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MICROBIAL GAS SYSTEM AND PROSPECTIVES OF HYDROCARBON EXPLORATION IN MIOCENE STRATA OF THE POLISH AND UKRAINIAN CARPATHIAN FOREDEEP

Maciej J. KOTARBA[1], Tadeusz M. PERYT[2] & Yuriy V. KOLTUN[3]

[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, Rakowiecka 4, 00-975 Warsaw, Poland, e-mail: tadeusz.peryt@pgi.gov.pl*
[3] *National Academy of Sciences of Ukraine, Institute of Geology and Geochemistry of Combustible Minerals, Naukova 3a, 79060 Lviv, Ukraine*

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Abstract: Molecular composition of natural gases accumulated in autochthonous Miocene strata of the Polish and Ukrainian Carpathian Foredeep is dominated by methane, which usually constitutes over 98 vol%. Methane was generated by the carbon dioxide reduction pathway of microbial processes. Ethane was generated both during microbial and thermogenic processes ("oil window") and propane at the initial stage of the low-temperature thermogenic processes, and also by the microbial processes. The rhythmic and cyclic deposition of Miocene clays and sands as well as the vigorous generation of microbial methane caused that the gas produced in claystone beds was accumulated in the overlaying sandstones, and capped, in turn, by the succeeding claystones. Such generation and accumulation system of microbial gases gave rise to the formation of multi-horizontal gas fields. Analysis of the distribution of immature humic dispersed organic matter in the Upper Badenian and Lower Sarmatian sequences indicates that it is practically homogeneous. A migration range of microbial gases was insignificant and locations of their accumulations would depend only on the existence of proper type of traps (compactional anticlines situated above basement uplifts, sealed by the Carpathian Overthrust and/or by faults; stratigraphic pinching out and stratigraphic traps related to unconformities). Another situation is encountered in the south, beneath the Carpathian Overthrust. The thickness of the autochthonous Miocene strata in this area is more than 1,500 metres. Geochemical studies reveal that from a depth of 2,500 metres starts the process of low-temperature thermogenic hydrocarbon generation ("oil window"). At greater depths, more than 7,500 metres, within the autochthonous Lower Miocene basin only the high-temperature methane ("gas window") could be produced and accumulated.

Key words: microbial gas, thermogenic gas, source rocks, hydrocarbon potential, organic geochemistry, prospectives of hydrocarbon exploration, autochthonous Miocene strata, Bilche-Volytsia Unit, Carpathian Foredeep, SW Poland, western Ukraine.

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INTRODUCTION

The main objective of our study is to present the hydrocarbon potential and geochemical characteristics of dispersed organic matter, origin of natural gases, model of microbial gas generation and prospectives of hydrocarbon exploration for the autochthonous Miocene strata of the Polish (Fig. 1A) and Ukrainian Carpathian Foredeep (Fig. 1B) between Kraków and Stryi.

Previous geochemical characteristics of dispersed organic matter were described by Kotarba *et al.* (1998b, 2005) and preliminary model of microbial and thermogenic gas generation by Kotarba *et al.* (1998a). Molecular and isotopic studies of natural gases accumulated within the autochthonous Miocene strata of the Polish and Ukrainian Carpathian Foredeep were presented by Głogoczowski (1976), Calikowski (1983), Jawor and Kotarba (1993), Kotarba (1992, 1998, 2011), Kotarba and Jawor (1993), Kotarba and Koltun (2006, 2011), Kotarba *et al.* (1987, 2005) and Shabo and Mamchur (1984).

GEOLOGICAL SETTING

The Carpathian Foredeep developed during the early and middle Miocene as a peripheral flexural foreland basin

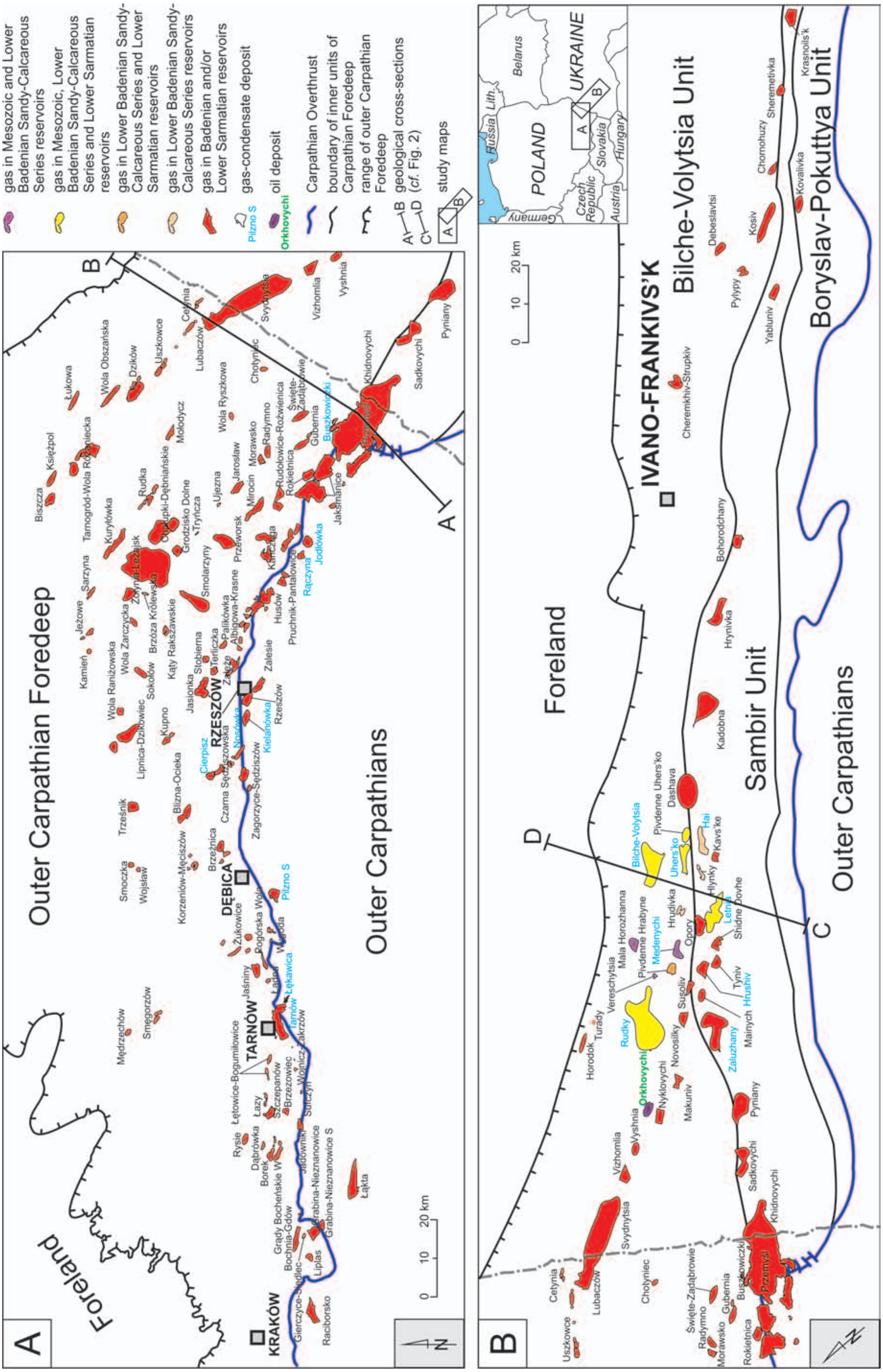

Fig. 1. Sketch map of location of gas and gas-condensate fields in the autochthonous Miocene strata of **(A)** the Polish and **(B)** Ukrainian parts of the Carpathian Foredeep

in front of the advancing Carpathian Overthrust (Oszczypko *et al.*, 2006). The highly complex epi-Variscan platform and its Permian–Mesozoic cover form the basement of the Carpathian Foredeep (Karnkowski, 1974; Danysh *et al.*, 2004; Oszczypko *et al.*, 2006; Buła & Habryn, 2011). The epi-Variscan platform developed on consolidated Proterozoic crystalline rocks and Proterozoic–Lower Palaeozoic metasedimentary rocks. In the area adjacent to the Polish-Ukrainian border, the Carpathian Foredeep is superimposed on the NW–SE trending Teisseyre–Tornquist Zone, a major crustal boundary between the West- and the East-European Cratons (Oszczypko *et al.*, 2006). This complex structure controlled the subsequent evolution, and in particular in the Polish-Ukrainian border area where during final, Badenian–Sarmatian development, the inherited Mesozoic rift-related tectonic zone was reactivated due to the combined effect of thrust wedge emplacement and slab-pull of foreland plate; this zone focused Miocene extension related to the flexure of the Carpathian foreland plate (Krzywiec, 1999).

The Carpathian Foredeep basin can be subdivided, based on the tectonic style and type of sediments, into two parts: inner and outer. The inner foredeep is located at the front and beneath the Carpathian Overthrust and is characterized by strongly folded Eggenburgian–Badenian strata: Sambir (Stebnik) Nappe and Zgłobice thrust-sheets in Poland and Boryslav-Pokuttya and Sambir Nappes in the Ukraine (Andreyeva-Grigorovich *et al.*, 1997, 2008); it contains up to 1,500 m of Lower to Middle Miocene autochthonous deposits that are overridden by thrust sheets (Oszczypko, 2006a, b; Oszczypko *et al.*, 2006). The outer foredeep (termed the Bilche-Volytsia zone in the Ukraine) is filled with generally undisturbed, flat-lying Middle Miocene (Badenian and Sarmatian) marine deposits, which range in thickness from a few hundred metres in the northern, marginal parts of the Foredeep to as much as 3.5 km in SE Poland (Wielkie Oczy graben – Oszczypko *et al.*, 2006) and 5 km in western Ukraine (Krukenychy Depression – Kurovets *et al.*, 2004). General structure of the Polish (Stebnik Unit and the Outer Carpathian Foredeep basin) and Ukrainian (Boryslav-Pokuttya, Sambir and Bilche-Volytsia units) parts of the Carpathian Foredeep is presented in Fig. 2A and Fig. 2B, respectively.

The Lower Miocene deposits of the Carpathian Foredeep formed a clastic wedge along the Carpathians, comparable with the Lower Freshwater Molasse of the Alpine Foreland (Oszczypko *et al.*, 2006); they formed from relatively shallow subaqueous turbidite currents as well as from subaerial debris flows. The early Badenian regional transgression (Oszczypko, 1998) resulted in variations in the palaeobathymetry of the early Badenian basin between upper bathyal depths in the axis of the basin to neritic and littoral ones in the marginal parts. The deepest part of the basin, which reached midbathyal depths, was located about 20 km south of the present-day position of the Carpathian front and it was dominated by deposition of dark-grey calcareous mudstones with sporadic intercalations of fine sandstones (Skawina, Balych and Bohorodchany formations; Oszczypko *et al.*, 2006). Some deposits revealed basinal turbidite characteristics, and the southern slope and its shelf with small embayments are dominated by calcareous mudstones (Oszczypko *et al.*, 2006).

There were three periods of intense foreland subsidence, namely during the early Miocene, early Badenian, and late Badenian to Sarmatian times. The Miocene convergence of the Carpathian wedge with the foreland caused outward migration of the depocentre of the foredeep and in its distal parts onlapping of successively younger deposits onto the foreland (Oszczypko, 2006a). Subsequent erosion was calculated, based on illite/smectite diagenesis, at some 400–800 m in SE Poland (Dudek, 1999).

The discussed area of the Carpathian Foredeep, subdivided by the Rzeszów Palaeoridge into the western and eastern parts (Oszczypko, 1999), contains a reduced section of the lower and middle parts of the Badenian section.

In the western part of the Carpathian Foredeep, the most widespread Lower Badenian unit is the Skawina Formation – deep-water, clayey-marly and clayey-muddy deposits with intercalations of sands and gravels that increase in abundance towards the south (Garlicki, 1979); the thickness of the Skawina Formation ranges from several tens of metres in the northern part of the foredeep to 800 m in the Gdów Bay (Ney *et al.*, 1974; Garlicki, 1979). It is followed by the Wieliczka Formation (30–100 m thick) composed of chlorides with siliciclastic intercalations accompanied by tuffites and bentonites. The Wieliczka Formation occurs along the Carpathian Overthrust and towards the north is passing into the Krzyżanowice Formation, mainly composed of laminated anhydrites 10–30 m thick (Peryt, 2000). The evaporites are overlain by the deposits of the Machów Formation – mostly marly clays with laminae and intercalations of fine-grained sandstones. The thickness of this formation, that includes the Upper Badenian and the Sarmatian, may reach 2000 m between Tarnów and Dąbrowa Tarnowska (Ney *et al.*, 1974; Krzywiec *et al.*, 2008).

In the area of the Rzeszów Palaeoridge, the substrate is covered by the Upper Badenian Grabowiec beds (60–300 m thick) – clayey-muddy deposits with tuffites and bentonites and local sandy intercalations, followed by a considerably thicker (1,000–2,000 m) complex of the Krakowiec beds having a similar lithology but included into the Sarmatian. South of the Rzeszów Palaeoridge, also older Badenian strata occur below the Grabowiec beds: Chodenice beds (up to 50 m thick), evaporites of the Krzyżanowice and Wieliczka formations (up to 30 m thick), and Skawina Formation (0– 150 m thick) (Kotlarczyk, 1991).

East of the Rzeszów Palaeoridge, the Badenian section begins with the Pińczów Formation in Poland and the Zhuriv Formation in the Ukraine (both formations in the older literature were also termed the Baranów beds) – quartz sandstones, sandy clays and clays, with common basal conglomerates. The thickness of the Baranów beds varies usually from several to 90 m, and increases towards the north and the east. They are overlain by laminated and brecciated anhydrites of the Krzyżanowice Formation (in Poland) and Tyras Formation (in the Ukraine), a few to over 40 metres thick, and these in turn by the clayey-marly and sandy deposits of the Machów Formation in Poland. Its lower member is the Spirialis Clays Member (100 m thick), passing toward the margin of the basin into the Pecten Clays

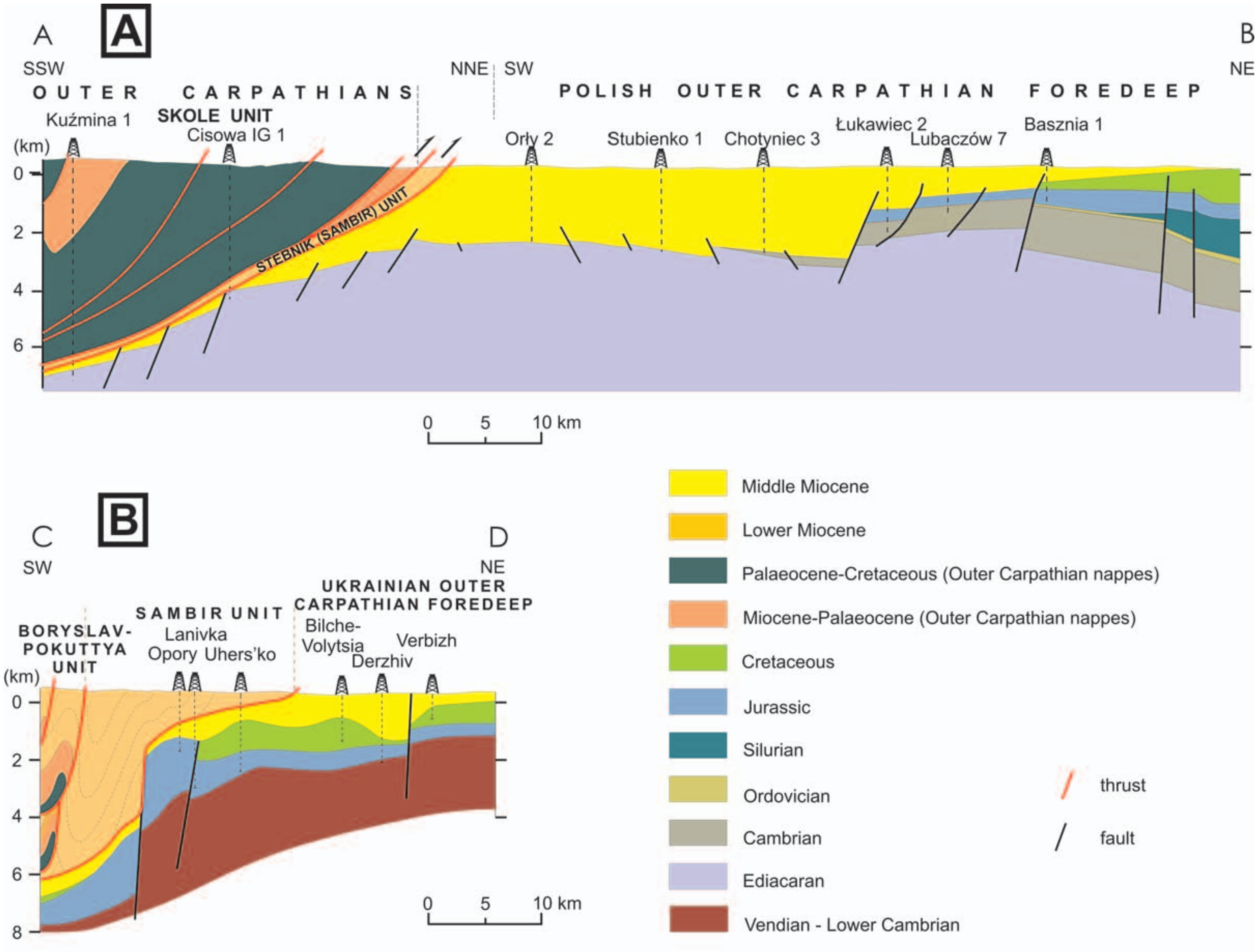

Fig. 2. Geological cross-sections through **(A)** the Polish and **(B)** Ukrainian parts of the Carpathian Foredeep; after Oszczypko *et al.* (2006), modified by authors. See Fig. 1 for location

