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ORIGIN OF NATURAL GASES IN THE AUTOCHTHONOUS MIOCENE STRATA OF THE POLISH CARPATHIAN FOREDEEP

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Abstract: Methane concentrations in natural gases accumulated in the autochthonous Miocene strata of the Polish Carpathian Foredeep (between Kraków and Przemyśl) usually exceeded 90 vol%. Methane and part of the ethane were generated during microbial reduction of carbon dioxide in the marine environment, mainly during the sedimentation of Miocene clays and muds. It is possible that this microbial process has continued even recently. Higher light hydrocarbons (mainly propane, butanes and pentanes) were generated during the diagenesis and the initial stage of the low-temperature thermogenic process. Very small changes in the values of geochemical hydrocarbon indices and stable isotope ratios of methane, ethane and propane with depth are evidence for similar gas generation conditions within the whole Badenian and Lower Sarmatian successions. Only in a few natural gas accumulations within the Upper Badenian and Lower Sarmatian reservoirs are thermogenic gases or thermogenic components present, both generated from mixed, type III/II kerogen. These thermogenic gases, now accumulated mainly in the bottom part of Miocene strata, probably resulted from thermogenic processes in the Palaeozoic–Mesozoic basement and then migrated to the Miocene strata along the fault zones. The presence of low hydrogen concentrations (from 0.00 to 0.26 vol%) within the Miocene strata is related to recent microbial processes. Carbon dioxide and nitrogen, which are common minor constituents, were generated in both microbial and low-temperature thermogenic processes. However, CO_2 has also undergone secondary processes, mainly dissolution in water during migration. Hydrogen sulphide, which occurs in natural gases of Lower Badenian strata, was most probably generated during microbial sulphate reduction of the Lower Badenian gypsum and anhydrites.

Key words: microbial methane, stable carbon isotopes, thermogenic hydrocarbon gases, carbon dioxide, nitrogen, sulphide hydrogen, autochthonous Miocene strata, Polish Carpathian Foredeep.

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INTRODUCTION

In the present paper the results of molecular analyses, stable carbon analyses of methane, ethane, propane, butanes, pentanes and carbon dioxide, stable hydrogen analyses of methane, and stable nitrogen isotopes analyses of gaseous nitrogen are related to the geological setting and geochemical data of dispersed organic matter in the autochthonous Miocene strata of the Polish Carpathian Foredeep. Interpretation of these data is aimed at explaining the conditions of generation, migration and accumulation of natural gases within these strata.

Previous molecular and isotopic studies of natural gases accumulated within the autochthonous Miocene strata of the Polish Carpathian Foredeep revealed that methane-dominated component was generated during microbial processes (Głogoczowski, 1976; Calikowski, 1983; Kotarba *et al.*, 1987, 2005; Jawor & Kotarba, 1993; Kotarba, 1992, 1998; Kotarba & Jawor, 1993; Kotarba & Koltun, 2006). The microbial methane is of vital economic importance (Rice & Claypool, 1981; Rice, 1992).

GEOLOGICAL SETTING AND PETROLEUM OCCURRENCE

The Carpathian Foredeep is the largest gas basin among all foredeep basins of the Alpine orogenic system in Europe. It is a tectonic depression, which extends along the front of the Carpathian Overthrust and partly also underlies the Carpathian nappes, ranging from the Vienna Forest in the west, through the Czech Republic, Slovakia, Poland and Ukraine up to the Iron Gate in Romania in the southeast (Fig. 1).

The Polish Carpathian Foredeep is divided into two basins: the outer and inner ones (Ney *et al.*, 1974; Oszczypko, 1997; Oszczypko *et al.*, 2006). The folded Miocene strata of the Zgłobice and the Stebnik units in the inner ba-

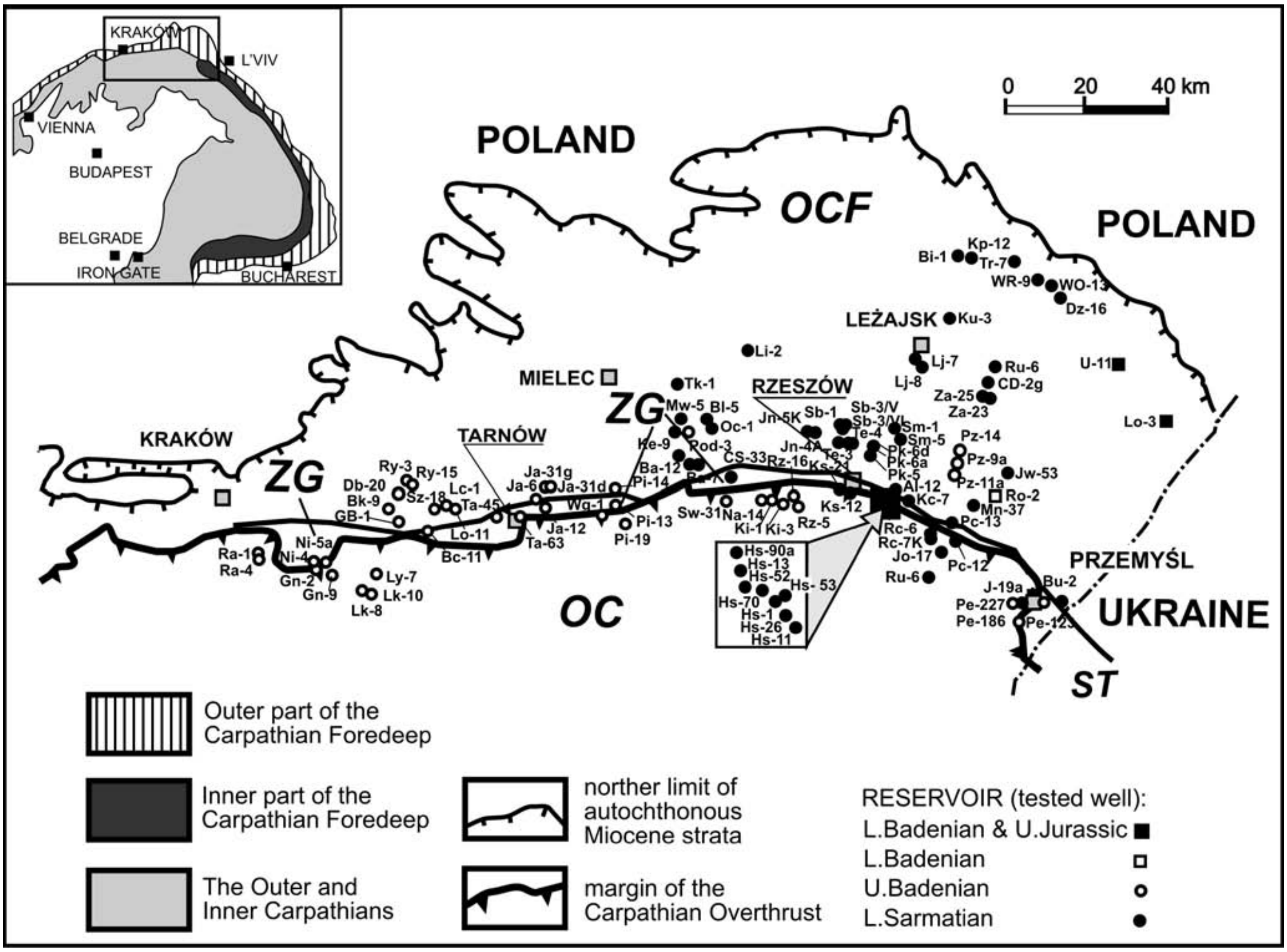

Fig. 1. Sketch map showing the major tectonic units of the Polish Carpathians with the locations of the gas sampling sites. OCF – outer part of the Carpathian Foredeep, ZG – Zgłobice Unit, ST – Stebnik Unit, OC – the Outer (Flysch) Carpathians

sin are too thin to become prospective plays for petroleum exploration. The formation of the outer Miocene basin of the Polish part of the Carpathian Foredeep is closely connected with multiphase orogenic movements: (i) the northward thrust of both the Outer (Flysch) Carpathian orogen and the inner basin units of the Carpathian Foredeep over the foreland platform of the Carpathian orogen, and (ii) deposition of succeeding suites of Badenian and Lower Sarmatian molasses at the front of the orogenic belt (Oszczypko, 1997; Oszczypko & Ślączka, 1989; Oszczypko *et al.*, 2006). The eastern part of the outer basin (between Kraków and Przemyśl) is filled with both Badenian and Lower Sarmatian strata of the following thicknesses: Lower and Middle Badenian – from 0 to 300 metres, Upper Badenian – from 0 to 1,700 metres, and Lower Sarmatian – from 0 to 2,900 metres (Ney *et al.*, 1974). Both the Upper Badenian and the Lower Sarmatian are represented by clay-sandy, mainly deltaic facies. On the other hand, the Lower and Middle Badenian strata comprise shallow-water, psammitic, argillaceous and chemical sediments. Recently, chemical sediments were rated to late Badenian (Andreyeva-Grigorovich *et al.*, 1997, 2008). The autochthonous Miocene strata of the outer basin of the Carpathian Foredeep have not been affected by orogenic movements and rest almost horizontally upon the Palaeozoic–Mesozoic basement (Oszczypko, 1997). Palaeobathymetric studies (Czepiec & Kotarba, 1998) revealed that the depth of the late Badenian sea did not exceed 200 metres, and the depth of the early Sarmatian sea was initially 30–50 metres and then became progressively shallower, reaching about 10 metres. In both the Upper Badenian and the Lower Sarmatian strata the gas-prone, Type III kerogen dominates whereas admixtures of algal Type II kerogen are very rare (Kotarba *et al.*, 1998a). The total organic carbon (TOC) contents vary from 0.02 to 3.22 wt% (mean: 0.68 wt%) (Kotarba *et al.*, 1998a).

In the autochthonous Upper Badenian and Lower Sarmatian strata of the outer basin of the Polish Carpathian Foredeep only methane-dominated gas fields have been discovered up to now. After the World War II about 100 gas deposits have been documented with estimated total resources over 200 billion cubic metres (Kotarba *et al.*, 2011). In 1958, the largest gas field in Poland, *i.e.*, the Przemyśl–Jaksmanice–Maćkowice multi-horizon pool, was discovered within these strata, holding about 100 billion cubic metres of total reserves. In the eastern part of the Polish Carpathian Foredeep, near the Polish-Ukrainian border, small gas deposits (Cetynia, Lubaczów, Roźwienica, Rokietnica, Wola Obszańska, Uszkowce) were also found within the Lower Badenian strata and the uppermost part of the Palaeozoic–Mesozoic basement (Karnkowski, 1999; Kotarba & Nagao, 2008; Myśliwiec *et al.*, 2004).

