



## Origin of hydrocarbon gases accumulated in the Middle Cambrian reservoirs of the Polish part of the Baltic region

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The origin of natural gases associated with oil and condensate accumulations within the Middle Cambrian sandstone reservoirs on the Polish part of the Baltic region was characterized by means of molecular analyses, stable carbon isotopes of methane, ethane and propane, and stable hydrogen isotopes of methane. Gases generated from the Upper Cambrian–Tremadocian source rock succession by hydrous pyrolysis at 330°C for 72 h was used to characterize thermogenic gas and to identify the microbial methane input in the natural gas accumulations. A insignificant component of microbial methane is only present in gases from the B3 offshore field and from two inflows in the B7-1/91 borehole. The traps within the Middle Cambrian sandstone reservoirs had already been formed and sealed between the Late Cambrian and the Early Ordovician time span when migration of microbial methane took place along the fault system. The traps were successively supplied with thermogenic gaseous hydrocarbons, condensate and oil generated from the same source organic matter of the Upper Cambrian–Tremadocian source rock succession at a successively higher maturation stage.

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Key words: Polish Baltic region, Upper Cambrian–Tremadocian source rock succession, thermogenic gases, microbial methane, hydrous pyrolysis, stable isotopes.

### INTRODUCTION

In the Polish onshore part of the Baltic region, the small arnowiec oil deposit was first discovered in 1970. Later, in this area two small oil accumulations at D bki in 1971 and Białogóra in 1991, and one gas-condensate accumulation at arnowiec-West in 1987 were discovered (Karnkowski, 1999; Dom alski *et al.*, 2004; Karnkowski *et al.*, 2010). In the Polish offshore part of the Baltic region, three oil accumulations in the B3 structure in 1981, B8 in 1983, and B34 in 1996, and four gas-condensate accumulations in the B4 structure in 1991, B6 in 1982, B16 in 1985, and B21 in 1996 were discovered in Middle Cambrian sandstone reservoirs (Dom alski *et al.*, 2004; Karnkowski *et al.*, 2010). The Upper Cambrian–Lower Ordovician (Tremadocian) succession contains the best source-rocks with low-organic sulphur and oil-prone Type-II kerogen (Wi cław *et al.*, 2010a). The Słupsk Block and the onshore part of the Łeba Block (Fig. 1) are the main petroleum

generation and expulsion areas that developed from the end of the Pridoli (latest Silurian) to the end of the Carboniferous (Kosakowski *et al.*, 2010; Wróbel and Kosakowski, 2010). The origin of oils accumulated in the Middle Cambrian reservoirs in the Polish part of the Baltic region is has been described by Wi cław *et al.* (2010b).

Details of the geology and petroleum occurrence in the Polish part of the Baltic region were published by Witkowski (1989), Karnkowski (1999), Dom alski *et al.* (2004), Karnkowski *et al.* (2010), Modli ski and Podhala ska (2010), Pokorski (2010), and in references therein.

The objective of this study is to determine the origin of hydrocarbon gases dissolved in oil and in condensate accumulations of the Middle Cambrian sandstone reservoirs of the Polish part of the Baltic region. The study involves molecular and stable-isotope characterization of natural gases and gases generated from Upper Cambrian–Tremadocian source rocks by hydrous pyrolysis (temperature 330°C and time 72 h).

