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Petroleum potential of Middle Jurassic rocks in the basement of the Carpathian Foredeep (Ukraine) and oil-to-source correlation with oil in Upper Jurassic reservoirs

JOHANNES F. RAUBALL[1,✉], REINHARD F. SACHSENHOFER[1] and ACHIM BECHTEL[1]

[1]Chair of Petroleum Geology, Montanuniversitaet Leoben, 8700 Leoben, Austria; ✉johannes.rauball@gmail.com

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Abstract: Organic matter-rich Middle Jurassic rocks occur in the Mesozoic basement of the Carpathian Foredeep in Ukraine. Eighty-nine core samples from the Mosty-2, Korolyn-6 and Korolyn-2 wells as well as three oil samples from the Kokhanivka and Orkhovychi oil fields in the Kokhanivka Zone, were investigated. Bulk geochemical data as well as maceral analysis have been determined, and a subset of these samples, including all oil samples, have been investigated for biomarker composition. Middle Jurassic strata are rich in organic matter (average: 4.19 wt. %) and reach TOC contents of up to 14.98 wt. %. However, HI values are low, typically around 100 mg HC/g TOC, and only reach a maximum of 242 mg HC/g TOC, indicating dominance of gas-prone, Type III kerogen. T_{max} values as well as random vitrinite reflectance measurements for the Mosty-2 (434 °C; 0.69–0.71 % Rr), Korolyn-6 (443 °C; 0.78–0.82 % Rr) and Korolyn-2 (448 °C; 0.85–0.90 % Rr) wells indicate that thermal maturity increases with depth from marginally mature to mature, suggesting that hydrocarbon generation may have occurred. However, biomarker data suggests no genetic link between these rocks and Upper Jurassic oils, as C_{27}–C_{28}–C_{29} sterane distributions, Pr/Ph ratios, DBT/Phenanthrene ratios and isotope data display significant differences between the two. New geochemical data, along with published biomarker data on Upper Jurassic rocks and crude oils belonging to the same oil family as the Upper Jurassic oils in the Ukrainian Carpathians, showed that Upper Jurassic rocks from the Korolyn-6 well present a better fit and are the source for the analysed oils.

Keywords: Ukrainian Carpathians, Mesozoic basement, Kokhanivka Zone, oil-source correlation, organic geochemistry, kerogen type, maturity.

Introduction

The East Carpathian Foredeep overlies the western margin of the East European Platform and is partly overthrusted by the Eastern Carpathians (Oszczypko et al. 2006). It hosts about 120 gas fields with total reserves of 2373 MMboe (Boote et al. 2018). The gas is mainly of microbial origin (Kotarba & Koltun 2011), sourced from immature Neogene shales (Kosakowski et al. 2013), which accumulated in Miocene sandstones and in Mesozoic carbonate and sandstone reservoirs (Popadyuk et al. 2006; Boote et al. 2018).

Apart from a microbial gas system, small oil fields (e.g., Kokhanivka, Orkhovychi; see Fig. 1b for location) in the Ukrainian sector of the foredeep (Glushko 1968; Vul et al. 1998; Kurovets et al. 2011) provide evidence for another petroleum system. The oil is reservoired in Upper Jurassic and Upper Cretaceous carbonate rocks. A Middle Jurassic source rock (Kokhanivka Fm.) is tentatively assumed as the source for the above accumulations (e.g., Koltun et al. 1998; Kotarba & Koltun 2006). Alternatively, thin intervals within the Upper Jurassic succession may have generated the sulphur-rich oil (Kotarba et al. 2011; Kosakowski et al. 2012).

In Ukraine, geological and geochemical data regarding potential source rock intervals in the Mesozoic basement of the Carpathian Foredeep are limited (Koltun et al. 1998; Kotarba & Koltun 2006; Kosakowski et al. 2012; Sachsenhofer & Koltun 2012). Additional information on the petroleum generation potential of these intervals and their petroleum systems may contribute to further exploration success in this area. Therefore, the primary objective of the present study is to determine the vertical and lateral variability of the hydrocarbon potential of the Middle Jurassic succession, and to analyse the genetic relationship between the Middle Jurassic rocks and the oil accumulations in the Upper Jurassic reservoirs.

Additional data from Upper Jurassic source rocks from the Voloshcha-1 and Korolyn-6 wells in Ukraine (Kosakowski et al. 2012) as well as for oil samples from the Opaka-1 (Więcław 2011) and Lubaczow-157 (Curtis et al. 2004) wells were taken into consideration for oil-to-source correlation.

Geological setting

The Carpathian Foredeep developed as a peripheral foreland basin in front of the advancing Carpathian orogenic wedge during early and middle Miocene times (Oszczypko 2006; Oszczypko et al. 2006). A generalized lithostratigraphic column of the Paleozoic and Mesozoic basement of the Carpathian Foredeep in eastern Poland and Ukraine is provided in Fig. 2.

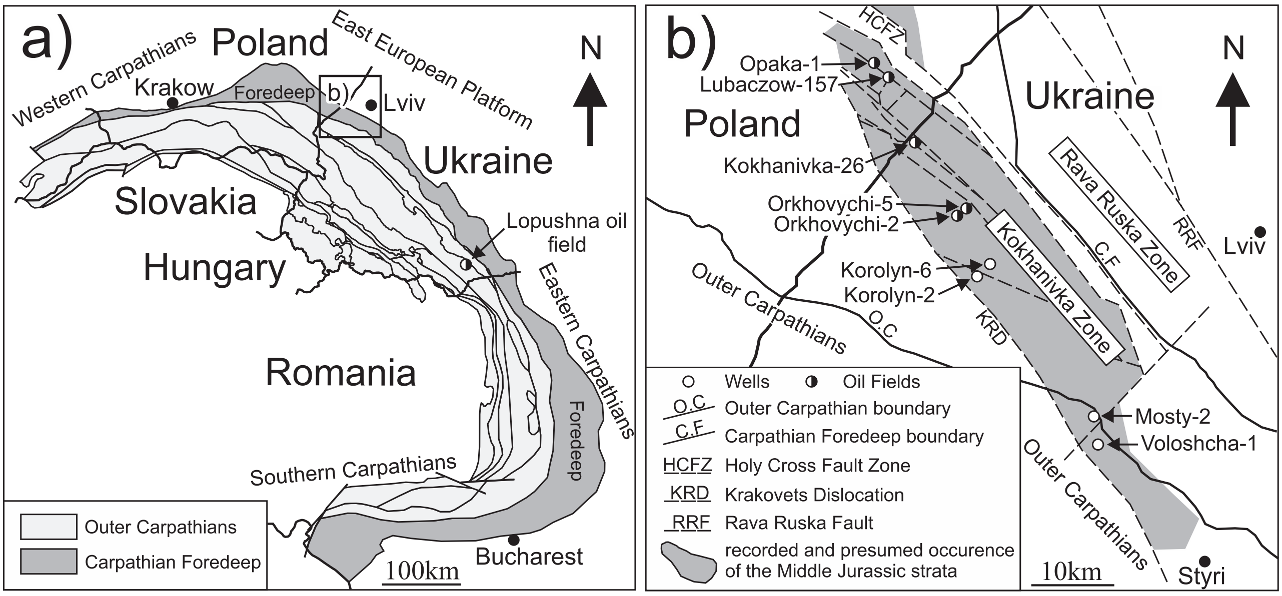

Fig. 1. a — Structural map of the Carpathian Fold-Thrust Belt and its foredeep basin (after Oszczypko et al. 2006; Slaczka et al. 2006; Nakapelyukh et al. 2018) showing the location of the study area in western Ukraine; **b** — Subcrop map of Middle Jurassic strata in the study area and the locations of the discussed wells (after Kosakowski et al. 2012).

The basement complex is traditionally referred to as the Kokhanivka and the Rava Ruska Zones in Ukraine (Fig. 1b), and as the Kielce Fold Belt and the Lysogory–Radom Block in Poland (Buła & Habryn 2011). The boundary between the Kokhanivka and the Rava Ruska Zones is formed by the Holy Cross Fault Zone. The south-western margin of the Kokhanivka Zone is formed by the Krakovets Dislocation (Fig. 1b). The Paleozoic strata include Cambrian, Ordovician and Silurian rocks (Drygant 2000; Buła & Habryn 2011; Jachowicz-Zdanowska 2011), partly with high TOC contents (e.g., Kotarba et al. 2011).

Jurassic rocks overlie the Paleozoic (Cambrian to Silurian) succession and comprise Lower–Middle Jurassic (Hettangian–Callovian) and Upper Jurassic–Lower Cretaceous (Oxfordian–Valanginian) sedimentary complexes (Kotarba et al. 2011). Lower Jurassic rocks are quartz arenite and mudstones with coal intercalations (Kurovets et al. 2011). The Middle Jurassic strata display variable thicknesses. In Poland Middle Jurassic sediments vary from dozens to several hundreds of metres, exceeding 100 m only in a few wells (Moryc 2004). In Ukraine, the Middle Jurassic complex in the Kokhanivka Zone shows a greater thickness and a more complete stratigraphic succession, as Middle Jurassic sediments reach up to 1000 m in thickness, likely due to deformations and tectonic repetition of sedimentary sequences. As a result, the true thickness of this sequence may only be in the order of hundreds of metres (Dulub et al. 1986, 2003; Moryc 2004; Swidrowska et al. 2008).

Middle Jurassic strata in the study area start with a sandstone-rich unit (e.g., Kurovets et al. 2011) grading upwards into organic matter-rich claystones and siltstones with scarce intercalations of sandstones (Fig. 2). This succession has been termed Kokhanivka Formation and ranges in age from Aalenian to Bathonian (Pieńkowski et al. 2008). The Kokhanivka Formation represents depositional systems varying from estuary/foreshore (lower part) to dysoxic shelf sediments. Sediments of a shallow carbonate–siliciclastic shelf accumulated during Callovian time (Javoriv Fm.; Pieńkowski et al. 2008) and have a much wider aerial extension than the underlying rocks. Dolomites and limestone with fossil remains, up to several centimetres thick, can be observed (Dulub et al. 2003).

The facies distribution during Late Jurassic/Early Cretaceous times has been described in detail by Gutowski et al. (2005a, b) and Krajewski et al. (2011). According to these authors, the south-western margin of the East European Platform was formed by a carbonate ramp (Oxfordian, lower Kimmeridgian) grading upwards into a rimmed platform (upper Kimmeridgian to Valanginian). Deep-water (marly) limestones overlain by a platform slope facies (Karolina Fm.) prevailed along the south-western margin of the Kokhanivka Zone near the Krakovets Fault (Anikeyeva & Zhabina 2002; Gutowski et al. 2005a; Krajewski et al. 2011). Carbonate buildups (Gutowski et al. 2005a, b) grading north-eastwards into an inner platform facies formed the platform margin facies. These shallow marine carbonates provide reservoir rocks for oil and gas fields in Ukraine (e.g., Kokhanivka, Orkhovychi) and Poland (e.g., Lubaczow) (Kotarba et al. 2011; Kurovets et al. 2011).