METHODOLOGY

Sampling procedure

Thirty-one natural gas samples were collected from producing wells drilled into the autochthonous Miocene reservoirs of the Polish Carpathian Foredeep (see Fig. 1 and Table 1). Free gases were collected directly at the producing wellheads in metal containers (volumes ~1,000 cm^3 and pressure from 2.0 to about 20.0 MPa) (Table 1). For interpretation, we also used the molecular and isotopic compositions of sixty nine natural gases from Miocene strata published by Kotarba (1992, 1998), Kotarba and Jawor (1993), Kotarba and Nagao (2008), and Kotarba *et al.* (2005) (Table 1). The locations of the sampling sites are listed in Table 1 and shown in Fig. 1.

Analytical procedures

Molecular compositions of collected natural gases (CH_4, C_2H_6, C_3H_8, iC_4H_{10}, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, C_6H_{14}, CO_2, O_2, H_2, N_2, He, Ar) were analysed in a set of columns on Hewlett Packard 5890 Series II and Chrom 5 gas chromatographs equipped with flame ionization (FID) and thermal conductivity (TCD) detectors.

Stable carbon, hydrogen, and nitrogen isotope analyses were carried out with Finnigan Delta Plus and Micromass VG Optima mass spectrometers. The stable carbon and hydrogen isotope data are presented in the δ-notation relative to the V-PDB and V-SMOW standards (Coplen, 1995), respectively. Analytical precision is estimated to be ±0.2‰ and ±3‰, respectively. The result of stable nitrogen isotope analysis is presented in the δ-notation relative to the air nitrogen standard. Analytical precision is estimated to be ±0.4‰.

For stable carbon isotope analyses methane, ethane, propane, butanes, propanes and carbon dioxide were separated chromatographically. The gases were combusted over hot copper oxide (850°C) and the carbon dioxide produced was transferred on-line to a mass spectrometer. For the stable hydrogen isotope analyses, water resulting from the combustion of methane was reduced to gaseous hydrogen with zinc (Florkowski, 1985). Gaseous nitrogen was separated chromatographically for stable nitrogen isotope analysis and was transferred to the mass spectrometer with the on-line system.

RESULTS AND DISCUSSION

Natural gases accumulated within the autochthonous Miocene strata of the Polish Carpathian Foredeep are variable in their molecular and isotopic compositions. Molecular and isotopic compositions as well as 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 are shown in Tables 2 and 3.

The occurrence and origin of gaseous hydrocarbons, hydrogen, carbon dioxide, nitrogen and hydrogen sulphide as well as the influence of mixing and secondary processes on molecular and stable isotope compositions are discussed below.

Hydrocarbon gases

For the classification of the hydrocarbon gases in terms of origin and formation mechanisms, the genetic diagrams after Berner and Faber (1996), Schoell (1988), Whiticar (1994) and Whiticar *et al.* (1986) 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 a "dogleg" trend, exemplified by relatively ^{13}C-depleted methane and ^{13}C-enriched propane as compared to ethane indicates that the corresponding reservoir gas was not generated from a single source rock or that it has undergone post-generation alterations (*e.g.*, secondary gas cracking, microbial oxidation or thermochemical sulphate reduction). Moreover, the contents of ^{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).

The measured stable carbon and hydrogen isotope compositions of methane in natural gases accumulated in the Upper Badenian and Lower Sarmatian reservoirs (Figs 2, 3) indicate that this gas was generated by microbial carbon dioxide reduction. This process occurs mainly in the marine environment (Whiticar *et al.*, 1986; Rice, 1992). Ethane was generated both by microbial and low-temperature thermogenic processes (Figs 4, 5, 6E). These data indicate that ethane was produced by microbial process in higher volumes than one molecule per one thousand molecules of methane (Oremland *et al.*, 1986). 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). Furthermore, stable carbon isotope composition of propane, butanes and propanes in the analysed samples (Figs 4, 5) suggests that these gases were produced as a result of diagenesis and/or an early stage of low-temperature thermogenic processes from the Type III kerogen of the autochthonous Miocene strata (Fig. 5).

The depths of sampled gas accumulations in both the Upper Badenian and Lower Sarmatian reservoirs vary from 161 to 2,621 metres and from 170 to 2,640 metres, respectively (Table 1, Fig. 6). Very small changes of the values of geochemical hydrocarbon indices (Fig. 6A, B) and isotopic ratios (Fig. 6D, E) with depth suggest quite uniform generation conditions of microbial methane and ethane in the whole Upper Badenian and Lower Sarmatian sequences.

Table 1

Characteristics of gas sample sites in the autochthonous Miocene strata

Well	Field	Sample code	Depth (m)
Age of reservoir: Lower Badenian & Upper Jurassic			
Lubaczów-3*	Lubaczów	Lo-3*	992-1,041
Uszkowce-11#	Uszkowce	Us-11#	1,077-1,084
Age of reservoir: Upper Badenian			
Roźwienica-2*	Roźwienica	Ro-2*	1,870-1,873
Borek-9*	Borek	Bk-9*	515-542
Brzezowiec-11*	Brzezowiec	Bc-11*	839-900
Dąbrówka-20***	Dąbrówka	Db-20***	807-809
Grabina-2*	Grabina-Nieznanowice	Gn-2*	350-357
Grabina-9	Grabina-Nieznanowice S	Gn-9	837-977
Grądy Bocheńskie-1	Grądy Bocheńskie	GB-1	651-658
Husów-13*	Husów	Hs-13*	2,398-2,442
Husów-70^	Husów	Hs-70^	2,419-2,455
Jaśniny-12*	Jaśniny Północ	Ja-12*	461-523
Jaśniny-6*	Jaśniny	Ja-6*	817-841
Jaśniny 31d	Jasniny	Ja-31d	1,168-1,164
Jaśniny 31g	Jasniny	Ja-31g	1,127-1,132
Kielanówka-1^	Kielanówka-Rzeszów	Ki-1^	2,320-2,348
Kielanówka-3**	Kielanówka-Rzeszów	Ki-3**	2,306-2,320
Łazy-7	Łazy	Ly-7	629-642
Łąkta-8	Łąkta	Lk-8	1,950-2,002
Łąkta-10***	Łąkta	Lk-10***	1,876-2,355
Łękawica-1	Łękawica	Lc-1	1,830-1,832
Łętowice-11	Łętowice	Lo-11	575-594
Nieznanowice-4	Grabina-Nieznznowice	Ni-4	245-305
Nieznanowice-5a*	Grabina-Nieznanowice	Ni-5a*	310-388
Nosówka-14**	Nosówka-Gaz	Na-14**	2,300-2,520
Pilzno-13^	Pilzno-Południe	Pi-13^	210-216
Pilzno-14***	Pilzno-Południe	Pi-14***	170-195
Pilzno-19	Pilzno-Południe	Pi-19	1,356-1,362
Podole-3	Brzeźnica	Pod-3	1,331-1,362
Przemyśl-123*	Przemyśl	Pe-123*	2,375-2,432
Przemyśl-186*	Przemyśl	Pe-186*	2,590-2,610
Przemyśl-227*	Przemyśl	Pe-227*	2,597-2,640
Raciborsko-1*	Raciborsko	Ra-1*	528-535
Raciborsko-4	Raciborsko	Ra-4	549-597
Rączyna-6	Jodłówka	Rc-6	1,825-1,852
Rysie-3*	Rysie	Ry-3*	601-624
Rysie-15	Rysie	Ry-15	617-631
Rzeszów-16**	Kielanówka-Rzeszów	Rz-16**	2,231-2,249
Rzeszów-5**	Kielanówka-Rzeszów	Rz-5**	2,243-2,257
Sędziszów-31	Zagorzyce-Sędziszów	Sw-31	1,970-1,976
Szczepanów-18	Szczepanów	Sz-18	815-841
Tarnów-45*	Tarnów	Ta-45*	2,243-2,257
Tarnów-63***	Tarnów	Ta-63***	462-468
Wygoda-1*	Wygoda	Wg-1*	592-625
Age of reservoir: Lower Sarmatian			
Albigowa-12	Husów	Al-12	755-835
Biszcza-1	Biszcza	Bi-1	855-860
Blizna-5**	Blizna-Ocieka	Bl-5**	603-623
Brzeźnica-12	Brzeźnica	Ba-12	350-412
Brzeźnica-7	Brzeźnica	Ba-7	433-438
Buszkowiczki-2*	Buszkowiczki	Bu-2*	2,199-2,215
Chałupki Dębiańskie-2g	Chałupki Dębiańskie	CD-2g	186-194
Czarna Sędziszowska-33	Czarna Sędziszowska	CS-33	385-481
Dzików-16	Dzików	Dz-16	742-748
Husów-1*	Husów	Hs-1*	1,934-1,939
Husów-11^	Husów	Hs-11^	1,882-1,901
Age of reservoir: Lower Sarmatian			
Husów-26*	Husów	Hs-26*	1,937-1,987
Husów-52*	Husów	Hs-52*	965-1,055
Husów-53*	Husów	Hs-53*	1,330-1,375
Husów-90a*	Husów	Hs-90a*	239-243
Jaksmanice-19a*	Przemyśl	Je-19a*	900-1,101
Jarosław-53*	Jarosław	Jw-53*	1,188-1,205
Jasionka-4A/X**	Jasionka	Jn-4A**	1,650-1,657
Jasionka-5K/A**	Jasionka	Jn-5K**	1,273-1,315
Jodłówka-17*	Jodłówka	Jo-17*	2,444-2,621
Kańczuga-7*	Kańczuga	Kc-7*	1,075-1,134
Korzeniów-9*	Korzeniów	Ke-9*	161-164
Krasne-12**	Krasne	Ks-12**	884-892
Krasne-21**	Krasne	Ks-21**	902-913
Księżpol-12	Księżpol	Kp-12	769-790
Kuryłówka-3*	Kuryłówka	Ku-3*	675-680
Leżajsk-7*	Żołynia-Leżajsk	Lj-7*	420-485
Leżajsk-8^	Żołynia-Leżajsk	Lj-8^	416-440
Lipnica-2**	Lipnica-Dzikowice	Li-2**	360-395
Męciszów-5	Korzeniów-Męciszów	Mw-5	515-530
Mirocin-37	Mirocin	Mn-37	1,432-1,449
Ocieka-1**	Blizna-Ocieka	Oc-1**	600-620
Palikówka-5**	Palikówka	Pk-5**	1,666-1,690
Palikówka-6/VIa**	Palikówka	Pk-6a**	1,304-1,313
Palikówka-6/VId**	Palikówka	Pk-6d**	1,374-1,383
Pruchnik-12*	Pruchnik-Pantalowice	Pc-12*	855-900
Pruchnik-13^	Pruchnik	Pc-13^	1,248-1,255
Przeworsk-11a^	Przeworsk	Pz-11a^	415-432
Przeworsk-14*	Przeworsk	Pz-14*	404-421
Przeworsk-9a*	Przeworsk	Pz-9a*	266-283
Rączyna-7K	Jodłówka	Rc-7K	1,948-1,959
Rudka-6	Rudka	Ru-6	1,188-1,197
Smolarzyny-1^	Smolarzyny	Sm-1^	375-455
Smolarzyny-5*	Smolarzyny	Sm-5*	395-420
Stobierna-1/III+IV**	Stobierna	Sb-1**	1,180-1,205
Stobierna-3/V**	Stobierna	Sb-3/V**	1,322-1,338
Stobierna-3/VI**	Stobierna	Sb-3/VI**	1,293-1,302
Tarnogród-7*	Tarnogród-Wola Różaniecka	Tr-7*	1,085-1,103
Terliczka-3A/X**	Terliczka	Te-3A**	1,064-1,091
Terliczka-3/VI**	Terliczka	Te-3**	939-954
Terliczka-4**	Terliczka	Te-4**	1,129-1,134
Trześnik-1**	Trześnik	Tk-1**	188-190
Wola Obszańska-13	Wola Obszańska	WO-13	721-762
Wola Róż.-9*	Tarnogród-Wola Róż.	WR-9*	940-945
Żołynia-23	Żołynia-Leżajsk	Za-23	503-507
Żołynia-25	Żołynia-Leżajsk	Za-25	195-200

