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Hydrocarbon potential of the Lower Cretaceous (Barremian–Albian) Shypot Formation in the Chornohora nappe, Ukraine

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Abstract: Organic matter-rich rocks occur in the Carpathians, both in the Lower Cretaceous and Oligocene. Whereas, the Oligocene Menilite Formation has been intensely studied, the hydrocarbon potential of Lower Cretaceous rocks is less well understood. In the present paper a 405 m thick succession of the lower part of the Shypot Formation in the Chornohora nappe (Ukraine) is studied using 94 outcrop samples. Maturity parameters for the Lower Cretaceous rocks indicate peak oil maturity (~0.85 % Rr) and organic carbon content averages 2.8 wt. % for all samples. As a result of the enhanced maturity, the hydrogen index (88 mg HC/g TOC) and the remaining petroleum potential (2 tHC/m²) are low. Comparisons with coeval rocks from the same tectonic unit, but with lower maturity suggest that the original petroleum potential was significantly higher (4 tHC/m²). Probably about 2 tHC/m² were generated during deep burial (6 km?), but were lost during uplift and erosion. Macerals analysis reveals a mixed type III-II kerogen, with domination of terrigenous components, which is also supported by HI values of nearby marginal mature samples (~200 mg HC/g TOC). Lower Cretaceous organic matter-rich rocks are found along the entire Carpathian arc. A compilation of published data for age-equivalent rocks across the Carpathian Fold-Thrust Belt shows that HI values are mainly controlled by maturity as well as the moderately high original HI values. Most of these rocks contain predominantly type III-II kerogen, whereas Lower Cretaceous rocks in the Skole-Skyba nappe near the Polish–Ukrainian border contain type (III-)IV kerogen.

Keywords: Carpathians, Lower Cretaceous, source rocks, organic geochemistry, Rock-Eval, kerogen type, organic matter, maturity.

Introduction

The Ukrainian Carpathians form the NE part of the Carpathian orogenic belt which stretches for approximately 1300 km from Vienna to the Iron Gate on the River Danube in Romania (Slaczka et al. 2006; Fig. 1a). They host one of the oldest petroleum-producing provinces in the world (Boote et al. 2018). Petroleum production began in 1854 with the discovery of the Boryslav oil field, one of the largest onshore oilfields in Europe (Kotarba et al. 2007). All oil and gas fields are located within the Outer Carpathians, bordered to the NE by a molasse-filled foredeep and to the SW by the Pieniny Klippen Belt. Internally, the Outer Carpathians consist of a series of structurally complex, NE-verging nappes which comprise rocks that are Lower Cretaceous to Lower Miocene in age (Slaczka et al. 2006; Nakapelyukh et al. 2018).

The Lower Oligocene to Lower Miocene Menilite Formation is the primary source rock interval in the Carpathians and has been studied extensively in the past (e.g., Curtis et al. 2004; Kotarba et al. 2007; Kosakowski et al. 2018, Sachsenhofer et al. 2018a, b; Jirman et al. 2019; Rauball et al. 2019 cum lit.). In contrast, information on organic matter-rich Lower Cretaceous rocks is limited (e.g., Kruge et al. 1996; Kotarba & Koltun 2006; Kotarba et al. 2013; Slaczka et al. 2014). For example, only a few data are available from the Barremian to Albian Shypot and Spas formations in the Ukraine (Koltun et al. 1998), as all economic hydrocarbon accumulations in the Ukrainian Carpathians have been correlated to the Menilite Formation (Kotarba et al. 2019), although the authors state that a contribution of Lower Cretaceous source rocks cannot be excluded.

The main goal of the present contribution is to provide an analysis of the vertical variation of organic matter content and hydrocarbon potential of the Lower Cretaceous Shypot Formation, a potential source rock, several hundred metres thick. For this, we selected a well-exposed outcrop section west of the village Bystrets in the Chornohora nappe (Fig. 1b). The study results are compared to source rock data from other areas in the Carpathian Fold-Thrust Belt and will contribute to a better understanding of the petroleum system, particularly in the internal parts of the fold-belt, which are still relatively unexplored.

Geological setting

Stratigraphy and tectonics

The Outer Carpathians comprise a series of nappes which have been thrust NE-ward, during Early Miocene tectonism, onto the SW margin of the East European Plate (Slaczka et al.

2006). In Ukraine, the following thrust sheets are distinguished from the NE (i.e. the most external part of the thrust-belt) to the SW (most internal): Sambir (Stebnyk), Boryslav-Pokuttya, Skyba (Skole), Krosno (Silesian), Dukla-Chornohora, Burkut, Magura, and Rakhiv (Nakapelyukh et al. 2018; Fig. 1b). The tectonic position of the Chornohora nappe is not completely clear (see Slaczka et al. 2006). According to Nakapelyukh et al. (2018), the Chornohora nappe corresponds to the Dukla nappe, and therefore is often regarded as the Dukla-Chronohora nappe.

Each thrust-sheet represents a separate or partly separate sedimentary sub-basin containing different lithostratigraphy and tectonic structures (Golonka et al. 2006). Strata in the Outer Carpathians range from Lower Cretaceous to Lower Miocene in age and may locally exceed thicknesses of 6 km (Slaczka et al. 2006). During overthrusting, the tectonic units became uprooted, and generally only the central parts of the basins are preserved (Slaczka et al. 2006).

Lithology of the Lower Cretaceous strata

Lower Cretaceous black shales make up the base of the flysch belt. They were deposited in oxygen-depleted marine conditions, which partly coincide with a global anoxic event during Barremian to Albian times (OAE-1; Schlanger & Jenkyns 1976; Jenkyns 1980), and are assigned to either the Shypot or the Spas Formation, depending on their tectonic position. The Spas Formation is confined to the Skole-Skyba Nappe and crops out locally in the NW part of the nappe (Vialov et al. 1988), whereas the Shypot Formation crops out frequently in the internal Krosno, Dukla-Chornohora and Burkut nappes.

Both formations are primarily composed of organic-rich black shales with minor siltstones and sandstones in their lower part and by thick-bedded sandstones in their upper part. The thickness of the organic-rich part of the Spas Formation in the Skyba Nappe (approximately 200 m; Kotlarczyk 1988) is typically lower than that of the Shypot Formation (up to 300 m; Slaczka et al. 2006). As described by Slaczka et al. (2006), the upper part of the Shypot Formation in the Chronohora nappe comprises 200 m of dark, quartzitic sandstone with black shale intercalations (Albian in age).

The studied section is located within the south-eastern part of the Ukrainian Outer Carpathians where Lower Cretaceous sediments outcrop within the Dukla-Chronohora nappe (Fig. 2).

Petroleum systems

The Ukrainian Outer Carpathians host two organic rich horizons: the Lower Cretaceous (Barremian–Albian) Shypot and Spas Formations and the Oligocene–Lower Miocene Menilite Formation (e.g., Sachsenhofer & Koltun 2012). The genetic potential of the source rocks increases from the Jurassic to the Oligocene–Lower Miocene Menilite Formation in the Outer Carpathians (Francu et al. 1996). The Menilite Formation is the primary source rock interval of the region (Kotarba & Koltun 2006) and contains very high TOC contents (locally exceeding 20 wt. %) with HI values up to 800 mg HC/g TOC (Rauball et al. 2019 cum lit.)

The Shypot and Spas formations are regarded as additional potential source rocks (Kotarba & Koltun 2006). Their TOC is generally greater than 2 wt. % and may reach as much as 8 wt. %. Rock-Eval data show that the shales contain a type III or II/III kerogen (Sachsenhofer & Koltun 2012). A type III kerogen is also indicated by the presence of high percentages of vitrinite (Kruge et al. 1996). Despite the occurrence of this potential source rock, no Cretaceous-sourced oil and gas has been identified across Ukrainian territory (Boote et al. 2018; Kotarba et al. 2019). However, according to Więcław et al. (2020), gaseous hydrocarbons in the eastern part of the Polish Outer Carpathians originated from Upper Cretaceous–Paleocene Istebna shales or Lower Cretaceous strata (Veřovice, Lgota and Spas shales).

Samples and methods

For this study, 94 samples from the Shypot Formation in the Chornohora nappe were collected from an outcrop along a small tributary of the river Bystrets, west of the village Bystrets (base of section: 48°07’18”N, 24°38’27”E), Iwano-Frankivsk, Ukraine. All samples were cleaned (using water), dried (at 30 °C in a drying-cabinet for two days) and pulverized (to a fraction below 0.2 mm; using a stone grinding machine) before laboratory analyses were performed.

The samples were analysed for their total carbon (TC), total sulphur (TS) and total organic carbon content (TOC) using an ELTRA Elemental Analyser and calcium carbonate (12.00 % Carbon) as a standard. 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 TC with the TOC. TIC was then used to calculate the calcite equivalent percentages (=TIC×8.333 – which is the stoichiometric factor or $CaCO_3$).

