

## Habitat and hydrocarbon potential of the Mesozoic strata in the Kraków–Rzeszów area (SE Poland)

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The Mesozoic strata in the southeastern Poland were geochemically characterized to determine their hydrocarbon potential on the basis of 483 core samples from 36 boreholes. The Lower and Middle Triassic, Middle and Upper Jurassic, and Lower and Upper Cretaceous turned out to be highly variable. Middle Jurassic rocks represent the highest geochemical quality. Their total organic carbon (TOC) contents range between 0.0 and 17.0 wt.%, with a median of 0.89 wt.%. The highest TOC was observed in the rocks of the Tarnawa 1 borehole. In the remaining boreholes analysed the organic carbon contents were much lower and usually did not exceed 1 wt.%. Gas-prone Type-III kerogen with an admixture of Type-II kerogen is present in the study area. The lowest TOC values were observed in the Cretaceous rocks, where median values were 0.05 wt.% and 0.04 wt.% for Upper Cretaceous and Lower Cretaceous strata respectively. Low TOC contents were also observed in the Lower Triassic and Upper Jurassic strata. Accordingly, those horizons could not be regarded as effective source rocks. The petroleum potential of these stratigraphic horizons is additionally significantly reduced by low maturity, below the threshold for the generation of hydrocarbons. The Mesozoic organic matter was found to be generally immature, i.e. below 0.5% of vitrinite reflectance.

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Key words: Carpathian Foredeep substratum, Mesozoic strata, Middle Jurassic source rock, petroleum geochemistry, quality of source rocks.

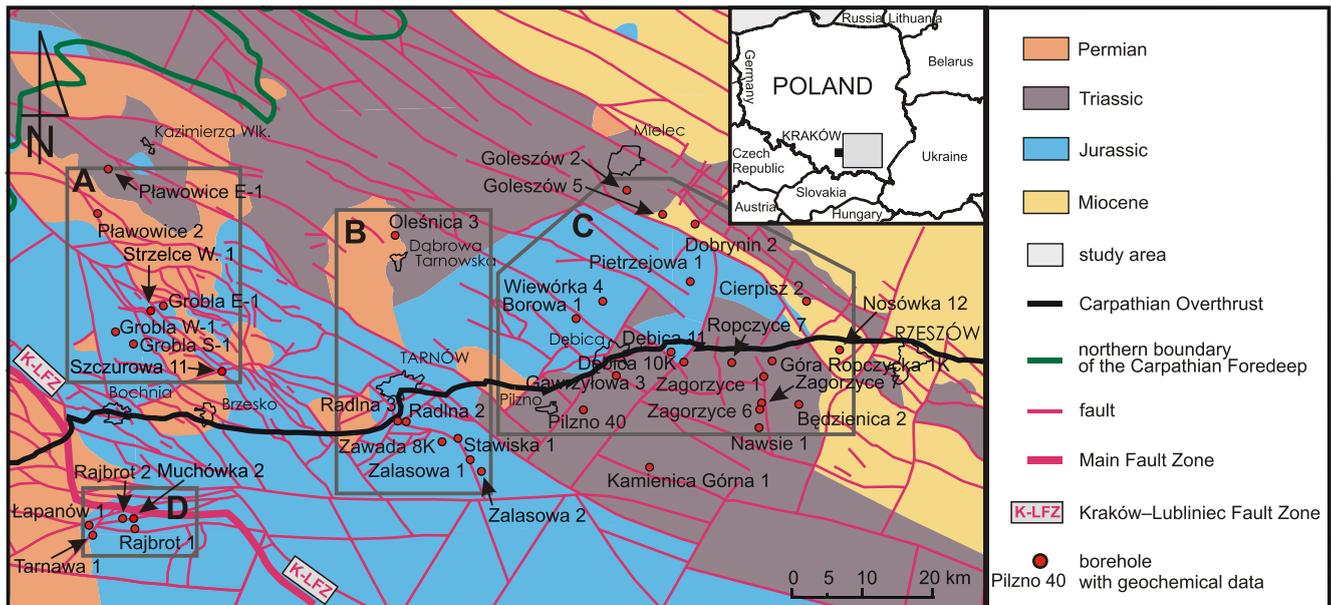
### INTRODUCTION

This study evaluates geochemical characteristics of organic matter (OM) in the Mesozoic stratigraphic succession in SE Poland related to the frontal part of the Carpathians, one of the oldest petroleum-producing regions in the world (Kotarba and Peryt, 2011), with a special emphasis on such factors as content of total organic carbon, genetic type of organic matter, its maturity and hydrocarbon potential. Lower and Middle Triassic, Middle and Upper Jurassic, and Cretaceous strata were the target of this investigation.

Petroleum studies performed so far in SE Poland have shown that, apart from the Carpathian flysch strata, only the Jurassic and Cretaceous strata have sufficient hydrocarbon potential to become an object of petroleum exploration (Moryc, 1992; Baran *et al.*, 1999; Darlak *et al.*, 2004; Gliniak and Urbaniec, 2005; Gliniak *et al.*, 2005, 2008; Kosakowski *et al.*, 2008, 2011; Kotarba *et al.*, 2011a). Discovered and documented hydrocarbon accumulations in the Upper Jurassic-Lower Cretaceous carbonates and Upper Cretaceous

sandstones, mainly connected with the upper part of these successions and usually situated close to regional dislocations, seem to confirm this thesis. The potential petroleum source rocks probably are Middle Jurassic strata in the basement and partly within the flysch strata of the Outer Carpathians. This hydrocarbon potential can be confirmed by geochemical analyses, quantitative analysis of OM content and degree of its transformation into hydrocarbons. Consequently, detailed analyses of the hydrocarbon generation process, indication of directions and range of their migration are necessary for evaluating the source potential of the Middle Jurassic strata in that part of Poland. By solving this issue the prospecting abilities in that area can be effectively increased.

A series of siliciclastic and carbonate rocks between Kraków and Rzeszów (Moryc, 1992, 2006; Buła and Habryn, 2008; Krajewski *et al.*, 2011) were evaluated geochemically based on 483 core and cuttings samples from 39 boreholes located in four zones: Bochnia–Kazimierza Wielka (A), Dąbrowa Tarnowska–Tarnów (B), Pilzno–Rzeszów–Mielec (C) and Tarnawa–Rajbrot (D) (Fig. 1) in the marginal area of the Silesian and Małopolska blocks.



**Fig. 1.** The occurrence of overburden rocks upon the top surface of the Carboniferous and older strata in the western part of the substratum of the Polish Carpathian Foredeep with location of sampled boreholes

Zones of organic matter characterization: **A** – Bochnia–Kazimierza Wielka, **B** – Dąbrowa Tarnowska–Tarnów, **C** – Pilzno–Rzeszów–Mielec, **D** – Tarnawa–Rajbrot

#### AN OUTLINE OF GEOLOGY AND STRATIGRAPHY OF MESOZOIC STRATA IN SE POLAND

The study area covers a part of the Neogene foredeep basin, i.e. the Carpathian Foredeep, and of the northern part of the Outer Carpathians. The natural northern boundary of the Carpathian Foredeep is the limit of the autochthonous Miocene marine sequence (Kotarba *et al.*, 2011b). The crystalline basement and the Paleozoic-Mesozoic sedimentary cover constitutes the substratum of the Carpathian Foredeep. This sedimentary cover occurs in two areas separated by a very distinct elevation (the Lower San Horst Structure; Buła and Habryn, 2011). This elevated structure influenced the palaeogeography, facies and thickness of strata. The study area is located to the west of the Lower San Horst Structure and extends from Kraków in the west to Rzeszów and Ropczyce in the east (Fig. 1). In the study area, the Precambrian and Paleozoic sequences form a regional unit called the Małopolska Block, representing a fragment of the epi-Variscan Central European Platform (Buła *et al.*, 2004; Mizerski and Stupka, 2005). The Paleozoic strata were subjected to multi-phase tectonic deformation and epigenetic erosion (Buła and Habryn, 2008). A characteristic feature is the presence of block structures built by Ediacaran metamorphic rocks surrounded by various Paleozoic rocks. Moreover, erosion resulted in the residual behavior of the substratum. The lower Paleozoic rocks occur in a few isolated patches located in the west of the city of Mielec and south of Tarnów–Rzeszów, and fill narrow troughs in the western part of the Małopolska Block (Buła and Habryn, 2011). Therefore, the thickness of the lower Paleozoic strata is small, usually less than 100 metres. The maximum thickness was observed in the Pilzno–Rzeszów–Mielec zone, where it exceeds 500 metres (Buła and Habryn, 2008). Smaller tectonic involvement, greater range and higher thickness

were observed for the lower Paleozoic complex. Devonian and lower Carboniferous strata cover almost the entire area west of the Lower San Horst Structure. Only locally, in the Dąbrowa Tarnowska–Tarnów zone and beneath the Carpathian Overthrust, south of Pilzno city, the upper Paleozoic strata have been eroded (Buła and Habryn, 2008). The total thickness of the Devonian and Carboniferous strata exceeds 2800 metres in the Słomniki 1 borehole.

