Annales Societatis Geologorum Poloniae (2011), vol. 81: 487–522.

PETROLEUM SYSTEMS IN THE PALAEOZOIC–MESOZOIC BASEMENT OF THE POLISH AND UKRAINIAN PARTS OF THE CARPATHIAN FOREDEEP

Maciej J. KOTARBA[1], Dariusz WIĘCŁAW[1], Paweł KOSAKOWSKI[1], Magdalena WRÓBEL[1], Jacek MATYSZKIEWICZ[1], Zbigniew BUŁA[2], Marcin KRAJEWSKI[1], Yuriy V. KOLTUN[3] & Jan TARKOWSKI[1]

[1] *AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Al. Mickiewicza 30, 30-059 Kraków, Poland, e-mail: kotarba@agh.edu.pl*
[2] *Polish Geological Institute – National Research Institute, Upper Silesian Branch, Królowej Jadwigi 1, 41-200 Sosnowiec, Poland*
[3] *National Academy of Sciences of Ukraine, Institute of Geology and Geochemistry of Combustible Minerals, 3a Naukova Street, 79060 Lviv, Ukraine*

Kotarba, M. J., Więcław, D., Kosakowski, P., Wróbel, M., Matyszkiewicz, J., Buła, Z., Krajewski, M., Koltun, Y. V. & Tarkowski, J., 2011. Petroleum systems in the Palaeozoic–Mesozoic basement of the Polish and Ukrainian parts of the Carpathian Foredeep. *Annales Societatis Geologorum Poloniae*, 81: 487–522.

Abstract: Comprehensive geochemical analyses (Rock-Eval pyrolysis, stable carbon isotopes, biomarkers and aromatic hydrocarbons and elemental composition of kerogen) provide an explanation of genetic relationships between dispersed organic matter in various source rock horizons of the Palaeozoic–Mesozoic basement in the Carpathian Foredeep and also the liquid (oils and condensates) and gaseous hydrocarbons accumulated in reservoirs in the area between Kraków and Ivano-Frankivs'k. The study region was divided into seven zones around oil, condensate and gas deposits for detailed determination of genetic oil – natural gas – source rock correlation. Based on source, reservoir, seal and overburden rocks, generation, expulsion, migration and accumulation of hydrocarbons and trap formation along with 1-D and 2-D modelling, two separated petroleum systems of the Palaeozoic–Mesozoic strata were established. One petroleum system occurs in the western part of the Małopolska Block, the second one in the eastern part of the Małopolska Block and western part of the Kokhanivka Zone (south-eastern Poland – western Ukraine). In addition, nine generation and expulsion areas were identified. The comparison of the two petroleum systems reveals that the western part of the Małopolska Block has considerably greater prospects for oil and gas exploration than the eastern part of the Małopolska Block and the western part of the Kokhanivka Zone.

Key words: source rock-oil/gas correlations, petroleum system, generation and expulsion areas, Palaeozoic–Mesozoic basement, Carpathian Foredeep, Poland, Ukraine.

Manuscript received 19 May 2011, accepted 13 October 2011

INTRODUCTION

In the Polish part of the Palaeozoic–Mesozoic basement of the Carpathian Foredeep twenty-six oil, condensate and gas deposits have been discovered since 1958. Here, the liquid and gas hydrocarbons accumulated in the Cambrian, Ordovician, Silurian, Middle and Upper Devonian, Lower Carboniferous, Upper Jurassic and Upper Cretaceous reservoirs (Karnkowski, 1999; Myśliwiec *et al.*, 2006). In the Ukrainian part of the Mesozoic basement of the Carpathian Foredeep only ten oil, condensate and gas deposits have been discovered since the World War II, and they all occur in the Upper Jurassic and Cretaceous reservoirs (Glushko, 1968; Vul *et al.*, 1998a, b).

The objective of this study is to define genetic relationships between dispersed organic matter in source rock horizons and the liquid (oils and condensates) and gaseous hydrocarbons accumulated in the Palaeozoic–Mesozoic basement. The results of geochemical analyses of the Palaeozoic (Więcław *et al.*, 2011; Więcław *et al.*, in press, a) and Mesozoic (Kosakowski *et al.*, in press, c, d) source rocks, petrophysical analyses (Kurovets *et al.*, 2011; Kosakowski *et al.*, in press, a), results of 1-D (Kosakowski & Wróbel, 2011; Kosakowski & Wróbel, in press; Kosakowski *et al.*, 2011; Kosakowski *et al.*, in press, b) and 2-D (Kosakowski *et al.*, in press, b; Wróbel *et al.*, in press) modelling of petroleum processes enable determination of the regional petroleum systems and areas were where hydrocarbon generation and expulsion processes proceeded.

GEOLOGICAL SETTING

Precambrian–Palaeozoic basement

In south-eastern Poland and western Ukraine, the Precambrian and/or Palaeozoic (from the Cambrian to Carboniferous) successions occur in the basement of the Carpathian Foredeep and in the marginal part of the Outer Carpathians, beneath discontinuous, locally developed, Permian–Mesozoic sedimentary cover. These deposits are members of regional tectonic units represented by the Małopolska (MB) and the Łysogóry-Radom (LRB) blocks (terranes) in Poland as well as the Leżajsk Massif (LM), the Kokhanivka (KZ) and Rava-Rus'ka (RRZ) zones in Ukraine (Fig. 1). These clearly inter-related units (Buła & Habryn, 2011) are situated within the Trans-European Suture Zone (TESZ) extending along the south-western edge of the East-European Craton (Baltica).

The sedimentary-diastrophic processes, occurring from the Precambrian to the Carboniferous (*e.g.*, Golonka *et al.*, 2006) with varying intensity within each of the above-mentioned tectonic units (that should be treated as separate lithospheric fragments/blocks), resulted in distinct geological structures. The boundaries between the units are marked by regional strike-slip fault zones that were repeatedly reactivated. The Precambrian rocks are siliciclastic flysch deposits, which underwent either low-grade metamorphism or intensive diagenesis and folding due to Cadomian movements recognised in both the MB and LM. Palynological and radiometric studies of Precambrian flysch in the MB and LM indicated their Ediacaran age (Żelaźniewicz *et al.*, 2009). These rocks form characteristic horst structures, of which one forms the prominent, Lower San River Horst Structure and its extension – the Leżajsk Massif in the Ukraine.

The fragmentary successions of the Lower, Middle and Upper Cambrian clastic deposits have been explored by drilling in the area of the Kielce Fold Belt (Fig. 1) and are composed of the SE parts of the MB, LRB, KZ and RRZ (Dziadzio & Jachowicz, 1996; Kowalska *et al.*, 2000; Jaworowski & Sikorska, 2006; Buła & Habryn, 2011; Jachowicz-Zdanowska, 2011). The Cambrian rocks represent claystones, sandy mudstones and quartz sandstones in variable proportions, often heterolithic (Fig. 2). It is impossible to estimate the total thickness of particular tectonic units because of fragmentary knowledge of the sections and variable dip angles of the strata.

The Ordovician and Silurian rocks form one structural complex developed in the MB, LRB, KZ and RRZ (Fig. 3 in Buła & Habryn, 2011). In the MB unit, these can be found within tectonic blocks in the Busko Zdrój-Dąbrowa Tarnowska, Pilzno-Rzeszów and Tarnogród-Lubaczów regions, beneath Palaeozoic, Mesozoic and Tertiary deposits (Fig. 4 in Buła & Habryn, 2011). Within the LRB and the RRZ, Ordovician–Silurian strata form a continuous cover beneath the Mesozoic suite and, locally, also beneath the Tertiary and Devonian successions (Buła & Habryn, 2011). The Ordovician deposits (Fig. 2) show distinct lithofacies variation (Modliński & Szymański, 2005; Buła & Habryn, *eds*, 2008; Buła & Habryn, 2011), particularly in the MB, where a carbonate platform facies grade into a graptolitic shale facies towards the basin centre. Claystones and mudstones with graptolites are the dominant lithologies in the Silurian. There is an increase of sandstone observed in sections corresponding to the Ludlow. Stratigraphic gaps comprise various parts of the Ordovician and Silurian in the MB.

Clear differences can be observed in the development of the Upper Silurian and Lower Devonian strata in the MB and LRB. The Silurian deposition in the MB had probably ceased in the Ludlow and the Pridoli deposits are lacking; the Silurian (or older) strata in this tectonic unit are overlain by Lower Devonian (Emsian) siliciclastics or Middle Devonian carbonates. Locally, younger deposits occur (Fig. 2). A discontinuous pattern of occurrence of the Ordovician and Silurian strata in the MB (Fig. 3 in Buła & Habryn, 2011) indicates that intensive erosion had occurred before the Emsian (Middle Devonian). In the Biłgoraj-Narol region of the LRB, Silurian sections (including Pridoli and Ludlow rocks) of variable thicknesses occur beneath Jurassic strata, and their thicknesses are many times greater than those of older Silurian stages (Modliński *et al.*, 1993). In the Łysogóry region of the Holy Cross Mts., Pridoli marine deposits grade without a sedimentary break into Lochkovian marine deposits (Malec, 2006; Kozłowski, 2008). The Silurian/Devonian transition of the RRZ shows similar features (Kruglov & Tsypko, *eds*, 1988; Drygant, 2000). The thickness of the Ordovician–Silurian complexes exceeds 400 m in the MB and increases from 100 to over 1,400 m towards the NE in the LRB (Buła & Habryn, 2011).

The Devonian and Carboniferous carbonates and siliciclastics of the Variscan structural complex occur in the western part of the MB (Fig. 2). The following lithostratigraphic complexes were distinguished (*e.g.*, Jawor & Baran, 2004; Buła & Habryn, 2011): (i) Lower Devonian siliciclastics (Old Red) represented by mottled quartz sandstones (quartzites), mudstones and claystones, 15 m to 150 m thick; (ii) Middle and Upper Devonian strata composed of various platform type limestones and dolomites, whose thickness varies from 87 m to over 1,000 m; (iii) Carbonate-siliciclastic complex "A" included in the Upper Tournaisian is composed of red and greyish-green sandstones, locally conglomeratic, as well as claystones and mudstones of similar colours interbedded with carbonates. This complex (up to 80 m thick) occurs in the Dębica region; (iv) Carbonate complex "B", also called the "Carboniferous Limestone", included in the Lower Visean and represented by crystalline, cryptocrystalline and micritic limestones and dolomites. Its thickness ranges from 80 m to 590 m; (v) Siliciclastic complex "C" (Culm), which ranges from the ?Middle Visean to the Lower Namurian A (Serpukhovian). It is composed of claystones, grey mudstones and fine- to medium-grained sandstones (Culm facies) of thickness up to 500 m.

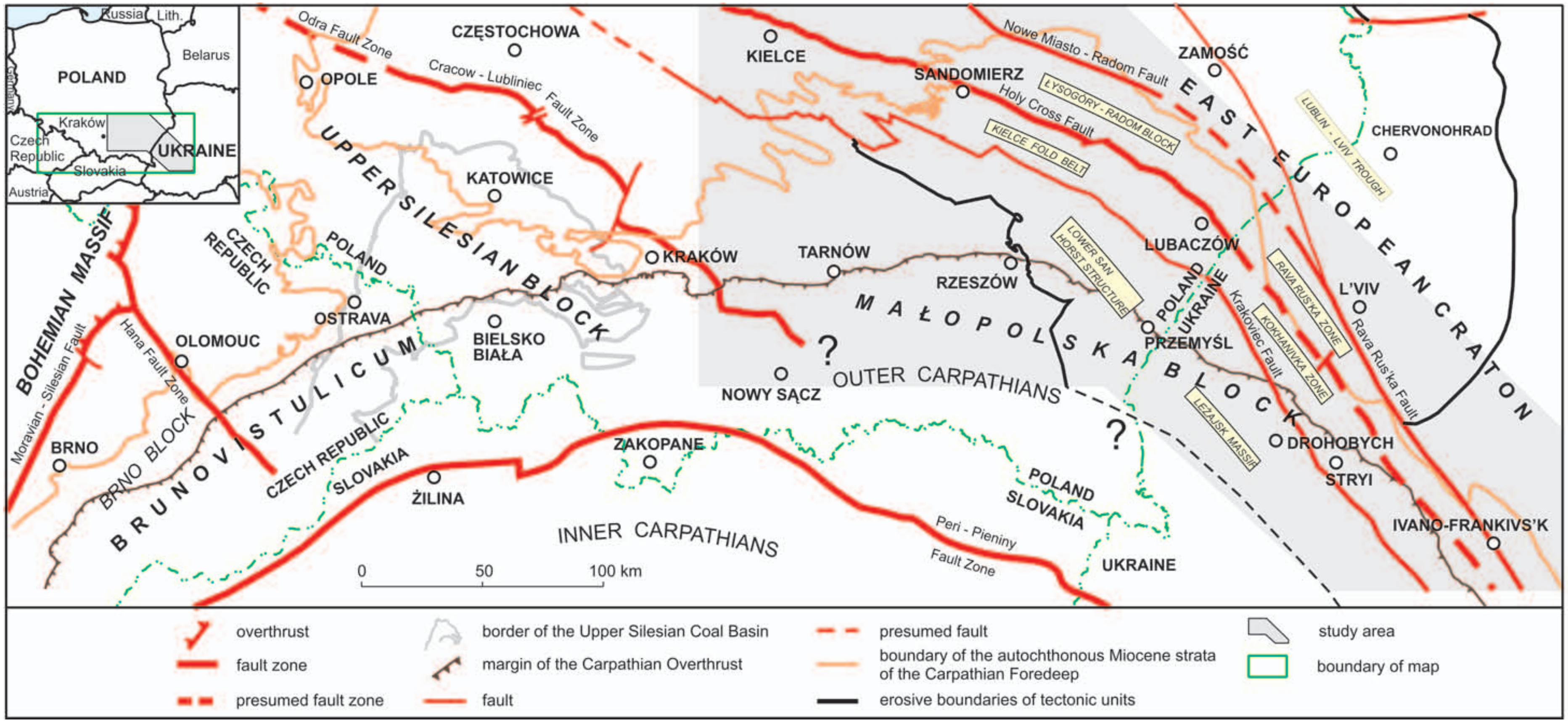

Fig. 1. Tectonic regional subdivision of the south-eastern part of Poland and western Ukraine at the sub-Permian–Mesozoic palaeosurface, after Buła and Habryn (2011)

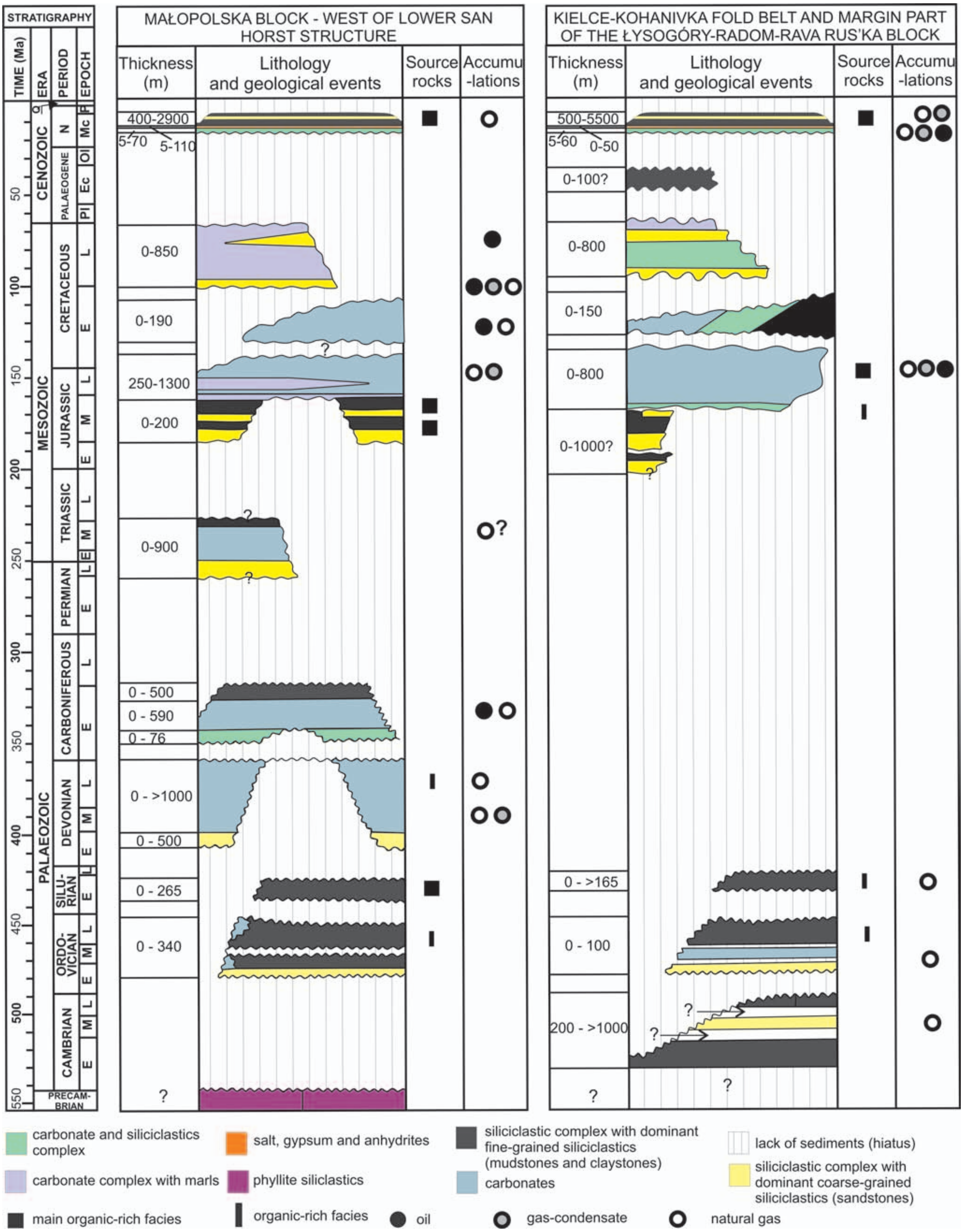

Fig. 2. Generalized lithostratigraphic columns of (left side) the Małopolska Block to the west of the Lower San Horst Structure and (right side) the Kielce-Kokhanivka Fold Belt and marginal part of the Łysogóry-Radom-Rava Rus'ka Block to the northeast of the Lower San Horst Structure (Leżajsk Massif), showing distribution of petroleum accumulations and organic-rich facies. E – Early, M – Middle, L – Late, Pl – Palaeocene, Ec – Eocene, Ol – Oligocene, N – Neogene, P – Pliocene

Mesozoic basement

The studies of the Carpathian Foredeep focused on a belt between Kraków (south-eastern Poland) and Ivano-Frankivs'k (western Ukraine) (Fig. 1). The southern boundary of the belt is marked by the Carpathian margin, and the northern one is determined by the extent of marine, autochthonous Miocene strata. In the Carpathian Foredeep basement the Mesozoic rocks occur in two zones, separated by the Lower San Horst Structure. The western part is situated between Kraków and Rzeszów, and the eastern one covers the area between Lubaczów and Stryi. These two zones differ in their facies development, thicknesses, completeness of successions and the structural pattern of the Mesozoic strata. The tectonic framework of the area between Kraków and Ivano-Frankivs'k is outlined, with certain simplification, by the extensive, Palaeozoic fault zones: Kraków-Lubliniec Fault Zone in the west, and Holy Cross Fault Zone in the east (Horodok Fault Zone in the Ukrainian part). The principal part of the study area belongs to the Palaeozoic Małopolska Block (Buła & Habryn, 2011). The block character of the Palaeozoic basement structure and the tectonic activity of the main transcontinental dislocations have generally influenced the development of Jurassic sedimentation in the basement of the Carpathian Foredeep (Krajewski & Matyszkiewicz, 2004; Jędrzejowska-Tyczkowska *et al.*, 2006; Matyszkiewicz *et al.*, 2006a, b; Krajewski *et al.*, 2011a, b).

In the Polish part of the Carpathian Foredeep basement, in the Kraków and Ropczyce areas, the Mesozoic sediments form three complexes: (i) the Triassic complex, (ii) the Middle Jurassic–Lower Cretaceous complex, and (iii) the Upper Cretaceous complex (Fig. 2). The thickness and extent of these complexes are related to the pre-Jurassic (late Triassic), early Jurassic, and Palaeogene erosion, as well as to the polyphase, mainly late Cretaceous–Palaeocene block tectonics (*e.g.*, Moryc, 2006). The Middle Jurassic–Lower Cretaceous complex appears to be the most important for geological structure of the Mesozoic in the Carpathian Foredeep.

In the central part of the Carpathian Foredeep basement, the Middle Jurassic strata (Bajocian–Bathonian–Callovian) are represented by sandstones, claystones, and siltstones with abundant plant detritus, and with carbonate intercalations in the upper part of the sequence (*e.g.*, Moryc, 2006). At the top of the Middle Jurassic sequence, a 1–2 m thick layer of nodular limestones appears locally. The total thickness of Middle Jurassic strata usually varies from a dozen or so up to several dozens of metres, only rarely exceeding 100 metres. The Middle Jurassic sediments represent a typical transgressive sequence. At the end of the Callovian, the Middle Jurassic sea covered a considerable part of the study area, whereas the emerging land areas formed an archipelago of the so-called "Małopolska islands".

A thick Upper Jurassic–Lower Cretaceous complex rests upon the Middle Jurassic, and locally, Triassic and Palaeozoic strata. The recent preservation of these strata varies depending on the extent of erosion. In the vicinity of Kraków this complex is about 300 m thick, while in the surroundings of Rzeszów (Dębica-Ropczyce area) the thickness reaches even 1,300 m. Geological studies carried out for years led to the distinguishing of Oxfordian, Kimmeridgian, Tithonian, Berriasian, Valanginian and perhaps Hauterivian sediments in the basement of the Carpathian Foredeep, between Kraków and Ropczyce (*e.g.*, Morycowa & Moryc, 1976; Golonka, 1978; Matyszkiewicz, 1997; Olszewska, 1999; Krajewski, 2001; Gutowski *et al.*, 2007; Matyja, 2009). These form three sedimentary successions: (i) Callovian–Oxfordian, (ii) Kimmeridgian, and (iii) Tithonian–Berriasian–Valanginian of various thicknesses and diversified contents of the marly-carbonate facies (Krajewski *et al.*, 2011a). The Oxfordian, Kimmeridgian, and Tithonian sediments correspond to the outer-mid platform facies, in which the pelitic and detrital sediments represent the bedded facies, and the predominant, microbial-sponge and microbial-coral-sponge facies correspond to the reef and biostrom complexes. At the end of the Tithonian, the mid platform facies sediments changed into the internal platform, high energy, ooidal-bioclastic shoals and open/restricted lagoon, mostly peloidal facies, predominating in the Berriasian–Valanginian sediments. The Lower Cretaceous (Berriasian–Valanginian) limestones and marly limestones up to 190 m thick are known from the Dębica region (*cf.* Urbaniec *et al.*, 2010). Sediments of the Middle Jurassic–Lower Cretaceous complex are covered with Upper Cretaceous and/or Tertiary ones.

