# Origin of natural gases in the Paleozoic-Mesozoic basement of the Polish Carpathian Foredeep

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**Abstract:** Hydrocarbon gases from Upper Devonian and Lower Carboniferous reservoirs in the Paleozoic basement of the Polish Carpathian Foredeep were generated mainly during low-temperature thermogenic processes ("oil window"). They contain only insignificant amounts of microbial methane and ethane. These gaseous hydrocarbons were generated from Lower Carboniferous and/or Middle Jurassic mixed Type III/II kerogen and from Ordovician–Silurian Type II kerogen, respectively. Methane, ethane and carbon dioxide of natural gas from the Middle Devonian reservoir contain a significant microbial component whereas their small thermogenic component is most probably genetically related to Ordovician–Silurian Type II kerogen. The gaseous hydrocarbons from the Upper Jurassic and the Upper Cretaceous reservoirs of the Mesozoic basement were generated both by microbial carbon dioxide reduction and thermogenic processes. The presence of microbial methane generated by carbon dioxide reduction suggests that in some deposits the traps had already been formed and sealed during the migration of microbial methane, presumably in the immature source rock environment. The traps were successively supplied with thermogenic methane and higher hydrocarbons generated at successively higher maturation stages of kerogen. The higher hydrocarbons of the majority of deposits were generated from mixed Type III/II kerogen deposited in the Middle Jurassic, Lower Carboniferous and/or Devonian strata. Type II or mixed Type II/III kerogen could be the source for hydrocarbons in both the Tarnów and Brzezówka deposits. In the Cenomanian sandstone reservoir of the Brzezowiec deposit and one Upper Jurassic carbonate block of the Lubaczów deposit microbial methane prevails. It migrated from the autochthonous Miocene strata.

**Key words:** Paleozoic-Mesozoic basement, Polish Carpathian Foredeep, isotope geochemistry, microbial hydrocarbon gases, thermogenic hydrocarbon gases, carbon dioxide origin, nitrogen origin.

## Introduction

This paper presents the results of molecular analyses, stable carbon isotope analyses of methane, ethane, propane, butanes, pentanes and carbon dioxide, stable hydrogen isotope analyses of methane, and stable nitrogen isotope analyses of gaseous nitrogen of natural gases accumulated within the Paleozoic-Mesozoic basement of the Polish Carpathian Foredeep between Kraków and the Polish-Ukrainian state border (Fig. 1). These results are related to the geological setting and the geochemical characterization of dispersed organic matter hosted in the autochthonous Miocene strata (Kotarba et al. 1998, 2005) as well as in the Middle Jurassic (Kosakowski et al. 2012a,b), Lower Carboniferous, Devonian and Ordovician-Silurian strata (Kotarba et al. 2011; Więcław et al. 2011, 2012) of the 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 and Ukrainian Carpathian Foredeep revealed that the methane, the dominating component of these gases, 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). In contrast, natural gases accumulated within the Paleozoic-Mesozoic basement of the Polish

Carpathian Foredeep represent various genetic types: (i) microbial, (ii) low-temperature, thermogenic gases associated with oil and condensate, and (iii) high-temperature, thermogenic, non-associated gases. Typical microbial gases, which have migrated from the autochthonous Miocene strata, are accumulated in the Upper Jurassic carbonate reservoir of one block of the Lubaczów field and in the Cenomanian sandstone reservoir of the Brzezowiec field (Jawor & Kotarba 1991, 1993; Kotarba & Jawor 1993; Kotarba & Koltun 2006).

## Geological setting and petroleum occurrence

The Polish Carpathian Foredeep consists of three structural complexes: (i) Precambrian-Paleozoic-Mesozoic basement, (ii) folded Zgłobice and Stebnik units, and (iii) autochthonous Miocene strata. The Carpathian Foredeep is divided into two basins: outer and inner (Oszczypko 1997). The eastern part of the outer basin, between Kraków and Przemyśl (Fig. 1) is filled with Badenian and Lower Sarmatian, mostly sandy-clayey sediments of total thickness up to 4500 m. The autochthonous Miocene sediments of the outer basin were affected by Alpine orogenic movements and rest almost horizontally upon the Precambrian-Paleozoic-Mesozoic basement (Oszczypko 1997; Oszczypko et al. 2006).

The Paleozoic-Mesozoic basement comprises two subunits: (i) Paleozoic basement, which includes Caledonian and
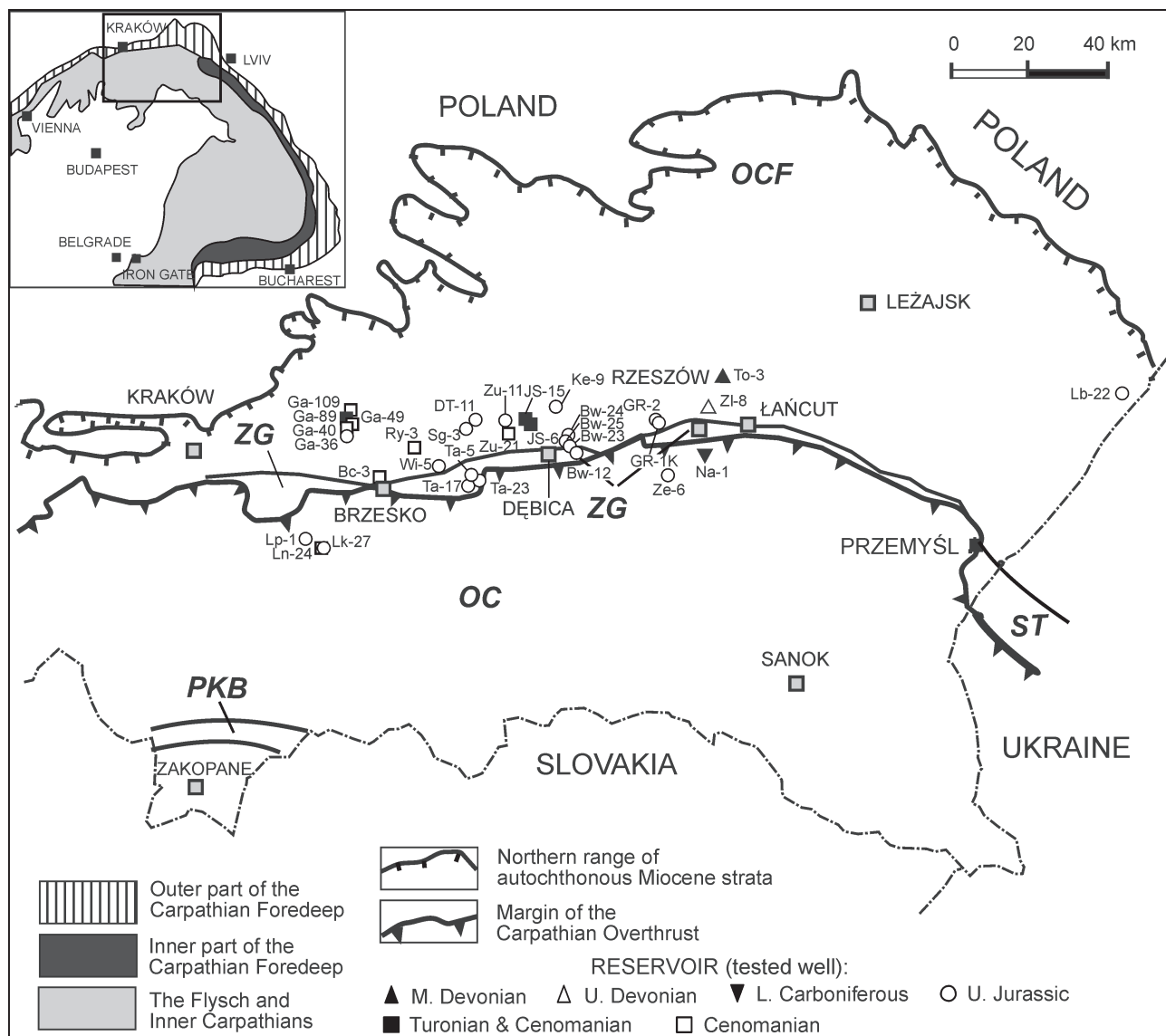
**Fig. 1.** Sketch map showing the major tectonic units of the Polish Carpathian region with the gas sampling locations. Names and codes of sampled wells are listed in Table 1. **OCF** — outer part of the Carpathian Foredeep; **ZG** — Zgłobice Unit; **ST** — Stebnik (Sambir) Unit; **OC** — the Outer (Flysch) Carpathians; **PKB** — Pieniny Klippen Belt.

Variscan orogens, and (ii) Mesozoic basement (the so-called Carpathian Foreland platform) built of Triassic, Middle–Upper Jurassic and Cretaceous strata. The Paleozoic-Mesozoic basement has highly diversified lithology, which reflects variable depositional environments, large stratigraphic and angular unconformities, and erosional morphology of the upper surface (Jawor 1970; Karnkowski 1999; Buła & Habryn 2011; Krajewski et al. 2011).

The Precambrian-Paleozoic-Mesozoic basement of the Carpathian Foredeep includes four main structural stages associated with strong and diversified diastrophic episodes: (i) Upper Proterozoic stage (Assynthian orogenic phase), (ii) Cambrian-Silurian stage (Caledonian orogeny), (iii) Devonian-Carboniferous stage (Variscan orogeny), and (iv) Zechstein-Mesozoic stage (Laramide orogenic phase) (Karnkowski 1999). Outlines of tectonics and lithostratigraphic sequence of the

Paleozoic/Mesozoic basement in the study area were described by Buła & Habryn (2011) and Krajewski et al. (2011). The generalized lithostratigraphic column of the Paleozoic-Mesozoic basement was presented in a number of publications, including Karnkowski (1999), Kotarba & Koltun (2006: Fig. 15) and Kotarba et al. (2011: Fig. 2).