Lower and Upper Cretaceous rocks comprising siliciclastic and carbonate successions conclude the Mesozoic succession, but are often missing due to erosion. Miocene molasse-type sediments follow above the major erosional unconformity. Partly the platform was overridden by the Outer Carpathians (Fig. 1b).

Petroleum systems

The East Carpathian Foredeep is mainly a gas province and hosts a microbial gas system and a thermogenic oil system.

More than 40 gas fields have been detected in the Ukrainian sector of the Carpathian Foredeep (Boote et al. 2018). The microbial gas, sourced from immature Neogene shales (Kosakowski et al. 2013) is trapped both in karstified Jurassic and Cretaceous carbonate and sandstone reservoirs, as well as in the overlying Miocene (Sarmatian and Badenian) sandstones (Boote et al. 2018). Minor thermogenic gas and condensate is sourced from mature Neogene depocenters (Kotarba & Koltun 2011).

The thermogenic petroleum system produced small fields with heavy oil (Kokhanivka and Orkhovychi) near the Polish–Ukrainian border. The oil is reservoired in Upper Jurassic and Cretaceous carbonates (Glushko 1968; Vul et al. 1998; Kurovets et al. 2011). Reservoir rocks in Ukraine (e.g., Kokhanivka, Orhkchivy) and Poland (e.g., Opaka, Lubaczow) are provided by carbonate buildups and inner platform sediments (Kotarba et al. 2011). Kurovets et al. (2011) distinguished three main types of reservoir rocks: (i) Fractured low-permeable limestones with small inter-granular porosity; (ii) Organo-detrital limestones with high porosity (15–20 %) and permeability (up to $100 \cdot 10^{-3}$ μm²); (iii) Fractured pseudo-oolitic limestones with high porosity (20–30 %), but low permeability. The reservoir rocks are sealed by Miocene shales. Potential source rocks include black shales in the middle Jurassic Kokhanivka Formation (e.g., Koltun et al. 1998; Kotarba & Koltun 2006) or deep-water carbonate mudstones within the Upper Jurassic Karolina Formation (Kotarba et al. 2011; Kosakowski et al. 2012).

Although located outside the study area, the Lopushna oil field (Popadyuk et al. 2006) in the south-eastern part of the Ukrainian foreland autochthon, beneath the Carpathian flysch nappes (for location see Fig. 1a) deserves mention. Here oil occurs in Upper Jurassic, Cretaceous and Paleogene reservoirs. Jurassic source rocks are not present in the area. Therefore, and based on the presence of oleanane, Koltun et al. (1998) and Kotarba & Koltun (2006) assumed that the oil was generated from the Oligocene Menilite shales from the Carpathian flysch sequence (Radkovets et al. 2016).

Samples and methods

For this study, a total of eighty-nine core samples from the Mosty-2, Korolyn-6 and Korolyn-2 wells, as well as three oil samples from the Kokhanivka-26, Orkhovychi-2 and Orkhovychi-5 wells, were collected for analyses. Core samples from the Mosty-2, Korolyn-6 and Korolyn-2 wells were taken at similarly spaced intervals (where possible), spanning from the uppermost part of the available core, to its base. The studied sections only represent a portion of the Middle Jurassic succession as overlying and underlying core samples from the selected wells were not available or do not exist. Before

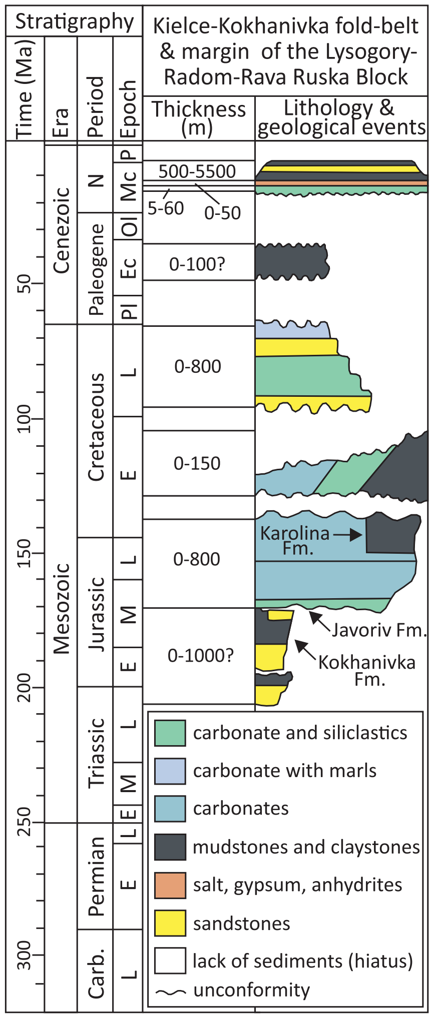

Fig. 2. Lithostratigraphic column of the pre-Miocene basement of the Carpathian Foredeep in the Ukrainian–Polish border region (after Kotarba et al. 2011).

laboratory analyses, all core samples were cleaned, dried and pulverized.

The core samples were analysed for their total carbon (TC), total sulphur (TS) and total organic carbon content (TOC) using an ELTRA Elemental Analyser. Samples measured for TOC were treated twice with 50 % phosphoric acid to remove inorganic carbon. Results are based on the averages of at least two corresponding measurements and are given in weight percent (wt. %). The total inorganic carbon (TIC) was determined by subtracting the TOC from the TC. TIC was then used to calculate the calcite equivalent percentages (=TIC*8.333).

Rock-Eval pyrolysis was carried out using a Rock-Eval 6 analyser in order to determine the S_1, S_2 (mg HC/g rock) and T_{max} for all core samples. S_1 determines the amount of hydrocarbons present in the rock, whereas S_2 determines the amount of hydrocarbons formed during pyrolysis. The petroleum potential (S_1+S_2 [mg HC/g rock]), the hydrogen index (HI=S_2/TOC*100 [mg HC/g TOC]) and the Production Index (S_1/[S_1+S_2]) were calculated using the S_1 and S_2 measurements.

T_{max} is a maturity parameter and indicates the temperature during Rock-Eval pyrolysis, at which the maximum amount of hydrocarbons can be generated (Espitalié et al. 1984). S_1, S_2 and T_{max} results are based on at least two measurements.

Based on the TOC contents and HI values, a total of 10 core samples were selected at similarly spaced intervals across the different wells, for biomarker analyses together with three oil samples. Rock samples were extracted in a Dionex ASE 200 accelerated solvent extractor using dichloromethane at 75° C and 50 bar for approximately 1 hour. Asphaltenes were precipitated from the solution using a hexane–dichloromethane solution (80:1) and then separated by centrifugation. The hexane-soluble fractions were separated into NSO compounds, saturated hydrocarbons and aromatic hydrocarbons using medium pressure liquid chromatography (MPLC) with a Köhnen–Willsch instrument (Radke et al. 1980). The saturated and aromatic hydrocarbon fractions were analysed by a gas chromatograph equipped with a 30 m DB-5MS fused silica column (i.d. 0.25 mm; 0.25 mm film thickness), coupled to a ThermoFischer ISQ Dual-quadrupole mass spectrometer. Using helium as the carrier gas, the oven temperature was set to increase from 70 °C to 300 °C at 4 $°C \cdot min^{-1}$, which was followed by an isothermal period of 15 min. With the injector temperature set to 275 °C, the sample was then injected with a split ratio of 10. The spectrometer was operated in the EI (electron ionization) mode over a scan range from m/z 50 to 650 (0.7 s total scan time). Data was processed using an Xcalibur data system where individual compounds were identified on the basis of retention time in the total ion current (TIC) chromatogram and by comparison of the mass spectra with published data. Percentages and absolute concentrations of various compound groups in the saturated and aromatic hydrocarbon fractions were calculated using peak areas from the gas chromatograms and their relations to the internal standards (deuterated *n*-tetracosane and 1,1'-binaphthyl, respectively). Concentrations were normalized to TOC.

The samples used for biomarker analysis were also selected for organic petrographic investigations (with the exception of two samples, where not enough material was available for further analysis). Some additional samples have been selected based on their TOC content. In total, 14 polished rock blocks were chosen and analysed using a single-scan method on approximately 1500 random distributed points per sample in white light and fluorescence (UV) mode (after Taylor et al. 1998). Depending on their origin, the macerals are divided into groups outlined by the International Committee for Coal Petrology (ICCP System 1998, 2001). For their maturity assessment, random vitrinite reflectance was measured in non-polarized light using a Leice DM4P microscope equipped with Hilgers FOSSIL MOT, with a 50× oil objective, following established procedures (after Taylor et al. 1998).

The MPI-1 was used to calculate vitrinite reflectance following the equation (Rc=0.60 MPI-1+0.40) proposed by Radke et al. (1982).

Results

Bulk parameters of organic matter and maceral composition

A summary of bulk parameters for the rocks from the Mosty-2, Korolyn-6 and Korolyn-2 wells are displayed in Fig. 3. Plots of hydrogen index (HI) versus T_{max} are shown in Fig. 4.

The Middle Jurassic section in well Mosty-2 ranges from 2268 to 2559 m. The studied samples cover the depth interval from 2361 to 2560 m. Carbonate contents are typically low (<2 wt. %), but reach 43 wt. % in marly sediments at 2512 and 2513 m depth. TOC contents range between 1.16 and 14.98 wt. % (average: 3.93 wt. %) and are especially high between 2512 and 2525 m depth. HI values (36–242 mg HC/g TOC) are low and reach a maximum at 2518 m depth. T_{max} (432–440 °C; average 434 °C), and low Production Index (PI: 0.01–0.05) values show that the organic matter is immature, whereas vitrinite reflectance (0.69–0.71 % Rr; Table 1) measurements indicate early oil window maturity. Sulphur contents are low (≤1.0 wt. %). TOC/S ratios typical for marine sediments (~2.8; Berner & Raiswell 1984) are observed in shallow samples (2361–2364 m), but TOC/S ratios are often significantly higher (max. 69.2) in the organic matter rich interval.

In well Korolyn-6, the Middle Jurassic succession ranges from 3037 to 4060 m. The studied samples represent the depth interval between 3418 and 3642 m. In this interval carbonate contents vary between 0.6 and 32.2 wt. % and are slightly higher than in Mosty-2. Even though the Mosty-2 and Korolyn-6 wells both contain an interval with significantly higher carbonate content (>30 wt. %) than the remaining samples, it is unlikely that these intervals can be correlated, considering their distance. The rocks contain high amounts of organic matter (TOC: 2.68–5.75 wt. %; average: 4.18 wt. %) with low HI values (average: 105 mg HC/g TOC). Whereas TOC contents show little vertical variation, HI values are especially low between 3430 and 3437 m depth, an interval characterized by silty plant-bearing, carbonate-free sediments. T_{max} (432–440 °C; average 434 °C), vitrinite reflectance (0.78–0.82 % Rr; Table 1) and PI values (0.15–0.23) are higher than in Mosty-2 and indicate early oil window maturity. Sulphur contents are moderately high (0.20–3.08 wt. %) and TOC/S ratios typically range from 1.3 to 6.6, but are higher (max: 29.4) is some samples near the base and in the middle part of the studied section.

