature	Kosakowski *et al.,* 2008
Dukla	Black schists of menilitic type	1.9–2.5	II/III	Mature	Jarmołowicz-Szulc, Jankowski, 2011
Silesian (Krosno)		2.1	III	Mature	
Boryslav-Pokuttya		2.9–3.2	III	Immature	
Skole		3.5–7.0	II	Immature	
Węglówka		1.2	II/ III	Mature	
Magura		1.2–2.0	II	Immature	

Values in tables rounded

Table 3

Isotopic determination for bitumens (carbon) from the Carpathian Silesian (Krosno) and Dukla units

Oznaczenia izotopowe dla bituminów (węgiel) z jednostek śląskiej (Krosno) i dukielskiej Karpat

	δ^{13}CPDB [‰]	References
Poland	(–26.3) – (–24.3)	Jarmołowicz-Szulc, Dudok, 2005
Ukraine	(–26.3) – (–25.9)	Jarmołowicz-Szulc, 2009b

CONCLUSIONS

Mineralogical, petrological and geochemical studies performed for the rocks, minerals and bitumens (organic matter) from different localities in the Western and Eastern Carpathians at the boundary between Poland and Ukraine roughly within last twenty years have shown a diversity of this study material and a complexity of the existing processes. Mineral forming, oil and gas generation and migration processes are to be mentioned here. Their nature was very complicated and they had many different stages. The results of successive multidirectional studies have given a solid basement for a wide interpretation (Kalyuzhnyi and Sachno, 1998; Dudok and Jarmołowicz-Szulc, 2000; Dudok *et al*., 2002; Jarmołowicz-Szulc and Dudok, 2005; Kotarba *et al*., 2007; Jarmołowicz-Szulc and Jankowski, 2008, 2011; Kosakowski *et al*., 2008; Naumko *et al.*, 2009; Jarmołowicz-Szulc *et al.*, 2010, 2011b).

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REFERENCES

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

BESSEREAU G., ROURE F., KOTARBA A., KUŚMIEREK J., STRZETELSKI W., 1996 — Structure and hydrocarbon habitat of the Polish Carpathians. *In*: Peri-tethys Memoir 2: Structure and prospects. Alpine basins and forelands (eds. P.A. Ziegler, F. Horvath). *Mémoires Musée Natural Histoire Naturelle*, **170**: 343–373.

BEZÁK V., BIELY A., ELEČKO M., KONEČNÝ V., MELLO J., POLK M., POFTAJ M., 2011 — A new synthesis of geological structure of Slovakia – the general geological map at 1:200 000 scale. *Geol. Quart*., **55**, 1: 1–8.

BEZÁK V., ELEČKO M., FORDINAL K., IVANIČKA J., KALIČIAK M., KONEČNY V., KOVAČIK M. (Košice), MAGLAY J., MELKO J., NAGY A., POLÁK M., POTFAJ M., BIELY A., BÓNA J., BROŠKA I., BUČEK S., FILO I., GAZDAČKO L., GRECULA P., GROSS P., HVARILA M., HÓK J., HRAŠKO L., JACKO S. ML., JACKO S. ST., JANOČKO I., KOBULSKÝ J., KOHÚT M., KOVAČIK M. (Bratislava), LEXA J., MADARÃS J., NEMÉTH Z., OLŠAVSKÝ M., PLAŠIENKA D., PRISTAŠ J., RAKÚS M., SALAJ J., SIMAN P., ŠIMON L., TE ÁK F., VASS D.,VOZÁR J., VOZÁROVÁ A., ŽEC B., 2008 — General geological map of the Slovak republic 1:200 000. 9 ed. V. Bezák. ŠGUDŠ.

BURRUSS R.C., 1991 — Practical aspects of fluorescence microscopy of petroleum inclusions. *In*: Luminescence microscopy, spectroscopy: qualitative and quantitative applications (eds. C.E. Barker, O. Kopp). *SEPM*, **25**: 1–7.