The complicated tectonics of the Kraków–Rzeszów area resulted in the Permian-to-Mesozoic strata overlying various Precambrian and Paleozoic rocks (Buła and Habryn, 2011; Fig. 1). The Mesozoic cover is composed of three units: Triassic, Middle Jurassic to Lower Cretaceous and Upper Cretaceous. They reflect separate stages of sedimentary basin development and were deposited during successive transgressive cycles of the European epicontinental basin (Dayczak-Calikowska, 1997; Dayczak-Calikowska and Moryc, 1988; Feldman-Olszewska, 1997). The transgressive pulses were related to the Tethys Ocean (Dayczak-Calikowska, 1997; Dayczak-Calikowska and Moryc, 1988). Hiatuses in the sedimentary section of the Mesozoic cover, which occur in the Lower and Upper Triassic, Lower and partly Middle Jurassic, and Lower Cretaceous, are related to terrestrial conditions during these intervals (Moryc, 2006; Krajewski *et al.*, 2011). In the area investigated the Triassic deposits are patchy (Moryc, 2006; Buła and Habryn, 2008). The Buntsandstein is represented by variegated, sandy and argillaceous deposits and the Roethian and Muschelkalk are developed in carbonate facies. The total thickness of the Triassic strata is over a hundred metres. The overlying Middle Jurassic strata are represented by sandstone and clay-silty deposits with abundant plant detritus and with carbonate intercalations (Moryc, 2006). The total thickness of the Middle Jurassic deposits usually varies from a dozen to several dozen metres, and

Table 1

## Geochemical characteristics of the Mesozoic strata in the substratum of the Polish Carpathian Foredeep

Zone	Bochnia–Kazimierza Wlk.		Dąbrowa Tarnowska–Tarnów				
Stratigraphy	Upper Jurassic	Upper Cretaceous	Middle Triassic	Middle Jurassic	Upper Jurassic	Lower Cretaceous	Upper Cretaceous
Indices							
TOC [wt.%]	$\frac{0.00 \text{ to } 0.39}{0.14}$ (43/5)	$\frac{0.00 \text{ to } 0.28}{0.21}$ (11/2)	0.33	$\frac{0.00 \text{ to } 1.55}{0.18}$ (6/2)	$\frac{0.00 \text{ to } 0.55}{0.05}$ (48/6)	$\frac{0.02 \text{ to } 0.10}{0.06}$ (5/1)	$\frac{0.00 \text{ to } 0.46}{0.04}$ (4/1)
S <sub>1</sub> + S <sub>2</sub> [mg HC/g rock]	$\frac{0.23 \text{ to } 0.69}{0.37}$ (12/4)	n.d.	0.28	$\frac{0.47 \text{ to } 0.66}{0.58}$ (3/2)	$\frac{0.23 \text{ to } 1.63}{0.47}$ (14/2)	n.d.	0.61
BR [mg bit./g TOC]	$\frac{38 \text{ to } 100}{91}$ (5/3)	n.d.	67	$\frac{13 \text{ and } 76}{44}$ (2/2)	$\frac{25 \text{ to } 129}{59}$ (6/2)	n.d.	24
HI [mg HC/g TOC]	$\frac{77 \text{ to } 200}{119}$ (12/4)	n.d.	79	$\frac{27 \text{ to } 121}{36}$ (3/2)	$\frac{85 \text{ to } 342}{138}$ (14/2)	n.d.	117
T <sub>max</sub> [°C]	$\frac{420 \text{ to } 428}{431}$ (12/4)	n.d.	430	$\frac{424 \text{ to } 429}{427}$ (3/2)	$\frac{422 \text{ to } 433}{426}$ (14/2)	n.d.	425
R <sub>o</sub> [%]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Type of kerogen	III?	n.c.	n.c.	III/II	III/II	n.c.	III?
Maturity	immature	n.c.	n.c.	immature/ early mature?	immature/ early mature?	n.c.	immature
Petroleum potential	no source/poor	n.c.	n.c.	poor to fair	poor to fair	n.c.	poor

TOC – total organic carbon content; S<sub>1</sub> + S<sub>2</sub> – genetic potential of source rocks; BR – bitumen ratio; HI – hydrogen index; T<sub>max</sub> – temperature at maximum S<sub>2</sub> generation; R<sub>o</sub> – vitrinite reflectance; geochemical parameters and indices are given as minimum and maximum values (numerator) and median values (denominator); in parentheses: number of samples from boreholes (numerator) and number of sampled boreholes (denominator); n.d. – not determined; n.c. – not classified

only in a few boreholes does it exceed 100 metres (Krajewski *et al.*, 2011). The Upper Jurassic–Lower Cretaceous relatively continuous carbonate sequence (Oxfordian to Valanginian – Olszewska, 2004; Gutowski *et al.*, 2007; Matyja and Barski, 2007; Krajewski *et al.*, 2011) is characterized progressively greater thicknesses (Callovian–Oxfordian *ca.* 150–250 metres, Kimmeridgian *ca.* 400 metres, Tithonian *ca.* 500 metres). The Lower Cretaceous succession is *ca.* 130 metres thick. The Upper Cretaceous succession begins with Cenomanian glauconitic sandstones and ends with greenish and light grey marls with cherts that are Santonian–Maastrichtian in age (Moryc, 2006). The thickness of these deposits varies from several dozen up to a few hundred metres.

The sedimentary profile is completed by Miocene strata filling the Neogene basin of the Carpathian Foredeep (Oszczypko *et al.*, 2006). The thickness of Miocene cover is highly variable: 0 to 300 metres for the lower and middle Badenian, 0 to 1700 metres for the upper Badenian, and 0 to 2900 metres for the lower Sarmatian (Ney *et al.*, 1974). The total thickness of the Miocene strata in the Polish part of the Carpathian Foredeep ranges from few hundred metres in the northern basin to 3500 metres at their maximum in the south (Wielkie Oczy graben; Oszczypko *et al.*, 2006). Lying almost horizontally upon the older strata, the autochthonous Miocene strata of the Carpathian Foredeep have not been affected by orogenic movements. Fur-

ther to the south of the area analysed the thick Miocene strata give place to the Outer Carpathian flysch. The succession of the Carpathian nappes is also very thick, exceeding 7500 m in the southernmost part of the area studied (Kuźmina 1 borehole – 7541 m) and its impact on the increase in organic matter maturity is thus unquestionable.

## SAMPLES

Rock samples were collected from cores representing Triassic, Jurassic and Cretaceous strata. A total of 483 core samples, mainly of carbonates as well as claystones and siltstones from 36 boreholes, were collected and analysed (Fig. 1). The distribution of the core sample material, its quality and representativeness in the study zones was very uneven. In zone A (Bochnia–Kazimierza Wielka), 54 samples were taken from the Grobla E-1, Grobla S-1, Grobla W-1, Pławowice E-1 and 2, Strzelce Wielkie 1 and Szczurowa 11 boreholes (Fig. 1). Zone B (Dąbrowa Tarnowska–Tarnów) was represented by 64 core samples from the Radlna 2 and 3, Stawiska 1, Zalasowa 1 and 2, and Zawada 8K boreholes. Zone C (Pilzno–Rzeszów–Mielec) was best represented; a total of 307 rock samples were taken from the Będzienica 2, Borowa 1, Cierpisz 2, Dębica 10K and 11, Dobrynin 2, Gawrzyłowa 3,

Table 2

Geochemical characteristics of the Mesozoic strata in the substratum of the Polish Carpathian Foredeep