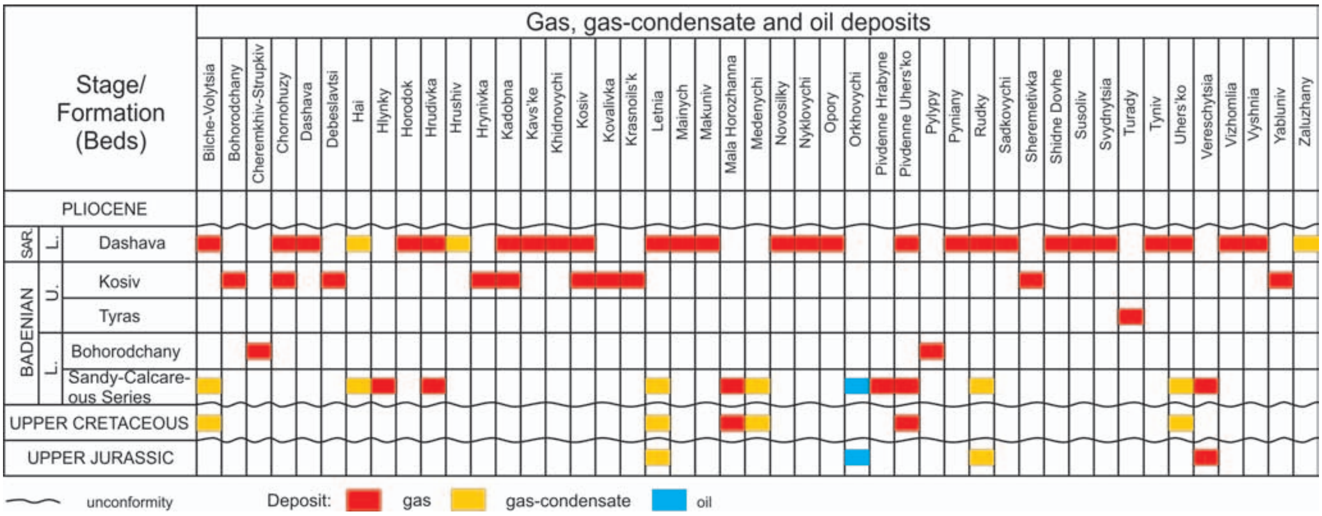

Fig. 3. Distribution of gas, gas-condensate and oil deposits of the lithostratigraphic formations of the Ukrainian Carpathian Foredeep. L. – Lower, U. – Upper

and Marls Member (Ney, 1969). The upper, Sarmatian part of the Machów Formation is composed of the Krakovets Clays (Ney *et al.*, 1974) that in the northern part of the foredeep are developed as the Syndesmia Clays Member (Ney, 1969). The thickness of the beds ranges from 200 m near Biłgoraj to 2,400 m in the Przemyśl region. The series consists mostly of clays with sandy laminae and towards the south the frequency and thickness of the sandy occurrences increase: they were interpreted as widespread delta deposits (Jawor, 1983; Karnkowski, 1989). In the Ukraine, the Upper Badenian strata are included into the Kosiv Formation (10–150 m thick) and the Sarmatian strata into the Dashava Formation that is further subdivided into two parts, the lower part (up to 3,500 m thick) and the upper part (up to 1,500 m thick) (see for details Kurovets *et al.*, 2004). The marginal facies of the Dashava Formation contains intercalations of limestones within mostly clayey series; it is up to 120 m thick and is termed the Volhynian beds.

In some well profiles of the Bilche-Volytsia Unit, various siliciclastic, often conglomerates and breccias, and carbonate deposits occur that are commonly regarded in the geological unpublished documentations as well as in the syntheses based on those documentations (*e.g.*, Vul *et al.*, 1998a; Krups'kyy, 2001) to be of Karpatian (and/or Palaeogene) age. These deposits are recently included into the Sandy-Calcareous Series and its Karpatian age is concluded (Vashchenko *et al.*, 2007), but the fossils quoted as supporters of such an age assignment have long ranges and indicate only their Miocene provenance. On the other hand, the regional stratigraphical correlations and palaeogeographic reconstructions do not support the presence of Karpatian strata in the Bilche-Volytsia Unit (*e.g.*, Andreyeva-Grigorovich *et al.*, 1997; Oszczypko *et al.*, 2006) and hence it is possible that the deposits included into the Sandy-Calcareous Series are transgressive Lower Badenian deposits that should be underlain by, or included into, the Bohorodchany Formation (Suite) (Fig. 3).

PETROLEUM OCCURRENCE

The frontal part of the Polish and Ukrainian Carpathians constitutes one of the oldest petroleum-producing regions in the world. The exploitation of oil started in 1853 in Bóbrka village near Krosno in Poland (in Austro-Hungarian Monarchy at that time) in the Outer (Flysch) Carpathians, and natural gas production in 1920 in Dashava village near Boryslav in Ukraine (in Poland at that time) in the autochthonous Miocene strata of the Bilche-Volytsia Unit of the Carpathian Foredeep (Vul *et al.*, 1998b; Karnkowski, 1999; Fedyshyn *et al.*, 2001). At the end of the 1930s, petroleum exploration started in the Carpathian Foreland, and in the years 1945–1955 petroleum industry in Poland and Ukraine had to be restored and reorganised. The exploration activity was focused mainly on the Outer (Flysch) Carpathians and partly on the Carpathian Foredeep (Karnkowski, 1994, 1999). Intensive development of petroleum exploration took place in the middle of the 1960s and in the 1970s (Karnkowski, 1999; Fedyshyn *et al.*, 2001; Myśliwiec *et al.*, 2006; Popadyuk *et al.*, 2006). Up to now, twenty-eight and eleven gas and gas-condensate fields within the Palaeozoic–Mesozoic basement of the Polish part of the Carpathian Foredeep (from 1948), and within the Mesozoic basement of the Ukrainian part of the Carpathian Foredeep (since 1944), respectively, were discovered. Hydrocarbon (mostly gas, and gas-condensate, and only locally oil) accumulations occur in the autochthonous Miocene strata (*e.g.*, Karnkowski, 1999; Boyko *et al.*, 2004; Fedyshyn *et al.*, 2001; Kurovets *et al.*, 2011) of the outer part of the Carpathian Foredeep. Gas accumulations occurring in the Middle Miocene strata show a clear pattern, and there are three zones that accordingly extend close to the margin of the Carpathian Overthrust, at the front of Carpathian orogen, and along the north-eastern limit of the outer Carpathian Foredeep (*e.g.*, Karnkowski, 1999; Krups'kyy, 2001); the largest gas deposits occur in the Lower Sarmatian strata close to the Carpathian Overthrust (Karnkowski, 1999; Fedyshyn *et al.*, 2001).

There are 101 gas and gas-condensate deposits (first discovery in 1945) in the autochthonous Miocene strata of the Polish Carpathian Foredeep as well as 44 gas and gas-condensate deposits and one oil deposit in the Bilche-Volytsia Unit of the Ukrainian Carpathian Foredeep (first discovery in 1920). Although the share of deposits discovered in the pre-Miocene strata has increased (Kotarba *et al.*, 2011a), the Miocene deposits remain the main host for gas deposits, and their significance is related to a low degree of tectonic disturbance and the presence of unrecognised, broad structures with perfect reservoir horizons (Karnkowski, 1999). The formation of various traps was significantly controlled by diversified basement palaeorelief and variable sedimentary conditions, which were crucial for the formation of various hydrocarbon traps, such as those related to pinch-outs and facies changes. Principally, layered and massive types of deposits occur there (Karnkowski, 1999).

Polish part of the Carpathian Foredeep

Petroleum deposits in the Polish sector of the Carpathian Foredeep are accumulated in both Neogene complex (Fig. 1A) and in its basement (Kotarba *et al.*, 2011b).

The petroleum reservoir rocks in the autochthonous Miocene strata of the outer part of the Polish Carpathian Foredeep are sandstones originated in various depositional environments (Myśliwiec *et al.*, 2006): (i) Lower Badenian glauconitic sandstones – the Baranów beds (Kuryłówka, Rokietnica and Sarzyna gas deposits), (ii) Middle Badenian evaporitic deposits (Rożwienica gas accumulation), (iii) Upper Badenian–Lower Sarmatian – sandstones deposited in submarine fan, deltaic and shallow marine environments (*e.g.*, Przemyśl, Jodłówka, Albigowa-Krasne, Husów, Żołynia, Rudka, Biszcza, Wola Obszańska, Księżpol, Łukowa, Dzików, Chałupki Dębniańskie, Grodzisko Dolne, Łazy, Łętowice, Wierzchosławice, Borek, Dąbrówka gas deposits), and (iv) Lower Sarmatian – massive sandstones (blocky sandstones of the Dzików gas deposit). Moreover, Eocene and Oligocene deposits were discovered in the north-eastern part of the Carpathian Foredeep. A gas accumulation in Oli- gocene sandstones was discovered in Luchów 3 well (My- śliwiec *et al.*, 2006). Oligocene sandstones have very good reservoirs parameters, with average porosity of 26% and average permeability equals to 1250 mD.

The sandstones deposited in the submarine fan and deltaic environments are the most important and productive Upper Badenian–Lower Sarmatian reservoir rocks. The submarine fan sandstone complex occurs at a depth interval of 1,000–3,500 m in the southern part of the Carpathian Foredeep – an area in front of and under the Carpathian Overthrust (Myśliwiec *et al.*, 2006). The thick beds of the submarine fan sandstones are the primary gas reservoirs in the Przemyśl, Jodłówka, Husów, Albigowa-Krasne areas (Myśliwiec *et al.*, 2006). The average porosity of the sandstone reservoirs, determined from cores, varies from 9 to 21% for the Przemyśl gas field (Karnkowski, 1999). A similar porosity value was evaluated for the Jodłówka, Albigowa-Krasne, and Husów reservoirs. The permeability is more divergent. For the Jodłówka area, the maximum value is only 200 mD, but in the Husów area it can be up to 800 mD (Karnkowski, 1999). Examples of reservoirs connected with deltaic sedimentary environments are the Biszcza, Wola Obszańska, Księżpol, Łazy, Łękawica gas deposits. The deltaic type of sediments occurs at a depth of 400–800 m in the Biszcza area. Their porosity is 15–32% and permeability 900 mD (Myśliwiec, 2004a). Glauconitic sandstones of characteristic green colour are good quality reservoir rocks with porosity ranging from 5 to 25% (Myśliwiec *et al.*, 2006). The secondary porosity of the Middle Badenian diagenetic anhydrites in the Rożwienica gas accumulation ranges between 4.3 and 16.1%; the increase in porosity and permeability was caused by the interaction between anhydrites and hydrocarbons (Myśliwiec, 2004a; Myśliwiec *et al.*, 2006). The so-called Dzików – blocky sandstones reservoir rocks are located along the fault zone of the Uszkowce-Lubaczów area. The blocky sandstones are excellent reservoir rocks, with a porosity of 15–35% and permeability of 200 mD (Myśliwiec *et al.*, 2006).

The occurrence of traps for gas accumulations in the Miocene was determined by two main factors: palaeomorphology of the pre-Miocene basement and deformation influence of the Carpathian Overthrust (Karnkowski, 1999; Myśliwiec, 2004b). The major type of traps in the Miocene of the Carpathian Foredeep are: (i) compactional anticlines situated above basement uplift (*e.g.*, Rudka, Palikówka, Kańczuga deposits), (ii) traps sealed by the Carpathian Overthrust plane (*e.g.*, Przemyśl, Albigowa-Krasne, Husów and Pilzno fields), (iii) traps sealed by faults (Mołodycz, Jarosław, Radymno and Sarzyna deposits), (iv) stratigraphic pinch-out traps (*e.g.*, the Husów field), and (v) stratigraphic traps related to unconformities (the Tarnów area and the deepest horizons of the Rudka deposit). In some cases, traps in Miocene strata may be formed by combined mechanism of sealing (*e.g.*, Husów, Przemyśl, and Rudka gas deposits).

Ukrainian part of the Carpathian Foredeep

Gas, gas-condensate and oil deposits (Fig. 1B) have been discovered within the autochthonous Miocene strata, combining Miocene and Mesozoic basement reservoirs in the Bilche-Volytsia Unit of the Ukrainian Carpathian Foredeep (Vul *et al.*, 1998b; Shcherba *et al.*, 1987).

Seven fields contain condensate and/or gas in the combined Mesozoic–Miocene reservoirs (Figs 1B, 3): the Rudky field – gas and condensate in the Upper Jurassic-reservoir and five gas accumulations in the Lower Dashava Formation of the Lower Sarmatian, the Vereschytsia field – gas in the Upper Jurassic–Lower Badenian Sandy-Calcareous Series, the Medenychi field – gas and condensate in the Upper Cretaceous–Lower Badenian Sandy-Calcareous Series, the Bilche-Volytsia field – gas and condensate in the Upper Cretaceous–Lower Badenian Sandy-Calcareous Series and four gas accumulations in the Lower Dashava For- mation of the Lower Sarmatian, the Uhers'ko – gas and condensate in the Upper Cretaceous–Lower Badenian Sandy- Calcareous Series an and five gas accumulations in the Upper and Lower Dashava Formation of the Lower Sarmatian, the

Pivdenne Uhers'ko – gas in the Upper Cretaceous– Lower Badenian Sandy-Calcareous Series and four gas accumulations in the Lower Dashava Formation of the Lower Sarmatian, and the Letnia field – gas and condensate in the Upper Jurassic–Lower Badenian Sandy-Calcareous Series, Upper Cretaceous–Lower Badenian Sandy-Calcareous Series and nine gas accumulations in the Lower Dashava Formation of the Lower Sarmatian strata. The Orkhovychi deposit contains oil in Upper Jurassic–Lower Badenian Sandy-Calcareous Series reservoir (Kotarba *et al.*, 2011b).