In well Korolyn-2, the Middle Jurassic strata was drilled between 3590 and 4212 m depth. Three depth intervals (3642–3652; 3696–3712; 3870–3996 m) were studied and contain rocks with low carbonate contents (0.6–13.9 wt. %). TOC contents are high (2.13–4.05 wt. %; average: 2.62 wt. %) in the upper intervals, but low (~0.1 wt. %) in the bright coloured deepest interval. HI values range from 55 to 105 mg HC/g TOC in the organic-rich intervals. T_{max} values (445–450 °C; average 448 °C) as well as vitrinite reflectance (0.85–0.90 % Rr) indicate that the organic matter is mature.

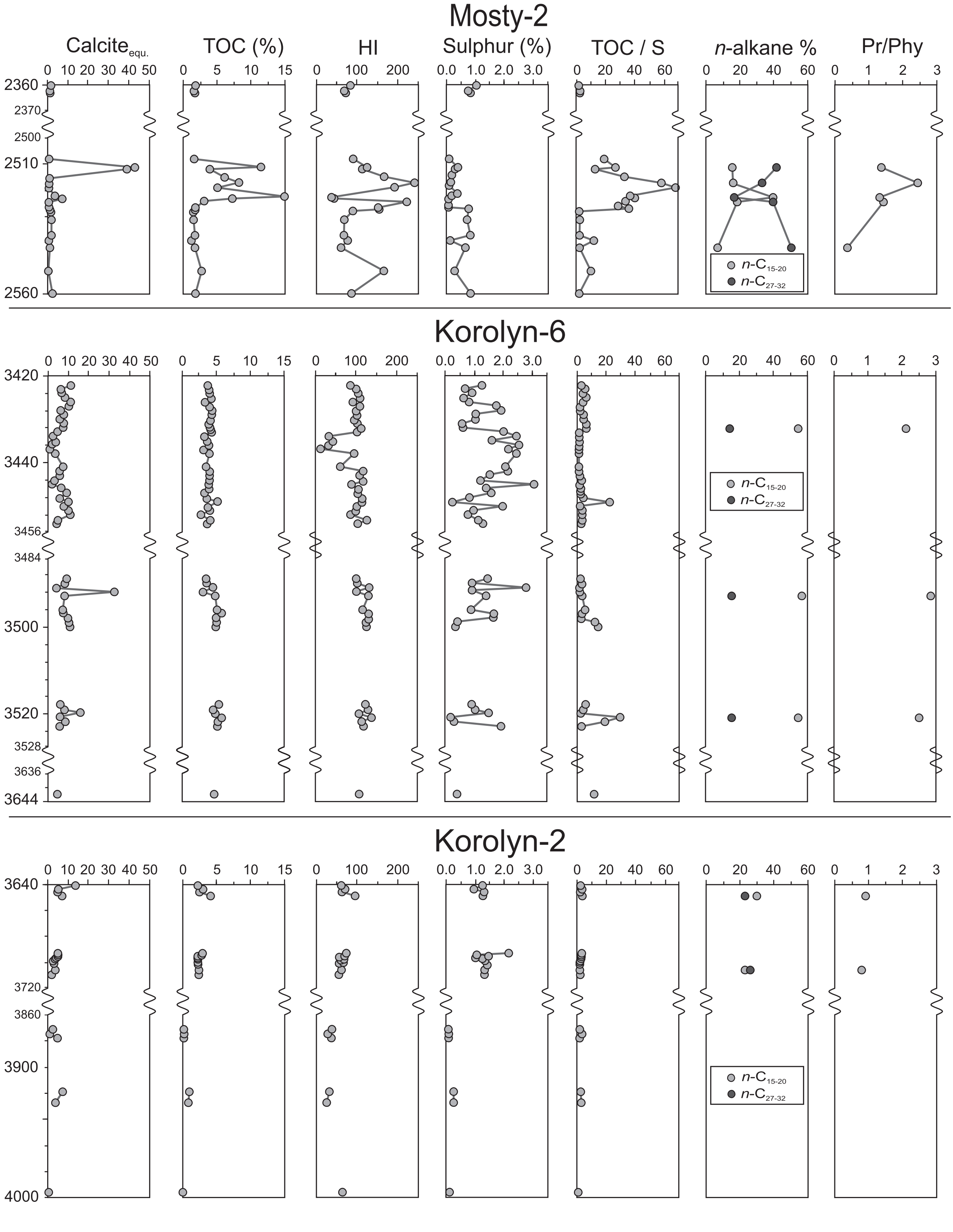

Fig. 3. Bulk geochemical data and important biomarker proxies versus depth for rocks from the Mosty-2, Korolyn-6 and Korolyn-2 wells.

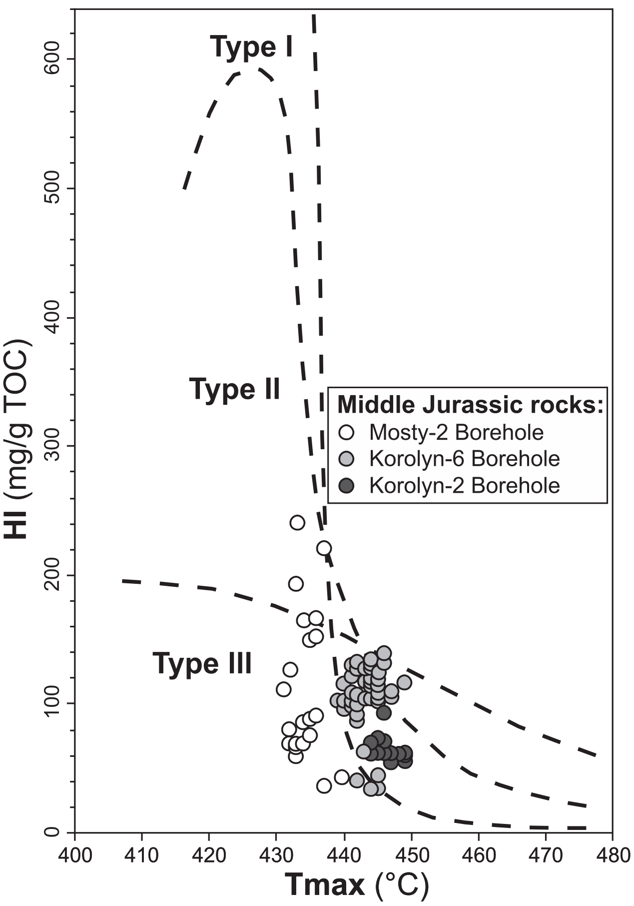

Fig. 4. Cross-plot of HI versus T_{max} (after Espitalié et al. 1984) for the rocks from the Mosty-2, Korolyn-6 and Korolyn-2 wells.

PI values (0.11–0.36) increase downwards and support oil window maturity.

Maceral assemblages (Table 1; Fig. 5) are similar in all studied samples and show a predominance of terrigenous maceral groups (detrovitrinite: 15–50 vol. %; inertinite: 7–49 vol. %; sporinite: 7–37 vol. %), whereas aquatic macerals (alginite: 14–46 vol. %) occur in variable amounts. Overall, slight differences are observed in the fluorescence colouring between the individual wells as the more mature rocks in Korolyn-6 and Korolyn-2 display darker and more red coloured liptinites, compared to the studied samples in Mosty-2 (Fig. 5). Despite the small sample-set, an attempt was made to correlate the HI values with the vitrinite and liptinite populations of the selected samples. However, these yielded inconclusive results as the data do not correlate.

The standard deviation for the random vitrinite reflectance measurements ranges from 0.07–0.13 and macerals were standardized to 100 % organic matter (% OM normalized; Table 1). In addition, the volume percentage of the mineral matrix (darker regions in the photomicrographs under white light; Fig. 5) and pyrite was determined, which allowed the calculation of the total maceral amount in comparison to the mineral matter (vol. %; Table 1).

Molecular composition of rock extracts

Geochemical data for Middle Jurassic rocks from the Mosty-2, Korolyn-6 and Korolyn-2 wells are listed in Table 2 and plotted versus depth in Fig. 3.

Yields of extractable organic matter (EOM) vary between 1.07–7.63 mg/g TOC. NSO compounds (29–59 % of the EOM) dominate in all samples, but asphaltene contents are elevated

Table 1: TOC, S, Calcite equ., HI, mean random vitrinite reflectance measurements and maceral composition for rocks from the Mosty-2, Korolyn-6 and Korolyn-2 wells. Depth — measured depth; TOC — total organic carbon; S — total sulphur; Calcite equ. — calcite equivalents; HI — Hydrogen Index; n# — measurements.

Depth	TOC	S	Calcite equ.	HI	Vitrinite		Standard	Vitrinite	Inertinite	Sporinite	Lamalginite	Telalginite	Maceral
[m]	[wt. %]			[mg/g TOC]	[% Rr]	n#	Deviation	[% OM normalized]					[vol. %]
Mosty-2													
2361	1.74	1.02	1.69	81	0.69	47	0.07	50	7	7	14	21	2.7
2512	11.57	0.42	42.68	126	*	*	*	19	49	16	10	5	15.7
2518	8.17	0.14	0.00	242	*	*	*	15	33	30	18	5	9.5
2525	3.25	0.09	0.07	221	*	*	*	30	8	33	23	8	5.5
2529	1.55	0.74	1.37	91	0.71	42	0.07	47	7	20	13	13	2.9
Korolyn-6													
3421	4.39	0.66	8.05	112	0.80	73	0.12	24	22	27	20	7	7.3
3428	4.07	0.63	7.40	116	*	*	*	27	8	37	19	10	7.3
3434	3.97	2.48	2.85	96	*	*	*	26	17	31	11	14	5.9
3445	5.20	0.24	9.62	117	0.82	68	0.13	27	19	24	14	16	6.6
3493	4.87	1.40	8.12	133	*	*	*	19	8	27	27	19	8.3
3521	5.75	0.20	6.23	141	0.78	74	0.13	26	14	26	17	17	7.7
Korolyn-2													
3652	4.05	1.25	7.34	93	0.85	70	0.11	33	25	21	13	8	4.2
3698	3.00	1.47	4.03	74	0.88	52	0.12	44	17	11	17	11	3.4
3708	2.48	1.30	3.41	61	0.90	50	0.11	26	21	21	11	21	3.4

in parts of the Mosty-2 well and both samples from the Korolyn-2 well.