Rock-Eval pyrolysis was carried out using a “Rock-Eval 6” analyser in order to determine the S_1, S_2 peaks (mg HC/g rock) and T_{max} for all samples. The S_1 peak records hydrocarbons volatilized at 300 °C and determines the amount of hydrocarbons present in the rock, whereas the S_2 peak is produced during gradual heating from 300 to 650 °C, and determines the amount of hydrocarbons formed during pyrolysis. The petroleum potential (S_1+S_2 [mg HC/g rock]), the hydrogen index (HI=S_2×100/TOC [mg HC/g TOC]) and the Production Index (S_1/[S_1+S_2]) were calculated. 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 the average of at least two measurements.

Based on the TOC contents and HI values (preferably higher values), a total of 24 samples were selected at similarly spaced

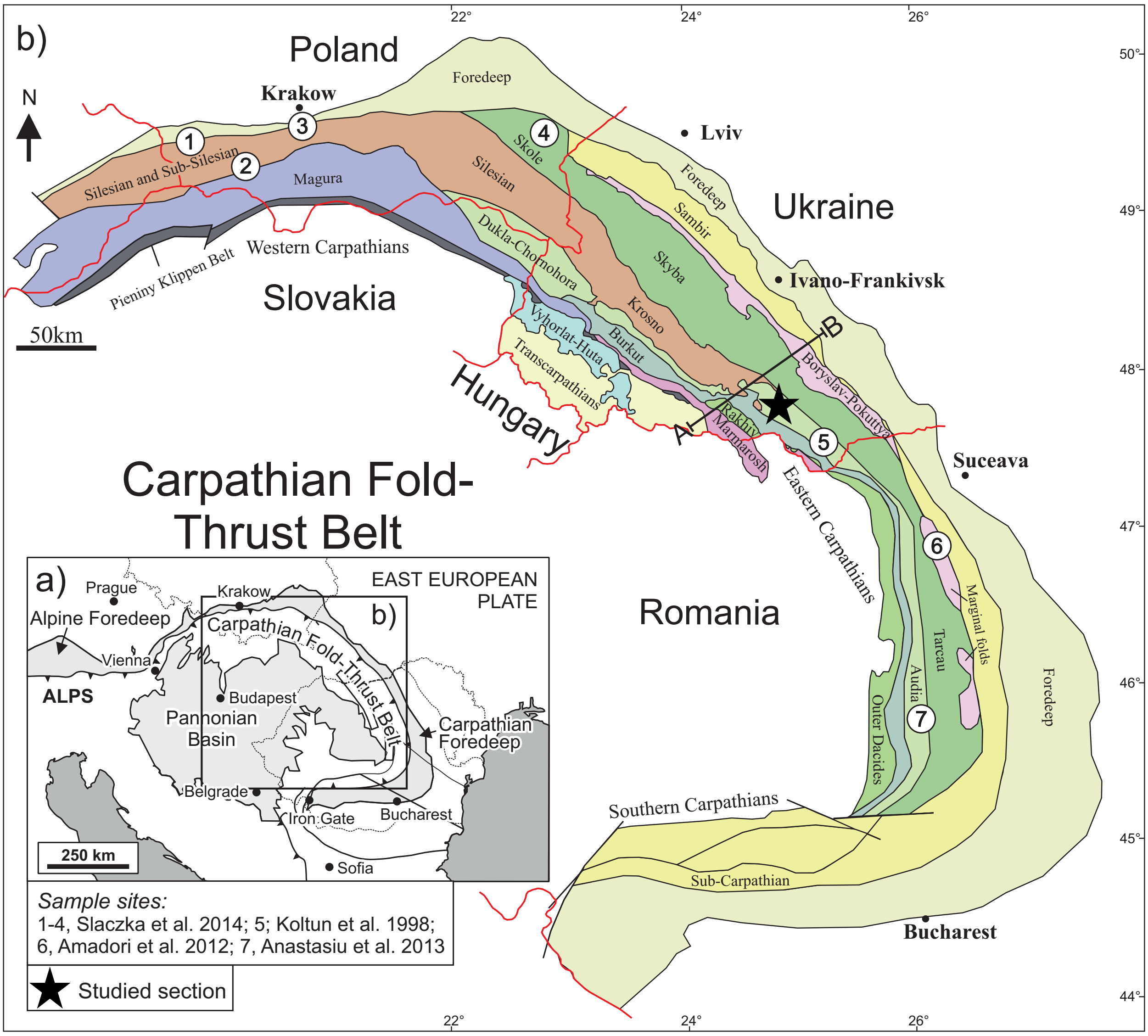

Fig. 1. **a** — Outline map of central-eastern Europe showing the location of the study area in the Carpathian orogenic belt. **b** — Structural map of the Carpathian Fold-Thrust Belt (after Oszczypko 2006; Slaczka et al. 2006; Nakapelyukh et al. 2018) with the location of the studied section in western Ukraine. Locations of profiles (1–9) with comparative samples are also shown.

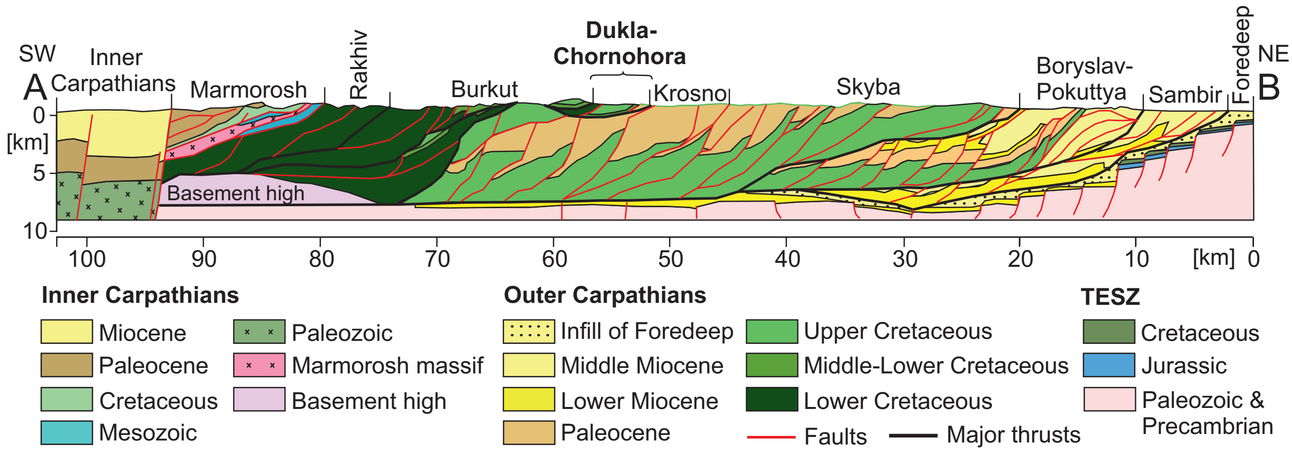

Fig. 2. Cross-section (A–B) of the Ukrainian Carpathians (modified after Shlapinskyi 2015; Nakapelyukh et al. 2018).

intervals across the Shypot Formation for biomarker analyses. 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 (1000 rpm). 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 μm; 0.25 μm film thickness), coupled to a ThermoFisher ISQ Dual-quadrupole mass spectrometer. Using helium as the carrier gas, the oven temperature of the GC was set to increase from 70 °C to 300 °C at 4 °C min^{-1}, which was followed by an isothermal period of 15 min. With the injector temperature set to 275 °C, the sample was 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 (e.g., Peters et al. 2007). 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 adjusted according to the TOC content of each sample.

The samples used for biomarker analysis were also selected for organic petrographic investigations (with the exception of one sample, where not enough material was available for further analysis). In total, 23 polished blocks were prepared for semi-quantitative maceral analysis. Maceral composition was determined using white light and fluorescent light. Vitrinite reflectance measurements were determined using a Leica microscope and following established procedures (Taylor et al. 1998).

The Methylphenanthrene Index-1 (MPI-1) was calculated following the equation: (1.5×(2-MP+3-MP)/(Phen+9-MP+1-MP)). The MPI-1 was then used to calculate vitrinite reflectance following the equation (Rc=0.60 MPI-1+0.40) proposed by Radke & Welte (1983); Phen – Phenanthrene, MP – Methylphenanthrene.

Results

Lithology

At the study location in the Chornohora nappe, the lower black shale part of the Shypot Formation is estimated to be about 400 m thick, which is slightly thicker than the 300 m thick lower part of the Shypot Formation analysed by Slaczka et al. (2006). The sandstone-rich upper part of the Shypot Formation (Slaczka et al. 2006) was not encountered and may be missing in this part of the Chornohora nappe. The base of the formation, which is marked by an unconformity, is fault-bound and underlying sediments were not exposed.