* after Kotarba (1998), ^ after Kotarba (1992), *** after Kotarba & Jawor (1993), # after Kotarba & Nagao (2008), ** after Kotarba *et al.* (2005)

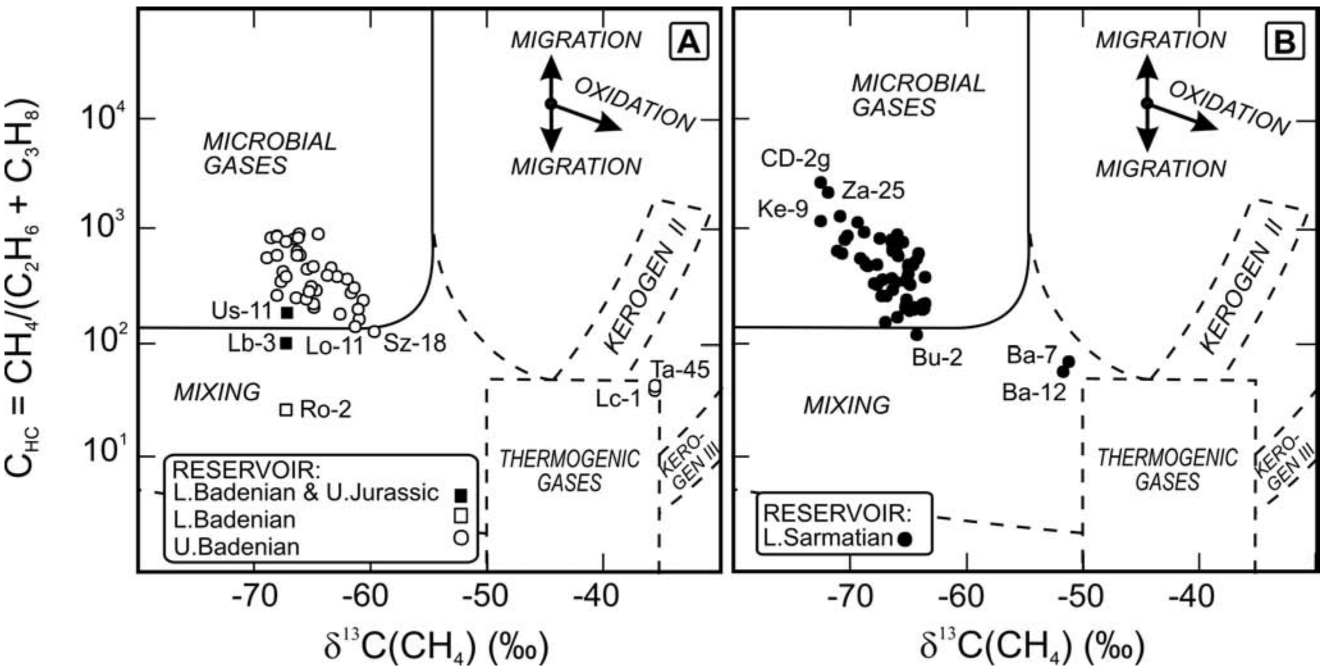

Fig. 2. Hydrocarbon index (C_{HC}) *versus* $\delta^{13}C(CH_4)$ for natural gases accumulated in (**A**) Badenian and (**B**) Lower Sarmatian reservoirs of the Polish Carpathian Foredeep. Compositional fields after Whiticar (1994). For explanation of sample codes see Table 1

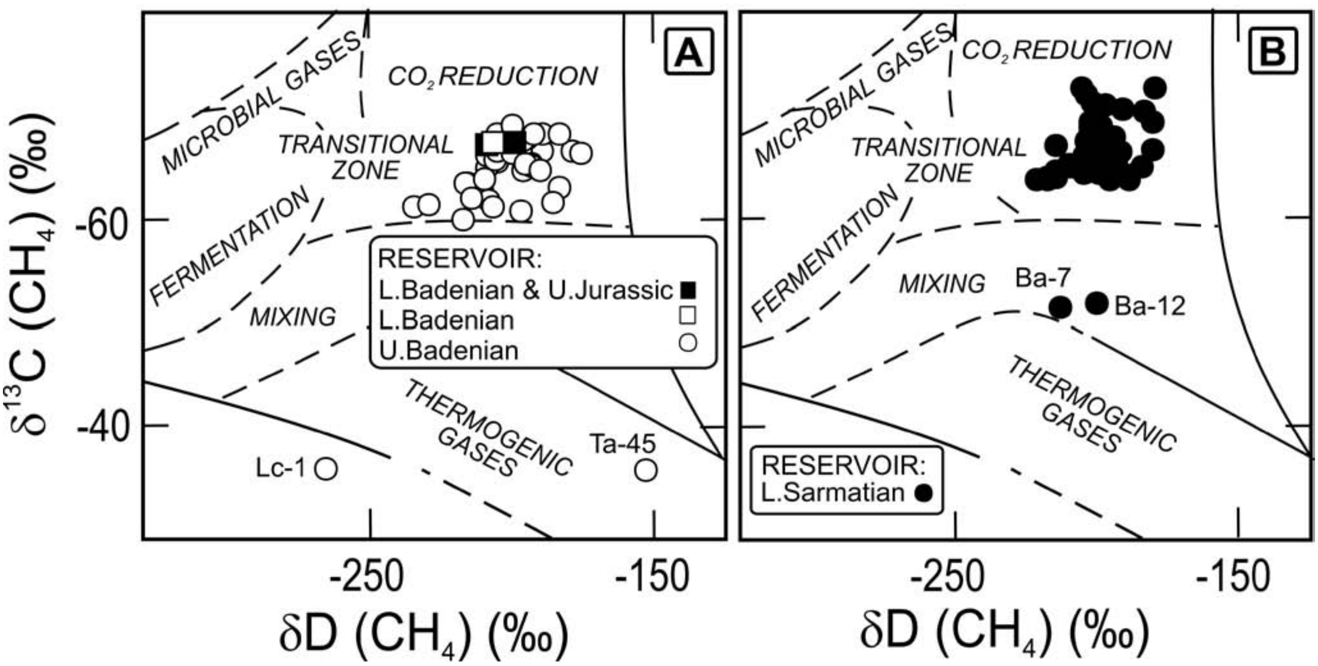

Fig. 3. $\delta^{13}C(CH_4)$ *versus* $\delta D(CH_4)$ for natural gases accumulated in (**A**) Badenian and (**B**) Lower Sarmatian reservoirs of the Polish Carpathian Foredeep. Compositional fields after Whiticar *et al.* (1986). For explanation of sample codes see Table 1

Similarly, the lack of changes of stable carbon isotope composition of propane with depth (Fig. 6F) also indicates similar diagenetic generation conditions for this hydrocarbon within the full Miocene succession.

Three small gas deposits were found within the Lower Badenian strata (Roźwienica – Ro-2 sample; Tables 1–3) as well as in both the Lower Badenian and the topmost Upper Jurassic strata (Lubaczów and Uszkowce – Lo-3 and Us-11 samples; Tables 1–3). Hydrocarbon gases of these accumulations are genetically very similar to the gases from the Upper Badenian and the Lower Sarmatian reservoirs (Figs 2–6).

The rhythmic and cyclic deposition of the clays and sands in the Miocene marine basin, and very high sedimen-

Table 2

Molecular composition of natural gases produced from the autochthonous Miocene strata