In the study area between Lubaczów and Ivano-Frankivs'k, the Mesozoic strata are represented by two sedimentary complexes: (i) the ?Lower-Middle Jurassic (?Hettangian–Callovian), and (ii) the Upper Jurassic–Lower Cretaceous (Oxfordian–Valanginian) ones. At present, this area is situated in the narrow Bilche-Volytsia tectonic zone (Lubaczów and Kokhanivka blocks) located at the SW edge of the East-European Platform and the NE margin of the Lower San River Horst Structure. This zone is bordered from the NE by the Horodok Fault (which is the SE continuation of the Holy Cross Fault Zone), and from the SW by the Krakovets Fault (Buła & Habryn, 2011). In the discussed part of the Carpathian Foredeep basement, the Jurassic sediments, deposited directly on the Palaeozoic, mainly Cambrian sequence (Buła & Habryn, 2011), reveal broad facies diversity. Sediments of the Middle Jurassic complex were documented in the SW part of the Ukrainian Carpathian Foredeep and in the Lubaczów area only. The position of Lower Jurassic deposits is disputable and remains stratigraphically undocumented (Dulub *et al.*, 2003; Moryc, 2004; Świdrowska *et al.*, 2008).

The Middle Jurassic strata show variable thicknesses. In the Lubaczów area, in various tectonic blocks the thickness of the Middle Jurassic sediments changes from several dozens up to several hundreds of metres (Moryc, 2004). In the Ukrainian part (the Kokhanivka Zone), the Middle Jurassic complex shows greater thickness and more complete stratigraphic sequence. In some areas the thicknesses of Middle Jurassic deposits reach about 1 km, what is most probably due to deformations and tectonic repetition of sedimentary sequences. The true thickness of these deposits is difficult to estimate; presumably it amounts to hundreds of metres (*cf.* Dulub *et al.*, 1986, 2003; Moryc, 2004; Świdrowska *et al.*, 2008). In the literature, the Middle Jurassic sediments were identified as the Bajocian, Bathonian, and

Callovian (*e.g.* Dulub *et al.*, 2003; Moryc, 2004), however, the boundaries between individual complexes were unclear. Lithology includes dark-grey claystones and siltstones with scarce intercalations of sandstones with coalified plant detritus and with pyrite. In the upper parts of successions, grey dolomites and limestones with fossil remains can be observed, up to several centimetres thick (Dulub *et al.*, 2003).

Both the Upper Jurassic and Lower Cretaceous strata cover a much larger area. In the Ukraine, these rocks occur in the whole area of the Carpathian Foredeep and enter the East-European Platform up to the Nizhniev area. Carbonate, evaporite, and siliciclastic facies were developed there (Gutowski *et al.*, 2005; Zhabina & Anikeyeva, 2007; Anikeyeva & Zhabina, 2002; Olszewska, 2010; Krajewski *et al.*, 2011b). In the Lubaczów area, Jurassic sediments are poorly preserved (Moryc, 2004; Olszewska, 2010). Facies development of the Upper Jurassic (Oxfordian–Tithonian)–Lower Cretaceous (Berriasian–Valanginian) complex in the narrow Bilche-Volytsia Zone demonstrates high diversity of sediments. In the Ukrainian part, deep-marine, radiolarian-saccocoma facies, gravity-flow platform slope facies, shallow-marine, ooidal-bioclastic marginal-platform facies and inner-platform, peri-tidal and peri-shore lacustrine facies were distinguished (Dulub *et al.*, 2003; Zhabina & Anikeyeva, 2007; Krajewski *et al.*, 2011b). These rocks represent mainly the Kimmeridgian and Tithonian. The Lower Cretaceous sediments reveal similar, ooidal-bioclastic facies development in most of the study area. Towards the East-European Platform, deep-water and platform slope facies grade in a narrow zone into the shallow-water, rimmed platform facies of lower thicknesses, laid down directly on the Palaeozoic strata. The platform-margin sediments are dominated by ooidal-bioclastic facies. The extent of Kimmeridgian and Tithonian sediments is closely related to the block structure of the basement, and to the course of the principal tectonic zones (Gutowski *et al.*, 2006; Zhabina & Anikyeva, 2007; Krajewski *et al.*, 2011b). In the Bilche-Volytsia Zone, located upon the Palaeozoic Kokhanivka Zone between the Krakovets and the Horodok faults, basin and platform-slope facies predominate. Platform facies are localized in the Rava Rus'ka Zone, between the Holy Cross and Rava Rus'ka faults (Fig. 1). The oolite-bioclastic barrier, which separates the platform slope from the inner-platform settings, runs along the fault system of the SW boundary of the Holy Cross Fault Zone.

The Lower Cretaceous strata are spread along the complete Ukrainian part of the Carpathian Foredeep. The facies change from carbonate in the northwestern part, adjacent to the Polish border, continuing in the Polish territory, to carbonate-terrigenous in the central part and terrigenous in the southeastern part. Lower Cretaceous sediments in the northwestern and central parts of the basement of the Ukrainian Carpathian Foredeep are of Valanginian–Hauterivian (Dulub, 1965) age and their thickness is from 140 to 150 m, while the Valanginian–Hauterivian sediments in the southeastern part are covered by the Barremian–Aptian (Gavrylyshyn, 1998; Ohorodnik, 2005) black shales and the thickness of the whole sequence is from 0 to 70 m (Shcherba & Radkovets, 2008; Radkovets, 2010).

PETROLEUM OCCURRENCE

The frontal part of the Polish and Ukrainian Carpathians is one of the oldest petroleum-producing regions in the world. The exploitation of oil started in 1853 in the Outer (Flysch) Carpathians and that of natural gas commenced in 1920 in autochthonous Miocene strata of the Carpathian Foredeep (Karnkowski, 1999; Vul *et al.*, 1998a, b). At the end of the 1930s, petroleum exploration started in the Carpathian Foreland. In the years 1945–1955 the Polish petroleum industry had undergone restoration and reorganization. The exploration activity was focused mainly on the Outer (Flysch) Carpathians and partly on the Carpathian Foredeep (Karnkowski, 1999). Intensive petroleum exploration took place in the middle of the 1960s and in the 1970s (Karnkowski, 1999; Myśliwiec *et al.*, 2006). Up to now, twenty-six oil, gas-condensate and gas fields were discovered within the Palaeozoic–Mesozoic basement of the Polish part of the Carpathian Foredeep (from 1948) (Figs 3, 4), and eleven deposits were found within the Mesozoic basement of the Ukrainian part of the Carpathian Foredeep (since 1944) (Fig. 3).

The Polish part of the Palaeozoic–Mesozoic basement of the Carpathian Foredeep

The major petroleum reservoir rocks in the Palaeozoic–Mesozoic basement include (Karnkowski, 1999; Florek *et al.*, 2006; Myśliwiec *et al.*, 2006): (i) Middle and Upper Devonian carbonates (Trzebownisko and Zalesie deposits, and Lachowice deposit beneath the Carpathian Overthrust, located SW from Kraków); (ii) Lower Carboniferous carbonates (Nosówka deposit); (iii) Malm limestones (Tarnów, Lubaczów, Korzeniów, Partynia-Podborze, Dąbrowa Tarnowska and Smęgorzów deposits); (iv) Cenomanian sandstones (Brzezowiec, Grobla, Łąkta and Rylowa deposits); and (v) Upper Cretaceous (Senonian) sandstones locally intercalated with Upper Cretaceous marls, Malm limestones and Cenomanian sandstones (Jastrząbka Stara and Swarzów deposits). Moreover, some hydrocarbon accumulations were discovered also in the Cambrian sandstones (small Cetynia deposit) and in the Ordovician/Silurian strata (small Uszkowce deposit) (Karnkowski, 1999).

The reservoir properties of the Cambrian sandstones in the Kielce Fold Zone are highly variable. Modal value of porosity is between 5 and 10%, and the filtration properties are poor. The filtration properties of the Cambrian sandstones are limited to fractures (Kosakowski *et al.*, in press, a).

The Cetynia gas deposit (Figs 3, 4) is a small accumulation of mixed, massive and layered type. The reservoirs are Cambrian sandstones as well as Lower Badenian Lithotamnion Limestones, Baranów Sandstones and the anhydrite series. The effective thickness of the Cambrian reservoir is about 20 m, porosity ranges up to about 4%, and permeability does not exceed 13 mD (Karnkowski, 1999).

The Uszkowce gas deposit (Figs 3, 4) comprises a few producing horizons, including the Ordovician, Silurian, Upper Jurassic and Middle Badenian strata (Karnkowski, 1999). The Uszkowce deposit was discovered in a narrow anticline cut by an oblique fault zone. Gas accumulated east

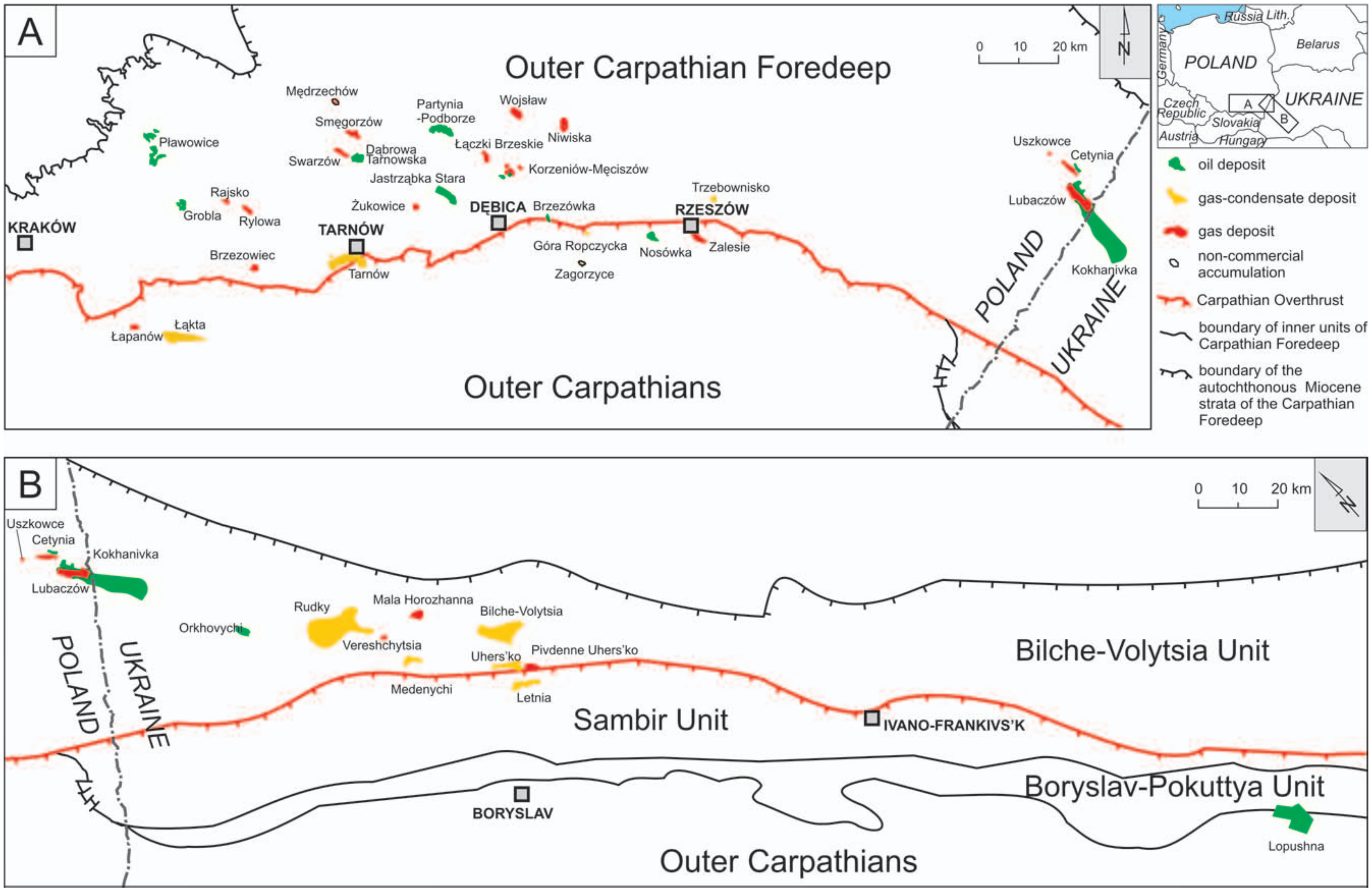

Fig. 3. Sketch map of location of the oil, gas-condensate and gas deposits in **(A)** the Palaeozoic–Mesozoic basement of the Polish, and **(B)** Ukrainian parts of the Carpathian Foredeep. Location of petroleum deposits modified after Vul *et al.* (1998a, b), Karnkowski (1999) and Myśliwiec *et al.* (2006). Lith. – Lithuania

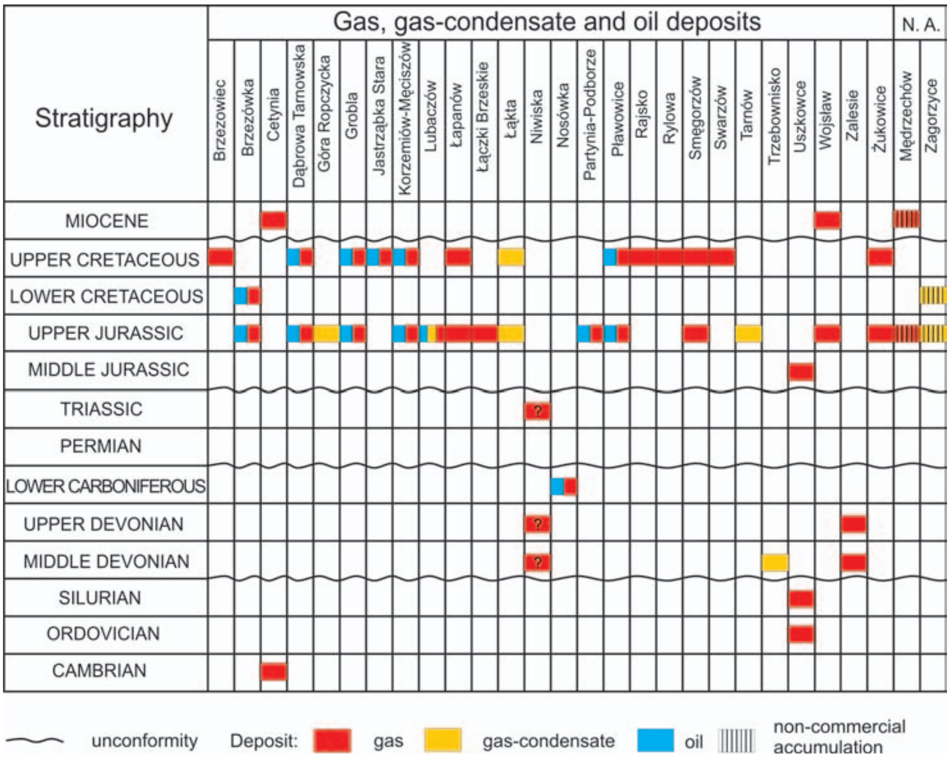

Fig. 4. Distribution of gas, gas-condensate and oil deposits of the lithostratigraphic formations of the Palaeozoic and Mesozoic basement of the Polish Carpathian Foredeep, modified after Karnkowski (1999), Myśliwiec *et al.* (2006) and unpublished data of the Polish Oil & Gas Company. N. A. – non-commercial accumulation

of the fault zone, whereas the producing Miocene strata can be found to the west of it. The eastern part of the gas deposit is of massive type, sealed by the Miocene strata. Gas horizons in the Miocene sequence form layered-type deposits. The massif-type part of the Uszkowce deposit shows variable permeability caused by its lithological diversity (Palaeozoic–Mesozoic reservoirs) (Karnkowski, 1999).

The first discovery of commercial gas accumulation in the Zalesie area, made in 1982, revealed the perspective character of Devonian reservoir rocks in the Rzeszów region (eastern part of the Carpathian Foredeep) (Figs 3, 4). Later, the Trzebownisko and Niwiska gas and condensate deposits were discovered in Devonian carbonates (Figs 3, 4) (Karnkowski, 1999).

The thickness of Devonian rocks increases to the south, beneath the Carpathian Overthrust and decreases to the north, northwest and northeast from the Zalesie field (Myśliwiec *et al.*, 2006). Lithology of the Devonian reservoir includes limestones and dolomites interbedded with fine-grained quartz sandstones and conglomerates (Myśliwiec *et al.*, 2006). Petrophysical analyses of Devonian carbonates showed that carbonates porosity in the entire Rzeszów region varies from 1.18 to 11.56%. Only in the Trzebownisko-3 well the Devonian rocks did demonstrate higher porosity, up to 16.7% (Kosakowski *et al.*, in press, a). These parameters indicated favourable filtration properties. The permeability was measured in a single sample (55 mD) only. According to Myśliwiec *et al.* (2006), the Devonian deposits are very promising reservoir rocks and in the Rzeszów area these strata were located on the most probable migration path.

The discovery of the Nosówka oil field (Figs 3, 4) in the Visean carbonates pointed to the Lower Carboniferous limestones and dolomites as potentially producing Palaeozoic reservoir rocks. The Lower Carboniferous deposits are well-developed only westward and southward from Rzeszów (Myśliwiec *et al.*, 2006). The roof surface of the Lower Carboniferous complex is erosional and is sealed by the Miocene shale-mudstone-sandstone complex. The Lower Carboniferous limestones are interbedded with sets of thin, mudstone-shale layers (Karnkowski, 1999). Only a small population of measured samples did show favourable reservoir properties. The intercrystalline porosity changes from 0 to 5%, whereas microfracture and cavernous porosities reach 17%. Permeability of the reservoir rocks does not exceed 30 mD (Karnkowski, 1999).

The Mesozoic reservoir rocks are present in the Upper Jurassic and Upper Cretaceous successions, and are the most important reservoirs containing the largest oil accumulations within the Carpathian Foredeep basement.

Hydrocarbon accumulations discovered in the Mesozoic basement of the Carpathian Foredeep between Kraków and Rzeszów (Fig. 2) are hosted mainly in structural and stratigraphic traps formed directly beneath the Miocene unconformity. The combined, structural-stratigraphic traps are located in the massive, erosional or tectonic blocks of the basement and are sealed by clayey Miocene strata or by marly Senonian–Turonian sediments, sometimes also by fault planes. The stratigraphic traps recognised in the Grobla and Pławowice oil and gas fields, and in the Łąkta gas field are pinch-outs of Cenomanian sandstones. In some cases the traps represent carbonate buildups (reefs) (Myśliwiec *et al.*, 2006).

The Lubaczów accumulation was the first discovered oil, gas and condesate field in the Mesozoic basement of the Carpathian Foredeep. It is reservoired in the Upper Jurassic limestones (Kimmeridgian) of the Tarnogród-Lubaczów area near the Polish-Ukrainian border (Fig. 3). The gas-saturated limestones show average porosity of 1.2%, locally 3.2%, and permeability from 0 to 677 mD (Karnkowski, 1999; Myśliwiec *et al.*, 2006). Another Uszkowce commercial gas field in that area is reservoired in Jurassic (Doggerian) clastics (Figs 3, 4). The high-methane gas is accumulated in sandstones characterized by porosity of about 13% and permeability up to 840 mD (Karnkowski, 1999; Myśliwiec *et al.*, 2006). Both deposits are located in structural-stratigraphic traps, in the massive, erosional or tectonic blocks of the basement. The carbonate and clastic reservoir facies are sealed by Miocene shales and by fault planes (Myśliwiec *et al.*, 2006).

In the Mesozoic basement of the Carpathian Foredeep between Kraków and Rzeszów, six hydrocarbon accumulations were discovered in the Upper Jurassic carbonates: Partynia-Podborze (oil), Wojsław, Łączki Brzeskie, Mędrzechów (gas), Góra Ropczycka and Tarnów (gas-condensate) (Figs 3, 4).

A few producing horizons were discovered in the Upper Jurassic and Upper Cretaceous successions of the Dąbrowa Tarnowska, Grobla, Korzeniów-Męciszów, Łapanów, Łąkta, Pławowice, Smęgorzów and Żukowice fields (Figs 3, 4). In the Brzezówka oil and gas field, the reservoirs are the Upper Jurassic and Lower Cretaceous carbonates, while inflow of gas and condensate in Zagorzyce came from the Upper Jurassic–Lower Cretaceous horizon (Figs 3, 4). Moreover, the Brzezowiec, Rajsko, Rylowa and Swarzów gas fields, and the Jastrząbka Stara oil field were discovered in the Upper Cretaceous sandstones only (Figs 3, 4) (Karnkowski, 1999; Maksym *et al.*, 2001; Florek *et al.*, 2006; Myśliwiec *et al.*, 2006).

The average porosity of Upper Jurassic carbonates is low and ranges from 2% in Partynia-Podborze and Łączki Brzeskie deposits, through about 6% in the Góra Ropczycka, Tarnów, Pławowice and Brzezówka fields, up to even 10% in the Dąbrowa Tarnowska and Łąkta fields (Karnkowski, 1999; Florek *et al.*, 2006; Myśliwiec *et al.*, 2006). The permeability of Upper Jurassic microfactured and fractured reservoirs changes from 5 mD in the Brzezówka field to over 180 mD in the Partynia-Podborze oil field. In the Pławowice field permeability of fractured reservoir reaches 150 mD (Karnkowski, 1999; Myśliwiec *et al.*, 2006). The effective thickness of this reservoir varies from 13 m in the Partynia-Podborze oil field to 30 m in the Łąkta gas and condensate field (Karnkowski, 1999; Florek *et al.*, 2006; Myśliwiec *et al.*, 2006).