The major petroleum reservoir rocks in the Paleozoic-Mesozoic basement are the following lithostratigraphic units (Karnkowski 1999): (i) Middle and Upper Devonian carbonates (Lachowice deposit, Trzebownisko-Krasne and Zalesie accumulations), (ii) Lower Carboniferous carbonates (Nosówka deposit), (iii) Triassic sandstones (Niwiska deposit), (iv) Malm limestones (Tarnów, Lubaczów, Korzeniów, Partynia-Podborze, Dąbrowa Tarnowska and Smęgorzów deposits), (v) Cenomanian sandstones alone (Brzezowiec, Grobla, Łąkta and Rylowa deposits), (vi) Upper Cretaceous (Turonian-

Senonian) sandstones locally intercalated with Upper Cretaceous marls, Malm limestones and Cenomanian sandstones (Jastrząbka Stara and Swarzów deposits).

The traps in oil and gas deposits of the Paleozoic/Mesozoic basement can be sealed either by the Miocene strata alone (e.g. Dąbrowa Tarnowska, Smęgorzów deposits), or by the Miocene cover and the Upper Cretaceous marls (e.g. Grobla, Rylowa, Wierzchosławice deposits). Moreover, the flysch strata of the Outer Carpathians provide an additional seal (e.g. Leszczyna-Łąkta) (Kotarba & Jawor 1993).

## Methodology

### Gas sampling procedure

Twenty-two natural gas samples were collected in the study area from the following producing wells drilled into Upper and Middle Devonian, Lower Carboniferous, Upper Jurassic and Upper Cretaceous reservoirs of the Paleozoic-Mesozoic basement (Table 1; Fig. 1). Free gases were collected directly at the producing wellheads into metal containers (volume ~1000 cm$^3$) and gases dissolved in oils were taken from separators to glass containers (volume ~500 cm$^3$) (Table 1). For interpretation, the results of molecular and isotopic analyses

of ten natural gases from the Paleozoic-Mesozoic basement published by Jawor & Kotarba (1991, 1993), Kotarba & Jawor (1993), Kotarba (1998), Kotarba et al. (2004) and Kotarba & Nagao (2008) were also used (Table 1). Information on the locations of sampling sites is given in Table 1 and in Fig. 1.

### Analytical procedures

The molecular composition of collected natural gases (CH$_4$, C$_2$H$_6$, C$_3$H$_8$, $i$C$_4$H$_{10}$, $n$C$_4$H$_{10}$, C$_5$H$_{12}$, C$_6$H$_{14}$, C$_7$H$_{16}$, unsaturated hydrocarbons, CO$_2$, O$_2$, H$_2$, N$_2$, He, Ar) were analysed with the Agilent 7890A and Chrom-5 gas chromatographs (GC). The Agilent GC is equipped with a three-valve system using three 1/8 inch packed columns (3 ft Hayesep Q 80/100 mesh, 6 ft Hayesep Q 80/100 mesh and 10 ft molecular sieve 13X 45/60 mesh) and a GS-Alumina capillary column (50 m×0.53 mm). The system consists of two independent channels. The channel using the FID for the detailed hydrocarbon analysis is a simple gas sampling valve injecting the sample into the GS-Alumina column. The second channel using packed columns is for determination of methane, ethane and non-hydrocarbon gases. The GC oven is programmed: initial temperature 60 °C held for 1 min, then increase to 90 °C at rate of 10 °C/min, next increase to 190 °C at rate of 20 °C/min and finally held for 5 min. Front detector (TCD) is operated with a temperature of 150 °C and

**Table 1:** Information on gas sample sites in the Paleozoic-Mesozoic basement.

| Well | Field | Sample | Lithology of reservoir | Age of reservoir | Depth (m) |
|---|---|---|---|---|---|
| Brzezowiec-3[#] | Brzezowiec | Bc-3[#] | Ss | Cenom. | 1346–1352 |
| Grobla-40 | Grobla-Pławowice | Ga-40 | Ss | Cenom. | 639–650 |
| Grobla-109 | Grobla-Pławowice | Ga-109 | Ss | Cenom. | 712–721 |
| Grobla-49 | Grobla-Pławowice | Ga-49 | Ss | Cenom. | 750–754 |
| Grobla-89 | Grobla-Pławowice | Ga-89 | Carb. & Cong. | Turonian & Cenom. | 664–702 |
| Jastrząbka Stara-6 | Jastrząbka Stara | JS-6 | Marls-Carb.-Ss | Turonian & Cenom. | 1295 |
| Jastrząbka Stara-15 | Jastrząbka Stara | JS-15 | Marls-Carb.-Ss | Turonian & Cenom. | 1290 |
| Leszczyna-24* | Łąkta | Ln-24* | Ss | Cenom. | 2268–2282 |
| Rylowa-3* | Rylowa | Ry-3* | Ss | Cenom. | 1035–1038 |
| Żukowice-21 | Żukowice | Zu-21 | Ss | Cenom. | 1320–1322 |
| Brzezówka-12 | Brzezówka | Bw-12 | Carb. | U.Jurassic | 1958–1985 |
| Brzezówka-23 | Brzezówka | Bw-23 | Carb. | U.Jurassic | 1930–1953 |
| Brzezówka-24*** | Brzezówka | Bw-24*** | Carb. | U.Jurassic | 1892–1913 |
| Brzezówka-25 | Brzezówka | Bw-25 | Carb. | U.Jurassic | 1902–1922 |
| Dąbrowa Tarnowska-11* | Dąbrowa Tarnowska | DT-11* | Carb. | U.Jurassic | 688-698 |
| Góra Ropczycka-1K | Czarna Sędziszowska | GR-1K | Carb.-Marls | U.Jurassic | 2040–2054 |
| Góra Ropczycka-2 | Czarna Sędziszowska | GR-2 | Carb. | U.Jurassic | 2049–2057 |
| Grobla-36 | Grobla | Ga-36 | Carb. | U.Jurassic | 766–781 |
| Lubaczów-22^ | Lubaczów | Lb-22^ | Carb. | U.Jurassic | 1020–1045 |
| Łapanów-1 | Łapanów | Lp-1 | Carb. | U.Jurassic | 1772–1776 |
| Łąkta-27 | Łąkta | Lk-27 | Carb. | U.Jurassic | 2258–2268 |
| Smęgorzów-3* | Smęgorzów | Sg-3* | Carb. | U.Jurassic | 473–470 |
| Tarnów-5 | Tarnów | Ta-5 | Carb. | U.Jurassic | 1650–1662 |
| Tarnów-17*** | Tarnów | Ta-17*** | Carb. | U.Jurassic | 1644–1670 |
| Tarnów-23 | Tarnów | Ta-23 | Carb. | U.Jurassic | 1660–1670 |
| Korzeniów-15 | Korzeniów | Ke-15 | Carb. | U.Jurassic | 1340–1375 |
| Wierzchosławice-5* | Łętowice-Wierzchosławice | Wi-5* | Carb.-Marls | U.Jurassic | 1450–1486 |
| Zagórzyce-6 | Zagórzyce | Ze-6 | Carb.-Marls | U.Jurassic | 2817–2871 |
| Żukowice-11 | Żukowice | Zu-11 | Carb.-Marls | U.Jurassic | 1292–1295 |
| Zalesie-8 | Zalesie | Zl-8 | Carb. | U.Devonian | 2765–2800 |
| Trzebownisko-3 | Krasne | To-3 | Carb. | M.Devonian | 2003–2065 |
| Nosówka-1** | Nosówka | Na-1** | Ss-Sh. | L.Carboniferous | 3465–3540 |

**U.** — Upper; **M.** — Middle; **L.** — Lower; **Cenom.** — Cenomanian (Upper Cretaceous); **Ss** — sandstones; **Cong.** — conglomerates; **Carb.** — Carbonates; **Sh.** — shales (mudstones & claystones); **#** — after Jawor & Kotarba (1993); **^** — after Kotarba (1998); **\*** — after Kotarba & Jawor (1993); **\*\*** — after Kotarba et al. (2004); **\*\*\*** — after Kotarba & Nagao (2008).

back detector (FID) — with a temperature of 250 °C. Helium is used as a carrier gas with flow through the TCD channel of 28 ml/min and through the FID channel of 7 ml/min. The concentration is determined on Chrom-5 GC equipped with TCD and 1/8 in. 2.5 m-long packed column with mixture of 4A and 5A molecular sieves (2 : 1 v/v) using argon as the carrier gas at a constant temperature of 25 °C. The Ar concentration is determined on the same GC at the same temperature program as helium using a 2.5 m-long packed column filled with molecular sieve 13X and hydrogen as carrier gas.

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, pentanes 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 using metallic 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 from Middle and Upper Devonian, and Lower Carboniferous reservoirs of the Paleozoic basement

The analysed gases of three samples collected from the Middle and Upper Devonian, and the Lower Carboniferous reservoirs of the Paleozoic basement of the Polish Carpathian Foredeep (Table 1) vary in their molecular and isotopic compositions. The molecular and isotopic compositions, and 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 the analysed gases (3 samples) are reported in Tables 2 and 3.