The studied section is primarily composed of organic-rich black shales with minor siltstone and sandstone beds. Organic-rich shale intervals are represented by brighter and darker shale intervals. Darker shales outnumber the lighter shales significantly throughout the entire section. Surprisingly, the lighter shales analysed at 0 m, 257.5 m, 324 m, 332 m, and 385 m (all positions are relative to the top of the formation) contain a lower carbonate content (average: 3.0 wt. %) than the darker shales (average: 8.0 wt. %). Carbonate content is highest in the middle of the formation (max. 38.5 wt. %) and generally decreases slightly towards the top. Sandstones are typically 30 to 40 cm thick (max. 1.5 m). They are fine- to medium-grained and occur frequently throughout the formation. The percentage of sandy sediments is in the order of approximately 35 %. Sedimentary structures such as dewatering structures are present in some sandstone beds.

Bulk parameters of organic matter and maceral composition

The TOC content of the black shales of the Shypot Formation in the Chornohora nappe averages 2.8 wt. % (Table 1; Fig. 3). Maximum TOC contents (up to 9.4 wt. %; Fig. 3) occur 280 to 325 m below the top of the section. HI values are low (average: 88 mg HC/g TOC; max. 185 mg HC/g TOC; Table 1; Figs. 3, 4) and increase slightly in the upper part of the section. On average, the grey shales contain a lower TOC content (average: 0.86 wt. %) and lower HI values (average: 49 mg HC/g TOC) than the black shales. T_{max} values (average: 456 °C; Table 2) show a general upward decreasing trend. Production Index (PI) values range from 0.06 to 0.26 (average 0.13). The calcite equ. varies considerably (Fig. 3), and reaches a maximum of 38.5 wt. % in the lower part of the section.

Sulphur contents reach a maximum of 2.5 wt.% (Fig. 3). TOC/S ratios (Fig. 3), which are commonly used as a parameter to distinguish between anoxic and oxic conditions, as well as between marine and freshwater deposits (Berner & Raiswell 1984), range from 0.7 to 5.2 (average 2.4) in samples with at least 0.3 wt. % TOC. TOC/S ratios generally increase slightly in the upper part of the section.

Yields of extractable organic matter (EOM) for a subset of samples from the Shypot Formation vary from 3.70 to 22.78 mg/g TOC (average: 9 mg/g TOC; Table 2). Extracts from all samples are primarily dominated by NSO compounds (31 to 81 % of the EOM), with the exception of sample 281 m (from the top of the section) which contains elevated Asphaltene content (80 % of the entire EOM).

The maceral composition for the Shypot Formation (Table 1) is characterized by a high abundance of vitrinite (34–60 vol. %; Fig. 5). Moderate amounts of sporinite (15–34 vol. %), lamalginite (9–19 vol. %) and telalginite (6–20 vol. %) make up

Table 1: Selected Bulk and Rock-Eval data, vitrinite reflectance and maceral composition for the Shypot Formation in the Chornohora nappe. TOC — total organic carbon; S — total sulphur; Calcite equ. — calcite equivalent; HI — Hydrogen Index; PI — Production Index; n# — number of measurements; * — not defined.

Position in relation to Top	TOC	S	Calcite equ.	HI	S1+S2	PI	Vitrinite reflectance	n#	Standard Deviation	Vitrinite	Inertinite	Liptinite			Maceral	Glauconite
												Sporinite	Lamalginite	Telalginite		
[m]	[wt. %]			[mg HC/ g TOC]	[mg HC/ g rock]		[%]		[%]	[% OM normalized]					[vol. %]	yes/no
5.0	3.1	1.7	4.4	75	2.6	0.13	0.85	51	0.12	40	6	30	18	6	5.6	n
49.0	1.9	0.8	2.6	143	3.2	0.13	*	*	*	40	0	30	10	20	1.9	y
56.5	2.6	0.6	0.6	126	3.6	0.10	0.82	32	0.10	39	9	26	17	9	4.3	y
63.0	3.2	1.1	0.0	125	4.4	0.10	0.83	17	0.09	39	3	34	17	7	4.7	y
75.5	5.3	1.5	3.9	185	10.6	0.07	*	*	*	34	6	28	19	13	9.4	y
84.0	5.6	1.1	6.2	168	10.1	0.07	0.83	26	0.09	31	10	26	23	10	6.6	y
96.0	4.5	1.4	7.0	158	7.7	0.08	*	*	*	48	2	26	13	11	7.4	n
118.0	4.0	1.2	12.8	171	7.5	0.09	*	*	*	50	6	22	11	11	3.8	y
133.0	4.9	1.4	4.4	105	5.7	0.09	0.74	39	0.09	36	7	30	17	10	5.9	y
159.0	1.8	1.1	12.0	80	1.7	0.15	*	*	*	52	6	24	12	6	3.1	y
170.0	3.1	1.0	5.7	81	2.9	0.13	*	*	*	45	9	17	13	16	6.2	y
194.0	3.8	2.2	10.3	111	4.7	0.11	0.85	52	0.10	38	6	22	18	16	5.5	y
228.0	1.8	2.1	21.3	90	1.9	0.18	*	*	*	43	7	29	14	7	2.2	y
248.0	2.1	1.2	23.7	74	1.8	0.16	*	*	*	49	6	19	13	13	3.4	y
257.0	3.8	1.9	11.3	89	4.0	0.16	*	*	*	59	7	16	11	7	5.3	y
281.0	8.0	2.2	0.7	127	11.2	0.09	0.8	67	0.11	49	8	16	16	11	7.9	y
294.0	7.5	2.5	6.1	124	10.4	0.11	*	*	*	60	6	14	11	9	7.0	y
313.0	8.2	2.3	5.6	157	14.0	0.09	0.85	43	0.11	37	5	26	19	13	11.3	y
323.8	9.4	2.3	3.8	124	12.8	0.09	*	*	*	47	7	20	15	11	9.6	n
361.0	2.8	1.2	4.8	77	2.5	0.12	0.86	43	0.11	43	7	29	14	7	5.5	y
382.0	3.6	2.0	14.7	110	2.1	0.13	*	*	*	54	5	23	9	9	4.4	y
394.0	2.6	1.3	11.1	66	2.4	0.12	*	*	*	44	4	26	17	9	4.1	y
402.3	4.2	2.1	2.2	86	4.1	0.10	0.86	32	0.09	55	9	15	12	9	7.1	y

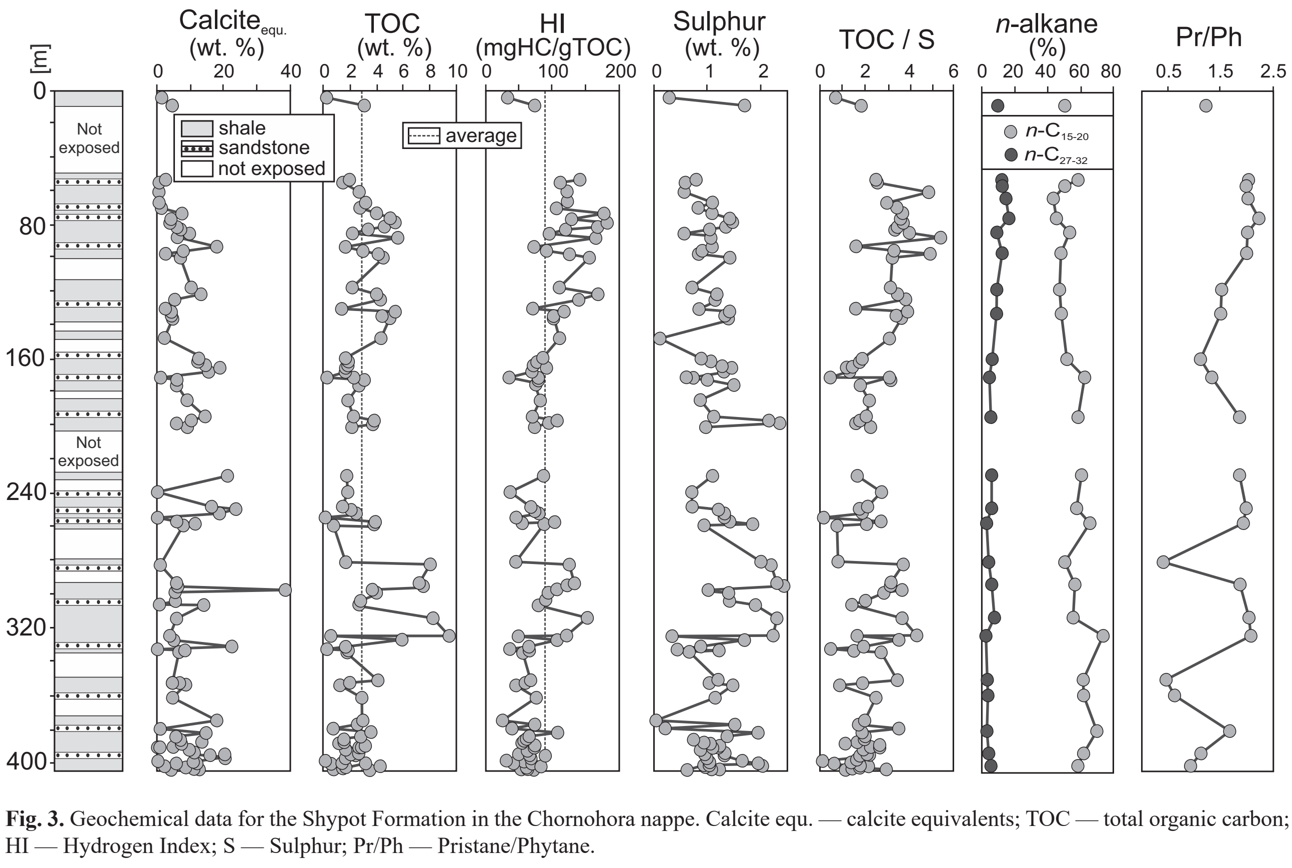

Fig. 3. Geochemical data for the Shypot Formation in the Chornohora nappe. Calcite equ. — calcite equivalents; TOC — total organic carbon; HI — Hydrogen Index; S — Sulphur; Pr/Ph — Pristane/Phytane.

