ORIGIN OF NATURAL GASES IN THE AUTOCHTHONOUS MIOCENE STRATA OF THE UKRAINIAN CARPATHIAN FOREDEEP AND ITS MESOZOIC BASEMENT

Maciej J. KOTARBA[1] **& Yuriy V. KOLTUN**[2]

[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] *National Academy of Sciences of Ukraine, Institute of Geology and Geochemistry of Combustible Minerals, 3a Naukova Street, 79060 Lviv, Ukraine*

Abstract: Methane concentrations in natural gases accumulated in the Lower and Upper Badenian and Lower Sarmatian reservoirs of the Bilche-Volytsia Unit in the western part of the Ukrainian Carpathian Foredeep usually exceed 96 vol%. Methane was generated by microbial reduction of carbon dioxide in the marine environment. Microbial methane and ethane were produced mainly during sedimentation of Miocene clays and muds. It is possible that this microbial process continues today. Higher light hydrocarbons (ethane in part, and mainly propane, butanes and pentanes) were generated during the diagenesis and the initial stage of the low-temperature, thermogenic processes from Type III and III/II kerogen deposited in Miocene strata and/or Middle and Upper Jurassic basement rocks. Limited variations in the values of geochemical hydrocarbon indices and stable isotope ratios of methane, ethane and propane with the depth indicate similar gas generation conditions within the whole Miocene succession. The microbial gases (methane and partly ethane) generated during microbial processes within the Miocene strata later migrated to the Upper Jurassic and the Upper Cretaceous (Cenomanian) reservoirs of the Mesozoic basement, and to the bottommost Lower Badenian reservoirs of the analysed Letnia, Orkhovychi, Rudky and Vereshchytsia fields. The low hydrogen concentrations within the Miocene strata as well as within the Upper Jurassic and the Upper Cretaceous (Cenomanian) reservoirs of the Mesozoic basement, and within the bottommost Lower Badenian reservoirs are also related to microbial processes. Carbon dioxide and nitrogen, which are common minor constituents, were generated by both microbial and low-temperature thermogenic processes. Moreover, CO_2 also underwent secondary processes, mainly dissolution in water, during migration. At least part of the nitrogen accumulated in the Rudky field, which is remarkably high in N_2 (96.9 vol%), is probably of atmospheric origin and was introduced to the reservoir by secondary recovery methods.

Key words: microbial gases, thermogenic gases, stable carbon isotopes, stable hydrogen isotopes, carbon dioxide, nitrogen, Miocene strata, Mesozoic strata, Ukrainian Carpathian Foredeep.

INTRODUCTION

The aim of this study is to analyse the conditions of generation, migration and accumulation of natural gases within the autochthonous Miocene strata of the Bilche-Volytsia Unit and the Mesozoic basement of the Ukrainian Carpathian Foredeep sector between the Polish-Ukrainian state border and Stryi (Fig. 1). The molecular composition of the gases, the stable carbon isotope ratios of methane, ethane, propane, butanes, pentanes and carbon dioxide, the stable hydrogen isotope ratios of methane, and the isotopic composition of the molecular nitrogen occurring in these gases are presented in the paper. These results are referred to the geological setting and the geochemical characteristics of the dispersed organic matter contained in the autochtho-

nous Miocene, Middle and Upper Jurassic and Ordovician–Silurian strata of the Carpathian Foredeep between Tarnogród and Stryi (southeastern Poland and western Ukraine) (Kotarba *et al.*, 2011b; Kosakowski *et al.*, in press; Więcław *et al.*, in press).

Previous molecular and isotopic studies of natural gases accumulated within the autochthonous Miocene strata of the Polish and Ukrainian Carpathian Foredeep have revealed that the methane-dominated component was generated by microbial processes (Głogoczowski, 1976; Shabo & Mamchur, 1984; Kotarba *et al.*, 1987, 2005; Kotarba, 1992, 1998, 2011; Jawor & Kotarba, 1993; Kotarba & Jawor, 1993; Kotarba & Koltun, 2006). Natural gases accumulated

Fig. 1.   Sketch map showing the major tectonic units of the Ukrainian Carpathian region and locations of gas sampling sites. EEP – East European Platform, B-V – Bilche-Volytsia Unit (outer part of the Carpathian Foredeep), SA – Sambir (Stebnik) Unit, B-P – Boryslav-Pokuttya Unit, OC – Outer (Flysch) Carpathians

within the Palaeozoic–Mesozoic basement of the Polish Carpathian Foredeep can be attributed to various genetic types. Studies revealed the presence of microbial and low-temperature, thermogenic varieties associated with oil and condensate, and a non-associated, high-temperature, thermogenic variety (Kotarba & Jawor, 1993). Moreover, in the Upper Jurassic carbonate reservoir forming one of the tectonic blocks of the Lubaczów gas field and in the Cenomanian sandstone reservoir of the Brzezowiec gas field typical microbial gases were found, which migrated from the autochthonous Miocene strata (Jawor & Kotarba, 1991, 1993; Kotarba & Jawor, 1993). Origin of natural gases in the Boryslav-Pokuttya Unit of the Ukrainian Outer Carpathians

was explained by Kotarba *et al*. (2009) and Sechman *et al.* (2009). Unfortunately, geochemical studies of natural gases accumulated within the Mesozoic basement of the Ukrainian part of the Carpathian Foredeep, which would explain their origin, have not been carried out to date.

GEOLOGICAL SETTING
AND PETROLEUM OCCURRENCE

The Ukrainian Carpathians form the middle segment of the Carpathian Arc located between the Polish and the Romanian Carpathians (Fig. 1). This part of the Carpathian

orogen consists of several tectonic units overthrust north-eastward (Dolenko, 1962; Vialov, 1965; Glushko, 1968; Kruglov *et al.*, 1985; Ślączka *et al.*, 2006).

In this part of the Carpathian orogen, the major part of both the oil and gas fields are located within the frontal tectonic units, mainly in the Carpathian Foredeep. The Foredeep includes three tectonic units, which differ in both the geological structure and the oil and gas potential. The Boryslav-Pokuttya Unit is the frontal nappe of the Outer Carpathian Belt. This is the main oil-bearing unit in the Ukrainian Carpathians. It is covered by overthrust folded molasse sediments belonging to the Sambir (Stebnik) Unit. No hydrocarbons have been found in the Sambir Unit to date. The outermost, Bilche-Volytsia Unit of the Carpathian Foredeep hosting the main gas fields in the area between Polish-Ukrainian border and Stryi (Fig. 1) is the subject of this study. To the southwest it underlies the Sambir and Boryslav-Pokuttya units and to the northeast it covers a fragment of the East-European Platform.

The Bilche-Volytsia Unit shows diversity of stratigraphic sequences and variable thicknesses of Miocene deposits (Shcherba *et al.*, 1987). The Miocene strata reach their maximum thickness of over 5 km in the Krukenychy Depression near the Ukrainian-Polish border (Kurovets *et al.*, 2004). In the northwestern part of the unit, the Miocene strata cover the Palaeozoic and Mesozoic formations. Gas fields occur not only in the Miocene sequence but also in both the Upper Jurassic and the Upper Cretaceous reservoirs. In the southeastern part of the Bilche-Volytsia Unit, the Palaeozoic and Mesozoic deposits also occur underneath the Miocene sequence but gas is accumulated only in the Miocene rocks.

The Miocene succession of the Bilche-Volytsia Unit consists of the Lower Badenian Sandy-Calcareous Series and Baraniv beds, Upper Badenian Tyras and Kosiv formations and Lower Sarmatian Dashava Formation (Andreyeva-Grigorovich *et al.*, 1997, 2008). In the bottom part of the Bilche-Volytsia Unit, various siliciclastic units, 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.*, 1998; Krups'kyy, 2001) to be Karpatian and/or Palaeogene in age. Based on recent regional stratigraphic correlations and palaeogeographic reconstructions, these deposits are included into the transgressive Lower Badenian Sandy-Calcareous Series (*e.g.*, Andreyeva-Grigorovich *et al.*, 1997; Oszczypko *et al.*, 2006). These deposits are mainly sandstones, up to several tens of metres thick. The Lower Badenian Baraniv beds, up to 80 m thick, are represented by argillites, sandstones and limestones. At the base of the Upper Badenian succession, up to 50 m thick Tyras Formation occurs. It is made up mainly of evaporate sediments, covered by the Kosiv Formation, up to 1,500 m thick, composed mainly of clayey sediments with sandstones intercalations.

The Lower Sarmatian sediments are represented by the Dashava Formation, which are sandstones with argillitic intercalations. They are subdivided into the lower part of the Dashava Formation with a maximum thickness of about 3,000 m and the upper part of the Dashava Formation with a

maximum thickness of about 1,900 m (Shcherba *et al.*, 1987). A characteristic feature of the whole Lower Sarmatian succession is the presence of a number of sandstone layers extending over the vast area. These layers are easily identified in well-logs and are best correlated in the northwestern part of the Bilche-Volytsia Unit. These sandstone horizons are gas reservoirs and the seal is provided by clayey layers. Such a development of the Lower Sarmatian succession allowed Vishniakov *et al.* (1979) to subdivide them into a number of cycles, which include sandstone horizons and enclosing clayey layers. In total, 17 such cycles were distinguished in the Lower Dashava Formation and another 14 were found in the Upper Dashava Formation. Each cycle has its own index (Kurovets *et al.*, 2004). Gas fields occur in all sandstone horizons, except for the upper four. Moreover, gas fields were discovered in all other Miocene stratigraphic units in the Lower and Upper Badenian. Gas reservoirs in the Badenian and Sarmatian successions are sandstone and siltstone layers, usually from 0.1 to 2 m (sometimes up to 5 m) thick. The porosity of sandstones usually ranges from 20 to 30%, but often is up to 40%. The sandstones of the Lower Badenian Sandy-Calcareous Series commonly form massive gas reservoirs together with the underlying Cretaceous sandstones. The porosity of the Lower Badenian sandstones ranges from 6 to 30% (Vul *et al.*, 1998).