For classification of the analysed hydrocarbon gases, the diagnostic diagrams (Figs. 2– 4) were applied after Whiticar et al. (1986), Schoell (1988), Whiticar (1994) and Berner & Faber (1996). An important implication for the interpretation is that a linear relationship of stable carbon isotopes of methane, ethane, propane, butanes and pentanes versus their reciprocal carbon number (Fig. 5) as assumed, for example, by Chung et al. (1988) and Rooney et al. (1995) is not a sufficient indicator of natural gas generated from a single source. Zou et al. (2007) and Kotarba et al. (2009) suggested that in this type of plot a "dogleg" trend, characterized by relatively $^{13}$C-depleted methane and $^{13}$C-enriched propane compared to ethane, is indicative of natural gas that was not generated from a single source rock (multiple source) or that has undergone post-generation alteration
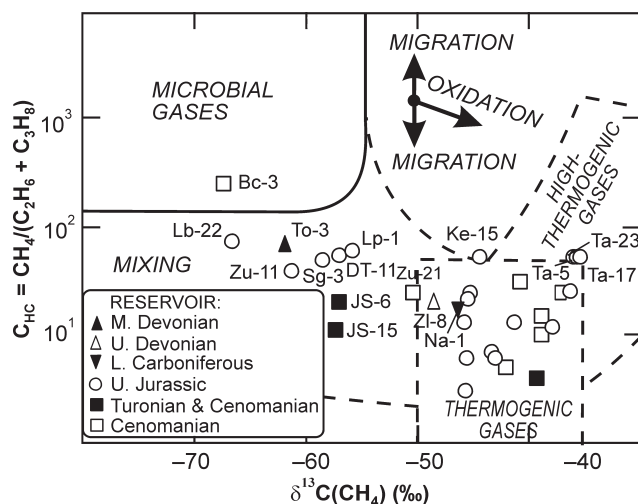


**Fig. 2.** Hydrocarbon index ($C_{HC}$) versus $\delta^{13}C(CH_4)$ for natural gases accumulated in Paleozoic-Mesozoic reservoirs of the basement of the Polish Carpathian Foredeep. Compositional fields after Whiticar (1994).
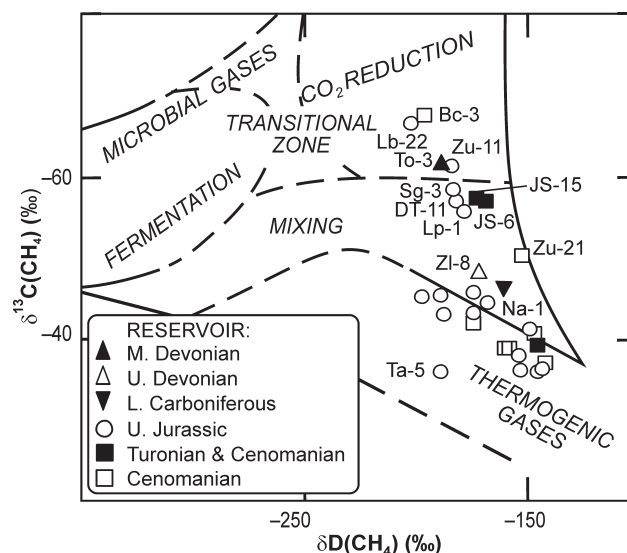


**Fig. 3.** $\delta^{13}C(CH_4)$ versus $\delta D(CH_4)$ for natural gases accumulated in Paleozoic-Mesozoic reservoirs of the basement of the Polish Carpathian Foredeep. Compositional fields after Whiticar et al. (1986).

(e.g. secondary gas cracking, microbial oxidation, thermochemical sulphate reduction). Moreover, the degree of $^{13}$C depletion of methane in relation to ethane can be applied to evaluate the mixing proportion of microbial methane and thermogenic gases (Kotarba & Lewan 2004; Kotarba et al. 2009).

The results of stable carbon and hydrogen isotope compositions of methane from natural gas accumulations in the Upper Devonian (Zl-8 sample) and the Lower Carboniferous (Na-1 sample) reservoirs (Figs. 2, 3) indicate that this gas was generated mainly during the low-temperature, thermogenic process. However, methane and ethane from these localities contain insignificant amounts of microbial components (Figs. 3, 4A). Ethane is generated in small quantities during microbial processes, for example, in the proportion of one molecule of ethane

**Table 2:** Molecular composition of natural gases from the Paleozoic-Mesozoic basement.

| Sample code | Molecular composition (vol. %) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $N_2$ | $CO_2$ | He | Ar | $H_2$ | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $iC_4H_{10}$ | $nC_4H_{10}$ | $iC_5H_{12}$ | $nC_5H_{12}$ | $C_6H_{14}$ |
| Bc-3[#] | 0.89 | 0.04 | 0.01 | 0.000 | 0.00 | 98.6 | 0.32 | 0.06 | 0.05 | 0.02 | 0.04 | n.a. | n.a. |
| Ga-40 | 14.3 | 0.63 | 0.02 | 0.03 | 0.05 | 77.7 | 3.32 | 1.86 | 0.68 | 0.80 | 0.37 | | 0.11 |
| Ga-109 | 13.1 | 0.36 | 0.03 | 0.04 | 0.81 | 76.7 | 4.40 | 3.21 | 0.60 | 0.41 | 0.012 | 0.05 | 0.34 |
| Ga-49 | 8.49 | 0.76 | 0.000 | 0.02 | 0.05 | 69.1 | 7.40 | 5.50 | 3.14 | 3.41 | 1.51 | | 0.49 |
| Ga-89 | 4.14 | 0.07 | 0.002 | 0.02 | 0.06 | 68.7 | 9.32 | 9.09 | 2.64 | 3.62 | 0.88 | 0.93 | 0.47 |
| JS-6 | 14.2 | 0.08 | 0.09 | 0.02 | 0.000 | 80.6 | 2.65 | 1.41 | 0.28 | 0.38 | 0.20 | | 0.25 |
| JS-15 | 14.7 | 0.00 | 0.00 | 0.03 | 0.000 | 76.6 | 4.15 | 2.77 | 0.60 | 0.67 | 0.20 | 0.16 | 0.13 |
| Ln-24* | 4.60 | 0.26 | 0.02 | 0.01 | 0.000 | 91.2 | 2.15 | 0.77 | 0.34 | 0.40 | 0.35 | | n.a. |
| Ry-3* | 37.4 | 0.09 | 0.10 | 0.000 | 0.000 | 59.4 | 1.63 | 0.76 | 0.13 | 0.27 | 0.20 | | 0.15 |
| Zu-21 | 31.2 | 0.11 | tr. | 0.16 | 1.10 | 64.7 | 2.26 | 0.38 | 0.03 | 0.05 | 0.02 | 0.000 | n.a. |
| Bw-12 | 3.14 | 0.16 | 0.009 | 0.005 | 0.001 | 89.0 | 5.10 | 1.69 | 0.30 | 0.35 | 0.12 | 0.101 | 0.06 |
| Bw-23 | 2.86 | 0.12 | 0.02 | 0.006 | 0.008 | 78.1 | 8.16 | 4.42 | 1.79 | 2.63 | 1.48 | | 0.44 |
| Bw-24*** | 4.07 | 0.08 | 0.02 | 0.008 | 0.002 | 80.0 | 7.37 | 3.56 | 1.30 | 1.91 | 1.19 | | 0.47 |
| Bw-25 | 0.93 | 0.11 | 0.004 | 0.005 | 0.005 | 70.2 | 15.0 | 6.82 | 2.22 | 2.76 | 1.52 | | 0.48 |
| DT-11* | 4.85 | 0.03 | 0.03 | 0.000 | 0.000 | 93.1 | 1.39 | 0.28 | 0.15 | 0.05 | 0.10 | 0.000 | 0.000 |
| GR-1K | 11.2 | 0.75 | 0.08 | 0.012 | 0.000 | 84.3 | 2.64 | 0.76 | 0.09 | 0.10 | 0.02 | 0.017 | 0.02 |
| GR-2 | 7.6 | 0.37 | 0.13 | 0.000 | 0.16 | 87.3 | 3.1 | 0.94 | 0.12 | 0.15 | 0.03 | 0.017 | 0.07 |
| Ga-36 | 8.7 | 0.19 | 0.02 | 0.04 | 0.003 | 74.5 | 7.3 | 5.10 | 1.27 | 1.63 | 0.40 | 0.45 | 0.41 |
| Lb-22^ | 4.79 | 0.33 | 0.07 | 0.000 | 0.09 | 92.4 | 0.75 | 0.47 | 0.29 | | 0.41 | | 0.17 |
| Lp-1 | 5.3 | 0.06 | 0.01 | 0.02 | 0.009 | 91.9 | 1.0 | 0.49 | 0.46 | 0.19 | 0.30 | 0.08 | 0.21 |
| Lk-27 | 1.24 | 0.27 | 0.12 | 0.005 | 0.000 | 89.4 | 4.06 | 2.64 | 0.64 | 0.88 | 0.27 | 0.27 | 0.18 |
| Sg-3* | 6.00 | 0.02 | 0.000 | 0.000 | 0.000 | 91.8 | 1.32 | 0.48 | 0.33 | 0.00 | 0.05 | | 0.02 |
| Ta-5 | 21.4 | 4.94 | 0.09 | 0.03 | 0.000 | 72.0 | 0.98 | 0.33 | 0.06 | 0.09 | 0.04 | 0.04 | 0.05 |
| Ta-17*** | 22.4 | 4.59 | 0.09 | 0.04 | tr. | 71.3 | 0.97 | 0.34 | 0.06 | 0.09 | 0.04 | 0.05 | 0.06 |
| Ta-23 | 22.4 | 4.54 | 0.09 | 0.03 | 0.03 | 71.4 | 0.98 | 0.34 | 0.06 | 0.09 | 0.04 | 0.04 | 0.05 |
| Ke-15 | 9.70 | 0.14 | 0.01 | 0.01 | 0.000 | 86.1 | 2.91 | 0.73 | 0.10 | 0.13 | 0.08 | | 0.03 |
| Wi-5* | 28.6 | 4.95 | 0.06 | 0.11 | 0.03 | 63.6 | 1.88 | 0.60 | 0.12 | 0.18 | 0.10 | | 0.05 |
| Ze-6 | 4.36 | 0.13 | 0.000 | 0.000 | 0.000 | 86.8 | 5.21 | 1.94 | 0.36 | 0.57 | 0.23 | 0.18 | 0.20 |
| Zu-11 | 4.66 | 0.04 | tr. | 0.01 | tr. | 92.5 | 1.60 | 0.70 | 0.18 | 0.16 | 0.16 | | 0.03 |
| Zl-8 | 8.60 | 0.07 | 0.01 | 0.000 | 0.007 | 85.4 | 2.98 | 1.00 | 0.34 | 0.37 | 0.33 | | n.a. |
| To-3 | 5.11 | 0.28 | 0.05 | 0.007 | 0.007 | 92.9 | 0.97 | 0.31 | 0.14 | 0.06 | 0.07 | 0.02 | 0.04 |
| Na-1** | 8.40 | 0.76 | 0.00 | 0.01 | 0.016 | 84.6 | 3.26 | 2.06 | 0.18 | 0.49 | 0.17 | | 0.06 |