BODNAR R.J., 1990 — Petroleum migration in the Miocene Monterey Formation, California, USA : constraints from fluid inclusion studies. *Mineral. Mag*., **54**: 295–304.

BROWN P., 1989 — FLINCOR: A microcomputer program for the reduction and investigation of fluid inclusion data. *Am. Min*., **74**: 1390–1393.

CURTIS J.B., KOTARBA M.J., LEWAN M.D., WIĘCŁAW D., 2004 — Oil/source rock correlations in the Polish Flysch Carpathians and Mesozoic basement and organic facies of the Oligocene Menilite Shales: insights from hydrobus pyrolysis experiments. *Organic Geochem*., **35**: 1573–1596.

DUDOK I.V., 1991 — Mineralogical-geochemical pecularities of vein fillings in flysch deposits in the Ukrainian Carpathians (in reference to oil-gas bearing ability). Unpublished thesis, Lvov (in Ukrainian).

DUDOK I.V., JARMOLOWICZ-SZULC K., 2000 — Hydrocarbon inclusions in vein quartz (the"Marmarosh diamonds") from the Krosno and Dukla zones of the Ukrainian Carpathians. *Geol. Quart*. **44**, 4: 415–423.

DUDOK I.V., KALYUZHNYJ V.A., VOZHNIAK D.K., 1997 — The particularities of phase composition and the problems of

systematics of the hydrocarbon fluid inclusions in "Marmarosh diamonds" of the Ukrainian Carpathians. XIV ECROFI: 96–97. Nancy, France.

DUDOK I.V., KOTARBA M., JARMOŁOWICZ-SZULC K., 2002 — Employment of pyrolitic meyhods in geochemical studies of organic matter of the vein formation in the flysch of the Carpathian Mts. *Geologia i Geokhimia Goriuchykh Kopalyn*, **1**: 76–87.

DZIADZIO P., MATYASIK I., 2006 — Reconstruction of petroleum systems based on integrated geochemical and geological investigations :selected examples from the Middle Outer Carpathians in Poland. *In*: The Carpathians and their foreland: Geology and hydrocarbon resources (eds. J. Golonka, F.J. Picha). *Am. Ass. Petrol. Geol. Mem*., **84**: 377–378.

ESPITALIÉ J., DEROO G., MARQUIS F., 1985 — La pyrolyse Rock Eval et ses applications. Revue IFP: 40–41, 563 –579, 755–784.

GOLONKA J., PICHA F.J. (eds.), 2006 — The Carpathians and their foreland: Geology and hydrocarbon resources. *Am. Ass. Petrol. Geology Mem*., **84**.

ten HAVEN H.L., LAFARGUE E., KOTARBA M., 1993 — Oil/oil and oil/source rock correlations in the Carpathian Foredeep and overthrust, south-east Poland. *Organic Geochem*., **20**: 935–959.

HURAI V., KIHLE J., KOTULOVA J., MARKO F., ŚWIERCZEWSKA A., 2002 — Origin of methane in quartz crystals from the Tertiary accretionary wedge and fore-arc basin of the Western Carpathians. *Appl. Geochem*.. **17**: 1259–1271.

JANKOWSKI L., JARMOŁOWICZ-SZULC K., 2009 — Particular tectonic zones (the mélange zones) as potential and significant paths for fluid migration and mineral formation. *Mineral. Rev*., **59**, 2: 42–55.

JANKOWSKI L., KOPCIOWSKI R., RYŁKO W. (eds.), 2007 — Geological map of the Outer Carpathians: borderlands of Ukraine and Romania, 1:200 000. Państw. Inst. Geol., Warszawa.

JANKOWSKI L., KOPCIOWSKI R., RYŁKO W., DANYCH V., TSARNENKO P., JANOČKO J., JACKO S. (eds.), 2004 — Geological map of the Outer Carpathians: borderlands of Poland, Ukraine and Slovakia, 1:200 000. Państw. Inst. Geol., Warszawa.

