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Source rock potential of the Oligocene Menilite Formation in the Czech sector of the Subsilesian Unit (Flysch Carpathians)

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Abstract: The Oligocene Menilite Formation represents the most important hydrocarbon source rock in the Flysch Carpathians. The formation is laterally uniform across long distances but shows strong vertical heterogeneity reflecting changes in depositional environments, which control the source rock potential. In the Czech Republic, the Menilite Formation is subdivided into the Subchert Member (nannofossil zone NP22), Chert Member (upper NP22 to lower NP23), Dynów Marlstone (NP23) and Šitbořice Member (upper NP23 to lower NP25). The present study describes in detail the Bystřice nad Olší section in the Subsilesian Unit where all four members are exposed including the uppermost part of the underlying Frýdlant Formation (Sheshory Marls). The present Frýdlant Formation has a negligible source rock potential compared to the Menilite Formation. The Menilite Formation in the Bystřice nad Olší section has mostly "good" source rock potential, although the TOC indicates "very good" potential. The Subchert Member (average TOC: 3.6 wt. %; HI up to 505 mg HC/g TOC) and the Chert Member (average TOC: 2.2 wt. %; HI up to 790 mg HC/g TOC) are the most prolific units. Based on organic petrography and HI, the kerogen is classified as type II and I. Indications of admixtures of type III kerogen are limited to samples with low TOC contents (<1 wt. %). The Source Potential Index (SPI) of the Menilite Formation in the Subsilesian Unit of the Czech Republic is estimated as ~1.15 t HC/m^2 which is comparable to SPI calculated for sections in the Silesian and Ždánice units in the Czech Republic and for the Waschberg Zone in Austria. Significantly higher SPI values estimated for the Polish and especially the Ukrainian Carpathians (up to 74.5 t HC/m^2) are caused by a wider stratigraphic range, several times greater thickness and higher total organic matter content.

Keywords: Menilite Formation, Paratethys, Outer Western Carpathian Flysch Belt, source rock potential, anoxia, organic petrography, thermal maturity.

Introduction

According to Klemme & Ulmishek (1991), Oligocene to Lower Miocene source rocks account for ~12.5 % of all discovered hydrocarbon reserves worldwide (see also Sorkhabi 2009). They are also the most important source rock in the Paratethys area, including the Carpathians (Sachsenhofer et al. 2018a, b), which represent one of the oldest petroleum-producing districts in the World (Boote et al. 2018) where hydrocarbons exploration and production began in the 1850s.

The Eocene–Oligocene boundary is characterized by a major extinction event followed by anoxic sedimentary conditions (Haq 1973; Aubry 1992; Prothero et al. 2000). The change from green-house into the ice-house conditions caused a significant sea-level drop and closing of marine gateways (Prothero et al. 2000). This, together with an overall increase of ocean fertility (e.g., Baldauf & Barron 1990; Salamy & Zachos 1999; Thomas et al. 2000), resulted in oxygen-depleted conditions and deposition of organic-rich rocks. The Oligocene to Early Miocene anoxic events in the Paratethys were controlled by climatic factors and episodic isolation of the region from the Mediterranean realm as a consequence of the progressing collision between African and Eurasian plates (Rögl 1999; Popov et al. 2004).

The Menilite Formation was first described by Glocker (1844) in the Moravia, Czech Republic. Recently, the Menilite Formation has been studied from Austria (Pupp et al. 2018), through the Czech Republic (Franců & Feyzullayev 2010; Jirman et al. 2018, 2019), Poland (Kosakowski et al. 2018 cum. lit.; Kotarba et al. 2019) and Ukraine (Sachsenhofer & Koltun 2012; Kotarba et al. 2019; Rauball et al. 2019) to Romania (Wendorff et al. 2017). Similar organic-rich rocks have been described in the Pannonian Basin (Bechtel et al. 2012), the Western Black Sea Basin (Sachsenhofer et al. 2009) and in the Eastern Paratethys between the Black Sea Basin and the Caspian region (Bechtel et al. 2013, 2014; Sachsenhofer et al. 2017).