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}	C_6H_{14}
Lo-3*	3.11	0.27	0.06	-	0.10	94.5	0.51	0.42	0.19	0.29	***0.36***		0.18
Us-11#	4.88	0.50	0.11	-	-	93.8	0.38	0.12	0.06	0.05	***0.06***		0.019
•Ro-2*	0.65	0.08	0.010	0.004	0.11	94.1	2.35	1.20	0.34	0.43	***0.53***		0.21
Bk-9*	3.19	0.05	0.02	0.04	0.004	96.4	0.20	0.02	0.009	0.009	***0.015***		n.a.
Bc-11*	0.10	0.04	0.21	0.009	-	99.5	0.12	0.03	0.010	0.003	***0.003***		n.a.
Db-20*	2.40	0.03	0.02	0.02	0.03	96.9	0.48	0.04	0.008	0.005	***0.006***		0.002
Gn-2*	0.48	0.09	0.011	0.007	-	99.3	0.10	0.02	0.005	0.002	***0.002***		tr.
Gn-9	0.35	0.03	0.005	0.004	0.000	99.5	0.09	0.014	0.006	0.001	0.0012	0.0000	0.000
GB-1	0.64	0.04	0.006	0.011	0.161	98.9	0.19	0.015	0.004	0.001	0.0013	0.0000	0.001
Hs-13*	2.20	0.007	-	0.045	-	97.2	0.20	0.07	0.02	0.009	***0.017***		0.013
Hs-70^	1.40	0.08	0.13	0.004	-	98.2	0.17	0.05	0.02	0.07	***0.012***		0.003
Ja-12*	1.13	0.05	0.007	-	-	98.7	0.11	0.001	0.0005	-	***0.0006***		0.0005
Ja-6*	0.72	0.05	0.007	-	0.004	99.0	0.20	0.02	0.008	0.003	***0.004***		0.001
Ja-31d	0.95	0.11	0.003	0.003	0.21	98.2	0.29	0.05	0.03	0.101	0.015	0.004	0.010
Ja-31g	0.82	0.13	0.004	0.006	0.000	98.8	0.24	0.03	0.008	0.005	0.006	0.005	0.013
Ki-1^	2.60	0.05	0.010	-	-	96.8	0.39	0.06	0.04	0.006	***0.036***		
Ki-3**	2.88	0.04	0.02	-	-	96.5	0.39	0.05	0.04	0.007	***0.038***		
Ly-7	0.74	0.03	0.011	0.005	0.02	98.5	0.52	0.08	0.03	0.01	0.015	0.005	0.008
Lk-8	0.49	0.09	0.008	0.003	0.000	99.1	0.20	0.05	0.03	0.01	0.013	0.0018	0.007
Lk-10*	0.54	0.10	-	-	-	98.8	0.31	0.07	***0.15***				n.a.
Lc-1	14.1	0.44	0.06	0.017	0.10	82.8	1.51	0.52	0.1	0.14	0.06	0.07	0.12
Lo-11	0.48	0.14	0.007	0.003	0.000	98.6	0.60	0.09	0.03	0.02	0.015	0.004	0.008
Ni-4	0.45	0.04	0.007	0.0003	0.000	99.4	0.10	0.014	0.004	0.001	0.0007	0.0004	0.003
Ni-5a*	0.39	0.06	0.010	0.003	-	99.4	0.09	0.013	0.005	0.002	tr.		-
Na-14**	1.44	0.04	0.02	-	0.03	97.8	0.24	0.12	0.14	0.04	***0.14***		
Pi-13^	0.75	0.11	-	-	-	99.0	0.11	***0.010***					n.a.
Pi-14*	1.46	0.92	-	-	-	97.4	0.16	0.008	***0.00***				n.a.
Pi-19	0.56	tr.	0.003	0.003	0.04	99.2	0.14	0.03	0.007	0.00	0.004	0.0007	0.003
Pod-3	0.94	0.04	0.02	0.003	0.07	98.6	0.18	0.06	0.019	0.01	0.009	0.0016	0.007
Pe-123*	0.74	0.18	0.006	0.003	0.003	98.6	0.28	0.11	0.07	0.019	***0.02***		0.006
Pe-186*	1.28	0.47	0.04	0.004	-	97.8	0.23	0.092	0.06	0.022	***0.04***		0.017
Pe-227*	1.17	0.51	0.03	0.005	-	97.9	0.23	0.07	0.04	0.018	***0.03***		0.010
Ra-1*	1.60	0.07	0.02	0.005	-	97.8	0.35	0.05	0.03	0.02	***0.008***		0.002
Ra-4	1.69	0.07	0.02	0.005	0.000	97.9	0.26	0.05	0.03	0.01	0.006	0.0015	0.004
Rc-6	0.52	0.10	0.004	0.007	0.000	99.2	0.13	0.03	0.012	0.00	0.006	0.0008	0.006
Ry-3*	1.29	0.05	0.03	0.016	-	98.5	0.11	0.003	-	-	-		-
Ry-15	1.62	0.05	0.02	0.009	0	98.1	0.15	0.007	0.004	0	0.0003	0.0000	0.003
Rz-16**	1.23	0.05	0.010	-	-	98.4	0.22	0.03	0.02	0.04	***0.020***		
Rz-5**	1.11	0.15	0.02	-	tr.	98.5	0.16	0.04	0.02	0.006	***0.019***		
Sw-31	2.16	tr.	0.02	0.002	0.26	97.2	0.27	0.07	0.03	0.008	0.017	0.006	0.013
Sz-18	0.86	0.08	0.010	0.007	0.000	98.2	0.66	0.11	0.04	0.02	0.03	0.009	0.012
Ta-45	20.18	0.47	0.049	0.020	-	77.0	1.34	0.47	0.10	0.18	***0.15***		0.085
Ta-63***	0.39	0.10	0.009	-	-	99.0	0.43	0.05	0.011		***0.007***		0.004
Wg-1*	0.72	0.08	0.006	0.009	-	99.1	0.09	0.012	0.003	0.002	***0.002***		tr.
Al-12	0.65	0.05	0.04	0.001	0.000	99.1	0.08	0.02	0.005	0.005	0.004	0.005	0.009
Bi-1	0.37	0.06	0.007	0.0008	0.000	99.4	0.10	0.02	0.007	0.001	0.002	0.0005	0.001
Bl-5**	2.50	0.08	0.05	-	-	97.1	0.23	0.010	0.004	0.001	tr.		
Ba-12	1.05	0.29	0.02	0.002	0.000	96.9	1.25	0.38	0.05	0.05	0.018	0.015	0.02
Ba-7	1.07	0.18	0.02	0.003	0.000	97.3	1.04	0.32	0.05	0.04	0.012	0.008	0.006
Bu-2*	0.60	0.38	0.010	0.001	-	97.3	0.44	0.35	0.34	0.16	0.30		0.14
CD-2g	3.20	0.04	0.02	0.04	0.04	96.6	0.03	0.000	0.000	0.000	0.0000	0.0000	0.000
CS-33	1.01	0.08	0.03	0.007	0.000	98.8	0.10	0.004	0.001	0.002	0.0015	0.0012	0.002
Dz-16	0.22	0.03	0.010	tr.	0.05	99.6	0.10	0.02	0.004	0.002	0.0013	tr.	0.000
Hs-1*	1.02	0.20	0.02	0.003	tr.	98.5	0.16	0.03	0.012	0.006	***0.007***		0.002
Hs-11^	2.40	0.04	-	-	-	96.9	0.37	***0.18***					n.a.
Hs-26*	0.75	0.07	0.010	0.001	0.06	98.8	0.23	0.03	0.014	0.003	0.008		0.007
Hs-52*	0.82	0.11	0.007	0.010	-	98.7	0.13	0.03	0.009	0.005	***0.005***		tr.
Hs-53*	0.87	0.05	-	-	-	98.8	0.19	***0.040***					n.a.

Table 2 continued

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}	C_6H_{14}
Hs-90a*	1.44	0.04	0.03	0.013	-	98.0	0.08	0.004	0.0005	0.001	tr.		tr.
Je-19a*	0.71	0.10	0.003	0.008	-	99.0	0.12	0.03	0.007	0.003	***0.004***		tr.
Jw-53*	0.72	0.11	-	0.005	-	98.7	0.31	0.05	0.03	0.007	***0.030***		0.014
Jn-4A**	6.51	0.10	0.10	-	0.014	92.8	0.31	0.13	0.04	0.021	***0.046***		
Jn-5K**	4.56	0.00	0.08	-	0.009	94.8	0.30	0.12	0.04	0.023	***0.047***		
Jo-17*	1.11	0.04	0.03	0.001	-	98.2	0.30	0.12	0.08	0.033	***0.061***		0.03
Kc-7*	0.77	0.04	0.08	-	-	98.4	0.27	0.09	0.04	0.019	***0.017***		0.003
Ke-9*	0.69	0.96	0.01	0.007	-	99.1	0.07	0.01	0.001	0.002	***0.002***		tr.
Ks-12**	1.23	0.21	0.03	-	-	98.4	0.09	0.02	0.006	0.002	***0.004***		
Ks-21**	2.35	0.15	0.08	-	-	97.1	0.20	0.06	0.02	0.011	***0.012***		
Kp-12	0.17	0.06	0.01	0.003	0.03	99.6	0.10	0.002	0.002	0.000	0.0002	0.0000	0.000
Ku-3*	9.21	0.10	0.05	0.003	-	90.2	0.43	0.004	0.013	tr.	***0.003***		n.a.
Lj-7*	2.44	0.15	0.04	-	-	97.2	0.19	0.001	0.001	-	-		-
Lj-8^	1.70	0.46	-	-	-	97.6	0.18	***0.002***					n.a.
Li-2**	3.04	0.10	0.08	-	-	96.7	0.06	tr.	-	-	-		
Mw-5	1.08	0.02	0.011	0.011	0.002	98.8	0.11	0.006	0.002	0.00	0.0006	0.0000	0.002
Mn-37	1.35	0.13	0.02	0.003	0.017	97.6	0.43	0.18	0.10	0.05	0.05	0.016	0.02
Oc-1**	2.61	0.09	0.04	-	-	97.0	0.27	0.010	0.007	tr.	-		
Pk-5**	1.71	0.06	0.05	-	tr.	97.8	0.23	0.08	0.04	0.01	***0.05***		
Pk-6a**	4.92	0.08	0.11	-	0.000	94.6	0.18	0.04	0.011	0.004	***0.013***		
Pk-6d**	5.77	0.07	0.10	-	0.000	93.8	0.19	0.04	0.010	0.005	***0.016***		
Pc-12*	0.65	0.08	0.00	0.008	-	98.9	0.24	0.04	0.018	0.003	***0.007***		0.002
Pc-13^	0.60	0.06	-	-	-	99.0	0.23	***0.06***					n.a.
Pz-11a^	2.00	0.09	-	-	-	97.7	0.14	***0.001***					n.a.
Pz-14*	0.59	0.11	0.02	-	-	99.1	0.16	0.008	0.02	0.006	***0.002***		0.0003
Pz-9a*	2.08	0.10	0.04	-	-	97.6	0.15	0.0002	-	-	-		-
Rc-7K	0.50	0.10	0.00	0.004	0.000	99.2	0.13	0.03	0.011	0.003	0.006	0.0009	0.005
Ru-6	7.27	tr.	0.08	0.006	0.016	92.2	0.29	0.08	0.014	0.006	0.004	0.0007	0.002
Sm-1^	5.40	0.04	-	-	-	94.2	0.22	***0.04***					n.a.
Sm-5*	5.10	0.05	0.11	0.011	-	94.5	0.24	0.002	0.003	-	***0.02***		0.0003
Sb-1**	2.32	tr.	0.09	-	0.03	97.0	0.33	0.11	0.04	0.016	***0.04***		
Sb-3/V**	3.67	0.00	0.08	-	0.05	95.6	0.33	0.12	0.05	0.021	***0.04***		
Sb-3/VI**	2.69	tr.	0.09	-	0.03	96.6	0.35	0.09	0.05	0.022	***0.04***		
Tr-7*	1.23	0.07	0.03	0.002	0.006	98.5	0.14	0.04	0.010	0.006	***0.006***		tr.
Te-3A**	4.94	0.00	0.08	-	0.002	94.5	0.32	0.11	0.03	0.019	***0.03***		
Te-3**	4.53	0.00	0.08	-	0.015	94.8	0.33	0.12	0.04	0.022	***0.04***		
Te-4**	4.43	tr.	0.08	-	0.005	94.9	0.33	0.12	0.04	0.026		0.04	
Tk-1**	1.19	0.13	0.03	-	-	98.6	0.07	0.00	-	-	-		
WO-13	0.78	tr.	0.03	0.001	0.109	98.9	0.12	0.03	0.004	0.002	0.0013	0.0000	0.002
WR-9*	0.68	0.08	0.02	0.003	-	99.0	0.13	0.02	0.007	0.003	***0.006***		-
Za-23	4.38	0.06	0.23	0.009	0.000	95.2	0.11	0.001	0.000	0.000	0.0000	0.0000	0.000
Za-25	2.52	0.09	0.29	0.03	0.05	97.2	0.04	0.000	0.000	0.000	0.0000	0.0000	0.000

* after Kotarba (1998), ^ after Kotarba (1992), *** after Kotarba & Jawor (1993), # after Kotarba & Nagao (2008), ** after Kotarba *et al.* (2005); tr. – traces; •Ro-2 - H_2S = 0.002 vol%; ***0.002*** – sum of higher hydrocarbons; n.a. – not analysed; - below of detection limit

tation rates, which exceeded 1,500 m/million years in the Late Badenian and 5,000 m/million years in the Early Sarmatian, facilitated intensive generation of microbial methane and ethane, as well as the formation and filling of multi-horizon traps within the Miocene strata. Microbial gases generated in a particular clay-mud horizon migrated to the overlying sand horizon, which, in turn, was covered by another clay-mud horizon (Kotarba, 1998; Kotarba *et al.*, 2005). It was found that microbial generation of methane and ethane was most intensive at the depth interval from 900 to 1,500 metres beneath the Miocene sea bottom (Kotarba *et al.*, 1998b). Microbiological studies revealed the presence of considerable quantities of methanogenic and methylotrophic bacteria in formation waters related to gas accumulations in the Miocene strata, thus, this process has been continuing until recent (Kotarba *et al.*, 1995).

