## Assessment of hydrocarbon potential of Jurassic and Cretaceous source rocks in the Tarnogród–Stryi area (SE Poland and W Ukraine)

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(Manuscript received November 22, 2011; accepted in revised form March 13, 2012)

**Abstract:** The Jurassic/Cretaceous stratigraphic complex forming a part of the sedimentary cover of both the eastern Małopolska Block and the adjacent Łysogóry-Radom Block in the Polish part as well as the Rava Rus'ka and the Kokhanivka Zones in the Ukrainian part of the basement of the Carpathian Foredeep were studied with geochemical methods in order to evaluate the possibility of hydrocarbon generation. In the Polish part of the study area, the Mesozoic strata were characterized on the basis of the analytical results of 121 core samples derived from 11 wells. The samples originated mostly from the Middle Jurassic and partly from the Lower/Upper Cretaceous strata. In the Ukrainian part of the study area the Mesozoic sequence was characterized by 348 core samples collected from 26 wells. The obtained geochemical results indicate that in both the south-eastern part of Poland and the western part of Ukraine the studied Jurassic/Cretaceous sedimentary complex reveals generally low hydrocarbon source-rock potential. The most favourable geochemical parameters: TOC up to 26 wt. % and genetic potential up to 39 mg/g of rock, were found in the Middle Jurassic strata. However, these high values are contradicted by the low hydrocarbon index (HI), usually below 100 mg HC/g TOC. Organic matter from the Middle Jurassic strata is of mixed type, dominated by gas-prone, Type III kerogen. In the Polish part of the study area, organic matter dispersed in these strata is generally immature ( $T_{max}$  below 435 °C) whereas in the Ukrainian part maturity is sufficient for hydrocarbon generation.

Key words: Jurassic, Cretaceous, Poland, Ukraine, petroleum geochemistry, source rock characteristics.

#### Introduction

The Jurassic/Cretaceous stratigraphic complex forming a part of the sedimentary cover of the eastern Małopolska Block and the adjacent Łysogóry-Radom Block (SE Poland) were studied with geochemical methods in order to evaluate the possibility of hydrocarbon generation. Both the blocks extend southeast, towards the territory of Ukraine, where these are named the Rava Rus'ka and the Kokhanivka Zones, respectively (Buła & Habryn 2011). In both areas the Jurassic/Cretaceous complex vary in the degree of geological and geochemical recognition. In the Polish part the complex is well-recognized geologically but geochemical and petrophysical data are insufficient (Kotarba et al. 2003; Kotarba 2004; Moryc 2004; Buła & Habryn 2008, 2011; Kosakowski et al. 2012a). In the Ukraine its geological and petrophysical recognitions are poor and geochemical data do not exist (e.g. Dulub et al. 2003; Gutowski et al. 2005; Krajewski et al. 2011; Kurovets et al. 2011). The available analytical results originate mostly from Middle Jurassic strata and partly from Upper Jurassic and Lower Cretaceous rocks. The population of samples collected from Mesozoic strata in the Ukrainian part of the Carpathian Foredeep is more numerous and the core samples represent all the stratigraphic units involved.

Geochemical characterization of organic matter in the analysed, Jurassic/Cretaceous complex from the Polish and

Ukrainian part of the Carpathian Foredeep includes: organic carbon content (TOC), petroleum potential, genetic type of kerogen and its maturity.

# Outline of geology and stratigraphy of the Mesozoic strata

The study area is located in the border part of the Polish and Ukrainian segments of the Carpathian Foredeep and covers an area between Tarnogród and Lubaczów towns in Poland, and Stryi town in Ukraine (Fig. 1). The geology of this part of the Carpathian Foredeep was extensively discussed e.g. by Oszczypko et al. (2006), Buła & Habryn (2011) and Krajewski et al. (2011).

In the study area several structural complexes were distinguished. The lower structural complex, which forms an uncontinuous cover of the older basement of the foredeep is composed of incomplete, Ordovician and Silurian successions (Figs. 2, 3). This succession fills tectonic troughs cutting the crystalline basement (Buła & Habryn 2008, 2011). The next structural complex is formed of Jurassic and Cretaceous strata. These strata constitute a fragment of a larger basin, which extends to the Polish-Ukrainian state border and which is a continuation of the Carpathian Foredeep outer zone (Figs. 2, 3; Kisłow 1966). The total thickness of Juras-



Fig. 1. Sketch map of the study area with location of sampled wells.

sic strata in the Polish part of this basin may reach up to 800 m and that of the Cretaceous sequence may be up to 600 m (Kowalska et al. 2000). In the Ukrainian part of the basin higher thicknesses are observed: the Jurassic succession has over 2000 m and the Cretaceous one over 600 m. The youngest Neogene complex fills the Carpathian Foredeep and is entirely composed of marine Miocene sediments up to 3400 m thick in the Polish part (e.g. in the tectonic trough south of Lubaczów) and over 5000 m thick in the Ukrainian part (Krukenychy Depression) (Obuchowicz 1963; Kurovets et al. 2004).

#### Samples

Samples used for geochemical characterization are very diverse in terms of quality and stratigraphic units. Moreover, there is also a significant difference in number of samples collected in Polish and Ukrainian parts of the study area.

A total of 469 core samples of Jurassic and Cretaceous rocks were collected from 37 wells and analysed. Considering the stratigraphic provenance, 31 samples from 5 wells originated from Lower Jurassic sediments in the Ukrainian part of the study area (Table 1, Fig. 1). 202 core samples were taken from 20 wells drilled into the Middle Jurassic horizon. The Upper Jurassic horizon was sampled in 2 wells in the Polish part and in 22 wells in the Ukrainian part of the study area (Fig. 1) supplying a total of 214 core samples. The Lower Cretaceous sediments were sampled only in the Tymce 1 (3 samples), Didushychi 2 (2 samples) and Pivnichno Girs'ke 1 (2 samples) wells (Fig. 1). The Upper Cretaceous strata were also insufficiently sampled, only in the Ukrainian part of the study area, namely from the Didushychi 2 (5 samples), Petrovetska 3 (1 sample), Pivnichno Girs'ke 1 (6 samples) and Verchany 1 (3 samples) wells (Fig. 1).

Table 1 shows the ranges and mean values of basic geochemical parameters and indicators for each stratigraphic complex together with the number of samples and wells in both the Polish and Ukrainian parts of the study area.

#### **Methods**

The pyrolysis was completed with the Delsi Model II Rock-Eval instrument, equipped with an organic carbon module (for analytical details see Espitalié et al. 1985;

Part		Polish			Uk	rainian		
Stratigraphy Indices	Middle Jurassic	Upper Jurassic	Lower Cretaceous	Lower Jurassic	Middle Jurassic	Upper Jurassic	Lower Cretaceous	Upper Cretaceous
TOC (wt. %)	$\frac{0.05 \text{ to } 25.9}{1.50} \frac{(102)}{(9)}$	$\frac{0.00 \text{ to } 0.46}{0.07} \frac{(16)}{(2)}$	$\frac{0.40 \text{ to } 2.03}{0.46} \frac{(3)}{(1)}$	$\frac{0.00 \text{ to } 0.17}{0.08} \frac{(31)}{(4)}$	$\frac{0.00 \text{ to } 8.3}{0.63} (\frac{100}{(11)})$	$\frac{0.00 \text{ to } 12.1}{0.08} \frac{(198)}{(22)}$	$\frac{0.01 \text{ to } 0.42}{0.08} \frac{(4)}{(2)}$	$\frac{0.01 \text{ to } 1.77}{0.42} \frac{(15)}{(4)}$
S <sub>1</sub> +S <sub>2</sub> (mg HC/g rock)	$\frac{0.09 \text{ to } 39.1}{0.75} \frac{(97)}{(9)}$	$\frac{0.19 \text{ and } 0.29}{0.24} \frac{(2)}{(1)}$	$\frac{0.05 \text{ to } 0.25}{0.06} \frac{(3)}{(1)}$	0.33	$\frac{0.09 \text{ to } 24.7}{0.78} \frac{(64)}{(7)}$	$\frac{0.03 \text{ to } 14.0}{0.67} \ \frac{(73)}{(13)}$	0.14	$\frac{0.05 \text{ to } 3.0}{1.13} \frac{(8)}{(2)}$
BR (mg bit./gTOC)	$\frac{10 \text{ to } 120}{29} \frac{(46)}{(9)}$	83	9	n.d.	$\frac{28 \text{ to } 158}{58} \frac{(56)}{(6)}$	$\begin{array}{r} \underline{22 \text{ to } 302} \\ \underline{56} \\ (9) \end{array}$	n.d.	$\frac{39 \text{ to } 117}{70} \frac{(7)}{(2)}$
HI (mg HC/g TOC)	$\frac{12 \text{ to } 153}{38} \frac{(97)}{(9)}$	$\frac{48 \text{ and } 63}{55} \frac{(2)}{(1)}$	$\frac{12 \text{ to } 13}{13} \frac{(3)}{(1)}$	141	$\frac{8 \text{ to } 289}{82} \frac{(64)}{(7)}$	$\frac{32 \text{ to } 557}{105} \frac{(73)}{(13)}$	21	$\frac{0 \text{ to } 143}{119} \frac{(8)}{(2)}$
T <sub>max</sub> (°C)	$\frac{412 \text{ to } 431}{423} \frac{(91)}{(9)}$	$\frac{416 \text{ and } 418}{417} \frac{(2)}{(1)}$	417	420	$\frac{412 \text{ to } 454}{437} \frac{(63)}{(6)}$	$\frac{417 \text{ to } 440}{431} \frac{(70)}{(13)}$	n.d.	$\frac{409 \text{ to } 429}{426} \frac{(8)}{(2)}$
R <sub>0</sub> (%)	$\frac{0.51 \text{ to } 0.65}{0.54} \frac{(5)}{(2)}$	n.d.	n.d.	$\frac{1.74 \text{ to } 1.99}{1.84} \frac{(3)}{(1)}$	$\frac{0.61 \text{ to } 0.65}{0.61} \frac{(3)}{(2)}$	$\frac{0.47 \text{ to } 1.41}{0.62} \ \frac{(11)}{(3)}$	n.d.	n.d.
Type of kerogen	III	III?	n.c.	n.c.	III/II	II/III	n.c.	III?
Maturity	immature	immature	n.c.	n.c.	immature/ mature	immature/ mature	n.c.	immature
Petroleum potential	poor to excellent	poor	n.c.	no source	poor to good	poor to good	n.c.	poor to fair