Systematic research generated detailed information about depositional environments, kerogen type, thermal maturity and source rock potential of the Menilite Formation (e.g., Sachsenhofer et al. 2018a cum. lit.). Although data are available from a section in the Czech Republic (e.g., Jirman et al. 2018, 2019), there is serious lack of data from the western part of Western Carpathians. In the present paper, we study the Bystřice nad Olší section in the Subsilesian Nappe. The section is located near the Polish border, allowing to study the differences of the Menilite Formation in the Czech Republic and Poland, where the Menilite Formation is much thicker (cf. Sachsenhofer et al. 2018a, b) and the proven source rock for hydrocarbons (e.g., Kotarba & Koltun 2006).

Geological settings

The Carpathians represents a part of the Alpine orogenic belt extending for more than 1300 km from the Austrian–Czech to the Serbian–Romanian border (Fig. 1; Golonka et al. 2006). The Flysch Belt on the territory of the Czech Republic forms a SW–NE trending segment of the Western Carpathians (Fig. 1). The Krosno–Menilite Group of Nappes comprises Pouzdřany, Ždánice, Zdounky, Subsilesian, Silesian, and Fore-Magura units (Pícha et al. 2006). The studied Bystřice nad Olší section is located within the Subsilesian Unit

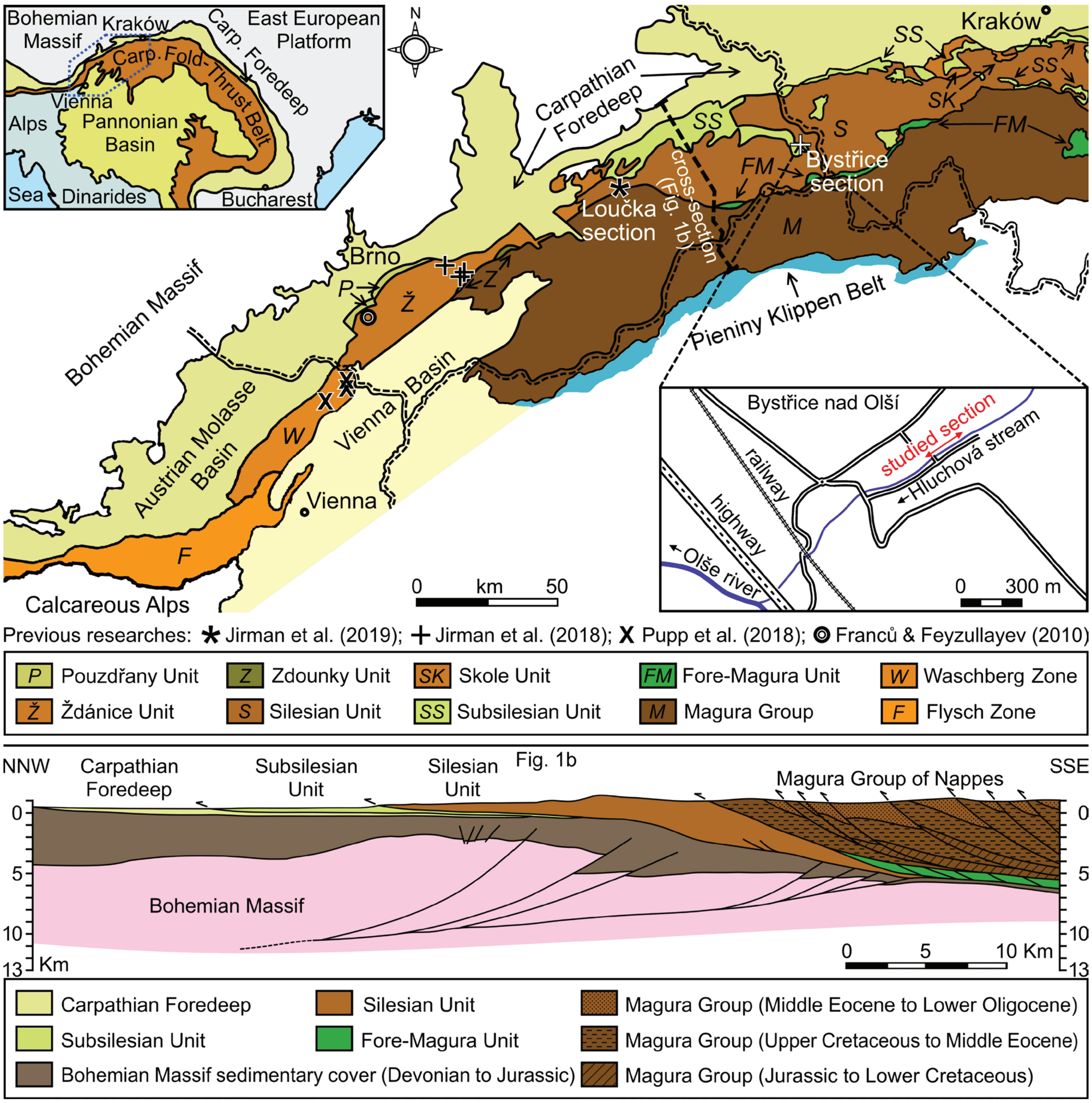

Fig. 1. Schematic geological map with studied Bystřice nad Olší section highlighted (white cross on the map). The studied localities of previous researches used for comparison purposes are shown as symbols in map. Cross-section through the Western Carpathian Flysch Belt according to Pícha et al. (2006).

(Fig. 1), which is equivalent to the Ždánice Unit and the Waschberg Zone in Austria forming a single major frontal thrust system of the Outer Western Carpathian Flysch Belt (Pícha et al. 2006).

The Menilite Formation on the territory of the Czech Republic

The Menilite Formation is mainly formed by pelitic, carbonate and siliceous rocks of pelagic origin (Bubík et al. 2016) which are typically rich in organic matter. In the area of the Czech Republic, the formation is formally subdivided according to Stráník et al. (1974) and Stráník (1981) into the Subchert Member (nannofossil zone NP22), Chert Member (upper NP22 to lower NP23), Dynów Marlstone (NP23) and Šitbořice Member (upper NP23 to lower NP25; Fig. 2).