Zone	Pilzno–Rzeszów–Mielec					Tarnawa–Rajbrot				
	Lower Triassic	Middle Jurassic	Upper Jurassic	Lower Cretaceous	Upper Cretaceous	Lower Triassic	Middle Jurassic	Upper Jurassic	Upper Cretaceous	
Stratigraphy										
Indices										
TOC [wt.%]	$\frac{0.02 \text{ to } 0.36}{0.13} \frac{(6)}{(2)}$	$\frac{0.08 \text{ to } 3.83}{0.93} \frac{(55)}{(4)}$	$\frac{0.00 \text{ to } 1.25}{0.05} \frac{(217)}{(16)}$	$\frac{0.00 \text{ to } 2.15}{0.05} \frac{(22)}{(4)}$	$\frac{0.04 \text{ to } 0.19}{0.04} \frac{(6)}{(2)}$	$\frac{0.04 \text{ to } 2.30}{0.25} \frac{(13)}{(1)}$	$\frac{0.00 \text{ to } 14.9}{0.20} \frac{(29)}{(4)}$	$\frac{0.01 \text{ to } 0.09}{0.02} \frac{(11)}{(1)}$	$\frac{0.01 \text{ to } 0.04}{0.03} \frac{(5)}{(1)}$	
S <sub>1</sub> + S <sub>2</sub> [mg HC/g rock]	$\frac{0.10 \text{ to } 0.67}{0.16} \frac{(3)}{(1)}$	$\frac{0.14 \text{ to } 4.33}{0.86} \frac{(54)}{(4)}$	$\frac{0.06 \text{ to } 5.06}{0.41} \frac{(63)}{(12)}$	$\frac{0.20 \text{ to } 2.46}{1.33} \frac{(2)}{(2)}$	n.d.	$\frac{0.15 \text{ to } 6.27}{0.43} \frac{(8)}{(1)}$	$\frac{0.40 \text{ to } 53.4}{22.8} \frac{(15)}{(2)}$	n.d.	n.d.	
BR [mg bit./g TOC]	n.d.	$\frac{24 \text{ to } 104}{39} \frac{(24)}{(4)}$	$\frac{28 \text{ to } 110}{67} \frac{(19)}{(10)}$	n.d.	n.d.	n.d.	$\frac{50 \text{ to } 184}{117} \frac{(14)}{(2)}$	n.d.	n.d.	
HI [mg HC/g TOC]	$\frac{36 \text{ to } 186}{76} \frac{(6)}{(1)}$	$\frac{17 \text{ to } 661}{78} \frac{(54)}{(4)}$	$\frac{10 \text{ to } 425}{108} \frac{(62)}{(12)}$	$\frac{38 \text{ and } 109}{73} \frac{(2)}{(2)}$	n.d.	$\frac{56 \text{ to } 264}{120} \frac{(8)}{(1)}$	$\frac{121 \text{ to } 507}{274} \frac{(15)}{(2)}$	n.d.	n.d.	
T <sub>max</sub> [°C]	$\frac{431 \text{ and } 434}{433} \frac{(2)}{(1)}$	$\frac{430 \text{ to } 445}{438} \frac{(48)}{(4)}$	$\frac{421 \text{ to } 430}{426} \frac{(55)}{(11)}$	437	n.d.	$\frac{421 \text{ to } 432}{431} \frac{(8)}{(1)}$	$\frac{410 \text{ to } 430}{423} \frac{(15)}{(2)}$	n.d.	n.d.	
Type of kerogen	n.c.	III/II	III/II	III?	n.c.	n.c.	III/II	n.c.	n.c.	
Maturity	n.c.	immature/mature	immature/early mature	n.c.	n.c.	n.c.	immature/early mature	n.c.	n.c.	
Petroleum potential	n.c.	poor to excellent	poor to good	poor	poor	n.c.	poor to excellent	n.c.	n.c.	

Explanations as in Table 1

Golezów 2 and 5, Góra Ropczycka 1K, Kamienica Górna 1, Nawsie 1, Nosówka 12, Pietrzejowa 1, Pilzno 40, Ropczyce 7, Wiewiórka 4, Zagorzyce 6 and 7 boreholes (Fig. 1). The marginal zone D of the Silesian and Małopolska blocks is represented by 58 samples from the Łapanów 1, Muchówka 2, Rajbrot 1 and 2, and Tarnawa 1 boreholes (Fig. 1). The boundaries of the study zones were generally determined by the extent of the Middle Jurassic strata, the main potential source rock horizon (Fig. 2; Kotarba *et al.*, 2003; Krajewski *et al.*, 2011).

In the population analysed of samples in all the zones, Triassic and Cretaceous strata had the poorest representation. Samples from the Upper Jurassic strata prevailed in the Dąbrowa Tarnowska–Tarnów and Bochnia–Kazimierza Wielka zones (Table 1). Despite the preponderance of materials for analysis from Upper Jurassic strata, the samples from the Middle Jurassic rocks in the Pilzno–Rzeszów–Mielec zone constitute a large proportion, that predominate in the sample population in the marginal zone of the Silesian and Małopolska blocks (Table 2). Tables 1 and 2 show the ranges and average basic geochemical pa-

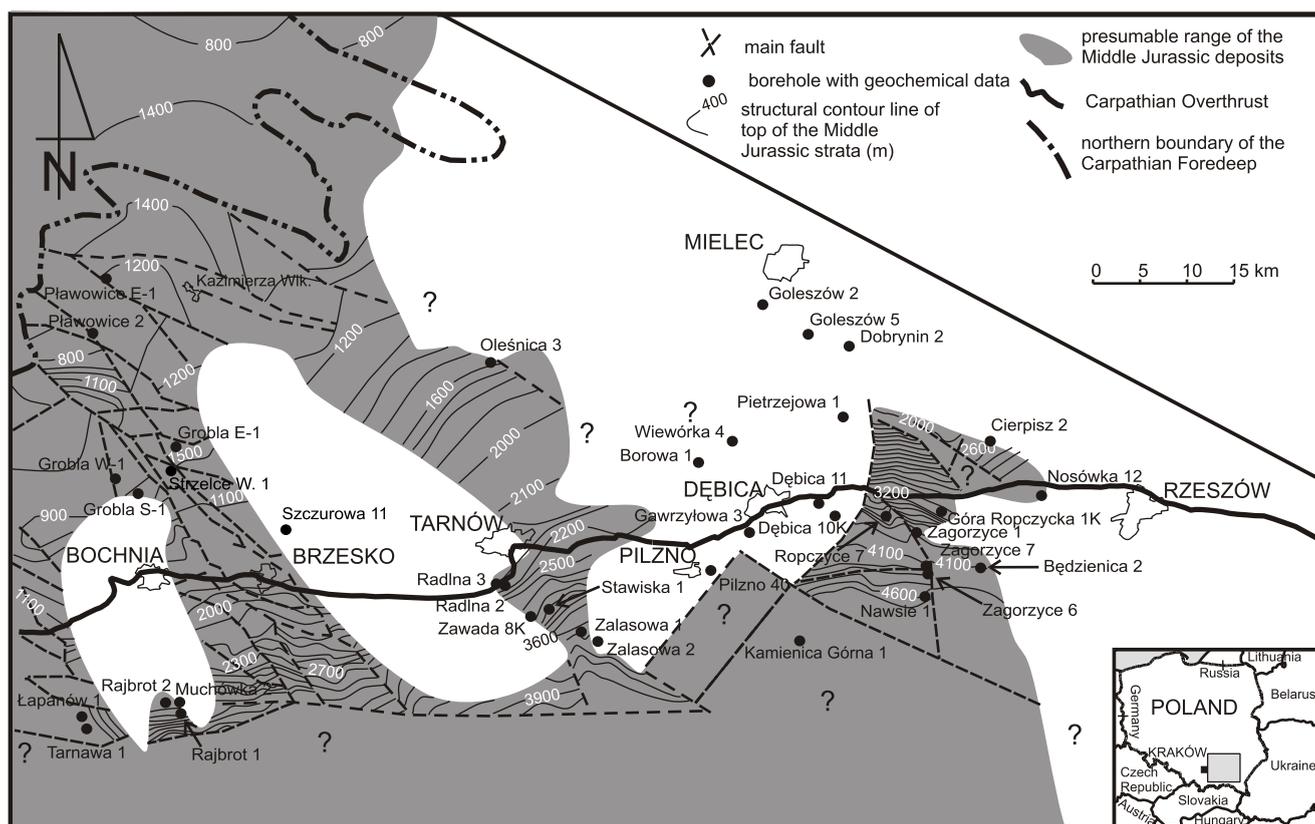


Fig. 2. Structural map of the top of the Middle Jurassic strata

rameters and indices for each stratigraphic horizon, together with the number of samples and boreholes.

## METHODS

Core samples were cleaned from mud contamination and crushed to 0.5–2 cm. 200 g samples were milled to below 0.2 mm diameter for geochemical analyses. Screening pyrolysis analyses of rock samples were carried on with a *Rock-Eval Model II* instrument equipped with an organic carbon module (Espitalié and Bordenave, 1993). Aliquots of the pulverised samples were extracted with dichloromethane:methanol (93:7 v/v) in a *SOXTEC*<sup>TM</sup> apparatus. The asphaltene fraction was precipitated with *n*-hexane. The remaining maltenes were then separated into compositional fractions of saturated hydrocarbons, aromatic hydrocarbons and resins by column chromatography, using alumina/silica gel (2:1 v/v) columns (0.8 × 25 cm). The fractions were eluted with *n*-hexane, toluene and toluene:methanol (1:1 v/v), respectively.

Stable carbon isotope analyses of the kerogen, bitumen and bitumen fractions were performed using a *Finnigan Delta Plus* mass spectrometer. Selected samples of kerogen were treated with hydrochloric acid prior to analysis. The stable carbon isotope data are shown in the  $\delta$ -notation relative to the V-PDB standard (Coplen, 1995), with an analytical precision estimated to be  $\pm 0.2\%$ .

Isolation of kerogen for elemental analysis was achieved by *SOXTEC*<sup>TM</sup> extraction of pulverised samples, decalcification of the solid residue with hydrochloric acid at room temperature, removal of silicates with concentrated hydrofluoric acid, removal of newly formed fluoride phases with hot concentrated HCl, heavy liquid separation (aqueous ZnBr<sub>2</sub> solution, density 2.1 g/ml), and repeated extraction with dichloromethane:methanol (93:7 v/v). Elemental analysis of isolated kerogen (C, H, N and S) was determined with a *Carlo Erba EA 1108* elemental analyser. The quantity of pyrite contaminating the kerogen was analysed as iron on a *Perkin-Elmer Plasma 40 ICP-AES* instrument after digesting the ash from burned kerogen (815°C, 30 min.) with hydrochloric acid. The organic sulphur content in kerogen was calculated as the difference between total and pyritic sulphur. The oxygen content was calculated as a difference to 100% taking into account C, H, N, S, moisture and ash contents.