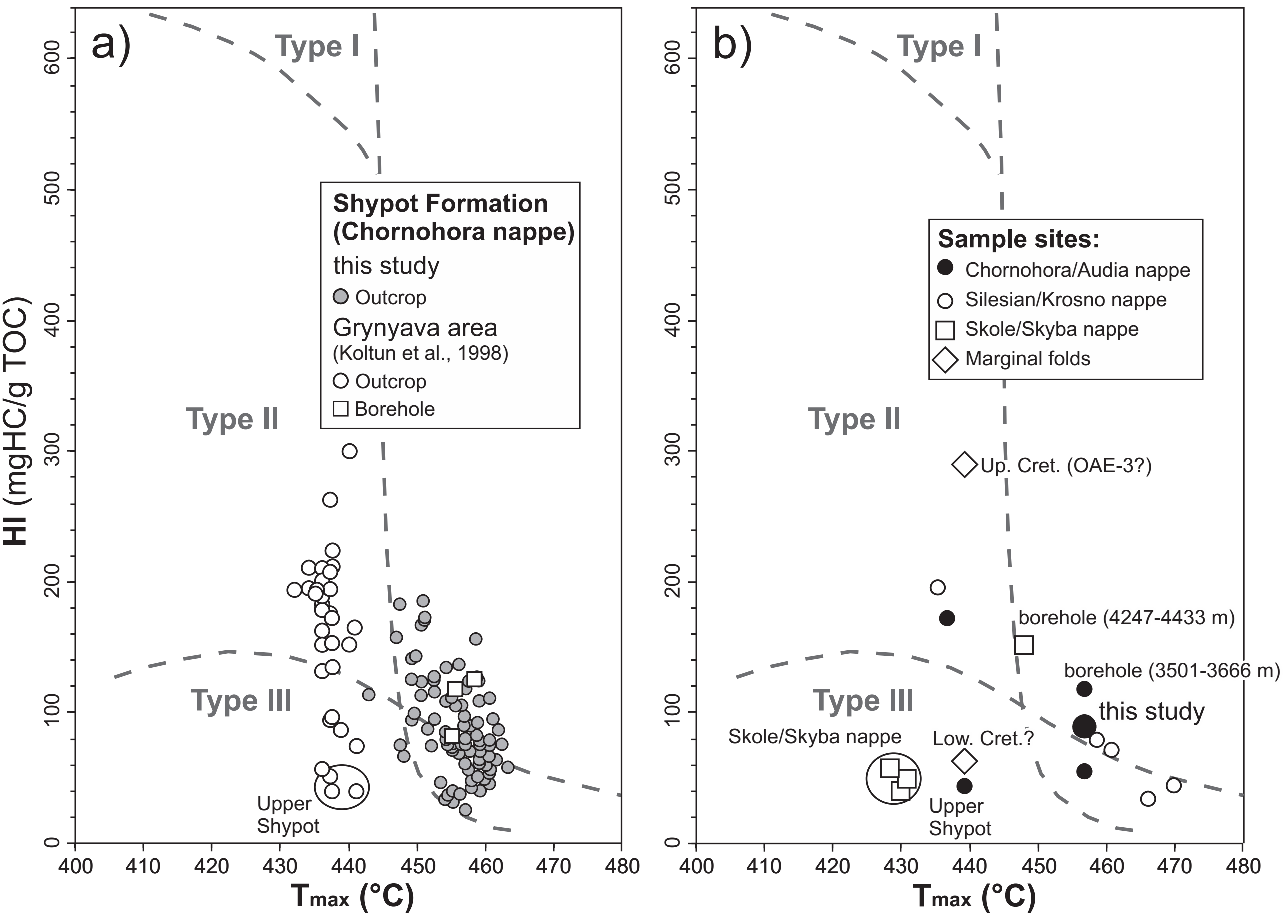

Fig. 4. HI vs. T_{max} (Espitalié et al. 1986). **a** — Shypot Formation in the Chornohora nappe. Data from additional samples in the Grynyava area (site 7 in Fig. 1; Koltun et al. 1998) are shown for comparison. **b** — Mean values of Lower Cretaceous outcrop and borehole samples from different nappes (data are from Koltun et al. 1998; Amadori et al. 2012; Anastasiu et al. 2013; Slaczka et al. 2014).

the remaining maceral composition. Inertinite (mainly fusinite) is observed frequently throughout the succession (max. 12 vol. %). Glauconite and authigenic carbonate minerals (Fig. 5) are also frequently present in most samples. Without a noticeable trend in the studied section, vitrinite reflectance ranges from 0.74 to 0.86 % (average: 0.83 %; Table 1).

Molecular composition of hydrocarbons

Geochemical data are listed in Table 2, and the vertical variations of important biomarker proxies versus depth are shown in Fig. 3.

n-alkanes and isoprenoids: Samples from the Shypot Formation contain high amounts of short-chain *n*-alkanes (n-$C_{15–20}$: 43–73 %) and very low amounts of long-chain *n*-alkanes (n-$C_{26–32}$: 2–16 %; Table 2, Fig. 6). The percentage of the long-chain *n*-alkanes slightly increases upwards.

Pristane/n-C_{17} (0.09–1.33) and phytane/n-C_{18} (0.05–0.61) ratios vary significantly and show a positive correlation with the percentage of long-chain *n*-alkanes (r^2=0.74 and 0.73, respectively; Fig. 6). CPI values (Bray & Evans 1961) range from 1.06 to 1.25 (Table 2), but do not show a clear depth trend.

Pristane/phytane (Pr/Ph) ratios are commonly used as redox indicators. Ratios <1.0 are attributed to strictly anoxic environments, whereas ratios >1 suggest a suboxic (1–3) to oxic (>3) environments (Didyk et al. 1978). Pr/Ph ratios for the Shypot Formation range from 0.41 to 2.23 (average: 1.58; Table 2, Fig. 3). Although it is suggested that they should be used with caution, ratios <1.0 are restricted to the lower part of the succession.

Steroids: Sterane concentrations are very low (0.02–2.32 µg/g TOC), likely due to an increased thermal maturity of the rocks (Tissot & Welte 1984). High steranes/hopanes ratios (1.30–8.54; Table 2), which are prone to maturity (Requejo 1994; Mißbach et al. 2016), are an indicator of marine organic matter with major contributions from algae, and can be observed throughout the formation (Moldowan & Fago 1986). The highest sterane concentrations, as well as the highest steranes/hopanes ratios, are both found 49 m below the top of the section.

The relative proportions of C_{27}, C_{28} and C_{29} steranes may provide paleoenvironmental information (Huang & Meinschein 1979). For the Shypot Formation, the relative proportions of C_{27} steranes (33–54 %) are slightly elevated compared to C_{28} (21–35 %) and C_{29} steranes (24–39 %; Fig. 7; Table 2).

Table 2: Organic geochemical data for samples from the Shypot Formation in the Chornohora nappe. EOM — Extractable Organic Matter; Sat. HC — Saturated Hydrocarbons; Aro. HC — Aromatic Hydrocarbons; Asph. — Asphaltene, Pr/Ph — Pristane/Phytane; CPI — Carbon Preference Index; Ts/Tm — Trisnorneohopane/Trisnorhopane; MPI-1 — Methylphenanthrene Index-1; DBT/Phen. — Dibenzothiophene/Phenanthrene; PAH — Polycyclic Aromatic Hydrocarbons; * — not defined.