JANOČKO J., PERESZLÉNYI M., VASS D., BEZÁK V., KOHÚT M., POLÁK M., MELLO J., JACKO Jr. S., JACKO S., 2006 — Geology and hydrocarbon resource of Inner Western Carpathians, Slovakia and Poland. *In*: The Carpathians and their foreland: Geology and hydrocarbon resources (eds. J. Golonka, F.J. Picha). *Am. Ass. . Petrol. Geol. Mem*., **84**: 429–463.

JARMOŁOWICZ-SZULC K., 2001 — Charakterystyka wypełnień żylowych w południowo-wschodniej części polskich Karpat (kalcyt, kwarc, bituminy). *Prz. Geol*., **49**, 2: 785–792.

JARMOŁOWICZ-SZULC K., 2009a — Recent contribution to mineralogical and geochemical studies in the Carpathians. *Mineral. Rev*., **59**, 2: 42–55.

JARMOŁOWICZ-SZULC K., 2009b — Geochemia izotopów pierwiastków lekkich – badania mineralogiczne i geochemiczne wypełnień szczelin w wybranych jednostkach Karpat. *Prz. Geol*., **57**, 4: 301.

JARMOŁOWICZ-SZULC K., 2009c — Mineralogical and geochemical approach to fissure fillings in selected Carpathian units. XX ECROFI Fluid and melt inclusions: using bubbles to decode the Earth. Programme and Abstracts: 119–120. Granada, Spain.

JARMOŁOWICZ-SZULC K., DUDOK I.V., 2005 — 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. *Geol. Quart*., **49**: 291–304.

JARMOŁOWICZ-SZULC K., JANKOWSKI L., 2008 — Problematyka mineralizacji w strefie melanżu w Bieszczadach. I Polski Kongres Geologiczny. Abstrakty: 42. Kraków.

JARMOŁOWICZ-SZULC K., JANKOWSKI L., 2011 — Analiza geochemiczna i korelacje genetyczne bituminów i skał typu czarnych łupków w jednostkach tektonicznych Karpat zewnętrznych w południowo-wschodniej Polsce i na obszarze przyległym. *Biul. Państw. Inst. Geol*., **444**: 73–98.

JARMOŁOWICZ-SZULC K., KARWOWSKI Ł., MARYNOWSKI L., 2011a — Fluid circulation and formation of minerals and bitumens in the sedimentary rocks of the Outer Carpathians – based on studies on the quartz–calcite–organic matter association. *J. Mar. Petrol. Geol*., DOI 10.1016/j.marpetgeo.2011.11.010.

JARMOŁOWICZ-SZULC K., KOZŁOWSKA A., KUBERSKA M., 2011b — Temperature and isotopic relations in the Middle Miocene sandstones from the Ukrainian Carpathian Foredeep Basin: a reconnaissance study. *Ann. Soc. Geol. Pol*., **81**: 79–86.

JARMOŁOWICZ-SZULC K., MATYASIK I., JANKOWSKI L., 2010 — Kontynuacja badań materii organicznej i minerałów w Karpatach – wyniki z obszaru pogranicza polsko-ukraińskiego. *Pr. Nauk. INiG*, **170**: 689–694.

KALYUZHNYI V.A., SACHNO B.E., 1998 — Prospects for prognostics of the useful materials on the base of typomorphic features of the hydrocarbon and carbon dioxide fluid inclusions. *Geochimia. i Geologia Goriuchykh Kopalyn*, **3**: 133–147.

KOLTUN Y.V., 1992 — Organic matter in oligocene Menilite formation rocks of the Ukrainian Carpathians:palaeoenvironment and geochemical evolution. *Org. Geochem*., **18**: 423–430.

KOLTUN Y.V., ESPALITIÉ J., KOTARBA M., ROURE F., ELLOUZ N., KOSAKOWSKI P., 1998 — Petroleum generation in the Ukrainian external Carpathians and the adjacent foreland. *J. Petrol. Geol*., **21**: 265–288.