The isolated saturated hydrocarbon fractions from the bitumens were diluted in isoctane and analysed by GC-MS for biomarker determination. The analysis was carried out with *Agilent 7890A* gas chromatograph equipped with *Agilent 7683B* automatic sampler, an *on-column* injection chamber and a fused silica capillary column (60 m × 0.25 mm i.d.) coated with 95% methyl/5% phenylsilicone phase (DB-5MS, 0.25  $\mu$ m film thickness). Helium was used as the carrier gas. The GC oven was programmed: 80°C held for 1 min, then increased to 120°C at the rate of 20°C/min, then increased further to 300°C

at the rate of 3°C/min and finally held for 35 min. The gas chromatograph was coupled with the 5975C mass selective detector (MSD). The MS was operated with an ion source temperature of 230°C, ionisation energy of 70 eV, and a cycle time of 1 sec in the mass range from 45 to 500 Daltons.

The aromatic hydrocarbon fractions were analysed by the GC-MS for phenanthrene, dibenzothiophene and their derivatives. The analysis was carried out using the same equipment as for the saturate hydrocarbon fraction. The GC oven was programmed from 40 to 300°C at the rate of 3°C/min. The MS was operated with a cycle time of 1 sec in the mass range from 40 to 600 Daltons.

Measurements of the mean random reflectance of vitrinite-like macerals ( $R_o$ ) were carried out with a *Zeiss-Opton* microphotometer at a wave-length of 546 nm, in oil. Sample preparation and point counts were carried out in accordance with the ICCP procedure (Taylor *et al.*, 1998).

## GEOCHEMICAL CHARACTERISTICS OF ORGANIC MATTER

Geochemical characterization of the Mesozoic strata between the cities of Kraków and Rzeszów (Fig. 1) was carried out for each of the sampled stratigraphic horizons of Triassic, Jurassic and Cretaceous in the four study zones. These zones reveal great diversity in quantity and quality of analytical materials, which has a significant impact on the credibility and accuracy of the performed characteristics and, therefore, they are discussed separately.

### BOCHNIA–KAZIMIERZA WIELKA ZONE

This zone is represented only by Upper Jurassic and Upper Cretaceous strata. All the geochemical characteristics are based on the results of analyses of 54 core samples from 7 boreholes (Table 1 and Fig. 1).

#### UPPER JURASSIC STRATA

Although having much better sample coverage, the TOC content in the Upper Jurassic strata turned out to be as low as in the Upper Cretaceous strata, and ranged from *ca.* 0 to 0.39 wt.%, with median 0.14 wt.% (Table 1). The highest TOC values concentrated in laminae and lenses of marly carbonates (Kotarba *et al.*, 2003). The hydrocarbons content ranges from *ca.* 0 to 0.69 mg HC/g of rock (Table 1). All samples had low hydrogen index (HI) values, and the median was equal to 119 mg HC/g TOC (Table 1 and Fig. 4A). The thermal maturity index  $T_{max}$  below 430°C indicates that the Upper Jurassic organic matter did not reach the threshold for thermogenic hydrocarbon generation (Table 1 and Fig. 4A). Therefore, it can be inferred that the Upper Jurassic strata do not meet the quantitative geochemical criteria of source rocks (Fig. 3A) and the geological prospects of these strata are restricted to the role of the reservoir rocks (Baran *et al.*, 1999; Darlak *et al.*, 2004; Gliniak *et al.*, 2004; Gliniak and Urbaniec, 2005).

### UPPER CRETACEOUS STRATA

The carbonate rocks of the Upper Cretaceous strata have very low total organic carbon (TOC) content, below 0.28 wt.% (Table 1). The hydrocarbon ( $S_1 + S_2$ ) content is below the sensitivity of the Rock-Eval apparatus. Though the strata were sampled only in two boreholes – Pławowice E-1 and 2 (11 core samples), it can be concluded that they did not fulfil the criteria of source rocks.

### DĄBROWA TARNOWSKA–TARNÓW ZONE

This zone is represented by a similar number of samples as the previous one. However, the samples represent a broader stratigraphic range, additionally the Lower Cretaceous and Middle Jurassic strata were included as well as one sample from the Middle Triassic (Table 1).

#### TRIASSIC STRATA

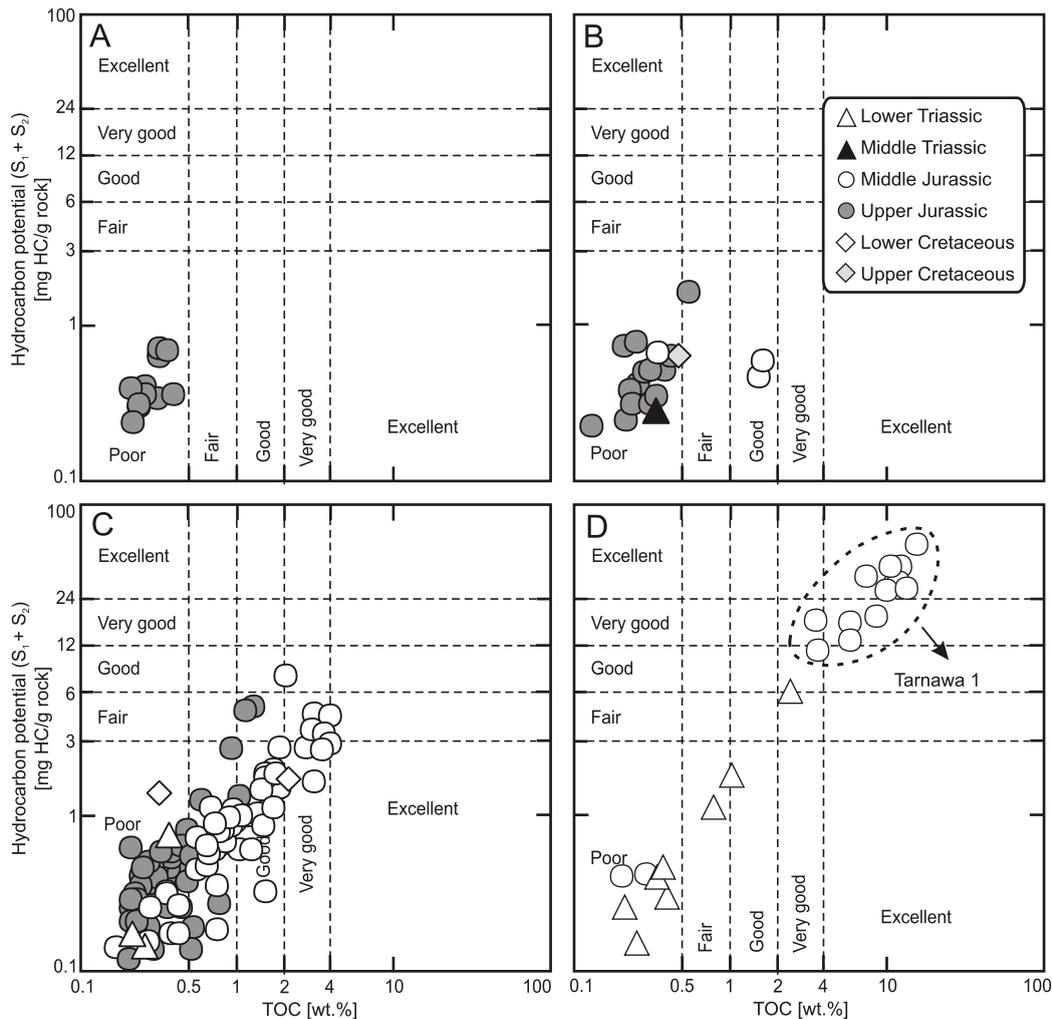
The Triassic strata are represented by one sample only. The TOC value is 0.33 wt.% and the content of hydrocarbons equals 0.28 mg HC/g rock (Table 1 and Fig. 3B). Because of this limited data, this stratigraphic horizon cannot be assessed from a petroleum potential point of view.

#### MIDDLE JURASSIC STRATA

The highest organic carbon contents in the Mesozoic profile of the study area were recorded in the Middle Jurassic strata. These strata were sampled only in the Zalasowa 1 (3 samples) and Oleśnica 3 (1 sample) boreholes (Fig. 1). Despite the large range of variation in the contents of TOC, ranging from 0 to 1.55 wt.%, the median value was only 0.18 wt.% (Table 1). Generally, low TOC values correspond to low contents of hydrocarbons, not more than 0.7 mg HC/g of rock (Table 1 and Fig. 3B). The hydrocarbon potential is also very low and reaches a maximum of 121 mg HC/g TOC. The low maturity, indicated by  $T_{max}$  below 430°C (Fig. 4B) reveals that the threshold for thermogenic transformation has not yet been reached. Consequently, these data show that the Middle Jurassic clastic rocks are generally lean and only locally may be considered as a source of thermogenic hydrocarbons (Fig. 3B; Kotarba *et al.*, 2003; Kotarba and Koltun, 2006).