The remaining thirty-seven deposits contain gas accumulations in Miocene reservoirs (Figs 1, 3). The Mala Horozhanna field contains gas in the Lower Badenian Sandy-Calcareous Series and Upper Badenian Tyras Formation. The Hai field contains gas and condensate in the Lower Badenian Sandy-Calcareous Series and in two of the Lower Dashava Formation of Lower Sarmatian horizons and gas in one Lower Sarmatian horizon. The Zaluzhany field contains gas and condensate in one and gas in twelve accumulations in the Upper and Lower Dashava Formation. The Hrushiv field contains gas and condensate in one and gas in two accumulations in the Lower Dashava Formation. The Hrudivka field contains gas in the Lower Badenian Sandy-Calcareous Series and in three of the Lower Dashava Formation, and the Hlynky and Pivdenne Hrabyne fields – in the Lower Badenian Sandy-Calcareous Series reservoirs. The Svydnytsia field contains gas in the Upper Dashava Formation of the Lower Sarmatian, and the Vyzhomlia, Nyklovychi, Makuniv, Novosilky, Mainych, Susoliv, Shidne Dovhe, Opory, Kavske, and Tyniv fields – in the Lower Dashava Formation; the Vyshnia, Khidnovychi, Sadkovychi, Pyniany, Dashava, and Horodok fields contain gas in the Upper and Lower Dashava Formation; the Kadobna, Kosiv, and Chornohuzy fields – in the Upper Badenian and Lower Sarmatian; the Turady, Hrynivka, Bohorodchany, Debeslavtsi, Yabluniv, Kovalivka, Sheremetivka, and Krasnoils'k fields – in the Upper Badenian; and the Cheremkhiv-Strupkiv and Pylypy fields – in the Lower Badenian reservoirs. They occur along the whole Bilche-Volytsia Unit, though a major part of them is concentrated in its north-western part (Fig. 1). In these deposits the traps are lithologically and tectonically-sealed. In particular, often the Stebnyk Overthrust serves as a seal, *e.g.*, in the Uhers'ko, Zaluzhany, Khidnovychi, Sadkovychi, Kavs'ke, and Hrynivka fields. However, in addition to this, the major part of the gas fields of the Bilche-Volytsia Unit occur in the elevated structures, *e.g.*, Svydnytsia, Rudky, Letnia, Bilche-Volytsia, Uhers'ko, Dashava and other fields.

Commonly, there are several producing horizons in a field: in the Bilche-Volytsia Unit 175 such horizons exist in 40 fields, and 165 in the Upper Badenian and Lower Sarmatian strata (Boyko *et al.*, 2004).

The Miocene sequence contains the major part of fields in the area and comprises several levels of reservoir rocks. The Lower Badenian Sandy-Calcareous Series, occurring at the base of the Miocene, are gas- and condensate-bearing in several fields in the north-western part of the Bilche-Volytsia Unit. The porosity of these rocks ranges between 6 and 31% (mean 13%), permeability is usually less than 0.1 mD, but locally reaches 270 mD (Shcherba *et al.*, 1987). The traps in the Lower Badenian Sandy-Calcareous Series and Baraniv beds are sealed by the Upper Badenian Tyras Formation deposits. The Badenian strata are gas-bearing mainly in the central and south-eastern parts, while the Lower Sarmatian strata contain the major part of gas fields of the north-western part of the Bilche-Volytsia Unit. The reservoir rocks represent sandstone layers with porosity of 20–30%, locally 30–40% and permeability from 0.1 mD to 1,595 mD. The Badenian reservoirs are often lithologically sealed within the Badenian sequence, while the Lower Sarmatian ones form anticlinal structures, sealed from the top by the Lower Sarmatian clayey rocks, and are often fault-sealed laterally.

HYDROCARBON POTENTIAL OF ORGANIC MATTER IN THE POLISH AND UKRAINIAN PARTS OF THE OUTER CARPATHIAN FOREDEEP

The results of organic geochemistry analyses enable the preliminary assessment of the dispersed organic matter (DOM) contained in autochthonous Miocene sequence of the Polish and Ukrainian parts of the Outer Carpathian Foredeep (Kotarba, 1999; Kotarba & Koltun, 2006; Kotarba *et al.*, 1998b, 2005, 2011a). The study was mainly focused on recognition of hydrocarbon potential of Upper Badenian and Lower Sarmatian strata due to the considerable thicknesses of those lithostratigraphic units and the enclosed great claystone-mudstone potential source rocks.

Small thicknesses of the Lower Badenian strata are the reason for poorer geochemical recognition. In the Lower Badenian Sandy-Calcareous Series, the Lower Badenian Baraniv beds and the Upper Badenian Tyras Formation of the Ukrainian Outer Carpathian Foredeep (Bilche-Volytsia Unit), the total organic carbon (TOC) contents are low and range from 0.00 to 0.76 wt% (average 0.28 wt%) (Kotarba & Koltun, 2006, 2011). This Miocene sequence consists of immature, terrestrial, gas-prone and marine, oil-prone organic matter, which has generated mainly the microbial methane and small amounts of microbial ethane. In the Lower Badenian Baraniv beds and in the Tyras Formation, an input of marine organic matter was discovered. Moreover, in the vicinity of Kokhanivka, the rocks of the Tyras Formation were deposited under hypersaline conditions, as revealed by the presence of marine plankton (Kotarba & Koltun, 2011).

In the Upper Badenian strata, the total organic carbon (TOC) contents vary from 0.02 to 1.48 wt% (average 0.75 wt%) in the Polish Carpathian Foredeep (Kotarba, 1999; Kotarba *et al.*, 1998b, 2005) and from 0.44 to 2.01 wt% (average 0.96 wt%) in the Ukrainian Carpathian Foredeep (Kotarba & Koltun, 2011). In the Lower Sarmatian strata, the TOC varies from 0.02 to 3.22 wt% (average 0.69 wt%) in the Polish Carpathian Foredeep (Kotarba, 1999; Kotarba *et al.*, 1998b, 2005) and from 0.01 to 1.45 wt% (average 0.71 wt%) in the Ukrainian Carpathian Foredeep (Kotarba & Koltun, 2011). Numerous TOC results from the Polish Oil & Gas Company laboratories (unpublished data) are very similar to those data and reach up to 5.1 wt% (average 0.88 wt%) and 3.4 wt% (average 0.82 wt%) in the Upper Badenian and the Lower Sarmatian strata, respectively

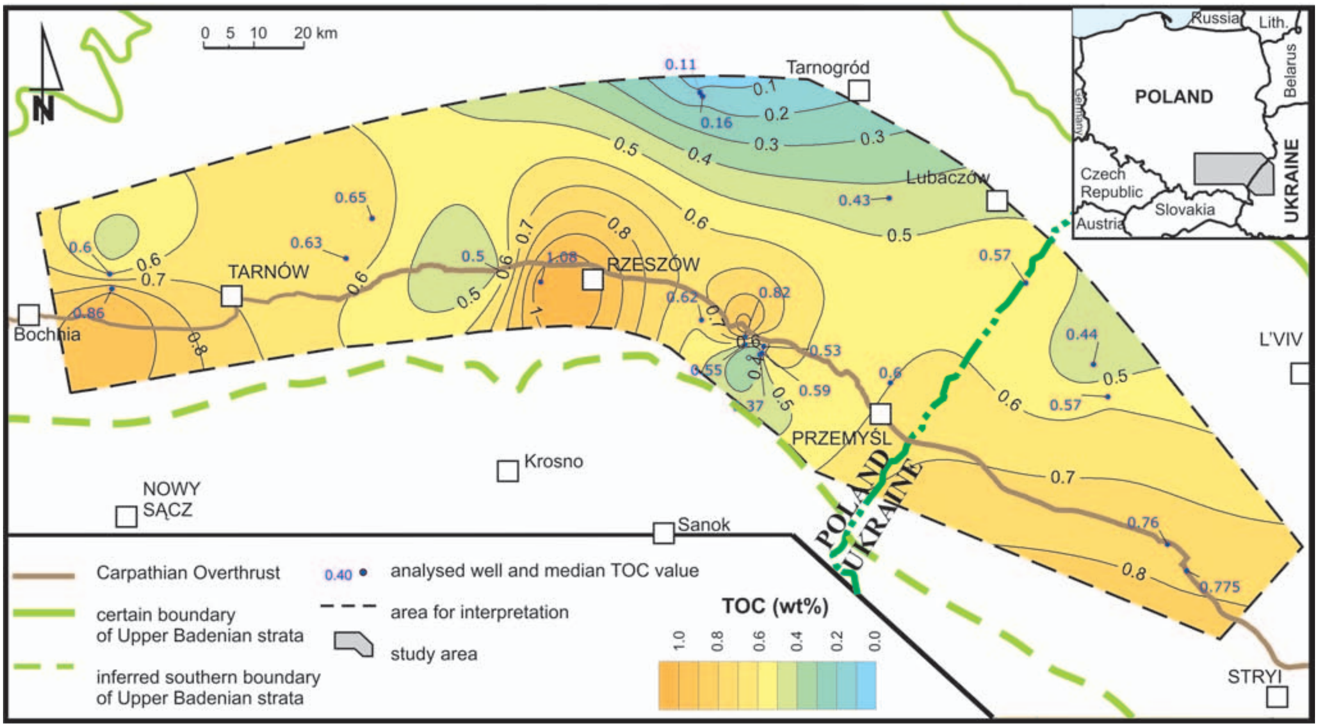

Fig. 4. Contour map of median values of the total organic carbon (TOC) content in sections of analysed wells within the Upper Badenian strata of the Carpathian Foredeep. Lith. – Lithuania

(Kotarba *et al.*, 1998b). According to Dickey and Hunt (1972), the TOC concentration over 0.5 wt% is required to qualify a rock as having hydrocarbon potential. Distributions of median TOC contents in the analysed profiles of wells in the Upper Badenian and Lower Sarmatian strata are shown in Figs 4 and 5, respectively. The distribution of median TOC contents in the Upper Badenian strata generally decreases from the south to the north (Fig. 4), while in the Lower Sarmatian strata the lowest values are observed in the southern zone near the Carpathian Overthrust, increasing northwards (Fig. 5).

Geochemical analyses (Rock-Eval, biomarkers and stable isotopes) of DOM (Kotarba *et al.*, 1998b, 2005; Kotarba & Koltun, 2006, 2011) indicate the general dominance of the terrestrial Type III kerogen in both the Upper Badenian and Lower Sarmatian sequences. This DOM mainly consists of vitrinite-group macerals (from 70.9 to 84.0 %) with the complete absence of the liptinite group macerals (Kotarba *et al.*, 1998b), which also supports the concept of its terrestrial origin. Moreover, such an origin has been also confirmed by the results of elemental analyses of the Miocene fossil remnants (Kotarba *et al.*, 1987). Terrestrial DOM dispersed in claystones/mudstones capable of generating and expelling oil should have HI values typically higher than about 200 (Hunt, 1991). Distribution of median HI values in the Upper Badenian and Lower Sarmatian strata usually does not exceed a value of 200 mg HC/g TOC (Figs 6, 7) and only in a small area of the Upper Badenian strata north of Leżajsk this value is increased up to 213 mg HC/g TOC (Fig. 6). The HI values close to that limit were found in a few samples from the Upper Badenian strata in the Rzeszów-Stryi area (Fig. 8C), which may suggest the presence of small amounts of algal (marine and/or non-marine) DOM. In the Kraków-Rzeszów area, only gas-prone Type III kerogen (Fig. 9C) has been found. The lack of obvious depth trends of both the T_{max} temperature and HI values (Figs 8B, C, 9B, C) advocates the immature gas-prone character of the entire Upper Badenian and Lower Sarmatian sequences. The immature terrestrial DOM shows Rock Eval T_{max} temperature below 435°C (Espitalié & Bordenave, 1993). The T_{max} temperature values at the bottom of the Upper Badenian and Lower Sarmatian strata varies from about 390 to 435°C (Figs 8B, 9B). Only in three samples from the Upper Badenian strata (Jo-4 and Rn-6 wells, depths 3,300–3,500 m), the T_{max} 435–438°C (Fig. 8B) was measured. Such T_{max} values together with no obvious depth trends (Figs 8B, 9B) indicate that down to the depths of 3,300–3,500 metres the Miocene terrestrial DOM is immature and generates almost exclusively microbial methane. The initial phase of low-temperature thermogenic process proceeds beneath these depths, under the Outer Carpathian Overthrust. Distribution of vitrinite reflectance values of the Miocene DOM with depth confirms its low maturity (Kotarba *et al.*, 1998b). The maturity of DOM in the Upper Badenian strata generally increases from the north to the south and the south-east from about 400 to about 435°C (Fig. 10), while in the Lower Sarmatian strata T_{max} changes only from about 420 to about 430°C, and decreases to the south-east (Fig. 11)

ORIGIN OF NATURAL GASES

The stable carbon and hydrogen isotopic composition of methane can be sensitive indicators of gas origin and migration. Carbon in methane has a wide range of $\delta^{13}C$ values

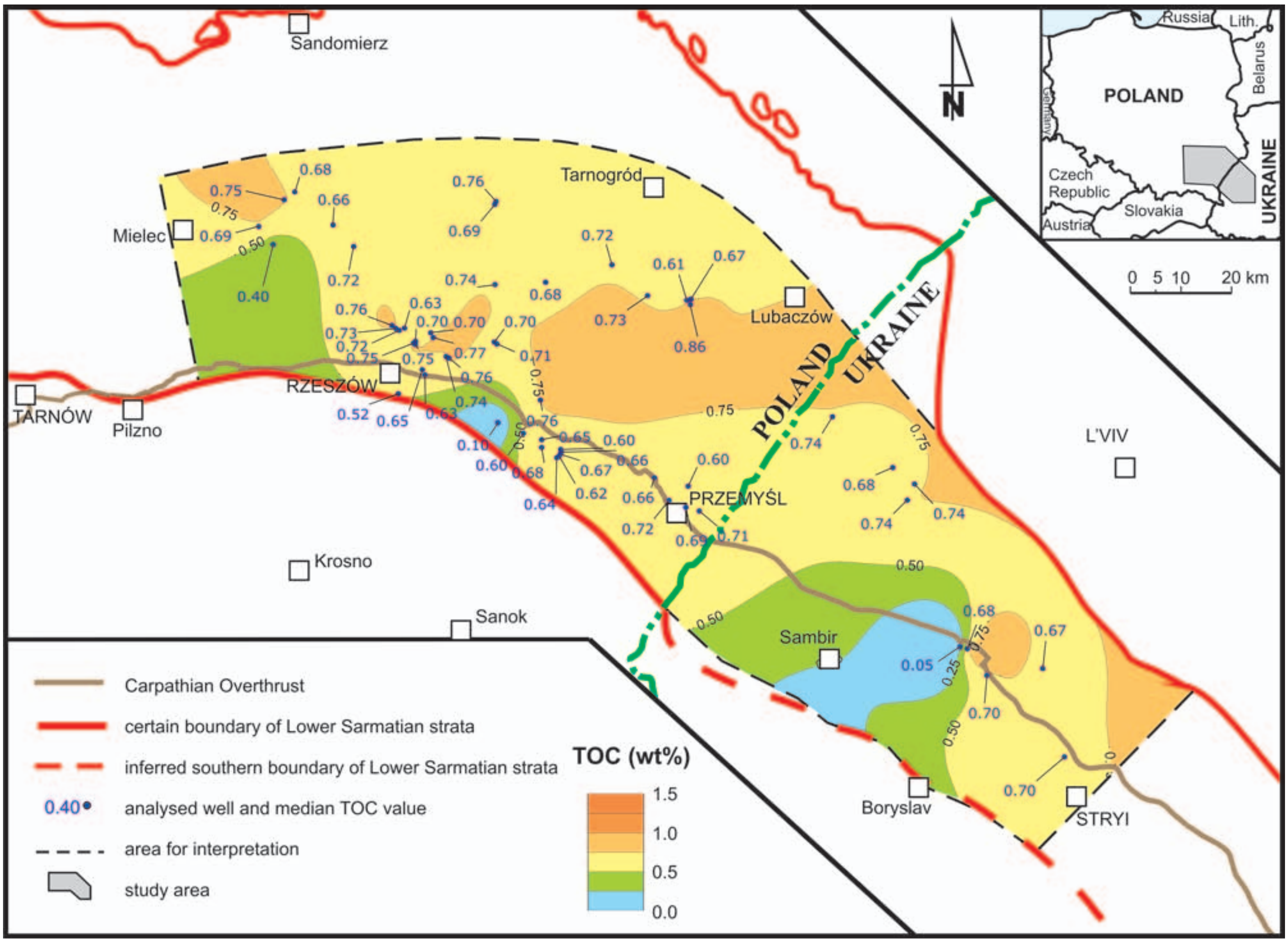

Fig. 5. Contour map of median values of the total organic carbon (TOC) content in sections of analysed wells within the Lower Sarmatian strata of the Carpathian Foredeep. Lith. – Lithuania