Table 1	Geoc	hemical	characteri	zation of	Mesozoia	e strata in	n the	Polish	1 and	Uk	rainiar	parts of	f the	Carpathian	Fored	eep.
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**TOC** — total organic carbon content;  $\mathbf{S}_1$  — oil and gas yield (mg HC/g rock);  $\mathbf{S}_2$  — residual petroleum potential;  $\mathbf{BR}$  — bitumen ratio;  $\mathbf{HI}$  — hydrogen index;  $T_{max}$  — temperature at maximum of  $\mathbf{S}_2$  peak;  $\mathbf{R}_0$  — vitrinite reflectance. Geochemical parameters and indices are given as minimum and maximum values (numerator) and median values (denominator); in parentheses: number of samples (numerator) and number of sampled wells (denominator); n.d. — not determined; n.c. — not classified.

Espitalié & Bordenave 1993). The basic parameters measured with Rock-Eval are: free hydrocarbons content (S<sub>1</sub>), residual hydrocarbons content (S<sub>2</sub>),  $T_{max}$  temperature, carbon dioxide produced during pyrolysis (S<sub>3</sub>) and residual organic carbon content (S<sub>4</sub>). The above parameters are the basis for calculation of indices used for quantitative and qualitative evaluation of organic matter in the analysed rock, namely total organic carbon (TOC) content, S<sub>2</sub>/S<sub>3</sub> ratio, production index (PI), hydrogen index (HI) and oxygen index (OI). Both the measured and calculated values provide a basis for characterization of organic matter, its quantity, genetic type and transformation degree (Espitalié et al. 1985; Hunt 1996).

After removal of carbonates with hydrochloric acid and extraction of bitumens, rock samples selected for stable carbon isotope analysis of kerogen were combusted in an on-line system. Preparation of previously extracted bitumens and their fractions for stable carbon isotope analyses was carried on with the same procedure. Stable carbon isotopes were analysed with the Finnigan Delta Plus mass spectrometer. The stable carbon isotope data were presented in the  $\delta$ -notation relative to the PDB standard, at an estimated analytical precision  $\pm 0.2 \%$ .

The isolation of kerogen for elemental analysis was carried on with the SOXTEC<sup>TM</sup> extraction of pulverized samples, decalcification of solid residue with HCl at room temperature, removal of silicates with concentrated HF, 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) (Więcław et al. 2010). The elemental (C, H, N and S) analysis of isolated kerogen was done with the Carlo Erba EA 1108 elemental analyser. The quantity of pyrite contaminating the kerogen was analysed as iron with the Perkin-Elmer Plasma 40 ICP-AES instrument after digesting the ash from the combusted kerogen (815 °C, 30 min.) with HCl. The organic sulphur content in kerogen was calculated as the difference between total and pyritic sulphur. The oxygen content was calculated as the difference to 100 %, taking into account the C, H, N, S, moisture and ash contents.

The saturated hydrocarbon fractions isolated from the bitumens were diluted in isooctane and analysed with the GC-MS for biomarker determination. The analysis was carried out with the Agilent 7890A gas chromatograph equipped with the 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 µm 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, further increased to 300 °C at the rate of 3 °C/min and finally held at 300 °C for 35 min. The gas chromatograph was coupled with the 5975C mass selective detector (MSD). The MS operated at ion source temperature 230 °C, ionization energy 70 eV, and a cycle time of 1 s in the mass range from 45 to 500 Daltons.

The aromatic hydrocarbon fractions were analysed with the GC-MS for phenanthrene, dibenzothiophene and their derivatives. The analysis was carried out using the same



Fig. 2. Sketch map of the bottom surface of Middle Jurassic strata in the study area.

equipment as for the saturate hydrocarbon fraction. The GC oven was programmed from 40 to 300 °C at the rate of 3 °C  $\cdot$  min<sup>-1</sup>. The MS operated with a cycle time of 1 s in the mass range from 40 to 600 Daltons.

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

#### Geochemical characteristics of organic matter

#### The Lower Jurassic rocks

The samples from Lower Jurassic strata reveal very low total organic carbon (TOC) contents, much below 0.5 wt. % (Table 1, Fig. 4). The median of TOC is 0.08 wt. %. Only in one sample genetic potential (Rock-Eval  $S_1+S_2$ ) of 0.33 mg/g of rock was measured (Table 1, Fig. 4). Despite the limited number and sampling area of analysed samples, it is concluded that the Lower Jurassic rocks cannot be considered as hydrocarbon source rocks in the study area.

#### The Middle Jurassic rocks

The highest TOC contents in the whole Mesozoic succession from the study area was recorded in the Middle Jurassic strata (Table 1, Fig. 2). The TOC contents in these strata vary significantly: from 0 up to 25.9 wt. %. Despite the similar variability range the lower TOC values were measured in samples coming from the Ukrainian part. In about 40 % of analysed samples the TOC contents were lower than 0.2 wt. %, and in about 45 % these were below 1 wt. % (Fig. 4). In samples from the Polish part TOC was below 1 wt. % in about 30 % of analysed samples and below 0.2 % in a few cases (Figs. 4, 5A). The maximum TOC value was measured in the Lubliniec 9/858.6 sample (Fig. 5A). The Mosty 2/2521-2529 sample also revealed an excellent hydrocarbon potential (Fig. 5B). The median of TOC values for the whole population of samples was 0.83 wt. % (Fig. 4); however, for samples from the Polish part this value was twice as high as for samples from the Ukrainian part (Table 1). The hydrocarbon content in the analysed samples varied in a similarly broad range: from 0.09 up to 39.1 mg/g of rock with the median value for all studied samples 0.77 mg HC/g of rock. No significant differences were observed between the Polish and the Ukrainian parts of the study area (Table 1, Figs. 4, 5A,B). The contents of extractable hydrocarbons indicate moderate to very good oil sourcing potential of the analysed rocks (Fig. 6A,B). Despite relatively high TOC and genetic potential, the analysed samples indicate

very low hydrocarbon potential, as documented by hydrogen index values (HI) which range from 13 to 289 mg HC/g TOC, with a median of merely 57 mg HC/g TOC (Table 1, Figs. 4, 7A,B). Such HI values found in the Middle Jurassic strata indicate the domination of terrigenous material (Type III kerogen) in the Polish part (Fig. 7A) and local inputs of marine Type II kerogen in the Ukrainian part (Fig. 7B) of the study area. These same Type III and III/II kerogens were observed in the western part of the Małopolska Block (Kosakowski et al. 2012b) and in central Poland (Marynowski et al. 2007). The maceral composition also indicates the presence of both terrestrial and marine materials. Their proportions vary from similar percentages of vitrinite and liptinite maceral groups, as in the Lubliniec 4 well, to predominance of terrestrial material, as in the Markowice 2 well (Table 2). Distribution of n-alkanes and isoprenoids in bitumens from Middle Jurassic rocks in the Polish part of the study area (Table 3, Fig. 8A) indicates domination of long-chain hydrocarbons (LTS<sub>HC</sub> ratio above 2, C<sub>max</sub> from 25 to 29), which suggests domination of the gas-prone, terrestrial organic matter (e.g. Peters et al. 2005). In the Ukrainian part of the study area admixture of the oil-prone Type II kerogen is documented by the  $LTS_{HC}$ ratio from 0.7 to 6.4 and C<sub>max</sub> from 20 to 27 (Table 3,



Fig. 3. Sketch map of the bottom surface of Upper Jurassic strata in the study area.