The Menilite Formation is underlain by Sheshory Marls (also termed Globigerina Marls; up to NP21), which form the uppermost part of the Upper Cretaceous to Eocene Frýdlant Formation (Eliáš 1998; also known as Submenilite Formation). The Frýdlant Formation (Fig. 2) is predominantly composed of variegated facies formed by grey, green and red shales.

The boundary between the Sheshory Marls and the Subchert Member (lower NP22) of the Menilite Formation is evidence for a drop of the CCD (calcite compensation depth) caused by the climate changes (Stráník 1981).

The Subchert Member, typically formed by brown stratified marls inter-bedded with dark laminated shales with fish scales (Pícha et al. 2006), represents the stepwise isolation from the world ocean (Švábenická et al. 2007).

The Chert Member consists of organic-rich laminated cherts and non-calcareous siliceous shales deposited in bathyal, anoxic conditions with limited influx of detrital material (Pícha & Stráník 1999). According to Krhovský (1981), the cherts are connected with long-lasting deposition of diatomites in a low salinity environment during a cooling period with increased seasonality. Anoxic conditions continued in the deep water during deposition of the Dynów Marlstone (NP23), which is composed of relatively homogeneous pelagic limestones and marlstones. Slightly increased surface salinity enabled blooms of calcareous nannoplankton, but was not yet high enough to enable the return of planktonic foraminifers (Krhovský 1981).

The base of the Šitbořice Member (uppermost NP23 to lowermost NP25) is often marked by slumps and debris flows with an erosional base (Stráník 1981) related to the Šitbořice event (Krhovský & Djurasinović 1993). The Šitbořice Member, characterized by brown non-calcareous shales, reflects the restoration of normal marine conditions. Anoxic conditions alternated with oxic episodes, as apparent from the alternation of light-coloured bioturbated layers and dark-coloured non-biodegraded "fish-shales". Predominantly hemipelagic depositional conditions turned to turbiditic conditions during deposition of the Šitbořice Member.