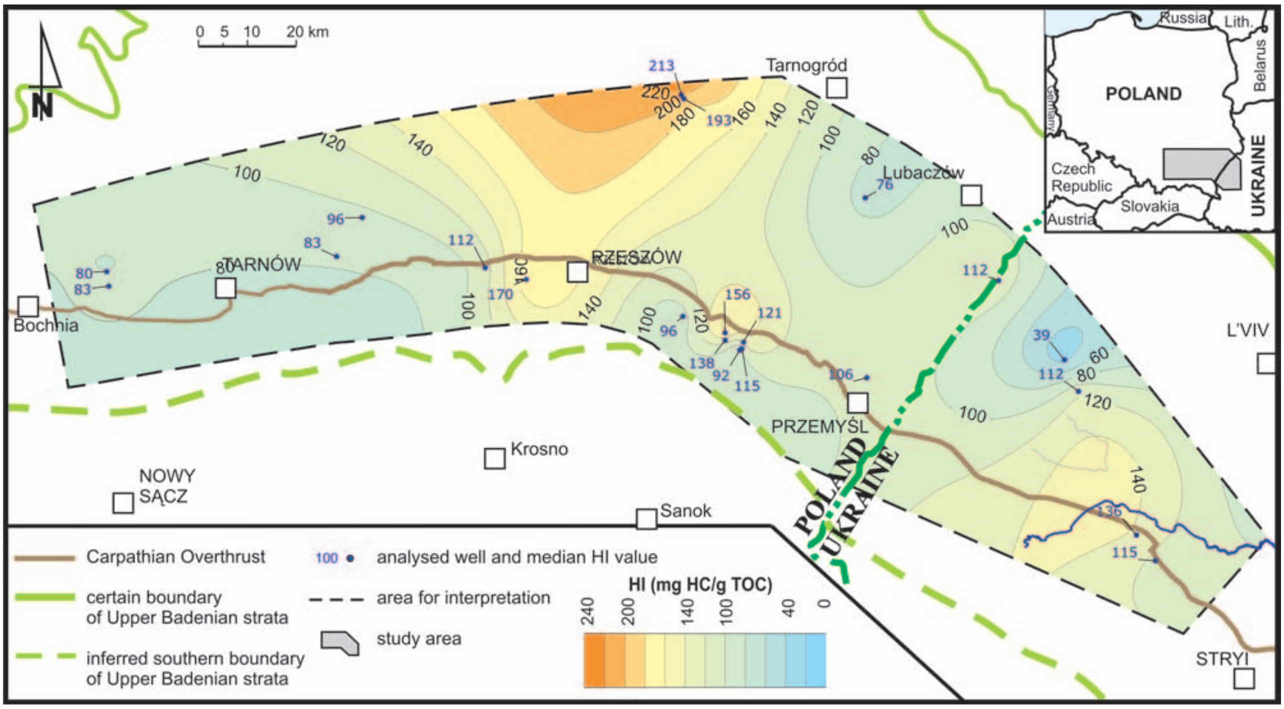

Fig. 6. Contour map of median values of the hydrogen index (HI) in sections of analysed wells within the Upper Badenian strata of the Carpathian Foredeep. Lith. – Lithuania

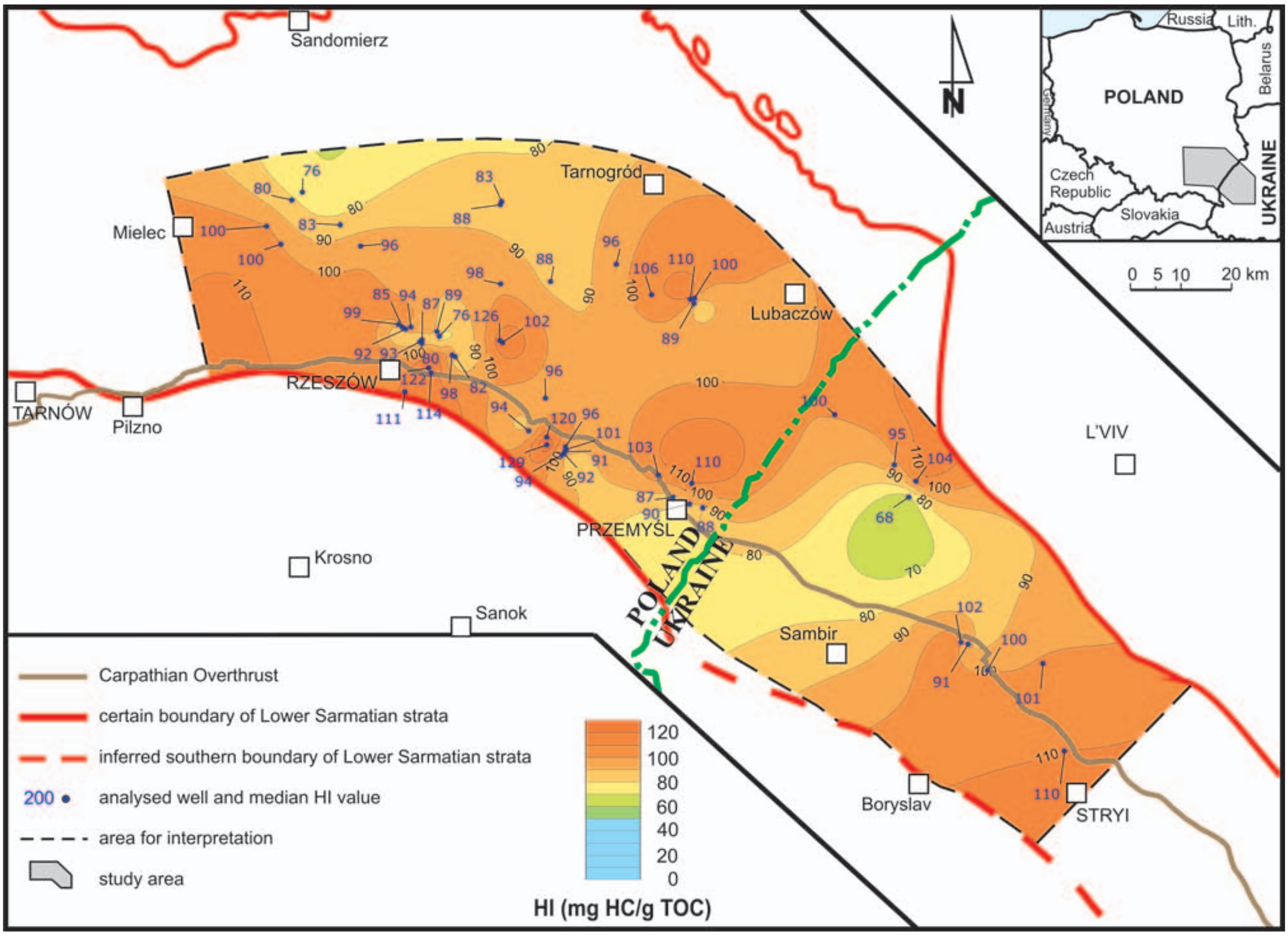

Fig. 7. Contour map of median values of the hydrogen index (HI) in sections of analysed wells within the Lower Sarmatian strata of the Carpathian Foredeep. Lith. – Lithuania

due to a variety of chemical, physical and microbial processes that cause significant variations in the isotopic compositions of the source organic matter and the daughter gases. The analyses of stable carbon and hydrogen isotopes in methane enables the identification of the source organic matter, from which gases were generated during microbial or thermogenic processes (*e.g.*, Berner & Faber, 1996; Kotarba, 1995). Methane generated during thermogenic processes from the sapropelic organic matter shows $\delta^{13}C$ values from –55 to –30‰ whereas that produced from the humic organic matter has $\delta^{13}C$ from –30 to –20‰. In contrast, microbially generated methane has typically very low $\delta^{13}C$ values (less than –55‰), even below –100‰. Microbial gases can be generated by two processes: methane fermentation and carbon dioxide reduction (Martini *et al.*, 1996, 1998; Whiticar *et al.*, 1986). Ethane, and in insignificant quantities, propane have been generated from microbial processes (Claypool, 1999; Gautier & Claypool, 1984; Hinrichs *et al.*, 2006; Jenden & Kaplan, 1986; Lillis, 2007; Oremland *et al.*, 1986; Taylor *et al.*, 2000). Results of stable carbon isotope analyses of ethane, propane, butanes and pentanes allowed the preparation of more precise genetic classification of natural gases, *i.e.* the distinguishing of genetic groups and enabled the identification of migration and mixing of either genetically different gases or gases produced from the same source organic matter but during the successive generation stages and migration distance (Berner & Faber, 1996; Kotarba *et al.*, 1994; Prinzhofer & Pernaton, 1997; Prinzhofer *et al.*, 2000; Whiticar, 1994). Both the experimental data and theoretical calculation demonstrated that stable carbon isotope studies of methane, ethane and propane are essential for determining the type and the maturation degree of the source organic matter in vitrinite reflectance scale (Berner & Faber, 1996; Whiticar, 1994). An important implication of the diagrams for genetic interpretation is that a linear dependence of carbon isotopes values in methane, ethane, propane, butanes and propanes to their reciprocal carbon number is not an exclusive indicator of the origin of natural gas from a single source, as it was assumed (*e.g.*, Rooney *et al.*, 1995). Instead, Kotarba *et al.* (2009) suggested that in such plots a "dogleg" trend, exemplified by relatively ^{13}C-depleted methane and ^{13}C-enriched propane in comparison to ethane, indicates that such natural gas was not generated from a single source rock or that it has underwent post-generation alterations (*e.g.*, secondary gas cracking, microbial oxidation or thermochemical sulphate reduction). Moreover, relatively more ^{13}C-depleted methane in relation to ethane can be applied to evaluate mixing proportions between microbial methane and thermogenic gases (Kotarba & Lewan, 2004; Kotarba *et al.*, 2009).

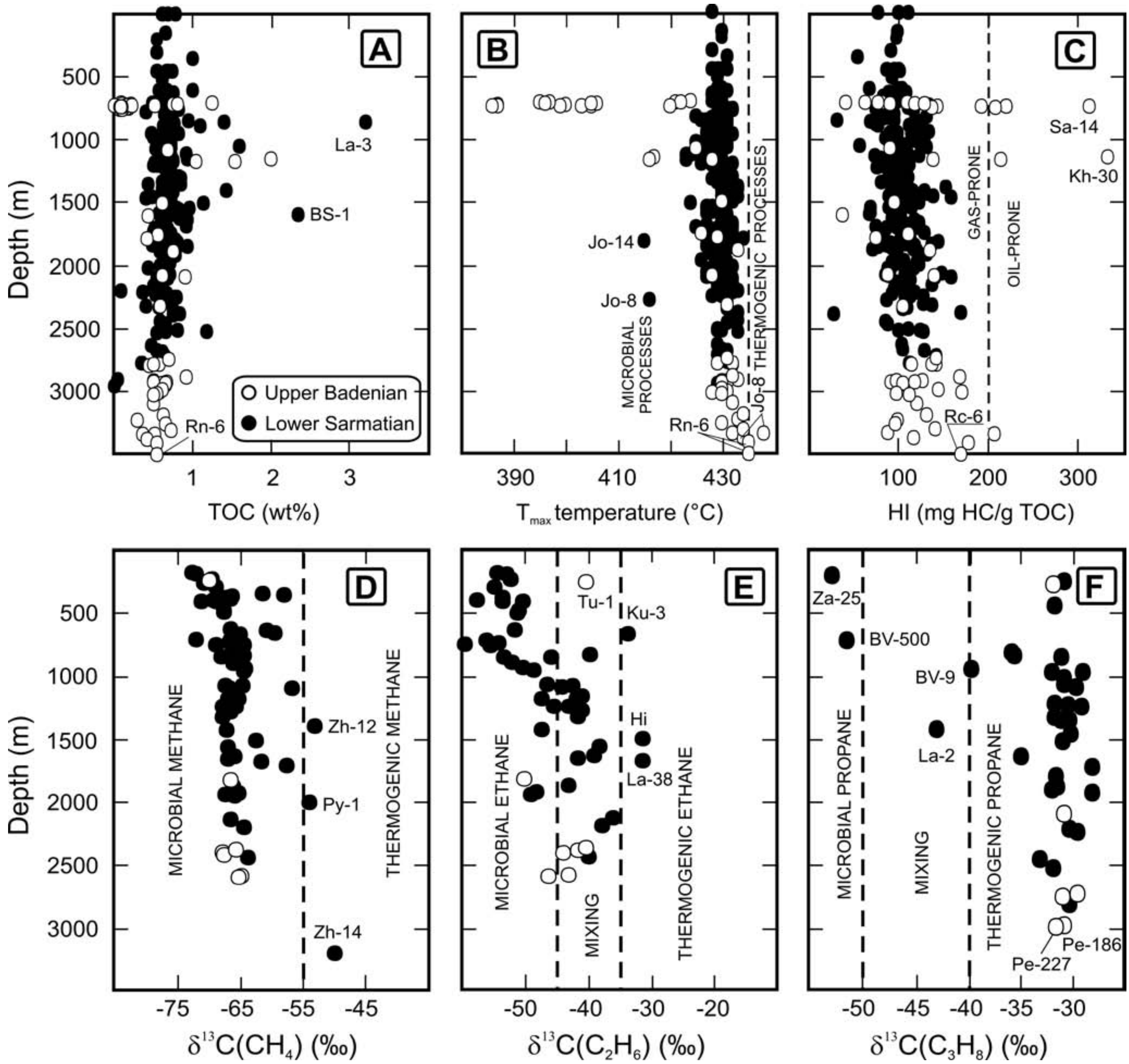

Fig. 8. (**A**) Total organic carbon, (**B**) Rock-Eval T_{max} temperature, (**C**) hydrogen index, (**D**) $\delta^{13}C(CH_4)$, (**E**) $\delta^{13}C(C_2H_6)$ and (**F**) $\delta^{13}C(C_3H_8)$ *versus* depth of (**A**, **B** and **C**) occurrence of organic matter and (**D**, **E** and **F**) natural gas accumulations within the Badenian and Lower Sarmatian reservoirs of the Carpathian Foredeep between Rzeszów and Stryi. Rock sample code (A, B and C) – see Kotarba *et al.* (1998b, 2005, 2011a), and gas sample code (D, E and F) – *cf.* Kotarba (1998, 2011), Kotarba and Koltun (2011) and Kotarba *et al.* (2005)

Most of the analysed gases were collected from the Upper Badenian and Lower Sarmatian strata (Kotarba, 1998, 2011). Results of stable carbon isotope analyses of methane, ethane, propane, butanes and pentanes, and stable hydrogen isotope analyses of methane (Figs 12–15) and spatial distributions of both $\delta^{13}C(CH_4)$ and $\delta^{13}C(C_2H_6)$ values in these strata (Figs 16–19) indicate that the gaseous hydrocarbons were mainly generated during microbial processes, and sporadically during low-temperature thermogenic processes.

Insignificant changes in values of stable carbon isotope ratios of methane and ethane with depth suggest quite uniform generation conditions of microbial methane and ethane in the entire Badenian and Lower Sarmatian sequences (Figs 8D, E and 9D, E). Thermogenic methane occurs only in the Brzeźnica, Łękawica and Tarnów accumulations in the Polish Carpathian Foredeep and Pyniany and Zaluzhany accumulations in the Ukrainian Carpathian Foredeep (Figs 8D, E and 9D, E). Moreover, thermogenic ethane occurs in the Kuryłówka (Ku-3), Hai and Letnia accumulations of the Rzeszów-Stryi area (Fig. 8E). Propane is mainly thermogenic in origin (Figs 8F, 9F, 14, 15). Microbial propane occurs in the Żołynia-Leżajsk (Zn-25) and Bilche-Volytsia (BV 500) accumulations of the Rzeszów-Stryi area (Fig. 8F).