#### UPPER JURASSIC STRATA

The most sampled Upper Jurassic strata demonstrate great variability of TOC and hydrocarbon contents. The variability of TOC content is similar to that in the previously described zone, ranging between *ca.* 0 and 0.55 wt.%, with a very low median 0.05 wt.% (Table 1). As with the TOC values, the residual hydrocarbon content is also low, generally less than 1 mg HC/g rock (Table 1 and Fig. 3B). Analogous to the Bochnia–Kazimierza Wielka zone, the Upper Jurassic strata, are reservoir rather than source rocks (Such, 1999; Gregosiewicz *et al.*, 2001; Kotarba and Koltun, 2006; Gliniak *et al.*, 2008).



**Fig. 3.** Petroleum source quality diagram for Mesozoic organic matter in (A) the Bochnia–Kazimierza Wielka zone, (B) the Dąbrowa Tarnowska–Tarnów zone, (C) the Pilzno–Rzeszów–Mielec zone and (D) the marginal zone of the Małopolska–Upper Silesian blocks – Tarnawa–Rajbrot zone

Classification after Hunt (1979), Peters and Cassa (2002)

#### CRETACEOUS STRATA

The geochemical characteristics of the Upper Cretaceous strata, based on the results of four analyses from the Radlna 2 borehole, does not differ from the characteristics of these strata in the adjacent Bochnia–Kazimierza Wielka zone (Figs. 1, 3B and Table 1). They also have a low content of organic carbon and an absence of hydrocarbons, except for one sample (Table 1). The Lower Cretaceous strata, sampled in the Radlna 3 borehole, also have low TOC content and hydrocarbons are absent (Table 1).

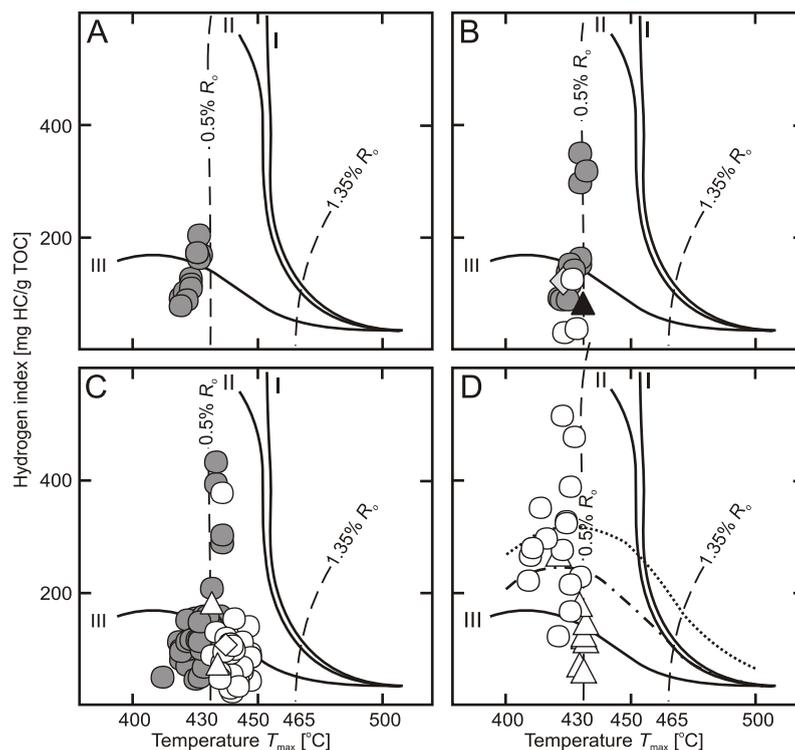
#### PILZNO–RZESZÓW–MIELEC ZONE

This zone was best represented with regard to the number of samples and the number of boreholes. The geochemical analyses were carried out for the Lower Triassic, Middle and

Upper Jurassic, Lower and Upper Cretaceous strata. In total results of geochemical analysis of 307 core samples taken from 19 boreholes were used (Table 2 and Fig. 1). The sample distribution, however, is uneven among these strata. In the Lower Triassic strata, only 6 samples were taken from 2 boreholes (Table 2). In the Lower Cretaceous strata 22 samples were taken, but only from 4 boreholes. A similar population of samples was collected in the Upper Cretaceous strata – 6 samples from 2 boreholes.

#### LOWER TRIASSIC STRATA

In the Lower Triassic strata, the TOC content is low. Measured TOC values range from 0.02 to 0.36 wt.%, with a median of 0.13 wt.% (Table 2) and the hydrocarbon ( $S_1 + S_2$ ) content ranges from 0.10 to 0.67 mg HC/g rock (Fig. 3C). The limited number of samples does not allow for direct assessment of the



**Fig. 4. Hydrogen index versus Rock-Eval  $T_{max}$  temperature for Mesozoic organic matter in (A) the Bochnia–Kazimierza Wielka zone, (B) the Dąbrowa Tarnowska–Tarnów zone, (C) the Pilzno–Rzeszów–Mielec zone and (D) the marginal zone of the Małopolska–Upper Silesian blocks – Tarnawa–Rajbrot zone**

Maturity paths of the main kerogen types after Espitalié *et al.* (1985); dashed-dotted line – boundary between kerogen types II and III (HI = 250) for transitional organic matter, and dotted line – boundary between kerogen types II and III (HI = 300) for coals; explanations as in Figure 3

source potential of this stratigraphic unit. However, these limited results (low TOC and hydrocarbon contents, low hydrocarbon potential, median of HI equal to 76 mg HC/g TOC), and some results from the adjacent zones suggest that the Lower Triassic strata in the Pilzno–Rzeszów–Mielec zone are poor gas-prone source rocks (Figs. 3C and 4C).

#### MIDDLE JURASSIC STRATA

In the Pilzno–Rzeszów–Mielec zone, the results of 55 samples from 4 boreholes located south of the Carpathian Overthrust range between Dębica and Rzeszów were used for the geochemical characterization of the source rocks (Table 2 and Figs. 1, 2) in the Middle Jurassic strata. Measured organic carbon content varies between 0.08 to 3.83 wt.%, with a median of 0.93 wt.% (Table 2). A similarly high variability is observed in the hydrocarbon content, from 0.14 up to 4.33 mg HC/g rock, predominantly below 1 mg HC/g rock (Table 2 and Fig. 3C). These values indicate that despite the relatively high organic carbon content, the hydrocarbon potential is generally low; local levels characterizing fair or good hydrocarbon potential were noted (Fig. 3C). This conclusion is supported by low hydrogen index values, usually below 100 mg HC/g TOC (Table 2 and Fig. 4C). The distribution of *n*-alkanes and isoprenoids and stable carbon isotope composition suggest

domination by terrestrial Type-III kerogen (Tables 3, 4 and Figs. 5, 6). This thesis is supported by strong domination  $C_{29}$  regular steranes over  $C_{27}$  steranes (Huang and Meinschein, 1979). Results of the elemental composition of kerogen of the single sample suggest the presence low-generative, reworked Type-IV kerogen (Table 6 and Fig. 7). The presence of mixed, Type-III/II kerogen indicated in these strata in previous publications (Kotarba *et al.*, 2003; Kosakowski *et al.*, 2008) was not detected here. The organic matter was deposited probably in anoxic conditions – the Pr/Ph ratio of the single sample is below 1.0 (Didyk *et al.*, 1978; Table 3). The thermal maturity of the organic matter has been determined only in the boreholes from the Rzeszów region. The  $T_{max}$  values (Table 2 and Fig. 4C), biomarker (Table 5 and Fig. 8) and aromatic hydrocarbon (Table 7) indices and  $R_o$  values (Table 8) indicate that the Middle Jurassic organic matter reached an early stage of thermogenic processes. The most mature levels, ranging from 0.75 to 0.8%  $R_o$ , were seen in the Zagorzyce 6 borehole profile (Table 8). Biomarker as well as aromatic hydrocarbon indices show that in the Nawisie 1 borehole profile (Tables 5, 7 and Fig. 8) organic matter also probably reaches a maturity of ca. 0.7%  $R_o$ .