Figs. 8B, 9). Moreover, the strong domination of  $C_{29}$  regular steranes (Table 4) supports this interpretation. Values of pristane/phytane ratio (Table 3) usually above one point to sub-oxic conditions during deposition of organic matter (Didyk et al. 1978; Moldowan et al. 1985; Peters et al. 2005). Low values of diasterane/regular sterane ratio (Table 4) reflect low maturity of organic matter rather than the influence of clay minerals (Seifert & Moldowan 1978).

The results of stable carbon isotope and elemental analyses are consistent with the above discussed data and indicate domination of the gas-prone kerogen in the Polish and mixed kerogen in the Ukrainian parts of the study area (Tables 5, 6, Figs. 10, 11). Highly generative Type IIS kerogen was recorded in only two samples collected from the Korolyn 6 and the Chornokuntsi 1 wells (Table 6).

The low maturity of organic matter dispersed in the Middle Jurassic strata is indicated by a number of analytical results and calculated geochemical indices:  $T_{max}$  values below 430 °C (Table 1, Figs. 4, 7), vitrinite reflectance varying from 0.51 to 0.65 % (Table 2), high values of CPI (Table 3), values of biomarker ratios (Table 4, Figs. 12, 13), results of elemental composition of kerogen (Table 6, Fig. 11) and values of indices calculated from methylphenantrenes and

dibenzothiophenes distribution (Table 7). All these results indicate somewhat higher maturity of organic matter in the Ukrainian part in comparison with the Polish part of the study area. Anyhow, the measured maturity fits into the early phase of the "oil window" (Kosakowski et al. 2011). In that case, the measured TOC and hydrocarbon contents could be regarded as initial or close to initial values. In the light of these facts, the Middle Jurassic clastic rocks in both the Ukrainian and Polish parts show moderate to high, and locally very high, oil-prone potential (Figs. 5A,B, 6A,B).

#### The Upper Jurassic rocks

Characterization of Upper Jurassic strata was based on the results of analyses of samples collected mostly in the Ukrainian part of the Carpathian Foredeep (Table 1, Fig. 4). In the Polish part of the study area only 16 core samples were taken from two wells: Tymce 1 and Sucha Wola 1 (Table 1, Fig. 1). The TOC values in the latter samples are very low, (namely less than 0.5 wt. % with median value 0.07 wt. % (Table 1, Figs. 4, 5B). Hydrocarbons are practically absent from these samples. Despite a much denser sampling grid, the TOC contents in Upper Jurassic rocks from the Ukrainian part of the study area are usually as low as in those from the Polish part, although horizons showing increased organic carbon contents were encountered, as well (Figs. 4, 5B). The TOC contents range from 0.0 to 12.1 wt. %, with very low median value (0.08 wt. %, Table 1, Fig. 4). The genetic potential  $(S_1 + S_2)$  are also very low in most samples (Figs. 4, 5B) and hydrocarbons were measured

only in about 40 % of analysed samples. They ranged from 0.18 to 14.0 mg/g of rock (Table 1, Fig. 5B). Despite such variability, low-hydrocarbon samples prevail and the median for the entire population is 0.67 mg/g of rock (Table 1). Most of the samples show low HI values and median value is up to 105 mg HC/g TOC (Table 1, Fig. 4). This low background contrasts with the results obtained in samples from the Voloshcha 1 and Korolyn 6 wells (Fig. 1), where both TOC contents, hydrocarbon contents and hydrocarbon index HI values are much higher. The TOC values measured in the Voloshcha 1 well, at the depth interval 2650-3300 m, are over 1.0 wt. % and locally reach up to 12.1 wt. % (Table 1). Genetic potential is also high, although the HI index values differ only slightly from the average ones. In samples from the Korolyn 6 well both the TOC and genetic potential is equally high and the HI values reach up to 557 mg/g of TOC (Table 1, Fig. 7B). In the remaining wells TOC contents, genetic potential values and HI are significantly lower (Fig. 5B). The probable presence of epigenetic hydrocarbon (Fig. 6B) indicates possible initiation of the hydrocarbon generation process.

In this stratigraphic unit organic matter is a mixture of Type II and Type III kerogens. In comparison to Middle



Fig. 4. Histograms of total organic carbon and hydrocarbon contents, hydrogen index and  $T_{max}$  temperature values for Jurassic and Cretaceous strata. Dashed line — median value for whole sample population.

Jurassic sediments, a higher proportion of oil-prone Type II kerogen is evident. Proportions of kerogen types can be estimated from analysis of maceral composition (Table 2), which ranges from dominating liptinite-group macerals (as in the Bortyatyn 1 well) indicating the presence of Type II kerogen, to dominating vitrinite-group macerals (as in the Voloshcha 1 well), typical of Type III kerogen (Hunt 1996). High values of hydrogen index HI (Fig. 7B), values of LTS<sub>HC</sub> ratio <1 and maximum intensities at short-chain *n*-alkanes (Table 3, Fig. 8C) as well as distribution of *n*-alkanes (Table 3, Fig. 9), composition of regular steranes (Table 4) as well as enrichment in light <sup>12</sup>C isotope (Table 5, Fig. 10B) and elemental composition of kerogen (Table 6, Fig. 11) indicate the presence of a good oil-prone source rock horizon in the succession of the Korolyn 6 well. Moreover, organic

matter from this well along with that encountered in the Chornokuntsi 1 well reveals high organic sulphur content (Type IIS kerogen), which enables the generation of hydrocarbons below the "typical" limits of the "oil window" (Orr 1986). The horizons which contain this type of kerogen occur only within narrow intervals of the Upper Jurassic strata. The Type IIS kerogen is the most probable source for extremely heavy, high-sulphur and viscous oils accumulated in the Upper Jurassic carbonates in the Kokhanivka and Orkhovychi deposits (Więcław et al. 2012). The occurrence of oil with the same properties in the Lubaczów deposit in Poland, ca. 10–20 km to the west of the Kokhanivka deposit (Więcław 2011), suggests the presence of one, continuous oil deposit. In the Polish part of the Upper Jurassic basin, this type of organic matter has not been recorded.



Fig. 6. Petroleum source quality diagram for organic matter from Mesozoic strata in (A) Polish and (B and C) Ukrainian parts of study area. Classification after Hunt (1979) and Leenheer (1984).

This kerogen was deposited under anoxic conditions, as defined by low values of pristane/phytane ratio (Didyk et al. 1978) (Table 3). In the other studied sequences gas-prone Type III kerogen dominates, as revealed by prevailing long-chain *n*-alkanes (Table 4, Fig. 8D), strong dominance of  $C_{29}$  over  $C_{27}$  regular steranes (Table 4), stable isotope composi-

tion (Table 5, Fig. 10B) and elemental composition of kerogen (Table 6, Fig. 11).

The thermal maturity index  $T_{max}$ , usually below 430 °C, indicates that the Upper Jurassic organic matter was immature and did not reach the threshold of thermogenic hydrocarbon generation (Table 1, Figs. 4, 7A,B). The vitrinite



reflectance (Table 2), biomarker indices (Table 4, Figs. 12, 13B) and elemental analysis (Fig. 11) suggest higher maturity, corresponding to the early and main phase of the "oil window". Hence, these strata are the effective source rocks, especially in the areas where highly generative, Type IIS kerogen was recorded.

#### The Lower Cretaceous rocks

The Lower Cretaceous strata are represented by only a few samples. The TOC ranges from 0.01 up to 2.03 wt. % and the median is 0.40 wt. % (Table 1, Fig. 4). Relatively moderate TOC contents are accompanied by very low genetic potential with median value of only 0.14 mg HC/g of rock (Table 1, Fig. 5C). Therefore, we can conclude that TOC value 2.03 wt. % confronted with the low genetic potential and low maturity cannot be regared as a reliable result. Probably, the carbonate matrix influenced this analytical value. Alternatively, it is possible that syn-sedimentary oxidation of organic matter (Marynowski et al.