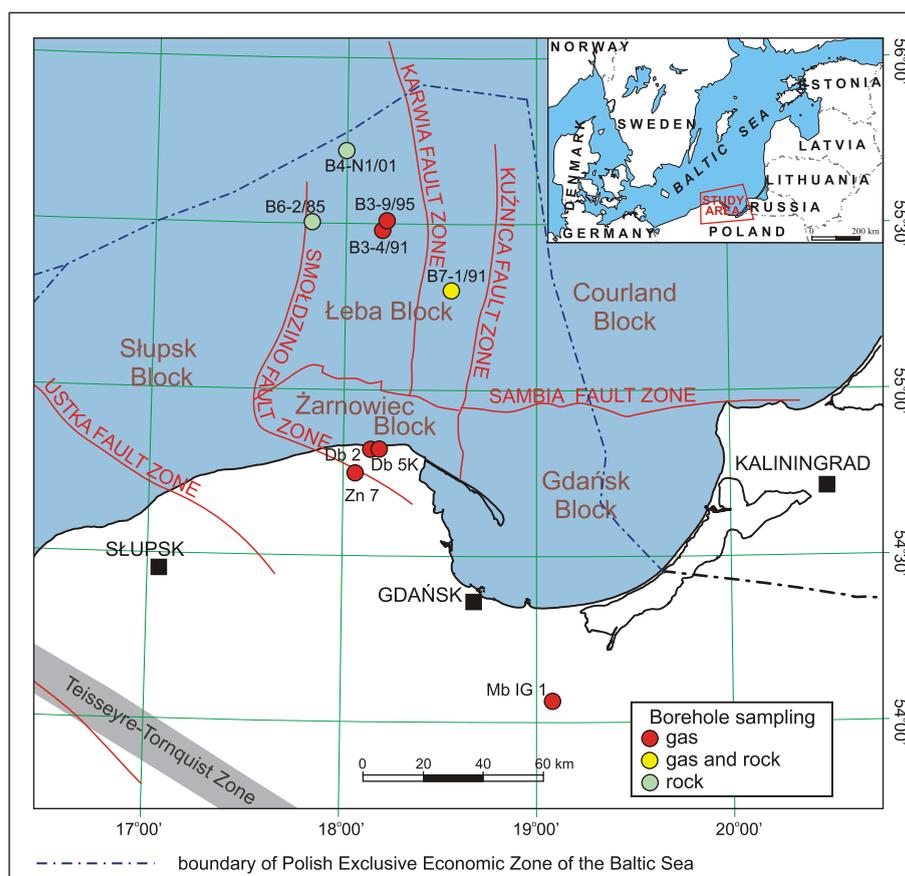


Fig. 1. Sketch map of the Polish Baltic region showing location of sampled rock and gas boreholes

Fault system after Pokorski (2010)

## SAMPLE DESCRIPTION

### ROCK SAMPLES

Hydrous pyrolysis experiments were conducted for three thermally immature samples representing Upper Cambrian and Tremadocian shales. One Upper Cambrian sample was taken from the B4-N1/01 borehole and the two Tremadocian samples originated from the B6-2/85 and B7-1/91 boreholes. All three boreholes are located in the Polish Exclusive Economic Zone of the Baltic Sea operated by the LOTOS Petrobaltic S.A. Company. The samples are ~2 kg composites collected from drill cores. The location of the sampling sites is shown in Figure 1 and sample depth is given in Table 1. The samples were crushed and sieved to gravel size (0.5–2.0 cm), and were not pre-extracted for the experiments.

### NATURAL GAS SAMPLES

Eight natural gas samples were collected from Middle Cambrian sandstones in the Polish part of the Baltic region (Fig. 1). Four of these samples were taken from offshore bore-

holes (B3-4/91, B3-9/95 and two intervals in B7-1/91), and four samples were collected from the onshore D bki 2 (Db 2), D bki 5K (Db 5K), Malbork IG 1 (Mb IG 1) and Żarnowiec 7 (Zn 7) boreholes (Fig. 1). Gases dissolved in oils (B3-4/91, B3-9/95, Db 2 and Db 5K samples) and condensates (Zn 7 sample) were collected from separators to glass or metal containers (~500 and ~1000 cm<sup>3</sup>, respectively). Gas samples from

Table 1

Description of rock samples subjected to hydrous pyrolysis and Rock-Eval data

Sample code	B4-N1 comp.	B7-1 comp.	B6-2 comp.
Depth [m]	1192–1197	2320–2323	1432–1438
Age	Cm3	O–Tr	O–Tr
TOC [wt.%]	13.0	9.6	10.6
$T_{max}$ [°C]	436	434	441
HI [mg/g TOC]	364	289	302

Cm3 – Upper Cambrian, O–Tr – Ordovician–Tremadocian; TOC – total organic carbon;  $T_{max}$  – maximum temperature; HI – hydrogen index; comp. – composite (an average sample from whole interval of lithostratigraphic unit)