The average porosity of Upper Cretaceous sandstones is high and in most fields exceeds 30% (Grobla oil and gas field, Jastrząbka Stara oil field, Rajsko gas field, Rylowa gas field). In the Pławowice oil and gas field, porosity of Cenomanian sandstones ranges from 6 to 13% (Karnkowski, 1999; Myśliwiec *et al.*, 2006). The permeability of this reservoir varies from a few dozens to even 2,630 mD in the Grobla field (Karnkowski, 1999; Myśliwiec *et al.*, 2006). The effective thickness of Upper Cretaceous reservoirs varies from 10 m in the Łąkta gas and condensate field, through 22 m in the Jastrząbka Stara oil field, up to 59 m in the Rylowa gas field (Karnkowski, 1999; Florek *et al.*, 2006). The Cenomanian reservoir sandstones show good and, locally, even very good reservoir properties (Myśliwiec *et al.*, 2006).

The traps in oil and gas deposits of the Palaeozoic–Mesozoic basement are sealed either by the Miocene strata alone (*e.g.*, Dąbrowa Tarnowska, Smęgorzów), or by the Miocene cover and the Upper Cretaceous marls (*e.g.,* Grobla, Rylowa, Wierzchosławice). The Carpathian Overthrust and the flysch strata provide an additional seal (*e.g.*, Leszczyna-Łąkta) (Kotarba & Jawor, 1993).

Ukrainian part of the Mesozoic basement of the Carpathian Foredeep

Eleven fields were discovered within the Mesozoic basement of the Ukrainian part of the Carpathian Foredeep (Vul *et al.*, 1998a, b; Shcherba *et al.*, 1987; Kurovets *et al.*, 2011). Three of them are oil fields: the Kokhanivka and Orkhovychi fields are heavy oil accumulations in Upper Jurassic reservoirs (Fig. 3), and the Lopushna oil field in the south-eastern part of the platform basement under the Carpathian Overthrust (Fig. 3) is in Upper Jurassic, Cretaceous (Albian–Cenomanian) and Eocene reservoirs. Seven fields contain condensate and/or gas in combined Mesozoic–Miocene reservoirs (Fig. 3) (Kurovets *et al.*, 2011). The Rudkivske – gas and condensate accumulation in the Upper Jurassic–Lower Badenian Sandy-Calcareous Series reservoir and 5 gas accumulations in Lower Sarmatian, Vereshchytsia – gas in the Upper Jurassic–Lower Badenian Sandy-Calcareous Series, Medenychi – gas and condensate in Upper Cretaceous–Lower Badenian Sandy-Calcareous Series, Bilche-Volytsia – gas and condensate in Upper Cretaceous–Lower Badenian Sandy-Calcareous Series and 4 gas accumulations in Lower Sarmatian, Uhers'ko – gas and condensate in Upper Cretaceous–Lower Badenian Sandy-Calcareous Series and 5 gas accumulations in Lower Sarmatian, Pivdenne Uhers'ko – gas in Upper Cretaceous–Lower Badenian Sandy-Calcareous Series and 4 gas accumulations in Lower Sarmatian and Letnia – gas and condensate in Upper Jurassic–Lower Badenian Sandy-Calcareous Series, Upper Cretaceous–Lower Badenian Sandy-Calcareous Series and 9 gas accumulations in Lower Sarmatian strata.

The Upper Jurassic strata of the Oparska and Nyzhnivska formations are reservoir rocks in several of the listed above oil and gas fields. They are represented by cavernous and fractured limestones and dolomites with porosity ranging from 2.3 to 29.6% and permeability of 0.001 to 26 mD (Scherba *et al.*, 1987; Vul *et al.*, 1998a, b; Kurovets *et al.*, 2011). The Cretaceous strata, reservoir rocks in several gas fields in the north-western part of the Bilche-Volytsia Unit and in the Lopushna oil field in its south-eastern part, are represented by 3 to 12-m-thick quartz-glauconitic sand-

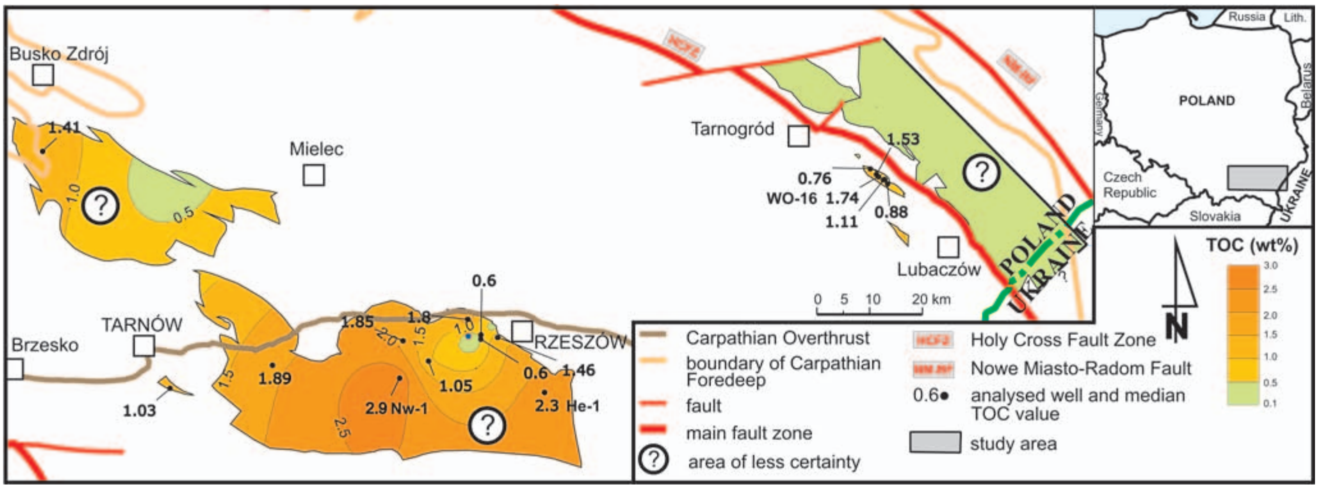

Fig. 5. Contour map of median values of total organic carbon (TOC) content of the Ordovician–Silurian source rocks in the area between Brzesko and Polish-Ukrainian border. Lith. – Lithuania

stones with porosity and permeability locally reaching 33.2% and 2,435 mD, respectively (Scherba *et al.*, 1987; Kurovets *et al.*, 2011). These Upper Jurassic and Upper Cretaceous reservoirs usually form an erosional ledge jointly with the Lower Badenian Sandy-Calcareous Series, and are sealed by the overlying Miocene beds. Palaeogene strata occur in the Carpathian foreland only locally, where in the Lopushna field they are up to few metres thick. The Eocene-age reservoir rocks are represented by sandstones with porosity of 12.5% and permeability of 0.7 mD (Vul *et al.*, 1998a, b) and are sealed by Badenian molasse deposits.

CHARACTERIZATION OF SOURCE ROCKS

Based on the results of geochemical analyses of samples collected from Palaeozoic and Mesozoic strata, five main petroleum source rock horizons were identified: Ordovician–Silurian rocks, Middle and Upper Devonian carbonates, Lower Carboniferous clastics (Culm), Middle Jurassic siliclastics and Upper Jurassic carbonates (Kosakowski *et al.*, in press, c, d; Więcław *et al.*, 2011; Więcław *et al.*, in press, a).

Ordovician and Silurian complex

Due to their comparable and continuous development Ordovician and Silurian strata were characterized as a single source rock for two separate areas (Buła & Habryn, *eds*, 2008): Busko Zdrój-Rzeszów and Tarnogród-Lubaczów (Figs 5–8). In the first area samples were collected from 15 wells and from 9 wells in the second one (Fig. 5). In the Ukrainian part of the Carpathian Foredeep only one sample was collected (Więcław *et al.*, in press, a) and thus our source rock interpretation is inconclusive.

In the Busko Zdrój-Rzeszów area, the best source rocks were found in the Nawsie-1 (Nw-1) and Hermanowa-1 (He-1) wells where the medians of TOC content were 2.9 and 2.3 wt%, respectively (Fig. 5). In the majority of wells the TOC contents exceeded 1 wt%, indicating generally high organic carbon content (Fig. 5). Medians of the hydrogen index (HI) values (from 135 to 548 mg HC/g TOC, Fig. 6) indicate reasonable hydrocarbon potential from the Type-II kerogen. Maturity changes from the initial phase of the "oil window" in the central part of the analysed area (Mielec-Tarnów) to the peak of the "oil window" in the eastern and western parts (Fig. 7). The estimated source rock thickness varies from 40 m to 220 m (Fig. 8).

Favourable source rocks with median TOC up to 1.74 wt% in Wola Obszańska-16 (WO-16) well were recorded in the Tarnogród-Lubaczów area, but in the small zone in the vicinity of above-mentioned well only (Fig. 5). The hydrocarbon potential of these rocks was rather low and in the individual wells the median values never exceeded 150 mg HC/g TOC (Fig. 6). This is probably due to the increased sample maturity (Fig. 7). The source rock thickness varies here from 20 m to 180 m (Fig. 8).

The results show that the Ordovician–Silurian complex from the Busko Zdrój-Rzeszów area has good source rock properties, whereas in Tarnogród-Lubaczów area such properties occur only locally, in the vicinity of Wola Obszańska.

Middle and Upper Devonian carbonates

The Middle and Upper Devonian strata are developed as carbonate deposits: dolomites, detrial limestones, dolomitic limestones, marls and marly limestones. Their thickness reaches 300–400 m in the vicinity of Rzeszów (Maksym *et al.*, 2003) and up to over 1,000 m in the Kraków-Brzesko area (Zając, 1984).

These strata are generally poor in organic matter. The total organic carbon (TOC) content is usually below 0.2 wt%. In the Grobla area (Grobla-28 and Rajsko-3 wells), source rock levels characterizing increased hydrocarbon potential: TOC up to 2.6 wt% and hydrocarbon contents up to 4.7 mg HC/g rock were recorded. Some parts of the section of the Grobla-28 well could have the initial hydrocarbon potential very good and even excellent (Więcław *et al.*, 2011). In the Middle and Upper Devonian carbonates the oil-prone

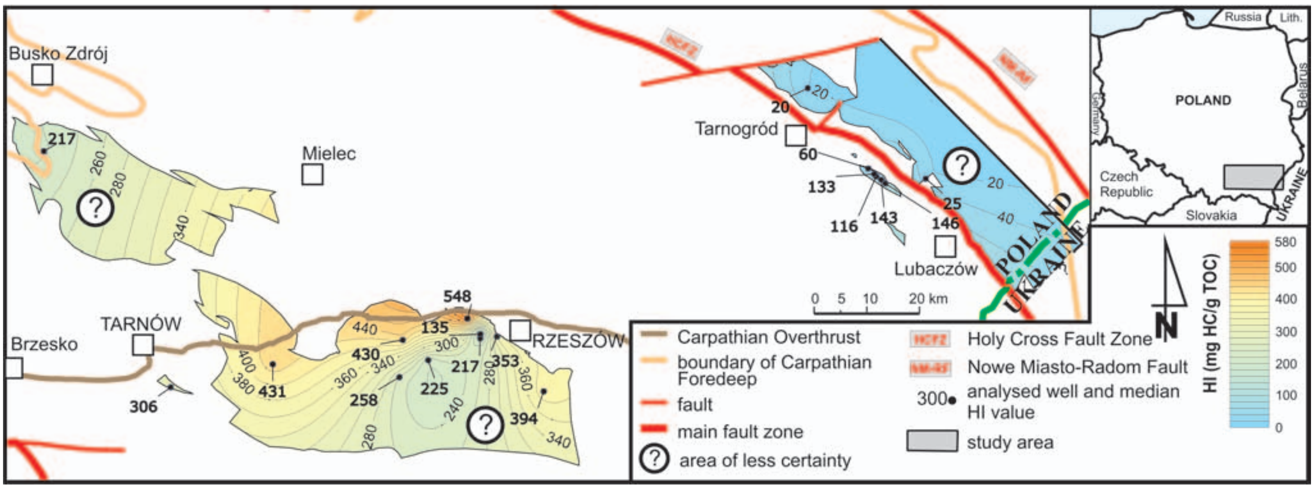

Fig. 6. Contour map of median values of hydrogen index (HI) of the Ordovician–Silurian source rocks in the area between Brzesko and the Polish-Ukrainian border. Lith. – Lithuania

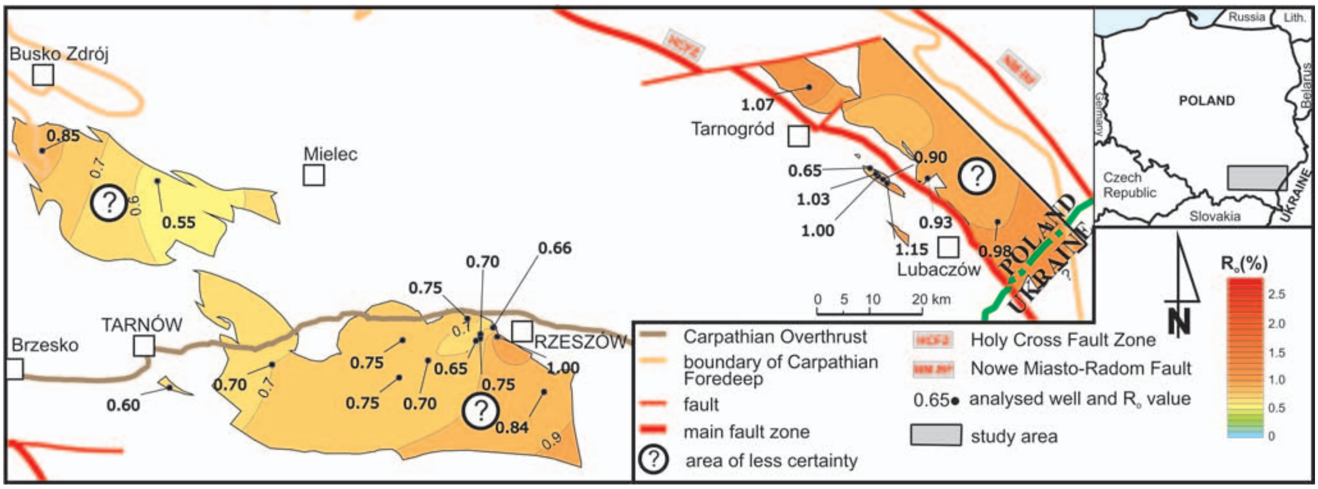

Fig. 7. Contour map of values of reflectance of vitrinite-like macerals (R_O) at the bottom of the Ordovician–Silurian strata in the area between Brzesko and the Polish-Ukrainian border. Lith. – Lithuania

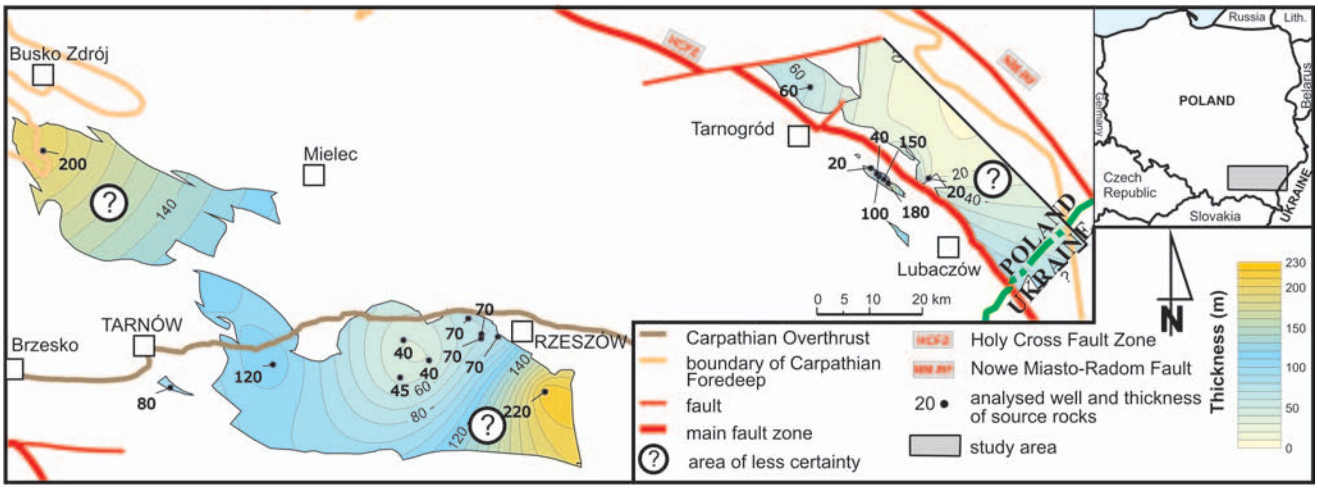

Fig. 8. Contour map of thickness of source rocks of the Ordovician–Silurian strata in the area between Brzesko and the Polish-Ukrainian border. Lith. – Lithuania

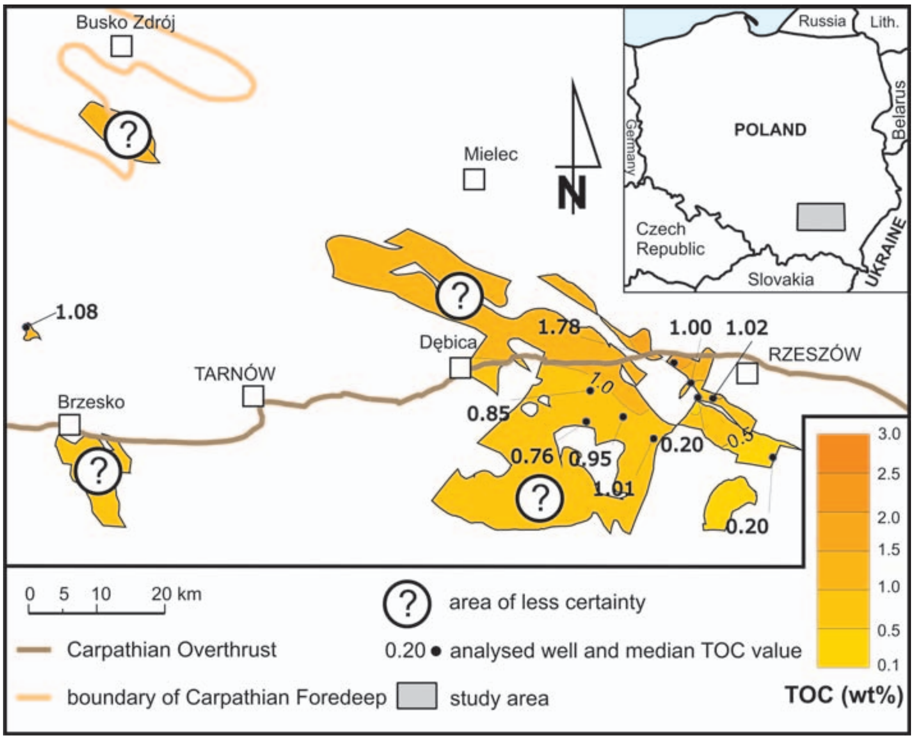

Fig. 9. Contour map of median values of total organic carbon (TOC) content of the Lower Carboniferous terrestrial source rocks in the Brzesko–Rzeszów area. Lith. – Lithuania

Type II kerogen dominates with local admixtures of the gas-prone Type III kerogen. Organic matter was deposited in anoxic carbonate environment (Więcław *et al.*, 2011). The thermal maturity of organic matter dispersed in these strata changes from the final stage of immature (microbial processes) in the vicinity of Rzeszów to the overmature zone (high-temperature thermogenic processes) in the western part of the analysed area near Grobla.

Lower Carboniferous clastic facies (Culm)

The Lower Carboniferous clastic facies (Culm) occurs in the Polish part of the study area only (Buła & Habryn, *eds*, 2008). Samples from 11 wells localized mostly between Dębica and Rzeszów towns (Figs 9–12) were analysed for this study. The median TOC content for the source rocks from individual wells is usually above 0.8 wt%, indicating generally high organic carbon content (Fig. 9). Hydrocarbon potential is low and usually does not exceed 100 mg HC/g TOC (Fig. 10) from the gas-prone, Type-III kerogen (Więcław *et al.*, 2011). Organic matter maturity, calculated to the bottom of the analysed strata, extends from the initial to the main phases of the "oil window" (Fig. 11), indicating that source rocks are capable of generating thermogenic hydrocarbons. The source rock thickness varies over a wide range: from 50 to 300 m (Fig. 12). The greatest thickness (300 m) was recorded in the Strzelce Wielkie-1 (SW-1) well (Fig. 12).

With respect to the TOC content, the best source rocks, with the highest hydrocarbon potential, maturity and thickness occur in the Dębica-Rzeszów area, beneath the Carpathian Overthrust.

Middle Jurassic strata

The Middle Jurassic strata were characterized in the Polish (20 wells sampled) and Ukrainian (10 wells sampled) parts of the study area (Figs 13–15) (Więcław *et al.*, 2010; Kosakowski *et al.*, in press, c, d). Median values of the TOC content vary over a wide range: from 0.0 to 6.4 wt% (Fig. 13). High median TOC value, above 2 wt%, occured in seven wells, in the various parts of the analysed area (Fig. 13). Generally, the median TOC content is above 1 wt%, being indicative of high organic carbon content. Hydrocarbon potential of dispersed organic matter is generally low and usually does not exceed 100 mg HC/g TOC (Fig. 14), indicating the presence of gas-prone, Type-III kerogen. Only in the Tarnawa-1 (Ta-1) well the HI median value is 260 mg HC/g TOC (Fig. 14) suggesting the admixture of Type-II kerogen. The maturity of organic matter changes from 0.4 to 0.7% R_o, evidencing the immaturity of rocks in the Kraków-Rzeszów area (Fig. 15). The highest maturities were recorded in the successions of deepest burial below the Carpathian Overthrust (Fig. 15). However, it was impossible to determine the source rock thickness due to insufficient sampling density.

Based on geochemical characteristics of the Middle Jurassic strata it can be concluded that the best source rocks, capable of generating thermogenic hydrocarbons, occur in the Dębica-Rzeszów area and in the Ukrainian part of the study area.