Fig. 7. Hydrogen index versus Rock-Eval  $T_{max}$  temperature for (A and C) Polish and (B and D) Ukrainian parts of study area. Maturity paths of individual kerogen types after Espitalié et al. (1985).

Well	Donth (m)	Stratigraphy	Pyrite	Ma	cerals	(%)	OM	$\mathbf{D}_{\mathbf{r}}(0_{\mathbf{r}})$	Dongo	No. of	$\mathbf{D}_{1}$ $(0/2)$
wen	Deptii (iii)	Stratigraphy	(%)	V	L	Ι	(%)	<b>N</b> <sub>0</sub> (%)	Kange	meas.	KOredep. (70)
Polish part											-
Lubliniec 4	730.4	M. Jurassic	5.5	3.2	3.1	1.0	7.3	0.54	0.46-0.76	97	0.90-1.20
Lubliniec 4	796.5	M. Jurassic	2.4	7.0	3.3	0.8	11.1	0.57	0.51 - 0.78	97	1.00-1.10
Lubliniec 4	837.5	M. Jurassic	2.1	4.0	1.0	0.2	5.2	0.65	0.52 - 0.90	115	1.00-1.20
Markowice 2	753.0	M. Jurassic	0.8	13.1	2.4	4.5	20.0	0.51	0.43-0.65	102	n.m.
Markowice 2	800.0	M. Jurassic	5.0	14.0	4.3	5.0	23.3	0.52	0.40-0.66	60	1.10-1.50
Ukrainian part											-
Rudky 300	3241.0-3246.0	L. Jurassic	2.4	0.1	ab.	ab.	0.1	1.74	1.44-2.00	29	n.m.
Rudky 300	3491.9-3495.5	L. Jurassic	1.7	< 0.1	ab.	ab.	<0.1	1.84	1.59-2.20	12	n.m.
Rudky 300	3902.0-3905.0	L. Jurassic	2.8	< 0.1	ab.	ab.	<0.1	1.99	1.74 - 2.30	17	n.m.
Bortyatyn 1	2846.0-2857.0	M. Jurassic	2.5	3.5	5.0	1.2	9.7	0.61	0.53-0.77	62	0.90-1.20
Podiltsi 1	3303.0-3306.1	M. Jurassic	5.2	1.7	0.6	0.4	2.7	0.65	0.57-0.73	61	1.10-1.55
Podiltsi 1	3475.0-3482.0	M. Jurassic	tr.	3.3	3.5	0.3	7.1	0.61	0.50-0.77	91	0.90-1.20
Bortyatyn 1	1820.0-1830.0	U. Jurassic	4.0	1.9	2.0	0.1	4.1	0.47	0.37-0.59	63	0.62-0.73
Bortyatyn 1	2522.0-2529.0	U. Jurassic	0.5	1.2	0.1	0.1	1.4	0.57	0.53-0.68	17	1.00-1.50
Moryanti 1	2263.0-2270.0	U. Jurassic	tr.	ab.	ab.	ab.	n.m.	n.m.	n.m.	n.d.	n.m.
Moryanti 1	2576.0-2582.0	U. Jurassic	0.1	0.1	ab.	ab.	0.1	0.78	0.71 - 0.88	13	1.0-1.20
Moryanti 1	3055.0-3063.0	U. Jurassic	0.1	0.3	ab.	tr.	0.3	0.9	0.68 - 1.10	37	1.10-1.25
Voloshcha 1	2255.0-2265.0	U. Jurassic	3.0	2.2	0.3	n.d.	2.5	0.54	0.42 - 0.67	68	0.86-1.25
Voloshcha 1	2500.0-2508.0	U. Jurassic	1.3	2.5	0.5	0.2	3.2	0.57	0.45-0.69	78	n.m.
Voloshcha 1	2651.0-2659.0	U. Jurassic	1.1	7.3	3.5	0.6	11.4	0.58	0.46-0.73	74	0.90-1.20
Voloshcha 1	2850.5-2860.5	U. Jurassic	2.7	25.0	5.1	4.2	34.3	0.65	0.52 - 0.77	93	1.00-1.20
Voloshcha 1	3296.0-3305.0	U. Jurassic	0.1	1.6	0.4	0.1	2.1	0.67	0.55 - 0.87	87	n.m.
Voloshcha 1	3547.0-3557.0	U. Jurassic	3.5	< 0.1	tr.	tr.	< 0.1	1.41	1.10 - 1.50	23	n.m.

Table 2: Maceral composition and vitrinite reflectance of organic matter from Jurassic strata in the Tarnogród-Stryi area.

In the Ukrainian part the depth of the sample is impossible to be accurately identified. M. — Middle; U. — Upper; V — vitrinite; L — liptinite; I — inertinite; OM — organic matter;  $R_0$  — vitrinite reflectance; meas. — measurements;  $R_{Oredep}$  — vitrinite reflectance of redeposited organic matter; tr. — traces; n.m. — not measured; ab. — absence; n.d. — no data.

Well	Depth (m)	Stratigraphy	CPI(17-31)	CPI(17-23)	CPI <sub>(25-31)</sub>	Pr/Ph	<b>Pr/n-C</b> <sub>17</sub>	Ph/n-C <sub>18</sub>	LTS <sub>HC</sub>	C <sub>max</sub>
Polish part										
Księżpol 18	869.6	M. Jurassic	n.c.	n.c.	1.80	n.c.	n.c.	0.62	5.54	25
Lubliniec 4	730.4	M. Jurassic	n.c.	n.c.	2.58	n.c.	n.c.	0.41	8.85	27
Łukowa 2	731.8	M. Jurassic	n.c.	n.c.	3.52	n.c.	n.c.	0.40	9.79	29
Łukowa 4	982.5	M. Jurassic	n.c.	n.c.	1.69	n.c.	n.c.	1,00	7.26	27
Markowice 2	800.0	M. Jurassic	n.c.	n.c.	2.86	n.c.	n.c.	0.52	9.33	27
Markowice 2	902.8	M. Jurassic	n.c.	n.c.	1.96	n.c.	n.c.	1.48	2.48	27
Ukrainian part										
Bortyatyn 1	2846.0-2857.0	M. Jurassic	1.23	1.00	1.55	1.39	4.93	0.71	1.8	25
Chornokuntsi 1	2096.0-2102.0	M. Jurassic	1.15	0.84	1.70	0.81	3.18	0.89	1.8	20
Korolyn 6	3421.8-3429.7	M. Jurassic	n.c.	n.c.	1.29	n.c.	n.c.	0.44	1.9	23
Korolyn 6	3517.3-3523.0	M. Jurassic	n.c.	n.c.	1.17	n.c.	n.c.	0.30	0.7	21
Mosty 2	2360.3-2364.4	M. Jurassic	n.c.	n.c.	1.99	n.c.	n.c.	1.01	3.0	25
Mosty 2	2521.0-2529.0	M. Jurassic	1.39	1.18	1.67	2.19	1.77	0.23	1.4	23
Mosty 2	2543.0-2549.0	M. Jurassic	1.29	0.93	1.75	1.51	3.42	0.59	3.1	27
Podiltsi 1	3214.8-3221.0	M. Jurassic	n.c.	n.c.	1.42	n.c.	n.c.	n.c.	6.4	23
Podiltsi 1	3316.0-3323.0	M. Jurassic	1.22	1.12	1.35	0.87	1.22	1.42	3.6	27
Korolyn 6	2144.0-2146.7	U. Jurassic	0.93	0.90	1.19	0.33	0.64	0.59	0.2	19
Korolyn 6	2293.0-2308.0	U. Jurassic	0.97	0.95	1.01	0.35	0.51	0.70	0.3	19
Lanivka 1	1590.0-1597.0	U. Jurassic	n.c.	n.c.	2.15	n.c.	n.c.	n.c.	4.0	22
Mosty 1	1790.0-1800.0	U. Jurassic	1.16	0.98	1.47	0.87	4.03	1.32	1.3	23
Voloshcha 1	2659.0-2667.0	U. Jurassic	n.c.	n.c.	1.64	n.c.	n.c.	n.c.	14.6	25
Voloshcha 1	2870.5-2880.0	U. Jurassic	n.c.	n.c.	1.66	n.c.	n.c.	0.81	1.9	23
Voloshcha 1	2903.7-2912.0	U. Jurassic	n.c.	n.c.	1.51	n.c.	n.c.	n.c.	10.3	25
Voloshcha 1	2952.0-2959.0	U. Jurassic	1.17	1.00	1.43	n.c.	n.c.	1.06	1.7	25
Voloshcha 1	3126.0-3134.0	U. Jurassic	n.c.	n.c.	1.57	n.c.	n.c.	0.53	1.9	25
Verchany 1	1811.0-1825.3	U. Jurassic	n.c.	n.c.	0.98	0.22	n.c.	2.74	0.9	22
Yuriyiv 1	2016.0-2025.0	U. Jurassic	n.c.	n.c.	1.20	0.99	n.c.	0.98	2.0	25
Chornokuntsi 1	1866.0-1871.0	U. Jurassic?	0.95	0.82	1.27	0.32	1.56	1.97	1.7	24
Didushychi 2	1100.0-1108.0	U. Cretaceous	n.c.	n.c.	3.23	n.c.	n.c.	2.99	2.1	22
Didushychi 2	1706.0-1712.0	U. Cretaceous	n.c.	n.c.	2.15	n.c.	n.c.	2.57	5.9	29
Pivn. Girs'ke 1	1391.2-1405.2	U. Cretaceous	n.c.	n.c.	3.11	< 1	n.c.	4.29	1.6	27
Pivn Girs'ke 1	1405 0-1414 0	U Cretaceous	nc	nc	2 5 2	< 1	nc	7.03	31	29