**#** — after Jawor & Kotarba (1993); **\*** — after Kotarba & Jawor (1993); **\*\*** — after Kotarba et al. (2004); **\*\*\*** — after Kotarba & Nagao (2008); **tr.** — traces; **n.a.** — not analysed.
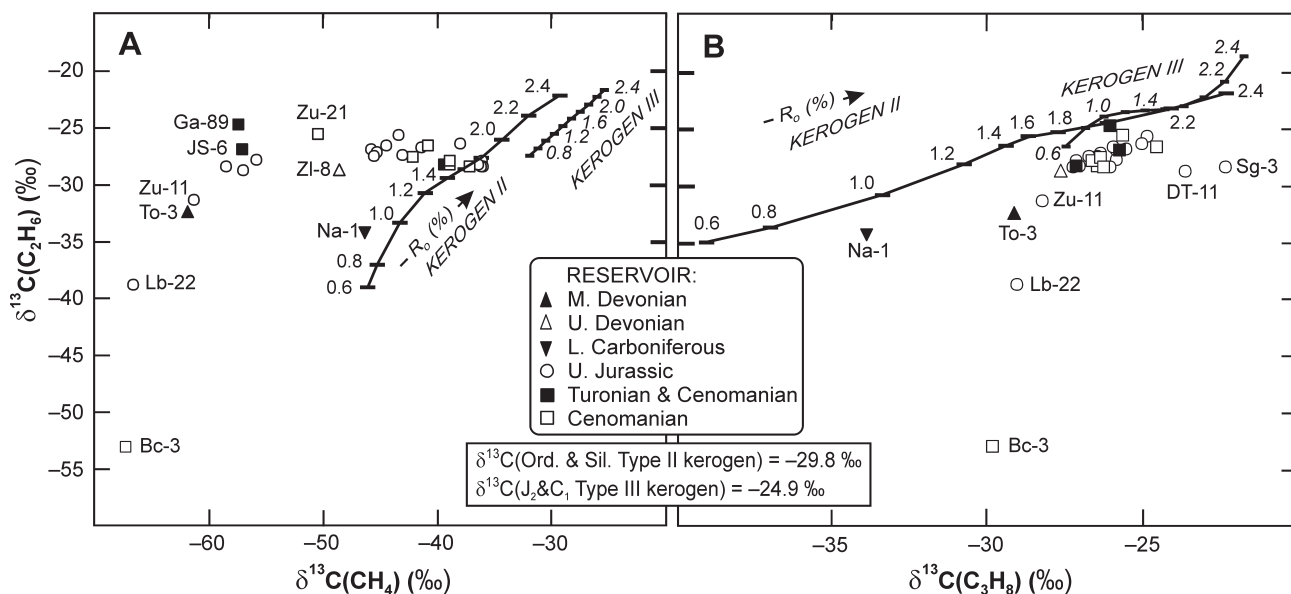


**Fig. 4.** $\delta^{13}C(C_2H_6)$ versus (**A**) $\delta^{13}C(CH_4)$ and (**B**) $\delta^{13}C(C_3H_8)$ for natural gases accumulated in Paleozoic-Mesozoic reservoirs of the basement of the Polish Carpathian Foredeep. Position of vitrinite reflectance curves for Type II and III kerogens after Berner & Faber (1996). Curves were shifted based on average $\delta^{13}C = -29.8$ ‰ for Ordovician and Silurian Type II kerogen (Więcław et al. 2011, 2012), average $\delta^{13}C$ values = $-24.9$ ‰ for Lower Carboniferous (clastic), and average $\delta^{13}C$ values = $-24.8$ ‰ for Middle Jurassic Type III kerogen (Kotarba et al. 2003; Więcław et al. 2011; Kosakowski et al. 2012a,b).

**Table 3:** Isotopic composition and gas ratios of natural gases from the Paleozoic-Mesozoic basement.

| Sample code | Stable isotopes (‰) | | | | | | | | | | Ratios | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\delta^{13}C$ (CH$_4$) | $\delta D$ (CH$_4$) | $\delta^{13}C$ (C$_2$H$_6$) | $\delta^{13}C$ (C$_3$H$_8$) | $\delta^{13}C$ ($i$C$_4$H$_{10}$) | $\delta^{13}C$ ($n$C$_4$H$_{10}$) | $\delta^{13}C$ ($i$C$_5$H$_{12}$) | $\delta^{13}C$ ($n$C$_5$H$_{12}$) | $\delta^{13}C$ (CO$_2$) | $\delta^{13}C$ (N$_2$) | C$_{HC}$ | CDMI | $i$CH$_4$ / $n$CH$_4$ |
| Bc-3[#] | –67.3 | –191 | –53.0 | –29.8 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 259 | 0.04 | 2.50 |
| Ga-40 | –38.9 | –159 | –28.3 | –26.4 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 15 | 0.81 | 0.84 |
| Ga-109 | –38.9 | –157 | –27.9 | –26.6 | –27.1 | –26.0 | n.a. | n.a. | –17.8 | 1.4 | 10 | 0.47 | 1.46 |
| Ga-49 | –42.1 | –173 | –27.6 | –26.3 | –27.2 | –26.4 | n.a. | n.a. | –16.6 | 1.2 | 5 | 1.09 | 0.92 |
| Ga-89 | –39.4 | –144 | –28.3 | –27.1 | –27.0 | –26.7 | n.a. | n.a. | n.a. | n.a. | 4 | 0.10 | 0.73 |
| JS-6 | –57.0 | –167 | –26.9 | –25.7 | –26.7 | –24.7 | –25.6 | –23.8 | –16.2 | 1.7 | 20 | 0.10 | 0.74 |
| JS-15 | –57.4 | –172 | –24.8 | –26.0 | –23.7 | –25.4 | –23.5 | n.a. | –27.2 | 1.7 | 11 | 0.00 | 0.90 |
| Ln-24* | –40.8 | –146 | –26.6 | –24.5 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 31 | 0.28 | 0.85 |
| Ry-3* | –37.2 | –141 | –28.4 | –26.2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 25 | 0.15 | 0.47 |
| Zu-21 | –50.4 | –151 | –25.6 | –25.6 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 25 | 0.17 | 0.60 |
| Bw-12 | –45.8 | –173 | –26.9 | –25.8 | –26.9 | –25.6 | n.a. | n.a. | –8.2 | 0.5 | 13 | 0.17 | 0.87 |
| Bw-23 | –45.6 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 6 | 0.15 | 0.68 |
| Bw-24*** | –43.4 | –173 | –25.7 | –24.8 | –26.1 | –24.6 | n.a. | n.a. | –8.6 | 0.7 | 7 | 0.10 | 0.68 |
| Bw-25 | –45.7 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 3 | 0.16 | 0.80 |
| DT-11* | –57.0 | –181 | –28.8 | –23.6 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 56 | 0.03 | 3.00 |
| GR-1K | –45.3 | –196 | –27.2 | –26.3 | –26.3 | –25.9 | n.a. | n.a. | –5.4 | 0.2 | 25 | 0.88 | 0.89 |
| GR-2 | –45.6 | –188 | –27.5 | –26.4 | –26.8 | –26.8 | –26.6 | –26.9 | –10.9 | 0.4 | 22 | 0.42 | 0.76 |
| Ga-36 | –43.1 | –187 | –27.5 | –26.7 | –27.6 | –26.5 | –26.9 | –26.2 | –15.5 | 1.4 | 6 | 0.26 | 0.78 |
| Lb-22^ | –66.6 | –201 | –38.8 | –29.0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 75 | 0.36 | n.c. |
| Lp-1 | –55.8 | –177 | –27.8 | –25.8 | –30.0 | –25.5 | –28.9 | –26.0 | –9.2 | 1.5 | 62 | 0.06 | 2.40 |
| Lk-27 | –41.4 | –148 | –26.8 | –25.5 | –26.9 | –25.3 | n.a. | n.a. | –10.4 | 1.1 | 13 | 0.30 | 0.73 |
| Sg-3* | –58.5 | –182 | –28.4 | –22.3 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 51 | 0.02 | 0.00 |
| Ta-5 | –36.1 | –188 | –27.9 | –27.1 | –27.4 | –27.3 | n.a. | n.a. | –5.8 | 2.0 | 55 | 6.42 | 0.71 |
| Ta-17*** | –36.0 | –144 | –28.4 | –26.0 | –27.5 | –26.7 | n.a. | n.a. | –6.0 | 2.0 | 54 | 6.05 | 0.70 |
| Ta-23 | –36.2 | –152 | –28.4 | –27.2 | –28.6 | –27.3 | n.a. | n.a. | –6.1 | n.a. | 54 | 5.98 | 0.71 |
| Ke-15 | –44.5 | –167 | –26.6 | –25.9 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 54 | 0.16 | 0.77 |
| Wi-5* | –36.4 | –142 | –28.3 | –27.0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 26 | 7.22 | 0.67 |
| Ze-6 | –38.0 | –153 | –26.4 | –25.0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 12 | 0.15 | 0.64 |
| Zu-11 | –61.3 | –183 | –31.4 | –28.2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 40 | 0.04 | 1.13 |
| Zl-8 | –48.6 | –171 | –28.7 | –27.6 | –28.2 | –27.1 | n.a. | n.a. | n.a. | n.a. | 21 | 0.08 | 0.92 |
| To-3 | –61.9 | –188 | –32.4 | –29.1 | –30.7 | –29.1 | n.a. | n.a. | –14.8 | –2.1 | 73 | 0.30 | 2.31 |
| Na-1** | –46.4 | –160 | –34.1 | –33.9 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 16 | 0.89 | 0.37 |