In general, the Middle Jurassic strata in the Pilzno–Rzeszów–Mielec zone show good source rock properties, but with high variability in geochemical characteristics

Table 3

Indices calculated based on distribution of the *n*-alkanes and isoprenoids in bitumen extracted from the Jurassic strata in the Pilzno–Rzeszów–Mielec zone

Borehole	Borehole code	Depth [m]	Stratigraphy	CPI <sub>(17-31)</sub>	CPI <sub>(17-23)</sub>	CPI <sub>(25-31)</sub>	Pr/Ph	Pr/ <i>n</i> -C <sub>17</sub>	Ph/ <i>n</i> -C <sub>18</sub>
Góra Ropczycka 1K	GRp-1K	3205.4	Middle Jurassic	n.c.	n.c.	1.82	n.c.	n.c.	n.c.
Nawsie 1	Nw-1	4530.5	Middle Jurassic	1.07	1.03	1.20	n.c.	n.c.	0.61
Zagorzycze 6	Ze-6	4027.5	Middle Jurassic	n.c.	n.c.	1.08	n.c.	n.c.	n.c.
Zagorzycze 6	Ze-6	3984.5	Middle Jurassic	1.11	0.93	1.39	0.56	1.58	0.39
Borowa 1	Br-1	1569.5	Upper Jurassic	1.11	0.82	1.58	0.19	1.48	1.48
Dębica 10K	Dc-10K	2882.4	Upper Jurassic	1.00	0.76	1.54	0.70	1.30	0.61
Goleszów 5	Go-5	1148.3	Upper Jurassic	1.01	0.76	2.97	0.19	1.49	1.47
Goleszów 5	Go-5	1098.3	Upper Jurassic	1.15	0.92	1.83	0.21	0.95	0.98
Nawsie 1	Nw-1	3807.5	Upper Jurassic	n.c.	n.c.	1.39	n.c.	n.c.	n.c.
Pilzno 40	Pi-40	2963.5	Upper Jurassic	1.30	1.05	1.73	0.87	1.52	0.73

Pr – pristane; Ph – phytane; n.c. – not calculated due to partly evaporation of hydrocarbons;  $CPI_{(17-31)} = [(C_{17} + C_{19} + \dots + C_{27} + C_{29}) + (C_{19} + C_{21} + \dots + C_{29} + C_{31})] / [2 * (C_{18} + C_{20} + \dots + C_{28} + C_{30})]$ ;  $CPI_{(17-23)} = [(C_{17} + C_{19} + C_{21}) + (C_{19} + C_{21} + C_{23})] / [2 * (C_{18} + C_{20} + C_{22})]$ ;  $CPI_{(25-31)} = [(C_{25} + C_{27} + C_{29}) + (C_{27} + C_{29} + C_{31})] / [2 * (C_{26} + C_{28} + C_{30})]$

Table 4

Fractions and stable carbon isotope composition of bitumen, its individual fractions and kerogen of the Jurassic strata in the Pilzno–Rzeszów–Mielec zone

Borehole code	Depth [m]	Stratigraphy	Fractions [wt.%]				$\delta^{13}C$ [‰]					
			Sat.	Aro.	Res.	Asph.	Sat.	Bit.	Aro.	Res.	Asph.	Ker.
GRp-1K	3205.4	Middle Jurassic	3	9	19	69	-28.9	-25.0	-26.4	-25.6	-24.5	-23.8
Nw-1	4530.5	Middle Jurassic	2	18	21	59	-27.6	-24.2	-24.3	-24.4	-23.9	-23.3
Ze-6	4027.5	Middle Jurassic	6	12	19	63	-28.5	-26.1	-26.2	-26.6	-25.7	-24.4
Ze-6	3984.5	Middle Jurassic	2	14	19	65	-27.2	-24.4	-24.5	-24.9	-24.2	-22.9
Br-1	1569.5	Upper Jurassic	11	6	32	51	-27.0	-25.0	-25.1	-25.2	-24.5	-22.0
Dc-10K	2882.4	Upper Jurassic	19	6	32	43	-30.7	-28.6	-29.1	-28.6	-27.6	-26.7
Go-5	1148.3	Upper Jurassic	12	8	41	39	-28.8	-28.3	-29.0	-28.6	-27.6	-26.0
Go-5	1098.3	Upper Jurassic	9	2	43	46	-28.8	-28.2	-27.7	-28.3	-28.1	-26.5
Nw-1	3807.5	Upper Jurassic	14	17	36	33	-29.8	-28.4	-29.1	-28.3	-27.5	-27.3
Pi-40	2963.5	Upper Jurassic	15	12	33	40	-29.6	-28.9	-29.6	-28.7	-28.6	-27.3

Aro. – aromatic hydrocarbons, Asph. – asphaltenes, Bit. – bitumen, Ker. – kerogen, Res. – resins, Sat. – saturated hydrocarbons

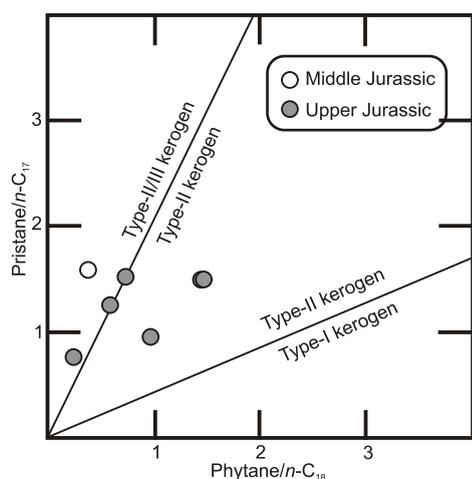


Fig. 5. Genetic characterization of bitumen from the Pilzno–Rzeszów–Mielec zone in terms of pristane/*n*-C<sub>17</sub> and phytane/*n*-C<sub>18</sub> according to the categories of Obermajer *et al.* (1999)

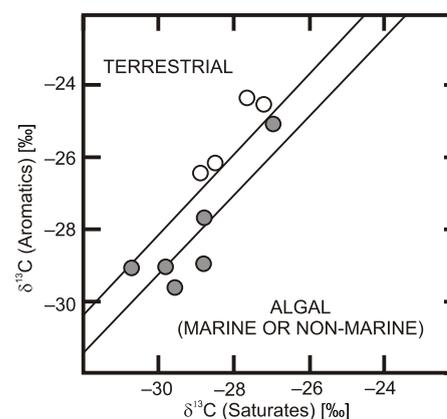


Fig. 6. Genetic characterization of bitumen from the Pilzno–Rzeszów–Mielec zone based on the stable carbon isotope composition of saturated and aromatic hydrocarbons

Genetic fields after Sofer (1984); explanations as in Figure 5

Table 5

## Selected biomarker characteristics of bitumen from the Jurassic strata in the Pilzno–Rzeszów–Mielec zone

Borehole code	Depth [m]	Stratigraphy	C <sub>27</sub>	C <sub>28</sub>	C <sub>29</sub>	C <sub>29</sub> /C <sub>27</sub> ster	Mor/Hop	H <sub>31</sub> S/(S+R)	H <sub>32</sub> S/(S+R)	C <sub>29</sub> SR	C <sub>29</sub>	C <sub>29</sub> Ts/C <sub>29</sub> H	Ts/Tm	Dia/Reg
GRp-1K	3205.4	Middle Jurassic	23	21	56	2.41	0.37	0.57	0.52	0.39	0.36	0.07	0.06	0.09
Nw-1	4530.5	Middle Jurassic	22	26	52	2.39	0.44	0.58	0.57	0.56	0.38	0.05	0.04	0.25
Ze-6	4027.5	Middle Jurassic	18	33	49	2.65	0.62	0.57	0.56	0.41	0.25	0.03	0.03	0.13
Ze-6	3984.5	Middle Jurassic	18	30	53	2.96	0.66	0.53	0.55	0.28	0.28	0.06	0.02	0.21
Br-1	1569.5	Upper Jurassic	38	17	45	1.17	0.45	0.22	0.21	0.27	0.11	0.02	0.12	0.04
Dc-10K	2882.4	Upper Jurassic	50	19	31	0.61	0.44	0.39	0.36	0.12	0.30	0.18	0.29	0.47
Go-5	1148.3	Upper Jurassic	44	18	38	0.88	0.63	0.25	0.45	0.10	0.29	0.43	0.31	0.11
Go-5	1098.3	Upper Jurassic	34	21	45	1.32	0.59	0.18	0.24	0.28	0.15	0.12	0.20	0.10
Nw-1	3807.5	Upper Jurassic	57	19	24	0.42	0.39	0.52	0.43	0.29	0.22	0.16	0.13	1.68
Pi-40	2963.5	Upper Jurassic	44	25	31	0.70	0.47	0.38	0.33	0.08	0.31	0.22	0.18	0.63

C<sub>27</sub> = C<sub>27</sub>ααα20R sterane/(C<sub>27</sub> + C<sub>28</sub> + C<sub>29</sub>)ααα20R steranes; C<sub>28</sub> = C<sub>28</sub>ααα20R sterane/(C<sub>27</sub> + C<sub>28</sub> + C<sub>29</sub>)ααα20R steranes; C<sub>29</sub> = C<sub>29</sub>ααα20R sterane/(C<sub>27</sub> + C<sub>28</sub> + C<sub>29</sub>)ααα20R steranes; C<sub>29</sub>/C<sub>27</sub>ster = ΣC<sub>29</sub> regular steranes/ΣC<sub>27</sub> regular steranes; Mor/Hop = moretane/17α hopane; H<sub>31</sub>S/(S+R) = homohopane 22S/(22S + 22R); H<sub>32</sub>S/(S+R) = bishomohopane 22S/(22S + 22R); C<sub>29</sub>SR = epimerisation of regular steranes C<sub>29</sub> ratio; C<sub>29</sub>ββ = ratio of ββ-epimeres of regular steranes C<sub>29</sub> to sum of ββ + αα steranes; C<sub>29</sub>Ts/C<sub>29</sub>H = C<sub>29</sub>18α norneohopane/C<sub>29</sub> norhopane; Ts/Tm = C<sub>27</sub>18α trisnorhopane/C<sub>27</sub>17α trisnorhopane; Dia/Reg = C<sub>27</sub>βα 20S diasterane/C<sub>29</sub>ααα 20R sterane