Table 3: Indices calculated from distribution of *n*-alkanes and isoprenoids in bitumens extracted from Jurassic and Cretaceous strata.

 $\begin{array}{l} Pr - pristane; Ph - phytane; CPI_{(17-31)} = [(C_{17}+C_{19}+...+C_{27}+C_{29})+(C_{19}+C_{21}+...+C_{29}+C_{31})]/2*(C_{18}+C_{20}+...+C_{28}+C_{30}); CPI_{(17-23)} = [(C_{17}+C_{19}+C_{21})+(C_{19}+C_{21}+C_{23})]/2*(C_{18}+C_{20}+C_{22}); CPI_{(25-31)} = [(C_{25}+C_{27}+C_{29})+(C_{27}+C_{29}+C_{31})]/2*(C_{26}+C_{28}+C_{30}); LTS_{HC} = (C_{27}+C_{28}+C_{29})/(C_{17}+C_{18}+C_{19}); n.c. - not calculated due to partial evaporation of hydrocarbons; values typed in italic are estimated due to co-elution of crocetane. \end{array}$ 

2011) or post-sedimentary oxidation related to erosion caused that kerogen recently observed in analysed rocks represents a non-generative residuum. The low hydrocarbon source potential of this kerogen, is revealed by the hydrocarbon index below 20 mg HC/g TOC (Table 1, Figs. 4, 7C). The low TOC content precludes detailed determination of its type and maturity but the obtained single values of  $T_{max}$  suggest its immaturity (Table 1, Figs. 4, 7C).

The overall assessment of Lower Cretaceous strata allows us to conclude that these sediments do not meet the criteria of hydrocarbon source rocks, mainly due to their low hydrocarbon content and immaturity (Figs. 4, 5C, 7C).

#### The Upper Cretaceous rocks

The characterization of Upper Cretaceous strata was also based on a small number of samples collected only in the Ukrainian part of the Carpathian Foredeep. Similarly to the Lower Cretaceous strata, the TOC range is also wide: from 0.01 to 1.77 wt. %, with nearly identical median value (0.44 wt. %, Table 1). The relatively high TOC content is associated with low genetic potential ( $S_1+S_2$ ) (Table 1, Figs. 4, 5D). This potential measured only for half the analysed samples reaches up to 3 mg HC/g of rock (Fig. 5D). The analysed samples point to the existence of very good oil potential, as revealed by relatively high efficiency of extractable hydrocarbons (Fig. 6C), which may be connected with the beginning of hydrocarbon generation process. All the analysed samples indicate low HI values (median 121 mg HC/g TOC), suggesting domination of gas-prone Type III kerogen (Figs. 4, 7D). This suggestion is supported by *n*-alkane distribution showing domination of long-chain hydrocarbons in the majority of analysed samples (Table 3, Fig. 8E). Regular sterane distribution (Table 4), stable carbon isotope composition (Fig. 10) as well as the elemental composition of kerogen (Fig. 11) indicate the input of oil-prone Type II kerogen. Increased concentrations of phytane in samples derived from the Pivnichno Girs'ke 1 well (Fig. 8E) may be connected with co-elution of crocetane (2, 6, 11, 15-tetramethylhexadecane), a biomarker of methanogenic and methanotrophic archea (Peters et al. 2005). In these samples the highlybranched isoprenoid C<sub>25</sub>[2,6,10,14-tetramethyl-7-(3-methylpenthyl) pentadecane] (HBI) was also detected (Fig. 8E). According to Volkman et al. (1994, 1998), this biomarker occurs in diatoms and is an indicator of diatoms' contribution to organic matter. In the Pivnichno Girs'ke 1/1405-1414 sample, the presence of 2, 6, 10, 15, 19-pentamethylicosane (PMI) was recorded (Fig. 8E). This isoprenoid is a common crocetane marker of methanogens in immature sediments (Noble & Henk 1998). The presence of all the above dis-

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per Jurassic strata in study area, in terms of pristane/n-C17 and phytane/n-C<sub>18</sub>. Categories after Obermajer et al. (1999).

O Middle Jurassic

Upper Jurassic



Fig. 8. Examples of ion chromatograms (m/z=71) showing the distributions of *n*-alkanes and isoprenoids in saturated hydrocarbons of bitumens from (A) and (B) Middle Jurassic, (C) and (D) Upper Jurassic, and (E) Upper Cretaceous strata. Pr — pristane, Ph — phytane, HBI — highly branched isoprenoid C<sub>25</sub>, PMI — 2,6,10,15, 19-pentamethylicosane.

Fig. 10. Genetic characterization of bitumens from Jurassic and Cretaceous strata in (A) Polish and (B) Ukrainian parts of the study area based on stable carbon isotope composition of saturated and aromatic hydrocarbons. Genetic fields after Sofer (1984).