Table 2

## Molecular composition of natural gases

Borehole	Sample code	Depth [m]	Molecular composition [mole%]												
			CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	<i>i</i> C <sub>4</sub>	<i>n</i> C <sub>4</sub>	<i>i</i> C <sub>5</sub>	<i>n</i> C <sub>5</sub>	C <sub>6+</sub>	N <sub>2</sub>	CO <sub>2</sub>	He	Ar	H <sub>2</sub>
B3-4/91	B3-4	1730–1755	50.88	25.75	14.35	0.82	2.27	n.a.	0.49	0.09	4.90	0.35	0.05	0.03	n.a.
B3-9/95	B3-9	1478–1479.8	45.00	25.10	17.10	1.35	3.01	0.32	0.38	0.15	6.37	0.22	0.01	n.a.	0.03
B7-1/91	B7-1(2)	2365.3–2374.4	67.60	5.86	2.00	0.07	0.19	n.a.	0.02	0.01	13.90	8.85	1.44	0.12	–
B7-1/91	B7-1(6)	2336.6–2365.0	34.90	17.26	14.15	0.82	2.48	n.a.	0.75	0.14	21.87	1.61	0.08	0.29	5.64
D bki 2	Db 2	2733–2753	71.80	14.40	7.60	0.63	1.48	n.a.	0.04	0.06	2.58	0.83	0.12	0.03	0.06
D bki 5K	Db 5K	2763–2785	57.30	19.30	14.60	1.30	3.27	n.a.	1.03	0.37	2.30	0.40	0.06	n.a.	n.a.
Malbork IG 1	Mb IG 1	3234–3261	61.49	15.36	7.11	1.49	2.38	n.a.	1.71	0.67	8.45	1.15	0.09	0.11	n.a.
arnowiec 7	Zn 7	2752–2775	73.40	13.70	6.43	0.64	1.57	n.a.	0.73	0.27	2.64	0.47	0.12	0.02	–

*i*C<sub>4</sub> – *i*C<sub>4</sub>H<sub>10</sub>; *n*C<sub>4</sub> – *n*C<sub>4</sub>H<sub>10</sub>; *i*C<sub>5</sub> – *i*C<sub>5</sub>H<sub>12</sub>; *n*C<sub>5</sub> – *n*C<sub>5</sub>H<sub>12</sub>; C<sub>6+</sub> = C<sub>6</sub>H<sub>14</sub> + C<sub>7</sub>H<sub>16</sub>; n.a. – not analysed

the B7-1/91 and Malbork IG 1 boreholes were collected to glass containers from gas and oil inflows. Sample depth intervals are given in Table 2.

## EXPERIMENTAL AND ANALYTICAL PROCEDURES

## HYDROUS PYROLYSIS

Hydrous pyrolysis (HP) experiments were conducted on 400 g of gravel-sized Upper Cambrian and Tremadocian shales. Samples were heated isothermally in the presence of liquid water in 1-L reactors made of *Hastelloy-C276* (Parr Instrument Company, Illinois, USA). It was calculated that 375 g of distilled/deionized water was sufficient to maintain liquid water in contact with the rock before, during, and after the experiments (Lewan, 1993). After loading and sealing of the reactor, the remaining headspace was evacuated and filled with helium. The reactor was then placed in an electric heater and brought to the desired experimental temperature within 65 minutes. Isothermal heating was conducted at time 72 h and temperature 330°C with standard errors less than ±0.5°C. This experimental condition for lignite (initially 0.34% *R*<sub>o</sub>) has been shown to be equivalent to a mean random vitrinite reflectance of 1.28% (Kotarba *et al.*, 2009). Cool-down times ranged from 18 to 24 h. At room temperatures, gas pressures and volumes were measured, and gases were collected in stainless-steel 304 dual-valve cylinders.

## ANALYTICAL PROCEDURE

Molecular compositions of the hydrous pyrolysis gases (C<sub>1</sub> to C<sub>6</sub> saturated and unsaturated hydrocarbons, H<sub>2</sub>S, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, He and Ar) were analysed by a set of columns on a *Hewlett Packard 6890* gas chromatograph configured by *Wasson Ece Instrumentation*. Mole percentages determined by this analysis were converted to moles with the ideal gas law and the recorded collection volumes, pressures, and temperatures. The results of analyses (Table 3) are given in mmoles/g TOC. He placed in the reactor as an internal standard is excluded from calculations. The generated gas analyses refer exclusively

to headspace gas and do not include gases dissolved in the water or oils generated by hydrous pyrolysis. Molecular compositions of natural gases were analysed with *Hewlett Packard 5890 Series II* and *Chrom 5* gas chromatographs equipped with flame ionization (FID) and thermal conductivity (TCD) detectors. The results of analyses are given in mole% and include the naturally occurring He (Table 2).

Stable isotope analyses were performed using *Finnigan Delta Plus* and *Micromass VG Optima* mass spectrometers. The stable carbon and hydrogen isotope data are presented in the δ notation relative to V-PDB and V-SMOW standards (Coplen, 1995; Hoeffs, 2007), respectively. Analytical precision is estimated to be ±0.2 and ±3‰, respectively. The stable isotope composition of hydrous pyrolysis and natural gases are presented in Tables 4 and 5, respectively.