***n*-alkanes and isoprenoids:** The carbon preference index (CPI) values (Bray & Evans 1961) are high in the Mosty-2 well (1.44–2.36), reflecting enhanced terrestrial input and low thermal maturity. CPI values for the deeper rocks (Korolyn-6: 1.20–1.27; Korolyn-2: 1.19–1.22) are lower. The relative amount of short-chain n-alkanes (n-$C_{15\text{-}20}$), which are typically derived from microbial organisms (Peters et al. 2007), depends on organic matter input and increases also with maturity. Hence, it is surprising that the highest relative amounts are present in the Korolyn-6 (n-$C_{15\text{-}20}$: 54–56 %) samples

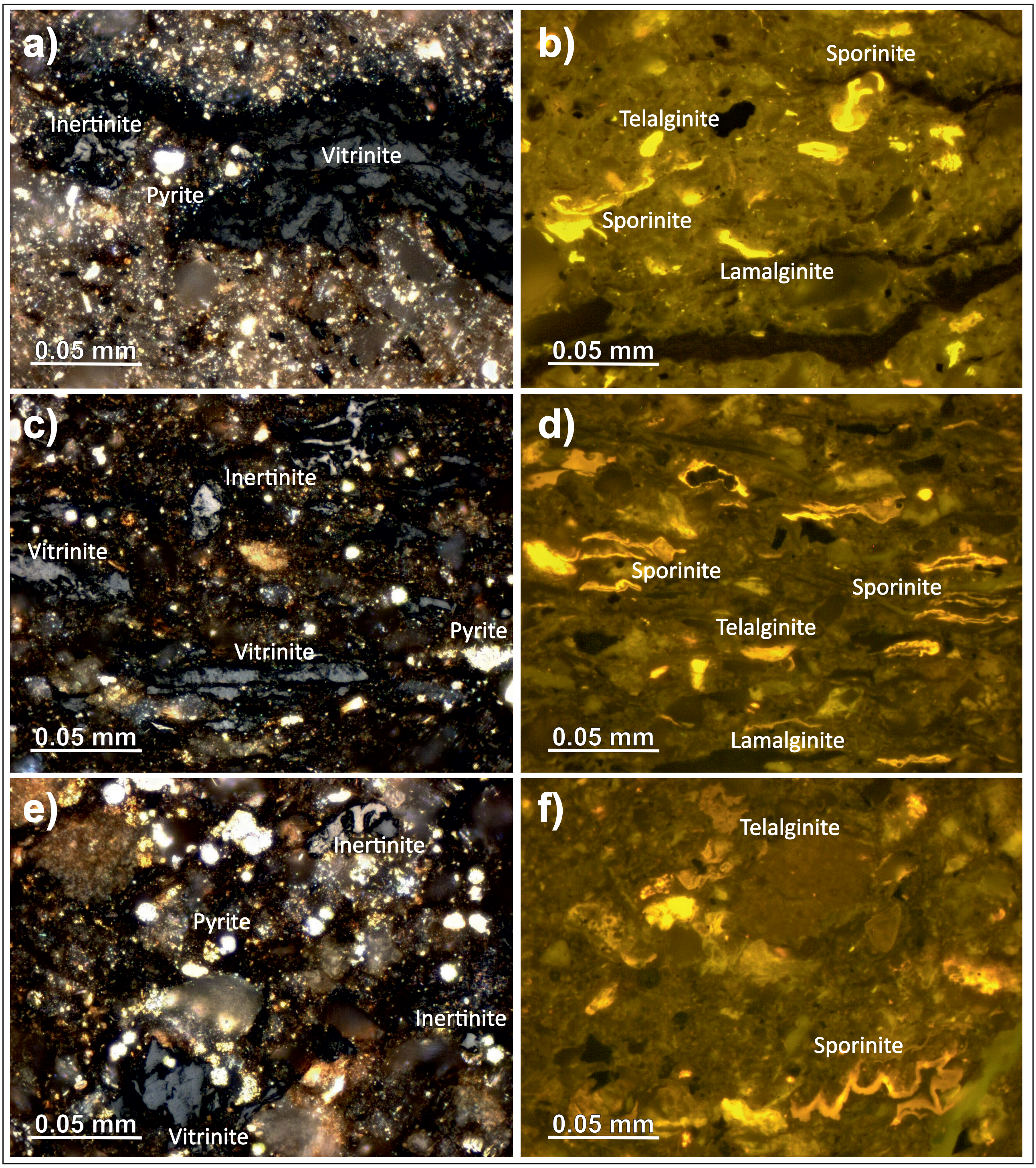

Fig. 5. Photomicrographs of samples from the Mosty-2 (**a**, **b**), Korolyn-6 (**c**, **d**) and Korolyn-2 (**e**, **f**) wells. **a, c, e** — Photomicrographs in white light showing inertinite, vitrinite and pyrite; **b, d, f** — photomicrographs in fluorescence mode illumination showing sporinite, lamalginite and telalginite.

Table 2: Organic geochemical data for rocks from the, Mosty-2, Korolyn-6, Korolyn-2 and Voloshcha-1 wells, as well as for oils from the Kokhanivka-26, Orkhovychi-5, Orkhovychi-2, Opaka-1 and Lubaczow-157 wells (*after Kosakowski et al. 2012; **after Więcław 2011; ***after Curtis et al. 2004).

Depth	TOC	HI	EOM	Sat. HC	Aro. HC	NSO	Asph.	$n\text{-}C_{15\text{-}20}/n\text{-}C_{15\text{-}32}$	$n\text{-}C_{21\text{-}26}/n\text{-}C_{15\text{-}32}$	$n\text{-}C_{27\text{-}32}/n\text{-}C_{15\text{-}32}$	Pr/Ph	Ts/Tm	DBT/ Phen	CPI	MPI-1	Sterane/ Hopanes	Moretane/ Hopanes	20S/ (20S+20R) C_{29} Steranes	ββ/(ββ+αα) C_{29} Steranes	22S/(S+R) C_{31} Hopanes	Diterpenoids	Steranes	Hopanes
[m]	[wt. %]	[mg/g TOC]	[μg/g TOC]	[wt. %]																	[μg/g TOC]		
Mosty-2	**Source rocks**																						
2512	11.57	126	4.43	0.04	0.09	0.59	0.29	0.15	0.43	0.42	1.42	0.03	0.12	1.97	0.46	0.21	0.42	0.29	0.41	0.54	4.20	0.08	0.36
2518	8.17	242	7.63	0.06	0.07	0.29	0.59	0.16	0.51	0.33	2.46	0.01	0.41	2.36	0.48	0.08	0.55	0.25	0.37	0.59	7.86	0.36	4.79
2523	14.98	36	1.07	0.08	0.13	n.d	0.80	0.40	0.43	0.17	1.33	0.11	0.13	1.44	0.43	0.55	0.28	0.16	0.30	0.57	7.26	0.20	0.36
2525	3.25	221	3.15	0.10	0.09	0.44	0.36	0.18	0.42	0.40	1.47	0.01	0.26	1.80	0.60	0.10	0.48	0.27	0.32	0.59	7.84	0.35	3.49
2543	1.69	60	3.55	0.04	0.04	0.35	0.57	0.06	0.44	0.50	0.30	0.01	0.10	1.90	0.64	0.10	0.51	0.21	0.41	0.56	37.51	0.50	5.00
Korolyn-6																							
3428	4.07	116	4.82	0.41	0.32	n.d	0.27	0.54	0.33	0.13	2.12	0.04	0.11	1.27	0.42	0.59	0.24	0.08	0.30	0.58	7.48	2.71	4.61
3493	4.87	133	5.61	0.23	0.46	n.d	0.31	0.56	0.30	0.14	2.84	0.03	0.09	1.26	0.44	0.31	0.21	0.11	0.33	0.60	3.80	0.56	1.80
3521	5.75	141	5.79	0.34	0.36	n.d	0.29	0.54	0.32	0.14	2.49	0.03	0.11	1.20	0.47	0.23	0.18	0.12	0.38	0.60	3.36	0.49	2.13
Korolyn-2																							
3652	4.05	93	5.32	0.07	0.08	0.34	0.52	0.30	0.47	0.23	0.94	0.04	0.02	1.19	0.54	0.13	0.16	0.43	0.63	0.61	12.41	0.32	2.50
3708	2.48	61	2.17	0.07	0.09	0.29	0.55	0.23	0.51	0.26	0.83	0.05	0.01	1.22	0.79	0.14	0.21	0.39	0.58	0.56	2.29	0.13	0.92
Korolyn-6*																							
2144-2147	n.a	n.a	n.a	0.05	0.22	0.16	0.57	n.a	n.a	n.a	0.33	0.19	n.a	0.93	0.59	n.a	0.08	n.a	n.a	0.52	n.a	n.a	n.a
2293-2308	n.a	n.a	n.a	0.08	0.23	0.30	0.39	n.a	n.a	n.a	0.35	0.08	n.a	0.97	0.60	n.a	0.09	n.a	n.a	0.57	n.a	n.a	n.a
Voloshcha-1*																							
2659-2667	n.a	n.a	n.a	0.08	0.15	0.32	0.45	n.a	n.a	n.a	n.a	0.30	n.a	n.a	n.a	n.a	0.54	n.a	n.a	0.47	n.a	n.a	n.a
2870-2880	n.a	n.a	n.a	0.03	0.09	0.26	0.62	n.a	n.a	n.a	n.a	0.19	n.a	n.a	n.a	n.a	0.44	n.a	n.a	0.54	n.a	n.a	n.a
2904-2912	n.a	n.a	n.a	0.04	0.16	0.33	0.47	n.a	n.a	n.a	n.a	0.12	n.a	n.a	n.a	n.a	0.45	n.a	n.a	0.54	n.a	n.a	n.a
2952-2959	n.a	n.a	n.a	0.02	0.17	0.25	0.56	n.a	n.a	n.a	n.a	0.29	n.a	n.a	n.a	n.a	0.47	n.a	n.a	0.52	n.a	n.a	n.a
3126-3134	n.a	n.a	n.a	0.04	0.14	0.26	0.56	n.a	n.a	n.a	n.a	0.11	n.a	n.a	n.a	n.a	0.41	n.a	n.a	0.55	n.a	n.a	n.a
Kokhanivka-26		**Oils**			[wt. %]																[μg/g Oil]		
n.a	n.a	n.a	n.a	0.09	0.19	0.50	0.22	0.46	0.30	0.12	0.54	0.16	2.76	0.96	0.46	0.54	0.08	0.47	0.67	0.59	7.11	344.60	634.31
Orkhovchi-2																							
n.a	n.a	n.a	n.a	0.11	0.20	0.50	0.19	0.44	0.31	0.11	0.29	0.14	2.91	0.96	0.52	0.50	0.07	0.44	0.69	0.61	8.58	357.77	718.74
Orkhovchi-5																							
n.a	n.a	n.a	n.a	0.08	0.15	0.57	0.20	0.48	0.29	0.11	0.43	0.15	3.15	0.94	0.52	0.56	0.07	0.46	0.69	0.59	4.58	306.57	550.81
Opaka-1**																							
1007-1057	n.a	n.a	n.a	0.10	0.41	0.16	0.33	n.a	n.a	n.a	0.37	0.07	3.70	1.05	0.63	n.a	0.09	0.50	0.50	0.50	n.a	n.a	n.a
Lubaczow-157***																							
1075-1130	n.a	n.a	n.a	0.28	0.31	0.16	0.25	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	0.11	n.a	n.a	n.a	n.a	n.a	n.a

compared to the shallower Mosty-2 (n-C_{15-20}: 6–40 %) and the deep Korolyn-2 (n-C_{15-20}: 23–30 %) samples. Conversely, long-chain n-alkanes, which are characteristic of higher land plants (Peters et al. 2007), are higher in the Mosty-2 (n-C_{26-32}: 17–50 %) and the Korolyn-2 (n-C_{26-32}: 23–26 %) rocks compared to the Korolyn-6 samples.