Well	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	C29ββαα	C <sub>29</sub> Ts/ C <sub>29</sub> H	Ts/Tm	Dia/Reg
Polish part		•												
Księżpol 18	869.6	M. Jurassic	21	20	58	2.72	0.79	0.34	0.23	0.12	0.42	0.03	0.05	0.14
Lubliniec 4	730.4	M. Jurassic	45	20	35	0.77	1.23	0.18	0.27	0.23	0.42	0.15	0.05	0.24
Łukowa 2	731.8	M. Jurassic	20	28	52	2.59	0.85	0.17	0.21	0.13	0.38	0.10	0.12	0.04
Łukowa 4	982.5	M. Jurassic	24	28	48	1.97	0.90	0.31	0.26	0.13	0.44	0.05	0.05	0.10
Markowiece 2	800.0	M. Jurassic	28	21	51	1.83	0.94	0.22	0.26	0.19	0.39	0.16	0.17	0.13
Markowiece 2	902.8	M. Jurassic	23	19	58	2.48	0.96	0.20	0.26	0.26	0.49	0.08	0.23	0.17
Ukrainian part														
Bortyatyn 1	2846.0-2857.0	M. Jurassic	25	21	54	2.21	0.46	0.56	0.56	0.36	0.32	0.11	0.03	0.24
Chornokuntsi 1	2096.0-2102.0	M. Jurassic	35	14	51	1.44	0.67	0.47	0.40	0.21	0.37	0.12	0.05	0.20
Korolyn 6	3421.8-3429.7	M. Jurassic	23	20	58	2.56	0.31	0.58	0.59	0.32	0.32	0.01	0.03	0.16
Korolyn 6	3517.3-3523.0	M. Jurassic	33	19	48	1.45	0.22	0.57	0.59	0.65	0.47	0.05	0.06	0.74
Mosty 2	2360.3-2364.4	M. Jurassic	33	26	42	1.28	0.48	0.54	0.44	0.16	0.40	0.10	0.07	0.26
Mosty 2	2521.0-2529.0	M. Jurassic	22	28	50	2.33	0.55	0.57	0.59	0.34	0.27	0.04	0.01	0.07
Mosty 2	2543.0-2549.0	M. Jurassic	36	20	44	1.21	0.42	0.57	0.56	0.31	0.45	0.09	0.07	0.44
Podiltsi 1	3214.8-3221.0	M. Jurassic	32	13	55	1.69	0.50	0.57	0.56	0.33	0.32	0.03	0.03	0.18
Podiltsi 1	3316.0-3323.0	M. Jurassic	25	27	48	1.91	0.41	0.58	0.59	0.45	0.34	0.01	0.03	0.14
Korolyn 6	2144.0-2146.7	U. Jurassic	33	22	44	1.33	0.08	0.52	0.60	0.52	0.53	0.10	0.14	0.19
Korolyn 6	2293.0-2308.0	U. Jurassic	35	22	42	1.21	0.09	0.57	0.60	0.52	0.57	0.11	0.27	0.08
Lanivka 1	1590.0-1597.0	U. Jurassic	23	34	43	1.84	0.19	0.33	0.41	0.07	n.c.	0.24	0.51	0.03
Mosty 1	1790.0-1800.0	U. Jurassic	31	27	42	1.36	0.22	0.59	0.57	0.34	0.29	0.28	0.40	0.18
Voloshcha 1	2659.0-2667.0	U. Jurassic	34	18	48	1.40	0.54	0.47	0.41	0.20	0.36	0.04	0.06	0.30
Voloshcha 1	2870.5-2880.0	U. Jurassic	21	28	51	2.45	0.44	0.54	0.50	0.28	0.33	0.02	0.02	0.19
Voloshcha 1	2903.7-2912.0	U. Jurassic	23	25	52	2.22	0.45	0.54	0.52	0.27	0.35	0.01	0.02	0.12
Voloshcha 1	2952.0-2959.0	U. Jurassic	18	22	60	3.39	0.47	0.52	0.49	0.34	0.65	0.09	0.04	0.29
Voloshcha 1	3126.0-3134.0	U. Jurassic	19	17	64	3.44	0.41	0.55	0.57	0.42	0.32	0.07	0.09	0.11
Verchany 1	1811.0-1825.3	U. Jurassic	31	22	47	1.50	0.22	0.45	0.49	0.29	0.35	0.07	0.20	0.15
Yuriyiv 1	2016.0-2025.0	U. Jurassic	32	18	51	1.61	0.67	0.41	0.30	0.15	0.43	0.08	0.04	0.42
Chornokuntsi 1	1866.0-1871.0	U. Jurassic?	38	20	42	1.12	0.09	0.54	0.56	0.16	0.25	0.12	0.28	0.05
Didushychi 2	1100.0-1108.0	U. Cretaceous	24	35	41	1.72	0.31	0.58	0.40	0.22	n.c.	0.37	0.40	0.04
Didushychi 2	1706.0-1712.0	U. Cretaceous	24	32	44	1.85	0.33	0.36	0.41	0.09	n.c.	0.32	0.32	0.03
Pivn. Girs'ke 1	1391.2-1405.2	U. Cretaceous	27	33	40	1.51	0.22	0.40	0.43	0.10	0.31	0.35	0.41	0.08
Pivn. Girs'ke 1	1405.0-1414.0	U. Cretaceous	47	26	28	0.60	0.09	0.35	0.36	0.08	n.c.	0.30	0.37	0.03

 Table 4: Selected biomarker characterization of bitumens from Jurassic and Cretaceous strata.

 $C_{27}=C_{27}\alpha\alpha\alpha\alpha20R \text{ sterane}/(C_{27}+C_{28}+C_{29})\alpha\alpha\alpha20R \text{ steranes}; C_{28}=C_{28}\alpha\alpha\alpha20R \text{ sterane}/(C_{27}+C_{28}+C_{29})\alpha\alpha\alpha20R \text{ steranes}; C_{29}=C_{29}\alpha\alpha\alpha20R \text{ sterane}/(C_{27}+C_{28}+C_{29})\alpha\alpha\alpha20R \text{ steranes}; C_{29}=C_{29}\alpha\alpha\alpha20R \text{ sterane}/(C_{27}+C_{28}+C_{29})\alpha\alpha\alpha20R \text{ steranes}; C_{29}=C_{29}\alpha\alpha\alpha20R \text{ sterane}/(C_{27}+C_{28}+C_{29})\alpha\alpha\alpha20R \text{ sterane}; Mor/Hop=moretane/17\alpha hopane; H_{31}S/(S+R)=homohopane 22S/(22S+22R); H_{32}S/(S+R)=bishomohopane 22S/(22S+22R); C_{29}SR=epimerisation of regular steranes C_{29} ratio; C_{29}\beta\beta\alpha\alpha=ratio of \beta\beta-epimeres of regular steranes C_{29} to sum of \beta\beta+\alpha\alpha$  steranes; C\_{29}Ts/C\_{29}H=C\_{29}18\alpha norneohopane/C<sub>29</sub> norhopane; Ts/Tm=C<sub>27</sub>18\alpha trisnorhopane/C<sub>27</sub>17\alpha trisnorhopane; Dia/Reg=C<sub>27</sub>  $\beta\alpha$  20S diasterane/C<sub>29</sub>  $\alpha\alpha\alpha$  20R sterane; n.c. — not calculated due to low intensities of biomarkers; M. — Middle; U. — Upper.



cussed biomarkers in the study area has already been described by Kotarba et al. (2011) for the overlying Miocene strata of the Carpathian Foredeep.

The immaturity of organic matter dispersed in analysed strata is evidenced by low  $T_{max}$  temperatures (below 430 °C, Table 1, Figs. 4, 7D), high CPI values (Table 3) and sterane ratios (Table 4, Fig. 13B). Moreover, hopane ratios also indicate low maturity of analysed organic matter, comparable to that from the Upper Jurassic rocks but higher than that from the Middle Jurassic sediments (Fig. 12).

The low maturity of analysed organic matter indicates that both the Upper and the Lower Cretaceous strata did not meet the criteria of hydrocarbon source rocks (Table 1, Figs. 5, 7).

#### Conclusions

The analysis of both the Jurassic and Cretaceous rocks from the south-eastern part of Poland and the western part of Ukraine, between Tarnogród and Stryi towns, generally reveals their low hydrocarbon source-rock potential. The lowest petroleum potential characterizes the Lower Jurassic and the Cretaceous strata where TOC contents, genetic potential

## **Fig. 11.** Genetic characterization of organic matter from Jurassic and Cretaceous strata in the analysed part of the Carpathian Foredeep. Fields representing natural maturity paths for individual kerogens after Hunt (1996).