Table 3

## Molecular composition (mmoles/g TOC)\* of gas generated by hydrous pyrolysis at 330°C for 72 h

Component	Sample code		
	B4-N1 comp.	B7-1 comp.	B6-2 comp.
Methane	0.2403	0.2396	0.1714
Ethane	0.1925	0.2175	0.1161
Ethene	0.0000	0.0005	0.0000
Propane	0.1736	0.1862	0.1165
Propene	0.0030	0.0028	0.0044
<i>n</i> -Butane	0.0618	0.0662	0.0489
<i>trans</i> -2-Butene	0.0015	0.0016	0.0020
<i>i</i> -Butene	0.0004	0.0005	0.0008
<i>i</i> -Butane	0.0149	0.0161	0.0130
<i>cis</i> -2-Butene	0.0013	0.0012	0.0016
<i>i</i> -Pentane	0.0081	0.0093	0.0080
<i>n</i> -Pentane	0.0161	0.0191	0.0156
<i>n</i> -Hexane	0.0034	0.0042	0.0038
<b>Total hydrocarbons</b>	<b>0.7168</b>	<b>0.7648</b>	<b>0.5023</b>

\* – acetylene, iso-butanenes, propadiene, neo-pentane, 1,3-butadiene, 3-methyl-1-butene, 2-methyl-2-butene, 1-pentene, neo-hexane, and benzene contents are less than 0.1 μmole/g TOC; other explanations as in Table 1

Table 4

## Molecular proportionality indices and stable isotope composition of hydrous pyrolysis gases (330°C and 72 h)

Sample code	Indices					Stable isotope [‰]			
	$\frac{CH_4}{C_2H_6}$	$\frac{C_2H_6}{C_3H_8}$	$\frac{C_3H_8}{C_4H_{10} +}$	$\frac{CH_4}{C_2H_6 + C_3H_8}$	$\frac{iC_4H_{10}}{nC_4H_{10}}$	$\delta^{13}C$ (CH <sub>4</sub> )	$\delta D$ (CH <sub>4</sub> )	$\delta^{13}C$ (C <sub>2</sub> H <sub>6</sub> )	$\delta^{13}C$ (C <sub>3</sub> H <sub>8</sub> )
B4-N1 comp.	1.25	1.11	1.66	0.66	0.24	-43.9	-328	-39.6	-34.5
B7-1 comp.	1.10	1.17	1.62	0.59	0.24	-42.4	-318	-39.3	-33.4
B6-2 comp.	1.48	0.99	1.30	0.74	0.27	-44.1	-322	-39.2	-35.1

Explanations as in Table 1;  $C_4H_{10+} = iC_4H_{10} + nC_4H_{10} + iC_5H_{12} + nC_5H_{12} + C_6H_{14} + C_7H_{16}$

Table 5

## Molecular proportionality indices and isotope composition of natural gases

Sample code	Indices					Stable isotope [‰]			
	$\frac{CH_4}{C_2H_6}$	$\frac{C_2H_6}{C_3H_8}$	$\frac{C_3H_8}{C_4H_{10} +}$	$\frac{CH_4}{C_2H_6 + C_3H_8}$	$\frac{iC_4H_{10}}{nC_4H_{10}}$	$^{13}C$ (CH <sub>4</sub> )	$\delta D$ (CH <sub>4</sub> )	$\delta^{13}C$ (C <sub>2</sub> H <sub>6</sub> )	$\delta^{13}C$ (C <sub>3</sub> H <sub>8</sub> )
B3-4	1.98	1.79	3.90	1.27	0.36	-50.9	-214	-42.3	-33.0
B3-9	1.79	1.47	3.28	1.07	0.45	-49.7	-260	-42.7	-34.2
B7-1(2)	11.53	2.93	6.94	8.60	0.37	-49.6	-232	-40.8	-30.0
B7-1(6)	2.02	1.22	3.38	1.11	0.33	-50.2	-230	-41.9	-32.8
Db 2	4.99	1.90	3.42	3.26	0.42	-48.1	n.a.	-39.0	n.a.
Db 5K	2.97	1.32	2.45	1.69	0.40	-47.1	-222	-38.0	-32.0
Mb IG 1	4.00	2.16	1.14	2.74	0.62	-47.4	-183	-36.2	n.a.
Zn 7	5.36	2.13	2.00	3.65	0.41	-47.1	-187	-38.0	n.a.