The Pristane/phytane (Pr/Ph) ratio is commonly used as redox parameter (Peters et al. 2007). Pr/Ph ratio is elevated in the Mosty-2 (1.33–2.46) and Korolyn-6 (2.12–2.84) wells, except for one sample in Mosty-2 at 2542 m with a Pr/Ph ratio of 0.30. The ratios for the Korolyn-2 (0.83–0.94) samples is lower. Highly-branched isoprenoid (HBI) alkanes were not detected in quantifiable concentrations in any of the rocks.

Steroids: With one exception (Korolyn-6; 3428 m: 2.7 µg/g TOC), sterane concentrations are typically very low (<0.6 µg/g TOC; Table 2). Diasteranes/steranes ratio range from 0.13 to 0.44 and steranes/hopanes ratio range from 0.08 to 0.59.

The relative abundances of C_{27}–C_{28}–C_{29} steranes are dominated by the source input (Fig. 6). The ratio does not change significantly throughout the oil-generative window, so it is possible to distinguish crude oils from different source rocks (Huang & Meinschein 1979). The relative proportions of C_{29} steranes are dominant (32–60 %) over the C_{28} (17–34 %) and C_{27} steranes (17–34 %; Fig. 6).

The 20S/(20S+20R) C_{29}-sterane isomerization ratio and the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ ratio can be used as a thermal maturity parameter, as the ratios rise with increasing maturity (Seifert & Moldowan 1986). 20S/(20S+20R) C_{29}-sterane isomerization ratios for the Mosty-2 (0.16–0.29) and Korolyn-6 (0.08–0.12) wells are lower, compared to the Korolyn-2 well (0.39–43). 20S/(20S+20R) C_{29}-sterane isomerization ratios observed in Korolyn-6 indicate thermal immaturity, which correspond to an approximately 0.5 % Ro (Callejon et al. 2003), which is lower than the measured vitrinite reflectance (ca. 0.8 % Rr). A similar trend is observed for the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ ratio (Mosty-2: 0.30–0.41; Korolyn-6: 0.30–0.38; Korolyn-2: 0.58–0.63).

Terpenoids: Hopanes are non-aromatic cyclic triterpenoids, which originate from precursors in bacterial membranes (Ourisson et al. 1979). Similar to sterane concentrations, concentrations are low in the rock extracts (0.36–5.00 µg/g TOC; Table 2).

The trisnorneohopane/trisnorhopane (Ts/Tm) is a thermal maturity parameter, which can be lithology and facies dependent and decreases in carbonate environments (Moldowan & Fago 1986; Peters et al. 2007). For Middle Jurassic rocks, the Ts/Tm ratios are extremely low (0.01–0.11). However, since Ts/Tm ratios are extremely vulnerable and are heavily influenced by the source of the organic matter and the lithology, this parameter should be taken with caution.

The moretane/hopane ratio can also be used as a thermal maturity parameter as the ratio of moretane to their corresponding hopanes decreases with increasing thermal maturity, from approximately 0.8 in immature sediments, to about 0.15–0.05 in mature source rocks (Mackenzie et al. 1980; Seifert & Moldowan 1980). Moretane/hopane ratios for Mosty-2 samples (0.28–0.55) are higher than in deeper samples (Korolyn-6: 0.18–0.24; Korolyn-2: 0.16–0.21; Table 2).

A widely used maturity parameter is the C_{31} 22S/(22S+22R) homohopane ratio. The ratio increases from 0 to 0.6 at equilibrium during maturation (Seifert & Moldowan, 1980). Most of the samples yield values near the equilibrium (0.54–0.61; Peters et al. 2007).

The **dibenzothiophene/phenanthrene** (DBT/Phen) ratio reflects the availability of free H_2S in the water column (Hughes et al. 1995). DBT/Phen ratios for the rocks are low (≤0.41; Table 2).

The ***Methylphenanthrene Index (MPI-1)*** is a maturity parameter and can be used to calculate vitrinite reflectance (% Rc; Radke et al. 1980). The calculated % Rc values for the Mosty-2 (0.66–0.79 % Rc), Korolyn-6 (0.62–0.68 % Rc) and Korolyn-2 (0.73–0.90 % Rc) rocks suggest early to peak oil window maturity.

Land-plant related biomarkers: Diterpenoids (e.g., cadalene, retene), which are gymnosperm-derived biomarkers (Wakeham et al. 1980; Simoneit 1986; Alexander et al. 1988), were encountered in all rocks (3.36 to 37.51 µg/g TOC; Table 2). Considering their Jurassic age, it is not surprising that pentacyclic non-hopanoid triterpenoids (incl. oleanane) were not detected in any of the studied samples.

Compound specific isotope analysis (CSIA) of individual n-alkanes can be used as a tool to

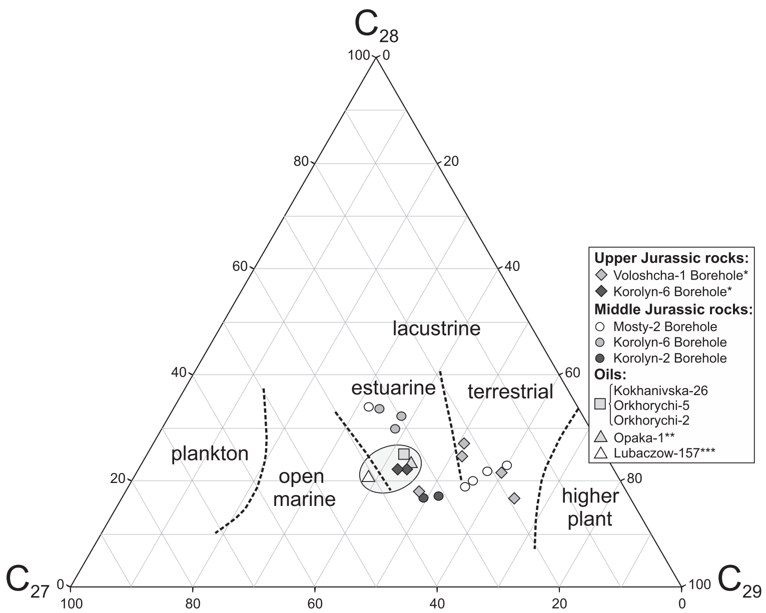

Fig. 6. Ternary diagram of regular steranes (C_{27}–C_{29}) showing the relationship between sterane compositions for rocks from the Voloshcha-1, Korolyn-6, Mosty-2, Korolyn-6 and Korolyn-2 wells, as well as oils from Kokhanivka-26, Orkhovychi-5, Orkhovychi-2, Opaka-1 and Lubaczow-157 wells (*after Kosakowski et al. 2012; **after Więcław 2011; ***after Curtis et al. 2004).

determine oil-source correlations, as the depositional setting of the source rock influences the shape of the *n*-alkane isotopic signature (Bechtel et al. 2012). Carbon isotope ratios of *n*-alkanes derived from Mosty-2 and Korolyn-6 samples range from −29 to −26 ‰. There is no distinct trend with chain length visible (Fig. 7).

Oil samples

Geochemical data for the oil samples from the Kokhanivka-26, Orkhovychi-2 and the Orkhovychi-5 wells are listed in Table 2. NSO compounds (50–57 %) dominate in all oil samples. Biodegradation was not observed in any of the studied samples (Fig. 8).

n-alkanes and isoprenoids: Oil samples are dominated by short-chain (44–48 %; Fig. 8) and mid-chain *n*-alkanes (29–31 %). Long-chain *n*-alkanes are rare (11–12 %) and show CPI values (Bray & Evans 1961) near unity. Pr/Ph ratios are very low (0.29–0.54). HBI alkanes were not detected in quantifiable concentrations.

Steroids: Sterane concentrations range from 300 to 350 µg/g oil; Table 2). Steranes/hopanes ratios are rather uniform (0.50–0.56) and diasteranes/steranes ratios are extremely low (0.01). C_{29} steranes (38–48 %) are slightly more abundant than C_{27} (33–41 %) and C_{28} (21–27 %; Fig. 6) steranes. 20S/(20S+20R) sterane isomerization ratios (0.44–0.47) and the $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ ratio (0.67–0.69) agree with oil window maturity.

Terpenoids: Concentrations of hopanes in oil samples ranges from 550–720 µg/g oil; Table 2. The Ts/Tm is extremely low for the oil samples (0.07–0.16). The moretane/hopane ratios of oil samples are close to the equilibrium values of 0.6 (Seifert & Moldowan 1980).

The **DBT/Phen** ratios of oil samples are significantly higher (2.76–3.70) compared to the studied rock samples.

Based on **MPI-1**, the oil samples were generated at oil window maturity (Kokhanivka-26: 0.68 % Rc; Orkhovychi-5: 0.71 % Rc; Orkhovychi-2: 0.71 % Rc).

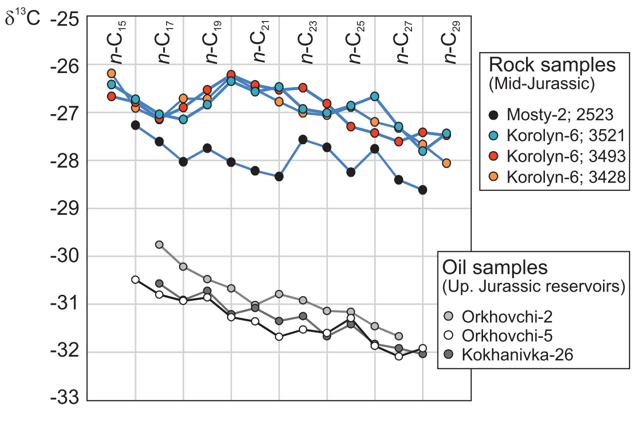

Fig. 7. Carbon isotopic composition of individual *n*-alkanes and acyclic isoprenoids in rock extracts and oil samples.

Land-plant related biomarkers: Gymnosperm-derived deterpenoids (Wakeham et al. 1980, Simoneit 1986; Alexander et al. 1988), were encountered in significant concentrations (4.58 to 7.11 µg/g TOC; Table 2), whereas oleanane was not detected (Fig. 8).

CSIA: δ^{13}C values of *n*-alkanes range from −31.9 to −29.8 ‰, showing that oil samples are isotopically lighter than the studied rock samples (Fig. 7).

Discussion

Middle Jurassic rocks

Maturity

T_{max} values as well as vitrinite reflectance measurements (% Rr) indicate that thermal maturity in the studied Middle Jurassic sample-set increases with depth of burial from immature to peak oil window maturity (Fig. 9). PI values also increase with depth and reach a value of 0.1, which is often considered as the top of the oil generating zone (e.g., Peters 1986), at approximately 3500 m depth.

In general, the fluoresecence colouring of the liptinite (sporinite, lamalginite and telalginite) macerals differs between the individual wells, and is consistent with their maturities. The more mature rocks in Korolyn-6 and Korolyn-2 typically display darker and more red coloured liptinites (sporinite, lamalginite and telalginite), compared to the rocks observed in Mosty-2, suggesting higher maturities (Fig. 5). It should be noted that in some cases the re-working of sediments may influence colouring, however, to our knowledge, this was not the case for any of the analysed samples.