In the Polish Carpathian Foredeep, in the Roźwienica field, gas is accumulated in the Lower (and partly Upper)

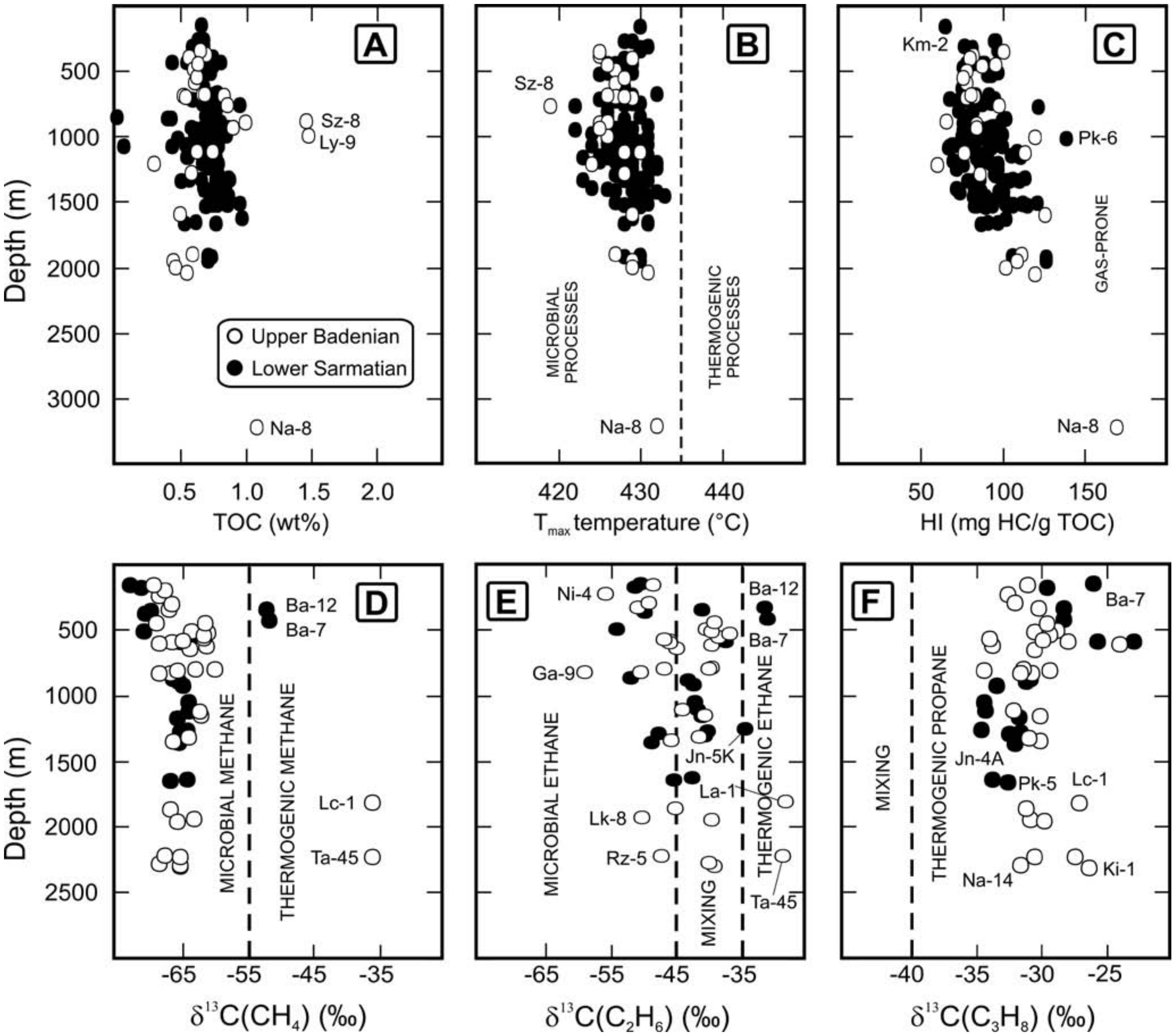

Fig. 9. (**A**) Total organic carbon, (**B**) Rock-Eval T_{max} temperature, (**C**) hydrogen index, (**D**) $\delta^{13}C(CH_4)$, (**E**) $\delta^{13}C(C_2H_6)$ and (**F**) $\delta^{13}C(C_3H_8)$ *versus* depth of (**A**, **B** and **C**) occurrence of organic matter and (**D**, **E** and **F**) natural gas accumulations within the Badenian and Lower Sarmatian reservoirs of the Carpathian Foredeep between Kraków and Rzeszów. Rock sample code (A, B and C) – see Kotarba *et al.* (1998b, 2005), and gas sample code (D, E and F) – *cf.* Kotarba (1998, 2011)

Badenian sequence; in the Lubaczów and Uszkowce deposits it occurs in the Lower Badenian strata and in the topmost parts of Upper Jurassic carbonates (Kotarba, 1998, 2011). The gas from the Tarnów, Łękawica and Brzeźnica deposits migrated from the Mesozoic basement to the Miocene strata and is typically thermogenic. This gas was generated from the oil-prone, marine organic matter (Type II kerogen) (Kotarba & Jawor, 1993; Kotarba, 2011). In both the Rożwienica and the Lubaczów deposits, a very small admixture of diagenetic (and/or low-temperature thermogenic) methane was identified (Kotarba, 1998). In the Lubaczów deposit the gas also filled up the trap in Upper Jurassic carbonates. Genetically, this gas is a typical microbial methane, which migrated to the Upper Jurassic trap from the autochthonous Miocene strata along a fault zone (Kotarba, 1998). In the Ukrainian Carpathian Foredeep, eight fields (Rudky, Vereschytsia, Medenychi, Mala Horozhanna, Bilche-Volytsia, Uhers'ko, Pivdenne Uhers'ko and Letnia) contain condensate and/or gas, and one Orkhovychi deposit contains oil in combined Mesozoic–Miocene reservoirs. The microbial gases (methane, hydrogen and partly ethane and propane) generated during microbial processes within the Miocene strata, then migrated to the Upper Jurassic and Upper Cretaceous (Cenomanian) reservoirs in the Mesozoic basement and to the bottommost Lower Badenian Sandy-Calcareous Series reservoirs of the traps of the above mentioned deposits (Kotarba & Koltun, 2011).

Increased $\delta^{13}C(CH_4)$ and $\delta^{13}C(C_2H_6)$ values in the Upper Badenian strata close to Tarnów town (Figs 16, 17) and in Lower Sarmatian strata near Dębica town (Figs 18, 19) in

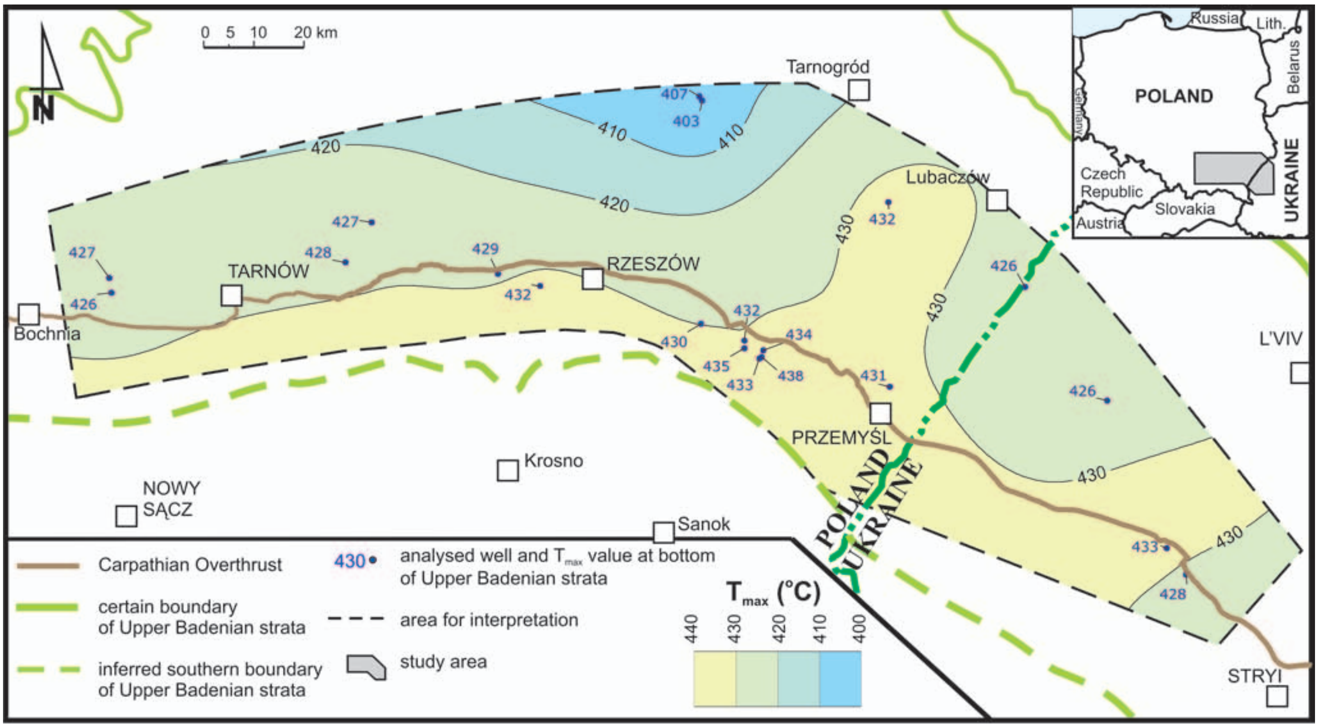

Fig. 10. Contour map of values of Rock-Eval T_{max} temperature at the bottom of the Upper Badenian strata of the Carpathian Foredeep. Lith. – Lithuania

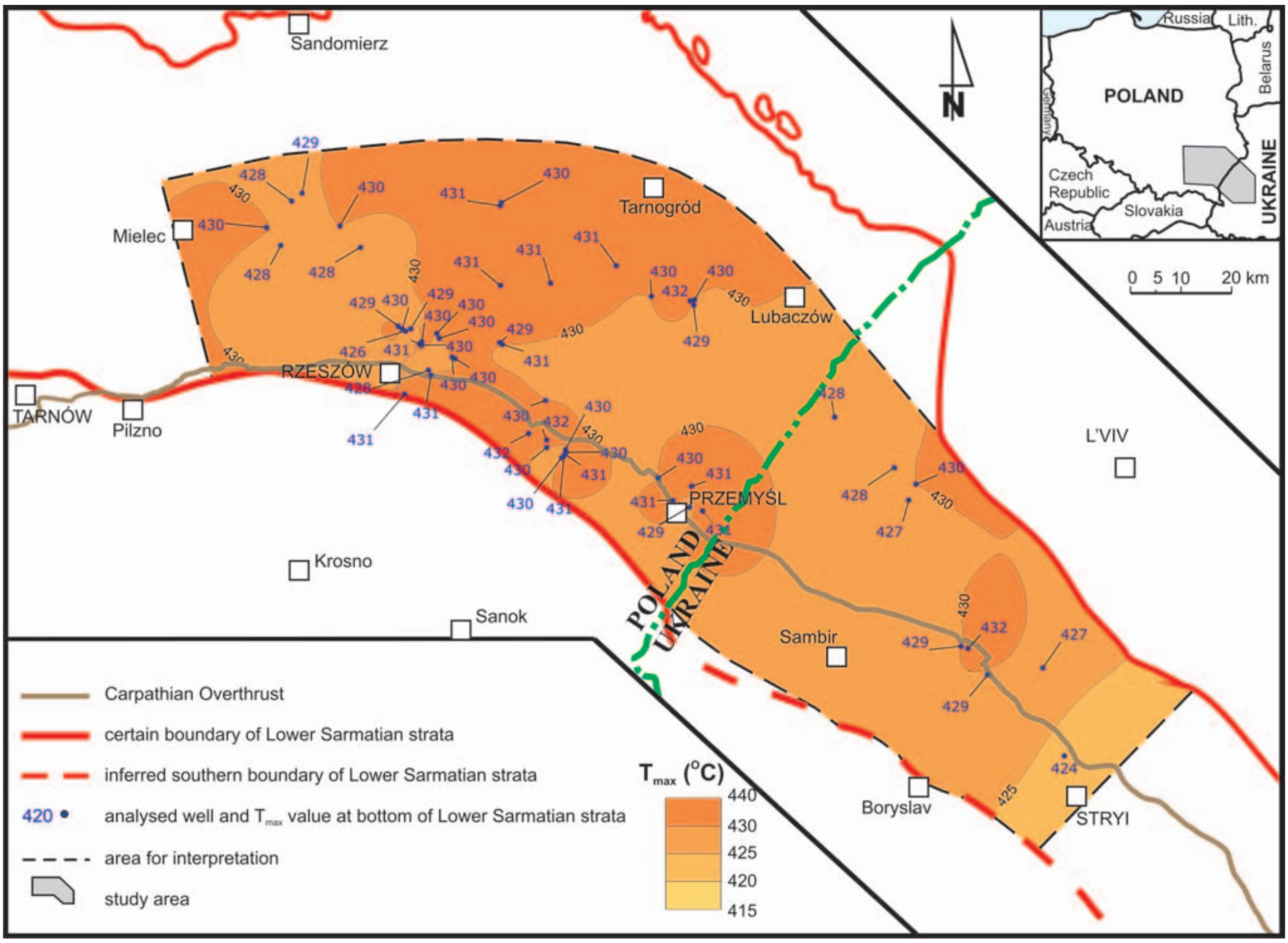

Fig. 11. Contour map of values of Rock-Eval T_{max} temperature at the bottom of the Lower Sarmatian strata of the Carpathian Foredeep. Lith. – Lithuania

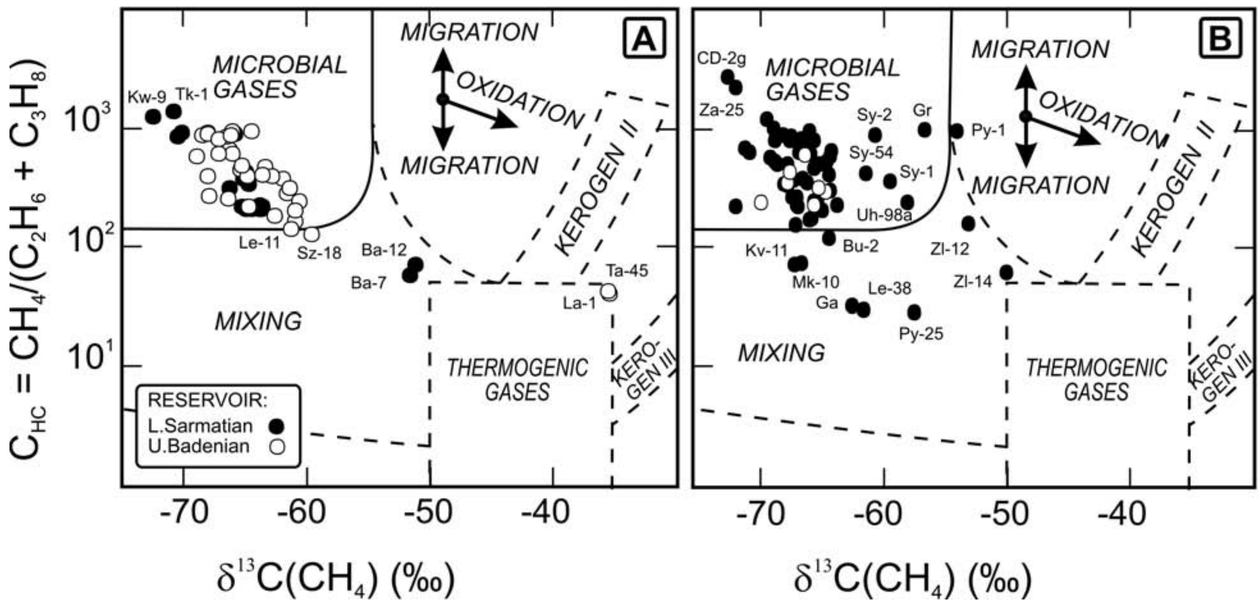

Fig. 12. Hydrocarbon index (C_{HC}) *versus* $\delta^{13}C(CH_4)$ for natural gases accumulated in the Miocene reservoirs of the Carpathian Foredeep in (**A**) Kraków – Rzeszów and (**B**) Rzeszów – Stryi areas. Compositional fields after Whiticar (1994). Gas sample code – see Kotarba (1998, 2011), Kotarba and Koltun (2011) and Kotarba *et al.* (2005). L. – Lower, U. – Upper

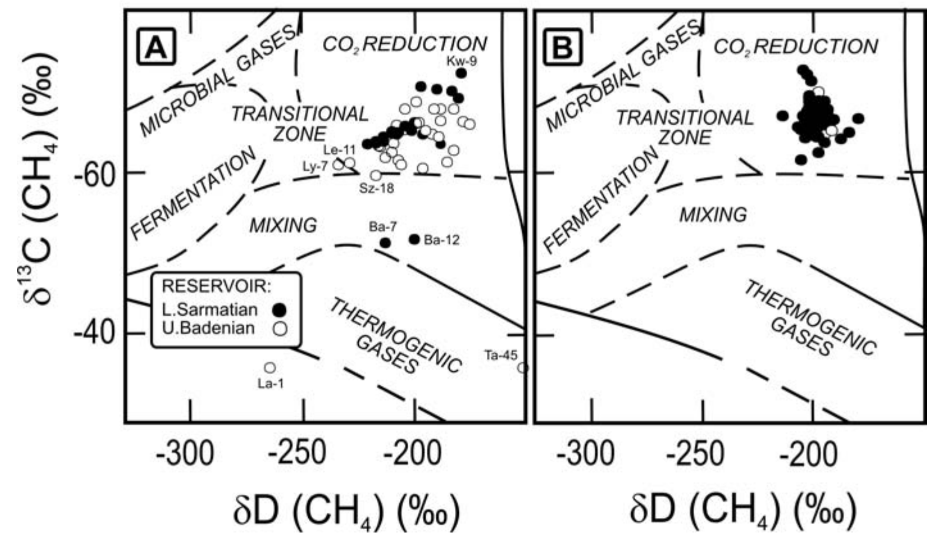

Fig. 13. $\delta^{13}C(CH_4)$ *versus* $\delta D(CH_4)$ for natural gases accumulated in the Miocene reservoirs of the Carpathian Foredeep in (**A**) Kraków – Rzeszów and (**B**) Rzeszów – Stryi areas. Compositional fields after Whiticar *et al.* (1986). Gas sample code – see Kotarba (1998, 2011), Kotarba and Koltun (2011) and Kotarba *et al.* (2005). L. – Lower, U. – Upper

the Polish part of the Carpathian Foredeep are caused by migration of thermogenic gases from the Mesozoic basement, while increased $\delta^{13}C(CH_4)$ and $\delta^{13}C(C_2H_6)$ values in the Lower Sarmatian strata near Boryslav, Drohobych and Sambir (Figs 18, 19) in the Ukrainian part of the Carpathian Foredeep are most probably caused by migration of thermogenic gases, which were generated within the Miocene strata beneath the Outer Carpathians at greater depths, from 3,500 to 12,000 metres (see chapter below).