In the studied sample set, only the Upper Badenian reservoirs from Ta-45 (Tarnów) and Lc-1 (Łękawica near Tarnów) wells did contain thermogenic gases whereas the Lower Sarmatian reservoirs from Ba-7 and Ba-12 (Brzeźnica) wells contained a significant thermogenic component (Figs 2–6) generated from mixed type II/III kerogen of about 1.1% in vitrinite reflectance scale (Fig. 4). Additionally, in gases from Ku-3 (Kuryłówka) and Jn-5K (Jasionka) wells a small thermogenic component was found (Figs 4, 6). These thermogenic gases were accumulated mainly in the

Table 3

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

Sample code	Stable isotopes (‰)										Ratios		
	$\delta^{13}C$ (CH_4)	δD (CH_4)	$\delta^{13}C$ (C_2H_6)	$\delta^{13}C$ (C_3H_8)	$\delta^{13}C$ (iC_4H_{10})	$\delta^{13}C$ (nC_4H_{10})	$\delta^{13}C$ (iC_5H_{12})	$\delta^{13}C$ (nC_5H_{12})	$\delta^{13}C$ (CO_2)	$\delta^{13}C$ (N_2)	C_{HC}	CDMI	$\frac{iC_4H_{10}}{nC_4H_{10}}$
Lo-3*	-67.3	-198	-	-	-	-	-	-	-	-	102	0.28	0.66
Us-11#	-67.2	-208	-43.4	-34.6	-30.9	-30.8	-	-	-27.2	-6.6	188	0.53	1.16
Ro-2*	-67.3	-206	-51.1	-31.2	-	-	-	-	-	-	27	0.08	0.79
Bk-9*	-63.4	-215	-39.9	-28.6	-	-	-	-	-	-	434.2	0.05	1.00
Bc-11*	-66.4	-198	-49.9	-30.5	-	-	-	-	-	-	663.3	0.04	3.33
Db-20*	-62.7	-210	-39.2	-31.2	-	-	-	-	-	-	186.3	0.03	1.60
Gn-2*	-66.6	-188	-50.5	-30.0	-	-	-	-	-	-	856	0.09	2.50
Gn-9	-68.1	-188	-58.6	-31.4	-	-	-	-	-9.9	-	920	0.03	7.00
GB-1	-63.5	-216	-44.4	-30.3	-	-	-	-	-	-	474	0.04	4.11
Hs-13*	-67.8	-194	-41.5	-30.8	-	-	-	-	-	-	357	0.01	2.56
Hs-70^	-67.6	-195	-43.8	-23.8	-	-	-	-	-	-	446	0.08	0.29
Ja-12*	-68.6	-	-	-	-	-	-	-	-	-	889	0.05	-
Ja-6*	-65.5	-204	-46.4	-29.1	-	-	-	-	-	-	458	0.05	2.67
Ja-31d	-61.7	-207	-40.1	-29.9	-31.1	-29.1	-	-	-9.9	-	289	0.12	0.28
Ja-31g	-62.0	-213	-43.5	-31.9	-30.3	-	-	-	-16.8	-	376	0.13	1.56
Ki-1^	-64.9	-208	-38.7	-26.2	-	-	-	-	-	-	215	0.05	6.33
Ki-3**	-64.9	-	-	-	-	-	-	-	-	-	219	0.04	5.00
Ly-7	-61.1	-234	-39.1	-33.5	-31.7	-32.5	-	-	-	-	165	0.03	2.26
Lk-8	-62.9	-182	-49.7	-30.6	-28.0	-29.5	-	-	-17.5	-	403	0.09	4.44
Lk-10*	-66.5	-178	-44.6	-31.0	-	-	-	-	-	-	260	0.10	-
Lc-1	-35.7	-265	-27.8	-26.9	-27.2	-27.0	-27.2	-26.7	-14.4	1.5	41	0.53	0.70
Lo-11	-61.4	-229	-38.0	-33.7	-32.2	-32.4	-30.8	-	-8.3	-	143	0.14	1.90
Ni-4	-68.1	-182	-55.3	-32.3	-	-	-	-	-0.7	-	895	0.04	4.2
Ni-5a*	-66.2	-175	-48.7	-31.8	-	-	-	-	-	-	947	0.06	2.50
Na-14**	-68.1	-204	-39.6	-31.4	-	-	-	-	-	-	272	0.04	3.41
Pi-13^	-67.3	-	-	-	-	-	-	-	-	-	825	0.11	-
Pi-14*	-69.0	-199	-48.1	-30.9	-	-	-	-	-	-	580	0.94	-
Pi-19	-66.1	-208	-45.3	-29.9	-30.0	-29.4	-	-	-	-	615	-	1.71
Pod-3	-63.8	-209	-41.0	-30.7	-30.3	-29.5	-	-	-	-	411	0.04	2.69
Pe-123*	-65.6	-205	-40.2	-29.4	-	-	-	-	-	-	253	0.18	3.47
Pe-186*	-64.7	-195	-43.0	-30.6	-	-	-	-	-	-	304	0.48	2.73
Pe-227*	-65.2	-192	-46.2	-31.4	-	-	-	-	-	-	323	0.52	2.22
Ra-1*	-60.7	-196	-39.2	-30.3	-	-	-	-	-	-	245	0.07	1.50
Ra-4	-61.5	-185	-36.4	-29.1	-	-	-	-	-15.0	-	317	0.07	5.09
Rn-6	-66.4	-204	-49.9	-30.7	-29.1	-29.1	-	-	-5.5	-	620	0.10	3.22
Ry-3*	-66.3	-199	-45.5	-27.8	-	-	-	-	-	-	872	0.05	-
Ry-15	-68.1	-191	-45.5	-23.8	-	-	-	-	-9.8	-	619	0.05	0.00
Rz-16**	-67.3	-	-	-	-	-	-	-	-	-	394	0.05	0.47
Rz-5**	-65.0	-192	-46.8	-30.3	-	-	-	-	-	-	493	0.15	2.83
Sw-31	-65.4	-195	-39.1	-29.6	-30.0	-29.5	-	-	-	-0.5	291	-	3.62
Sz-18	-59.8	-217	-39.5	-34.1	-31.0	-32.4	-30.0	-29.5	-11.8	-	128	0.08	2.11
Ta-45*	-35.7	-151	-28.1	-27.2	-	-	-	-	-	-	43	0.61	0.52
Ta-63***	-61.1	-206	-38.6	-29.4	-	-	-	-	-	-	206	0.10	-
Wg-1*	-64.6	-189	-46.3	-29.7	-	-	-	-	-	-	962	0.08	1.50
Al-12	-68.9	-198	-59.4	-30.9	-	-	-	-	-13.9	-	1017	0.05	0.98
Bi-1	-65.6	-193	-53.1	-31.8	-	-	-	-	0.2	-	821	0.06	6.73
Bl-5**	-63.7	-188	-36.9	-22.8	-	-	-	-	-	-	405	0.08	4.0
Ba-12	-51.8	-200	-30.9	-28.1	-28.2	-27.4	-26.5	-26.6	-5.1	-	59	0.29	1.00
Ba-7	-51.4	-213	-30.7	-28.1	-27.2	-27.4	-27.6	-27.4	-4.9	-	72	0.18	1.11
Bu-2*	-64.4	-199	-37.6	-31.7	-	-	-	-	-	-	123	0.39	2.09
CD-2g	-72.6	-205	-54.1	-	-	-	-	-	-	-	2801	2801	0.04
CS-33	-70.3	-183	-49.4	-	-	-	-	-	-8.9	-	927	927	0.08
Dz-16	-66.6	-180	-54.0	-35.4	-	-	-	-	-	-	843	843	0.03
Hs-1*	-65.2	-202	-48.0	-30.1	-	-	-	-	-	-	510	510	0.20
Hs-11^	-66.0	-197	-42.9	-	-	-	-	-	-	-	176	176	0.04
Hs-26*	-67.3	-	-	-	-	-	-	-	-	-	380	380	0.07
Hs-52*	-64.3	-204	-48.5	-29.5	-	-	-	-	-	-	602	602	0.11