Biomarker ratios are in general agreement with the thermal maturity trend suggested by Rock-Eval data. For example, average CPI values decrease from 1.89 in Mosty-2 to 1.24 in Korolyn-6 and 1.21 in Korolyn-2. Moretane/hopane ratios decrease in the same direction from 0.45 (Mosty-2) to 0.21 (Korolyn-6) and 0.18 (Korolyn-2). However, plots of 20S/(20S+20R) versus Ts/Tm and $\beta\beta/(\beta\beta+\alpha\alpha)$ for the C_{29} steranes (Fig. 10), shows that sterane-based maturity parameters pretend a lower maturity for Korolyn-6 samples compared to the shallower, immature Mosty-2 samples. Probably this discrepancy reflects a facies influence on sterane proxies. Within this context, it is worth noting that rocks from the Korolyn-6 well typically contain higher sulphur contents than those from Mosty-2 and Korolyn-2. However, low DBT/Phen ratios show that organic sulphur contents are probably low.

C_{31} 22S/(22S+22R) homohopane ratios are similar and near the equilibrium value and do not contribute to the maturity assessment. MPI-1 ratios and calculated Rc values for the Mosty-2 (average: 0.71 % Rc; Table 2) and Korolyn-2 (average: 0.82 % Rc; Table 2) are in line or slightly below the vitrinite reflectance measurements for these wells (0.69–0.71 % Rr and 0.85–0.90 % Rr, respectively). In contrast, similar to sterane isomerization, the MPI-derived vitrinite

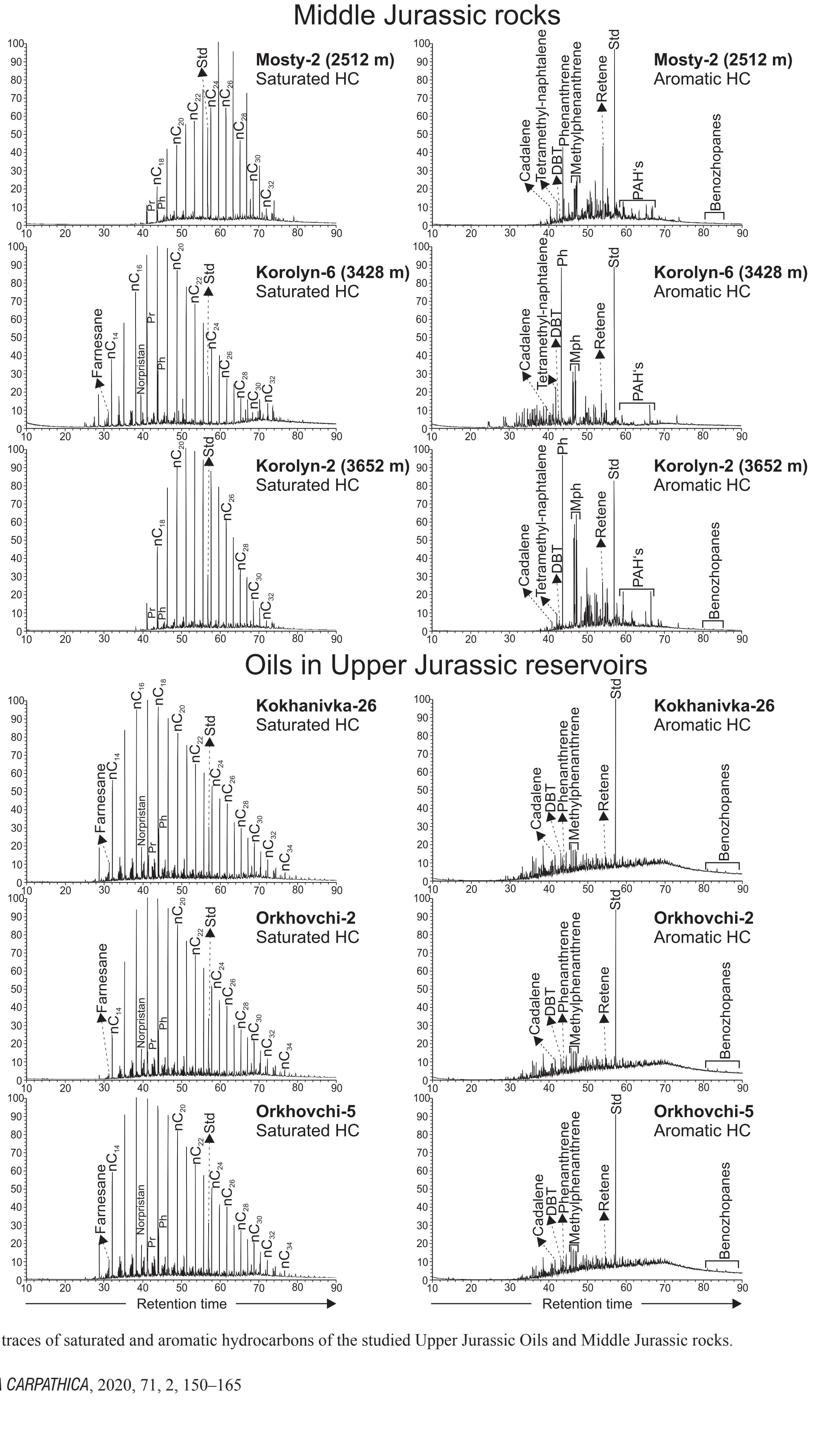

Fig. 8. Ion traces of saturated and aromatic hydrocarbons of the studied Upper Jurassic Oils and Middle Jurassic rocks.

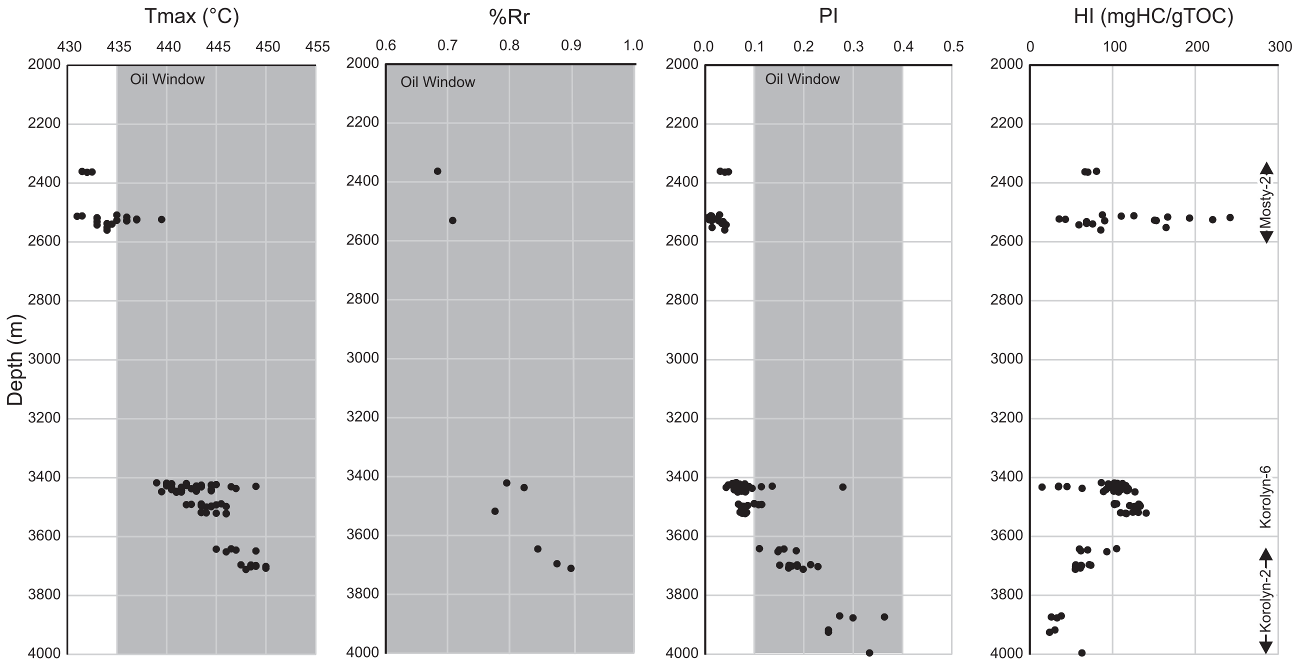

Fig. 9. Depth plot of T_{max}, Production Index (PI), Hydrogen Index (HI) and Vitrinite reflectance (% Rr) measurements for Middle Jurassic rocks in Mosty-2, Korolyn-6 and Korolyn-2 wells.

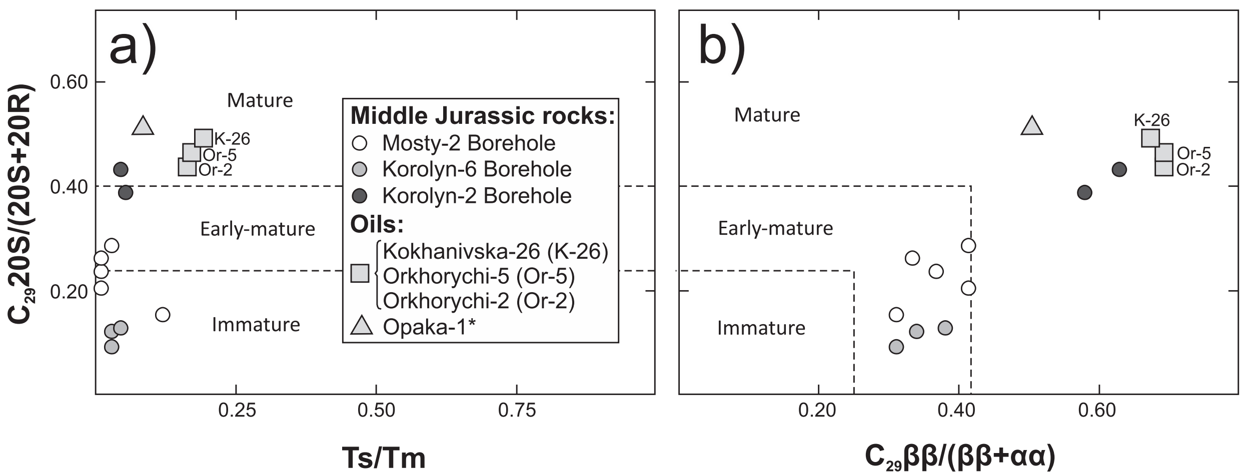

Fig. 10. Plots of Sterane C_{29} 20S/(20S+20R) versus Ts/Tm and ββ/(ββ+αα) (after Peters et al. 2007) for Middle Jurassic rocks and oil samples from Upper Jurassic carbonate reservoirs.

reflectance value in Korolyn-6 (average: 0.66 % Rc; Table 2) is significantly lower than the measured value (ca. 0.80 % Rr).

Hydrocarbon potential

Differences in thermal maturity have to be considered when assessing the hydrocarbon potential. The original potential can be determined for Mosty-2 samples, whereas the hydrocarbon potential of Korolyn-6 rocks may be slightly lower, and that of Korolyn-2 rocks significantly reduced due to advanced maturity. A decrease in HI for Korolyn-2 rocks is clearly evident in Fig. 9. However, a downward increase in HI is observed in the lowermost sample (3996 m), likely due to extremely low TOC and S2 values. Hence only a remaining petroleum potential can be determined for Korolyn-2.