MODEL OF MICROBIAL AND THERMOGENIC GAS GENERATION

The hydrocarbon generation conditions in the autochthonous Miocene were analysed in nine selected test areas (Figs 20, 21). The A (Tarnów), B (Mielec-Leżajsk), F (Pidluby) and (G) Rudky areas represent the part of the Carpathian Foredeep located north of the present margin of the Outer Carpathians. The C (Rzeszów), D (Przemyśl) and

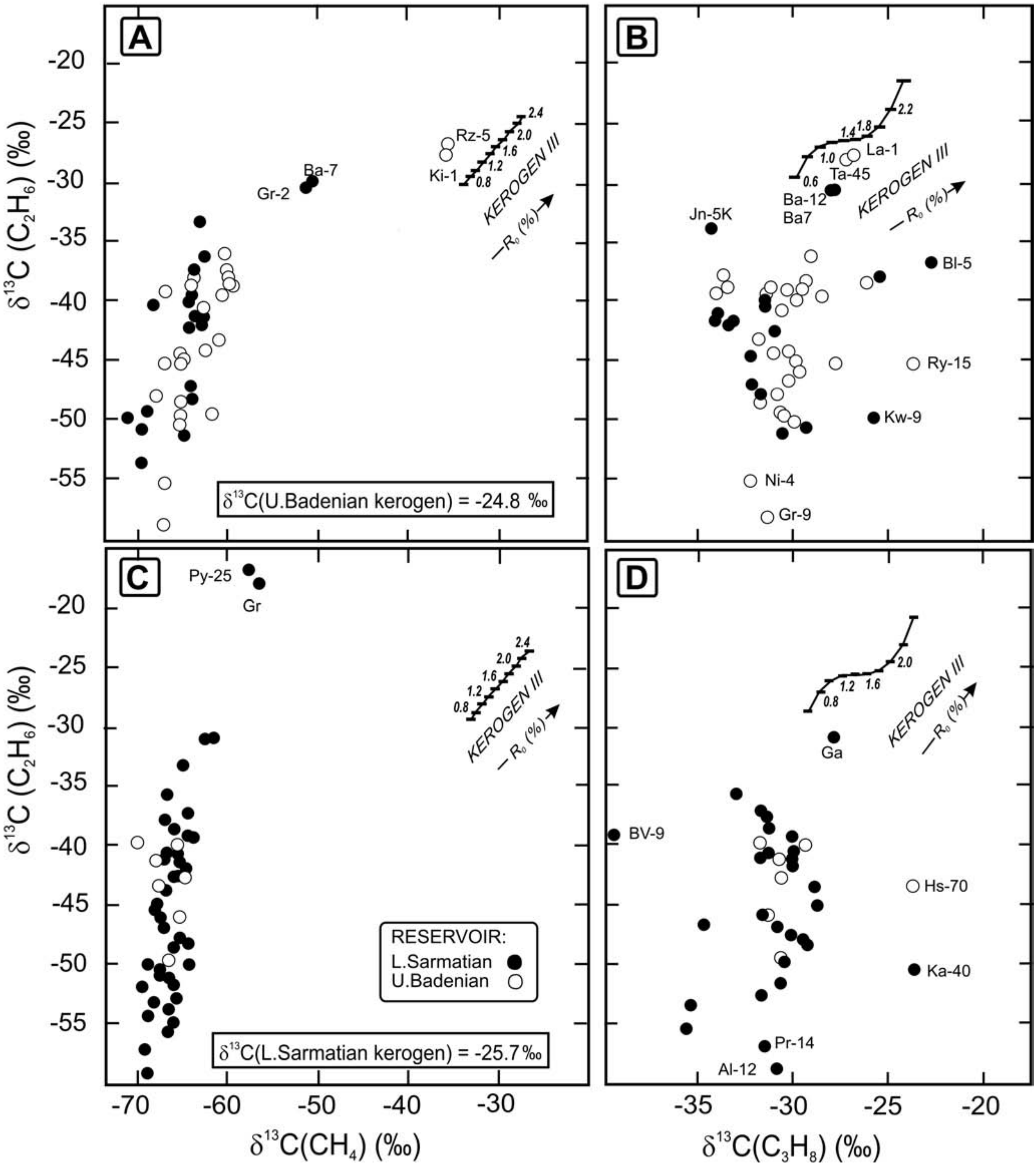

Fig. 14. $\delta^{13}C(C_2H_6)$ *versus* $\delta^{13}C(CH_4)$ (**A** and **C**) and $\delta^{13}C(C_3H_8)$ (**B** and **D**) for natural gases accumulated in the Miocene reservoirs of the Carpathian Foredeep in the (**A** and **B**) Kraków-Rzeszów and (**C** and **D**) Rzeszów – Stryi areas. Position of vitrinite reflectance curves for type III kerogen after Berner and Faber (1996). Curves were shifted based on average values of $\delta^{13}C$ = –24.8‰ for (A and B) Upper Badenian kerogen and $\delta^{13}C$ values = –25.7‰ for (C and D) Lower Sarmatian kerogen from the autochthonous Miocene strata (Kotarba *et al.*, 1998a, 2005). Gas sample code – see Kotarba (1998, 2011), Kotarba and Koltun (2011) and Kotarba *et al.* (2005). L. – Lower, U. – Upper

H (Zaluzhany-Sambir) areas are located in the autochthonous Miocene outer basin along the present edge of the Outer Carpathians (Figs 20, 21). The E (Krosno-Sanok) and I (Skole) areas were chosen as an example of hypothetical deepest levels where the autochthonous Lower Miocene strata might have existed at a depth of about 11–12 km. The hydrocarbon generation modelling used the time-temperature (TTI) method (Waples, 1980). The time scale and regional Miocene correlation were based upon Gradstein *et al.* (2004), Czepiec & Kotarba (1998) and Oszczypko

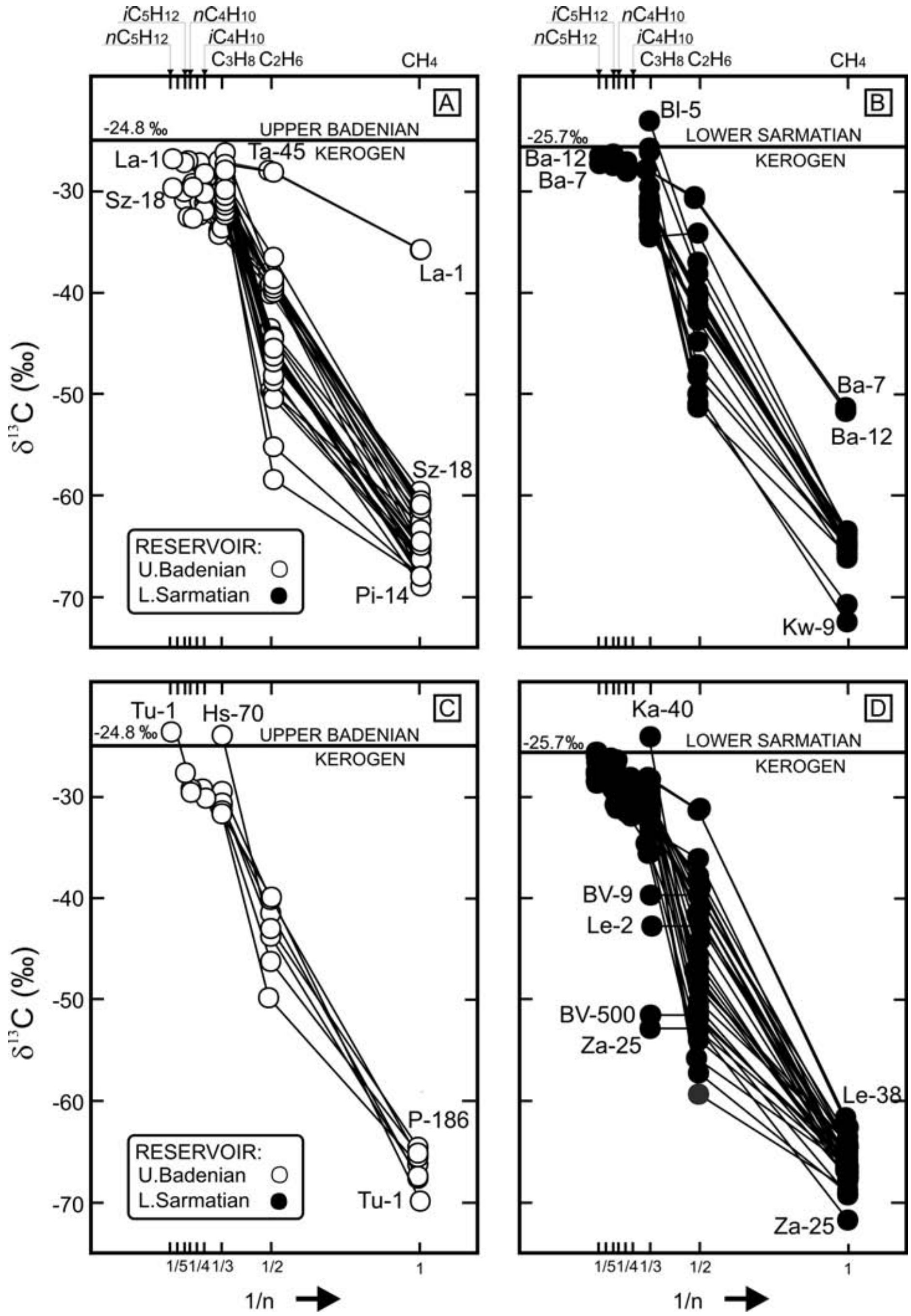

Fig. 15. (**A** and **B**) Stable carbon isotope composition of methane, ethane, propane, butanes and propanes *versus* the reciprocal of their carbon number for natural gases accumulated in (**A** and **C**) the Upper Badenian and (**B** and **D**) Lower Sarmatian reservoirs of the Carpathian Foredeep (**A** and **B**) in the Kraków – Rzeszów and (**C** and **D**) Rzeszów – Stryi areas. Structure of the graph for methane, ethane and propane after Rooney *et al.* (1995). Average values of $\delta^{13}C$ = –24.8 ‰ for Upper Badenian kerogen (A and C), and $\delta^{13}C$ values = –25.7 ‰ for Lower Sarmatian kerogen (B and D) from the autochthonous Miocene strata (Kotarba *et al.*, 1998a, 2005). Gas sample code – Kotarba (1998, 2011), Kotarba and Koltun (2011) and Kotarba *et al.* (2005)

(2006a) whereas the geothermal gradient – 33°C/10^{-3} m is the average value obtained from palaeotemperature calculations for the Miocene basin (Szafran, 1990) and calibrated with vitrinite reflectance values (Kotarba *et. al.*, 1998a). Thicknesses of stratigraphic units were taken from the results of drillings in the analysed parts of the outer basin. The estimated erosional reduction was 100 metres in A, B, F and G test areas and 250 metres in the remaining ones. TTI modelling in the outer basin (test areas A to D and F to H) was related to the bottom of the Upper Badenian succession as the datum surface. The top of the Lower Badenian Sandy-Calcareous Series sequence was the datum surface in the test areas E and I.

The modelling for the test E and I areas indicated the possibility of generation of the higher gaseous hydrocarbon (and even liquid hydrocarbons) beneath the Carpathian Overthrust, at about 7,500 m of depth (Fig. 21). At greater depths, within the relics of autochthonous Lower Miocene

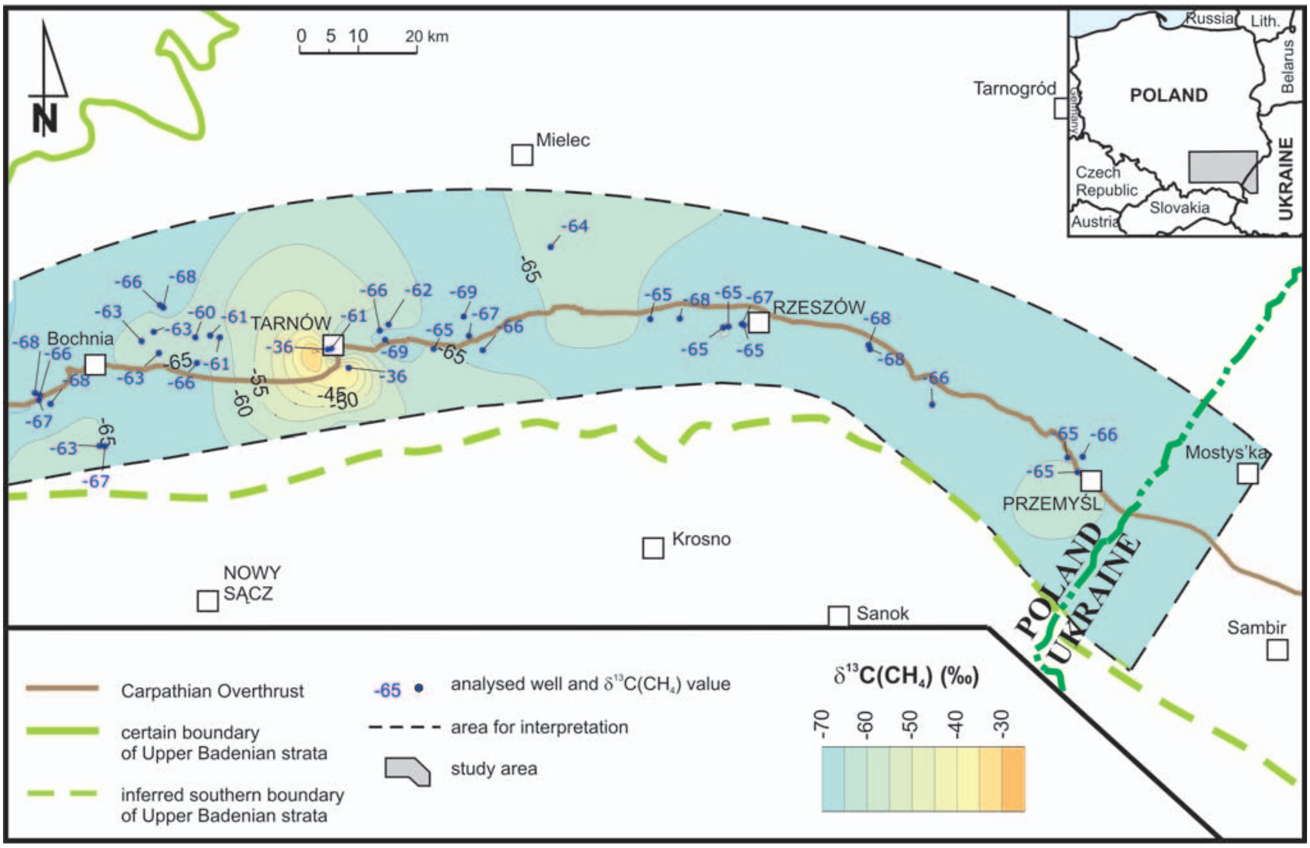

Fig. 16. Contour map of values of $\delta^{13}C(CH_4)$ at the bottom of the Upper Badenian strata of the Carpathian Foredeep. Lith. – Lithuania