Position in relation to Top [m]	TOC	HI	EOM	Sat. HC	Aro. HC	NSO	Asph.	n-C_{15-20} /n-C_{15-32}	n-C_{21-26} /n-C_{15-32}	n-C_{27-32} /n-C_{15-32}	Pr/Ph	CPI	Steranes conc.	% C_{27} Steranes	% C_{28} Steranes	% C_{29} Steranes	Sterane/ Hopanes	C_{28}/C_{29} Steranes	Hopanes conc.	22S/(S+R) C_{31} hopanes	Moretane/ Hopanes	Ts/ Tm	DBT/ Phen	MPI-1	PAH conc.
	[wt. %]	[mg/ g TOC]	[mg/ g TOC]	[wt. %]									[µg/ g TOC]						[µg/ g TOC]						[µg/ g TOC]
5.0	3.08	75	5.95	13	11	49	27	0.50	0.41	0.09	1.24	1.19	0.06	0.46	0.28	0.25	3.06	1.11	0.02	0.40	0.08	3.32	0.01	0.89	155.1
49.0	1.94	143	10.79	27	11	40	22	0.58	0.31	0.11	2.03	1.07	2.32	0.42	0.30	0.28	8.54	1.06	0.27	0.72	0.18	2.38	0.00	0.91	88.0
56.5	2.62	126	8.68	24	11	37	28	0.50	0.38	0.12	2.00	1.08	0.67	0.40	0.25	0.35	2.77	1.27	0.24	0.66	0.12	2.08	0.00	0.76	83.9
63.0	3.18	125	9.39	16	9	41	34	0.43	0.43	0.14	2.03	1.12	0.33	0.38	0.34	0.27	2.49	0.69	0.13	0.63	0.07	3.17	0.00	0.74	83.3
75.5	5.33	185	15.08	15	13	34	38	0.45	0.39	0.16	2.23	1.06	0.57	0.38	0.25	0.37	2.38	0.89	0.24	0.68	0.10	1.61	0.01	0.69	125.3
84.0	5.60	168	14.01	7	9	31	53	0.53	0.38	0.09	2.01	1.09	0.27	0.43	0.27	0.30	1.61	0.64	0.17	0.77	0.16	0.67	0.01	0.72	153.9
96.0	4.45	158	11.59	10	10	36	44	0.48	0.40	0.12	2.00	1.08	0.27	0.36	0.25	0.39	1.30	0.69	0.21	0.78	0.20	0.45	0.01	0.73	186.6
118.0	3.99	171	11.72	9	9	*	*	0.47	0.44	0.09	1.53	1.18	0.32	0.36	0.26	0.38	3.72	1.12	0.09	0.49	0.07	4.17	0.00	0.75	124.0
133.0	4.93	105	8.47	9	11	*	*	0.48	0.43	0.09	1.52	1.17	0.18	0.33	0.35	0.32	3.02	1.00	0.06	0.69	0.14	1.34	0.01	0.72	46.8
159.0	1.83	80	4.03	25	13	48	14	0.51	0.43	0.06	1.12	1.17	0.04	0.42	0.29	0.29	4.61	0.74	0.01	0.69	0.27	2.15	0.01	0.84	59.4
170.0	3.07	81	5.48	16	13	48	23	0.62	0.34	0.04	1.34	1.23	0.02	0.34	0.28	0.38	2.60	1.17	0.01	0.63	0.10	1.71	0.01	0.73	28.6
194.0	3.78	111	7.71	15	15	53	17	0.58	0.37	0.05	1.88	1.21	0.09	0.41	0.32	0.27	2.94	0.62	0.03	0.65	0.13	2.62	0.00	0.62	78.3
228.0	1.77	90	6.65	29	11	46	14	0.60	0.35	0.05	1.88	1.19	0.02	0.45	0.21	0.34	5.14	0.82	0.01	0.38	0.16	3.29	0.00	0.75	39.6
248.0	2.05	74	5.40	25	14	50	11	0.57	0.38	0.05	2.00	1.22	0.33	0.40	0.27	0.33	1.57	0.71	0.21	0.85	0.23	1.28	0.00	0.74	36.8
257.0	3.77	89	7.45	17	16	51	16	0.65	0.32	0.03	1.95	1.21	0.06	0.33	0.28	0.39	3.28	0.70	0.02	0.46	0.09	4.05	0.01	0.73	87.8
281.0	7.99	127	10.47	1	3	81	15	0.50	0.46	0.04	0.41	1.19	0.56	0.37	0.26	0.37	5.93	0.99	0.09	0.69	0.15	2.12	0.01	0.80	79.3
294.0	7.51	124	11.80	6	12	33	49	0.56	0.38	0.06	1.88	1.24	0.81	0.51	0.24	0.25	2.83	0.75	0.29	0.48	0.07	3.96	0.02	0.73	114.2
313.0	8.15	157	22.78	3	5	12	80	0.55	0.38	0.07	2.05	1.20	0.63	0.44	0.24	0.32	3.09	0.79	0.20	0.43	0.07	3.56	0.01	0.80	45.4
323.8	9.39	124	13.50	10	18	54	18	0.73	0.25	0.02	2.08	1.24	0.16	0.44	0.25	0.32	4.12	0.88	0.04	0.55	0.07	3.92	0.02	0.68	87.6
350.5	4.04	69	4.49	11	12	54	23	0.61	0.36	0.03	0.47	1.15	0.06	0.54	0.22	0.24	3.47	1.04	0.02	0.79	0.32	1.00	0.01	0.91	51.0
361.0	2.80	77	3.70	13	14	51	22	0.61	0.36	0.03	0.63	1.19	0.06	0.48	0.27	0.25	6.62	1.09	0.01	0.74	0.17	1.46	0.01	1.01	65.2
382.0	3.56	110	7.23	15	15	56	14	0.69	0.28	0.03	1.67	1.18	0.03	0.46	0.28	0.26	3.18	1.07	0.01	0.72	0.32	1.32	0.01	0.78	120.6
394.0	2.64	66	4.88	18	14	55	13	0.61	0.35	0.04	1.14	1.16	0.12	0.41	0.31	0.29	3.77	1.09	0.03	0.70	0.28	1.82	0.01	0.91	65.4
402.3	4.23	86	5.87	8	11	38	43	0.57	0.37	0.06	0.93	1.25	0.23	0.36	0.33	0.31	3.51	0.73	0.07	0.56	0.09	2.06	0.01	0.85	52.0

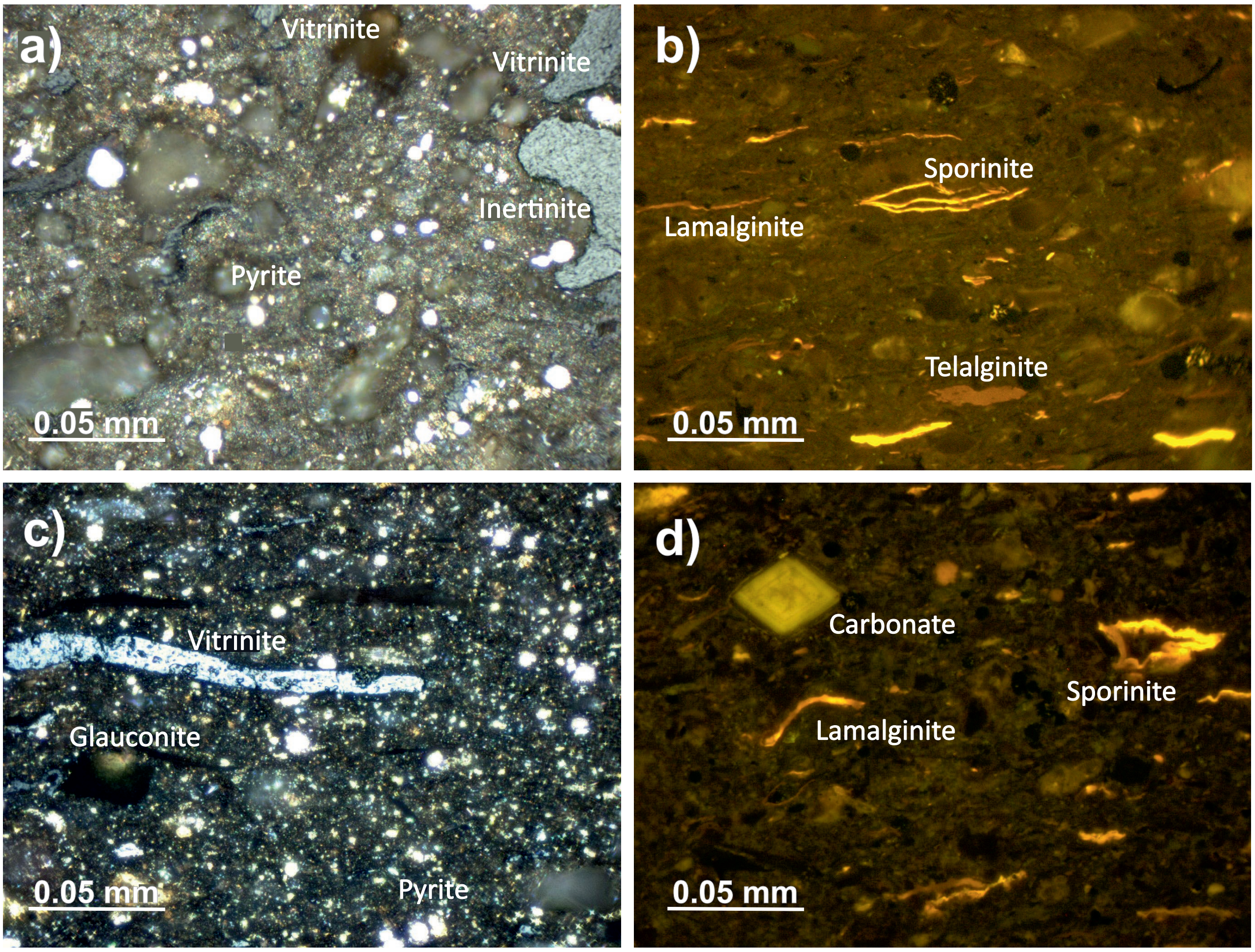

Fig. 5. Photomicrographs of samples from the Shypot Formation in the Chornohora nappe. **a, c** — Photomicrographs in white light showing inertinite, vitrinite, glauconite and pyrite; **b, d** — Photomicrographs in fluorescence mode illumination showing lamalginite, sporinite, telalginite and carbonate.