Irrespective of maturity, TOC contents for the Mosty-2, Korolyn-6 and Korolyn-2 rocks are high (Fig. 3) and average 3.93, 4.17, and 2.75 wt. %, respectively. Low TOC contents are observed only in Middle Jurassic rocks between 3870 and 3996 m depth in Korolyn-2 (max. 0.13 wt. %). HI values of immature to marginally mature samples in the Mosty-2 (average 112; max. 242 mg HC/g TOC) and Korolyn-6 (average

105 mg HC/g TOC) wells show the presence of type III kerogen, which is also supported by a strong predominance of terrigenous macerals.

A cross-plot of Rock-Eval S_1+S_2 (petroleum potential) versus TOC (Fig. 11) indicates strongly varying source potential for Mosty-2 samples ranging from poor to good. A fair to good source potential is also visible for Korolyn-6 samples, however, the original potential of rocks from this well may have been slightly higher. In contrast, the poor (remaining) potential of the Korolyn-2 samples is clearly a result of their higher maturity.

Oil samples: Thermal maturity and implications for source rocks

The three studied oil samples are from Upper Jurassic reservoirs in the Kokhanivka Zone in Ukraine. Two nearby oil samples from the extension of this zone in Poland (Lubaczow-157; Opaka-1) have been studied by Curtis et al. (2004) and Więcław (2011) and are included in this discussion. Well locations are shown in Fig. 1b and available data is listed in Table 2.

The MPI-1 (Table 2) values for the Kokhanivka-26 (0.68 % Rc), Orkhovychi-2 (0.71 % Rc), Orkhovychi-5 (0.71 % Rc) and Opaka-1 (0.78 % Rc) wells indicate early oil window maturity. In contrast, moretane/hopane ratios (0.07–0.08), C_{31} 22S/(22S+22R) homohopane ratios (~0.6), CPI values (0.94–0.96) as well as the 20S/(20S+20R) versus ββ/(ββ+αα) for the C_{29} steranes and Ts/Tm (Fig. 10) suggest peak oil maturity.

Pr/Ph ratios are very low (0.29–0.54; Table 2) indicating strongly oxygen-depleted conditions during deposition of the rocks. Very high DBT/Phen ratios (Table 2) indicate that free H_2S was elevated in the water column. On a cross-plot of Pr/Ph vs. DBT/Phen (Fig. 12b; Hughes et al. 1995), the studied oils plot in Zone 1 (A and B sub-zones), which denotes a marine carbonate depositional environment. This is further supported by very low diasteranes/steranes ratios observed in the oil samples, as well as the low CPI (<1). In addition, distributions of *n*-alkanes in the crude oil samples display a maximum in short-chain hydrocarbons (Table 2), reflecting hydrocarbons generated from marine organic matter (Peters et al. 2007), which was deposited in a carbonate-rich environment. Since oleanane was not detected in any of the oils, the age of the source rock most probably is Jurassic or older. However, it is important to consider that the absence of oleanane does not always necessary indicate pre-Cretaceous source rocks.

Elevated asphaltene content (Table 2) in the analysed oil samples, generally around 20 wt. % (max: 33 wt. %), is higher than in oils from the Outer Carpathians (Boryslav–Pokuttya Unit; Więcław et al. 2012). Więcław et al. (2012) used this fact as an indication for short-distance migration and postulated that the source rock is in close proximity to the reservoir rocks.

Oil-source correlation

An important aspect of the study was to correlate oils within Upper Jurassic reservoirs with the potential Middle Jurassic source rocks (Kokhanivka Fm.). However, because biomarker and isotope data are not compatible with a genetic link between the oils and the Middle Jurassic rocks (see below), data from Upper Jurassic source rocks (Kosakowski et al. 2012) are also taken into account.

The main arguments against a genetic link between accumulated oils and the Middle Jurassic rocks are derived from plots of DBT/Phenathrene ratios versus pristane/phytane ratios (Fig. 12b). DBT/Phenanthrene ratios are very high for the oil samples compared to the Middle Jurassic rocks. The mismatch is also evident in plots of pristane/nC_{17} vs. phytane/nC_{18} ratios (Fig. 12a), isotopic signatures (Fig. 7) and in differing sterane distributions (Fig. 6).

This shows that the studied section of the Middle Jurassic Kokhanivka Formation is not the source rock for the accumulated oil. Hence an alternative solution has to be found.

According to Kosakowski et al. (2012), the TOC contents in Upper Jurassic rocks from the study area are usually low (median: 0.08 wt. %), but samples from the Voloshcha-1 and Korolyn-6 (for location see Fig. 1b; for selected data, see Table 2) wells contain high amounts of organic matter. TOC values in samples between 2650 and 3300 m depth from

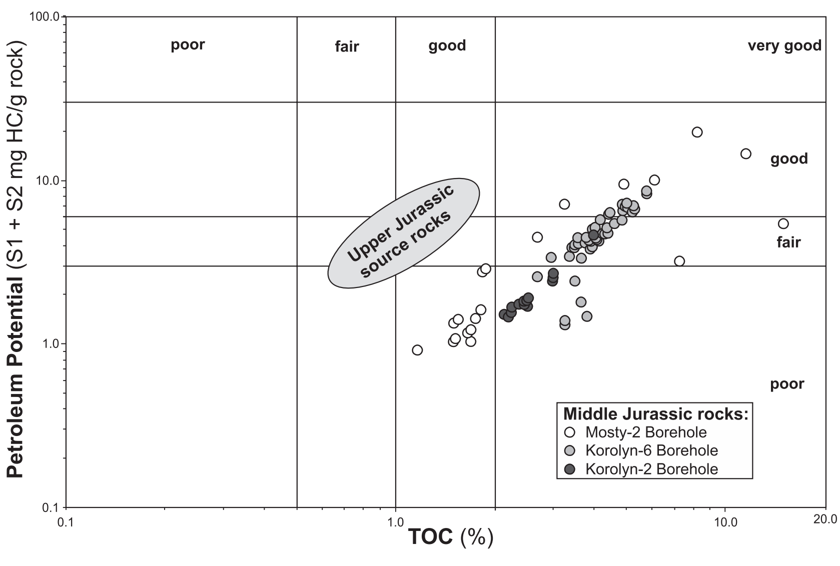

Fig. 11. Petroleum potential vs. TOC for the rocks from the Mosty-2, Korolyn-6 and Korolyn-2 wells. Grey field represents Upper Jurassic source rocks after Kosakowski et al. (2012).

the Voloshcha-1 well displayed average TOC content of over 1 wt. % (max: 12.1 wt. %), but low HI values (~100 mg HC/g TOC), indicating the presence of type III kerogen, which is also supported by maceral data and high CPI values (Kosakowski et al. 2012).

In contrast, Upper Jurassic rocks from the Korolyn-6 well (1973–3037 m depth) contain layers with very high HI (max: 557 mg HC/g TOC), but moderately high TOC (max. 1.5 wt. %; Kosakowski et al. 2012) in the depth interval between 2140 and 2500 m, which can be considered as having a fair to good hydrocarbon potential (Fig. 11). High organic sulphur contents classify the kerogen as type IIS (Kosakowski et al. 2012), which may generate hydrocarbons below the typical limits of the oil window. The potential source rocks are also compatible with the high DBT/Phenanthrene ratios detected in oil samples. Furthermore, two Upper Jurassic samples from the Korolyn-6 well yield the best fit in the steranes triangular diagram with the oil samples (Fig. 6). Hence, it is very likely that the oil was generated from platform slope deposits preserved in the south-western part of the Kokhanivvka Zone in a narrow strip along the Krakovets Fault (Fig. 1b; Krajewski et al. 2011). This study, therefore, confirms earlier models published by Kotarba et al. (2011) and Kosakowski et al. (2012).

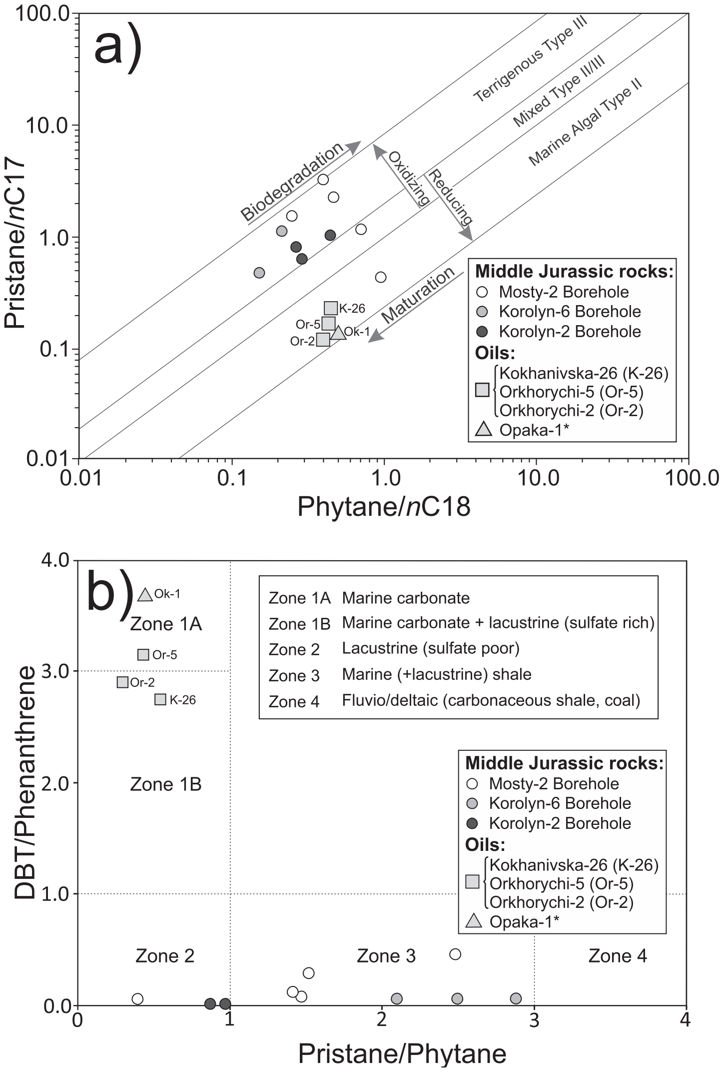

Fig. 12. a — Pristane/nC_{17} versus phytane/nC_{18} for rocks and oil samples after Peters et al. 2007. **b** — A cross-plot of the dibenzothiophene (DBT)/phenanthrene ratio versus the pristane/phytane ratio. Classification of source kerogen sedimentation conditions after Hughes et al. 1995. Data from Opaka-1 according to Więcław 2011.