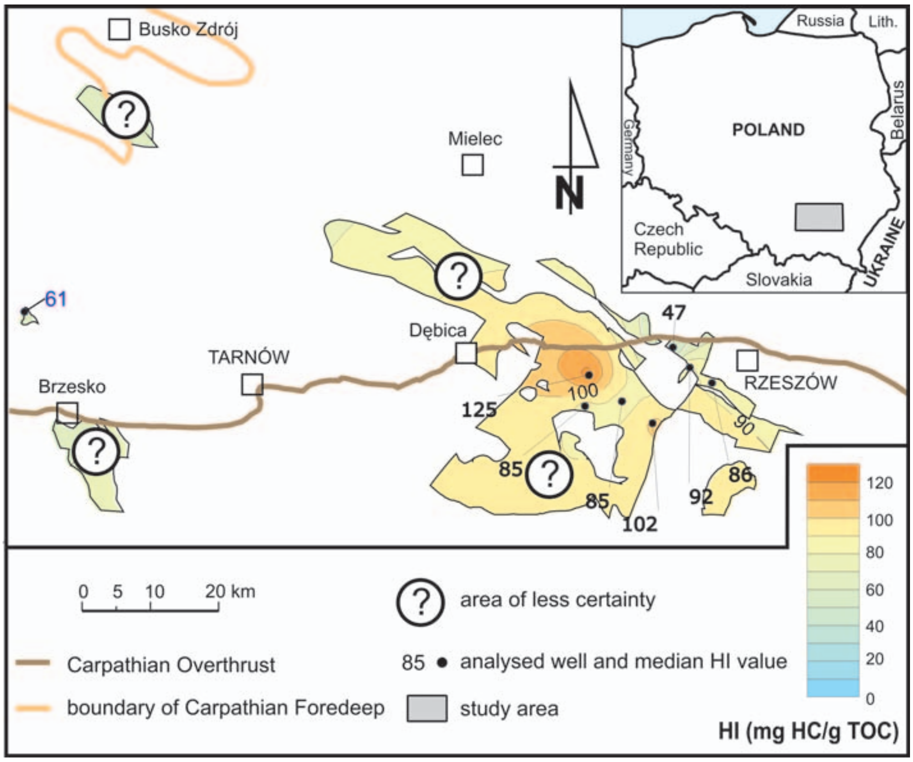

Fig. 10. Contour map of median values of hydrogen index (HI) of the terrestrial Lower Carboniferous source rocks in the Brzesko–Rzeszów area. Lith. – Lithuania

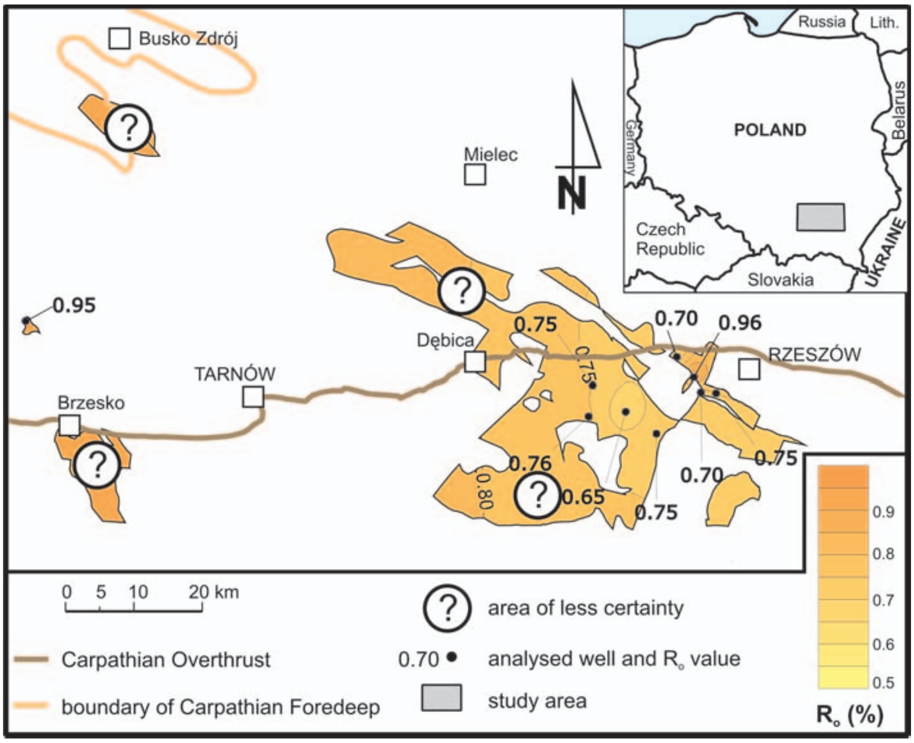

Fig. 11. Contour map of values of vitrinite reflectance (R_o) at the bottom of the Lower Carboniferous terrestrial strata in the Brzesko–Rzeszów area. Lith. – Lithuania

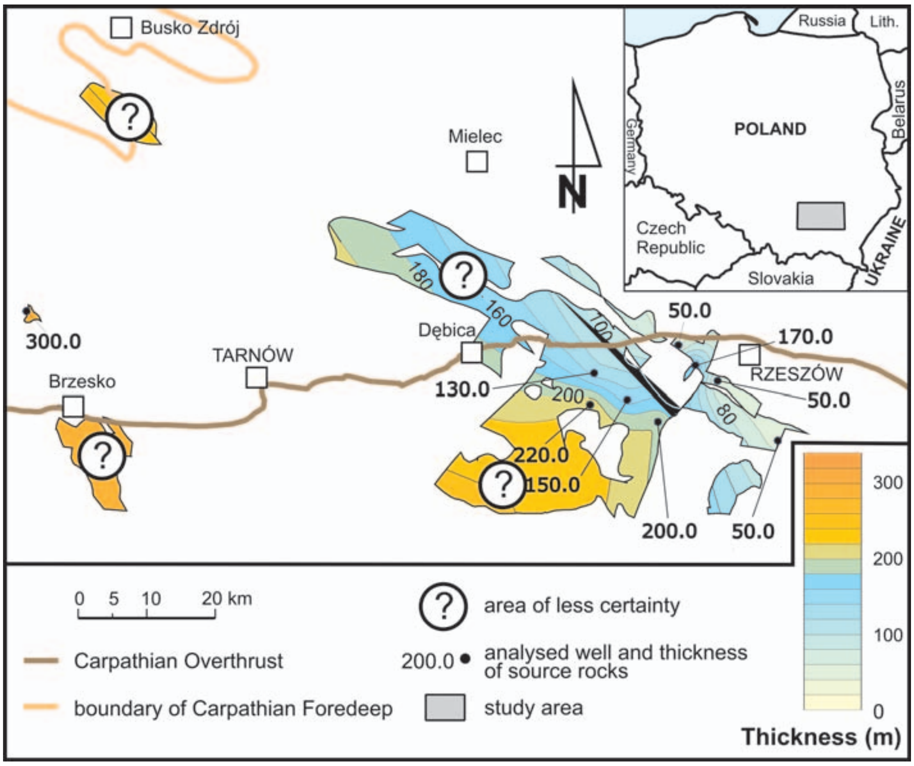

Fig. 12. Contour map of thickness of source rocks within the Lower Carboniferous terrestrial strata in the Brzesko–Rzeszów area. Lith. – Lithuania

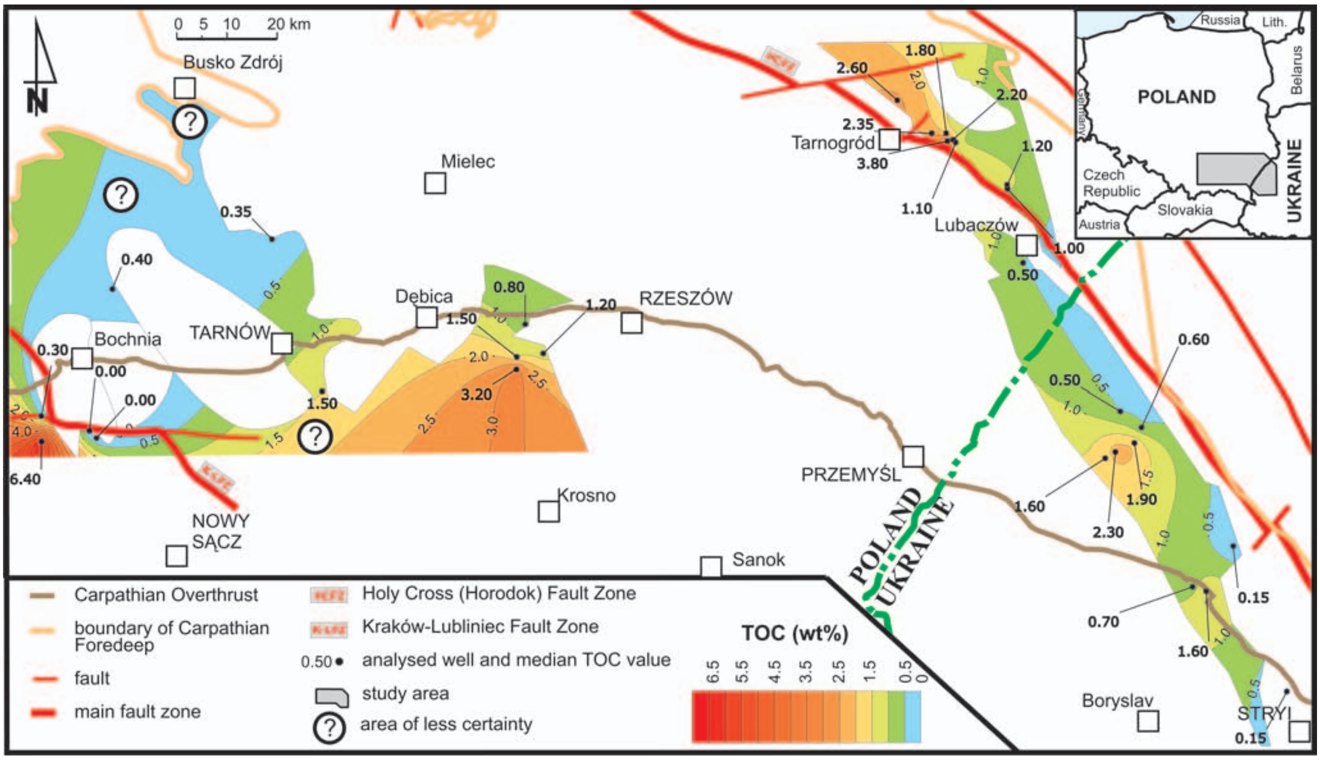

Fig. 13. Contour map of median values of total organic carbon (TOC) content of the Middle Jurassic source rocks in the area between Bochnia and Stryi towns. Lith. – Lithuania

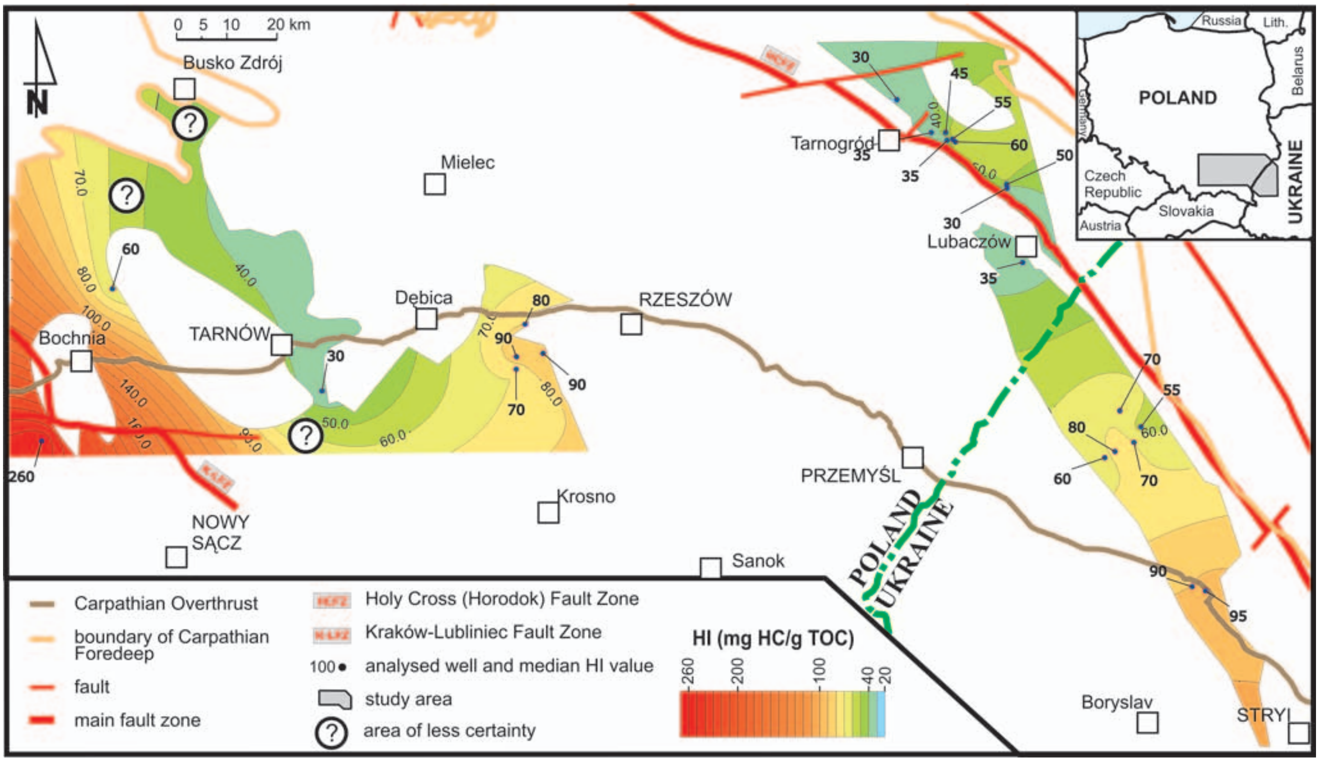

Fig. 14. Contour map of median values of hydrogen index (HI) of the Middle Jurassic source rocks in the area between Bochnia and Stryi towns. Lith. – Lithuania

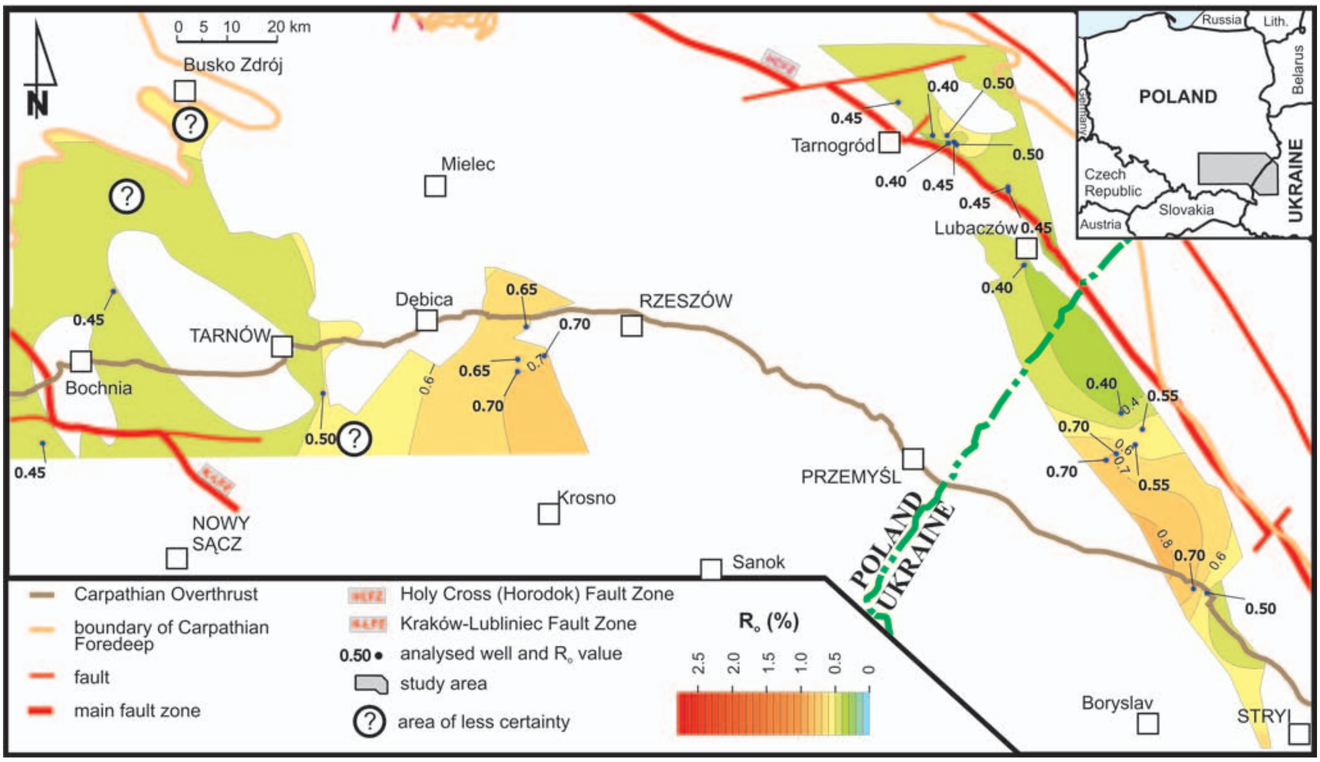

Fig. 15. Contour map of values of reflectance of vitrinite-like macerals (R_o) at the bottom of the Middle Jurassic strata in the area between Bochnia and Stryi towns. Lith. – Lithuania

Upper Jurassic strata

In the Polish part of the Carpathian Foredeep, the Upper Jurassic carbonates are usually low in organic matter and only locally show medium TOC concentrations (Kosakowski *et al.*, in press, c, d). The generally low hydrocarbon potential and maturity correspond to the final phase of microbial processes and the initial phase of the "oil window". Hence, these rocks can be considered only as a secondary source of hydrocarbons (Kosakowski & Wróbel, in press; Kosakowski *et al.*, 2011). The source rocks of Jurassic strata in the Polish Outer Carpthians were evaluated by Golonka *et al.* (2009).

In the Ukrainian part, the Upper Jurassic strata show a variable organic carbon content, from 0.0 up to 2.1 wt% (Fig. 16). The highest hydrocarbon potential, up to 375 mg HC/g TOC, is observed in the vicinity of Mostys'ka and Horodok (Fig. 17) indicating the highest content of oil-prone, Type-II kerogen. Low maturity of the analysed strata is comparable to that observed in the Polish part of the study area (Fig. 18), but the presence of the highly-reactive Type-IIS kerogen (Kosakowski *et al.*, in press, d) suggests capability of Upper Jurassic source rocks for oil and gas generation. The most favourable area for thermogenic hydrocarbon generation is in the Mostys'ka-Horodok zone.

OIL – NATURAL GAS – SOURCE ROCK CORRELATION

The application of comprehensive methods (stable carbon isotopes, biomarkers and aromatic hydrocarbons) allows for an explanation of the genetic relationships between dispersed organic matter and liquid (oils and condensates) and gaseous hydrocarbons accumulated in the Palaeozoic–Mesozoic basement strata of the Carpathian Foredeep in the Kraków and Ivano-Frankivs'k area (Figs 3, 4, 19). Moreover, in the case of oil-source rock correlation, the possibility of hydrocarbon migration from the Menilite Shales of the flysch sequence of the Outer Carpathians to the base-

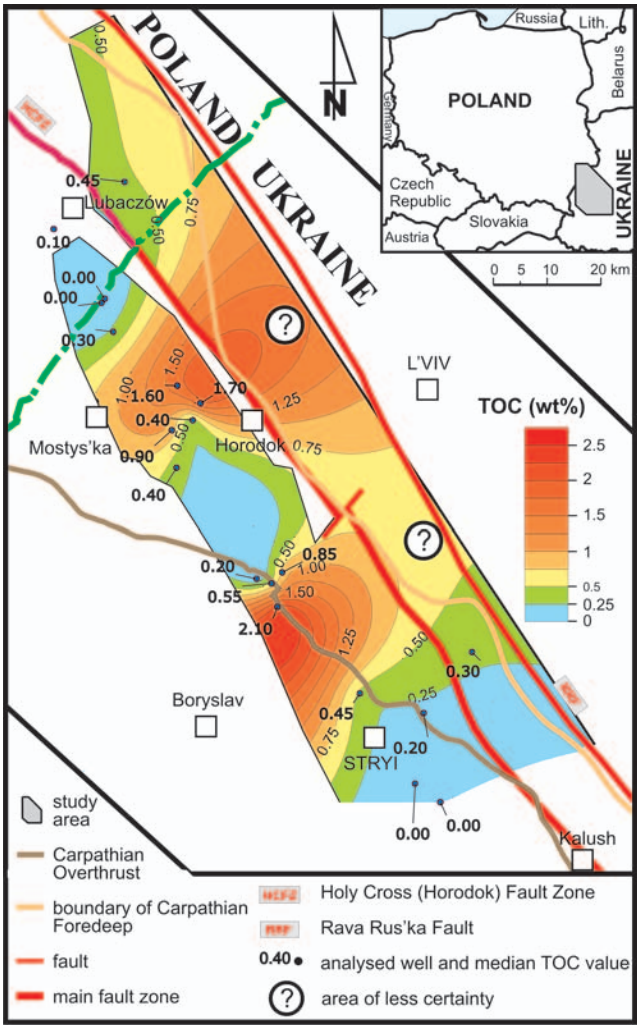

Fig. 16. Contour map of median values of total organic carbon (TOC) content of the Upper Jurassic source rocks in the area between Lubaczów and Kalush towns. Lith. – Lithuania

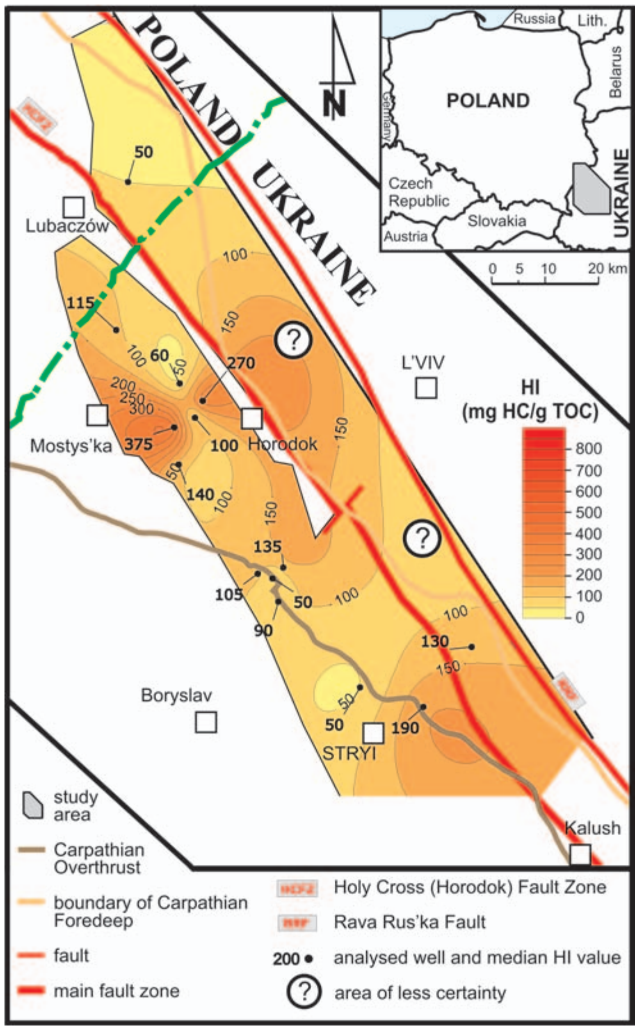

Fig. 17. Contour map of median values of hydrogen index (HI) of the Upper Jurassic source rocks in the area between Lubaczów and Kalush towns. Lith. – Lithuania

ment was considered. The entire study region was divided into seven zones around the discovered oil and/or condensate deposits for the detailed determination of genetic oil – source rock correlation (Fig. 19).