Explanations as in Table 4

Methane, ethane and propane were separated chromatographically for stable carbon isotope analyses. The gases were combusted separately over hot copper oxide (850°C) produced by the on-line system and then transmitted to a mass spectrometer. Water resulting from the combustion of methane for stable hydrogen isotope analyses was reduced to gaseous hydrogen with zinc (Florkowski, 1985).

The rock samples for Rock-Eval analyses were pulverized to the fraction less than 0.2 mm. Pyrolysis assay was conducted on *Delsi Model II* Rock-Eval instrument equipped with an organic carbon module, which determined total organic carbon (TOC).

## RESULTS AND DISCUSSION

The gaseous hydrocarbons generated at 330°C for 72 h by hydrous pyrolysis are shown in Table 3. The quantities of generated gaseous hydrocarbons range from 0.5 to 0.8 μmoles/g TOC and show no correlation to original concentration of TOC and hydrogen index (Table 1). These generated quantities do not represent maximum hydrocarbon yields, and higher experimental temperatures may reveal better correlations with the initial geochemical parameters. All the hydrous-pyrolysis gases generally have similar order of magnitude of molecular proportionalities ( $C_1/C_2$ ,  $C_2/C_3$ ,  $C_3/C_{4+}$ , and  $iC_4/nC_4$ ) as shown in Table 4, which may indicate that organic matter in the ana-

lysed rock samples contains the same Type-II kerogen of similar maturity.

Although the dryness of a gas, as measured here by the  $C_1/C_2$  ratio, is generally considered to increase with the thermal maturity of a source rock, Whiticar (1994) notes that this trend is typical of Type-I and -II kerogens. The greater dryness observed in natural gases relative to pyrolysis gases generated in the laboratory has been documented (Mango, 1992). Price and Schoell (1995) contend that such dryness discrepancy between natural and pyrolysis gases may be the result of the former being preferentially enriched in methane during secondary migration after expulsion from a source rock.

Although the proportionality of methane to ethane in natural gas is not simulated in the thermogenic gases generated by hydrous pyrolysis and in other pyrolysis methods (Mango, 1992; Price and Schoell, 1995), the distributions of ethane, propane and butanes in natural gases is similar to those known from thermogenic gases generated by hydrous pyrolysis. Another possible reason for higher  $C_1/C_2$  ratios in natural gases (Table 5) than in hydrous pyrolysis gases (Table 4) can be due to the presence of a small component of microbial methane in natural gases. The traditional plot of gas dryness ( $C_1/[C_2+C_3]$ ) versus  $\delta^{13}C$  of methane (Fig. 2) reveals that natural gases include thermogenic gas and varying mixtures of thermogenic and microbial gases. Typically, the  $C_2/C_3$  ratios for natural gases range from 1.5 to 5.0 (Nikonov, 1972). In the samples studied the  $C_2/C_3$  ratios for analysed hydrous pyrolysis vary

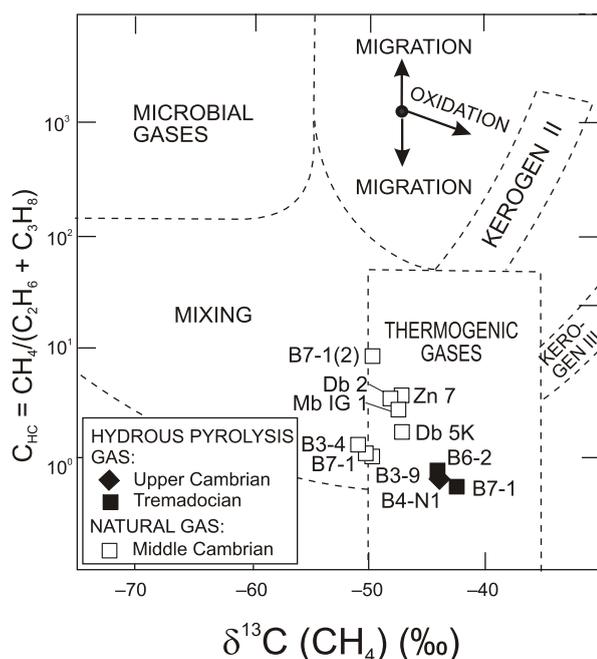


Fig. 2. Hydrocarbon index  $C_{HC}$  (i.e.,  $CH_4/[C_2H_6+C_3H_8]$ ) versus  $\delta^{13}C$  of methane for natural gases accumulated in the Middle Cambrian reservoir and for hydrolysis gases generated from kerogen of the Upper Cambrian–Tremadocian source rock succession at 330°C and 72 h