Well	Donth (m)	Stuatignaphy	F	ractio	ns (wt	.%)			<b>δ</b> <sup>13</sup> C	C (%o)		
vv en	Deptii (iii)	Straugraphy	Sat	Aro	Res	Asph	Sat	Bit	Aro	Res	Asph	Ker
Polish part												
Księżpol 18	869.6	M. Jurassic	1	16	17	66	-27.4	-24.4	-25.0	-24.6	-23.7	-23.1
Lubliniec 4	730.4	M. Jurassic	5	10	23	62	-27.8	-25.5	-26.6	-26.3	-24.9	-23.9
Łukowa 2	731.8	M. Jurassic	8	10	35	47	-29.3	-26.2	-27.0	-26.5	-25.2	-24.1
Łukowa 4	982.5	M. Jurassic	3	16	29	52	-27.1	-24.1	-24.7	-24.5	-23.6	-22.9
Markowice 2	800.0	M. Jurassic	10	11	30	49	-28.5	-26.2	-27.2	-26.5	-25.3	-23.7
Markowice 2	902.8	M. Jurassic	7	15	19	59	-28.3	-24.5	-25.7	-24.8	-23.7	-22.8
Ukrainian part		•										
Bortyatyn 1	2846.0-2857.0	M. Jurassic	4	10	18	68	-28.0	-24.3	-24.8	-24.7	-23.4	-23.8
Chornokuntsi 1	2096.0-2102.0	M. Jurassic	4	10	28	58	-30.2	-29.7	-30.1	-29.7	-29.4	-29.1
Korolyn 6	3421.8-3429.7	M. Jurassic	6	21	25	48	-27.5	-24.7	-24.6	-25.1	-24.1	-23.7
Korolyn 6	3517.3-3523.0	M. Jurassic	4	12	31	53	-27.4	-24.6	-24.7	-24.8	-24.3	-23.5
Mosty 2	2360.3-2364.4	M. Jurassic	5	13	29	53	-28.2	-25.0	-25.1	-25.5	-24.5	-23.5
Mosty 2	2521.0-2529.0	M. Jurassic	8	14	27	51	-30.3	-26.2	-27.7	-26.2	-25.1	-24.5
Mosty 2	2543.0-2549.0	M. Jurassic	8	9	25	58	-29.0	-25.6	-26.4	-25.9	-25.0	-24.4
Podiltsi 1	3214.8-3221.0	M. Jurassic	4	17	32	47	-27.1	-24.2	-24.3	-24.3	-23.8	-23.2
Podiltsi 1	3316.0-3323.0	M. Jurassic	4	19	19	58	-27.1	-24.4	-24.9	-24.7	-24.4	-23.8
Korolyn 6	2144.0-2146.7	U. Jurassic	5	22	16	57	-29.0	-29.0	-29.6	-28.7	-29.1	-28.4
Korolyn 6	2293.0-2308.0	U. Jurassic	8	23	30	39	-30.2	-29.7	-30.1	-29.7	-29.4	-29.1
Lanivka 1	1590.0-1597.0	U. Jurassic	12	9	36	43	-26.9	-26.3	-26.0	-25.6	-26.7	-23.4
Mosty 1	1790.0-1800.0	U. Jurassic	18	15	38	29	-27.6	-27.6	-26.5	-28.3	-27.3	-25.1
Voloshcha 1	2659.0-2667.0	U. Jurassic	8	15	32	45	-28.9	-25.9	-26.2	-26.0	-25.3	-24.2
Voloshcha 1	2870.5-2880.0	U. Jurassic	3	9	26	62	-26.9	-23.9	-24.2	-24.1	-23.7	-22.6
Voloshcha 1	2903.7-2912.0	U. Jurassic	4	16	33	47	-27.5	-24.3	-24.7	-24.4	-23.8	-23.4
Voloshcha 1	2952.0-2959.0	U. Jurassic	2	17	25	56	-27.3	-23.7	-24.0	-24.1	-23.4	-22.6
Voloshcha 1	3126.0-3134.0	U. Jurassic	4	14	26	56	-28,0	-25.1	-25.1	-25.4	-24.8	-24.3
Verchany 1	1811.0-1825.3	U. Jurassic	8	8	44	40	-28.7	-26.9	-26.8	-26.9	-26.7	-24.3
Yuriyiv 1	2016.0-2025.0	U. Jurassic	3	8	18	71	-28.2	-24.5	-25.1	-25.0	-23.8	-23.5
Chornokuntsi 1	1866.0-1871.0	U. Jurassic?	17	17	37	29	-26.6	-25.6	-25.6	-25.4	-25.3	-24.9
Didushychi 2	1100.0-1108.0	U. Cretaceous	13	6	40	41	-28.1	-27.3	-27.4	-27.2	-27.2	-24.6
Didushychi 2	1706.0-1712.0	U. Cretaceous	9	7	31	53	-28.3	-26.9	-27.2	-27.0	-26.5	-25.0
Pivn. Girs'ke 1	1391.2-1405.2	U. Cretaceous	11	8	52	29	-27.7	-26.5	-26.7	-26.6	-26.0	-24.8
Pivn, Girs'ke 1	1405.0-1414.0	U. Cretaceous	24	12	37	27	-28.0	-26.2	-26.6	-25.8	-25.6	-25.0

Table 5: Stable carbon isotope compositions of bitumens, their individual fractions and kerogen from Jurassic and Cretaceous strata.

In the Ukrainian part the depth of the sample is impossible to be accurately identified. M. — Middle; U. — Upper; Sat — saturated hydrocarbons; Aro — aromatic hydrocarbons; Res — resins; Asph — asphaltenes; Bit — bitumen; Ker — kerogen.

and hydrocarbon index values prove that these stratigraphic horizons were not significant sources of hydrocarbons. However, our results demonstrate the increasing values of these quantitative parameters as well as local enrichment in organic carbon and hydrocarbon content within the Upper Cretaceous strata in the eastern part of the study area. Unfortunately, the effective hydrocarbon sourcing in these horizons is significantly limited by low maturity of organic matter, which does not guarantee its transformation into hydrocarbons. In conclusion, the above-mentioned stratigraphic horizons are of minor importance as potential source rocks of hydrocarbons in the study area.

**Fig. 12.** Plots of moretane/ $17\alpha$  hopane ratio versus (A) Ts/Tm and (B) C<sub>29</sub>Ts/C<sub>29</sub>H ratios.

**Fig. 13.** Plots of sterane  $C_{29}20S/(20S + 20R)$  ratio versus  $C_{29}\beta\beta/(\beta\beta + \alpha\alpha)$  ratio for organic matter from Jurassic strata in the (**A**) Polish and (**B**) Ukrainian parts of the Carpathian Foredeep. Maturity fields after Peters & Moldowan (1993).



Well	Depth (m)	Stratigraphy	Ele	ment (da	al con f, wt.	npos %)	ition		Atom	ic ratio	)		Mole f	raction	
	_		С	Н	0	Ν	S	H/C	<b>O/C</b>	N/C	S/C	H/(H+C)	0/(0+C)	N/(N+C)	S/(S+C)
Polish part															
Księżpol 18	869.6	M. Jurassic	75.0	4.1	16.5	1.6	1.9	0.65	0.16	0.018	0.009	0.39	0.14	0.017	0.009
Łukowa 2	982.5	M. Jurassic	73.1	3.8	20.1	1.4	1.6	0.63	0.21	0.016	0.008	0.38	0.17	0.016	0.008
Markowice 2	902.8	M. Jurassic	74.5	4.0	19.3	1.6	0.6	0.64	0.19	0.018	0.003	0.39	0.16	0.017	0.003
Ukrainian part															
Bortyatyn 1	2846.0-2857.0	M. Jurassic	79.9	4.6	12.6	2.1	0.8	0.70	0.12	0.022	0.004	0.41	0.11	0.022	0.004
Korolyn 6	3517.3-3523.0	M. Jurassic	81.4	4.4	11.7	2.1	0.4	0.65	0.11	0.023	0.002	0.39	0.10	0.022	0.002
Mosty 2	2521.0-2529.0	M. Jurassic	80.7	5.0	11.9	1.7	0.7	0.74	0.11	0.018	0.003	0.42	0.10	0.018	0.003
Podiltsi 1	3214.8-3221.0	M. Jurassic	82.1	3.9	11.0	1.9	1.1	0.57	0.10	0.020	0.005	0.36	0.09	0.019	0.005
Korolyn 6	2293.0-2308.0	U. Jurassic	75.8	7.2	4.8	1.3	10.8	1.13	0.05	0.015	0.054	0.53	0.05	0.015	0.051
Kokhanivka 26	1090.9–1095.0	U. Jurassic	68.8	5.9	18.6	1.6	5.1	1.03	0.20	0.020	0.028				1
Lanivka 1	1590.0-1597.0	U. Jurassic	70.3	7.2	14.7	2.5	5.3	1.23	0.16	0.030	0.028	0.55	0.14	0.029	0.028
Voloshcha 1	2659.0-2667.0	U. Jurassic	78.8	5.3	12.6	1.9	1.4	0.81	0.12	0.021	0.007	0.44	0.11	0.021	0.007
Voloshcha 1	2903.7-2912.0	U. Jurassic	81.6	3.7	12.2	1.8	0.6	0.55	0.11	0.019	0.003	0.35	0.10	0.019	0.003
Yuriyiv 1	2016.0-2025.0	U. Jurassic	79.6	4.1	13.4	1.6	1.3	0.62	0.13	0.017	0.006	0.38	0.11	0.017	0.006
Chornokuntsi 1	1866.0-1871.0	U. Jurassic?	68.2	6.0	13.9	1.3	10.6	1.05	0.15	0.016	0.059	0.51	0.13	0.016	0.055
Pivn. Girs'ke 1	1405.2-1414.0	U. Cretaceous	44.6	4.6	51.5	1.2	1.1	1.17	0.13	0.023	0.009	0.55	0.46	0.022	0.009

 Table 6: Elemental composition of kerogen from Jurassic and Cretaceous strata.

In the Ukrainian part the depth of the sample is impossible to be accurately identified. daf — dry, ash — free basis. M. —Middle, U. — Upper.

Table 7: Maturity indices calculated from distribution of phenanthrene and dibenzothiophene, and their methyl derivatives in bitumens from Jurassic and Cretaceous strata.