**#** — after Jawor & Kotarba (1993); **^** — after Kotarba (1998); ***** — after Kotarba & Jawor (1993); ****** — after Kotarba et al. (2004); ******* — after Kotarba & Nagao (2008); **C$_{HC}$** = CH$_4$/(C$_2$H$_6$+C$_3$H$_8$); **CDMI** = [CO$_2$/(CO$_2$+CH$_4$)]100 (%); **n.a.** — not analysed.

per one thousand molecules of methane (Oremland et al. 1986). Microbial ethane enriched in $^{12}$C (–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). Stable carbon isotope compositions of ethane, propane, butanes and pentanes (Figs. 4, 5) suggest that hydrocarbons from the Nosówka deposit (Na-1 sample) were generated from Ordovician-Silurian Type II kerogen (Fig. 5I) of maturity about 1.0 % on the vitrinite reflectance scale (Fig. 4) whereas gases from the Zalesie deposit (Zl-8 sample) were most probably produced from the Lower Carboniferous or Middle Jurassic, mixed Type III/II kerogen (Fig. 5F) of maturity about 1.1 % on the vitrinite reflectance scale (Fig. 4). Oil from the Nosówka deposit was generated from the same source of organic matter (Więcław 2011). Methane and ethane contained in the natural gas from the Middle Devonian reservoir of the Trzebownisko deposit (To-3 sample) reveals a significant microbial component (Figs. 2, 3, 4A, 5F, 6D). The small thermogenic component is most probably genetically related to the Ordovician-Silurian Type II kerogen (Fig. 5F). In all analysed gases the microbial component is genetically related to carbon dioxide reduction (Fig. 3), which occurs mainly in the marine environment (Whiticar et al. 1986; Rice 1992).

The hydrogen concentrations in the analysed gases vary from 0.007 to 0.016 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 (dissociation of water molecules bombarded by alpha particles) and natural nuclear reactions (Zobell 1947; Zinger 1962; Hawkes 1972; Whiticar et al. 1986; Dubessy et al. 1988; Savary & Pagel 1997). Hydrogen is a very reactive and mobile gas, hence, its retention in petroleum traps and in sedimentary rocks is rather ephemeral. Thus, its presence in natural gases indicates that it is either recently generated in secondary reactions within the reservoir and/or in the adjacent source beds, or it is ascending from deep-seated sources (Hunt 1996). Corrosion should be mentioned as a potential H$_2$ source. Depending on the well conditions and casing it may be even the most important process. Analysis of deuterium content in the analysed gases can perhaps be used to better constrain its origin.

The carbon dioxide concentrations and the values of the carbon dioxide-methane index (CDMI) in the analysed natural gases hosted in the Middle and Upper Devonian, and in the Lower Carboniferous reservoirs vary from 0.07 to 0.76 vol. % and from 0.08 to 0.89, respectively (Tables 2, 3). The $\delta^{13}C(CO_2)$ value in the To-3 sample is –8.2 ‰ (Table 3). The $\delta^{13}C(CH_4)$ versus $\delta^{13}C(CO_2)$ indicate that this carbon dioxide was generated by microbial processes (Fig. 7).

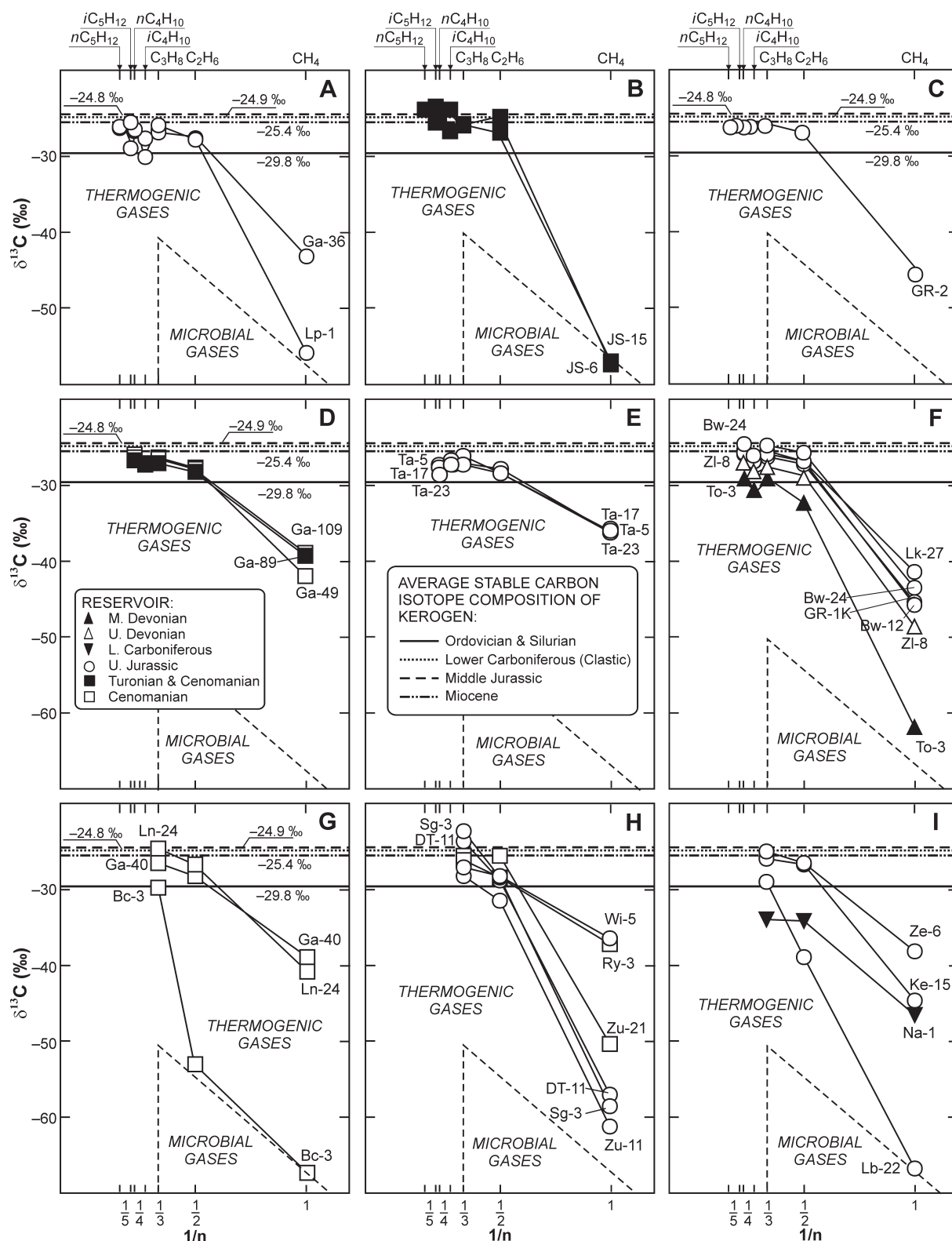**Fig. 5.** (**A**, **B** and **C**) Stable carbon isotope composition of methane, ethane, propane, butanes and pentanes (**D**, **E** and **F**), stable carbon isotope composition of methane, ethane, propane and butanes and (**G**, **H** and **I**) stable carbon isotope composition of methane, ethane and propane versus the reciprocal of their carbon number for natural gases accumulated in the Paleozoic-Mesozoic strata of (**A**, **D** and **F**) Kraków-Brzesko zone, (**B**, **E** and **H**) Brzesko-Dębica zone, and (**C**, **F** and **I**) Dębica-state border zone (for information on locations see Fig. 1). Structure of the graph (**G**, **H** and **I**) 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. 2011, 2012), $\delta^{13}C$ = –24.9 ‰ for Lower Carboniferous (clastic) kerogen (Więcław et al. 2011), $\delta^{13}C$ = –24.8 ‰ for Middle Jurassic kerogen (Kotarba et al. 2003; Kosakowski et al. 2012a,b), and $\delta^{13}C$ values = –24.6 ‰ for Miocene kerogen (Kotarba et al. 1998, 2005).