Table 3 continued

Sample code	Stable isotopes (‰)										Ratios		
	$\delta^{13}C$ (CH_4)	δD (CH_4)	$\delta^{13}C$ (C_2H_6)	$\delta^{13}C$ (C_3H_8)	$\delta^{13}C$ (iC_4H_{10})	$\delta^{13}C$ (nC_4H_{10})	$\delta^{13}C$ (iC_5H_{12})	$\delta^{13}C$ (nC_5H_{12})	$\delta^{13}C$ (CO_2)	$\delta^{13}C$ (N_2)	C_{HC}	CDMI	$\frac{iC_4H_{10}}{nC_4H_{10}}$
Hs-53*	-67.8	-194	-41.5	-30.8	-	-	-	-	-	-	520	0.05	-
Hs-90a*	-69.4	-202	-52.0	-30.7	-	-	-	-	-	-	1241	0.04	0.50
Je-19a*	-66.0	-198	-51.9	-30.7	-	-	-	-	-	-	678	0.10	2.33
Jw-53*	-67.0	-214	-47.2	-30.8	-	-	-	-	-	-	274	0.11	4.29
Jn-4A**	-64.0	-214	-42.1	-33.5	-	-	-	-	-9.4	-	211	0.11	1.95
Jn-5K**	-64.0	-217	-34.0	-34.4	-	-	-	-	-	-2.3	226	0.00	1.52
Jo-17*	-63.7	-195	-39.6	-30.1	-	-	-	-	-	-	234	0.04	2.33
Kc-7*	-67.4	-198	-46.3	-31.6	-	-	-	-	-	-	274	0.04	1.84
Ke-9*	-72.6	-179	-50.0	-25.9	-	-	-	-	-	-	1271	0.96	0.50
Ks-12**	-66.0	-204	-51.4	-30.6	-	-	-	-	-	-	895	0.21	3.00
Ks-21**	-65.3	-210	-42.7	-31.0	-	-	-	-	-	-	374	0.15	2.00
Kp-12	-66.0	-194	-55.2	-	-	-	-	-	-13.8	-	968	0.06	-
Ku-3*	-65.0	-184	-33.4	-	-	-	-	-	-	-	208	0.11	-
Lj-7*	-68.6	-	-	-	-	-	-	-	-	-	509	0.15	-
Lj-8^	-68.8	-202	-50.2	-	-	-	-	-	-	-	536	0.47	-
Li-2**	-69.4	-180	-40.7	-	-	-	-	-	-	-	-	0.10	-
Mw-5	-70.6	-190	-53.7	-	-	-	-	-	-	-	859	0.02	4.75
Mn-37	-67.1	-194	-47.2	-34.7	-31.5	-30.8	-28.4	-28.1	-15.5	-	160	0.13	2.09
Oc-1**	-64.9	-196	-38.0	-25.5	-	-	-	-	-	-	345	0.09	-
Pk-5**	-66.4	-200	-44.8	-32.3	-	-	-	-	-	-	316	0.06	4.0
Pk-6a**	-65.1	-210	-47.2	-32.2	-	-	-	-	-8.6	-3.1	430	0.08	2.75
Pk-6d**	-65.2	-207	-48.2	-31.8	-	-	-	-	-9.9	-2.9	408	0.07	2.00
Pc-12*	-68.0	-200	-45.6	-28.8	-	-	-	-	-	-	353	0.08	6.00
Pc-13^	-67.8	-202	-45.2		-	-	-	-	-	-	341	0.06	-
Pz-11a^	-71.2	-201	-53.3	-	-	-	-	-	-	-	693	0.09	-
Pz-14*	-69.2	-202	-57.4	-31.5	-	-	-	-	-	-	590	0.11	3.67
Pr-9a*	-70.8	-	-	-	-	-	-	-	-	-	650	0.10	-
Rc-7K	-65.9	-200	-48.8	-29.4	-	-	-	-	-9.2	-	627	0.10	3.56
Ru-6	-65.3	-206	-41.6	-30.1	-30.3	-28.6	-	-	-	-4.6	253	-	2.23
Sm-1^	-66.2	-	-	-	-	-	-	-	-	-	362	0.04	-
Sm-5*	-66.5	-	-	-	-	-	-	-	-	-	391	0.05	-
Sb-1**	-65.4	-201	-40.5	-31.5	-	-	-	-	-	-2.5	221	-	2.56
Sb-3/V**	-65.1	-208	-40.1	-31.5	-	-	-	-	-	-2.7	212	0.00	2.24
Sb-3/VI**	-65.0	-208	-39.8	-31.4	-	-	-	-	-	-2.4	220	-	2.27
Tr-7*	-64.6	-202	-42.2	-30.2	-	-	-	-	-	-	538	0.07	1.67
Te-3A**	-63.7	-221	-41.6	-34.1	-	-	-	-	-	-2.4	220	0.00	1.79
Te-3**	-64.6	-214	-41.8	-33.2	-	-	-	-	-	-2.5	211	0.00	2.00
Te-4**	-63.8	-217	-41.3	-34.0	-	-	-	-	-	-2.2	211	-	1.62
Tk-1**	-70.9	-197	-50.9	-29.4	-	-	-	-	-	-	1409	0.13	-
WO-13	-66.5	-191	-55.9	-35.6	-29.4	-	-	-	-	-	701	-	2.75
WR-9*	-64.2	-188	-50.2	-30.6	-	-	-	-	-	-	656	0.08	2.33
Za-23	-67.5	-203	-51.0	-	-	-	-	-	-9.7	-3.9	880	0.07	0.00
Za-25	-72.0	-203	-52.8	-	-	-	-	-	-13.9	-1.9	2283	0.09	0.00

* after Kotarba (1998), ^ after Kotarba (1992), *** after Kotarba & Jawor (1993), # after Kotarba & Nagao (2008), ** after Kotarba *et al.* (2005); $C_{HC} = CH_4/(C_2H_6+C_3H_8)$; CDMI = $[CO_2/(CO_2+CH_4)]100$ (%), - not analysed

bottom part of Miocene strata. It is suggested that these gases were generated by thermogenic processes in the Palaeozoic–Mesozoic basement and have subsequently migrated to the Miocene strata along the fault zones (Kotarba & Jawor, 1993). Finally, diagenetic and early thermogenic ethane, propane, butanes and propanes might have also been generated from dispersed organic matter within the Miocene strata, as suggested by the data from Bl-5 (Blizna-Ocieka), Oc-1 (Ocieka) and Ke-9 (Korzeniów) wells (Fig. 4D).

Hydrogen

Hydrogen concentrations in the analysed Miocene gases vary from 0.00 to 0.26 vol% (mean 0.02 vol%) (Table 2). Natural hydrogen is generated by various biogenic and abiogenic processes: microbial fermentation of sedimentary organic matter, microbial carbon dioxide reduction, thermal decomposition of sedimentary organic matter, hydrolysis, water radiolysis and natural nuclear reactions (*e.g.*, Zobell, 1947; Zinger, 1962; Hawkes, 1972; Dubessy *et al.*, 1988; Whiticar *et al.*, 1986; Savary & Pagel, 1997). Hydrogen is a

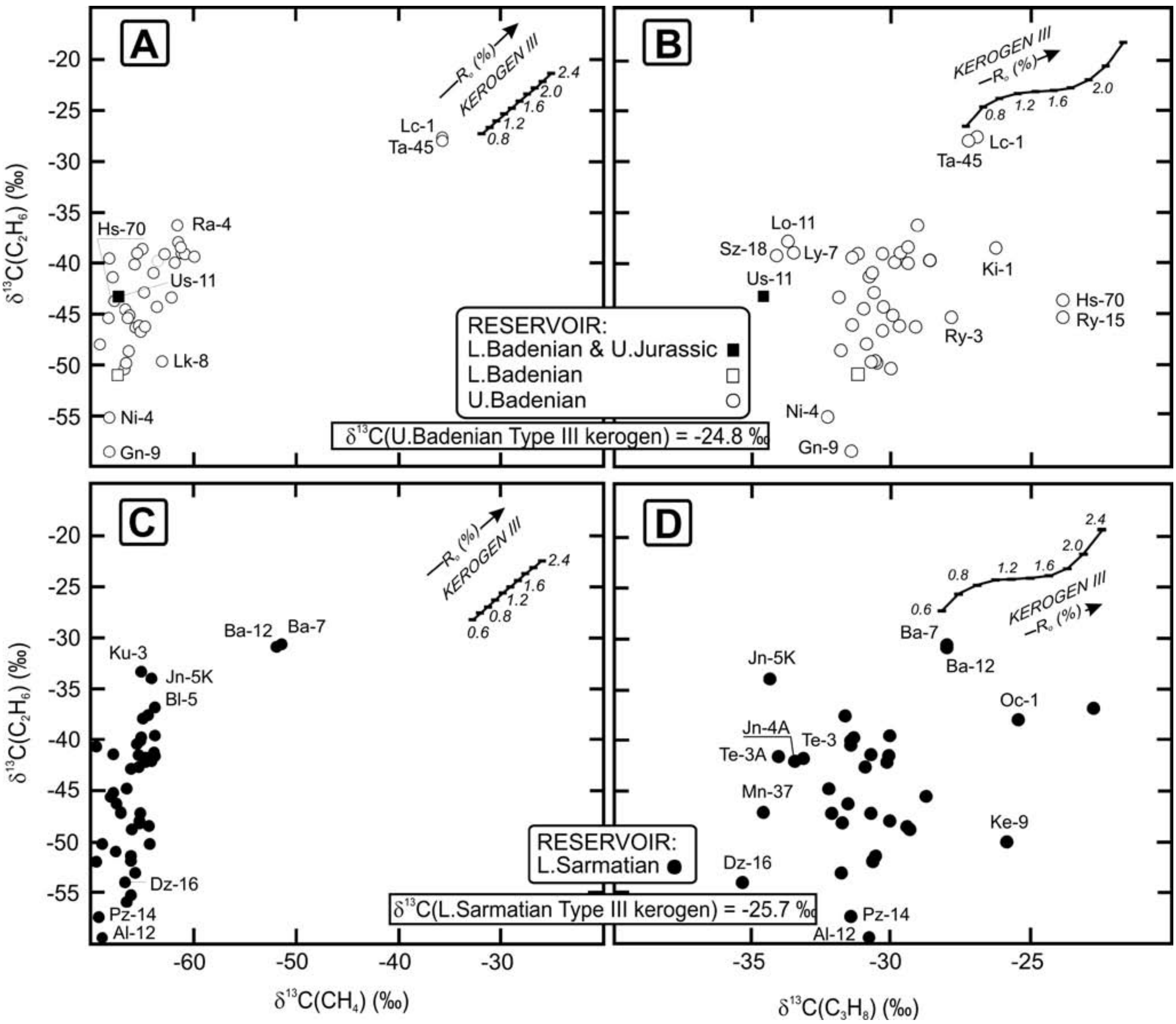

Fig. 4. $\delta^{13}C(C_2H_6)$ *versus* $\delta^{13}C(CH_4)$ (**A** and **C**) and $\delta^{13}C(C_3H_8)$ (**B** and **D**) for natural gases of Badenian (**A** and **B**) and Lower Sarmatian (**C** and **D**) reservoirs of the Polish Carpathian Foredeep. Included are the vitrinite reflectance curves for type III kerogens after Berner & Faber (1996). Curves were shifted based on the 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). For explanation of sample codes see Table 1

very reactive and mobile gas, so its retention in petroleum traps and, more generally, in sedimentary rocks is rather ephemeral. Thus, its presence in natural gases indicates its relatively recent origin in microbial processes.

Carbon dioxide

The carbon dioxide concentrations and the values of carbon dioxide-methane (CDMI) index in the natural gases analysed here are listed in Tables 2 and 3.