Grobla-Pławowice zone (A)

In the Grobla-Pławowice zone (A), five oil and five natural gas samples from Grobla and two oil samples from Pławowice deposits were collected and analysed (Kotarba, in press; Więcław, 2011).

The stable carbon isotope composition of saturated and aromatic hydrocarbons indicates the presence of one family of oils and its genetic correlation with bitumen extracted from Silurian and Devonian strata (Fig. 20A). Also, some levels of the Menilite Shales from the Dukla and Silesian units of the Outer Carpathians correlate with analysed oils (Fig. 20A), though the results of other (Rock-Eval, biomarkers, aromatic hydrocarbons) analyses (Więcław, 2002) reveal that their maturity is too low for generation of oils. Curtis *et al.* (2004) recorded a different stable carbon isotope composition for oils from Grobla deposit and oils generated from the Menilite Shales during hydrous pyrolysis (HP) experiments. These facts and high H_2S content in the gas accompanying oil in the Grobla-Pławowice deposit (Kotarba, in press) suggest the generation from organic matter in the carbonates, which do not occur in the Palaeogene flysch section of the Outer Carpathians. Thus, the idea of genetic connection of oils from Grobla and Pławowice deposits with the Oligocene Menilite Shales (ten Haven *et al.*, 1993) must be rejected. The correlation with Jurassic organic-rich rocks in the Outer Carpathian flysch and carbonates (Mikulov Marls) of the Carpathian foreland (Golonka *et al.*, 2009) was not studied yet. The biomarker and aromatic hydrocarbons data support correlation of the Silurian and Devonian source rocks with analysed oils (Figs 21A, 22A). The lack of correlation between oils (Fig. 22A) and one Devonian rock sample is a result of its low maturity. However, Devonian samples from Grobla showed maturities corresponding to the final phase of the "oil window" (Więcław *et al.*, 2011).

Molecular and isotopic compositions of natural gases associated with oils from the Grobla deposit show that they were generated from Type-II kerogen with significant component of Type-III kerogen, the maturity of which is about 1.3% in vitrinite reflectance scale (Kotarba & Jawor, 1993; Kotarba, in press). These gases lack the microbial component (Kotarba, in press) and the data suggest a Devonian source.

Łąkta-Tarnów zone (B)

In the Łąkta-Tarnów zone (B), nine oils and condensates and six gas samples were collected and analysed.

The stable carbon isotope composition of saturated and aromatic hydrocarbons of oils shows the presence of two oil families (Fig. 20B). One oil family, enriched in ^{13}C isotope, consists of Łąkta-27 (Lk-27) condensate and Tarnów-47 (Ta-47) oil and the second family constitute all the remaining oils and condensates (Fig. 20B). Oils from the first family correlate very well with the Middle Jurassic strata from the basement and Oligocene Menilite Shales from the Dukla and Silesian units (Fig. 21B). The genetic correlation based on C_{27}, C_{28} and C_{29} regular $\alpha\alpha\alpha$ steranes of oils from the second family and bitumen extracted from Silurian strata is visible (Fig. 21B). Also some levels of the Menilite Shales from the Dukla Unit correlate with these oils (Fig. 21B), but the maturity of those rocks is too low for generation of oils (Więcław, 2002). The geochemical data characterizing the Upper Palaeozoic strata in this zone are limited, but Dudek *et al.* (2003) and Więcław *et al.* (2011) showed enough organic matter in levels in the Devonian and Lower Carboniferous strata and we cannot exclude these as source rocks.

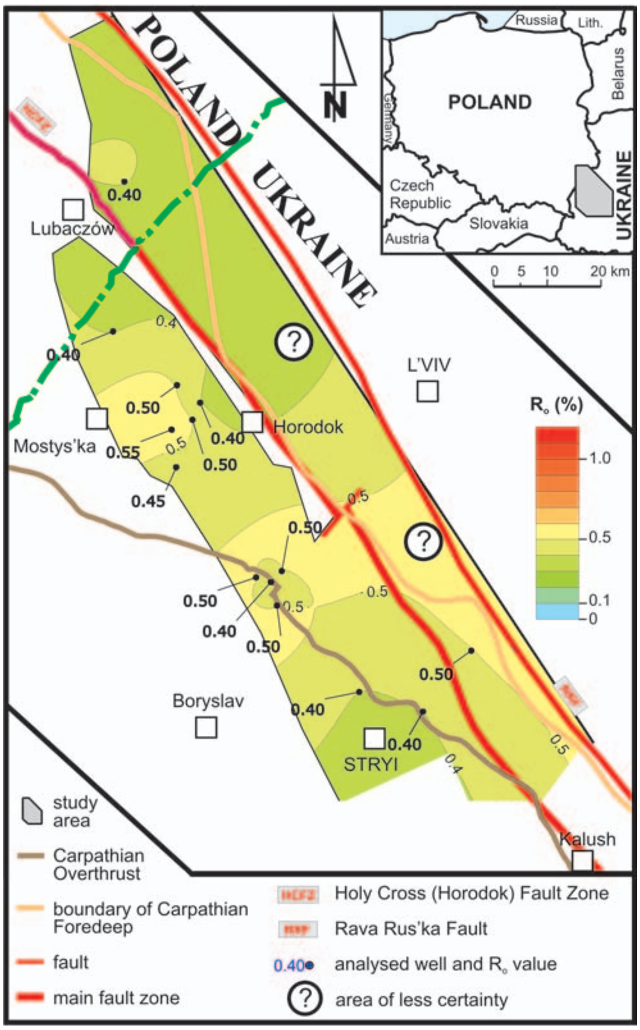

Fig. 18. Contour map of values of reflectance of vitrinite-like macerals (R_o) at the bottom of the Upper Jurassic strata in the area between Lubaczów and Kalush towns. Lith. – Lithuania

The most probable source rock for the other oils are the Silurian strata (Figs 20B, 21B). The visible differences in MDR values of oils and bitumen (Fig. 22B) are probably caused by oil migration.

Molecular and isotopic compositions of natural gases from Łąkta-Leszczyna, Wierzchosławice, Rylowa, and Tarnów deposits indicate that they are generated from Type-II kerogen with significant component of Type-III kerogen.

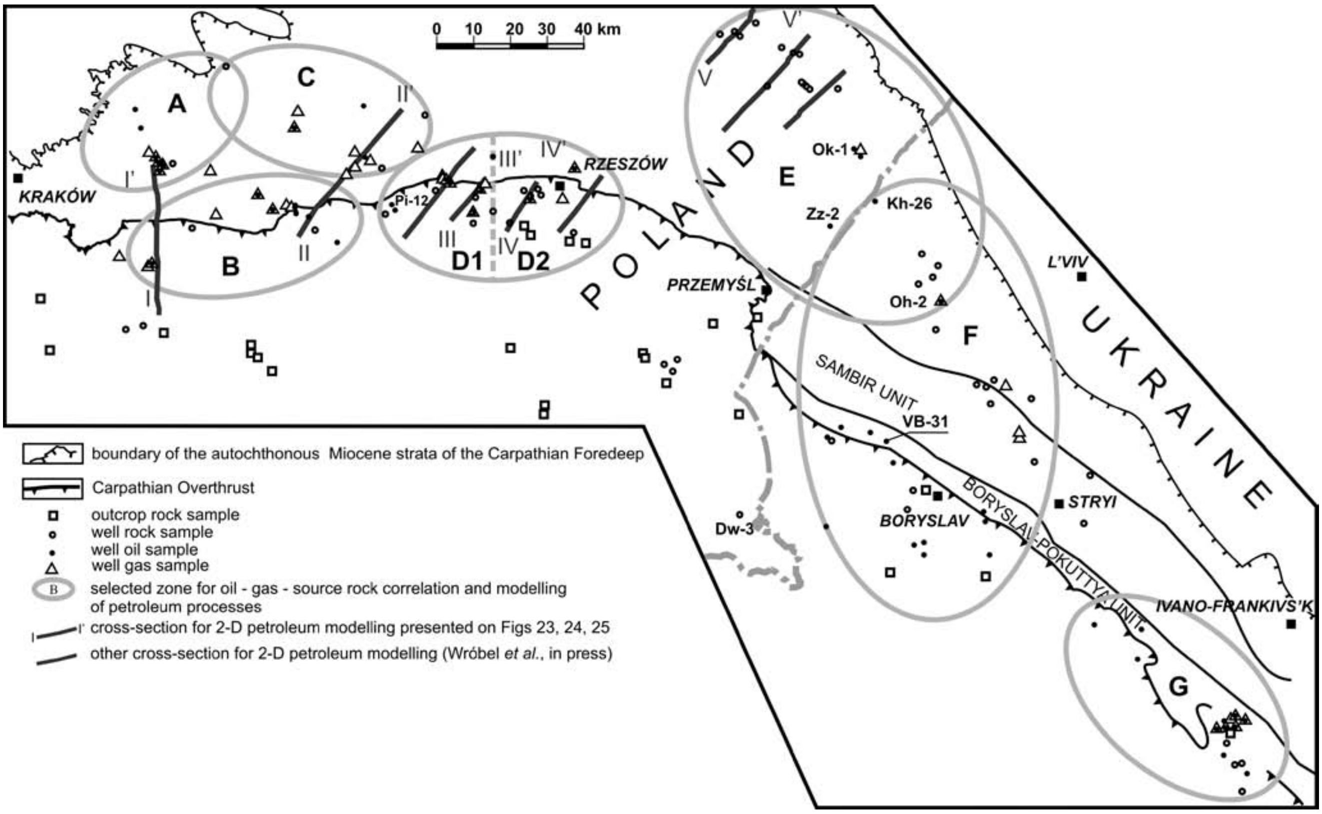

Fig. 19. Sketch map of location of zones selected for oil – gas – source rock correlation and modelling of petroleum processes in the Palaeozoic–Mesozoic basement of the Polish and Ukrainian parts of the Carpathian Foredeep. Zones: (A) Grobla-Pławowice, (B) Łąkta-Tarnów, (C) Jastrząbka Stara-Partynia Podborze, (D) Pilzno-Rzeszów: (D1) Pilzno-Będzienica, (D2) Będzienica-Rzeszów, (E) Lubaczów-Orkhovychi, (F) Kokhanivka-Boryslav and (G) Letisivka–Bytkiv. Codes of wells: Dw-3 – Dwernik-3, Oh-2 – Orkhovychi-2, Ok-1 – Opaka-1, Kh-26 – Kokhanivka-26, VB-31 – Vola Blazhivska-31, Zz-2 – Załazie-2

Their maturity from vitrinite reflectance is about 1.3% (Kotarba & Jawor, 1993; Kotarba, in press). Natural gas from Łapanów accumulation has a significant thermogenic component, but also includes a microbial origin component. These data suggest that Middle Jurassic and probably Devonian kerogens are their source (Kotarba, in press). Molecular and isotopic compositions of natural gas from Brzezowiec accumulation indicate that it was generated in the autochthonous Miocene strata and migrated to a Cenomanian trap (Kotarba & Jawor, 1993; Kotarba & Koltun, 2006).

Jastrząbka Stara-Partynia Podborze zone (C)

In the Jastrząbka Stara-Partynia Podborze zone (C), three oil and six gas samples from Dąbrowa Tarnowska, Jastrząbka Stara, Partynia-Podborze, Smęgorzów and Żukowice deposits (Figs 3A, 19) were analysed (Figs 20–22). The Silurian, Devonian, Carboniferous and Jurassic source rocks also were examined (Figs 20–22).

The stable carbon isotope composition of saturated and aromatic hydrocarbons of oils proves the presence of one oil family (Fig. 20C), where distribution of regular ααα steranes show little differences between the oil of Jastrząbka Stara deposit and the remaining oils (Fig. 21C). The direct isotopic correlation of oils and bitumen demonstrate a genetic relation of oils with Menilite Shales from the Silesian Unit (Fig. 20C) in Dwernik-3 (Dw-3) section near the Ukrainian border (Fig. 19). Considering the 100 km distance between this rock and oil deposits we believe that oil migration is rather impossible. A good isotopic and biomarker correlation between oils and the Middle Jurassic strata is observed (Figs 20C, 21C), which negates a Menilite Shales relation. The organic matter in these rocks is immature and could not generated the analysed oils (Fig. 22C). Biomarker and methyldibenzotiophenes data also reveal probable sourcing of oils from the Devonian rocks (Figs 21C, 22C). All data and high sulphur content in oils (Więcław, 2011) indicate that the Middle and Upper Devonian and Lower Carboniferous carbonates are the most probable source rock for these oils. Also, a Silurian source could not be excluded (Figs 21C, 22C). Some differences in $\delta^{13}C$ values of saturated and aromatic hydrocarbons of oils and bitumens (Fig. 20C) may be an effect of maturity, as demonstrated by Curtis *et al.* (2004) from hydrous pyrolysis experiments made on samples from the Oligocene Menilite Shales. During transformation, organic matter generates oil enriched in ^{13}C and gas is depleted in this isotope (*e.g.*, Lewan, 1983). The presence in oils of oleanane reported by ten Haven *et al.* (1993) and Curtis *et al.* (2004) is probably caused by its elution and other biomarkers originated from angiosperms by migrating oil through the Cretaceous strata.

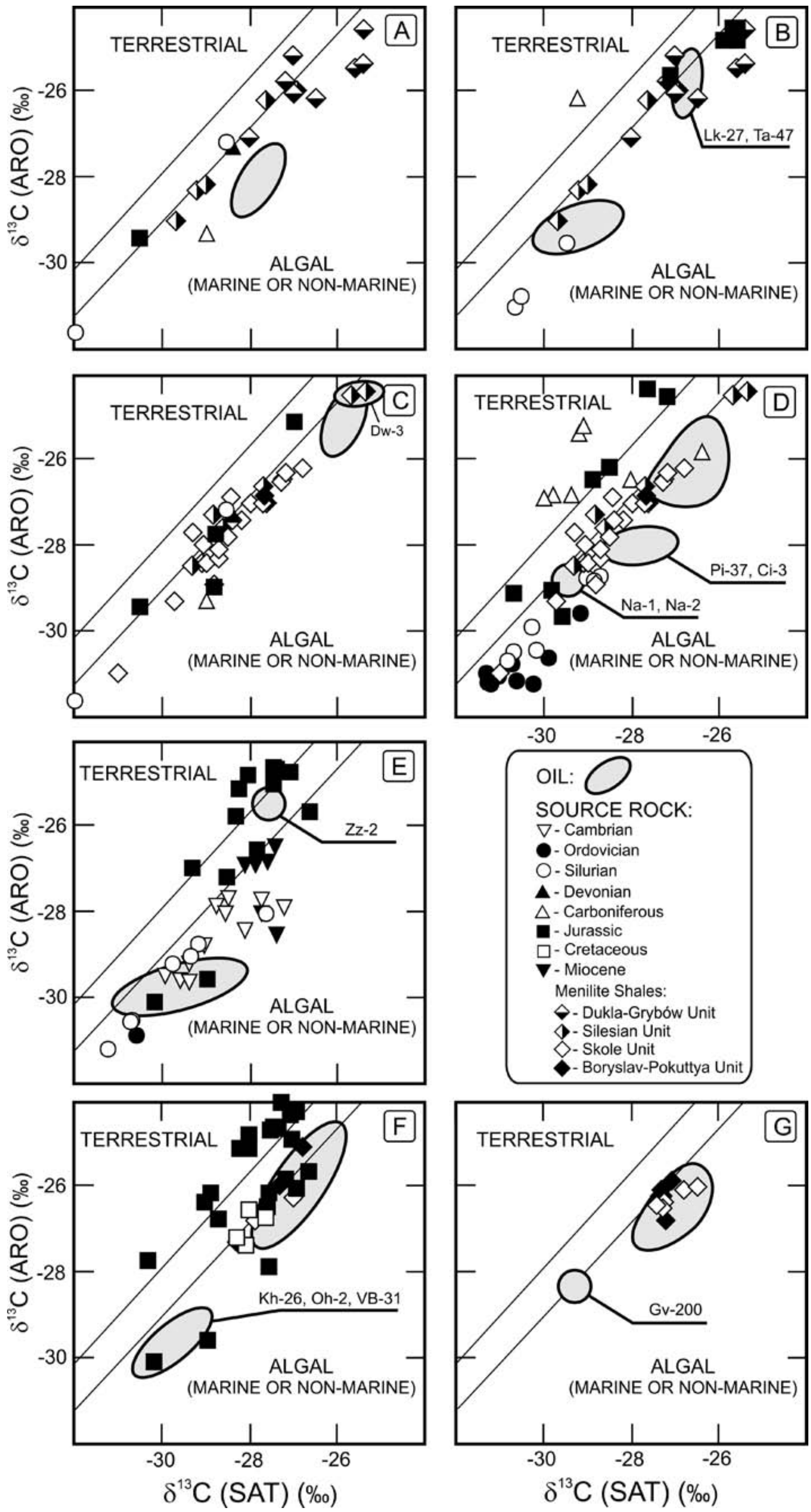

Fig. 20. $\delta^{13}C$ (aromatic hydrocarbons) *versus* $\delta^{13}C$ (saturated hydrocarbons) in oils and bitumens in areas **A** to **G** selected for oil–source rock correlation in the Palaeozoic–Mesozoic basement of the Polish and Ukrainian parts of the Carpathian Foredeep and the Oligocene Menilite Shales of the Outer Carpathians. Genetic fields after Sofer (1984). Explanation of sample codes – see Więcław (2011) and Więcław *et al.* (2011c)

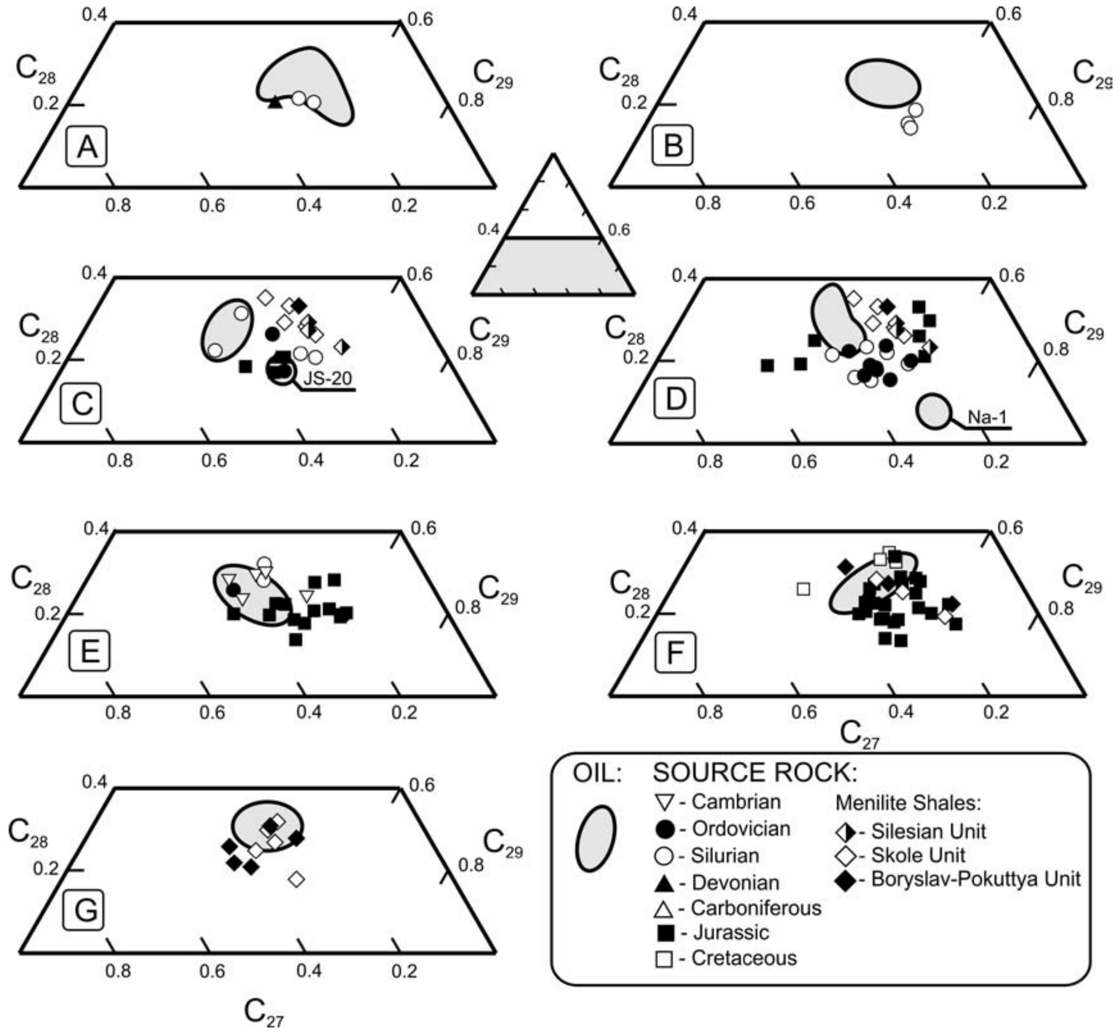

Fig. 21. Ternary diagrams of C_{27}, C_{28} and C_{29} regular ααα steranes in bitumens and oils for oil–source rock correlation in areas (**A** to **G**) of the Palaeozoic–Mesozoic basement of the Polish and Ukrainian parts of the Carpathian Foredeep and the Oligocene Menilite Shales of the Outer Carpathians

Molecular and isotopic compositions of natural gases from the Dąbrowa Tarnowska, Jastrząbka Stara, Smęgorzów and Żukowice deposits indicate that these gases include both thermogenic and microbial components (Kotarba & Jawor, 1993; Kotarba, in press) with the microbial component being dominant (about 60–70%). The thermogenic component is from Type-III kerogen, with insignificant component of Type-II kerogen on maturity 1.1–2.0% in vitrinite reflectance scale. These data suggest that most probably the Lower Carboniferous and also Devonian kerogens are the source of these gases (Kotarba, in press).