**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 in the basement of the Polish Carpathian Foredeep.

Nitrogen is produced in large quantities during both the microbial processes and the thermogenic transformation of organic matter (Kotarba 1988; Krooss et al. 1995). For instance, coalification of 1 kg of humic coal is associated with a change volatile matter ($VM^{daf}$) yield from initially 40 down to 4 % generates about 3.5 $dm^3$ of $N_2$ (Kotarba 1988). Sapropelic organic matter is richer in nitrogen, therefore, more molecular nitrogen can be produced from it than from the humic matter (Maksimov et al. 1982). The process of molecular nitrogen generation from organic matter was also documented by pyrolytic experiments (Gerling et al. 1997). The $\delta^{15}N$-values of molecular nitrogen from natural gases change from –15 to 18 ‰ (Gerling et al. 1997). This isotopic fractionation results from both, the primary genetic factors and the secondary processes taking place during gas migration through the gas-rock and gas-reservoir fluids interfaces

(Stahl 1977; Gerling et al. 1997; Zhu et al. 2000; Ballentine & Sherwood Lollar 2002; Krooss et al. 2005). Nitrogen concentrations in the analysed natural gases vary from 5.11 to 8.60 vol. % and $\delta^{15}N(N_2)$ in the To-3 sample is –2.1 ‰ (Tables 2, 3). The position of the To-3 sample in Fig. 8 can suggests that nitrogen was generated by both the microbial processes and the thermal transformation of organic matter. However, I cannot exclude that at least part of the nitrogen found in the analysed samples might have originated from the atmosphere during sedimentation.

### Natural gases from the Upper Jurassic and Upper Cretaceous reservoirs of the Mesozoic basement

The analysed gases (29 samples) collected from both the Upper Jurassic and the Upper Cretaceous reservoirs of the
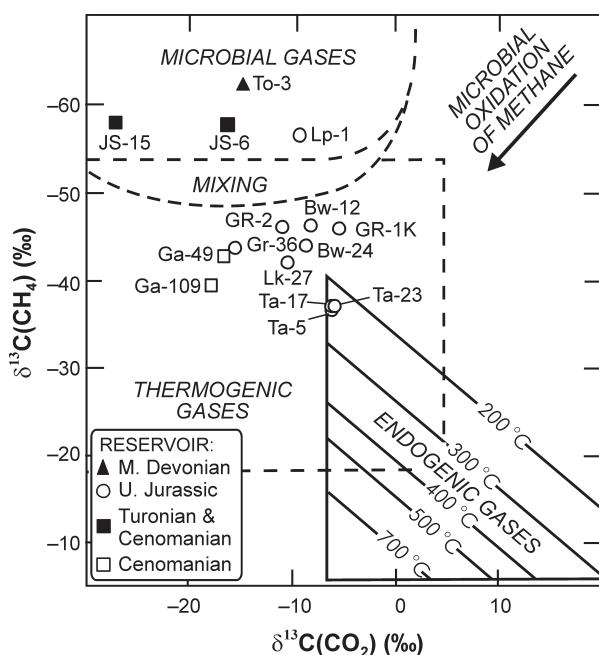
**Fig. 7.** $\delta^{13}C(CH_4)$ versus $\delta^{13}C(CO_2)$ for natural gases accumulated in Paleozoic-Mesozoic reservoirs of the basement of the Polish Carpathian Foredeep. Compositional fields modified from Gutsalo & Plotnikov (1981) and Kotarba (1988).
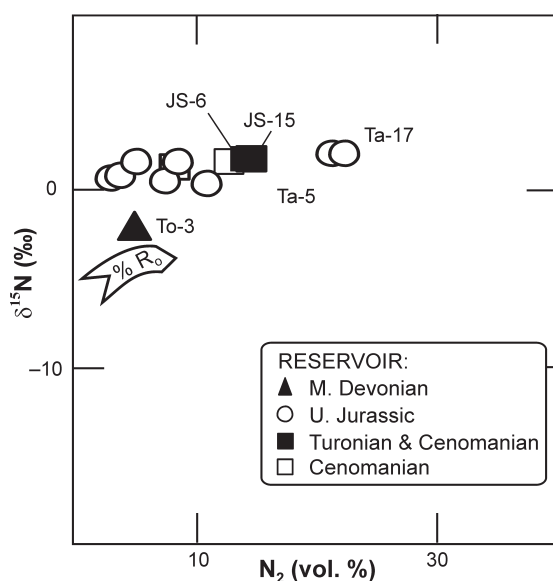


**Fig. 8.** $\delta^{15}N(N_2)$ versus $N_2$ concentration of natural gases accumulated in Paleozoic-Mesozoic reservoirs of the basement of the Polish Carpathian Foredeep. Direction of increasing source rock maturity after Gerling et al. (1997).

Mesozoic basement of the Polish Carpathian Foredeep (Table 1) also vary in their molecular and isotopic compositions.

The stable carbon and hydrogen isotope compositions of methane from natural gas accumulated within the Upper Jurassic and the Upper Cretaceous reservoirs of the Mesozoic basement (Figs. 2, 3) indicate that this gas was generated by both, microbial carbon dioxide reduction and thermogenic

processes. In the Brzezowiec deposit (sample Bc-3) and in one block of the Lubaczów deposit (sample Lu-22) microbial methane prevails (Figs. 2–6). It was generated by carbon dioxide reduction (Fig. 3). This microbial methane migrated from the autochthonous Miocene strata to the Cenomanian sandstone and the Upper Jurassic carbonate reservoirs (Jawor & Kotarba 1993; Kotarba & Koltun 2006). Significant microbial gas components occur in natural gases from the Swarzów (Sw-3), Dąbrowa Tarnowska (DT-11), Żukowice (Zu-11) and Łapanów (La-1) deposits (Figs. 2, 3, 4A, 5, 6). The presence of microbial methane generated by microbial carbon dioxide reduction (Fig. 3) suggests that in these deposits the traps had already been formed and sealed during the migration of microbial methane. The traps have been successively supplied with thermogenic methane and higher hydrocarbons generated from Type III/II kerogen (Fig. 5) at successively higher maturation stages (Fig. 4). Microbial methane was also generated by the same process within the autochthonous Miocene strata (Kotarba 2011). Therefore, under favourable geological conditions partial migration of Miocene-sourced microbial methane into the basement cannot be excluded (Kotarba & Jawor 1993).

The remaining deposits (Brzezówka, Czarna Sędziszowska-Góra Ropczycka, Grobla, Korzeniów, Łąkta-Leszczyna, Rylowa, Tarnów, Wierzchosławice and Zagórzyce) are dominated by thermogenic methane (Figs. 2–6). Comparison of stable carbon isotope values of propane, butanes and pentanes with those for different types of kerogen (Fig. 5) indicates the presence of mixed, Type III/II kerogen with a broad maturity range (from 1.1 to 2.2 % in the vitrinite reflectance scale) in the Middle Jurassic (Kosakowski et al. 2012a,b) and/or the Lower Carboniferous strata (Więcław et al. 2011), as the source of these thermogenic gases (Fig. 4). Type II or mixed Type II/III kerogen could be the source of hydrocarbons in the Tarnów (Fig. 5E) and the Brzezówka (Fig. 5F) deposits. A kerogen of similar type in the Middle and Upper Devonian strata could be at least partly the source of the hydrocarbons in the Grobla and Rylowa deposits (Kotarba et al. 2011; Więcław et al. 2011). A "dogleg" trend of the isotopic curves in Fig. 5 suggests that thermogenic gases were generated in at least two phases: first, the low-temperature, thermogenic gases associated with oil and condensate were produced, followed by the second, high-temperature, thermogenic, non-associated gases.

The carbon dioxide concentrations and the values of the carbon dioxide-methane index (CDMI) in the analysed natural gases vary from 0.02 to 4.95 vol. % and from from 0.02 to 7.22 vol. %, respectively (Tables 2, 3). The $\delta^{13}C(CO_2)$ values range from –17.8 to –5.4 ‰ (Table 3). The $\delta^{13}C(CH_4)$ versus $\delta^{13}C(CO_2)$ plot (Fig. 7) indicates that carbon dioxide was generated both in microbial and thermogenic processes. Microbial carbon dioxide almost exclusively occurs in the natural gases from the Jastrząbka Stara and the Łapanów deposits. On the contrary, thermogenic carbon dioxide dominates in the Brzezówka, Czarna Sędziszowska-Góra Ropczycka, Grobla, Łąkta-Leszczyna and Tarnów deposits (Fig. 7). The vertical distribution of carbon dioxide-methane index (CDMI) and the $\delta^{13}C(CO_2)$ values are presented in Fig. 6B and C. Such variations in concentration and stable isotope composition of car-

bon dioxide with depth indicate the influence of secondary processes, mainly $CO_2$ dissolution in water during migration.

The $N_2$ concentrations in the natural gases from the Mesozoic basement vary from 0.89 to 37.4 vol. % and $\delta^{15}N(N_2)$ values range from 0.2 to 2.0 ‰ (Tables 2, 3). Correlation between $\delta^{15}N(N_2)$ and $N_2$ concentration (Fig. 8) could suggests that nitrogen was generated by both, microbial processes and thermal transformation of organic matter. However, it cannot be excluded that atmospheric gases would have been introduced into the source rocks or into the pathways of gas migration to the surface, as for example, in the natural gases accumulated in the Upper Jurassic reservoir of the Tarnów deposit (Kotarba & Nagao 2008). The notably high $H_2$ (1.10 vol. %) and $N_2$ (31.2 vol. %, Table 2) contents in the Zu-21 sample are attributed to secondary recovery methods applied in the Żukowice field.

The hydrogen sulphide concentrations in the natural gases from the Mesozoic basement in the Grobla and Tarnów deposits vary from 0.10 to 0.12 vol. % and from 0.04 to 0.07 vol. % (Table 2). The origin of hydrogen sulphide is one of the most complex problems in petroleum geochemistry. Hydrogen sulphide can be generated in a number of processes, namely: (i) microbial sulphate reduction (MSR), (ii) thermochemical sulphate reduction (TSR), (iii) thermal decomposition 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). Stable sulphur isotope ($\delta^{34}S$) compositions of hydrogen sulphide, sulphates, sulphides, and elemental sulphur, as related to the geological and geothermal conditions in a given petroleum basin, may be used to recognize the origin of hydrogen sulphide, though not all of 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). Preliminary results of stable sulphur isotope analyses of hydrogen sulphide from the Grobla and Tarnów deposits suggest that this gas component was generated during thermal decomposition of organic sulphur components of oil and fossil organic matter (Kotarba & Hałas, unpublished data).