Compositional fields are from Whiticar (1994)

from 1.00 to 1.17 (Table 4) and those for natural gases from 1.22 to 2.93 (Table 5). The lower  $C_2/C_3$  ratios of both natural and pyrolysis gases may indicate that natural gases accumulated within Middle Cambrian sandstones were generated from organic matter of the Upper Cambrian–Tremadocian source rock succession. The  $iC_4H_{10}/nC_4H_{10}$  ratios of hydrolysis gases generated (from 0.24 to 0.27; Table 4) and natural gases analysed (from 0.33 to 0.62; Table 5) generally correspond to the prescribed trend of Oudin (1993) who predicted this ratio to be  $<1$  for thermogenic gases generated during the catagenesis. Therefore, with the exception of the proportionality of methane to other hydrocarbon gases, hydrolysis is a reasonable approach to simulating the natural generation of thermogenic gas. In particular, the geochemical characteristics of gas generated during hydrolysis (Figs. 2–5) serves as a model for a comparative diagram for thermogenic gases which have not undergone secondary processes during migration and accumulation, and mixing with microbial methane.

The  $\delta^{13}C$  values of hydrocarbon gases generated during hydrolysis are given in Table 4 and displayed in a reciprocal carbon number plot in Figure 3 together with the natural gas data. The simulation of thermogenic gas generation by hydrolysis from the Upper Cambrian–Tremadocian source rock succession shows that the stable carbon isotope composition increases in the methane-ethane-propane system (Fig. 3). In this system (Fig. 3), all the hydrocarbon gases generated show “dog-leg” trends, which are different from the more linear trends reported by Chung *et al.* (1988). An important implication of these experimental results is that a linear relationship of methane, ethane and propane carbon isotopes with their reciprocal carbon number is not an exclusive indicator of a natural

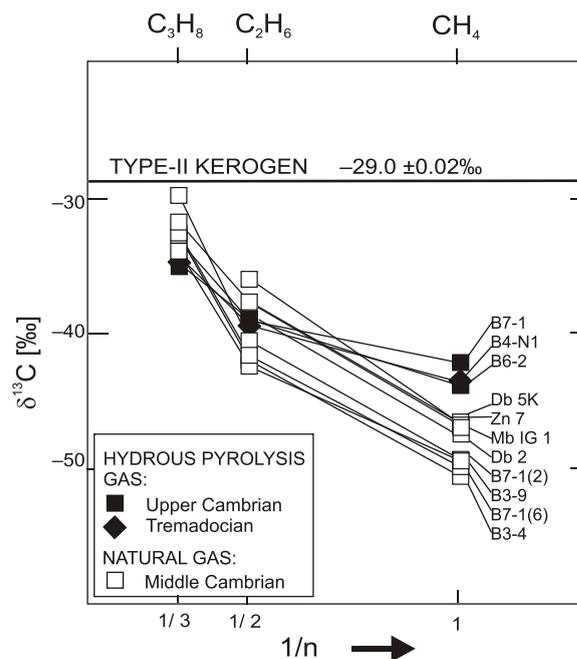
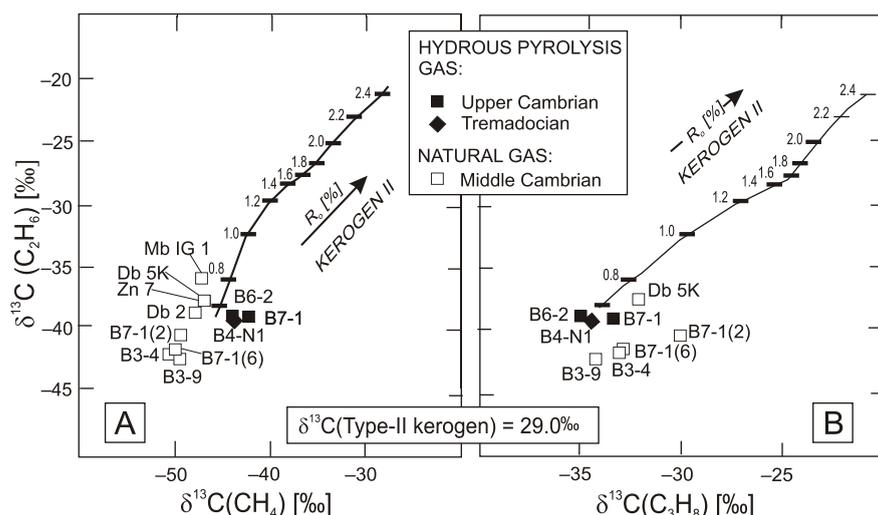