The plot of $\delta^{13}C(CH_4)$ versus $\delta^{13}C(CO_2)$ (Fig. 7) indicates that carbon dioxide was generated mainly by microbial processes. Only the data for Lc-1 (Łękawica near Tarnów, Upper Badenian reservoir) (Fig. 7A) and Ba-7 and Ba-12 (Brzeźnica, Lower Sarmatian reservoir) (Fig. 7B) lie in the "thermogenic gas" ranges of these diagrams. In these gases accumulated in the bottom part of the Miocene succession, small amounts of CO_2 (0.44, 0.18 and 0.29%, respectively, Table 2) were probably generated together with methane by thermogenic processes in the basement and then migrated upward. The vertical distribution of the carbon dioxide-methane (CDMI) index and the $\delta^{13}C(CO_2)$ values are presented in Fig. 6B & C. Such variations in concentration and stable isotope composition of carbon dioxide with depth also indicate both the multiple origins of this component of the analysed gases and the influence of secondary processes, mainly CO_2 dissolution in water during migration.

Nitrogen

Nitrogen is produced during the microbial processes and thermogenic transformation of organic matter (Kotarba,

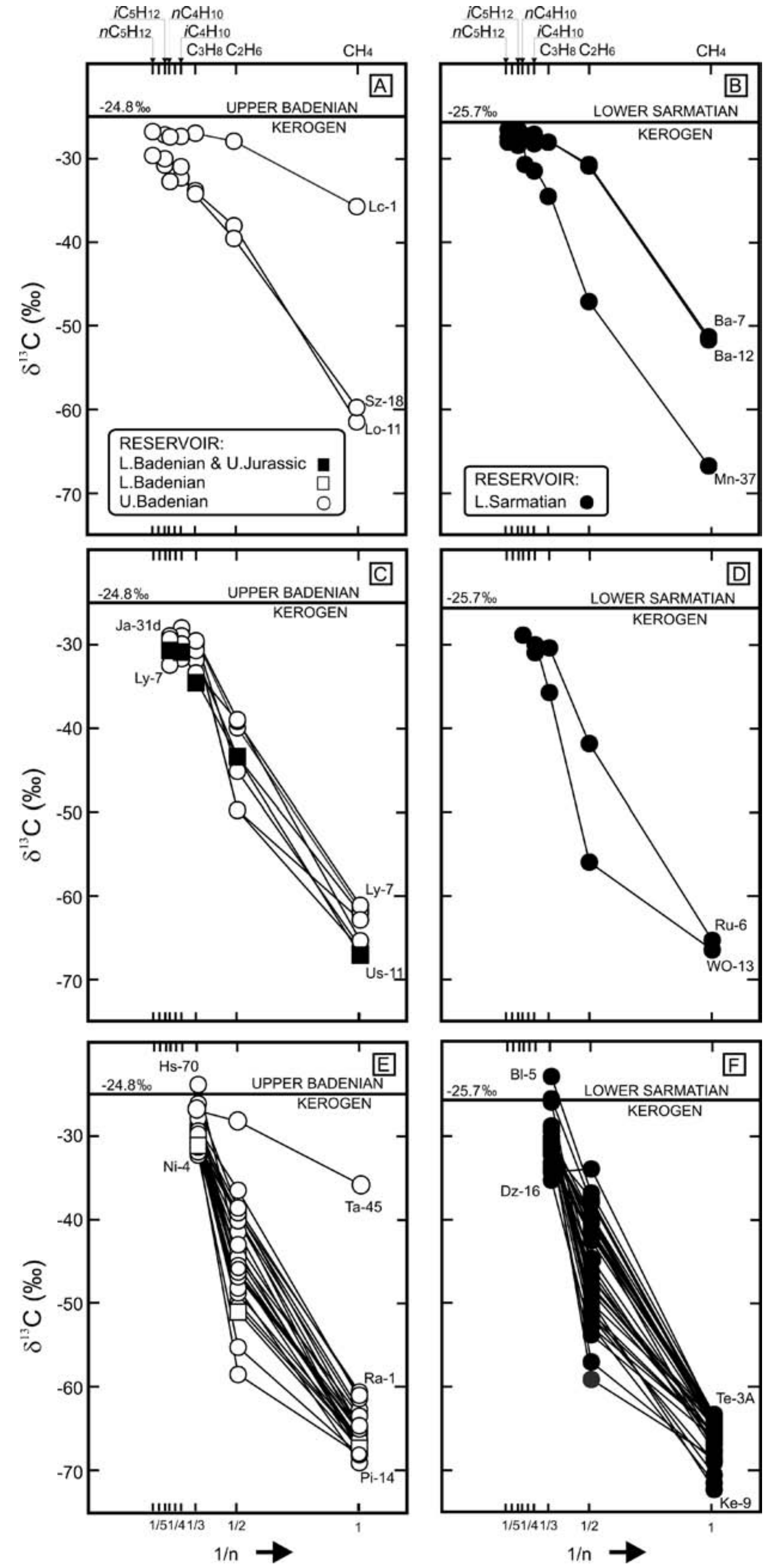

Fig. 5. Stable carbon isotope composition of methane, ethane, propane, butanes and pentanes (**A** and **B**), stable carbon isotope composition of methane, ethane, propane and butanes (**C** and **D**), and stable carbon isotope composition of methane, ethane and propane (**E** and **F**) *versus* the reciprocal of their carbon number for natural gases accumulated in Badenian (**A, C** and **E**) and Lower Sarmatian (**B, D** and **F**) reservoirs of the Polish Carpathian Foredeep. Structure of the graph for methane, ethane and propane (**E** and **F**) after Rooney *et al.* (1995). Average values of $\delta^{13}C = -24.8‰$ for Upper Badenian kerogen (**A, C** and **E**), and $\delta^{13}C$ values = –25.7 ‰ for Lower Sarmatian kerogen (**B, D** and **F**) from the autochthonous Miocene strata (Kotarba *et al.*, 1998a, 2005) . For explanation of sample codes see Table 1

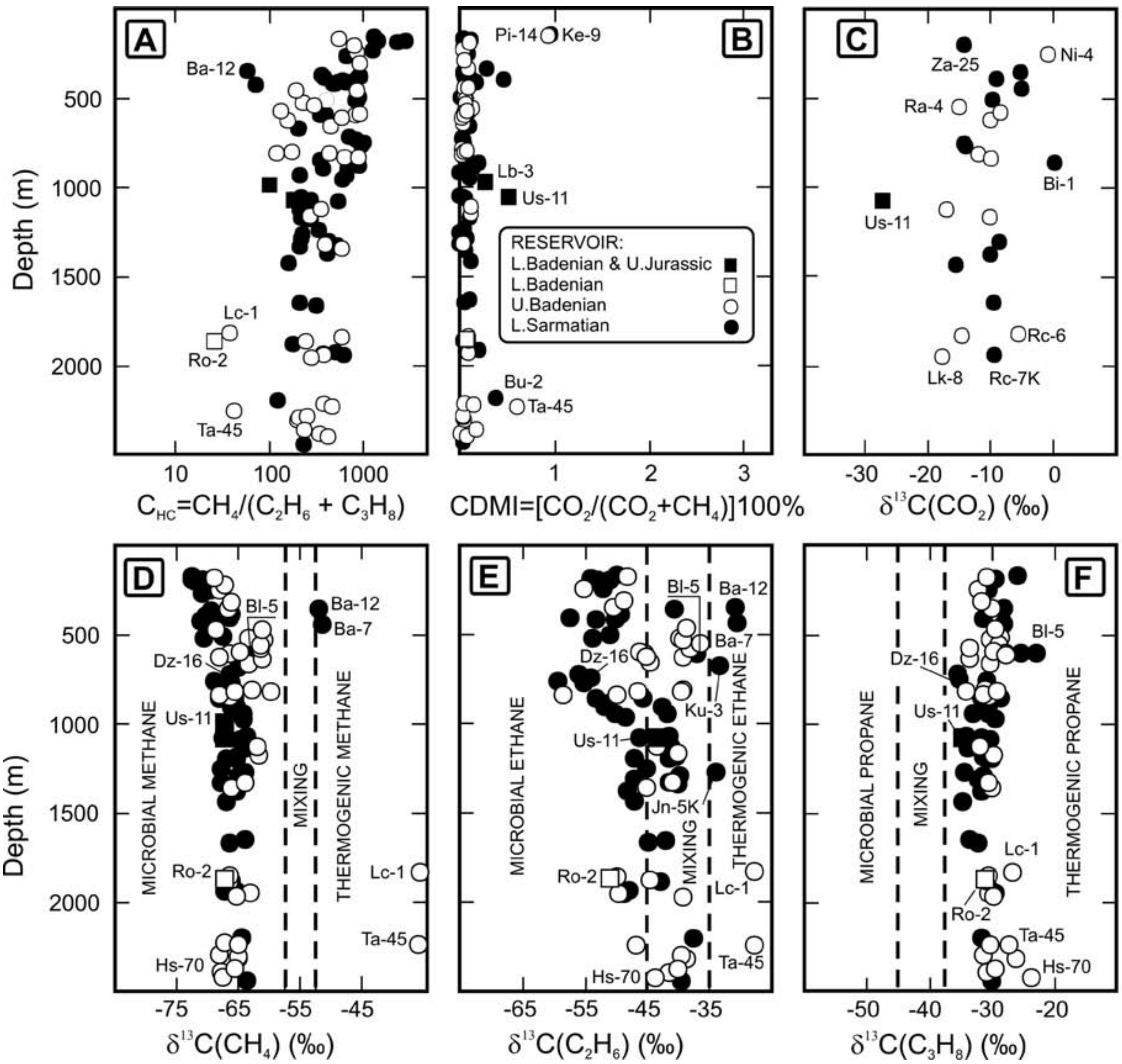

Fig. 6. (**A**) Hydrocarbon index, (**B**) carbon dioxide-methane index, (**C**) $\delta^{13}C(CO_2)$, (**D**) $\delta^{13}C(CH_4)$, (**E**) $\delta^{13}C(C_2H_6)$ and (**F**) $\delta^{13}C(C_3H_8)$ *versus* depth of natural gas accumulations within Badenian and Lower Sarmatian reservoirs of the Polish Carpathian Foredeep. For explanation of sample codes see Table 1

1988; Krooss *et al.*, 1995). For instance, during coalification of 1 ton of humic coals with a change in volatile matter (VM^{daf}) content from 40 to 4%, about 3.5 m^3 of N_2 are produced (Kotarba, 1988). Sapropelic organic matter is richer in nitrogen components, therefore, 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 of natural gases range from –15 to 18‰ (Gerling *et al.*, 1997). This isotopic fractionation results from both primary genetic factors and secondary processes taking place during migration at the gas-rock and gas-reservoir fluids interfaces (Stahl, 1977; Gerling *et al.*, 1997; Krooss *et al.*, 2005; Ballentine & Sharwood Lollar, 2002; Zhu *et al.*, 2000).