## Conclusions

The results of molecular and stable isotopic analyses of natural gases from the Paleozoic-Mesozoic basement of the Polish Carpathian Foredeep lead to the following conclusions:

1. Hydrocarbon gases from the Upper Devonian (Zalesie deposit) and the Lower Carboniferous (Nosówka deposit) reservoirs were generated mainly by a low-temperature, thermogenic process ("oil window"). Methane and ethane from these accumulations contain insignificant microbial components. The thermogenic hydrocarbon gases in the Nosówka deposit were generated from Ordovician-Silurian Type II kerogen at a maturity level corresponding to around 1.0 % in the vitrinite reflectance scale, and those from the Zalesie deposit were most probably produced from Lower Carboniferous and/or Middle Jurassic, mixed Type III/II kerogen with a vitrinite reflectance around 1.1 %;

2. Methane, ethane and carbon dioxide in the Middle Devonian reservoir of the Trzebownisko deposit contain a significant microbial component. The small thermogenic component is most probably genetically related to Ordovician-Silurian Type II kerogen;

3. The microbial components of all analysed gases from the Paleozoic basement are related to carbon dioxide reduction, which occurs mainly in the marine environment;

4. The nitrogen component of Paleozoic gases was generated by both, microbial and thermogenic processes but its partial atmospheric origin cannot be excluded;

5. Hydrocarbon gases from the Upper Jurassic and the Upper Cretaceous reservoirs of the Mesozoic basement were generated by both the microbial carbon dioxide reduction and the thermogenic processes;

6. In the Cenomanian sandstone reservoir of the Brzezowiec deposit and an Upper Jurassic carbonate block of the Lubaczów deposit, microbial methane prevails; according to its isotopic signature it was generated by carbon dioxide reduction. This gas has migrated from the autochthonous Miocene strata to the Mesozoic reservoirs;

7. Significant portions of microbial gas occur in the Swarzów, Dąbrowa Tarnowska, Żukowice, and Łapanów deposits. The presence of microbial methane generated by carbon dioxide reduction suggests that in these deposits the traps had already been formed and sealed during the migration of microbial methane produced presumably from immature source-rocks. The traps have been successively supplied with thermogenic methane and higher hydrocarbons generated from Type III/II kerogen at successively higher maturation stages;

8. Microbial methane was generated by the same process within the autochthonous Miocene strata. Therefore, partial migration of Miocene-sourced microbial methane into the basement may have occurred under favourable geological conditions;

9. Natural gases from the Czarna Sędziszowska-Góra Ropczycka, Grobla, Korzeniów, Łąkta-Leszczyna, Rylowa, Wierzchosławice and Zagórzyce deposits hosted in the Mesozoic basement are dominated by thermogenic methane. These gaseous hydrocarbons were generated from the mixed Type III/II kerogen of the Middle Jurassic, Lower Carboniferous and/or Devonian strata, which extends over a broad range of maturity — from 1.1 to 2.2 % in the vitrinite reflectance scale;

10. Type II or mixed Type II/III kerogen may have been the sources of hydrocarbons in the Tarnów and the Brzezówka deposits;

11. Thermogenic gases found in both, Upper Jurassic and Upper Cretaceous deposits were generated in at least two phases: first, low-temperature, thermogenic gases associated with oil and condensate were formed, followed by, high-temperature, thermogenic, non-associated gases. Thus, the traps in these deposits were supplied during a long time span corresponding to the successive hydrocarbon generation phases;

12. Carbon dioxide found in both, Upper Jurassic and Upper Cretaceous deposits was generated by both, microbial and thermogenic processes. Microbial carbon dioxide is predominant in natural gases of the Jastrząbka Stara and the

Łapanów deposits, whereas in the Brzezówka, Czarna Sędziszowska-Góra Ropczycka, Grobla, Łąkta-Leszczyna and Tarnów deposits thermogenic carbon dioxide prevails;

13. Nitrogen found in both the Upper Jurassic and Upper Cretaceous deposits was generated by both, microbial processes and thermal transformation of fossil organic matter. However, it cannot be excluded, that atmospheric gases were introduced into the source rocks or into the ascension pathways of gases to the surface, as for example, the Upper Jurassic reservoir of the Tarnów deposit;

14. Hydrogen sulphide found in the Grobla and Tarnów deposits was most probably generated by thermal decomposition of organic sulphur components of oil and fossil organic matter.

# References

Anissimov L. 1995: Origin of $H_2S$ in natural gases: Identification of geochemical processes. In: Grimalt J.O. & Dorronsoro C. (Eds.): Organic geochemistry: developments and applications to energy, climate, environment and human history. *Selected papers from the 17th International Meeting on Organic Geochemistry*, Donostia-San Sebastian, 1113–1114.

Ballentine C.J. & Sherwood Lollar B. 2002: Regional groundwater focusing of nitrogen and noble gases into the Hugoton-Panhandle giant gas field, USA. *Geochim. Cosmochim. Acta* 66, 2483–2497.

Berner U. & Faber E. 1996: Empirical carbon isotope/maturity relationships for gases from algal kerogens and terrigenous organic matter, based on dry, open-system pyrolysis. *Org. Geochem.* 24, 947–955.

Buła Z. & Habryn R. 2011: Precambrian and Palaeozoic basement of the Carpathian Foredeep and the adjacent Outer Carpathians (SE Poland and western Ukraine). *Ann. Soc. Geol. Pol.* 81, 221–239.

Chung H.M., Gormly J.R. & Squires R.M. 1988: Origin of gaseous hydrocarbons in subsurface environments: theoretical considerations of carbon isotope distribution. *Chem. Geol.* 71, 91–103.

Coplen T.B. 1995: Reporting of stable carbon, hydrogen, and oxygen isotopic abundances. In: Reference and intercomparison materials for stable isotopes of light elements. Proceedings of a consultants meeting held in Vienna, 1–3 December 1993. *Inter. Atom. Energy Agency*, Vienna, 31–34.

Dubessy J., Pagel M., Beny J.M., Christensen H., Hickel B., Kosztolanyi C. & Poty B. 1988: Radiolysis evidenced by $H_2$-$O_2$ and $H_2$-bearing fluid inclusions in three uranium deposits. *Geochim. Cosmochim. Acta* 52, 1155–1167.

Florkowski T. 1985: Sample preparation for hydrogen isotope analysis by mass spectrometry. *Inter. J. Appl. Radiat. Isotopes* 36, 991–992.

Gerling P., Idiz E., Everlien G. & Sohns E. 1997: New aspects on the origin of nitrogen in natural gas in Northern Germany. *Geol. Jb.* D103, 65–84.

Głogoczowski J.J. 1976: Versuch der Aufstellung eines neuen "Hydrat" modells der Erdgasgenerierung im Miözan der Karpatenvorsenke. *Z. Angew. Geol.* 26, 156–158.

Gutsalo L.K. & Plotnikov A.M. 1981: Carbon isotopic composition in the $CH_4$-$CO_2$ system as a criterion for the origin of methane and carbon dioxide in Earth natural gases. *Dokl. Akad. Nauk SSSR* 259, 470–473 (in Russian, English summary).

Hałas S., Lis J., Szaran J. & Żuk W. 1973: Variability of isotopic composition of $H_2S$ in presence of deposits of natural gas. *Przegl. Geol.* 21, 5, 280–281 (in Polish, English summary).

Hawkes H.E. 1972: Free hydrogen in genesis of petroleum. *AAPG Bull.* 56, 2268–2277.

Hinrichs K-U., Hayes J.M., Bach W., Spivack A.J., Hmelo L.R., Holm N.G., Johnson C.G. & Sylva S.P. 2006: Biological formation of ethane and propane in the deep marine sediments. *Proc. Nat. Acad. Sci.* 103, 14684–14689.

Hunt J.M. 1996: Petroleum geochemistry and geology. 2nd Edition. *Freeman,* New York, 1–743.

Jawor E. 1970: The structure of the deep substratum in the region east of Cracow. *Acta Geol. Pol.* 20, 709–769 (in Polish, Englis summary).

Jawor E. & Kotarba M. 1991: Origin of natural gas accumulated in Paleozoic-Mesozoic basement complex in western and central parts of Carpathian Foredeep: geological and isotopic interpretation. *Nafta* 47, 149–155 (in Polish, English summary).

Jawor E. & Kotarba M. 1993: Origin of natural gas accumulated in Cenomanian and Miocene reservoirs in Brzezowiec field. *Nafta* 49, 47–53 (in Polish, English summary).

Karnkowski P. 1999: Oil and gas deposits in Poland. *Geol. Soc. "Geos"*, Kraków, 1–380.

Kosakowski P., Więcław D., Kotarba M.J. & Kowalski A. 2012a: Hydrocarbon potential of the Mesozoic strata between Kraków and Rzeszów (SE Poland). *Geol. Quart.* 56, 139–152.

Kosakowski P., Więcław D., Kowalski A. & Koltun Y.V. 2012b: Assessment of hydrocarbon potential of Jurassic and Cretaceous source rocks in the Tarnogród–Stryi area (SE Poland and W Ukraine). *Geol. Carpathica* 63, 4, 319–333.

Kotarba M. 1988: Geochemical criteria of origin of gases accumulated in the Upper Carboniferous coal-bearing strata of the Wałbrzych basin. *Zesz. Nauk. AGH* 1199, *Geol.* 42, 1–119 (in Polish, English summary).

Kotarba M. 1992: Bacterial gases in Polish part of the Carpathian Foredeep and the Flysch Carpathians: isotopic and geological approach. In: Vially R. (Ed.): Bacterial Gas. *Editions Technip*, Paris, 133–146.