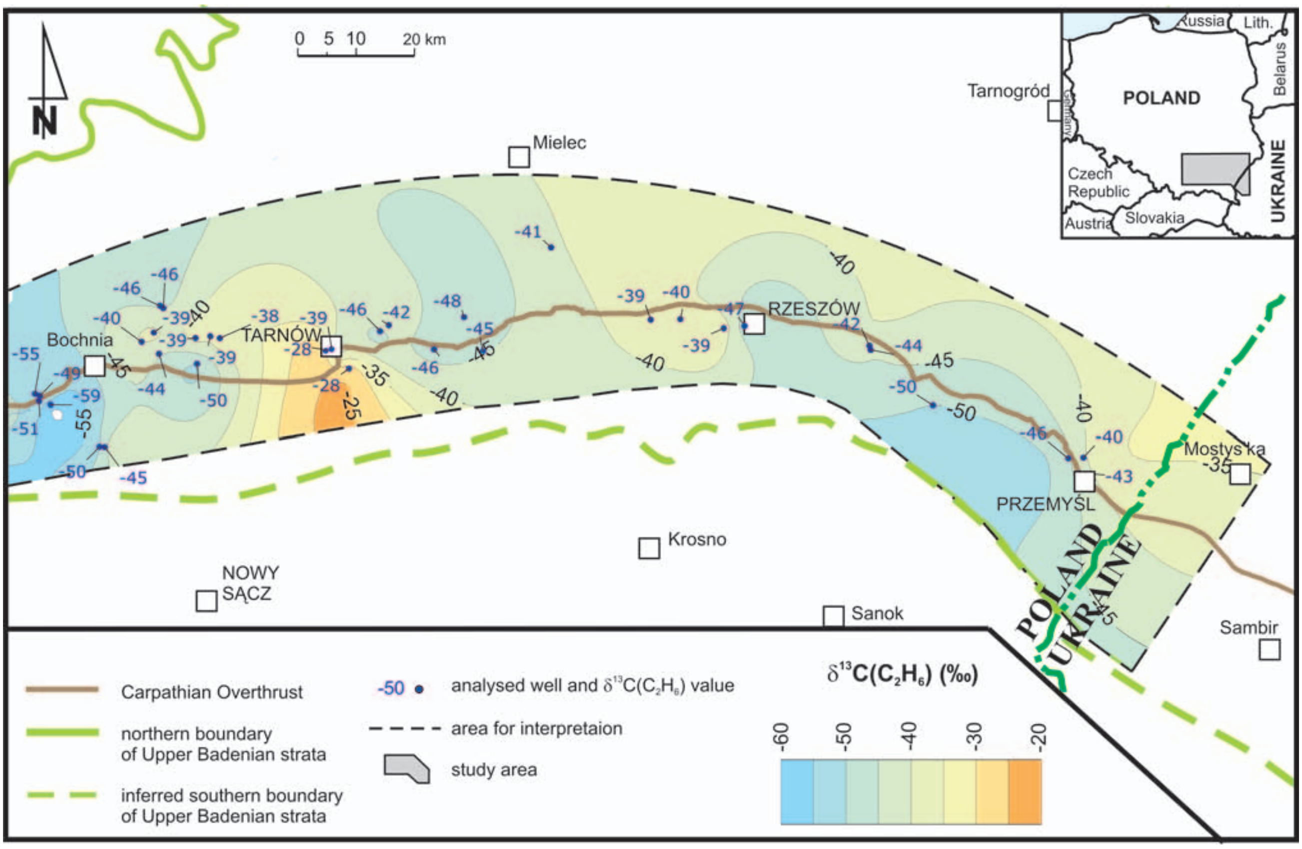

Fig. 17. Contour map of values of $\delta^{13}C(C_2H_6)$ at the bottom of the Upper Badenian strata of the Carpathian Foredeep. Lith. – Lithuania

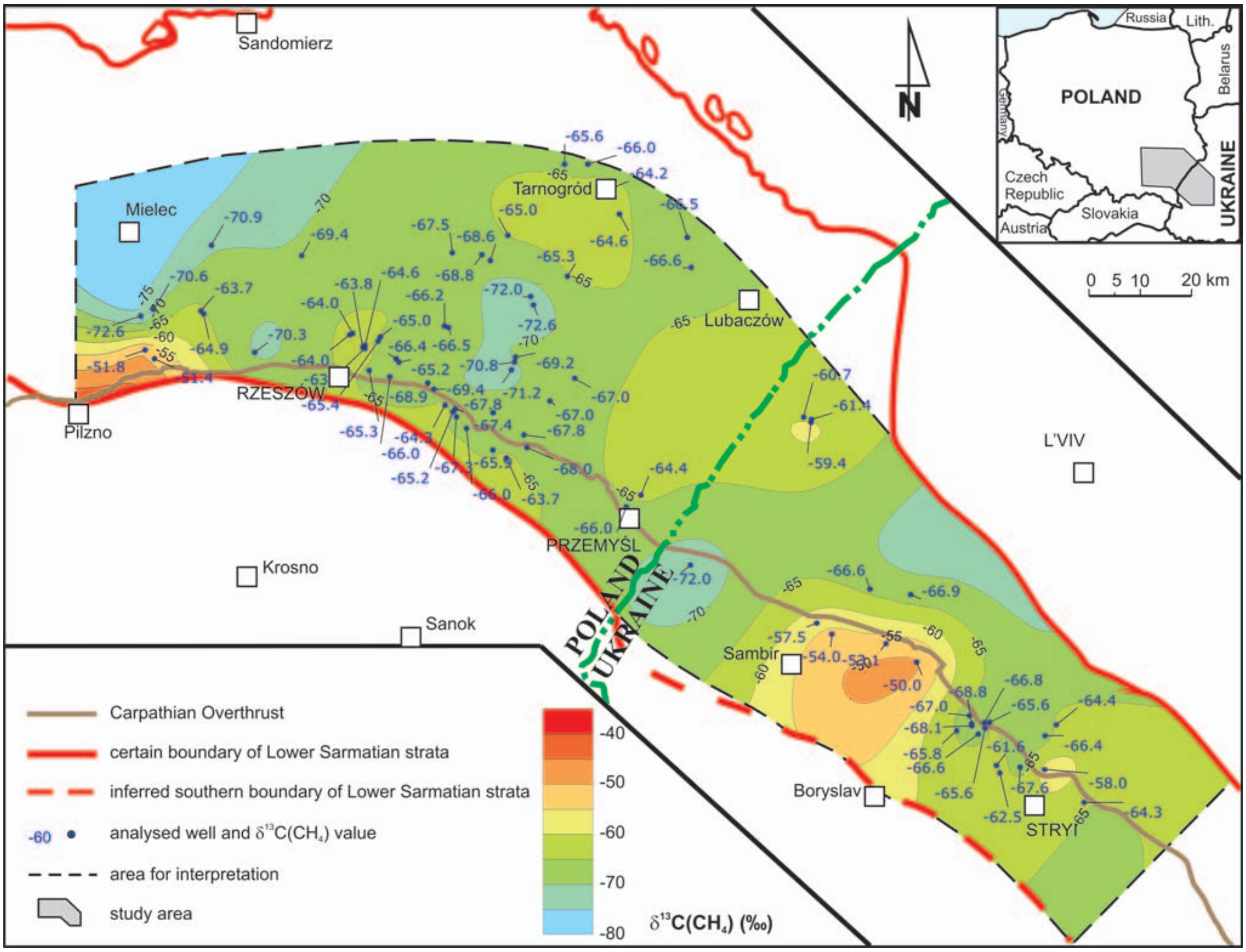

Fig. 18. Contour map of values of $\delta^{13}C(CH_4)$ at the bottom of the Lower Sarmatian strata of the Carpathian Foredeep. Lith. – Lithuania

strata of the inner basin, only the high-temperature methane could be produced. The northern range of generation of thermogenic hydrocarbons was presented in Fig. 20.

The results of modelling revealed that in the A, B, F and G test areas (north of the margin of the Carpathians) the TTI values were 0.05 to 1 (Fig. 21) proving that thermogenic gases had not been generated. At the edge of the Carpathian orogen, the maximum TTI values were: 21 at a depth of about 3,600 metres in C test area, 4 at a depth of about 2,600 metres in D area, and 480 at a depth of about 5,000 metres in D area. These values suggest the appearance of low-temperature thermogenic processes within the autochthonous Miocene strata beneath the Carpathian Overthrust, *i.e.* beneath 2,500 m depth.

The results of modelling for all the test areas proved the generation of microbial methane in almost entire thickness of autochthonous Miocene of the outer basin. Taking into account the quantitative criteria for microbial gas generation (Clayton, 1992), the intensity of methane production was calculated for the generalized sedimentation conditions of the Miocene marine basin. It was found that generation processes of microbial methane were most intensive at the depth interval of 700 to 1,500 m beneath the Miocene sea floor (Fig. 21). The maximum yield of microbially-produced methane was about 5 cubic metres of CH_4 per one cubic metre of source rock. The volume of produced microbial methane is spatially variable within the basin and depends on the burial history. As no dramatic changes of thermal conditions have been deduced within the basin since the Sarmatian, these microbial generation processes have presumably continued until recent (Kotarba *et al.*, 1995). Even the folding and uplift of the Carpathian orogen and the consequent regression of the Miocene sea at the break of the early and late Sarmatian did not impede the microbial processes.

The results of modelling revealed that both in the hypothetical deepest test areas E and I the TTI values were 10^9 and 10^{10}, respectively, thus prompting a conclusion that high-temperature thermogenic zone started below depth of 7,500 m (Fig. 21).

HYDROCARBON ACCUMULATION AND EXPLORATION PROSPECTIVES

The composition of natural gases accumulated in autochthonous Miocene strata of the Polish and Ukrainian Outer Carpathian Foredeep is dominated by methane, which usu-

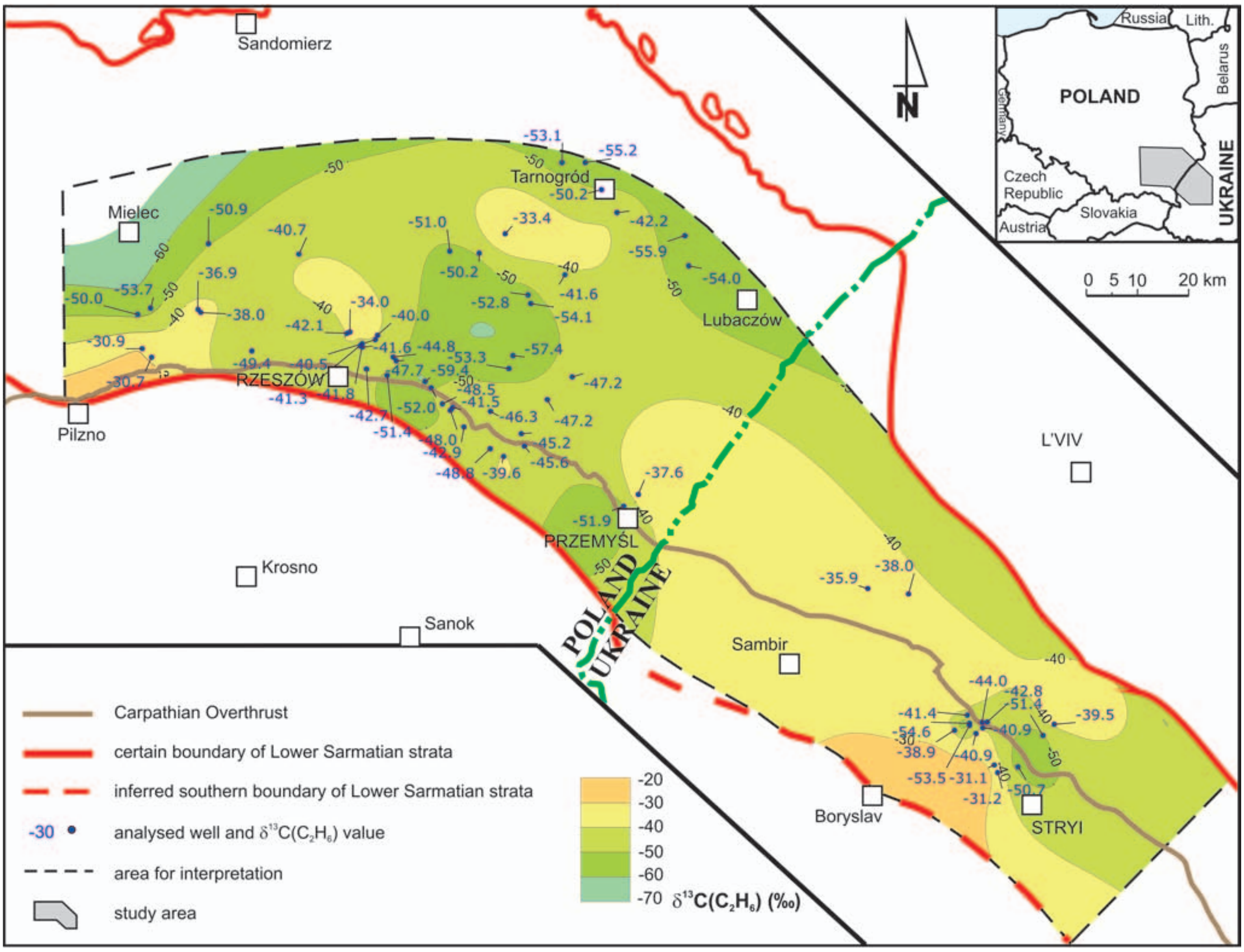

Fig. 19. Contour map of values of $\delta^{13}C(C_2H_6)$ at the bottom of the Lower Sarmatian strata of the Carpathian Foredeep. Lith. – Lithuania

ally constitutes over 98 vol%. Methane was generated by the carbon dioxide reduction pathway of microbial processes (Kotarba, 1998; 2011; Kotarba & Koltun, 2006, 2011; Kotarba *et al.*, 2005). Higher gaseous hydrocarbons (mainly ethane and propane) are usually minor constituents (concentrations less than 0.2 vol%). Ethane was generated during both microbial processes and at the initial stage of the low-temperature thermogenic processes. Propane was generated mainly at the initial stage of the low-temperature thermogenic processes and also during microbial processes (Kotarba, 2011). The microbial methane is of vital economic importance (Rice & Claypool, 1981; Rice, 1992, 1993).

Stable carbon isotope compositions of methane and ethane (Figs 16–19) reveal that natural gases in autochthonous Upper Badenian and Lower Sarmatian strata of the Polish and Ukrainian Carpathian Foredeep north of the Carpathian Overthrust were mainly generated during microbial processes from dispersed organic matter inside this Miocene complex. The occurrence of thermogenic hydrocarbons near the bottom sequence of the Miocene strata near Tarnów (Figs 16, 17) was caused by an inflow from the Mesozoic basement to Miocene strata (Więcław, 2011). Isotopic anomalies near Dębica (Figs 18, 19) in the Polish part and Boryslav, Drohobych and Sambir (Figs 16–19) in the Ukrainian part of the Carpathian Foredeep were most probably caused by the migration of thermogenic gases, which were generated within the Miocene strata beneath the Outer Carpathians.