In the gases of the Lower Badenian and the Upper Jurassic reservoirs, N_2 concentrations vary from 0.65 to 4.88 vol% and the $\delta^{15}N(N_2)$ measured for one sample (Us-11) was –6.6‰. In the Upper Badenian reservoirs they range from 0.10 to 20.2 vol% (mean 1.92 vol%), and from –0.5 to 1.5‰, respectively, and from 0.17 to 9.21 vol%, and $\delta^{15}N(N_2)$ from –4.6 to –1.9‰, respectively, in the Lower Sarmatian reservoirs (Tables 2, 3). $\delta^{15}N(N_2)$ versus N_2 concentration (Fig. 8) can suggests that nitrogen was generated during both the microbial processes and the thermal transformation of organic matter.

Hydrogen sulphide

The origin of hydrogen sulphide is one of the most complex problems in organic geochemistry. Hydrogen sulphide can be generated in a number of processes, such as: (i) microbial sulphate reduction (MSR), (ii) thermochemical sulphate reduction – TSR), (iii) thermal destruction of organic sulphur components of oil and fossil organic matter, (iv) reaction of elemental sulphur and fossil organic matter (hydrocarbons), and (v) magmatic reactions (abiogenic, volcanic and/or plutonic processes). Results of stable sulphur isotope ($\delta^{34}S$) analyses of hydrogen sulphide, sulpha-

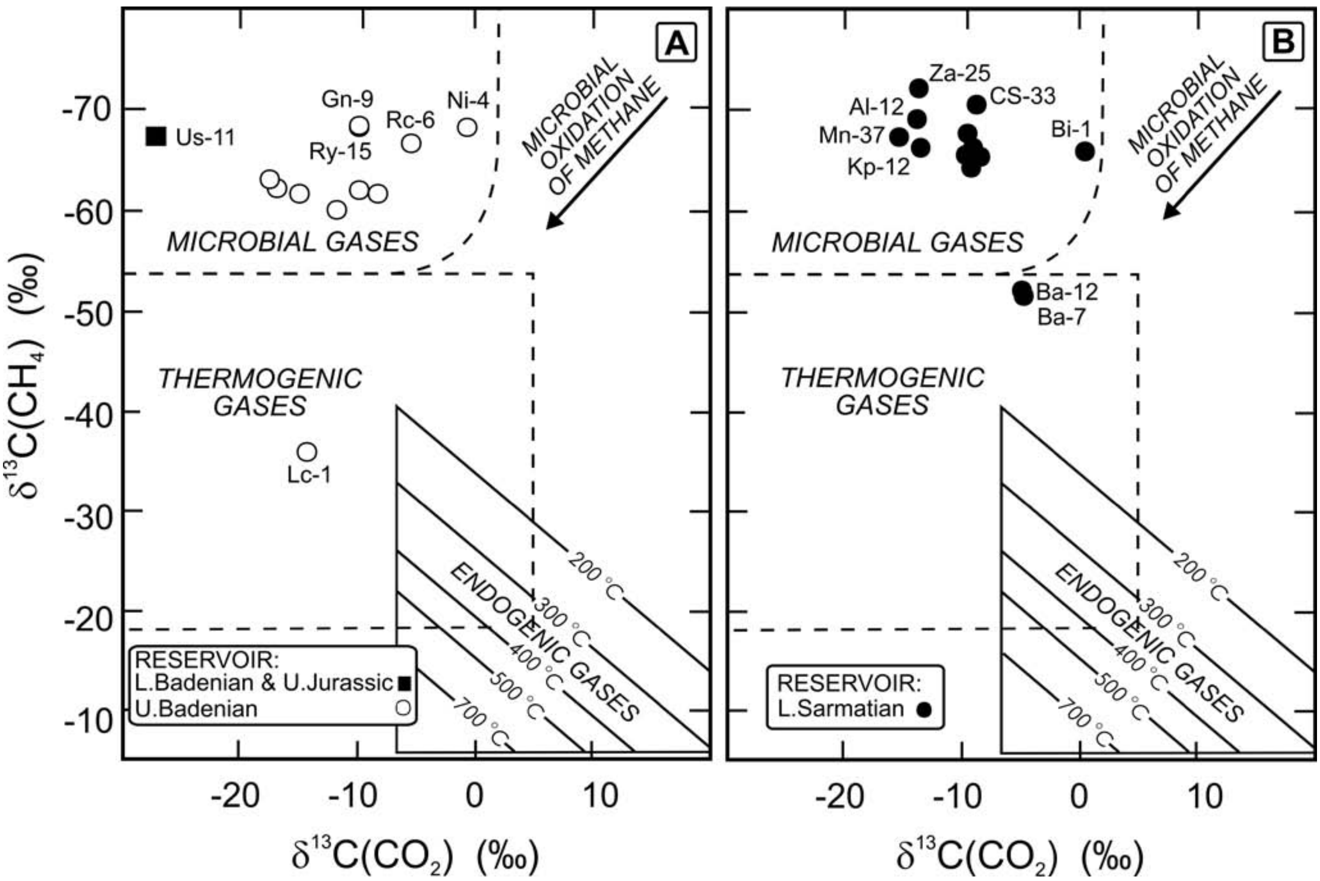

Fig. 7. $\delta^{13}C(CH_4)$ *versus* $\delta^{13}C(CO_2)$ for natural gases accumulated in (**A**) Badenian and (**B**) Lower Sarmatian reservoirs of the Polish Carpathian Foredeep. Compositional fields modified from Gutsalo & Plotnikov (1981) and Kotarba (1988). For explanation of sample codes see Table 1

tes, sulphides, and elemental sulphur, as related with geological and geothermal conditions in a given petroleum basin, enable one to recognise the origin of hydrogen sulphide, though not all its generation mechanisms have been fully explained so far (*e.g.*, Anissimov, 1995; Hałas *et al.*, 1973; Krouse, 1980; Krouse *et al.*, 1988; Worden *et al.*, 1995; Zhang *et al.*, 2008).

The concentration of hydrogen sulphide in the natural gas from the Lower Badenian Baranów beds in Roźwienica deposit equals 0.002 vol% (Table 2). Moreover, hydrogen sulphide concentration of 0.35 vol% and 0.15 vol% were found in the natural gases of the Wola Obszańska deposit and the Rokietnica deposit in Baranów beds, respectively (Karnkowski, 1999; Myśliwiec *et al.*, 2004). H_2S also occurs in natural gases of the Cetynia, Lubaczów and Uszkowce deposits within Lower Badenian Baranów beds, in the Upper Badenian chemical sediments and in the uppermost part of the Palaeozoic–Mesozoic basement (Karnkowski, 1999). Preliminary results of stable sulphur isotope analyses of hydrogen sulphide from Roźwienica deposit suggest that this gas component was generated during microbial sulphate reduction of the Lower Badenian gypsum and anhydrites (Kotarba, 1995).

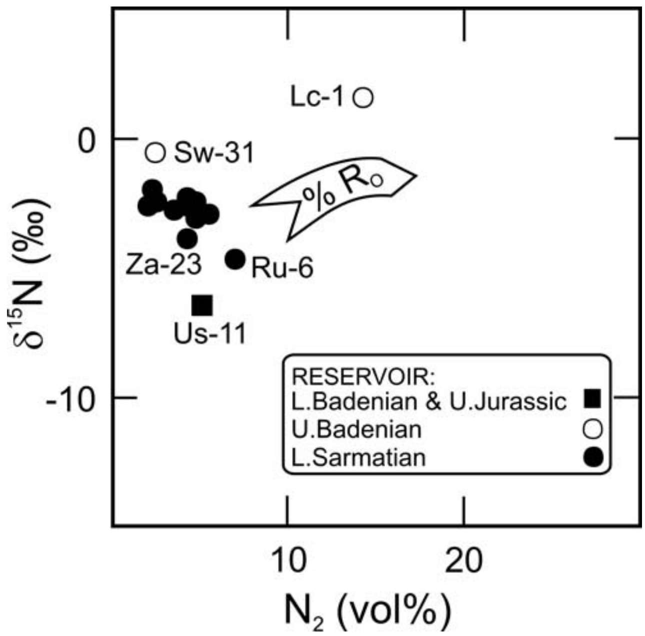

Fig. 8. $\delta^{15}N(N_2)$ *versus* N_2 concentration of natural gases accumulated in autochthonous Miocene reservoirs of the Polish Carpathian Foredeep. Direction of maturity of source rock after Gerling *et al.* (1997). For explanation of sample codes see Table 1

CONCLUSIONS

Methane concentrations in natural gases accumulated in the autochthonous Miocene strata of the Polish Carpathian Foredeep (between Kraków and Przemyśl) usually exceed 90 vol%. According to the common classification schemes, the gas was generated by microbial reduction of carbon dioxide in marine depositional environments, mainly during sedimentation of the Miocene clays and muds. It is likely that this microbial generation continues up to now. The higher light hydrocarbons (mainly propane, butanes and pentanes) were generated during diagenesis and at the initial stage of the low-temperature thermogenic processes. Very small changes in values of geochemical hydrocarbon indices and stable isotope ratios of methane, ethane and propane with depth evidence similar gas generation conditions within the whole Badenian and Lower Sarmatian sections.

Generation and accumulation of microbial methane and ethane, and the formation and the loading of multiply stacked Miocene reservoirs of the Polish Carpathian Foredeep were facilitated by rhythmic and cyclic deposition of clays, muds and sands at very high sedimentation rates.

The Upper Badenian reservoirs produced *via* the Ta-45 (Tarnów) and Lc-1 (Łękawica near Tarnów) wells are exceptions because they contain thermogenic gases. This holds also true for the Lower Sarmatian reservoirs accessed by the Ba-7, Ba-12 (Brzeźnica), Ku-3 (Kuryłówka) and Jn-5K (Jasionka) wells, which contain thermogenic gases. In both cases gases are generated from mixed type II/III kerogen. These thermogenic gases occur mainly in the bottom part of the Miocene succession. They were presumably generated by thermogenic processes in the Palaeozoic–Mesozoic basement and then ascended to the Miocene strata along the fault zones. The diagenetic and early thermogenic ethane, propane, butanes and propanes might have also been generated from dispersed organic matter within the Miocene strata.

Molecular hydrogen in concentrations up to 0.26 vol% was encountered in the Miocene gases. These hydrogen occurrences might be related to recent microbial processes.

Carbon dioxide concentrations in the analysed Miocene natural gases vary from 0.00 to 0.96 vol%. This gas was generated by both the microbial and low-temperature processes, and was subsequently subjected to secondary processes, mainly CO_2 dissolution in water during migration.

Nitrogen concentrations in the analysed Miocene natural gases vary from 0.65 to 4.88 vol%. It was probably generated during both the microbial and low-temperature thermogenic processes.

Hydrogen sulphide occurring in the Rożwienica deposit most probably was generated by microbial sulphate reduction of the Upper Badenian gypsum and anhydrites.

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