Kotarba M.J. 1998: Composition and origin gaseous hydrocarbons in the Miocene strata of the Polish part of the Carpathian Foredeep. *Przegl. Geol.* 46, 751–758.

Kotarba M.J. 2011: Origin of natural gases in the autochthonous Miocene strata of the Polish Carpathian Foredeep. *Ann. Soc. Geol. Pol.* 81, 409–424.

Kotarba M. & Jawor E. 1993: Petroleum generation, migration and accumulation in the Miocene sediments and Paleozoic-Mesozoic basement complex of the Carpathian Foredeep between Cracow and Pilzno (Poland). In: Spencer A.M. (Ed.): Generation, accumulation and production of Europe's hydrocarbons. *Spec. Publ. European Assoc. Petrol. Geol.*, 3, *Springer*, Heidelberg, 295–301.

Kotarba M.J. & Koltun Y.V. 2006: The origin and habitat of hydrocarbons of the Polish and Ukrainian Parts of the Carpathian Province. In: Golonka J. & Picha F.J. (Eds.): The Carpathians and their foreland: geology and hydrocarbon resources. *AAPG Mem.* 84, 395–442.

Kotarba M.J. & Lewan M.D. 2004: Characterizing thermogenic

coalbed gas from Polish coals of different ranks by hydrous pyrolysis. *Org. Geochem.* 35, 615–646.

Kotarba M.J. & Nagao K. 2008: Composition and origin of natural gases accumulated in the Polish and Ukrainian parts of the Carpathian region: Gaseous hydrocarbons, noble gases, carbon dioxide and nitrogen. *Chem. Geol.* 255, 426–438.

Kotarba M., Szafran S. & Espitalié J. 1987: A study of organic matter and natural gases of Miocene sediments in the Polish part of the Carpathian Foredeep. *Chem. Geol.* 64, 197–207.

Kotarba M.J., Wilczek T., Kosakowski P., Kowalski A. & Więcław D. 1998: A study of organic matter and habitat of gaseous hydrocarbons in the Miocene strata of the Polish part of the Carpathian Foredeep. *Przegl. Geol.* 46, 742–750.

Kotarba M.J., Więcław D., Kosakowski P., Zacharski J. & Kowalski A. 2003: Evaluation of source rock and petroleum potential of Middle Jurassic strata in the south-eastern part of Poland). *Przegl. Geol.* 51, 1031–1040 (in Polish, English summary).

Kotarba M.J., Burzewski W., Jawor E., Baran U., Kosakowski P. & Buła Z. 2004: Generation element of petroleum system and evaluation of hydrocarbon accumulation potential of Carboniferous strata in the southern part of the Upper Silesian and Małopolska blocks). In: Kotarba M.J. (Ed.): Hydrocarbon generation potential of Carboniferous rocks in the southern part of the Upper Silesian and Małopolska blocks. *Towarzystwo Badania Przemian Środowiska "Geosfera",* Kraków, 117–141 (in Polish, English summary).

Kotarba M.J., Więcław D., Kosakowski P. & Kowalski A. 2005: Hydrocarbon potential of source rocks and origin of natural gases accumulated in Miocene strata of the Carpathian Foredeep in Rzeszów area. *Przegl. Geol.* 53, 67–76 (in Polish, English summary).

Kotarba M.J., Curtis J.B. & Lewan M.D. 2009: Comparison of natural gases accumulated in Oligocene strata with hydrous pyrolysis gases from Menilite Shales of the Polish Outer Carpathians. *Org. Geochem.* 40, 769–783.

Kotarba M.J., Więcław D., Kosakowski P., Wróbel M., Buła Z., Matyszkiewicz J., Krajewski M., Kowalski A. & Koltun Y.V. 2011: Petroleum systems and prospectives of hydrocarbon exploration in the Palaeozoic-Mesozoic basement (SE Poland and western Ukraine). *Ann. Soc. Geol. Pol.* 81, 487–522.

Krajewski M., Matyszkiewicz J., Król K. & Olszewska B. 2011: Facies of the Upper Jurassic–Lower Cretaceous deposits from the southern part of the Carpathian Foredeep basement in the Kraków–Rzeszów area (southern Poland). *Ann. Soc. Geol. Pol.* 81, 269–290.

Krooss B.M., Littke R., Müller B., Frielingsdorf J., Schwochau K. & Idiz E.F. 1995: Generation of nitrogen and methane from sedimentary organic matter: implications on the dynamics of natural gas accumulations. *Chem. Geol.* 126, 291–318.

Krooss B.M., Friberg L., Gensterblum Y., Hollenstein J., Prinz D. & Littke R. 2005: Investigation of the pyrolytic liberation of molecular nitrogen from Paleozoic sedimenraty rocks. *Int. J. Earth Sci.* 94, 1023–1038.

Krouse H.R. 1980: Stable isotope geochemistry of non-hydrocarbon constituents of natural gas. *Proc. 10th World Petroleum Congress,* Bucharest 10, 85–92.

Krouse H.R., Viau C.A., Eliuk L.S., Ueda A. & Halas S. 1988: Chemical and isotopic evidence of thermochemical sulfate reduction by light hydrocarbon gases in deep carbonate reservoirs. *Nature* 333, 415–419.

Lillis P.G. 2007: Upper Cretaceous microbial petroleum systems in north-central Montana. *Mountain Geologist* 44, 11–35.

Maksimov S.P., Ancupov P.V., Botnieva T.A., Niecajev O.L.,

Karnkowski P., Korab Z., Stepniewska E. & Calikowski A. 1982: Natural gases from Zechstein Main Dolomite. *Nafta* 38, 41–44 (in Polish).

Oremland R.S., Whiticar M.J., Strohmaier F.S. & Kiene R.P. 1986: Bacterial ethane formation from reduced, ethylated sulphur compounds in anoxic sediments. *Geochim. Cosmochim. Acta* 52, 1895–1904.

Oszczypko N. 1997: The Early–Middle Miocene Carpathian peripheral foreland basin (Western Carpathians, Poland). *Przegl. Geol.* 45, 1054–1063.

Oszczypko N., Krzywiec P., Popadyuk I. & Peryt T. 2006: Carpathian Foredeep Basin (Poland and Ukraine): its sedimentary, structural, and geodynamic evolution. In: Golonka J. & Picha F.J. (Eds.): The Carpathians and their foreland: geology and hydrocarbon resources. *AAPG Mem.* 84, 261–318.

Rice D.D. 1992: Controls, habitat, and resource potential of ancient bacterial gas. In: Vially R. (Ed.): Bacterial gas. *Editions Technip*, Paris, 91–117.

Rooney M.A., Claypool G.E. & Chung H.M. 1995: Modeling thermogenic gas generation using carbon isotope ratios of natural gas hydrocarbons. *Chem. Geol.* 126, 219–232.

Savary V. & Pagel M. 1997: The effects of water radiolysis on local redox conditions in the Oklo, Gabon, natural fission reactors 10 to 16. *Geochim. Cosmochim. Acta* 61, 4479–4494.

Schoell M. 1988: Multiple origins of methane in the Earth. *Chem. Geol.* 71, 1–10.

Shabo Z.V. & Mamchur G.P. 1984: The perspectives of gas bearing of the deep horizons of the Carpathian Foredeep based on carbon isotope composition. *Geol. Zhurnal* 1, 50–57 (in Russian).

Stahl W. 1977: Carbon and nitrogen isotopes in hydrocarbon research and exploration. *Chem. Geol.* 20, 121–149.

Whiticar M.J. 1994: Correlation of natural gases with their sources. In: Magoon L.B. & Dow W.G. (Eds.): The petroleum system — from source to trap. *AAPG Mem.* 60, 261–283.

Whiticar M.J., Faber E. & Schoell M. 1986: Biogenic methane formation in marine and freshwater environments: $CO_2$ reduction vs. acetate fermentation — Isotope evidence. *Geochim. Cosmochim. Acta* 50, 693–709.

Więcław D. 2011: Origin of liquid hydrocarbons in the Miocene strata of the Polish Carpathian Foredeep and its Palaeozoic-Mesozoic basement. *Ann. Soc. Geol. Pol.* 81, 443–458.

Więcław D., Kotarba M.J., Kowalski A. & Kosakowski P. 2011: Habitat and hydrocarbon potential of the Palaeozoic source rocks in the Kraków-Rzeszów area (SE Poland). *Ann. Soc. Geol. Pol.* 81, 375–394.

Więcław D., Kosakowski P., Kotarba M.J., Koltun Y.V. & Kowalski A. 2012: Assessment of hydrocarbon potential of the Lower Palaeozoic strata in the Tarnogród-Stryi area (SE Poland and western Ukraine). *Ann. Soc. Geol. Pol.* 82, 65–80.

Worden R.H., Smalley P.C. & Oxtoby N.H. 1995: Gas souring by thermochemical sulphate reduction at 140 ºC. *AAPG Bull.* 79, 854–863.

Zhu Y., Shi B. & Fang C. 2000: The isotopic compositions of molecular nitrogen: implications on their origins in natural gas accumulations. *Chem. Geol.* 164, 321–330.

Zinger A.S. 1962: Molecular hydrogen in gas dissolved in waters of oil-gas fields, Lower Volga Region. *Geochemistry* 10, 1015–1023.

Zobell C.R. 1947: Microbial transformation of molecular hydrogen in marine sediments, with particular reference to petroleum. *AAPG Bull.* 31, 1709–1751.

Zou Y.-R., Cai Y., Zhang Ch., Zhang X. & Peng P. 2007: Variations of natural gas carbon isotope-type curves and their interpretation — A case study. *Org. Geochem.* 38, 1398–1415.