Pilzno-Rzeszów zone (D)

In the Pilzno-Rzeszów zone (D), eleven oil and condensate samples and eleven gas samples from Brzezówka, Korzeniów, Góra Ropczycka, Zagorzyce (Upper Jurassic), Cierpisz and Pilzno (Miocene), Nosówka (Lower Carboniferous), Trzebownisko and Zalesie accumulations (Devonian) and oil from the inflow of Pilzno-12 well were analysed (Figs 3A, 19). The Ordovician, Silurian, Lower Carboniferous and Middle Jurassic source rocks also were examined (Figs 20–22).

The collected oils appear to be derived from three families: (i) Nosówka deposit (Na-1 and Na-2 wells), (ii) Pilzno and Cierpisz deposits (Pi-37 and Ci-3 wells) of the Miocene reservoir, and (iii) the remaining oils from Brzezówka, Góra Ropczycka, Trzebownisko and Zagorzyce deposits (Fig. 20D). The last two families have very similar isotopic characteristics. Distribution of regular ααα steranes indicate only two oil families (Fig. 21D) because no biomarkers were recorded in the Miocene condensates (Więcław, 2011). Biomarker and aromatic hydrocarbon indices reveal a changeable maturity of the analysed oils (Fig. 22D). The condensate collected from the Góra Ropczycka deposit (GRp-1 well) is less mature than oil from the Brzezówka deposit (Bw-24 well). The isotope and biomarker compositions of oils from the Nosówka deposit directly correlate with bitumen from Ordovician and Silurian rocks (Figs 20D, 21D). The stable isotope composition of the Miocene condensates from the Cierpisz and Pilzno deposits is the

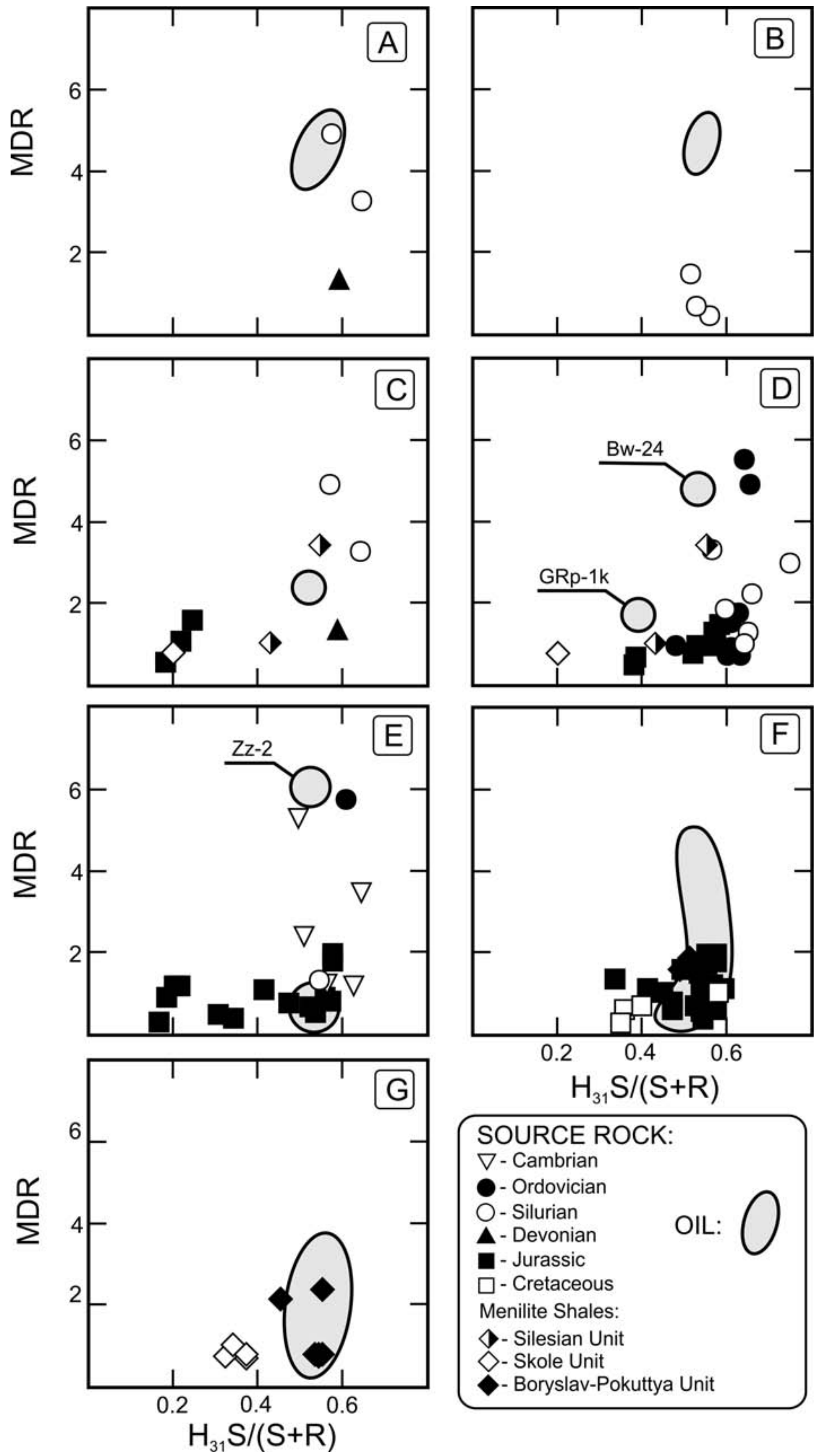

Fig. 22. Methyldibenzotiofene ratio (MDR) *versus* S/(S+R) ratio for C_{31} homohopane in bitumens and oils in areas **A** to **G** selected for oil–source rock correlation in the Palaeozoic–Mesozoic basement of the Polish and Ukrainian parts of the Carpathian Foredeep and the Oligocene Menilite Shales of the Outer Carpathians. Explanation of sample codes – see Więcław (2011)

same as in bitumen extracted from these strata presented by Kotarba *et al.* (2005b) identifying their genetic correlation. The remaining oils correlate best with the Menilite Shales from the Skole, Silesian and Boryslav-Pokuttya units (Fig. 20D). Besides the above mentioned Menilite Shales there is a good isotopic correlation between oils and the local levels of Carboniferous and Jurassic strata (Fig. 20D), although organic matter in these rock is immature for oil generation (Fig. 22D). Biomarker and methyldibenzotiophenes data also suggest probable sourcing of oils from the Ordovician and Silurian rocks (Figs 21D, 22D). Taking into consideration all presented data and the fact that these oils are generally high-sulphur ones (Więcław, 2011), the Lower Carboniferous carbonates are most probable source rocks for these oils. Also, sourcing from the Ordovician and Devonian carbonates and mixing with the Upper Jurassic and also Miocene bitumen can not be excluded (Figs 21C, 22C). Some differences in $\delta^{13}C$ values for saturated hydrocarbons and aromatics of oils and bitumen (Fig. 20C) may be an effect of maturity, migration and mixing. The oleanane presence in oils reported by ten Haven *et al.* (1993) and Curtis *et al.* (2004) is probably caused by elution of angiosperm biomarkers by oil migrating through the Cretaceous and probably also Miocene strata, sealing the deposits from the top.

Molecular and isotopic compositions of natural gases from the Nosówka and Trzebownisko deposit reveal that they are generated from Type-II kerogen on maturity about 1.1–1.2% in vitrinite reflectance scale (Kotarba & Jawor, 1993; Kotarba *et al.*, 2004a; Kotarba, in press). The gases from the Trzebownisko deposit contain significant microbial component. These data suggest that most probably Ordovician–Silurian kerogen is the source of these gases. The thermogenic gases from the Brzezówka, Góra Ropczycka, Korzeniów, Zalesie and Zagorzyce accumulations are generated from Type-II kerogen with an admixture of Type-III kerogen on maturity about 1.0–1.6 % in vitrinite reflectance scale (Kotarba, in press). These data suggest, that most probably, Lower Carboniferous kerogen is source of these gases (Kotarba, in press).

Lubaczów-Orkhovychi zone (E)

In the Lubaczów-Orkhovichi zone (E), five oil and two gas samples were analysed from the Lubaczów, Kokhanivka and Orkhovychi deposits and oil from the inflows of the Opaka-1 (Ok-1) and Załazie-2 (Zz-2) wells (Figs 3A, 19). The Cambrian, Ordovician, Silurian, Jurassic and Miocene source rocks were analysed as well (Figs 20–22).

The stable carbon isotope composition of saturated and aromatic hydrocarbons of oils evidences the presence of two separate oil families (Fig. 20E). One of them, enriched in ^{13}C isotope, consists of Załazie-2 (Zz-2) oil, and the second one comprises all the remaining oils (Fig. 20E). Oil from the first family correlates very well with the Jurassic and Miocene strata (Fig. 20E). Because the Załazie-2 well is located in the Lower San Horst Structure (Fig. 19), where the autochthonous Miocene strata lie directly on the Cambrian or Precambrian rocks (Buła & Habryn, 2011), the analysed oil could not be generated from the Jurassic source rocks. Biomarker and aromatic hydrocarbons indices reveal high maturity of that oil (Fig. 22E). The only explanation of origin of this oil is its sourcing from the Cambrian rocks. The differences in the stable carbon isotope composition of oil and bitumen extracted from the Cambrian strata (Fig. 20E) are a result of high maturity of the analysed oil (Fig. 22E). The genetic correlation of oils from the second family and bitumen extracted from the Cambrian, Ordovician, Silurian and some levels of Jurassic strata is visible (Fig. 20E). These oils are heavy, high-sulphur ones. They were generated from high-sulphur organic matter (kerogen Type-IIS) deposited in carbonates (Więcław, 2011; Więcław *et al.*, in press, b). From the above mentioned strata only Type-IIS kerogen was reported in the Upper Jurassic carbonates (Kosakowski *et al.*, in press, d), hence, these strata are considered as the source rock for the discussed heavy oils.

In one block of the Lubaczów deposit (sample Lu-22) and in the Orkhovychi deposit (sample Oh-2), the microbial methane prevails which was generated by carbon dioxide reduction process. This microbial methane migrated from the autochthonous Miocene strata to the Upper Jurassic reservoir of the Lubaczów deposit and the Upper Jurassic–Lower Badenian Sandy-Calcareous Series reservoir of the Orkhovychi deposit (Kotarba, 2011; Kotarba & Koltun, 2011).

Kokhanivka-Boryslav zone (F)

In the Kokhanivka-Boryslav zone (F), fourteen oil samples were analysed from the Kokhanivka (Kh) and Orkhovichi (Oh) deposits from the basement of the Carpathian Foredeep, Blazhiv (Bh), Nova Shidnytsya (NS), Oriv (Or), Pivdenno Stynava (PS), Pivdenny Monastyrets (PM), Ulychno (Ul), Vola Blazhivska (VB) and Stary Sambir (SS) deposits from Boryslav-Pokuttya Unit, and Zvorivska (Zv), Vovchenska (Vv), Nova Shidnytsya (NS) and Verchnyo Maslovetska (VM) deposits from the Skiba Unit (Figs 3B, 19).

Moreover, four gas samples were analysed in this zone from the Letnia, Rudky and Vereshchytsia accumulations (Fig. 3B). The origin of gas from the Orkhovychi accumulation was considered in previous chapter (E zone). In this zone, the source rocks from Jurassic and Cretaceous strata of the basement of the Carpathian Foredeep and the Outer Carpathians, and Oligocene Menilite Shales from the Boryslav-Pokuttya and Skiba (Skole) units were analysed (Figs 20–22).

The stable carbon isotope composition of saturated and aromatic hydrocarbons of oils indicates the presence of two oil families (Fig. 20F). One of them, depleted in ^{13}C isotope, consists of the Kokhanivka-26 (Kh-26), Orkhovichi-2 (Oh-2) and Vola Blazhivska-31 (VB-31) oils and the second family is formed by all the remaining oils (Fig. 20F). The oil from the first family correlates very well with the selected levels of the Jurassic strata (Fig. 20F). Also, sterane composition evidences correlation of these oils with the Jurassic source rocks. It is worth mentioning that oil from the Vola Blazhivska-31 well came from the Boryslav-Pokuttya Unit, very close to other oils accumulated in this unit, having a different stable carbon isotope composition (Więcław *et al.*, in press, b). The isotopic composition of all other oils accumulated in the Boryslav-Pokuttya and Skiba (Skole) units changes in a narrow range indicating that they had one source. Kotarba *et al.* (2007) reported Menilite Shales of the Boryslav-Pokuttya Unit as the source rock for oils accumulated in the Carpathian units in this zone. Current data confirm this thesis.

Molecular and isotopic compositions of natural gases from the Letnia, Orkhovychi, Rudky and Vereshchytsia deposits reveal that they are generated during microbial processes (Kotarba & Koltun, 2011). The microbial gases (methane, ethane and hydrogen) generated during microbial processes within the Miocene strata have later migrated to the Upper Jurassic and Upper Cretaceous (Cenomanian) reservoirs of the Mesozoic basement, and to the bottommost Lower Badenian Sandy-Calcareous Series reservoirs (Kotarba & Koltun, 2011).

Lytisivska-Bytkiv zone (G)

In the Lytisivska-Bytkiv zone (G), eleven oil samples from the Chechvynska (Cv), Monastyrchany (Mo), Markova (Ma), Gvizd (Gv) and Bytkiv (By) from Boryslav-Pokuttya Unit, and Letisivka (Lyt), Vilkhivka (Vi) and Cherlenska (Ce) deposits and five gas samples from Gvizd, Monastyrchany, Markova and Starunia (Nadzieja-1 well) accumulations from the Boryslav-Pokuttya Unit were collected and analysed (Kotarba *et al.*, 2005a). The Oligocene Menilite Shales source rocks from the Boryslav-Pokuttya and Skiba units were also examined (Figs 20–22).

The stable carbon isotope composition of saturate and aromatic hydrocarbons of oils evidences the presence of two oil families (Fig. 20G). One of them, depleted in ^{13}C isotope, consists of the Gvizd-200 oil and the second one comprises the remaining oils (Fig. 20G). No rocks correlating with the Gvizd-200 oil were sampled or analysed (Fig. 20G). All analysed Menilite samples correlate very well with oils forming the second family (Fig. 20G). The distinct oil was probably generated from other organic facies in the Menilite Shales, or similarly to oil collected from Vola Blazhivska-31 well, was generated by Mesozoic strata deposited in the Carpathian basement. The most probable source for this oil is the first solution because of the oil from Gvizd-200 has low sulphur content and was generated from organic matter deposited in shales (Kotarba *et al.*, 2005a). The sterane composition of all oils is similar and evidences correlation of all oils with the Menilite Shales from the Boryslav-Pokuttya and Skiba (Skole) units (Fig. 21G). Taking into consideration maturity indices (Fig. 22G), a direct correlation of oils and the Menilite Shales from the Boryslav-Pokuttya Unit is observed (Fig. 22G). The Menilite Shales from the Skiba Unit are immature for generation of liquid hydrocarbons (Fig. 22G).

Gases accumulated in the Oligocene and Eocene reservoirs of the Borislav-Pokuttya Unit were generated during low-temperature thermogenic processes (“oil window”) at a maturity level 0.7 to 0.9% on the vitrinite reflectance scale based on the assumption that Type-II/III kerogen occurs in the Menilite Shales (Kotarba *et al.*, 2005a).

MODELLING OF THE PETROLEUM PROCESSES

Both the 1-D and 2-D modelling of petroleum processes was carried out in sequences of twenty-seven wells and along nine cross-sections (Kosakowski & Wróbel, 2011; Kosakowski & Wróbel, in press; Kosakowski *et al.*, in press b; Wróbel *et al.*, in press; Wróbel *et al.*, 2010). Results of these modellings are discussed for the following deposits: Grobla-Pławowice (A), Łąkta-Tarnów (B), Jastrząbka Stara-Partynia Podborze (C), Pilzno-Będzienica (D1), Będzienica-Rzeszów (D2) and Lubaczów-Orkhovychi (E) zones (Fig. 19).

The Grobla-Pławowice zone (A)

Petroleum modelling in the Grobla zone indicated that the Devonian carbonates were the best source rocks for hydrocarbon generation (Wróbel, *et al.*, 2010). Maturity of the Devonian source rocks reached the late phase of the “oil window”. The maturity of Carboniferous source rock did not exceed 1.0% R_o. Generation of hydrocarbons started in the late Carboniferous, but the main stage took place in the late Neogene, during Miocene deposition in the Carpathian Foredeep basin of the Małopolska Block (Wróbel, *et al.*, 2010). The maximum amount of hydrocarbons generated from the Devonian source rocks reached 420 mg/g TOC (Figs 23A, 24A) whereas the volume of generated oil from the Carboniferous source horizon did not exceed 220 mg/g TOC (Fig. 23A).

The petroleum expulsion process occurred in the Devonian source rocks only. The highest volume of expelled hydrocarbons was noticed in the Grobla zone – up to 0.024 m^3/m^3 rock. The accumulation of hydrocarbons in the reservoir took place almost exclusively in the Miocene, during the overthrusting of the Carpathian tectonic units. Hydrocarbons were expelled from the Upper Palaeozoic strata and migrated to the Upper Jurassic and Upper Cretaceous structural and stratigraphic traps located in the tectonic blocks (Wróbel, *et al.*, 2010). Both the migration and accumulation processes proceeded also during the overthrusting of the Outer Carpathians. In the Grobla region, the Upper Jurassic carbonates and the Upper Cretaceous sandstones were characterized as best reservoirs (Myśliwiec *et al.*, 2006). Vertical migration connected with a dense fault system moved the hydrocarbon mass to the Upper Jurassic carbonates and the Upper Cretaceous sandstones. The volume of oil accumulation ranged to 0.45 m^3/m^3 rock, and the gas accumulation volume did not exceed 0.025 m^3/m^3 rock in the Grobla field zone (Fig. 25A).

The Łąkta-Tarnów (B) and Jastrząbka Stara-Partynia Podborze zones (C)

In the Łąkta-Partynia Podborze zone, the main source rocks occur in the Silurian succession, where they achieved maturity in the late phase of the “oil window”, similarly to the second analysed source rocks in the Carboniferous strata (Kosakowski & Wróbel, 2011; Wróbel, *et al.*, 2010; Wróbel *et al.*, in press). Hydrocarbon generation process started in the early Cretaceous, though the main phase of generation took place during the Neogene (Kosakowski & Wróbel, 2011; Wróbel *et al.*, in press). The maximum amount of generated oil reached 350 mg/g TOC whereas that of gas generation did not exceed 100 mg/g TOC (Figs 23B, 24B).