The major part of the Bilche-Volytsia Unit is underlain by Jurassic and Cretaceous rocks. The northwestern part of the Bilche-Volytsia Unit rests upon the Lower, Middle and Upper Jurassic strata. The Lower Jurassic sequence, up to 1,000 m thick, comprises mainly terrigenous sediments whereas the Middle Jurassic sequence is dominated by black shales of the Kokhanivka Formation, reaching a thickness of 500 m (Dulub *et al.*, 1986). The Upper Jurassic strata unconformably overlie the Mesozoic rocks or the pre-Mesozoic basement. These are predominantly limestones over 800 m thick. The outline of tectonics and lithostratigraphy of the Palaeozoic–Mesozoic basement in the study area can be found in Buła and Habryn (2011) and in Krajewski *et al.* (2011). The major part of the southwestern margin of the East-European Platform is covered by Cretaceous sediments, Neocomian to Maastrichtian in age, reaching a thickness of over 500 m (Vul *et al.*, 1998). The general structure of the Ukrainian Carpathian Foredeep is presented in Fig. 2B in Kotarba *et al.* (2011a). The Upper Cretaceous sandstones and the Upper Jurassic carbonates provide reservoirs for oil and gas in several fields located in the basement of the Bilche-Volytsia Unit.

Fourty-four gas and gas-condensate deposits and one oil and gas deposit were discovered in the Miocene strata of the Bilche-Volytsya Unit of the Ukrainian Carpathian Foredeep (Kotarba *et al.*, 2011a). These fields are scattered within the whole Bilche-Volytsia Unit, though they are mainly clustered in the northwestern part. These fields comprise over 160 accumulations. In both the Badenian and Sarmatian fields the traps are lithologically and tectonically sealed. Commonly, the Sambir Overthrust plays the role of the seal. The major part of the gas fields hosted in the Bilche-Volytsia Unit occur in elevated structures. In 1920, one of the first gas-producing wells in the world started pro-

Gas sample sites in the autochthonous Miocene strata and Mesozoic basement of the Carpathian Foredeeep

Well	Field	Sample code	Lithology of reservoir	Lithostratigraphy	Age of reservoir	Depth (m)
Autochthonous Miocene strata (Bilche-Volytsya unit)						
Hlynky-1*	Hlynky	Hl-1*	Sandstones	Sandy-Calcareous Series	Lower Badenian	1,192-1,222
Mala Horozhanna-5	Mala Horozhanna	MH-5				430-463
Pivdenne Hrabyne-10	Pivdenne Hrabyne	PH-10				1,336-1,344
Turady-1	Turady	Tu-1		Tyras Formation	Upper Badenian	254-275
Bilche Volytsia-9*	Bilche-Volytsia	BV-9*		Dashava Formation	Lower Sarmatian	841-940
Bilche Volytsia-500*		BV-500*				636-650
Dubanevychi-1	Makuniv	Du-1				1,570-1,600
Hai-4, -5,-6, -30, -32	Hai	Ha				1,512-1,650
Kavs'ke-40	Kavs'ke	Ka-40				488-491
Letnia-2*	Letnia	Le-2*				1,245-1,267
Letnia-21		Le-21				1,098-1,152
Letnia-38		Le-38				1,686-1,694
Letnia-52		Le-52				1,168-1,181
Letnia-60		Le-60				1,283-1,302
Letnia-64		Le-64				1,643-1,660
Makuniv-10	Makuniv	Mk-10				2,138-2,155
Opory-22a	Opory	Op-22a				380-422
Opory-40		Op-40				296-298
Shidne Dovhe-10	Shidne Dovhe	SD-10				1,660-1,675
Khidnovychi-133^	Khidnovychi	Khi-133^				719-830
Dashava-65^	Dashava	Dh-65^				754-770
Hrynivka-17, -51^	Hrynivka	Hk^				1,100-1,300
Pyniany-1^	Pyniany	Py-1^				2,000-2,200
Pyniany-25^		Py-25^				1,712-1,735
Svydnytsia-54^	Svydnytsia	Svy-54^				350-450
Svydnytsia-48, -51, -61^		Svy-48, -51, -61^				640-644
Svydnytsia-55, -62^		Svy-55, -62^				660-667
Uhers'ko-98a^	Uhers'ko	Uh-98a^				365-369
Zaluzhany-12^	Zaluzhany	Zh-12^				1,400-1,600
Zaluzhany-14^		Zh-14^				3,200-3,400
Mesozoic basement						
Orkhovychi-2	Orkhovychi	Oh-2	Carbonates & Sandstones		Upper Jurassic & Lower Badenian	1,881-1,915
Rudky-228	Rudky	Ru-228				1,293-1,380
Vereshchytsia-4	Vereshchytsia	Ve-4				1,419-1,490
Letnia-13	Letnia	Le-13	Carbonates		Upper Jurassic	1,590-1,595
Letnia-65		Le-65	Sandstones		Cenomanian & Lower Badenian	1,578-1,593

* – after Kotarba and Koltun (2006), ^ – after Shabo and Mamchur (1984)

duction from the Dashava deposit hosted in the Bilche-Volytsia Unit (Vul *et al.*, 1998). Eleven oil, gas-condensate and gas fields were discovered within the Mesozoic basement of the Ukrainian part of the Carpathian Foredeep (Kotarba *et al.*, 2011c). The Miocene rocks of the adjacent tectonic blocks often serve as seals for the Mesozoic fields.

Our study provides geochemical characteristics of gases from reservoirs of different ages and types (Table 1), and attempts to explain the origin of these gases.

METHODOLOGY

Sampling procedure

The gas samples were collected from 15 producing wells drilled into the autochthonous Miocene (Lower and Upper Badenian and Lower Sarmatian) reservoirs of the Bilche-Volytsia Unit of the Ukrainian Carpathian Foredeep and five wells accessing the Upper Jurassic and Upper Cretaceous (Cenomanian) reservoirs of the Mesozoic basement
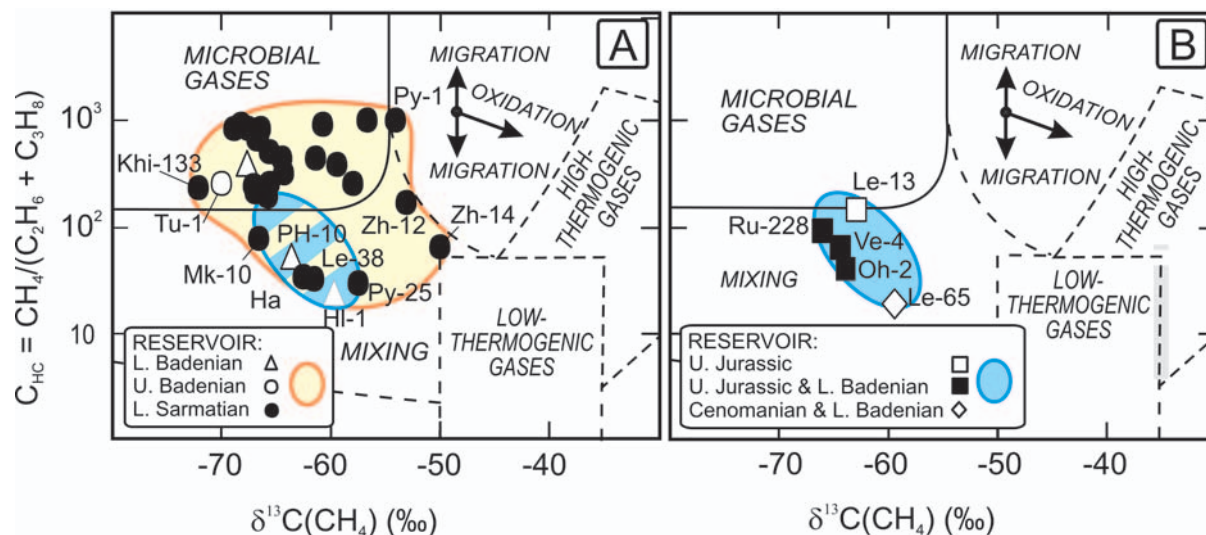
Fig. 2. Hydrocarbon index (C$_{HC}$) *versus* δ^{13}C(CH$_4$) for natural gases accumulated in **(A)** Miocene and **(B)** Upper Jurassic, Upper Cretaceous (Cenomanian) and Lower Badenian reservoirs of the Ukrainian Carpathian Foredeep and its basement. Compositional classification fields modified after Whiticar (1994)

and the bottommost Lower Badenian reservoirs. The names of the wells and fields are listed in Table 1 and their locations are shown in Fig. 1. Free gases were collected directly at the producing wellheads in metal containers (volume ~1,000 cm^3) and gases dissolved in oils were taken from separators to glass containers (volume ~500 cm^3) (Table 1). For interpretation purposes, we also used earlier molecular and isotope compositions of four natural gases (Hl-1, BV-9, BV-500 and Le-2) from Miocene strata published by Kotarba and Koltun (2006), and stable carbon isotope composition of eleven natural gases from the Lower Sarmatian Dashava Formation of Dashava, Khidnovyhchi, Pyniany, Svidnycia, Uhers'ko and Zaluzhany gas fields provided by Shabo and Mamchur (1984).

Analytical procedure

Analytical methods of measurements of the molecular and isotopic compositions of natural gases were described in another paper in this volume (Kotarba, 2011).