Locally, the Jasło Limestone with intercalations of laminated shaly carbonates was recognized within the Šitbořice Member (Jucha 1958). Bubík (1987) observed the Jasło limestone horizon associated with non-laminated Zagórze-type limestone (Haczewski 1989) in the studied Bystřice nad Olší section. The Menilite Formation in the Subsilesian Unit locally contains additional thick facies of slump conglomerates and debris flows containing clasts of crystalline basement and Paleozoic to Paleogene sedimentary rocks (Pícha et al. 2006).

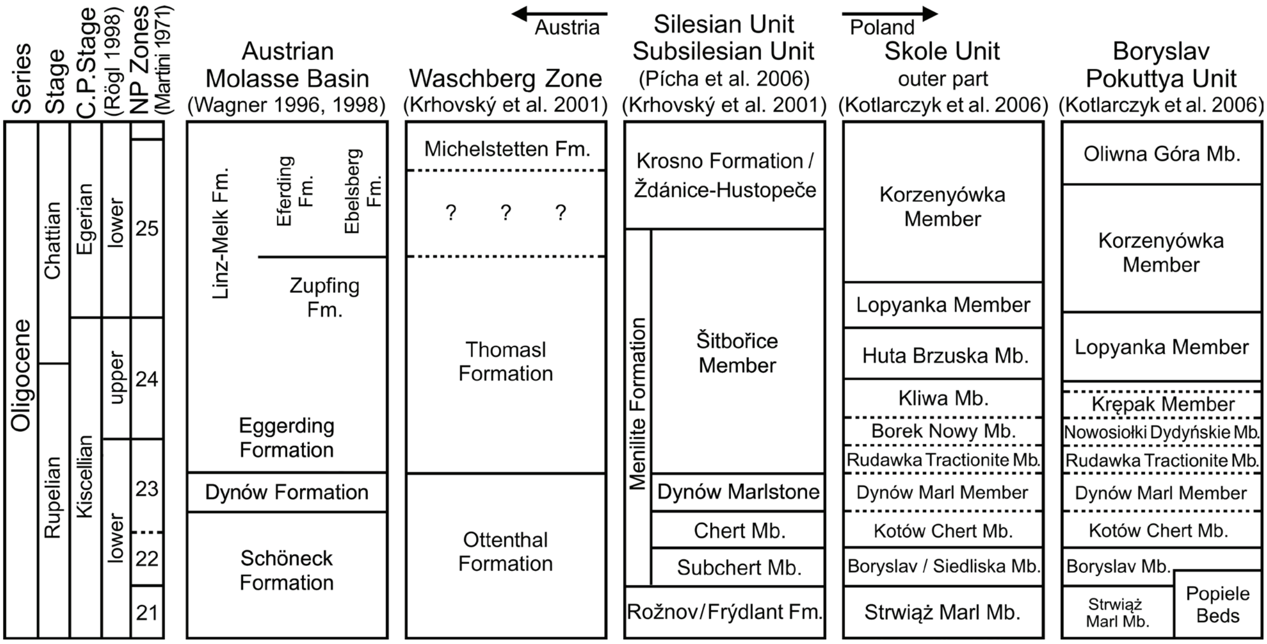

Fig. 2. Simplified Oligocene stratigraphic correlation of selected Carpathian Flysch Belt units in Austria, Czech Republic and Poland. Modified according to Krhovský et al. (2001) for Czech territory, Wagner (1996, 1998) for Austrian territory and Kotlarczyk et al. (2006) for Polish territory. Stages of the Central Paratethys are according to Rögl (1998); NP Zones according to Martini (1971).

The total thickness of the Menilite Formation in the Subsilesian Unit is typically below 50 m, but does not exceed 100 m.