Fig. 3.  $\delta^{13}C$  of methane, ethane, and propane versus the reciprocal of their carbon number for natural gases accumulated in the Middle Cambrian reservoir with hydrolysis gases in gray at 330°C and 72 h for the rock sample analysed

Order according to Rooney *et al.* (1995)

gas from a single source as sometimes assumed by e.g., Chung *et al.* (1988) and Rooney *et al.* (1995). Zou *et al.* (2007) suggest that in this type of plot a “dog-leg” trend, exemplified by relatively  $^{13}C$ -depleted methane and enriched propane compared to ethane, results from the fact that natural gas might have not been generated from a single source rock or that it may have undergone post-generation alterations (e.g., secondary gas cracking, microbial oxidation, thermochemical sulphate reduction). However, a “dog-leg” trend for the thermogenic gases generated by hydrolysis experiments of the Upper Cambrian–Tremadocian source rock succession (Table 4 and Fig. 3) as well as of Oligocene Menilite Shales of the Polish Outer Carpathians (Kotarba *et al.*, 2009) allow one to propose a single source rock.

The Figure 4 shows plots of  $\delta^{13}C$  of ethane versus  $\delta^{13}C$  of methane and  $\delta^{13}C$  of propane along with the empirical maturity trend for Type-II kerogen proposed by Berner and Faber (1996). The later maturity trend takes into account the  $\delta^{13}C$  of the original kerogen from which gas was generated. The Type-II trend is based on the average  $\delta^{13}C$  value ( $-29.0 \pm 0.02\text{‰}$ ) of kerogen from the Upper Cambrian–Tremadocian source rock succession (Wi cław *et al.*, 2010a). The results of stable carbon isotope analyses of ethane and propane of natural gases accumulated in the Middle Cambrian sandstone reservoir (Table 5 and Fig. 4B) and their comparison with gas components generated by hydrolysis (Table 3 and Fig. 4B) suggest that these natural gases were generated during low-temperature thermogenic processes from Type-II kerogen of maturity 0.6–0.7% in the vitrinite reflectance scale contained in the Upper Cambrian–Tremadocian source rock succession.  $\delta^{13}C(C_2H_6)$  values deviate from the related trend (Fig. 4) which



**Fig. 4.**  $\delta^{13}\text{C}$  of ethane versus A –  $\delta^{13}\text{C}$  of methane and B –  $\delta^{13}\text{C}$  of propane for natural gases accumulated in the Middle Cambrian reservoir and for hydrolysis gases generated from kerogen of the Upper Cambrian–Tremadocian source rock succession at  $330^\circ\text{C}$  and 72 h

Vitrinite-reflectance trend line for Type-II kerogen is based on equation reported by Berner and Faber (1996)

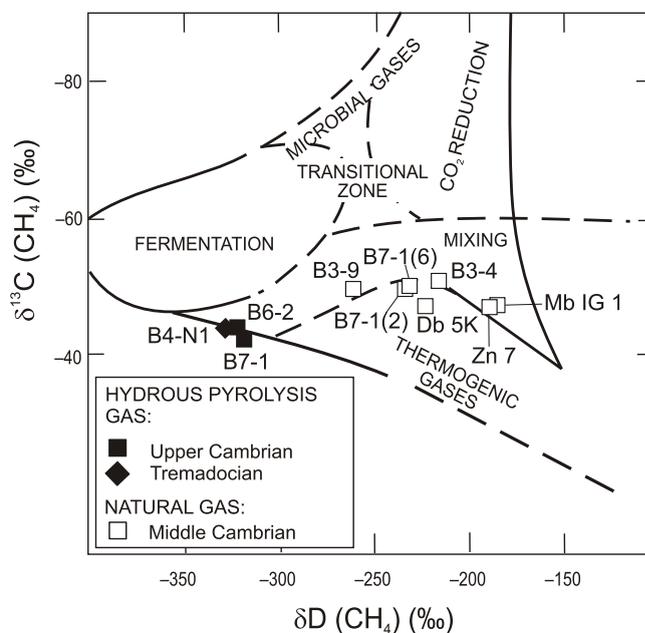
can be caused by the contribution of microbial ethane. Claypool (1999) documents that ethane can be also generated during microbial processes.