RESULTS AND DISCUSSION

Natural gases from the autochthonous Miocene reservoirs

The gases collected from the autochthonous Miocene (Lower and Upper Badenian and Lower Sarmatian) strata (19 samples) and gases from the Lower Sarmatian strata (Shabo & Mamchur, 1984) of the Bilche-Volytsia Unit of the Ukrainian Carpathian Foredeep (11 samples) vary in their molecular and isotopic compositions. Molecular and isotopic compositions, and hydrocarbon (C$_{HC}$) [C$_{HC}$ = CH$_4$/(C$_2$H$_6$ + C$_3$H$_8$)], carbon dioxide-methane (CDMI) {CDMI = [CO$_2$/ (CO$_2$ + CH$_4$)] 100 (%)} and iC$_4$H$_{10}$/nC$_4$H$_{10}$ gas indices of analysed gases are summarized in Tables 2 and 3.

For classification of the analysed hydrocarbon gases in terms of origin and generation mechanism, the genetic diagrams described by Whiticar *et al.* (1986), Schoell (1988), Whiticar (1994) and Berner and Faber (1996) were used (Figs 2–4). Figure 5 shows the plots of the carbon isotopes values of methane, ethane, propane, the butanes and pentanes *vs*. their reciprocal carbon numbers. As proposed, by *e.g.*, Chung *et al.* (1988) and Rooney *et al.* (1995), linear trends of these plots are indicative of a single source for thermogenic gases. Zou *et al.* (2007) and Kotarba *et al.* (2009) suggest that in this type of plot a "dogleg" trend, exemplified by relatively ^{13}C-depleted methane and ^{13}C-enriched propane as compared to ethane, results from the presence of natural gas that was not generated from a single source rock or that underwent post-generation alteration (*e.g.*, secondary gas cracking, microbial oxidation or thermochemical sulphate reduction). Moreover, the increased ^{13}C-depletion of methane in relation to ethane has been applied used to evaluate the mixing proportion between microbial methane and thermogenic gases (Kotarba & Lewan, 2004; Kotarba *et al.*, 2009).

The diagnostic plots of stable carbon and hydrogen isotope data in Figs 2 and 3 indicate that the methane in the Lower and Upper Badenian and Lower Sarmatian reservoirs was mainly generated by microbial carbon dioxide reduction with occasional admixture of low-temperature, thermogenic gases. The microbial carbon dioxide reduction process occurs mainly in the marine environment (Whiticar *et al.*, 1986; Rice, 1992). The stable carbon isotope compositions of ethane, propane, butanes and pentanes (Figs 4, 5) suggest that ethane results mainly from microbial processes whereas propane, butanes and pentanes were produced during diagenesis and/or the early stages of low-temperature, thermogenic processes. Comparison of stable carbon isotope composition of propane, butanes and pentanes with that of kerogen (Fig. 5A–C) indicates the thermogenic gas components were sourced by type III kerogen of the Miocene strata or at least partly from the Middle and Upper Jurassic strata (Kotarba *et al.*, 2011b; Kosakowski *et al.*, in press). Ethane was generated in insignificant quantities by

Table 2

Molecular composition of natural gases produced from the autochthonous Miocene strata and Mesozoic basement

Sample code	Molecular composition (vol%)											
	N_2	CO_2	He	Ar	H_2	CH_4	C_2H_6	C_3H_8	iC_4H_{10}	nC_4H_{10}	iC_5H_{12}	nC_5H_{12}
Autochthonous Miocene strata (Bilche-Volytsya unit)												
Hl-1*	2.00	0.08	0.04	0.013	n.a.	92.6	2.26	1.65	0.36	0.52	n.a.	n.a.
MH-5	1.61	0.27	0.02	0.011	0.016	97.8	0.20	0.06	0.016	0.01	0.007	0.003
PH-10	2.83	0.14	0.04	0.019	0.000	94.2	0.98	0.81	0.27	0.31	0.17	0.12
Tu-1	2.22	0.25	0.03	0.013	0.000	96.9	0.25	0.14	0.07	0.06	0.05	0.02
BV-9*	1.21	0.14	0.013	0.008	n.a.	98.4	0.18	0.05	0.015	0.006	n.a.	n.a.
BV-500*	0.95	0.14	0.008	0.008	n.a.	98.8	0.11	0.010	0.005	0.001	n.a.	n.a.
Du-1	0.68	0.25	0.013	0.004	0.000	98.4	0.33	0.14	0.10	0.03	0.05	0.01
Ha	0.90	0.13	0.007	0.008	0.000	95.1	1.66	1.23	0.25	0.36	0.13	0.12
Ka-40	0.57	0.09	0.005	0.007	0.000	99.2	0.11	0.012	0.005	0.001	0.002	0.000
Le-2*	1.09	0.08	0.007	0.008	n.a.	98.6	0.16	0.05	0.02	0.007	n.a.	n.a.
Le-21	2.26	0.09	0.000	0.011	0.004	97.4	0.12	0.03	0.010	0.005	0.006	0.004
Le-38	0.94	0.13	0.006	0.007	0.000	94.6	1.73	1.32	0.27	0.40	0.16	0.17
Le-52	0.69	0.06	0.007	0.20	0.11	98.6	0.28	0.11	0.02	0.04	0.02	0.03
Le-60	0.95	0.38	0.003	n.a.	0.08	98.4	0.09	0.07	0.04	0.02	0.02	0.008
Le-64	0.45	0.02	0.009	0.008	0.03	98.5	0.32	0.22	0.11	0.08	0.08	0.04
Mk-10	1.03	0.47	0.013	0.003	0.000	95.9	0.61	0.66	0.74	0.25	0.10	0.09
Op-22a	0.55	0.01	0.004	0.006	0.000	99.3	0.10	0.007	0.004	0.0000	0.000	0.000
Op-40	0.34	0.04	0.005	0.02	0.000	99.5	0.11	0.011	0.002	0.0000	tr.	0.000
SD-10	0.78	0.14	0.006	0.07	0.000	98.3	0.26	0.17	0.09	0.06	0.06	0.03
Khi-133^	n.a.	0.10	n.a.	n.a.	n.a.	98.6	0.35	0.09	0.12			
Dh-65^	n.a.	0.20	n.a.	n.a.	n.a.	99.4	0.23	0.09	0.10			
Hk^	n.a.	0.10	n.a.	n.a.	n.a.	99.3	0.07	0.03	0.04			
Py-1^	n.a.	0.75	n.a.	n.a.	n.a.	98.0	0.08	0.02	0.02			
Py-25^	n.a.	0.40	n.a.	n.a.	n.a.	94.9	1.83	1.42	0.42			
Svy-54^	n.a.	0.08	n.a.	n.a.	n.a.	99.3	0.09	0.14	0.10			
Svy-48, -51, -61^	n.a.	0.08	n.a.	n.a.	n.a.	99.4	0.04	0.07	0.06			
Svy-55, -62^	n.a.	0.10	n.a.	n.a.	n.a.	99.3	0.10	0.17	0.12			
Uh-98a^	n.a.	0.20	n.a.	n.a.	n.a.	97.6	0.32	0.08	0.07			
Zh-12^	n.a.	4.80	n.a.	n.a.	n.a.	92.9	0.52	0.05	0.10			
Zh-14^	n.a.	0.89	n.a.	n.a.	n.a.	95.1	0.97	0.54	1.76			
Minimum value	0.34	0.01	0.000	0.003	0.000	92.6	0.04	0.007	0.002	0.0000	0.000	0.000
Maximum value	2.83	4.80	0.04	0.20	0.11	99.5	2.26	1.65	0.76	0.52	0.17	0.17
Mesozoic basement												
Oh-2	2.57	0.79	0.01	0.02	0.000	92.9	1.17	1.24	0.35	0.57	0.19	0.15
Ru-228	96.9	0.19	tr.	n.a.	0.20	2.71	0.017	0.014	0.006	0.42	0.007	0.004
Ve-4	3.05	0.40	0.01	0.008	0.006	94.0	0.85	0.71	0.24	0.27	0.15	0.11
Le-13	1.98	0.19	0.03	0.008	0.005	97.0	0.46	0.23	0.03	0.04	0.02	0.014
Le-65	6.60	0.49	0.03	0.05	0.05	86.7	2.60	1.99	0.42	0.55	0.21	0.18
Minimum value	1.98	0.19	tr.	0.008	0.000	2.71	0.017	0.014	0.006	0.04	0.007	0.004
Maximum value	96.9	0.79	0.03	0.05	0.20	97.0	2.60	1.99	0.42	0.57	0.21	0.18

* – after Kotarba and Koltun (2006), ^ – after Shabo and Mamchur (1984) – for these gases $\Sigma(C_4 + C_5)$ were analysed, tr. – traces, n.a. – not analysed

microbial processes, but more than the proposed ethanogenesis rate (Oremland *et al.*, 1986) of one molecule of ethane per one thousand molecules of methane. Microbial ethane with ^{12}C enrichment (–61.2 to –52.5‰) has been reported in producing microbial gas accumulations (Lillis, 2007) and

microbial propane in some deep marine sediments (Hinrichs *et al.*, 2006).