Materials and methods

Materials

The Bystřice nad Olší section is located in the Subsilesian Unit of the Western Carpathian Flysch Belt in Silesia, Czech Republic. The section contains four separate outcrops, up to 1 m high, in a bed of the Hluchová stream (Fig. 3). The total length of the section is about 180 m, whereas the total true vertical thickness of the composite section is ~33 m (Fig. 4). Since the times of measuring and sampling the section, stream banks and some parts of the stream bed were reinforced by sandstone blocks to prevent stream erosion. These blocks and newly deposited gravel sediments cover most of the section at the present time.

The Bystřice nad Olší section exposes the uppermost part of the Frýdlant Formation (Sheshory Marls) and all members of the Menilite Formation (Fig. 3). However, the members are not complete because the section, mostly overturned, is dissected by four faults (*α*, *β*, *γ*, *δ*) causing stratigraphic gaps. Nevertheless, a composite section of the profile was created (Fig. 4). The outcrops 3 and 4 expose two limbs of a fold as indicated by the tectonically repeated Jasło Limestone horizon (Fig. 3).

The exposed formations were lithologically described and 39 samples were collected (Appendix), partly below the water table of the Hluchová stream. Any weathered material was removed from the fresh outcrop samples. The sampling interval was chosen according to outcrop conditions and lithology variations and was reduced within the lithological divers Subchert Member and in the vicinity to the Jasło Limestone in the Šitbořice Member. Outcrop 3 (Fig. 3) was poorly exposed during the sampling campaign. Therefore, another 9 samples (1 from Dynów Marlstone and 8 from the Šitbořice Member) from the archive of M. Bubík were added for this study. From the total 48 samples, 3 samples represent the Frýdlant Formation (Sheshory Marls) and 45 the Menilite Formation (Subchert Member: 11 samples, Chert Member: 3 samples; Dynów Marlstone: 3 samples; Šitbořice Member: 28 samples).

Methods

The samples were cleaned, dried and pulverized. All samples were analysed for bulk geochemical parameters and Rock-Eval pyrolysis. Contents of total carbon (TC), total organic carbon (TOC) and total sulphur (TS, all in [wt. %]) were analysed using an ELTRA S/C Element Analyser. TOC was measured after decarbonatization of the samples with concentrated phosphoric acid. All samples were measured at least twice, final data (Appendix) represent average values free of outliers. Total inorganic carbon (TIC, [wt. %]) was calculated as TC–TOC. The content of calcite equivalent (Calc. Eq., [wt. %]) was calculated as TIC · 8.333, which is the stoichiometric factor for $CaCO_3$.

The Rock-Eval 6 instrument was used to determine the free hydrocarbons content S_1 [mg HC/g rock], remaining hydrocarbon potential S_2 formed during pyrolysis [mg HC/g rock] and temperature T_{max} [°C] at the S_2 peak maximum. The hydrogen index $HI = 100 \cdot S_2/TOC$ [mg HC/g TOC] and the production index $PI = S_1/(S_1+S_2)$ [mg HC/g rock] were calculated following Lafargue et al. (1998). The determination of HI_{true} is based on TOC_{live} which represents pyrolysable (or reactive) portion of overall TOC (Dahl et al. 2004). The genetic potential GP [mg HC/g rock] is represented by the sum of Rock-Eval S_1+S_2 peaks.

The amount of hydrocarbons, which can be generated below 1 m² of surface area, was calculated using the source potential index (SPI [t HC/m^2]) according to Demaison & Huizinga (1991). The SPI for particular source rock ($_{SR}$)=thickness$_{SR}$× GP$_{SR}$×bulk density$_{SR}$/1000.

Nine samples of the Menilite Formation (Subchert Member: 2 samples, Chert Member: 3 samples; Dynów Marlstone: 2 samples; Šitbořice Member: 2 samples) were selected for maceral analysis. Polished blocks were prepared following procedures outlined in ISO 7404-2 (2009). The maceral composition was determined following the ISO 7404-3 (2009). The macerals were identified under reflected white and blue light using a reflecting light microscope Olympus BX51 with fluorescence system coupled to an automatic point counter PELCON attached to a mechanical stage. The nomenclature and terminology used for maceral identification has been adopted from the ICCP System 1994 (ICCP 1998, 2001), Sýkorová et al. (2005) and Pickel et al. (2017).