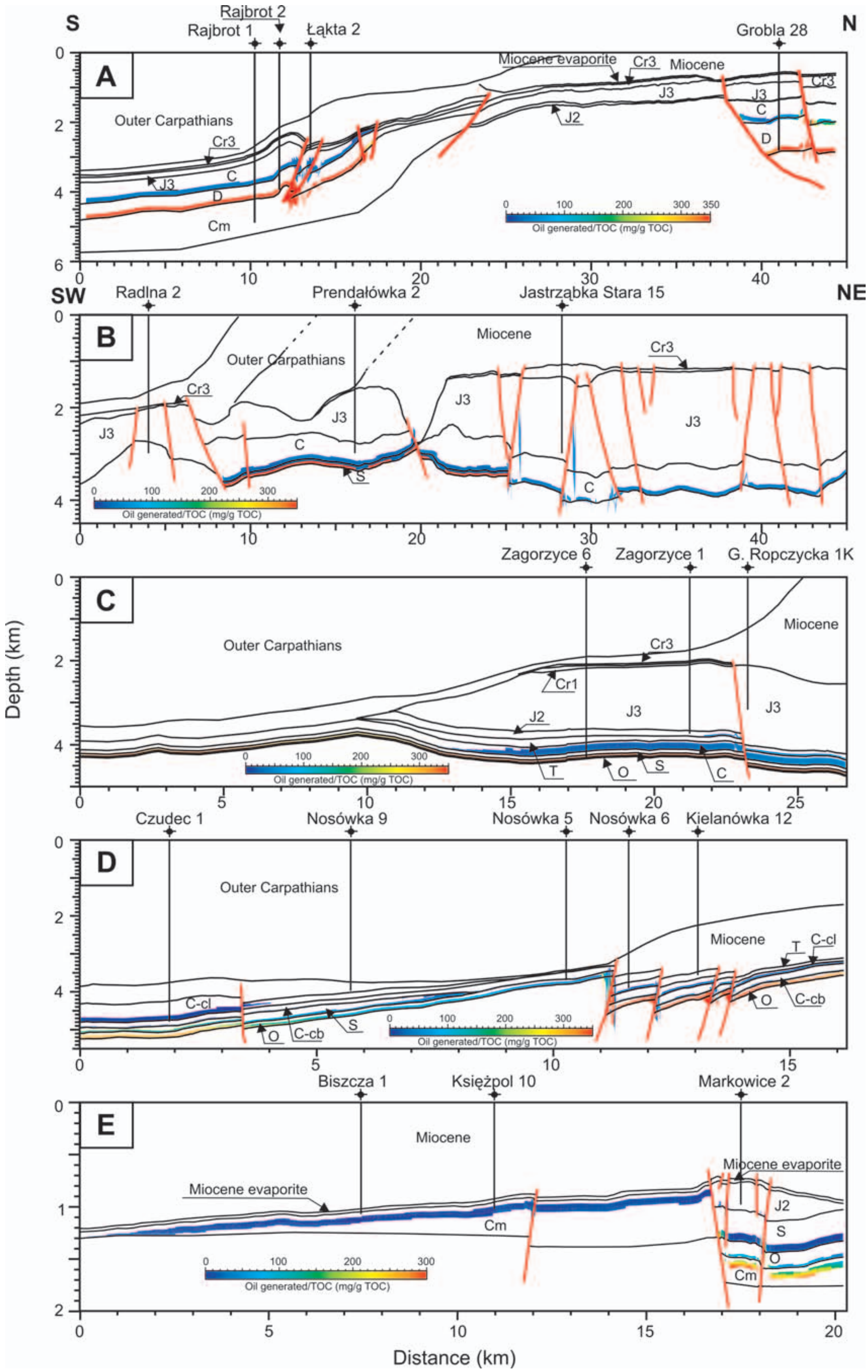

Fig. 23. Amount of generated oil along the I – I' **(A)**, II – II' **(B)**, III – III' **(C)**, IV – IV' **(D)**, and V – V' **(E)** cross-sections. Cr3 – Upper Cretaceous, Cr1 – Lower Cretaceous, J3 – Upper Jurassic, J2 – Middle Jurassic, T – Triassic, C – Carboniferous, Ccl – clastic facies of the Carboniferous, Ccb – carbonate facies of the Carboniferous, D – Devonian, S – Silurian, O – Ordovician, Cm – Cambrian. For location of cross-sections see Fig. 19. Some of the wells were projected on the cross-sections; for details see Wróbel *et al.* (in press)

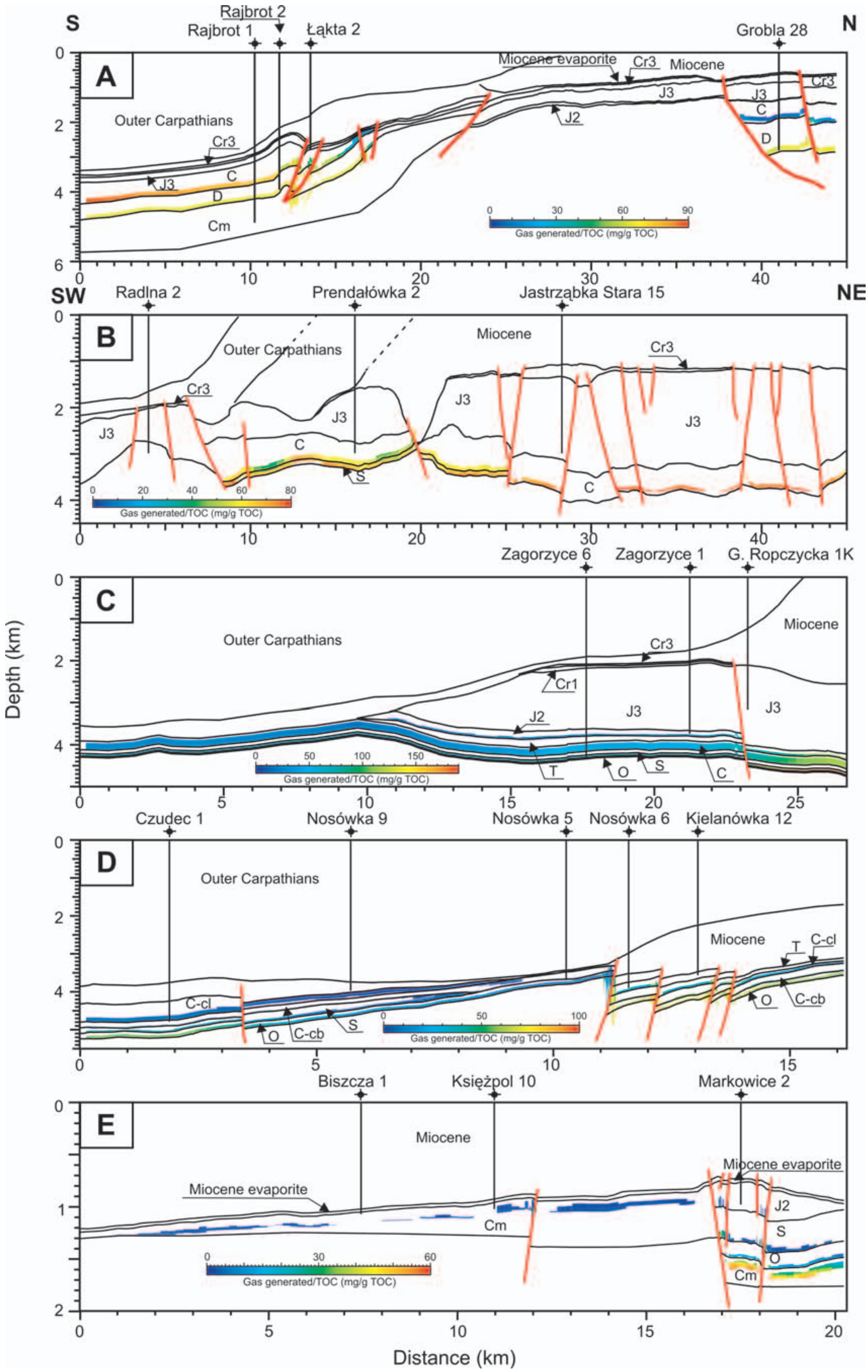

Fig. 24. Amount of generated gas along the I – I' **(A)**, II – II' **(B)**, III – III' **(C)**, IV – IV' **(D)**, and V – V' **(E)** cross-sections. For abbreviations see Fig. 23

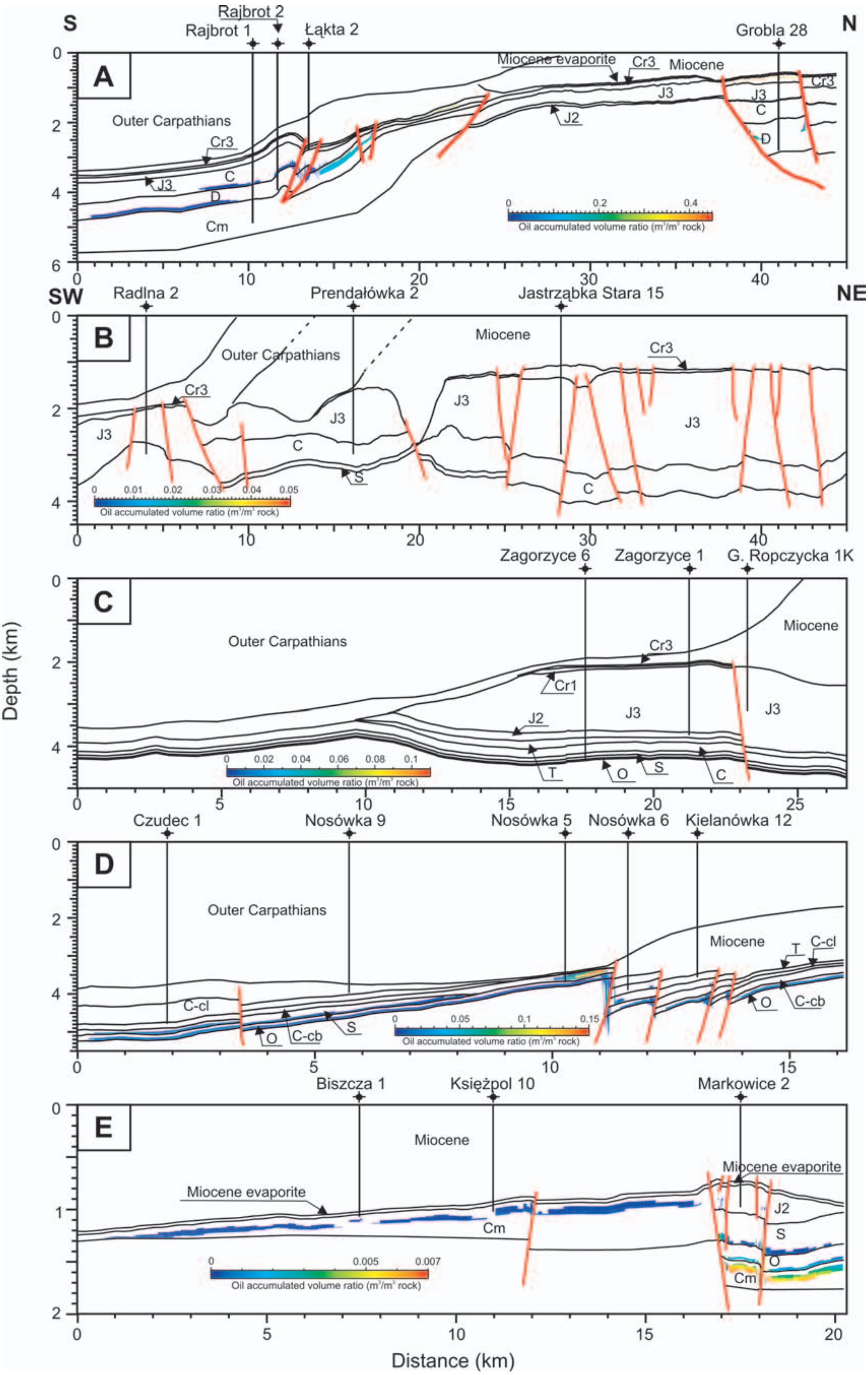

Fig. 25. The volume of oil accumulation along the I – I' **(A)**, II – II' **(B)**, III – III' **(C)**, IV – IV' **(D)**, and V – V' **(E)** cross-sections. For abbreviations see Fig. 23

The expulsion occurred only from the Silurian source rock and its maximum amounted up to 0.01 m^3/m^3 rock for oil and 0.01 m^3/m^3 rock for gas. The migration of both the oil and gas took place during the Miocene, and transferred hydrocarbons to the Upper Jurassic carbonates and the Upper Cretaceous sandstones. The accumulation of hydrocarbons in structural and stratigraphic traps took place in the Neogene during the overthrusting of the Outer Carpathian units (Wróbel *et al.*, in press). The oil accumulation amounted up to 0.05 m^3/m^3 rock and the gas accumulation volume reached 0.04 m^3/m^3 rock (Fig. 25B).

The Pilzno-Będzienica zone (D1)

In the Pilzno-Będzienica zone, the main source rocks were found within the Ordovician and Silurian successions. The organic matter attained maturity in the late phase of the "oil window" (Kosakowski & Wróbel, 2011). Hydrocarbon generation took place mainly during the late Jurassic and the early Cretaceous (Kosakowski & Wróbel, 2011; Wróbel *et al.*, in press). Maximum amount of generated oil reached 350 mg/g TOC and gas generation did not exceed 200 mg/g TOC (Figs 23C, 24C). The expulsion occurred only from the Upper Palaeozoic source rocks and its maximum amounted up to 0.04 m^3/m^3 rock for oil and 0.01 m^3/m^3 rock for gas. The migration of oil and gas took place during the Miocene, when hydrocarbons have travelled to the Upper Jurassic carbonates and sandstones. Accumulation of hydrocarbons in structural and stratigraphic traps coincided with the overthrusting of the Outer Carpathian flysch units (Wróbel *et al.*, in press). The amount of oil accumulation ranged from 0.05 to 0.25 m^3/m^3 rock, and the gas accumulation volume did not exceed 0.05 m^3/m^3 rock (Fig. 25C).

The Będzienica-Rzeszów zone (D2)

Like in the Pilzno-Będzienica zone, in the Będzienica-Rzeszów zone the main source rocks are located within the Ordovician and Silurian formations (Kosakowski & Wróbel, 2011). The petroleum processes had two significant periods of development: the Jurassic and the Neogene. In the north-eastern part of this zone, the analysed source rocks have already attained higher maturity in the Jurassic, while in the south-eastern part their maturity in the main phase of the "oil window" was reached at the end of the Neogene (Kosakowski & Wróbel, 2011; Wróbel *et al.*, in press). Hydrocarbon generation took place in both the Ordovician and the Silurian source rocks, and reached average values of 350 mg/g TOC of oil and 70 mg/g TOC of gas (Figs 23D, 24D). Hydrocarbons were expelled almost exclusively from the Ordovician and Silurian source horizons. The oil expulsion did not exceed 0.012 m^3/m^3 rock and the gas expulsion was about 0.004 m^3/m^3 rock. It is worth noting that in the Hermanowa area expulsion was absent. Hydrocarbons were accumulated in the Carboniferous carbonate facies to which migration took place during the overthrusting of the Outer Carpathian units (Wróbel *et al.*, in press). The volume of accumulated oil and gas did not exceed 0.2 m^3/m^3 rock (Fig. 25D).

The Lubaczów-Orkhovychi zone (E)

In the Lubaczów-Orkhovychi zone, the Cambrian, Ordovician, Silurian and Middle Jurassic source rocks were tested in the petroleum modelling. The petroleum processes were noticed in two periods. The first period lasted from the end of the Devonian till the end of the early Carboniferous, and the second one took place in the late Jurassic (Kosakowski *et al.*, in press, b). The Lower Palaeozoic source rocks reached the full range of the "oil window", and locally, even the "gas window" in the early Carboniferous. The transformation ratio of Cambrian kerogen varies from 30 to 100%. The highest transformation ratio was attained in the Łysogóry-Radom Block (Kosakowski *et al.*, in press, b). For the Ordovician and Silurian source rock, transformation reached 80% only in the central part of the study area, whereas in the northern and southern parts it was below 40% (Kosakowski *et al.*, in press, b). The highest oil and gas generation ratios were also noticed in the Łysogóry-Radom Block, and the maximum amount of generated hydrocarbons varied from 60 m/g TOC for Silurian source rocks to about 400 mg/g TOC for Cambrian and Ordovician source rocks (Figs 23E, 24E).

The maturity of the Middle Jurassic source rocks did not exceed 0.7% R_o (Kosakowski *et al.*, 2011). The maximum transformation ratio reached 50% and the amount of generated oil and gas did not exceed 70 mg/g TOC. The increase of maturity and intensity of generation process took place during the late Jurassic (Kosakowski *et al.*, 2011).

In the Ukrainian part of the study area, the results of geochemical analyses revealed that the Upper Jurassic strata have met the criteria for source rocks (Kosakowski *et al.*, 2011). The source rock horizons were found in, *e.g.*, the Korolyn-6, Mosty-2 and Voloshcha-1 wells (Fig. 19). The maturity of organic matter in the Upper Jurassic strata was similar to that in the Middle Jurassic succession. The Upper Jurassic source rocks locally exceeded 10% transformation ratio (Kosakowski *et al.*, 2011). The Upper Jurassic source rocks reached similar generation levels as the Middle Jurassic ones. The average amount of hydrocarbons generated from the Upper Jurassic source rocks was 100 mg HC/g TOC, with maximum expulsion of 30% (Kosakowski *et al.*, 2011).

The expulsion from all the modelled source rocks was low and appeared only locally in the Łysogóry-Radom Block (Kosakowski *et al.*, 2011). In most of the modelled source rocks, the expulsion threshold was not exceeded and the hydrocarbons remained within the source rocks. Thus, accumulation of hydrocarbons should be treated as saturation of the source horizons with generated but not expelled hydrocarbons. The hydrocarbon saturation was observed in both the Upper Palaeozoic and Middle Jurassic source rocks (Kosakowski *et al.*, in press, b). The volume of total oil and gas saturation did not exceed 0.01 m^3/m^3 rock in both the Cambrian and Ordovician strata; in the Silurian it amounted up to 0.0012 m^3/m^3 rock and in the Middle Jurassic it ranged from 0.0008 to 0.0025 m^3/m^3 rock (Fig. 25E).

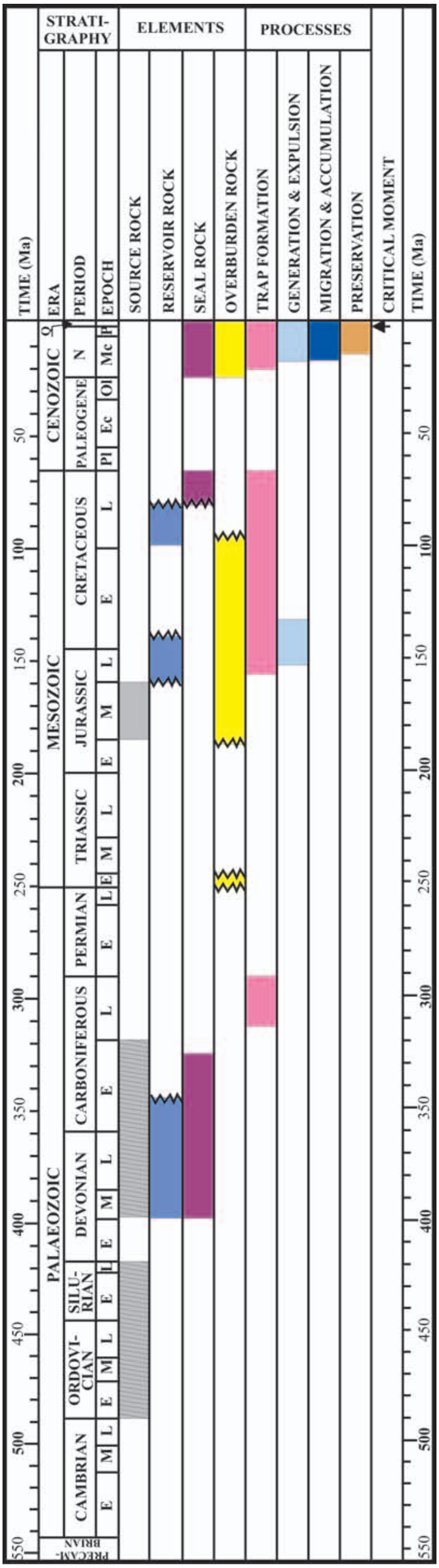

Fig. 26. Event chart of the Palaeozoic–Mesozoic petroleum system of the western part of the Małopolska Block. Pl – Palaeocene, Ec – Eocene, Ol – Oligocene, N – Neogene, Mc. – Miocene, P – Pliocene, Q – Quaternary, E – Early, M – Middle, L – Late

PETROLEUM SYSTEMS

The petroleum system is in use worldwide for oil and gas exploration (*e.g.,* Magoon & Dow, 1994; Biteau & Perrodon, 2003). With regard to differentiations of geological settings, elements (source, reservoir, seal and overburden rocks) and course of processes (generation, expulsion, migration and accumulation of hydrocarbons, and trap formation), two separate events charts for: (i) the Palaeozoic–Mesozoic petroleum system of the western part of the Małopolska Block (Figs 1, 26), and (ii) the Palaeozoic–Mesozoic petroleum system of the eastern part of the Małopolska Block and western part of the Kokhanivka Zone (SE Poland – western Ukraine) (Figs 1, 27) were prepared.

The petroleum system and hydrocarbon generation and expulsion areas were established based on all results of geochemical analyses of source rocks, oil and gas as well as source rock – oil – gas correlations, one- and two-dimensional modelling of petroleum processes and analyses of geological, reservoir and sealing conditions. Petroleum system in the Polish Outer Carpathians was worked out by Leśniak *et al.* (2010).

Palaeozoic–Mesozoic petroleum system of the western part of the Małopolska Block

In the Palaeozoic–Mesozoic petroleum system of the western part of the basement of the Carpathian Foredeep (region between Kraków and Rzeszów; Figs 1, 3, 19) five horizons of source rocks – the Ordovician, Silurian, carbonate Upper Devonian–Lower Carboniferous, clastic Lower Carboniferous and Middle Jurassic, were defined based on geochemical studies. Their geochemical characteristics and petroleum potential were widely described by Kosakowski *et al.* (in press, c) and Więcław *et al.* (2011).

The Silurian and Middle Jurassic strata contained the best source rock horizons (Fig. 26). The TOC content was up to 6.6 wt% in the Silurian claystones and siltstones, and ranged from few to 17 wt% in the Middle Jurassic claystones and siltstones (Kosakowski *et al.*, in press, c; Więcław *et al.*, 2011). The TOC content of the Ordovician carbonates and claystones reached maximally 2.9 wt%, but the median was below 0.3 wt%. The Devonian–Lower Carboniferous carbonates and Lower Carboniferous clastic complex had much lower quantities of organic carbon, but also in these strata levels with elevated TOC contents were observed (Więcław *et al.*, 2011).

The laboratory studies of reservoir parameters and interpreted well logs indicated that the best reservoir rocks in the study area were the Upper Jurassic carbonates and the Upper Cretaceous sandstones. In the Devonian–Lower Carboniferous carbonates, only locally the raise of the reservoir features and hydrocarbon saturation of reservoir were found (Kosakowski *et al.*, in press, a).

The autochthonous Miocene, covering the Palaeozoic and Mesozoic strata, played the role of the main seal rock and simultaneously was a very important reservoir rock for accumulations of microbial gases (Kotarba, 2011; Kotarba *et al.*, 2011). Locally, the seal was represented by Turonian and Santonian strata (Fig. 26).

The overburden rocks depended on the region, because the Mesozoic cover differed in its facies development, thickness, profile completeness, and also the structural plan of the Mesozoic deposits (Fig. 26). The present Mesozoic section consists of incomplete strata of the Lower Triassic, Middle and Upper Jurassic, Lower and Upper Cretaceous (Oszczypko *et al.*, 2006; Krajewski *et al.*, 2011a).

The time of trap formation was probably connected with two tectonic events (Fig. 26). The Variscan tectonic movements in the study area affected the Devonian and Carboniferous strata, and resulted in formation of traps mainly in the Devonian–Lower Carboniferous carbonates (Buła & Habryn, 2011). The Late Cretaceous–Early Palaeocene phase formed the Upper Jurassic, Lower and Upper Cretaceous structural-stratigraphic traps. The Miocene erosional troughs in the basement, fault zones and big organogenic buildups had the main influence on the formation of the Mesozoic traps (Myśliwiec *et al.*, 2006). The overthrusting of the Outer Carpathians also influenced the formation of traps.