The depth of the sampled gas accumulations in the Lower and Upper Badenian and Lower Sarmatian reservoirs varied from 254 to 3,400 m (Table 1, Fig. 6). Insignifi-
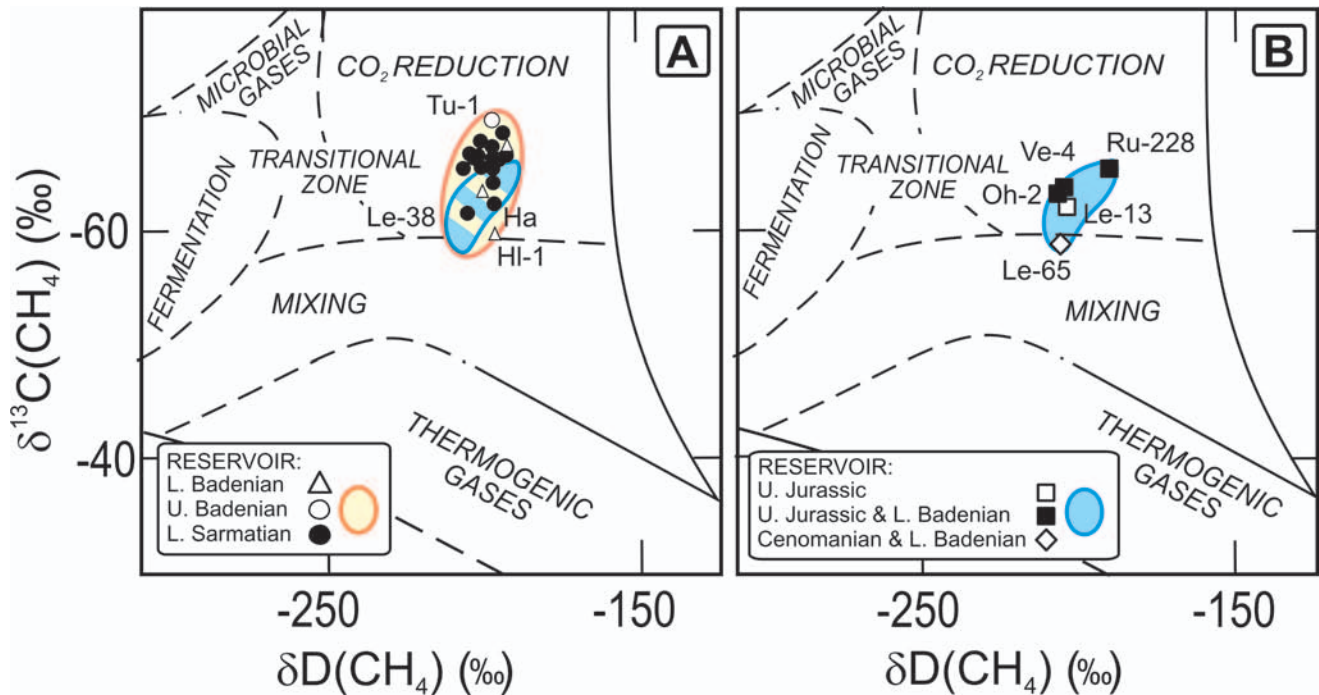
Fig. 3. $\delta^{13}C(CH_4)$ *versus* $\delta D(CH_4)$ for natural gases accumulated in **(A)** Miocene and **(B)** Upper Jurassic, Upper Cretaceous (Cenomanian) and Lower Badenian reservoirs of the Ukrainian Carpathian Foredeep and its basement. Compositional classification fields after Whiticar *et al.* (1986)

cant variations in the values of geochemical hydrocarbon indices (Fig. 6A) and the stable carbon isotope ratios in methane (Fig. 6D) with depth suggest quite uniform generation conditions of microbial methane in the Miocene strata down to about 1,200 m depth (Fig. 5D). A decrease in the hydrocarbon (C_{HC}) index (Fig. 6A) and an increase in stable carbon isotope ratios in methane and ethane (Fig. 6D, E) suggest the occurrence of significant amounts of diagenetic and/or low-temperature, thermogenic gases beneath 1,200 m depth. Moreover, the absence of a depth trend of stable carbon isotope composition of propane with depth (Fig. 6F) also indicates similar, thermogenic generation conditions within the Miocene succession. Most probably the thermogenic components were generated beneath the Outer Carpathians and migrated from the south (Kotarba *et al.*, 2011a).

In the Polish Carpathian Foredeep, the rhythmic and cyclic deposition of clays and sands in the Miocene marine basin and very high sedimentation rates, which exceeded 1,500 m/million years and 5,000 m/million years in the late Badenian and the early Sarmatian, respectively, facilitated the intense generation of microbial methane and ethane, as well as the formation and filling of multihorizon traps within the autochthonous Miocene strata. Microbial gases generated in a particular clay-mud horizon migrated to the overlying sand horizon which, in turn, is covered by another clay-mud layer (Kotarba, 1998; Kotarba *et al.*, 1998). Microbial generation of methane and ethane was apparently most intensive in the depth interval from 900 to 1,500 metres beneath the Miocene sea floor (Kotarba *et al.*, 1998). Microbiological studies revealed the presence of considerable quantities of methanogenic and methylotrophic bacteria in waters connected with gas accumulations in the Mio-

cene strata and that microbial methanogenesis may still continue (Kotarba *et al.*, 1995).

The hydrogen concentrations in the analysed Miocene gases vary from 0.000 to 0.11 vol% (Table 2). Natural hydrogen is generated in various biogenic and abiogenic processes: microbial fermentation of sedimentary organic matter, microbial carbon dioxide reduction, thermal decomposition of sedimentary organic matter, hydrolysis, water radiolysis (dissociation of water molecules bombarded by alpha particles) and natural nuclear reactions (Zobell, 1947; Zinger, 1962; Hawkes, 1972; Dubessy *et al.*, 1988; Whiticar *et al.*, 1986; Savary & Pagel, 1997). Hydrogen is a very reactive and mobile gas, hence, its retention in petroleum traps and in sedimentary rocks is rather ephemeral. Consequently, its presence in natural gases indicates that it was either generated recently by microbial processes (Balabane *et al.*, 1987) in secondary reactions within the reservoirs and/or in adjacent source beds, or it has ascended from deep-seated sources (Hunt, 1996). As stated before, in the Miocene strata considerable quantities of methanogenic and methylotrophic bacteria were found (Kotarba *et al.*, 1995). Therefore, it seems very probable that the presence of hydrogen within the Miocene strata is related to recent microbial processes.

The carbon dioxide concentrations and the values of the carbon dioxide-methane (CDMI) index in the analysed natural gases from the Lower and Upper Badenian and Lower Sarmatian reservoirs vary from 0.01 to 4.80 vol% and from 0.01 to 4.9, respectively (Tables 2 and 3). The $\delta^{13}C(CO_2)$ values range from –21.2 to –8.2‰ (Table 3). The $\delta^{13}C(CH_4)$ *versus* $\delta^{13}C(CO_2)$ (Fig. 7) indicate that carbon dioxide was generated exclusively by microbial processes. The vertical

Table 3

Isotopic composition and gas ratios of natural gases produced from the autochthonous Miocene strata and the Mesozoic basement

Sample code	Stable isotopes (‰)										Ratios		
	$\delta^{13}C$ (CH$_4$)	δD (CH$_4$)	$\delta^{13}C$ (C$_2$H$_6$)	$\delta^{13}C$ (C$_3$H$_8$)	$\delta^{13}C$ (iC$_4$H$_{10}$)	$\delta^{13}C$ (nC$_4$H$_{10}$)	$\delta^{13}C$ (iC$_5$H$_{12}$)	$\delta^{13}C$ (nC$_5$H$_{12}$)	$\delta^{13}C$ (CO$_2$)	$\delta^{13}C$ (N$_2$)	C$_{HC}$	CDMI	$\dfrac{i\text{C}_4\text{H}_{10}}{n\text{C}_4\text{H}_{10}}$
Autochthonous Miocene strata (Bilche-Volytsya unit)													
Hl-1*	-59.8	-197	-30.1	-27.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	24	0.09	0.69
MH-5	-67.6	-193	-44.2	-31.0	-28.8	-28.9	n.a.	n.a.	-17.6	n.a.	390	0.28	1.90
PH-10	-63.7	-201	-33.6	-30.8	-30.4	-28.8	-26.8	-27.4	-13.2	-3.3	53	0.14	0.89
Tu-1	-69.9	-198	-40.1	-31.7	-30.3	-29.6	-27.8	-23.6	-21.2	-3.0	245	0.26	1.16
BV-9*	-64.4	-198	-39.5	-29.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	424	0.14	2.50
BV-500*	-66.4	-196	-51.4	-29.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	823	0.14	5.00
Du-1	-66.9	-194	-38.0	-31.4	-31.7	-30.7	-29.0	-28.0	-13.1	n.a.	209	0.26	3.78
Ha	-62.5	-198	-31.2	-28.0	-28.7	-26.1	-26.8	-25.5	-14.3	n.a.	33	0.13	0.69
Ka-40	-67.6	-198	-50.7	-23.8	n.a.	n.a.	n.a.	n.a.	-13.2	n.a.	820	0.09	5.00
Le-2*	-65.6	-198	-42.8	-29.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	481	0.08	2.86
Le-21	-66.8	-202	-44.0	-29.0	-28.0	-26.6	-26.1	-27.5	-15.1	-0.3	654	0.10	2.02
Le-38	-61.6	-206	-31.1	-28.0	-28.9	-26.3	-26.5	-25.5	-13.5	n.a.	31	0.13	0.67
Le-52	-65.6	-207	-40.9	-31.5	-30.2	-29.3	-27.5	-27.7	-15.4	n.a.	249	0.06	0.63
Le-60	-66.6	-198	-40.9	-30.0	-30.2	-27.5	-28.2	-26.0	-8.2	n.a.	642	0.38	2.12
Le-64	-65.8	-202	-38.9	-31.3	-31.3	-29.8	-28.4	-28.5	-14.9	n.a.	182	0.02	1.30
Mk-10	-66.6	-204	-35.9	-33.0	-31.7	-31.0	-28.2	-28.4	-15.5	n.a.	76	0.49	2.93
Op-22a	-68.1	-202	-53.5	n.a.	n.a.	n.a.	n.a.	n.a.	-13.8	n.a.	895	0.01	0.00
Op-40	-68.8	-195	-54.6	n.a.	n.a.	n.a.	n.a.	n.a.	-15.8	n.a.	822	0.04	0.00
SD-10	-67.0	-205	-41.4	-31.8	-31.3	-29.5	-28.3	-26.4	-13.6	n.a.	232	0.14	1.54
Khi-133^	-72.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-12.5	n.a.	224	0.10	n.a.
Dh-65^	-64.3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	311	0.20	n.a.
Hk^	-56.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-18.1	n.a.	993	0.10	n.a.
Py-1^	-54.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	980	0.76	n.a.
Py-25^	-57.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-17.1	n.a.	29	0.42	n.a.
Svy-54^	-61.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	432	0.08	n.a.
Svy-48, -51, -61^	-60.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	904	0.08	n.a.
Svy-55, -62^	-59.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	368	0.10	n.a.
Uh-98a^	-58.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	244	0.20	n.a.
Zh-12^	-53.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-13.6	n.a.	163	4.90	n.a.
Zh-14^	-50.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	63	0.93	n.a.
Minimum value	-72.0	-207	-54.6	-33.0	-31.7	-31.0	-29.0	-28.5	-21.2	-3.3	24	0.01	0.00
Maximum value	-50.0	-193	-30.1	-23.8	-28.0	-26.1	-26.1	-23.6	-8.2	-0.3	993	4.90	5.00
Mesozoic basement													
Oh-2	-63.9	-207	-36.6	-34.8	-31.6	-32.3	-30.4	-30.7	-12.6	n.a.	39	0.84	0.61
Ru-228	-65.9	-191	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-16.6	0.4	89	6.39	0.81
Ve-4	-64.3	-205	-34.6	-31.7	-31.1	-29.2	-28.0	-27.1	-13.5	-2.2	61	0.42	0.92
Le-13	-62.8	-204	-37.1	-32.4	-30.4	-30.1	-28.5	-27.8	-3.8	n.a.	141	0.19	0.73
Le-65	-59.5	-207	-30.8	-28.1	-28.0	-26.5	-25.8	-25.9	-12.5	n.a.	19	0.56	0.77
Minimum value	-65.9	-207	-37.1	-34.8	-31.6	-32.3	-30.4	-30.7	-16.6	-2.2	19	0.19	0.61
Maximum value	-59.5	-191	-30.8	-28.1	-28.0	-26.5	-25.8	-25.9	-3.8	0.4	141	6.39	0.92