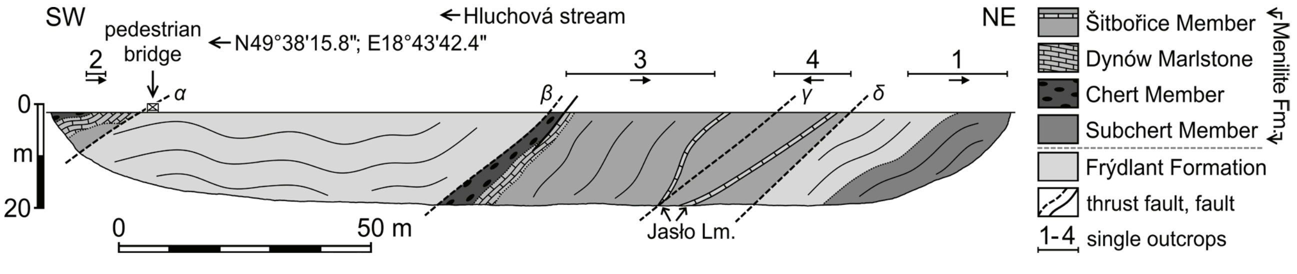

Fig. 3. Geological sketch of the Bystřice nad Olší section composed of four separate outcrops (1–4) exposing the Menilite Formation and the upper part of the underlying Frýdlant Formation. For the location of the section see Fig. 1. Small arrows indicate direction upward.