Table 6

## Elemental composition of kerogen from the Jurassic strata

Borehole code	Depth [m]	Stratigraphy	Elemental composition [daf, wt.%]					Atomic ratio			
			C	H	O	N	S	H/C	O/C	N/C	S/C
Nw-1	4530.5	Middle Jurassic	78.9	3.8	15.2	1.4	0.7	0.57	0.14	0.015	0.003
Nw-1	3807.5	Upper Jurassic	79.2	7.3	9.7	1.7	2.1	1.11	0.09	0.018	0.010

daf – dry, ash-free basis

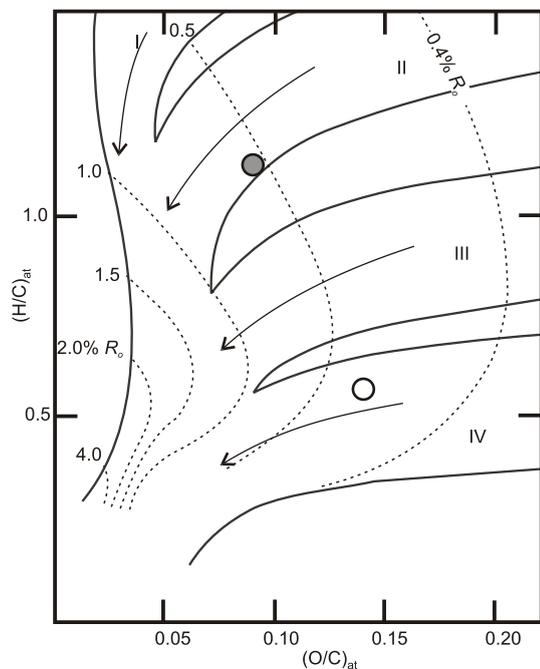


Fig. 7. Genetic characterization of Jurassic organic matter in the Polish part of the Carpathian Foredeep

Fields representing natural maturity paths for individual kerogens after Hunt (1996); explanations as in Figure 5

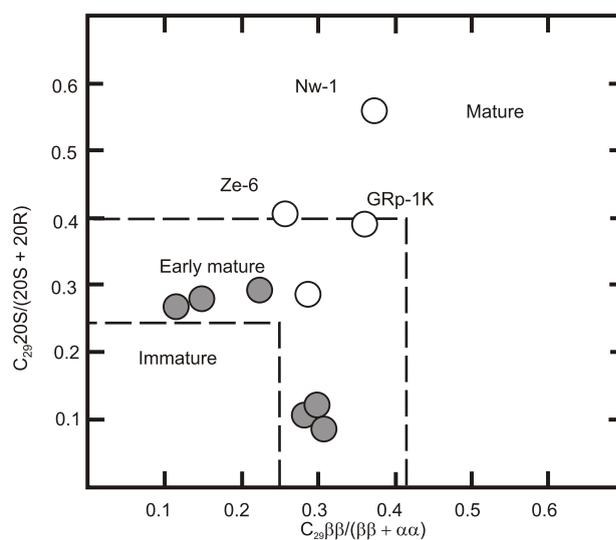


Fig. 8. Sterane C<sub>29</sub>20S/(20S + 20R) ratio versus C<sub>29</sub>ββ/(ββ + αα) ratio for Jurassic organic matter in the Polish part of the Carpathian Foredeep

Maturity fields after Peters and Moldowan (1993); explanations as in Figure 5

Table 7

**Maturity indices calculated based on distribution of phenanthrene and dibenzothiophene and their methyl derivatives in bitumen of the Jurassic strata in the Pilzno–Rzeszów–Mielec zone**

Borehole code	Depth [m]	Stratigraphy	MPI1	MPR	MPR1	$R_{cal}$ [%]	$R_{cal(MPR)}$ [%]	MDR	$R_{cal(DBT)}$ [%]	$T_{max(DBT)}$ [°C]
GRp-1K	3205.4	Middle Jurassic	0.56	0.63	0.33	0.70	0.57	1.3	0.6	430
Nw-1	4530.5	Middle Jurassic	0.58	0.70	0.40	0.72	0.73	2.4	0.7	435
Ze-6	4027.5	Middle Jurassic	0.62	0.68	0.41	0.74	0.75	1.0	0.6	428
Ze-6	3984.5	Middle Jurassic	0.43	0.43	0.32	0.63	0.55	1.2	0.6	429
Br-1	1569.5	Upper Jurassic	0.80	0.75	0.37	0.85	0.66	1.1	0.6	428
Dc-10K	2882.4	Upper Jurassic	0.39	0.54	0.35	0.61	0.63	0.6	0.6	426
Go-5	1148.3	Upper Jurassic	0.97	0.89	0.41	0.95	0.76	0.5	0.5	426
Go-5	1098.3	Upper Jurassic	0.53	0.88	0.44	0.69	0.83	1.6	0.6	431
Nw-1	3807.5	Upper Jurassic	0.60	0.63	0.37	0.73	0.67	0.8	0.6	427
Pi-40	2963.5	Upper Jurassic	0.38	0.41	0.28	0.60	0.46	0.6	0.6	426

MPI1 =  $1.5(2 - MP + 3 - MP)/(P + 1 - MP + 9 - MP)$ ; P – phenanthrene, MP – methylphenanthrene; MPR =  $2 - MP/1 - MP$ ; MPR1 =  $(2 - MP + 3 - MP)/(1 - MP + 9 - MP + 2 - MP + 3 - MP)$ ;  $R_{cal} = 0.60MPI1 + 0.37$  for MPR < 2.65 (Radke, 1988);  $R_{cal(MPR)} = -0.166 + 2.242(MPR1)$  (Kvalheim *et al.*, 1987); MDR =  $4 - MDR/1 - MDR$ ; MDR – methyl dibenzothiophene;  $R_{cal(DBT)} = 0.51 + 0.073MDR$ ;  $T_{max(DBT)} = 423 + 5.1MDR$  (Radke and Willsch, 1994)

Table 8

**The macerals composition and vitrinite reflectance of the Jurassic and Cretaceous strata in the Pilzno–Rzeszów–Mielec zone**

Borehole code	Depth [m]	Stratigraphy	Macerals [%]			OM [%]	$R_o$ [%]	Range	No. of meas.	$R_{o\ redep.}$ [%]
			V	L	I					
Be-2	4364.5	Middle Jurassic	5.5	15.0	2.0	22.5	0.66	0.55–0.77	125	1.00–1.40
Be-2	4592.5	Middle Jurassic	0.9	4.8	0.1	5.8	0.66	0.48–0.84	61	n.m.
Be-2	4594.5	Middle Jurassic	0.9	4.2	ab.	5.1	0.64	0.49–0.73	60	n.m.
GRp-1K	3205.4	Middle Jurassic	3.4	4.5	1.3	9.2	0.63	0.50–0.66	50	n.m.
GRp-1K	3212.7	Middle Jurassic	4.5	3.8	1.0	9.3	0.59	0.48–0.72	108	0.90–1.10
Ze-6	3983.5	Middle Jurassic	3.2	1.1	0.2	4.5	0.75	0.57–0.90	90	1.10–1.50
Ze-6	4027.3	Middle Jurassic	5.5	2.0	1.1	8.6	0.78	0.63–0.95	78	1.10–1.30
Dc-10K	2882.4	Upper Jurassic	tr.	ab.	ab.	tr.	n.m.	n.m.	n.d.	0.90–1.50
Nw-1	3807.5	Upper Jurassic	0.1	0.3	0.1	0.5	0.6	0.46–0.67	15	1.00–1.35
Nw-1	3867.5	Upper Jurassic	0.6	0.2	0.1	0.9	n.m.	n.m.	n.d.	1.00–1.32
Nw-1	4008.5	Upper Jurassic	0.1	0.1	0.1	0.3	0.69	0.63–0.79	12	0.98–1.16
Nw-1	4232.5	Upper Jurassic	0.1	0.3	0.1	0.5	n.m.	0.60–0.80	8	0.95–1.30
Ze-6	3579.6	Upper Jurassic	0.1	0.2	tr.	0.3	n.m.	0.41–0.44	11	1.20–1.32
Ze-6	3681.4	Upper Jurassic	tr.	0.1	ab.	0.1	n.m.	n.m.	n.d.	1.25–1.30
Ze-6	3800.7	Upper Jurassic	tr.	0.1	ab.	0.1	n.m.	0.44–0.49	10	1.00–1.10
Ze-6	2817.0	Lower Cretaceous	0.1	ab.	ab.	0.1	1.28	1.16–1.43	13	1.22–1.60

Be-2 – Będzienia 2 borehole; abbreviations of others boreholes see Table 3; V – vitrinite group; L – liptinite group; I – inertinite group; OM – organic matter;  $R_o$  – vitrinite reflectance; meas. – measurements;  $R_{o\ redep.}$  – vitrinite reflectance of redeposited organic matter; ab. – absent; n.d. – no data; n.m. – not measured; tr. – traces

(Fig. 3C). The majority of the Jurassic section has a low hydrocarbon potential, but locally this potential is excellent. The thermal maturity of the organic matter is sufficient for generating hydrocarbons (Figs. 4C and 8). In the zone analysed from the Mesozoic profile, the Middle Jurassic strata are the main gas-prone source rock.