* – after Kotarba and Koltun (2006), ^ – after Shabo and Mamchur (1984), n.a. – not analysed

C_{HC} = CH$_4$/(C$_2$H$_6$+C$_3$H$_8$); CDMI = [CO$_2$/(CO$_2$+CH$_4$)]100 (%)
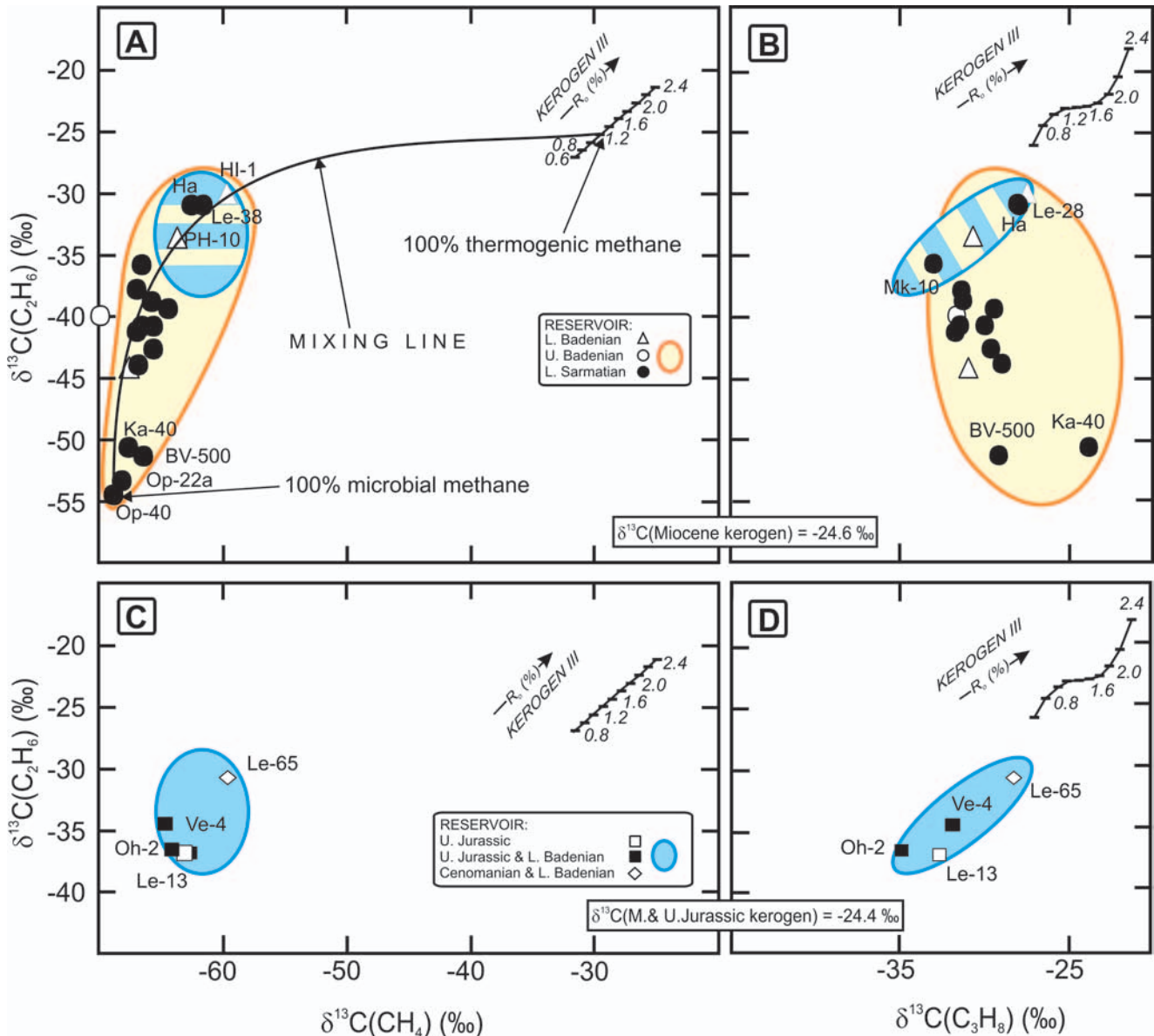
Fig. 4. $\delta^{13}C(C_2H_6)$ *versus* (**A** and **C**) $\delta^{13}C(CH_4)$ and (**B** and **D**) $\delta^{13}C(C_3H_8)$ for natural gases accumulated in (**A** and **B**) Miocene reservoirs and (**C** and **D**) in Upper Jurassic, Upper Cretaceous (Cenomanian) and Lower Badenian reservoirs of the Ukrainian Carpathian Foredeep and its basement. Position of vitrinite reflectance curve for Type III kerogen after Berner and Faber (1996). Curve was shifted based on average values of (**A** and **B**) $\delta^{13}C = -24.6$ ‰ for Miocene kerogen from Bilche-Volytsia Unit (Kotarba *et al.*, 2011b), and (**C** and **D**) $\delta^{13}C$ values = -24.4‰ for Middle and Upper Jurassic kerogen (Kosakowski *et al.*, in press)

distributions of the carbon dioxide-methane (CDMI) index and of the $\delta^{13}C(CO_2)$ values are presented in Fig. 6B, C. The variations observed in these diagrams indicate the occurrence of microbial gas generation throughout the whole Miocene sequence and/or the influence of secondary processes, mainly CO_2 dissolution in water (*e.g.*, Hałas *et al.*, 1997; Leśniak & Zawidzki, 2006), that caused isotopic fractionation during migration.

Nitrogen is produced during microbial processes and the thermogenic transformation of organic matter (Kotarba, 1988; Krooss *et al.*, 1995). For instance, during coalification of 1 kg of humic coal with the volatile matter (VM^{daf}) content between 40 and 4%, about 3.5 dm^3 of N_2 are produced (Kotarba, 1988). As sapropelic organic matter is