The high sedimentation rates together with rhythmic and cyclic deposition of Miocene clays and sands as well as the vigorous generation of microbial methane caused that the gas produced in claystone beds was accumulated in the overlaying sandstones, and capped, in turn, by the succeeding claystones. Results of the distribution of immature humic dispersed organic matter in the Upper Badenian and Lower Sarmatian sequences indicates that it is practically homogeneous (Figs 4–7, 8A–C, 9A–C). The migration range of microbial gases was insignificant and locations of their accumulations would depend only on the existence of proper type of traps (compactional anticlines situated above basement uplift, sealed by the Carpathian Overthrust, and sealed by faults, stratigraphic pinch-out and stratigraphic traps related to unconformities). Such a generation and accumulation system of microbial gases gave rise to the formation of multi-horizontal gas fields, *e.g.*, Przemyśl and Husów gas fields. Recent introduction of interpretation of 2-D and 3-D seismic sections and application of DHI (direct

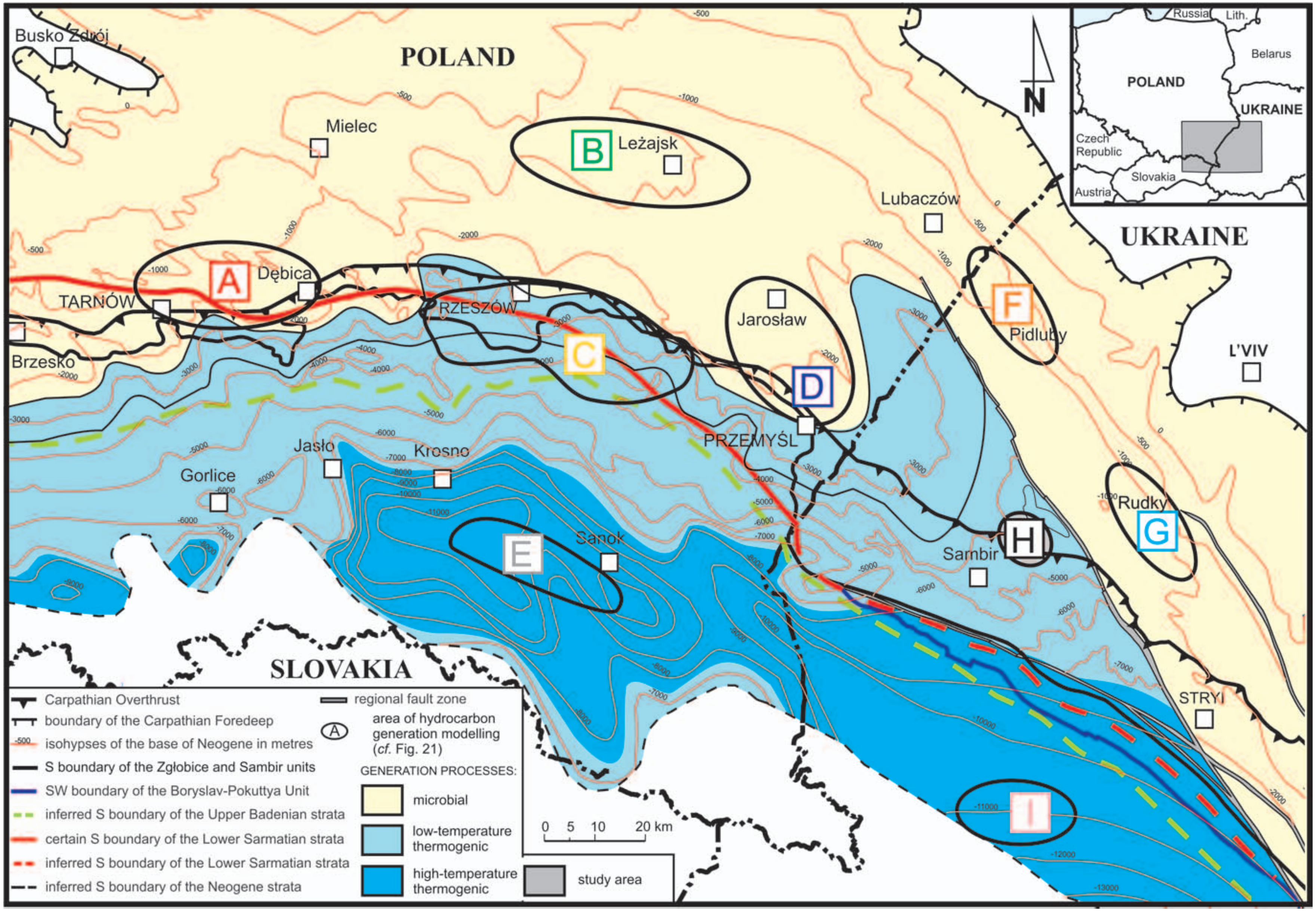

Fig. 20. Sketch map of the central and eastern parts of the Polish and Ukrainian Carpathian Foredeep and locations of the TTI (Time Temperature Index) hydrocarbon generation test areas and zones of microbial and thermogenic processes. TTI hydrocarbon generation test areas modified after Kotarba *et al.* (1998a)

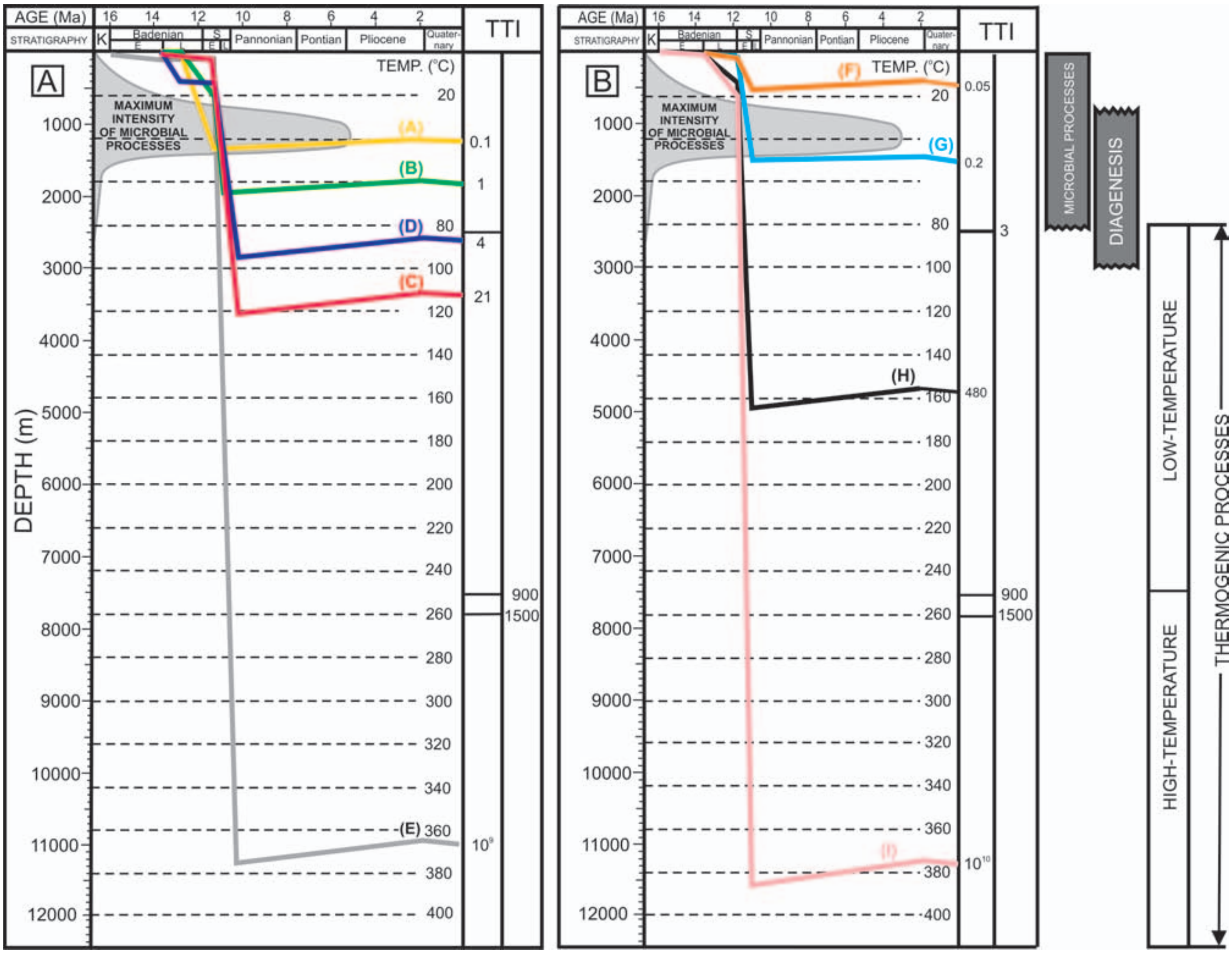

Fig. 21. Model of gas generation within the autochthonous Miocene basin and family of burial-history subsurface temperature grid and TTI (Time Temperature Index) values for (**A**) Tarnów, (**B**) Mielec-Leżask, (**C**) Rzeszów, (**D**) Przemyśl, (**E**) Krosno-Sanok, (**F**) Pidluby, (**G**) Rudky, (**H**) Zaluzhany, and (**I**) Skole areas. Model for A to D areas modified after Kotarba *et al.* (1998a). S – Sarmatian, E – early, L – late

hydrocarbon indicator) on the seismic data enables location of areas of hydrocarbon prospecting (Baran & Jawor, 2009; Myśliwiec, 2004a, b; Myśliwiec *et al.*, 2006).

An idea has been put forward in the geochemical literature that microbial methane might have been accumulated as hydrate beneath the Miocene seafloor (Kotarba, 1992). However, the results of bathymetric analyses (Czepiec & Kotarba, 1998) revealed that the Badenian sea was presumably only slightly deeper than the outer shelf, *i.e.* about 300 m, at most. Initially, the Sarmatian sea was about 30–50 m deep and has shallowed to only about 10 m. Both the Badenian and Sarmatian seas were the warm basins of surface water temperatures of 17–20°C (Czepiec & Kotarba, 1998). Taking into account these data, the concept that natural methane hydrate zone formed beneath the Miocene seafloor must be rejected.

Geochemical studies and TTI modelling within the autochthonous Miocene strata of the Carpathian Foredeep occurring south beneath the Carpathian Overthrust reveal that the low-temperature thermogenic process starts from a depth of 2,500 m, the high-temperature thermogenic process begins from a depth of 7,500 m, and three generation zones were established: microbial, low-temperature thermogenic and high-temperature thermogenic (Figs 20, 21).

All hydrocarbon deposits discovered in the autochthonous Miocene strata of the Polish and Ukrainian Carpathian Foredeep, north and along the present edge of the Outer Carpathians, occur within the microbial zone (Figs 1, 20). Gases accumulated in this zone are mainly of microbial origin. Oil from one Orkhovychi deposit and from petroleum inflows near Tarnów migrated to the Miocene strata from the Mesozoic basement (Kotarba & Jawor, 1993; Więcław, 2011; Więcław *et al.*, in press). The entire surface of this zone has a very good seismic and drilling record. In the Polish Carpathian Foredeep, the gas resources were assessed to 200–220 billion cubic metres, and about 160 billion cubic metres have been already discovered.

The current interpretation (Oszczypko, 2006b; Oszczypko *et al.*, 2006) assumes that the Upper Badenian deposits south of the Carpathian Overthrust continue over a distance of some 10–20 km, and farther south only Lower Miocene deposits occur; and the southern extent of Lower Sarmatian deposits is decreased as compared to the Upper Badenian. The inferred southern boundaries of the Upper

Badenian and Lower Sarmatian strata follow such an interpretation (*cf.* Figs 4–7, 10, 11, 16–19), however, the general pattern of distribution of Miocene facies below the Carpathian nappes is very well established only west of the "Cracow bolt" (Ney, 1968) where a sufficient documentation by wells exists (*e.g.*, Oszczypko & Oszczypko-Clowes, 2003; Oszczypko *et al.*, 2006). In other areas, the well control is poor and it is not certain if the pattern established in the Silesian part of the Carpathian Foredeep is valid for its other area that is related to the Małopolska block (Buła & Habryn, 2011), considering the recorded differences in palaeotopography of the western and eastern parts of the Carpathian Foredeep basin (Buła *et al.*, 2008). During the Palaeogene, the area of the Carpathian Foredeep was subject to intensive erosion that resulted in highly variable morphology. The maximum height difference exceeded 2,000 m and the valley depths reached 1,000 m (Karnkowski & Ozimkowski, 2001); in these deep valleys Palaeogene conglomerates and sandy-silty deposits up to 300 m thick have been found in some places (Moryc, 1995). Considering that the palinspastic reconstruction assumes that bathyal deposition took place in the major part of the early Badenian basin (Oszczypko *et al.*, 2006, Fig. 18) and that these deep basin conditions continued during the subsequent Tyras and Kosiv deposition in western Ukraine (Peryt, 2006), it is highly probable that the southern Badenian extent, in particular in SE Poland and western Ukraine, does not differ significantly from the Miocene extent as shown in Fig. 20.

North and along the present edge of the Carpathian Overthrust in the Ukraine, the Lower Badenian Sandy-Calcareous Series contains twelve gas and gas-condensate deposits, and one oil deposit (Fig. 1B). As the lithofacies development of the Lower Miocene strata resembles the development of the Upper Badenian and Lower Sarmatian strata, it can also contain a similar quantity and similar genetic type of gas-prone kerogen. Their thickness beneath the Carpathian Overthrust exceeds even 1.5 km (Oszczypko, 2006b). All these facts may indicate that in both low- and high-temperature thermogenic zones considerable quantities of gases could be generated and accumulated.

CONCLUSIONS

The Carpathian Foredeep developed during the early and middle Miocene as a peripheral flexural foreland basin in front of the advancing Carpathian Overthrust. The outer foredeep (termed the Bilche-Volytsia zone in the Ukraine) is filled with generally undisturbed, flat-lying autochthonous Middle Miocene marine deposits, which range in thickness from a few hundred metres in the northern, marginal parts of the Foredeep to as much as 3.5 km in SE Poland and 5 km in western Ukraine.

Since 1920, within the autochthonous Miocene strata north and along the present edge of the Carpathian Overthrust, 101 gas and gas-condensate deposits in the Polish Carpathian Foredeep (mainly in the Upper Badenian and Lower Sarmatian strata and locally in the Lower Badenian strata), and 44 gas and gas-condensate deposits and one oil deposit in the Ukrainian Carpathian Foredeep (mainly in the Upper Badenian and Lower Sarmatian strata and locally in the Lower Badenian Sandy-Calcareous Series) have been discovered. The molecular composition of natural gases accumulated in autochthonous Miocene strata of the Polish and Ukrainian Carpathian Foredeep is dominated by methane, which usually constitutes over 98 vol%. Methane was generated by the carbon dioxide reduction pathway of microbial processes. Ethane was generated by both microbial and thermogenic processes and propane at the initial stage of the low-temperature thermogenic processes, and also by microbial processes.

In the Upper Badenian strata, the total organic carbon (TOC) contents vary from 0.02 to 1.48 wt% (average 0.75 wt%) in the Polish Carpathian Foredeep and from 0.44 to 2.01 wt% (average 0.96 wt%) in the Ukrainian Carpathian Foredeep. In the Lower Sarmatian strata, the TOC varies from 0.02 to 3.22 wt% (average 0.69 wt%) in the Polish Carpathian Foredeep and from 0.01 to 1.45 wt% (average 0.71 wt%) in the Ukrainian Carpathian Foredeep. This dispersed organic matter in marine Miocene sediments is gas-prone, terrestrial (humic) in origin.

The high sedimentation rates together with rhythmic and cyclic deposition of Miocene clays and sands as well as the vigorous generation of microbial methane caused that the gas produced in claystone beds was accumulated in the overlaying sandstones, and capped, in turn, by the succeeding claystones. A migration range of microbial gases was insignificant and locations of their accumulations would depend only on the existence of proper type of traps (compactional anticlines situated above basement uplift, sealed by the Carpathian Overthrust, and sealed by faults, stratigraphic pinching out and stratigraphic traps related to unconformities). Such generation and accumulation system of microbial gases gave rise to the formation of multi-horizontal gas fields.

Another situation is encountered in the autochthonous Miocene strata south beneath the Carpathian Overthrust. As the lithofacies development of the Lower Miocene strata resembles the development of the Upper Badenian and Lower Sarmatian strata, it can also contain a similar quantity and similar genetic type of gas-prone kerogen. Their thickness beneath the Carpathian Overthrust exceeds even 1.5 km. Geochemical studies reveal that from the depth of 2,500 m starts the process of low-temperature thermogenic hydrocarbon generation ("oil window"). At greater depths, more than 7,500 m, within the autochthonous Lower Miocene basin existed the high-temperature methane generation zone ("gas window"). All these facts may evidence that in both low- and high- temperature thermogenic zones considerable quantities of gases might have generated and accumulated.

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