KOSAKOWSKI P., KOTARBA M.J., WIĘCŁAW D., KOLTUN Y.V., WIĘCŁAW D., KUŚMIEREK J., 2008 — Macierzystość warstw menilitowych i rozwój procesów ropotwórczych w przygranicznej strefie jednostki skolskiej i borysławsko-pokuckiej polskich i ukraińskich Karpat zewnętrznych. I Polski Kongres Geologiczny, Abstrakty, PTG: 56. Kraków.

KOTARBA M., KOLTUN Y.V., 2006 — Origin and habitat of hydrocarbons of the Polish and Ukrainian parts of the Carpathian Province. *In*: The Carpathians and their foreland: Geology and hydrocarbon resources (eds. J. Golonka, F.J. Picha). *Am. Ass. Petrol. Geol. Mem*., **84**: 395–443.

KOTARBA M., WIĘCŁAW D., KOLTUN Y.V., LEWAN M.D., MARYNOWSKI L., DUDOK I.V., 2005 — Organic geochemical study and genetic correlations between source rocks and hydrocarbons from surface seeps and from deep accumulations in the Starunia area, fore-Carpathian region, Ukraine. *In*: Polish and Ukrainian geological studies (2004–2005) at Starunia – the area of discoveries of woolly rhinoceroses (ed. M.J. Kotarba): 125–145. Państw. Inst. Geol., Warszawa – Kraków.

KOTARBA M., WIĘCŁAW D., KOLTUN Y.V., MARYNOWSKI L., KUŚMIEREK J., DUDOK I.V., 2007 — Organic geochemical study and genetic correlation of natural gas, oil and Menilite source rocks in the area between San and Stryi riv-

ers (Polish and Ukrainian Carpathians). *Org. Geochem*., **38**: 1431–1456.

KOTLARCZYK J., LEŚNIAK T., 1990 — Lower part of the Menilite Formation and related Futoma Diatomite Member in the Skole Unit in the Polish Carpathians. AGH, Kraków.

KÖSTER J., KOTARBA M., LAFARGUE E., KOSAKOWSKI P., 1998 — Source rock habitat and hydrocarbon potential of Oligocene Menilite Formation (Flysch Carpathians, southeast Poland): an organic geochemical and isotope approach. *In*: Advances in organic geochemistry (eds. B. Horsfield, M. Radke, R.G. Schaefer, H. Wilkes). *Org. Geochem*., **29**: 543–558.

KRUGE M.A., MASTALERZ M., SOLECKI A., STANKIEWICZ B.A., 1996 — Organic geochemistry and petrology of oil source rocks, Carpathian overthrust region, southeastern Poland – implications for petroleum generation. *Org. Geochem*., **24**: 897–912.

LAZARIENKO E.K., LAZARIENKO E.A., BARYSHNIKOV E.K, MALYGINA O.A., 1963 — Mineralogy of Carpathians. Izdat. Lvov. Univ., Lvov.

LUMB D.M., 1978 — Organic luminescence. *In*: Luminescence spectroscopy (ed. D.M. Lumb): 93–148. Acad. Press, New York.

MALATA T., 1996 — Analysis of standard lithostratigraphic nomenclature and proposal of division of Skole unit in the Polish Flysch Carpathians. *Geol. Quart*., **40**, 4: 543–554.

MATYASIK I., JARMOŁOWICZ-SZULC K., JANKOWSKI L., 2010 — Analiza charakteru materii organicznej w rejonie przygranicznym Karpat Zachodnich i Wschodnich. *Pr. Nauk. INiG*, **17**: 675–680.

NAUMKO I., BONDAR R., SVOREN YO., SAKHNO B., NECHEPURENKO O., 2009 — Pecularities of the gas phase of the metamorphic-metasomatic minerogenesis fluids in the rock-ore complexes of the Marmarosh massif north-western part (from data of fluid inclusion researches). *Mineral. Rev*., **59**, 1: 84–94.