richer in nitrogen components, much more molecular nitrogen can be produced from it than from the humic matter (Maksimov *et al.*, 1982). The process of molecular nitrogen production from organic matter was also documented by pyrolytic experiments (Gerling *et al.*, 1997). The $\delta^{15}N$ values of molecular nitrogen from natural gases range from –15 to 18‰ (Gerling *et al.*, 1997). This isotopic fractionation results from both the primary genetic factors and the secondary processes operating during gas migration through the gas-rock and gas-reservoir fluids interfaces (Stahl, 1977; Gerling *et al.*, 1997; Zhu *et al.*, 2000; Ballentine & Sharwood Lollar, 2002; Krooss *et al.*, 2005). Nitrogen concentrations and $\delta^{15}N(N_2)$ values in the analysed natural gases vary from 0.34 to 2.83 vol% and from –3.3 to –0,3‰, respectively (Ta-
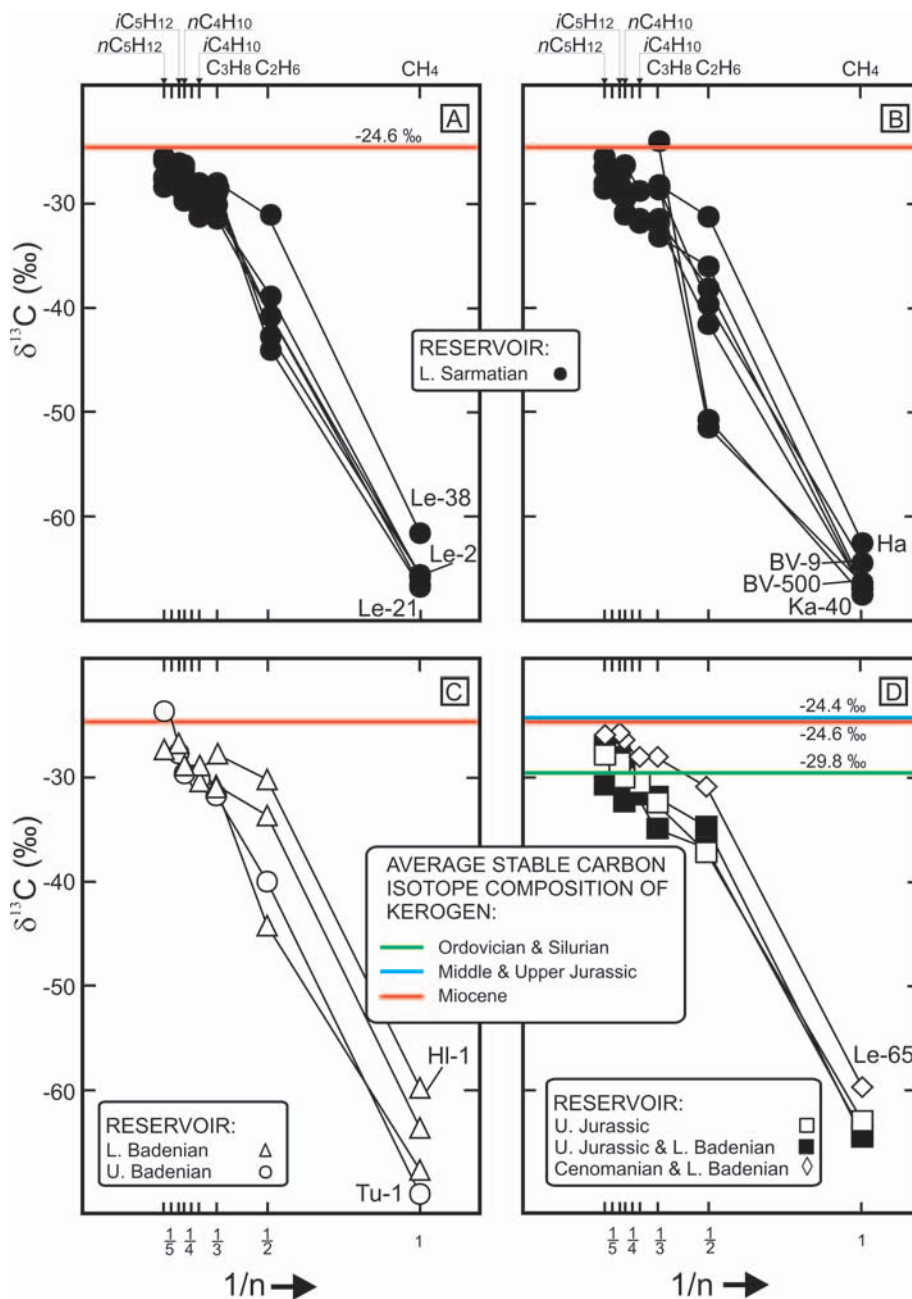
Fig. 5. Stable carbon isotope composition of methane, ethane, propane, butanes and pentanes *versus* reciprocal carbon numbers for natural gases from **(A)** the Letnia field and **(B)** other fields with Lower Sarmatian reservoirs, and **(C)** gases accumulated in Lower and Upper Badenian reservoirs and **(D)** in Upper Jurassic, Upper Cretaceous (Cenomanian) and Lower Badenian reservoirs of the Ukrainian Carpathian Foredeep and its basement. Structure of the order for methane, ethane and propane after Rooney *et al.* (1995). Average values of $\delta^{13}C = -29.8$ ‰ for Ordovician and Silurian kerogen (Więcław *et al.*, in press), $\delta^{13}C = -24.4$ ‰ for Middle and Upper Jurassic kerogen (Kosakowski *et al.*, in press), and $\delta^{13}C$ values = -24.6 ‰ for Miocene kerogen from Bilche-Volytsia Unit (Kotarba *et al.*, 2011b)

bles 2, 3). Absence of correlation between $\delta^{15}N(N_2)$ and N_2 concentration (Fig. 8) suggests that nitrogen was generated during both the microbial processes and the thermal transformation of organic matter.

Natural gases from the Upper Jurassic, Cenomanian and bottommost Lower Badenian reservoirs

The gases collected from both the Upper Jurassic and Upper Cretaceous (Cenomanian) reservoirs of the Mesozoic

basement, and from the bottommost Lower Badenian reservoirs of the Ukrainian Carpathian Foredeep show variations in their molecular and isotopic compositions. Molecular and isotopic compositions, hydrocarbon (C_{HC}) [C_{HC} = CH_4/(C_2H_6 + C_3H_8)], carbon dioxide-methane (CDMI) {CDMI = [CO_2/(CO_2 + CH_4)] 100 (%)} and iC_4H_{10}/nC_4H_{10} gas indices of analysed gases (5 samples) vary within the ranges given in Tables 2 and 3.

The stable carbon and hydrogen isotope compositions of methane in this sequence (Figs 2, 3) indicate that, similar
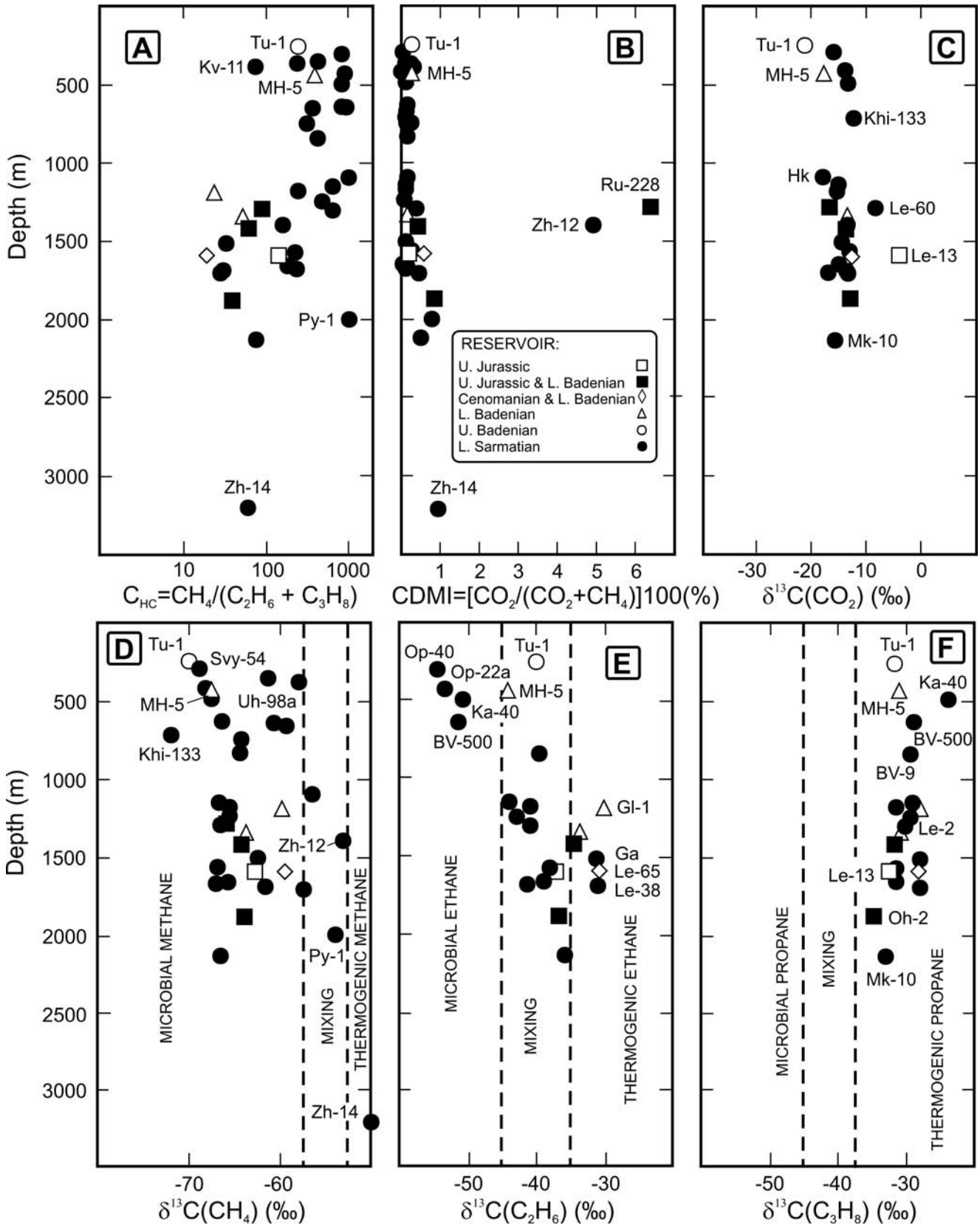
Fig. 6. **(A)** Hydrocarbon index, **(B)** carbon dioxide-methane index, **(C)** $\delta^{13}C(CO_2)$, **(D)** $\delta^{13}C(CH_4)$, **(E)** $\delta^{13}C(C_2H_6)$ and **(F)** $\delta^{13}C(C_3H_8)$ *versus* depth of natural gas accumulations within Miocene and Mesozoic reservoirs of Ukrainian Carpathian Foredeep and its basement
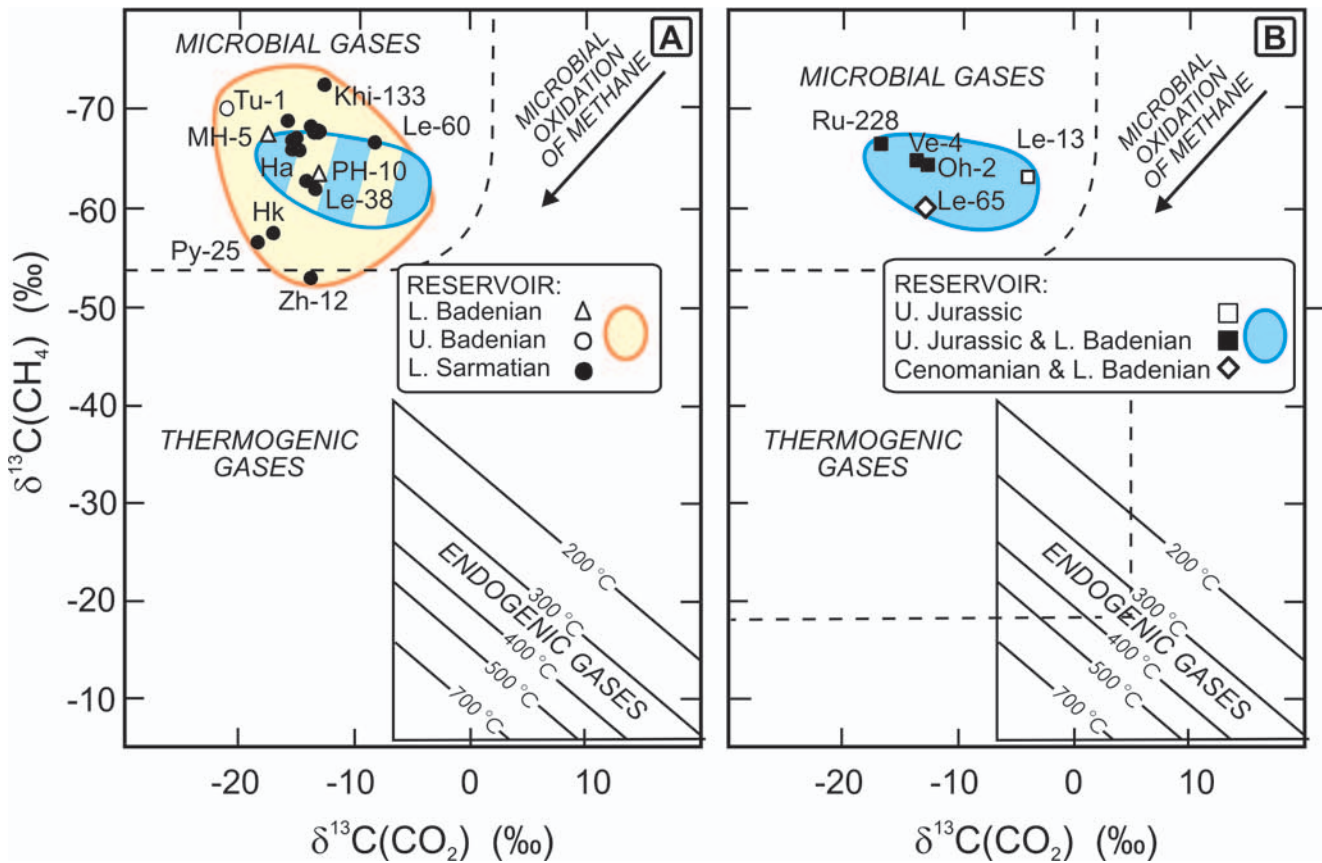
Fig. 7. $\delta^{13}C(CH_4)$ *versus* $\delta^{13}C(CO_2)$ for natural gases from **(A)** Miocene and **(B)** Upper Jurassic, Upper Cretaceous (Cenomanian) and Lower Badenian reservoirs of the Ukrainian Carpathian Foredeep and its basement. Compositional classification fields modified from Gutsalo and Plotnikov (1981) and Kotarba (1988)