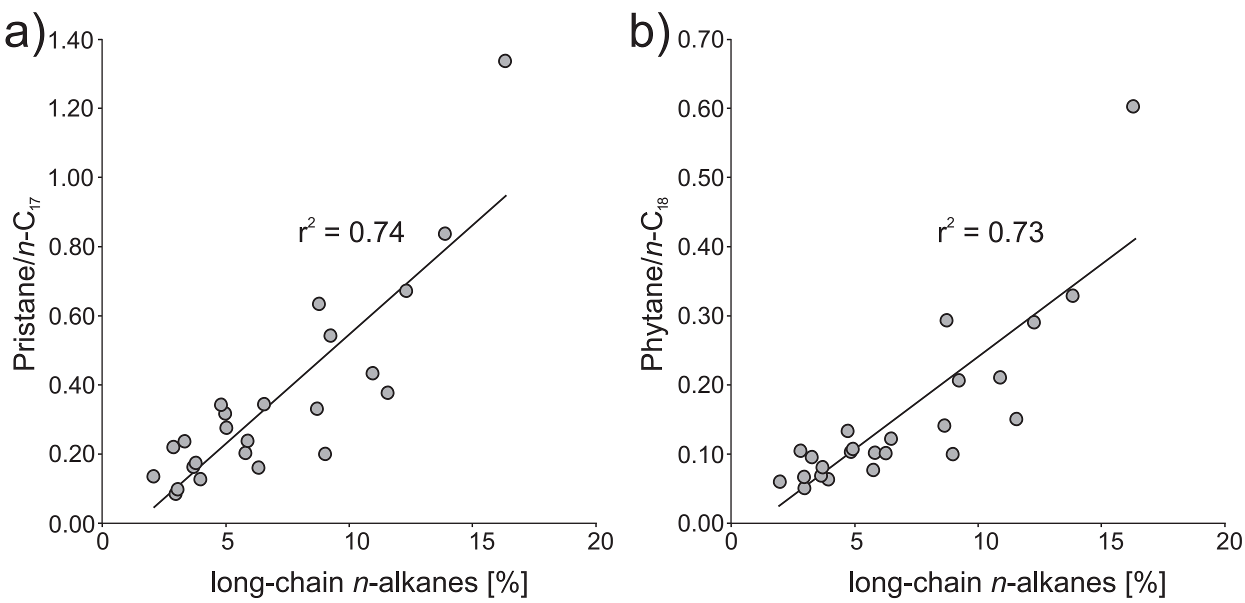

Fig. 6. Cross-plot of relative concentration of long-chain *n*-alkanes versus (**a**) pristane/*n*-C_{17} and (**b**) phytane/*n*-C_{18} ratios.

The ratio of C_{28}/C_{29} steranes in marine source rocks increases during geological history (Grantham & Wakefield 1988). In the Shypot Formation, the C_{28}/C_{29} steranes ratio varies widely (0.64–1.27; Table 2), but the average ratio of 0.90 agrees with the Lower Cretaceous age of the rocks.

Terpenoids: Hopanes originate from precursors in bacterial membranes (Ourisson et al. 1979). Similar to sterane concentrations, hopane concentrations range from 0.01 to 0.29 (µg/g TOC; Table 2), whereas the 22S/(22S+22R) isomerization ratio of C_{31} hopanes varies between 0.40 to 0.85 (average: 0.63; Table 2).

Moretane/hopane and trisnorneohopane/trisnorhopane (Ts/Tm) ratios are thermal maturity parameters, but are also influenced by different sources of organic matter and depositional environment (Moldowan & Fago 1986; Peters et al. 2007). The moretane/hopane ratio varies from 0.07 to 0.32 (average: 0.15), whereas the Ts/Tm ratio ranges between 0.45 to 4.17 (average: 2.31).

Considering the Lower Cretaceous age of the Shypot Formation, it is not surprising that oleanane was not detected in any of the studied samples.

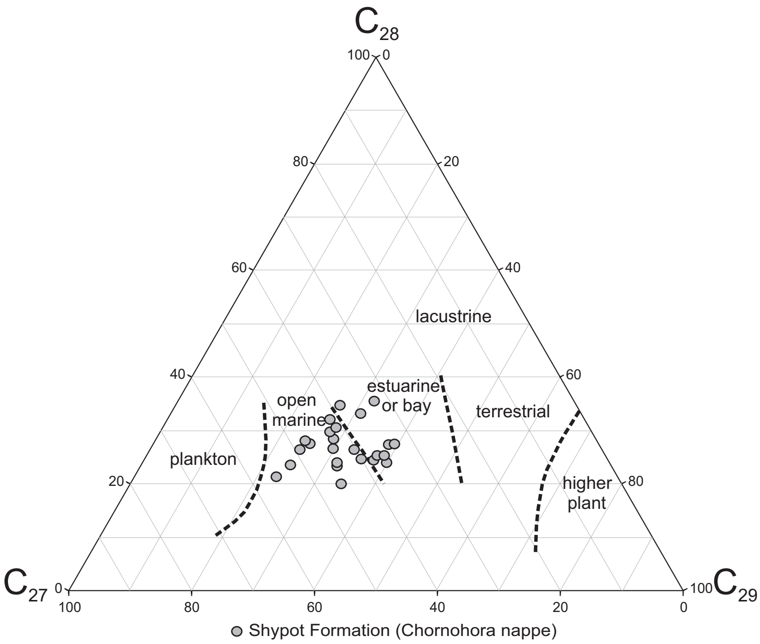

Fig. 7. Triangle diagram of C_{27}, C_{28} and C_{29} regular sterane composition for the Shypot Formation in the Chornohora nappe. Modified after Huang & Meinschein (1979).

Polycyclic aromatic hydrocarbons (PAH) and S-containing compounds

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 Shypot Formation are extremely low (≤0.02) as a result of low DBT concentrations which are generally insufficient for quantification.

The Methylphenanthrene Index-1 (MPI-1) is a maturity parameter and can be used to calculate vitrinite reflectance (Rc) of a sample (Radke & Welte 1983). The calculated Rc for the Shypot Formation ranges from 0.77 to 1.01 % (average: 0.87 %).

Polycyclic aromatic hydrocarbons, including Chrysene, Perylene, which are typically found in coal deposits and may be used as an indicator for forest fires, are found in high concentrations (28.6–186.6 µg/g TOC) throughout the succession.

Discussion

Maturity and burial depth

Vitrinite reflectance values (average: 0.82 %) indicate peak oil window maturity for the Shypot Formation at the study location. T_{max} values (average: 456 °C) and vitrinite reflectance calculated using MPI-1 values (average 0.87 %) agree with a peak oil window maturity. A subtle downward increase in maturity with depth of burial is indicated by T_{max} values and a downward increase in short-chain *n*-alkanes, which are mainly controlled by the advanced maturity of the studied section. In addition, since pristane/*n*-C_{17} and phytane/*n*-C_{18} ratios correlate positively with the percentage of long-chain *n*-alkanes (r^2=0.74 and 0.73, respectively), isoprenoid/*n*-alkane ratios and the percentage of long-chain *n*-alkanes are also mainly controlled by maturity. Furthermore, maturity parameters, including CPI (1.06–1.25), hopane isomerization (average 0.63), moretane/hopane ratios (0.07–0.32; average: 0.15) and Ts/Tm ratios (average: 2.31), support oil window maturity for rocks in the studied section.

Compared to another outcrop locality in the Chornohora nappe (Gryniava, site 7 in Fig. 1; 433–441 °C; Koltun et al. 1998), T_{max} values in the studied profile are significantly higher and similar T_{max} values (454–458 °C) are observed only at 3.5 km depth (borehole Gryniava-1; Koltun et al. 1998; Fig. 3). Koltun et al. (1998) reconstructed a maximum burial depth of about 6 km for the Lower Cretaceous rocks in the Gryniava-1 well and a similar burial depth has to be assumed for the Shypot Formation exposed at the study location.