The generation process for the Palaeozoic and Mesozoic source rocks took place mainly during the Neogene, though in the central part of study area the late Palaeozoic source rocks started the generation of hydrocarbons in the late Jurassic and lasted to the early Cretaceous. The generation process was renewed in the Miocene time during thrusting of the Outer Carpathian nappes over the autochthonous Miocene strata and the Palaeozoic–Mesozoic basement. The generation of hydrocarbons occurred from all five source rocks, but the highest one was observed from the Ordovician and Silurian source horizons (Kosakowski & Wróbel, 2011; Kosakowski & Wróbel, in press; Wróbel *et al.*, in press).

The expulsion processes occurred almost exclusively from the Ordovician and the Silurian source rocks (Fig. 26). This process began in the early Cretaceous, but the maximum expulsion was achieved in the Neogene (Kosakowski & Wróbel, 2011; Wróbel *et al.*, in press). The expulsion from the Devonian and Carboniferous source rocks was not significant. In the Jurassic source rocks, expulsion was observed only in the Ukrainian part of the eastern part of the Małopolska Block and the western part of the Kokhanivka Zone (Kosakowski *et al.*, 2011).

The migration process took place during Miocene and Pliocene time and was strictly connected with the fault system and the Carpathian Overthrust (Wróbel *et al.*, in press). The hydrocarbons expelled from the Lower Palaeozoic source rocks migrated along the fault surface to the top of anticlinal structures and were accumulated in the Devonian–Lower Carboniferous or Upper Jurassic–Upper Cretaceous strata.

It was found out that the preservation time and critical moment occurred after the formation of the Carpathian Overthrust.

The above mentioned oil-source rock and gas-source rock correlations indicate that the Palaeozoic–Mesozoic petroleum system of the western part of the Carpathian Foredeep represents a known petroleum system, after criteria introduced by Magoon and Dow (1994).

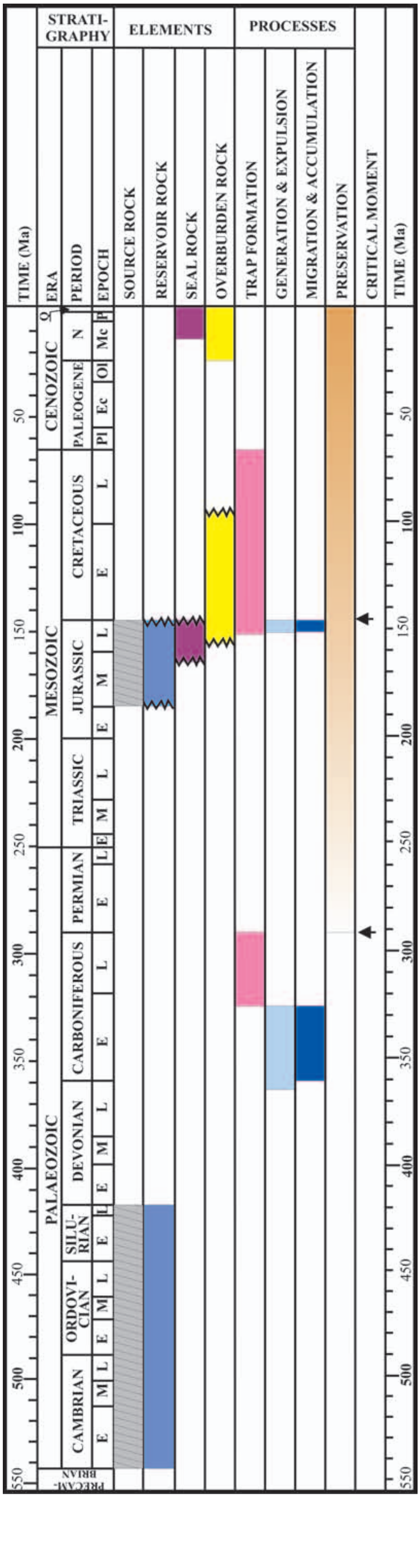

Fig. 27. Event chart of the Palaeozoic–Mesozoic petroleum system of the basement of the Carpathian Foredeep. Pl – Palaeocene, Ec – Eocene, Ol – Oligocene, N – Neogene, Mc. – Miocene, P – Pliocene, Q – Quaternary, E – Early, M – Middle, L – Late

Palaeozoic–Mesozoic petroleum system of the eastern part of the Małopolska Block and the western part of the Kokhanivka Zone (south-eastern Poland – western Ukraine)

The Palaeozoic–Mesozoic petroleum system of the basement of the Carpathian Foredeep comprises the Kielce Fold Belt (Poland) and Kokhanivka Zone (Ukraine), as well as Łysogóry-Radom Block (Poland) and Rava Rus'ka Zone (Ukraine) between the Krakoviec Fault and the Nowe Miasto-Radom-Rus'ka Fault (Fig. 1). Four source rocks horizons – the Cambrian, Ordovician, Silurian and Middle Jurassic ones, were defined there based on the results of geochemical studies (Fig. 27). Their petroleum characteristics and potential were widely described by Kosakowski *et al.* (in press, d) and Więcław *et al.* (in press, a).

The Cambrian and Ordovician source rocks have a low TOC content below 1 wt%, and only the TOC content for Silurian source rocks reaches up to 2.6 wt% (Więcław *et al.*, in press, a). The Middle Jurassic source rocks have good quantitative sourceness, but it is reduced by low hydrocarbon potential, usually below 100 mg HC/g TOC (Kosakowski *et al.*, in press, d). In the Ukrainian part of the study area, also the Upper Jurassic strata contained good source rock horizons (Kosakowski *et al.*, in press, d).

In the study area, the Cambrian, Ordovician, Silurian, Middle and Upper Jurassic strata have reservoir rock horizons. Their reservoir properties were presented by Karnkowski (1999) and Kurovets *et al.* (2011). The Lower Palaeozoic reservoir rocks had weak reservoir features; the porosity did not exceed 10 %. In the Middle and Upper Jurassic strata good reservoir properties were observed and then confirmed for the Mesozoic complex by well logs (Kosakowski *et al.*, in press, a).

The main seal was created by the autochthonous Miocene strata, the thickness of which could reach even 5,000 m (Kurovets *et al.*, 2004). Locally, the seal was created by the Upper Jurassic carbonates. The overburden rocks were also Miocene strata, but in the north-eastern side of the Holy Cross Fault Zone the Upper Jurassic and the Cretaceous strata (Krajewski *et al.*, 2011b) were partly present.

The tectonic movements influenced the trap formation. Variscan movements comprised the Devonian and Lower Carboniferous strata. The Variscan uplift and erosion took place during late Carboniferous time (Buła & Habryn, 2011) and was responsible for the formation and/or destruction of the Palaeozoic traps . The following uplift and erosion took place after Jurassic and after Cretaceous times (Oszczypko *et al.*, 2006) and caused formation and destruction of the Mesozoic traps.

The generation process took place from the end of the Devonian to the end of the early Carboniferous for the Lower Palaeozoic source rocks, and during the late Jurassic – early Cretaceous for the Middle and Upper Jurassic source rocks. A slight, local expulsion was observed for all four source rocks in the analysed area (Kosakowski *et al.*, in press, b). Insignificant expulsion was observed in the Jurassic source rocks (Kosakowski *et al.*, 2011). The amount of hydrocarbons expelled from the source rocks even reached 30% of generated hydrocarbons. The effect of a small amount of expelled hydrocarbons was the presence of only small accumulations, like the Lubaczów-Kokhanivka and Orkchovychi deposits.

No migration process was observed, and the accumulation was a result of saturation by hydrocarbons generated from source rocks. The time of saturation was concurrent with the generation process (Kosakowski *et al.*, in press, b).

The preservation time had a long time interval from the late Carboniferous till present, with two critical moments. Critical moments were assumed at the end of the Variscan inversion of the study area and at the end of the late Cretaceous–early Palaeocene uplift and erosion. These two moments took place at the end of the generation process. The lack of the remaining petroleum processes caused that the petroleum system in the study area was almost complete in these two moments.

The ambiguous petroleum-source rocks correlation, caused by insufficient information about the Lower Palaeozoic source rocks in the Ukrainian part of study area, made the recognition of the Palaeozoic–Mesozoic petroleum system a little more credible. Due to this petroleum system of SE Poland – western Ukraine could be distinguished as a hypothetical petroleum system after criteria introduced by Magoon and Dow (1994).

DETERMINATION OF HYDROCARBON GENERATION AND EXPULSION AREAS – SUMMARY

The comparison of Palaeozoic–Mesozoic petroleum systems reveals that the western part of the Małopolska Block has a considerably greater prospective for oil and gas exploration than the eastern part of the Małopolska Block and the western part of the Kokhanivka Zone. Based on the results of geochemical analyses conducted for Palaeozoic (Więcław *et al.*, 2011; Więcław *et al.*, in press) and Mesozoic (Kosakowski *et al.*, in press, c, d) source rocks, results of 1-D (Kosakowski & Wróbel, 2011; Kosakowski & Wróbel, in press; Kosakowski *et al.*, 2011; Kosakowski *et al.*, in press, b) and 2-D (Kosakowski *et al.*, in press, b; Wróbel *et al.*, in press) modelling of petroleum processes, and analysis of petroleum systems, nine areas were established where hydrocarbon generation and expulsion processes at the largest scale proceeded (Fig. 28). Seven generation and expulsion areas occur in the western part of the Małopolska Block and only two areas exist within the basement of the Carpathian Foredeep in south-eastern Poland and western Ukraine. These areas could be a starting point for determining prospective zones for petroleum exploration.

I area

This area lies beneath the Carpathian Overthrust at the border of the Upper Silesian and Małopolska blocks (Figs 1, 28). The source rock horizons are hosted in the Devonian and Carboniferous strata. The Devonian carbonates are usually poor in organic carbon content. Oil-prone kerogen is mature for generation of thermogenic hydrocarbons (Kotarba *et al.*, 2001). The Lower Carboniferous clastic and carbonate rocks have changeable contents of early- or mid-mature gas-prone organic matter. In the Upper Carbonifer-

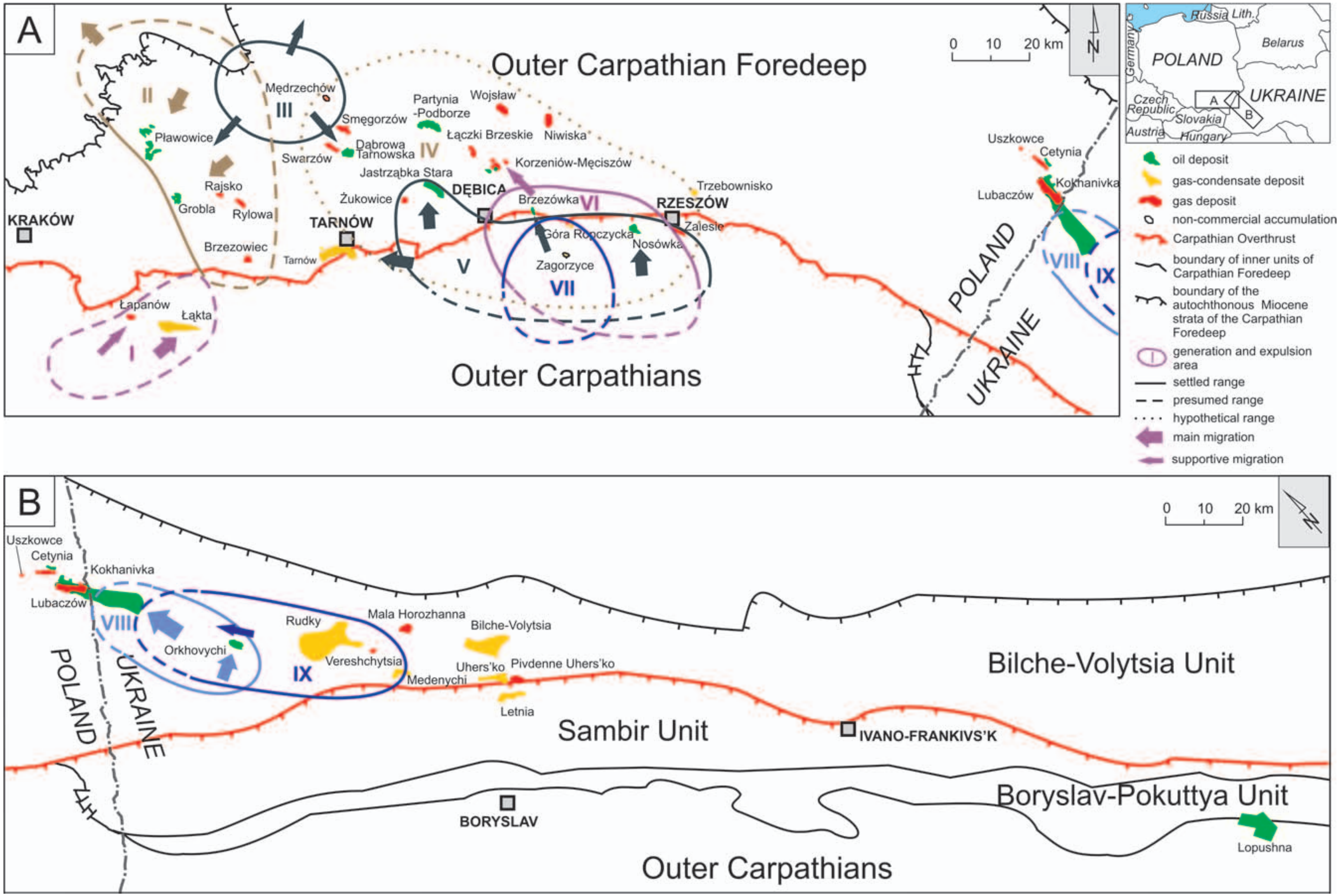

Fig. 28. Sketch map of location of generation and expulsion areas and the oil, gas-condensate and gas deposits (see Fig. 3) in **(A)** the Palaeozoic–Mesozoic basement of the Polish and **(B)** Ukrainian parts of the Carpathian Foredeep. Main source rocks in generation and expulsion areas: I – Lower and Upper Carboniferous, II – Middle-Upper Devonian and Lower Carboniferous (?), III – Ordovician and Silurian, IV – Devonian, V – Ordovician and Silurian, VI – Lower Carboniferous, VII – Middle Jurassic, VIII – Upper Jurassic, IX – Middle Jurassic. Lith. – Lithuania

ous strata, lenses of bituminous coals were recorded (Kotarba *et al.*, 2004b). Generation of hydrocarbons started in the late Carboniferous, but the main stage of this process took place during the overthrusting of the Outer Carpathians on the Upper Silesian Block. The petroleum expulsion process proceeded from the Devonian and Carboniferous source rocks, but the expulsion from the Carboniferous source horizon was repeatedly smaller. The migration connected with intensive fault system moved the expelled oil to the Upper Jurassic carbonates and the Upper Cretaceous sandstones. The accumulation of hydrocarbons in the reservoir also took place during overthrusting of the Carpathian nappes in the Miocene time. Condensate and gas accumulated in the Łąkta deposit were most probably generated from Type-III kerogen contained in Carboniferous strata.

II area

The source rock horizons of the II area (Fig. 28) are hosted in the Middle and Upper Devonian and locally in the Lower Carboniferous strata. They are usually poor in organic matter content, but horizons of elevated TOC contents are recorded. In Devonian strata oil-prone organic matter occurs and in Carboniferous gas-prone one dominates. The maturity of the whole complex corresponds with the middle or final phase of the "oil window". Generation of hydrocarbons from the Devonian and Lower Carboniferous source rocks started in the late Carboniferous, but the main stage of this process took place in the late Neogene during the deposition of the autochthonous Miocene strata in the Małopolska Block. The petroleum expulsion process occurred only from the Devonian source rock. Vertical migration connected with intensive fault system moved the hydrocarbon mass to the Upper Jurassic carbonates and the Upper Cretaceous sandstones. The migration and accumulation processes occurred during the overthrusting of the Outer Carpathians. Thermogenic liquid and gas hydrocarbons generated and expelled from the Middle and Upper Devonian source rocks in this area filled the traps of the Grobla and Pławowice oil deposits and the Rajskie and Rylowa gas fields. The Cenomanian trap of the Brzezowiec deposit was filled up with microbial gas, which migrated from the autochthonous Miocene strata.

III area

The Ordovician and Silurian source rocks in the III area (Fig. 28) are usually rich in TOC. The maturity of the oil-prone Type-II kerogen present in these strata corresponds with the middle phase of the "oil window" and increases in the NW direction. Generation and expulsion of hydrocarbons from the Silurian source rock took place in the late Carboniferous. All petroleum processes ended with the beginning of the Variscan tectonic rebuilding. Thermogenic liquid and gas hydrocarbons generated and expelled from the Ordovician and Silurian source rocks in this area could have filled up at least partly the traps of the Dąbrowa Tarnowska and Grobla oil deposits.

IV area

The Devonian strata are probably the perspective source rocks in the IV area (Fig. 28). The geochemical characteristic of this level was conducted only in a restricted area in the vicinity of Rzeszów (Więcław *et al.*, 2011; Matyasik *et al.*, 2004). The present oil-prone Type-II kerogen is mature for generation of thermogenic hydrocarbons (early and middle phase of the "oil window"). The range of this perspective generation and expulsion area is hypothetical and needs additional geochemical studies. Probably, hydrocarbons generated and expelled from the Devonian source rocks at least partly filled the traps of all oil deposits in this area.

V area

The Ordovician and Silurian strata in the V area (Fig. 28) are rich in organic matter content. The best source rocks occur in the southern part of the area. Oil-prone kerogen has high hydrocarbon potential at maturity level corresponding with the initial and middle phase of the low-temperature thermogenic processes ("oil window"). The generation process started at the turn of the late Jurassic and early Cretaceous, though the main phase of generation took place during the Neogene. The expulsion occurred from both the Silurian and Ordovician source rocks. The expulsion started in the Miocene time. The migration of oil and gas took place during the Miocene, and moved hydrocarbons to the Upper Jurassic carbonates and the Upper Cretaceous sandstones. The accumulation of hydrocarbons in structural, anticlinal traps occurred during the overthrusting of the Outer Carpathians in Miocene time. Thermogenic liquid and gas hydrocarbons generated and expelled from the Ordovician and Silurian source rocks in this area probably filled up the traps of Nosówka and, at least partly, Jastrząbka Stara and Brzezówka oil deposits.

VI area

The Lower Carboniferous clastic source rocks in the VI area (Fig. 28) have the TOC content of *ca.* 1 wt%. Low hydrocarbon potential usually below 100 mg HC/g TOC evidences domination of gas-prone Type-III kerogen. Maturity of the organic matter corresponds with the middle phase of the "oil window". The petroleum processes had two significant periods of development: the Jurassic and the Neogene. In the north-eastern part of the VI area, the Lower Carboniferous source rocks started generation already in the Jurassic, while in the south-eastern part in the end of the Neogene. The magnitude of generation differs over the VI area, with the biggest intensity in Góra Ropczycka-Zagorzyce region. Expulsion was slight and also local in character. Hydrocarbons were accumulated in the carbonate strata of the Carboniferous, and the migration took place during overthrusting of the Outer Carpathians.

VII area

The VII area (Fig. 28) represents an exceptional place in the Polish part of the Carpathian Foredeep basement, where the Middle Jurassic strata have sufficient maturity for thermogenic hydrocarbons generation. Also, TOC content is high there, *i.e.* up to 3.2 wt%, but low hydrocarbon potential shows that only gaseous hydrocarbons may be generated from these strata. The generation process from the Middle Jurassic source rock took place during the Miocene time. The expulsion process has not been observed there.

VIII area

The Upper Jurassic strata in the VIII area (Fig. 28) have high organic carbon contents, up to 1.7 wt%. Also, the highest hydrocarbon potential, up to 375 mg HC/g TOC, is observed identifying the highest share of the oil-prone Type-II kerogen. The maturity of these strata corresponds with transition from microbial to low-temperature thermogenic processes, though the presence of high-reactive Type-IIS kerogen suggests that the Upper Jurassic source rocks are capable of generating thermogenic oil and gas. The generation process from the Upper Jurassic source rock took place from the end of the late Jurassic to the end of the overthrusting of the Outer Carpathians in the Miocene. Expulsion from this source rock occurred at the end of the overthrusting. Thermogenic liquid and gas hydrocarbons generated and expelled from the Upper Jurassic source rocks in this area filled up the traps of the Lubaczów-Kokhanivka and Orkhovychi oil fields. The Upper Jurassic trap of the block of the Lubaczów deposit (L-22 well) was filled up with microbial gas, which migrated from the autochthonous Miocene strata.

IX area

In the Middle Jurassic strata, the TOC content generally exceeds 1 wt% in the IX area (Fig. 28). Hydrocarbon potential of dispersed organic matter is generally low and usually does not exceed 100 mg HC/g TOC (Fig. 14) pointing to the presence of gas-prone Type-III kerogen there. Maturity of organic matter changes from 0.6 to 0.8% in the vitrinite reflectance scale, evidencing its capability for generation of low-temperature thermogenic hydrocarbons ("oil window"). The highest maturity was recorded in the most buried areas below the Carpathian Overthrust. Generation process from the Middle Jurassic source rocks took place from the end of the late Jurassic to the end of overthrusting of the Outer Carpathians in Miocene times. Most of the generation process occurred during the overthrusting. No expulsion has been observed since the Middle Jurassic in this area.

Acknowledgements

The research was undertaken as the project No. UKRAINE/193/2006 of the Ministry of Science and Higher Education carried out at the AGH University of Science and Technology in Kraków and the Polish Geological Institute – National Research Institute in Warsaw. Scientific work was financed from the funds in the years 2007–2010. Paweł Karnkowski, Frank Picha and Andrzej Ślączka provided very constructive reviews, which greatly improved the discussion and working hypotheses presented in the manuscript. We also thank Mark Pawlewicz of the U. S. Geological Survey in Denver for improvement of English manuscript. Technical editorial work by Joanna Gawęda-Skrok, Marek Hajto, Tomasz Kowalski, Hieronim Zych and Sebastian Ptak from the AGH University of Science and Technology in Kraków is gratefully acknowledged. The authors would like to thank Mr. Andrzej Urbaniec and Ms. Agnieszka Kowalska-Skulig from the Sanok Branch of Polish Oil & Gas Company for providing archival information about oil and gas deposits.

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