to the Miocene gases, this methane was generated by microbial carbon dioxide reduction and was occasionally mixed with low-temperature, thermogenic gases. The stable carbon isotope compositions of ethane, propane, butanes and pentanes (Figs 4, 5) suggest that ethane was generated mainly by microbial processes whereas propane, butanes and propanes were formed during diagenesis and/or early stage of low-temperature, thermogenic processes. Comparison of stable carbon isotope compositions of propane, butanes and pentanes with kerogen (Fig. 5D) indicates that the source of these thermogenic gas components is type III kerogen from the Middle and Upper Jurassic (Kosakowski *et al.*, in press) and/or from Miocene strata (Kotarba *et al.*, 2011b). Moreover, type II kerogen occurring in the Ordovician–Silurian sediments (Więcław *et al.*, in press) obviously is not the source of these gases.

The depths of the sampled gas accumulations in the Upper Jurassic and the Upper Cretaceous (Cenomanian) reservoirs of the Mesozoic basement, and in the bottommost Lower Badenian reservoirs varies from 1,293 to 1,915 metres (Table 1, Fig. 6). Insignificant changes in values of geochemical hydrocarbon indices (Fig. 6A) and stable carbon isotope ratios in methane (Fig. 6D) with depth suggest quite uniform generation conditions of microbial methane, very similar to those in the whole autochthonous Miocene sequence. Increasing stable carbon isotope ratios in ethane (Fig. 6E) imply that significant amounts of this gas occur

beneath 1,000 m depth. Moreover, the lack of variation in stable carbon isotope composition of propane with depth (Fig. 6F) also indicates similar, diagenetic and/or low-temperature, thermogenic generation conditions for this component. Most probably, the microbial gases generated within the Miocene strata then migrated into the Mesozoic reservoirs. Possible migration pathways of microbial gases from autochthonous Miocene strata to Mesozoic reservoirs in the Rudky and the Bilche-Volytsia fields, and in the Opory and the Letnia ones are documented in Figs 9 and 10, respectively. The thermogenic component (Fig. 5) may have been generated within both from the Miocene kerogen beneath the Carpathian Overthrust and from the Upper and Middle Jurassic kerogens (Kosakowski *et al.*, in press). The condensates occurring in the Mesozoic–Lower Badenian reservoirs, *e.g.*, in the Bilche-Volutsia, Rudky (Fig. 9) and Letnia deposits (Fig. 10) were also generated mainly in the Upper and Middle Jurassic and/or Miocene strata most probably beneath the Outer (Flysch) Carpathian Overthrust and migrated from the south (Kotarba *et al.*, 2011a). Natural gas accompanying oil (Oh-2 sample) in the Upper Jurassic–Lower Badenian reservoir of the Orhonovichi deposit contains significant microbial components (Figs 2 to 5).

The hydrogen concentrations in the analysed natural gases in the Upper Jurassic and Upper Cretaceous (Cenomanian) reservoirs of the Mesozoic basement and in the bottommost Lower Badenian reservoirs vary from 0.000 to

0.20 vol% (Table 2). As shown before, considerable quantities of recent methanogenic and methylotrophic bacteria were found in the Miocene strata (Kotarba *et al.*, 1995). Therefore, it seems very probable that hydrogen was generated during microbial processes within the Miocene strata and then it migrated into the Mesozoic reservoirs.