Remaining and original source rock potential

The high maturity of the Shypot Formation implies that hydrocarbons have already been generated (see also PI values exceeding 0.1). Hence, HI values and the petroleum potential (S_1+S_2) cannot be considered original. Consequently, a plot of the petroleum potential vs. TOC provides information on the remaining source rock potential only (Fig. 8). Based on the (remaining) petroleum potential, the Shypot Formation is

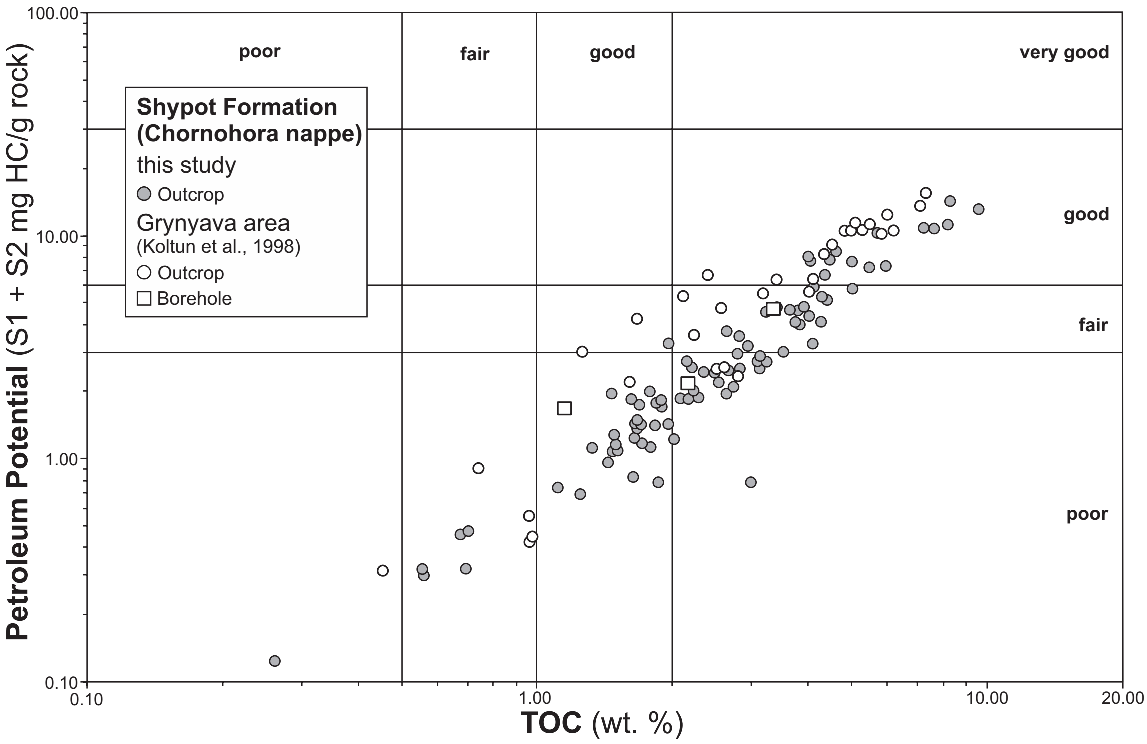

Fig. 8. Petroleum potential vs. TOC for the Shypot Formation in the Chornohora nappe. Data from additional outcrop and borehole samples in the Grynyava area (site 7 in Fig. 1; Koltun et al. 1998) are shown for comparison. Classification after Peters & Cassa (1994).

a poor to good source rock (Fig. 8), despite the very high TOC contents (max. 9.4 wt. %).

The remaining source potential of the Shypot Formation was calculated following the equation for the Source Potential Index (SPI) proposed by Demaison & Huizinga (1994) (SPI= thickness×[S_1+S_2]×bulk density/1000). Assuming a net source rock thickness of 263 m (65 % of the total thickness of the studied section), as well as an average remaining petroleum potential of 3.3 mg HC/g rock and an average density of 2.3 t/m³ (Demaison & Huizinga 1994), an SPI of 2.0 tons of hydrocarbons per square metre surface area can be calculated (tHC/m²).

HI values of the marginal mature outcrop samples at Gryniava (average T_{max}: 437 °C; see Fig. 3) may be used for a very rough estimate of the original SPI. At that locality, HI values range from 58 to 300 mg HC/g TOC and the average HI is 172 mg HC/g TOC (Koltun et al. 1998). The average HI at the studied section is 88 mg HC/g TOC, suggesting that about 50 % of the original potential has already been generated during burial and heating. Hence, the original SPI may have been in the order of 4.0 tHC/m², implying that about 2 tHC/m² have been generated and expelled.

If the generated hydrocarbons formed any accumulations, it is reasonable to assume that these accumulations were destroyed during major uplift and erosion. Based on the thermochronological data, major uplift commenced 12 to 10 Ma ago and post-dated nappe stacking and shortening (Nakapelyukh et al. 2018).

Organic matter type and depositional environment

Maceral analysis (Table 1; Fig. 5) reveals a high percentage in terrestrial organic matter (vitrinite: 34–60 vol. %; inertinite: 0–12 vol. %; sporinite: 15–34 vol. %). However, aquatic macerals (alginite: 18–32 vol. %) also occur in significant amounts. This suggests a mixture of type III and II kerogen, which is also supported by HI values of marginal mature samples (ca. 40–300 mg HC/g TOC) from the Chornohora nappe (Koltun et al. 1998). In contrast, high maturity of the Bystrets section prohibits the use of HI for kerogen classification (Fig. 4).

Relatively high amounts of alginite are reflected by high concentrations of C_{27} steranes (Fig. 7). Nevertheless, considering the maceral percentages, the content in C_{29} steranes, characteristic for woody land-plant input, is surprisingly low.

Preservation of the organic matter was supported by an oxygen-deficient environment, indicated by Pr/Ph ratios, which are low and range between 1.0 to 2.3. Pr/Ph ratios below 1 reflect strict anoxic conditions, and are only observed in the lower part of the studied succession. This, together with relatively high TOC/S ratios (Berner & Raiswell 1984), shows that strictly anoxic conditions were rare. Very low DBT/Phen ratios, partly due to low DBT concentrations, suggest that free H_2S was not available in the water column, providing an additional argument against strict anoxic conditions. Oxygen-depletion may be related to the late Barremian to Albian global anoxic event (OAE 1; Jenkyns 1980).

Glauconite is formed in oxygen-depleted shallow marine environments. Its appearance in most samples (Table 1) suggests detrital input from near-shore environments, which is in line with the high percentages of land plant-derived macerals (esp. vitrinite and sporinite).

Vertical trends show that the environment did not change significantly during deposition of the lower, shaly part of the Shypot Formation.

Comparison with coeval rocks in the Carpathian Basin

Stratigraphic rocks equivalent to the Shypot Formation are found in different nappes along the entire Carpathian Belt. However, many parts of these rocks are unexplored and therefore only a few source rock data are available. The following discussion summarizes bulk geochemical data from Lower Cretaceous rocks according to their tectonic position.

The most external nappe is the **Boryslav-Pokuttya – Marginal Folds nappe**. Lower Cretaceous rocks are absent in the Boryslav-Pokuttya nappe in Ukraine. In contrast, the Sarata Formation in Romania has been traditionally considered Lower Cretaceous (e.g., Melinte-Dobrinescu & Roban 2011; Roban et al. 2017). However, according to Amadori et al. (2012) and Guerrera et al. (2012), only the lower member of the Sarata Formation may be Lower Cretaceous, whereas the middle and upper member are probably Upper Cretaceous (Campanian–Maastrichtian) in age. Silicified black shales occur in the lower and in the middle member and contain on average of 1.49 wt. % and 1.37 wt. % TOC, respectively (Fig. 9d; Amadori et al. 2012). Similar TOC contents (0.3–1.5 wt. %) have been reported recently by Roban et al. (2017). Both successions are marginal mature (439 °C), but HI values vary considerably (Fig. 4b). Organic matter in the lower member has low HI values (47–111 mg HC/g TOC; average: 76 mg HC/g TOC), whereas the middle member displays relatively high HI values (196–394 mg HC/g TOC; average: 290 mg HC/g TOC; based on four samples only), which is the highest recorded value for all Cretaceous rocks in the entire Carpathian Basin. However, as pointed out by Amadori et al. (2012), these rocks are probably Upper Cretaceous in age and may represent the Coniacian to Lower Campanian OAE 3. Relatively high TOC contents (~3 wt. %) also occur in thin shaly layers within the Cenomanian/Turonian succession (Roban et al. 2017).