The discrepancy between the stable carbon isotope composition of the gases analysed (Fig. 4) and the isotopic curves of Berner and Faber (1996) can be explained in part by differences in the kinetics for recombination/condensation reactions responsible for vitrinite reflectance and the wide variation in kinetics for free radical cracking reactions responsible for petroleum generation (Lewan, 1985). On the other hand, this discrepancy can potentially provide evidence that the Berner-Faber plot is not valid for the HP gases.

The  $\delta\text{D}$  values of methane generated by hydrolysis vary from  $-328$  to  $-318$ ‰ (Table 4 and Fig. 5). As previously discussed by Kotarba and Lewan (2004) and Kotarba *et al.* (2009),  $^2\text{H}$ -depleted methane can be explained by the  $^2\text{H}$ -depleted distilled waters used in the hydrolysis experiments. The ability of water to be a source of hydrogen during the thermal cracking of hydrocarbons has been shown experimentally (Hoering, 1984; Lewan, 1997; Schimmelmann *et al.*, 1999, 2001) and has been advocated in natural methane generation (Smith *et al.*, 1982; Schoell, 1988). Therefore, unlike the importance of kerogen influencing the  $\delta^{13}\text{C}$  values for generated hydrocarbon gases,  $\delta\text{D}$  values of hydrocarbon gases can be influenced by the formation waters present in a source rock during their generation.

Stable carbon isotope analysis of methane from natural gas accumulated in the Middle Cambrian reservoirs (Table 5) compared with methane generated during hydrolysis indicates that a microbial component (Table 4 and Figs. 2–5) also exists. A insignificant component of microbial methane is present only in gases from the B3-4, B7-1 and B3-9 samples (Figs. 3 and 5). Concluding so far, the traps within the Middle Cambrian sandstone reservoirs had already been formed and sealed during migration of microbial methane which was generated from immature organic matter of the Upper Cam-

brian–Tremadocian succession. The thermogenic generation and expulsion processes were initiated in the Pridoli (latest Silurian) and lasted until the Carboniferous (Kosakowski *et al.*, 2010; Wróbel and Kosakowski, 2010). The fault system in the Baltic region has old Neoproterozoic roots and was activated in the Cambrian and Ordovician (Poprawa, 2006; Poprawa *et al.*, 2006). Therefore, microbial methane and ethane might have migrated from the Upper Cambrian–Tremadocian source rock



**Fig. 5.**  $\delta^{13}\text{C}$  versus  $\delta\text{D}$  of methane for natural gases accumulated in the Middle Cambrian reservoir and for hydrolysis gases generated from kerogen of the Upper Cambrian–Tremadocian source rock succession at  $330^\circ\text{C}$  and 72 h

Compositional fields are from Whiticar *et al.* (1986)

succession to the Middle Cambrian sandstone traps in the Late Cambrian to Early Ordovician interval. Isotopic data also suggest that thermogenic generation and expulsion processes themselves were of at least one-phase type, and that traps already containing microbial gases were supplied by new portions of thermogenic gaseous hydrocarbons as well as by condensate and oil.

## CONCLUSIONS

The trend between  $\delta^{13}\text{C}$ -values of methane, ethane and propane of gases generated by hydrous pyrolysis of a representative Upper Cambrian–Tremadocian source-rock succession containing Type-II kerogen and their reciprocal carbon number is not always linear, as prescribed by some investigators. Experimental determination of a “dog-leg” trend of the hydrous pyrolysis gases and how it changes during petroleum generation provides a correlation parameter that can help assess thermogenic gas end-members and microbial gas input in natural gases.

Isotopic characterization of natural hydrocarbon gases accumulated in the Middle Cambrian sandstone reservoir compared to hydrous pyrolysis gases in the Polish part of the Baltic region revealed that these natural gases were mainly generated by thermogenic processes from oil-prone Type-II kerogen contained in the Upper Cambrian–Tremadocian source rock succession. In the B3 offshore oil and gas field and in petroleum inflows to the B7-1/91 borehole an insignificant micro-

bial component was found. The traps within the Middle Cambrian sandstone reservoir had already been formed and sealed between the Late Cambrian and the Early Ordovician time span when migration of microbial methane took place along the fault system. The thermogenic generation and expulsion were at least one-phase processes. Subsequently, the gases have undergone migration and mixing. The traps already containing microbial gases were supplied by new portions of thermogenic gaseous hydrocarbons as well as by condensate and oil.

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