Well	Depth (m)	Stratigraphy	MPI1	MPR	MPR1	R <sub>cal</sub> (%)	R <sub>cal(MPR)</sub> (%)	MDR	R <sub>cal(DBT)</sub> (%)	T <sub>max(DBT)</sub> (°C)
Polish part										
Księżpol 18	869.6	M. Jurassic	0.57	0.72	0.39	0.72	0.71	1.0	0.6	428
Lubliniec 4	730.4	M. Jurassic	0.55	0.58	0.34	0.70	0.60	1.1	0.6	429
Łukowa 2	731.8	M. Jurassic	0.70	0.61	0.35	0.79	0.63	0.3	0.5	425
Łukowa 4	982.5	M. Jurassic	0.66	0.58	0.36	0.77	0.65	0.5	0.5	425
Markowice 2	800.0	M. Jurassic	0.67	0.63	0.37	0.77	0.67	1.2	0.6	429
Markowice 2	902.8	M. Jurassic	0.79	0.89	0.44	0.84	0.83	1.2	0.6	429
Ukrainian part										
Bortyatyn 1	2846.0-2857.0	M. Jurassic	0.49	0.57	0.36	0.66	0.65	0.9	0.6	428
Chornokuntsi 1	2096.0-2102.0	M. Jurassic	0.49	0.50	0.34	0.66	0.60	0.8	0.6	427
Korolyn 6	3421.8-3429.7	M. Jurassic	0.63	0.88	0.43	0.75	0.79	1.8	0.6	432
Korolyn 6	3517.3-3523.0	M. Jurassic	0.79	0.99	0.46	0.84	0.87	2.0	0.7	433
Mosty 2	2360.3-2364.4	M. Jurassic	0.61	0.82	0.43	0.74	0.80	1.5	0.6	431
Mosty 2	2521.0-2529.0	M. Jurassic	0.47	0.39	0.30	0.65	0.52	0.6	0.6	426
Mosty 2	2543.0-2549.0	M. Jurassic	0.70	0.63	0.38	0.79	0.68	1.1	0.6	428
Podiltsi 1	3214.8-3221.0	M. Jurassic	0.72	0.67	0.38	0.80	0.69	1.2	0.6	429
Podiltsi 1	3316.0-3323.0	M. Jurassic	0.51	0.77	0.40	0.68	0.72	1.0	0.7	433
Korolyn 6	2144.0-2146.7	U. Jurassic	0.59	0.85	0.41	0.73	0.76	0.7	0.6	426
Korolyn 6	2293.0-2308.0	U. Jurassic	0.60	0.83	0.39	0.73	0.70	0.8	0.6	427
Lanivka 1	1590.0-1597.0	U. Jurassic	0.67	0.73	0.38	0.77	0.68	1.4	0.6	430
Moryanti 1	1848.2-1853.1	U. Jurassic	0.65	0.71	0.39	0.76	0.71	1.0	0.6	428
Mosty 1	1790.0-1800.0	U. Jurassic	0.57	0.66	0.39	0.71	0.71	1.1	0.6	429
Voloshcha 1	2659.0-2667.0	U. Jurassic	0.79	0.68	0.36	0.85	0.65	0.6	0.6	426
Voloshcha 1	2870.5-2880.0	U. Jurassic	0.44	0.40	0.31	0.64	0.54	0.4	0.5	425
Voloshcha 1	2903.7-2912.0	U. Jurassic	0.50	0.45	0.31	0.67	0.52	1.1	0.6	428
Voloshcha 1	2952.0-2959.0	U. Jurassic	0.49	0.65	0.39	0.66	0.71	1.7	0.6	431
Voloshcha 1	3126.0-3134.0	U. Jurassic	0.55	0.57	0.38	0.70	0.69	1.9	0.6	433
Verchany 1	1811.0-1825.3	U. Jurassic	0.83	0.89	0.43	0.87	0.81	1.0	0.6	428
Yuriyiv 1	2016.0-2025.0	U. Jurassic	0.56	0.58	0.38	0.70	0.69	1.1	0.6	429
Chornokuntsi 1	1866.0-1871.0	U. Jurassic?	0.40	0.68	0.30	0.61	0.50	0.5	0.5	426
Didushychi 2	1100.0-1108.0	U. Cretaceous	0.81	0.78	0.39	0.85	0.72	1.0	0.6	428
Didushychi 2	1706.0-1712.0	U. Cretaceous	0.81	0.68	0.35	0.86	0.63	0.6	0.6	426
Pivn. Girs'ke 1	1391.2-1405.2	U. Cretaceous	0.49	0.47	0.31	0.66	0.54	0.7	0.6	426
Pivn. Girs'ke 1	1405.0-1414.0	U. Cretaceous	0.52	0.55	0.34	0.68	0.60	0.3	0.5	424

 $\begin{array}{l} \mathbf{MPI1} = 1.5(2-\mathrm{MP}+3-\mathrm{MP})/(\mathrm{P}+1-\mathrm{MP}+9-\mathrm{MP}); \ \mathbf{P} & - \ \mathrm{phenanthrene}; \ \mathbf{MP} & - \ \mathrm{metylphenanthrene}; \ \mathbf{MPR} = 2-\mathrm{MP}/1-\mathrm{MP}; \ \mathbf{MPR1} = (2-\mathrm{MP}+3-\mathrm{MP})/(1-\mathrm{MP}+9-\mathrm{MP}+2-\mathrm{MP}+3-\mathrm{MP}); \ \mathbf{R}_{cal} = 0.60\mathrm{MPI1} + 0.37 \ \mathrm{for} \ \mathrm{MPR} < 2.65 \ (\mathrm{Radke} \ 1988); \ \mathbf{R}_{cal}(\mathrm{MPR}) = -0.166 + 2.242\mathrm{MPR1} \ (\mathrm{Kvalheim} \ \mathrm{et} \ \mathrm{al}. \ 1987); \ \mathbf{MDR} = 4-\mathrm{MDBT}/1-\mathrm{MDBT}; \ \mathbf{MDBT} & - \ \mathrm{metylphenanthrene}; \ \mathbf{MDR} = 0.51 + 0.073\mathrm{MDR}; \ \mathbf{Tmax}(\mathbf{DBT}) = 423 + 5.1\mathrm{MDR}; \ (\mathrm{Radke} \ \& \ \mathrm{Willsch} \ 1994); \ \mathbf{M} & - \ \mathrm{Middle}; \ \mathbf{U} & - \ \mathrm{Upper}. \end{array}$ 

Both the Middle and Upper Jurassic strata reveal different geochemical characterizations. The Middle Jurassic strata show relatively the best source rock parameters. This is particularly evident from the Polish part of the study area, where nearly all analysed samples meet the quantitative hydrocarbon sourcing criteria. In the Ukrainian part one can observe equally high TOC content and genetic potential, although in about 40 % of analysed samples TOC contents are below the threshold. Good quantitative sourcing characterization is reduced by low HI values, generally below 100 mg HC/g TOC. Organic matter in the Middle Jurassic strata is of mixed type, dominated by gas-prone Type III kerogen. The Rock-Eval  $T_{max}$  temperature together with the biomarker ratios and vitrinite reflectance indicate that the organic matter is immature. Hence, despite positive hydrocarbon sourcing properties, the Middle Jurassic sediments are mature enough to be the effective hydrocarbon source rocks only in the Ukrainian part of the study area.

Similar geochemical characteristics were found for the Upper Jurassic rocks in which highly variable TOC contents and genetic potential, very low medians and low hydrocarbon index were observed. This indicates that the Upper Jurassic strata are poor source rock although horizons with high TOC contents and high genetic potential may locally exist. The Middle Jurassic strata reveal the low thermal maturity, which makes them rather poor hydrocarbon source rocks except for some isolated horizons found in the vicinity of the Korolyn 6 and Chornokuntsi 1 wells where highly generative, high-sulphur Type IIS kerogen was recorded.

The overall assessment of both the Jurassic and Cretaceous rocks reveals that these are poor, ineffective hydrocarbon source rocks. Horizons capable of generating hydrocarbons contain Type IIS kerogen and occur only locally within the Upper Jurassic strata. In the Polish part of the Upper Jurassic basin this type of organic matter was not observed.

Acknowledgments: The research was undertaken as Project No. UKRAINE/193/2006 of the Ministry of Science and Higher Education carried out at the AGH University of Science and Technology in Kraków and at the Polish Geological Institute — National Research Institute in Warsaw in the years 2007-2010. Analytical work by Mr. Hieronim Zych and Mr. Tomasz Kowalski from the AGH University of Science and Technology in Kraków is gratefully acknowledged. The authors are indebted to Ms. Izabella Grotek from the Polish Geological Institute — National Research Institute in Warsaw for measurements of vitrinite reflectance and maceral composition. The authors want to express their sincere thanks to Tadeusz Peryt (Polish Geological Institute — National Research Institute), and to the anonymous reviewers for their valuable comments, which helped to prepare the final text.

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