Data from the **Skole-Skyba-Tarcau nappe** are available from Poland and Ukraine. In both countries (sites 4 and 5 in Fig. 1) Hauterivian to Aptian aged rocks (Lower Spas Formation) are immature (average T_{max}: 429 °C) and contain high amounts of organic matter (Ukraine: 2.02–6.19 wt. % TOC; average 3.30 wt. % TOC; Poland: max. 4.53 wt. % TOC; average: 2.85 wt. %). HI values are very low (~50 mg HC/g TOC) in spite of low maturity. Deep borehole samples in Ukraine (~4400 m; site 6 in Fig. 1) are mature (448 °C) and contain even higher TOC contents (4.05 wt. %; max. 7.84 wt. %) with an average HI of 153 mg HC/g TOC; max. 235 mg HC/g TOC) (Figs. 4b, 9c). Melinte-Dobrinescu & Roban (2011) report high TOC contents (average: 3.2 wt. %; max. 5.5 wt. %) from the Tarcau nappe in Romania. Unfortunately, Rock Eval data are not available.

Data from the **Silesian-Krosno nappe** are available from the Polish Carpathians (sites 1–3 in Fig. 1; Slaczka et al. 2014). Only samples from site 2 are immature to marginal mature (T_{max}: 435 °C). They contain high amounts of organic matter (average 2.5 wt. %, max. 3.72 wt. % TOC) with HI values ranging from 92 to 267 mg HC/g TOC (average 196 mg HC/g TOC). Average TOC contents (1.6 wt. %) of mature to overmature samples at sites 1 and 3 are slightly lower, although the maximum content is similar (3.70 wt. %). HI values are low (average 65 mg HC/g TOC), due to advanced maturity. High TOC contents (2.0–3.7 wt. %) were also reported from the western Czech part of the nappe (Pavlus & Skupien 2014).

Lower Cretaceous rocks in the **Dukla-Chornohora-Audia nappe** have been studied in this paper and by Koltun et al. (1998) in its Ukrainian sector (Chornohora nappe) and by Anastasiu et al. (2013) in its Romanian sector (Audia nappe). The average TOC content in immature to marginal mature outcrops of the Lower Shypot Beds in the Grynyava area (T_{max} 437 °C) is 4.6 wt. % (max. 7.5 wt. %) and the average HI is 177 mg HC/g TOC. Mature outcrop samples in Ukraine (this study) and Romania (site 9 in Fig. 1) and mature samples from a deep borehole are characterized by an average T_{max} of 456 °C. The average TOC (1.3–2.8 wt. %) and HI values (56–109 mg HC/g TOC) for these regions varies significantly. According to Melinte-Dobrinescu & Roban (2011), TOC contents in the Audia nappe range from 1.05 to 3.35 wt. %. Marginal mature outcrop samples from the Upper Shypot Beds (439 °C) contain low amounts of organic matter (ca. TOC 1.0 wt. %) with very low HI values (ca. 45 mg HC/g TOC).

Overall, the comparison generally shows a strong dependency of HI values on maturity (Fig. 4b). Black shales with a remarkably low potential occur in the north-western part of the Skole-Skyba nappe and in the upper Shypot Beds (Chornohora nappe). The interpretation of data from the Marginal Folds in Romania is complicated by the uncertain age data. Apart from that, most sections contain TOC-rich samples, but HI values are relatively low even in immature samples, indicating the presence of an original type III-II kerogen. Nevertheless, their hydrocarbon potential should be considered, although the Menilite formation clearly contains source rocks with a better quality (Sachsenhofer et al. 2018a, b).

Conclusion

The Shypot Formation in the Chornohora nappe comprises organic-rich shales with interbedded siltstones and sandstones at the studied section near the village of Bystrets. The succession is approximately 405 m thick and is characterized by high organic matter content. TOC content exceeds 9 wt. % in one sample in the lower part of the succession and averages 2.8 wt. % for the entire section. HI values (average 88 mg

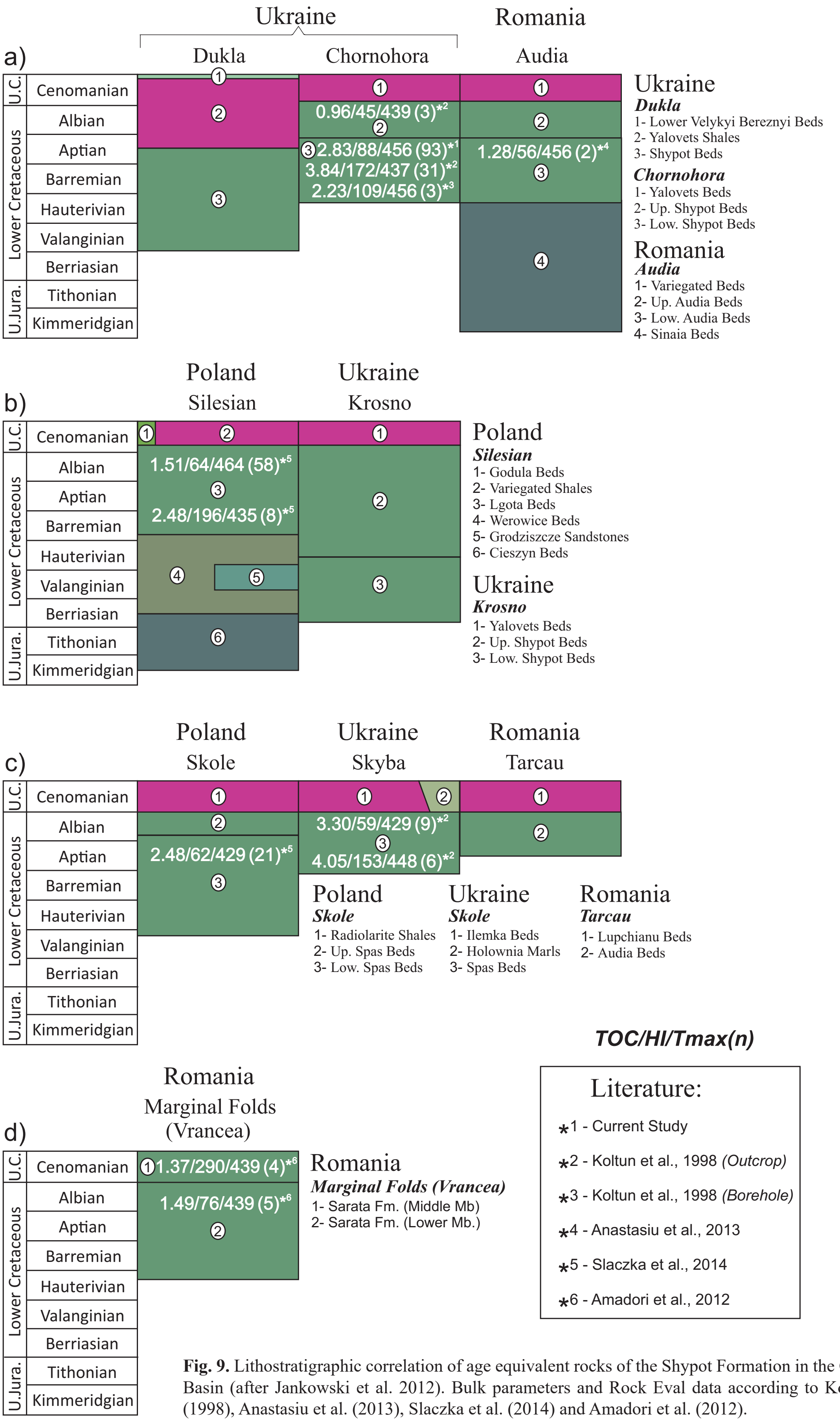

Fig. 9. Lithostratigraphic correlation of age equivalent rocks of the Shypot Formation in the Carpathian Basin (after Jankowski et al. 2012). Bulk parameters and Rock Eval data according to Koltun et al. (1998), Anastasiu et al. (2013), Slaczka et al. (2014) and Amadori et al. (2012).

HC/g TOC), suggest a gas-prone type III kerogen, but increase slightly towards the top of the formation. The Shypot Formation is thermally mature (average vitrinite reflectance: 0.82 % Rr; T_{max}: 456 °C). Pr/Ph ratios (0.41 to 2.23) argue for oxygen-depleted conditions during deposition. Ratios below 1.0 are restricted to the lower part of the succession. Compared to other parts of the Carpathian Basin, the Shypot Formation in the study area is slightly more mature, but displays similar TOC content compared to other coeval rocks.

The TOC suggests very good source rock potential, however according to the petroleum potential, the formation is a poor to good source rock. The high maturity of the Shypot Formation implies that hydrocarbons have likely already been generated. Hence, HI values and the petroleum potential (S_1+S_2) cannot be considered as the original amount. The remaining Source Potential Index (SPI) shows that 1.8 tons of hydrocarbons per m² can be generated, whereas the original SPI, which is a rough estimate based on the marginal mature outcrop samples from previous data on the Shypot Formation in the Chornohora nappe, yields an SPI in the order of 4 tHC/m², implying that about 2 tHC/m² have been generated.

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