Conclusion

The investigation of 89 samples representing the Middle Jurassic Kokhanivka Formation in the basement of the Ukrainian Carpathian Foredeep and of three oil samples from Upper Jurassic reservoirs yielded important insights into the petroleum system:

- Middle Jurassic rocks contain high organic matter contents (average TOC: 4.19 wt. %; max.: 14.98 wt. %). The organic matter is dominated by terrigenous macerals from a nearby hinterland. Therefore, HI values are generally low (max: 242 mg HC/g TOC), classifying the organic matter a gas-prone type III kerogen (with rare transitions to type II kerogen).
- Despite the high TOC contents, Middle Jurassic rocks can be considered “fair” source rocks. Based on the total petroleum potential (Rock-Eval S_1+S_2), only a few horizons display “good” source rock potential.
- As a consequence of the high terrestrial input, Pr/Ph ratios are often high (max: 2.84). DBT/Phen ratios for these rocks are generally low, arguing for an absence of salinity stratification of the water column.
- Thermal maturity of the Middle Jurassic rocks is mainly controlled by depth of burial. Mosty-2 samples (2361–2560 m depth) are marginally mature, whereas Korolyn-6 (3418–3523 m) and Korolyn-2 samples (3642–3996 m) reach peak oil window maturity. Major hydrocarbon generation started at about 3500 m depth.
- Oil samples derived from Upper Jurassic reservoir rocks are sulphur-rich and show very high DBT/Phen ratios. In contrast, Pr/Ph (<0.6) and diasterane/sterane (0.01) ratios are very low.
- Major differences in DBT/Phen ratios, Pr/Ph ratios and carbon isotope ratios between oil and rock samples clearly show that the oils have not been charged from Middle Jurassic rocks.
- A comparison with published data from Upper Jurassic rocks (Kosakowski et al. 2012) suggests that the oils have been generated from platform slope deposits preserved in a narrow strip along the south-western part of the Kokhanivvka Zone.

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Supplement

Table S1: Bulk geochemical data and depths for the Middle Jurassic rocks analysed from the Mosty-2 and Korolyn-2 wells.

Depth [m]	S_1 [mgHC/gRock]	S_2	T_{max} [°C]	**TOC** [%]	**S** [%]	**TOC/S** [–]	**HI** [mgHC/gTOC]	**PI** [–]	**TIC** [%]	**Calc. Equ.** [%]	**Biomarker**
Middle Jurassic rocks											
Mosty-2											
2361	0.05	1.41	432	1.74	1.02	1.70	81	0.03	0.20	1.69	
2363	0.05	1.00	433	1.50	0.71	2.11	67	0.05	0.18	1.49	
2364	0.05	1.20	432	1.70	0.78	2.17	70	0.04	0.15	1.28	
2509	0.04	1.32	435	1.50	0.08	19.02	88	0.03	0.00	0.01	
2512	0.18	14.56	432	11.57	0.42	27.59	126	0.01	5.12	42.68	x
2513	0.06	4.40	431	3.97	0.31	12.65	111	0.01	4.69	39.06	
2516	0.09	10.11	436	6.07	0.18	33.21	167	0.01	0.06	0.51	
2518	0.14	19.78	433	8.17	0.14	59.50	242	0.01	0.02	0.00	x
2520	0.08	9.55	433	4.95	0.07	69.17	193	0.01	0.02	0.00	
2523	0.13	5.33	437	14.98	0.41	36.53	36	0.02	0.45	3.73	x
2524	0.08	3.15	440	7.28	0.18	40.38	43	0.02	0.87	7.28	
2525	0.06	7.19	437	3.25	0.09	34.51	221	0.01	0.01	0.07	x
2527	0.04	2.77	435	1.83	0.06	30.02	151	0.01	0.03	0.26	
2528	0.04	2.88	436	1.88	0.05	36.56	153	0.01	0.01	0.00	
2529	0.04	1.40	436	1.55	0.74	2.09	91	0.03	0.16	1.37	
2532	0.04	1.05	433	1.53	0.73	2.10	69	0.04	0.16	1.35	
2538	0.04	1.14	434	1.65	0.83	1.98	69	0.03	0.20	1.64	
2540	0.04	0.89	435	1.16	0.10	12.18	76	0.04	0.02	0.13	
2543	0.05	1.01	433	1.69	0.67	2.52	60	0.04	0.11	0.92	x
2552	0.07	4.43	434	2.69	0.24	11.10	165	0.01	0.03	0.00	
2560	0.07	1.56	434	1.82	0.83	2.18	86	0.04	0.22	1.82	
Korolyn-2											
3643	0.26	1.34	445	2.23	1.22	1.82	60	0.16	1.67	13.90	
3646	0.37	2.09	447	2.98	0.93	3.22	70	0.15	0.65	5.43	
3649	0.36	1.57	449	2.53	1.31	1.93	62	0.18	0.55	4.60	
3652	0.66	3.78	446	4.05	1.25	3.25	93	0.15	0.88	7.34	x
3696	0.59	2.17	448	3.01	2.13	1.41	72	0.21	0.53	4.45	
3697	0.28	1.22	449	2.20	1.04	2.12	56	0.19	0.66	5.53	
3698	0.40	2.22	449	3.00	1.47	2.04	74	0.15	0.48	4.03	
3699	0.32	1.56	449	2.51	0.97	2.58	62	0.17	0.31	2.56	
3700	0.30	1.41	449	2.25	1.22	1.84	63	0.17	0.39	3.23	
3701	0.32	1.50	449	2.44	1.33	1.83	62	0.18	0.55	4.62	
3702	0.34	1.46	450	2.36	1.28	1.85	62	0.19	0.34	2.82	
3703	0.35	1.18	449	2.13	1.40	1.52	55	0.23	0.29	2.39	
3708	0.31	1.52	450	2.48	1.30	1.91	61	0.17	0.41	3.41	x
3712	0.35	1.39	448	2.51	1.30	1.93	55	0.20	0.25	2.08	
3870	0.02	0.04	n.d	0.10	0.06	1.81	38	0.27	0.31	2.56	
3874	0.02	0.04	n.d	0.13	0.06	2.22	26	0.36	0.12	0.97	
3877	0.02	0.04	n.d	0.11	0.06	1.92	33	0.30	0.54	4.53	
3918	0.01	0.03	n.d	0.10	0.06	1.63	31	0.25	0.84	7.01	
3926	0.01	0.03	n.d	0.12	0.06	2.12	24	0.25	0.42	3.53	
3996	0.01	0.02	n.d	0.03	0.12	0.28	63	0.33	0.07	0.56	

Table S2: Bulk geochemical data and depths for the Middle Jurassic rocks analysed from the Korolyn-6 well.

Depth [m]	S_1 [mgHC/gRock]	S_2	T_{max} [°C]	TOC [%]	S [%]	TOC/S [−]	HI [mgHC/gTOC]	PI [−]	TIC [%]	Calc. Equ. [%]	Biomarker
Middle Jurassic rocks											
Korolyn-6											
3418	0.22	3.18	439	3.67	1.32	2.78	87	0.06	1.34	11.13	
3419	0.26	3.97	440	3.89	0.68	5.71	102	0.06	0.74	6.18	
3420	0.29	4.28	442	4.04	0.93	4.32	106	0.06	0.80	6.68	
3421	0.29	4.93	441	4.39	0.66	6.63	112	0.06	0.97	8.05	
3422	0.28	3.19	440	3.36	0.84	4.01	95	0.08	1.41	11.73	
3423	0.32	4.26	441	3.81	1.81	2.11	112	0.07	1.25	10.40	
3424	0.29	4.47	445	4.39	1.95	2.25	102	0.06	0.74	6.19	
3425	0.25	4.46	445	4.30	1.06	4.05	104	0.05	0.92	7.63	
3426	0.21	4.15	444	4.13	1.04	3.97	100	0.05	0.65	5.41	
3427	0.24	4.07	442	3.90	0.59	6.56	104	0.06	0.89	7.39	
3428	0.40	4.73	440	4.07	0.63	6.48	116	0.08	0.89	7.40	x
3429	0.31	4.52	443	4.30	2.02	2.12	105	0.06	0.58	4.84	
3430	0.18	1.14	449	3.27	2.45	1.34	35	0.14	0.22	1.83	
3431	0.16	1.64	447	3.64	1.64	2.22	45	0.09	0.42	3.48	
3432	0.17	1.32	444	3.79	2.55	1.49	35	0.11	0.28	2.29	
3433	0.17	1.29	442	3.26	2.19	1.49	40	0.11	0.07	0.62	
3434	0.17	3.81	441	3.97	2.48	1.60	96	0.04	0.34	2.85	
3437	0.24	2.23	447	3.51	2.09	1.68	63	0.10	0.85	7.07	
3438	0.40	4.71	443	3.95	2.17	1.82	119	0.08	0.65	5.42	
3439	0.28	4.48	443	4.01	1.59	2.52	111	0.06	0.69	5.78	
3440	0.36	4.83	445	4.04	1.22	3.31	120	0.07	0.38	3.17	
3441	0.28	3.61	441	3.91	3.08	1.27	92	0.07	0.21	1.79	
3442	0.28	4.45	442	4.04	1.40	2.89	110	0.06	0.74	6.16	
3443	0.29	3.69	442	3.43	1.58	2.17	107	0.07	1.13	9.39	
3444	0.35	4.22	442	3.56	0.82	4.33	118	0.08	0.68	5.69	
3445	0.45	6.11	445	5.20	0.24	22.06	117	0.07	1.15	9.62	
3446	0.30	3.94	443	3.76	1.98	1.90	105	0.07	0.93	7.74	
3447	0.33	4.09	441	4.02	1.03	3.92	102	0.07	1.16	9.64	
3448	0.22	2.39	440	2.68	0.78	3.42	89	0.08	1.27	10.54	
3449	0.48	5.33	442	4.19	1.13	3.72	127	0.08	0.55	4.57	
3450	0.28	3.87	441	3.61	1.30	2.78	107	0.07	0.50	4.14	
3489	0.40	3.58	446	3.49	1.48	2.36	102	0.10	1.08	9.04	
3490	0.42	3.74	444	3.55	0.95	3.74	105	0.10	0.99	8.29	
3491	0.43	5.87	443	4.45	2.80	1.59	132	0.07	0.50	4.17	
3492	0.40	3.05	442	2.97	0.94	3.17	102	0.11	3.86	32.15	
3493	0.79	6.46	445	4.87	1.40	3.48	133	0.11	0.97	8.12	x
3496	0.59	6.18	444	5.12	0.91	5.60	121	0.09	0.83	6.91	
3497	0.60	7.67	445	5.74	1.71	3.35	134	0.07	0.87	7.22	
3498	0.57	6.67	446	5.01	1.65	3.05	133	0.08	1.16	9.71	
3499	0.53	6.58	445	5.20	0.44	11.84	127	0.07	1.20	9.99	
3500	0.50	6.24	444	4.91	0.35	13.94	127	0.07	1.27	10.56	
3518	0.50	6.54	444	5.25	0.94	5.58	125	0.07	0.71	5.89	
3519	0.54	5.82	444	4.43	1.06	4.17	131	0.08	0.93	7.75	
3520	0.46	5.32	444	4.84	1.52	3.18	110	0.08	1.85	15.40	
3521	0.74	8.09	445	5.75	0.20	29.38	141	0.08	0.75	6.23	x
3522	0.50	6.15	446	5.31	0.28	18.99	116	0.08	0.95	7.93	
3523	0.54	6.03	446	5.15	1.95	2.65	117	0.08	0.70	5.87	
3642	0.60	4.85	447	4.62	0.40	11.54	105	0.11	0.58	4.84	