The carbon dioxide concentrations and the values of carbon dioxide-methane (CDMI) index in the natural gases from the Upper Jurassic and Upper Cretaceous (Cenomanian) reservoirs of the Mesozoic basement, and from the bottommost Lower Badenian reservoirs vary from 0.19 to 0.79 vol% and from 0.01 to 0.49, respectively (Tables 2, 3). The $\delta^{13}C(CO_2)$ values range from –16.6 to –3.8‰ (Table 3). The $\delta^{13}C(CH_4)$ *versus* $\delta^{13}C(CO_2)$ (Fig. 7) indicate that carbon dioxide was also generated by microbial processes. Vertical distributions of the carbon dioxide-methane (CDMI) index and $\delta^{13}C(CO_2)$ values are presented in Fig. 6B and C. Such variations in concentration and stable isotope composition of carbon dioxide with depth indicate that, most probably, carbon dioxide has migrated together with microbial methane, ethane and hydrogen from the auto-
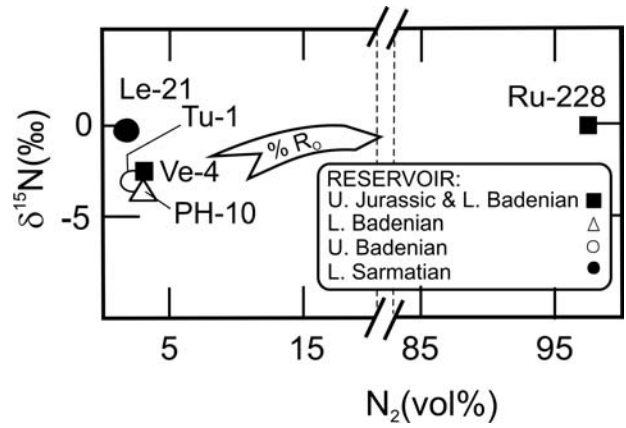
Fig. 8. $\delta^{15}N(N_2)$ *versus* N_2 concentration of natural gases accumulated in Upper Jurassic and Miocene reservoirs of the Ukrainian Carpathian Foredeep and its basement. Maturity of source rock after Gerling *et al.* (1997)
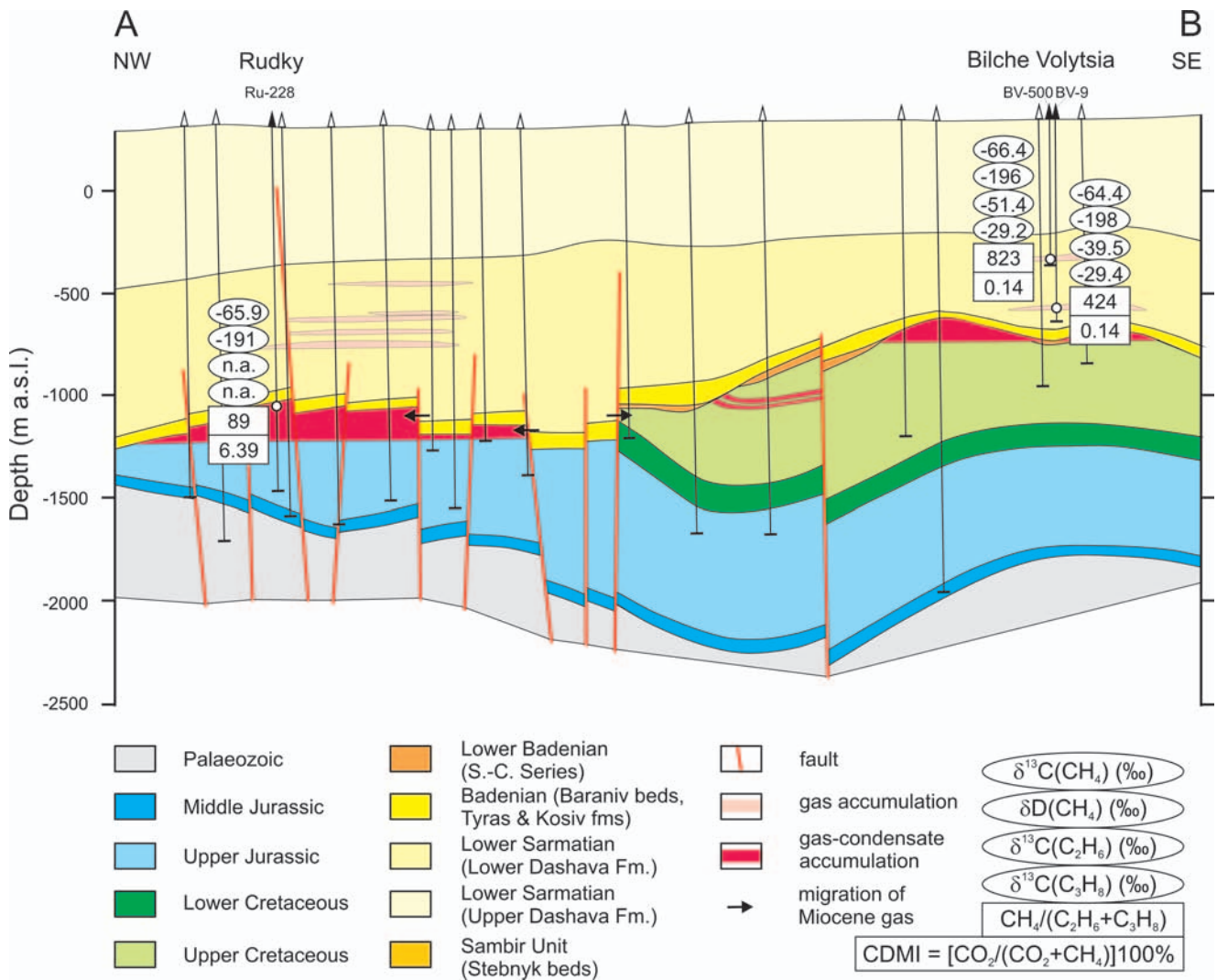
Fig. 9. Schematic geological cross-section through the Rudky and Bilche-Volytsia fields (modified after Shcherba *et al.*, 1987) with molecular and isotopic ratios for gas (Table 3). For location, see Figure 1. S.-C. – Sandy-Calcareous, Fm. – Formation, fms – formations
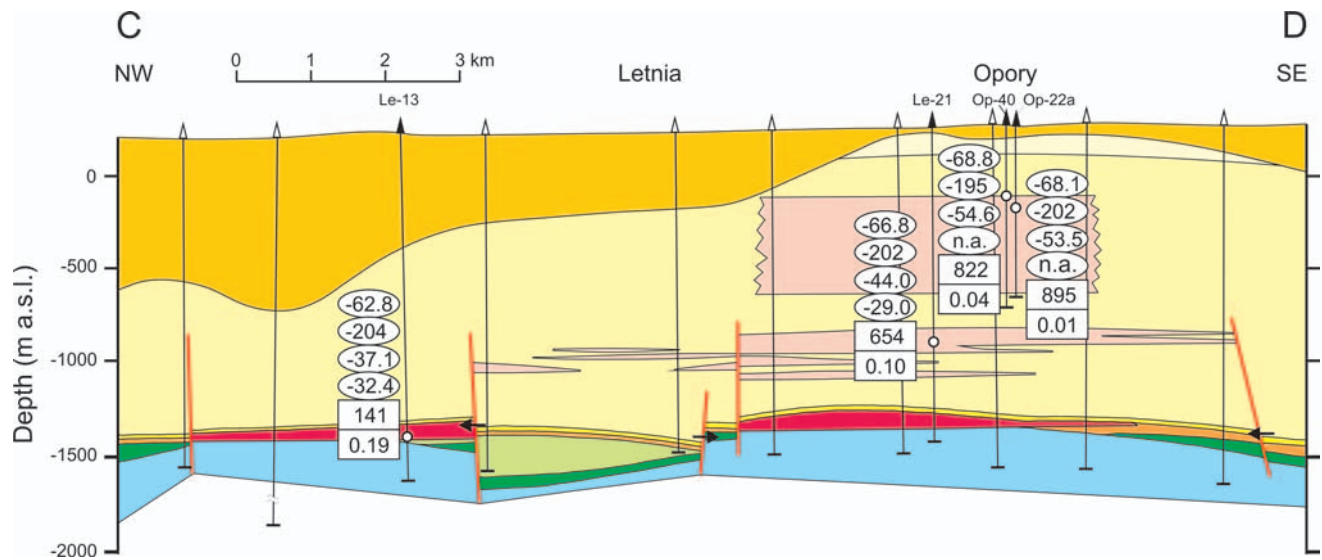
Fig. 10. Schematic geological cross-section through the Letnia and Opory fields (modified after Vul *et al.*, 1998) with molecular and isotopic ratios for gas (Table 3). For location, see Figure 1. Key for lithostratigraphy and geochemical data – see Figure 9

chthonous Miocene strata and that it was influenced during migration by secondary processes, mainly CO_2 dissolution in water.

The nitrogen concentrations in the natural gases vary from 1.98 to 6.60 vol% (4 samples) and 96.9 vol% in Ru-228 samples. The $\delta^{15}N(N_2)$ values are –2.2 and 0.4‰ (Tables 2, 3). Absence of correlations between $\delta^{15}N(N_2)$ and N_2 concentration (Fig. 8) suggests that nitrogen was generated during both microbial processes and thermal transformation of organic matter.

The notably high N_2 content in the Ru-228 sample (96.9 vol%, Table 2) is probably related with the secondary recovery methods, when the atmospheric air was injected into the Rudky field. The $\delta^{15}N(N_2)$ measured in this gas sample was 0.4 ‰ (Table 3), which is indicative of atmospheric nitrogen. Oxygen as very reactive agent reacted quickly. This gas sample also contains a significant percentage of H_2 (0.20 vol%) in relation to the other gas samples (Table 2). This may be attributed to sequential, secondary microbial oxidation and fermentation in the reservoir by microbes that were injected with the chemicals in separate recovery process than atmospheric air injection. A similar phenomenon was observed in the Wańkowa field, in the Polish Outer Carpathians (Kotarba *et al.*, 2009). However, it cannot be excluded that atmospheric gases have been introduced into the source regions or into the passage of gases to the surface, similar as in natural gases in the Upper Jurassic reservoir in Tarnów deposit in the Polish Carpathian Foredeep (Kotarba & Nagao, 2008).

CONCLUSIONS

The methane concentrations in natural gases accumulated in the Lower and Upper Badenian and Lower Sarmatian reservoirs of the Bilche-Volytsia Unit of the Ukrainian Carpathian Foredeep (between the Polish-Ukrainian state border and Stryi) usually exceed 96 vol%. Methane was generated by microbial reduction of carbon dioxide in the marine environment. Presumably methane and ethane were produced mainly during the sedimentation of Miocene clays and muds. It is possible that this microbial process continues today.

Both the generation and the accumulation of microbial methane and ethane as well as the formation and the loading of multiple-stacked Miocene reservoirs of the Ukrainian Carpathian Foredeep were facilitated by rhythmic and cyclic deposition of clays, muds and sands at very high sedimentation rates.

The higher light hydrocarbons (mainly propane, butanes and pentanes) were generated during diagenesis and the initial stage of the low-temperature, thermogenic processes from type III kerogen accumulated in the Miocene strata of the Foredeep and/or in the Middle and Upper Jurassic basement sediments. Absence of variations in the values of geochemical hydrocarbon indices and stable isotope ratios of methane, ethane and propane with depth indicate similar gas generation conditions within the whole Miocene succession.

Methane and in part ethane were generated by 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 reservoirs of the analysed Letnia, Orkhovychi, Rudky and Vereshchytsia fields.

Hydrogen (concentrations to 0.20 vol%) encountered within the Miocene strata as well as in the Upper Jurassic and the Upper Cretaceous (Cenomanian) reservoirs of the Mesozoic basement, and also within the bottommost Lower Badenian reservoirs are also attributed to microbial processes. Carbon dioxide and nitrogen, which are minor components, were generated in both microbial and the low-temperature, thermogenic processes. However, at least part of the nitrogen accumulated in the notably high-nitrogen Rudky field (96.9 vol% N_2) is of atmospheric origin injected to the reservoir during the secondary recovery operations.

Acknowledgements

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