NAUMKO I.M., KOVALYSHYN Z.I., SVOREN J.M., SAKHNO B.E., 1999 — On conditions of forming of vein mineralization in sedimentary oil- and gas-bearing layers of the Carpathian region (obtained by data of fluid inclusion research). *Biul. Państw. Inst. Geol*., **387**: 141–142.

O'NEIL J.R., 1979 — Stable isotope geochemistry of rocks and minerals. *In*: Lectures in isotope geology (eds. E. Jäger, J.C. Hunziker): 235–263. Springer-Verlag, Berlin.

OSZCZYPKO N., KRZYWIEC P., POPPADYUK I., PERYT T., 2006 — Carpathian Foredeep Basin (Poland and Ukraine): Its sedimentary, structural and geodynamic evolution. *In*: The Carpathians and their foreland: Geology and hydrocarbon resources (eds. J. Golonka, F.J. Picha). *Am. Ass. Petrol. Geol. Mem*., **84**: 261–318.

PAGEL M., WALGENWITZ F., DUBESSY J., 1986 — Fluid inclusions in oil and gas bearing sedimentary formations. Therm. Model. Sediment. Basins. 1st IFP Explor. Res. Conf.: 565–583. Paris.

REYNOLDS T.J., 1993 — Temperature calibration standards by SYNFLINC. Fluid Inc. Denver, unpubl. manuscript.

ROEDDER E., 1984 — Fluid inclusions. *Rev. Mineral*., **12**.

ŚLĄCZKA A., KRUGLOV S., GOLONKA J., OSZCZYPKO N., POPADYUK I., 2006 — Geology and hydrocarbon resources of the Outer Carpathians, Poland, Slovakia and Ukraine: general geology. *In*: The Carpathians and their foreland: geology and hydrocarbon resources (eds. J. Golonka, F.J. Picha). *Am. Ass. Petrol. Geol. Mem*., **84**: 221–258.

ŚWIERCZEWSKA A., TOKARSKI A. K., HURAI V., 2000 — Joints and mineral veins during structural evolution: a case study from the Outer Carpathians (Poland). *Geol. Quart*., **44**, 3: 333–339.

ZIRKENNAGEL U., 1978 — Cathodoluminescence of quartz and its silica application of sandstone petrology. *Contrib. Sediment*., **8**.

SUMMARY

For many years the area of the Outer Carpathians has been under a permanent research in different aspects. That has concerned a complex geological structure and rocks of different character and genesis as well as all sorts of minerals present. The mineralogical, petrological and geochemical analyses have been conducted mostly in reference to search on hydrocarbons.

A hitherto conducted research and analytical procedures in the area of the Polish-Ukrainian Carpathians comprised many stages. They were conducted in the fields of tectonics and carthography, mineralogy, petrology and geochemistry. First of all, that concerns field works and sampling (e.g. Dudok and Jarmołowicz-Szulc, 2000; Jankowski *et al*., 2004; Jankowski *et al*., 2007). Further – preparation and macroscopic and microscopic evaluation of the material from the point of view of minerals, organic matter and inclusions; detailed microscopic determinations and auxiliary studies (e.g. Jarmołowicz-Szulc and Dudok, 2005). The microscopic analyses in detail correspond to the following steps (as in short is shown by Jankowski and Jarmołowicz-Szulc, 2009): – standard analysis of thin sections and mineral pieces; – cathodoluminescence studies; – fluorescence studies; – microthermometry.

Multifold studies that have been conducted in the period of last two decades have led to numerous petrological, mineralogical and geochemical data. The examples of these data will be shown in the present paper aiming at detailed presentation of the analytical stages

In conclusion, mineralogical, petrological and geochemical studies performed for the rocks, minerals and bitumens (organic matter) from different localities in the Western and Eastern Carpathians at the boundary between Poland and Ukraine roughly within last twenty years have shown a diversity of this study material and a complexity of the existing processes. Mineral forming, oil and gas generation and migration processes are to be mentioned here. Their nature was very complicated and they had many different stages. The results of successive multidirectional studies have given a solid basement for a wide interpretation.