#### UPPER JURASSIC STRATA

Most samples of the Upper Jurassic strata do not differ in their geochemical characteristics from the adjacent zones. Measured TOC values in the 217 core samples from 16 bore-

holes vary across a relatively wide range, from 0 to 1.25 wt.% (Table 2 and Figs. 1, 3C). However, as in other zones, the organic carbon content is very low, with median of 0.05 wt.% (Table 2). The hydrocarbon content is highly variable and ranges from values close to zero up to 5.1 mg HC/g rock (Table 2 and Fig. 3C). Higher contents of TOC and hydrocarbons observed in the Dobrynin 2, Nawsie 1 boreholes and partly in the Pilzno 40 borehole (Table 2 and Fig. 1), may be associated with intercalations of either OM-rich clays, or may be the result of stratigraphic misidentification of the Mesozoic profile. The median of hydrocarbon potential (HI index) does not exceed 110 mg HC/g TOC, but individual values reach up to

425 mg HC/g TOC (Table 2). This diversity is probably a result of genetic diversity in the types of deposited organic matter. Correlation between the hydrogen index HI and  $T_{\max}$  temperature (Fig. 4C), results of biomarker distribution (Tables 3, 5 and Fig. 5), isotopic composition (Table 4 and Fig. 6) and kerogen elemental composition (Table 6 and Fig. 7) show the presence of both gas-prone Type-III and oil-prone Type-II kerogens with a domination by the latter. According to the *n*-alkane and isoprenoid distribution, organic matter generally was deposited in anoxic conditions (Pr/Ph <1; Table 3). The Upper Jurassic organic matter is generally immature or at most early mature, i.e.  $T_{\max}$  temperature is below 430°C and vitrinite reflectance ( $R_o$ ) below 0.7% (Tables 2 and 8, Fig. 4C). Also, indices calculated based on biomarker and aromatic hydrocarbon distribution (Tables 5, 7 and Fig. 8) show a low maturity of the strata investigated. Maturity indices of samples Br-1/1569.5 and Go-5/1148.3 calculated based on methylphenanthrenes distribution (Table 7) suggesting their increased maturity (middle phase of the oil window) are probably overstated because these used are dedicated for terrigenous Type-II OM (Radke, 1988), whereas in the Upper Jurassic carbonates oil-prone Type-II kerogen dominates. Only in the eastern part of the zone, near the Nawsie 1 and Zagorzyce 1 boreholes, maturity increases slightly and reaches the early mature stage (Figs. 4C and 8). Results of geochemical analyses of the Upper Jurassic rocks confirm poor source rock characteristics in the zone studied, but the presence of hydrocarbons in these strata indicates their good reservoir properties (Gliniak *et al.*, 2005).

#### CRETACEOUS STRATA

Geochemical analyses confirm that the Cretaceous strata have geochemical characteristics similar to those in the zones discussed above (Fig. 3C). In the Upper Cretaceous strata, TOC content ranges from *ca.* 0.04 up to 0.19 wt.%, with a median of 0.04 wt.%, while in the Lower Cretaceous rocks it reaches as much as 2.15 wt.%, though the median for both these stratigraphic horizons is very similar (Table 2). The highest TOC values here were observed in a single sample from the Kamienica Górna 1 borehole (Figs. 1 and 3C). Such high TOC values may result from the presence of clay laminae in carbonate rocks, erroneous stratigraphy, or some error during sampling for geochemical analysis.

#### TARNAWA–RAJBROT ZONE

The Tarnawa–Rajbrot zone is located in the marginal parts of the Małopolska and Silesian blocks. In this zone, Lower Triassic, Middle and Upper Jurassic, and Upper Cretaceous strata were geochemically characterized. The characteristics of the individual stratigraphic divisions correspond to their trends in the remaining areas. The Middle Jurassic and Upper Cretaceous strata, as in the adjacent zones, contain a small amount of organic carbon and hydrocarbons, close to zero (Table 2 and Fig. 3D). They do not exhibit characteristics of good source rocks (Kotarba *et al.*, 2001). Only in the Tarnawa 1 borehole the Middle Jurassic strata present high organic carbon and hydrocarbon contents, up to 14.9 wt.% and 53.4 mg HC/g TOC, respectively. Slightly higher contents of TOC and hydrocarbons are observed in the Lower Triassic strata, but they are not considered to be representative because the samples were collected only from one borehole – Tarnawa 1 (Fig. 1).

The median of TOC is low – 0.25 wt.%, but a maximum content is as high as 2.3 wt.% (Table 2). Also, the hydrocarbon content ( $S_1 + S_2$ ) is variable and can reach the maximum value of 6.27 mg HC/g rock (Table 2 and Fig. 3D). The amount of hydrocarbon potential HI is low, with the median equal to 120 mg HC/g TOC (Table 2). The genetic type of organic matter was determined based on Rock-Eval pyrolysis that indicated gas-prone Type-III kerogen (Fig. 4D). In general, the potential of the Lower Triassic rocks is low (Fig. 3D), and they can only locally constitute a source of hydrocarbons (Kotarba *et al.*, 2001). The Middle Jurassic strata have definitely the best source rock parameters. Although the values of individual geochemical parameters and indices vary considerably, the medians are relatively high (Table 2 and Fig. 3D). Most of the increased organic carbon content values were measured in samples collected from lenses of lignites. These samples also have very high hydrocarbon contents, up to 53.4 mg HC/g rock (Table 2 and Fig. 3D). In the other sampled boreholes – Łapanów 1, Rajbrot 1 and 2 (Fig. 1), the Middle Jurassic rocks are lean in organic carbon, close to 0. The results of Rock-Eval pyrolysis, biomarker distributions and stable carbon isotope compositions (Kotarba *et al.*, 2001) indicate that mixed Type-III/II kerogen dominates. The Middle Jurassic strata are immature or at an early stage of the “oil window” (Table 2 and Fig. 4D).

#### CONCLUSIONS

The geochemical analysis of the Mesozoic profile in the southeastern part of Poland, in four separate zones between the cities of Kraków and Rzeszów, reveals their generally low source-rock potential for hydrocarbons. The Triassic, Upper Jurassic and Cretaceous strata have generally very low TOC and hydrocarbon ( $S_1 + S_2$ ) contents. Only in the eastern part of the area, near Rzeszów, was an increase in their contents observed. This particularly relates to the Upper Jurassic carbonates, in which the TOC content reaches 1.25 wt.% and hydrocarbons up to 5.1 mg HC/g rock. Good, and sometimes even very good source quality is observed in interbeds containing oil-prone Type-II kerogen, occurring within the generally poor carbonate strata. Under such circumstances, these interbeds can be local source rocks. However, the low maturity of dispersed organic matter limits their source potential.

The Middle Jurassic strata represent a stratigraphic horizon with the best geochemical characteristics for source rocks. These strata were found in the entire study area, but they do not form a continuous strata cover. In the three zones: Dąbrowa Tarnowska–Tarnów, Pilzno–Rzeszów–Mielec and Tarnawa–Rajbrot, the Middle Jurassic source rocks have both the highest organic carbon contents and hydrocarbon potential ( $S_1 + S_2$ ). The TOC content and hydrocarbon potential in the first zone ranges from 0 to 1.55 wt.% (median value 0.18 wt.%) and 0.47 to 0.66 mg HC/g rock (median value 0.58 mg HC/g rock), respectively, in the Pilzno–Rzeszów–Mielec zone from 0 to 3.83 wt.% (median value 0.93 wt.%) and from 0.14 to 4.33 mg HC/g rock (median value 0.86 mg HC/g rock), and in Tarnawa–Rajbrot from 0 to 14.9 wt.% (median value 0.20 wt.%) and 0.40 to 53.4 mg HC/g rock (median value 22.8 mg HC/g rock), respectively. Their hydrocarbon potential is variable, but the maximum values indicate the presence of excellent source rock intercalations. Such intercalations of exquisite qualities were most likely a source of hydrocarbons in

the discovered and documented accumulations in the Mesozoic strata, especially in Upper Jurassic-Lower Cretaceous carbonates and Upper Cretaceous sandstones.

Organic matter in the Middle Jurassic strata is of mixed type, dominated by gas-prone Type-III kerogen. Rock-Eval  $T_{max}$  temperature values indicate that organic matter is immature, or mature in the early phase of the low-temperature thermogenic process (“oil window”). The maturity of kerogen increases towards and beneath the Outer Carpathians.

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