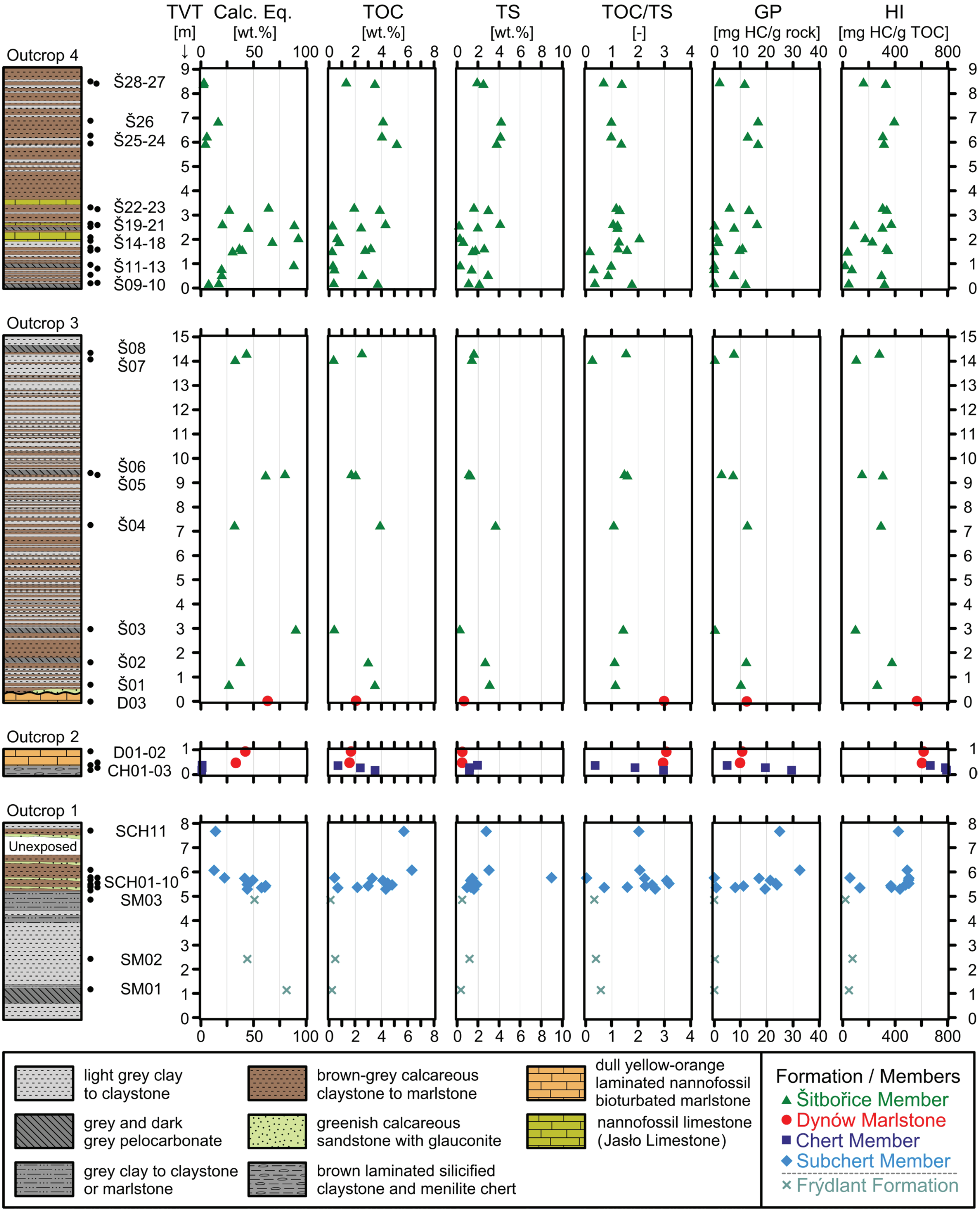

Fig. 4. Depth trends of geochemical proxies and Rock-Eval data of the Menilite Formation and uppermost Frýdlant Formation within the Bystřice nad Olší section. TVT=true vertical thickness; Calc. Eq=calcite equivalent; TOC=total organic carbon; TS=total sulphur; GP=genetic potential (Rock-Eval S_1+S_2 values); HI=hydrogen index.

Results

Lithological composition

The exposed part of the Frýdlant Formation (Sheshory Marls) is 5.3 m thick. It consists of light grey clay to claystone or marlstone with few pelocarbonate beds.

The overlying Subchert Member of the Menilite Formation (Figs. 3 and 4) is 2.3 m thick and dominated by brown-grey calcareous claystone to marlstone. The claystone includes thin layers of greenish calcareous sandstone with glauconite. The carbonate content is high in the lower part and low in the upper part (Fig. 4).

The exposed upper part of the Chert Member is only 0.5 m thick and consists of brown laminated silicified non-calcareous claystone and menilite cherts.

The lower- and uppermost parts of the Dynów Marlstone are present in outcrops 2 and 3, respectively (Fig. 4), whereas the middle part is missing. Hence, only 0.75 m of Dynów Marlstone is exposed. The Dynów Marlstone is a homogeneous dull yellow-orange laminated nannofossil marlstone (Figs. 3 and 4). The carbonate content increases upwards from 34 to 64 wt. % (Appendix).

The exposed part of the Šitbořice Member is about 23.5 m thick. The lower part in outcrop 3 (Figs. 3 and 4) comprises alternations of light grey claystone to marlstone and brown-grey calcareous claystone to marlstone. Both lithotypes attain similar total thickness, but brown-grey calcareous claystone to marlstone prevails in the upper part (outcrop 4 in Fig. 3 and 4). The Jasło Limestone is a brownish/creamy laminated nannofossil limestone. Its carbonate content (~83 wt. %) is higher than that of the Šitbořice Member *sensu stricto* (without the Jasło Limestone; ~32 wt. %).

Bulk geochemical proxies and Rock-Eval data

The Frýdlant Formation (Sheshory Marls) has very low TOC contents (average 0.30 wt. %, range 0.17–0.50 wt. %) and GP in order of 0.04 to 0.40 mg HC/g rock. The average HI reaches 51 mg HC/g TOC only. The TOC/TS ratio is <1.

Each Menilite Formation member was evaluated individually despite of the small number of Chert Member and Dynów Marlstone samples. A summary of TOC and Rock-Eval data is provided in Table 1. All data are plotted versus depth in Fig. 4 and are listed in Appendix.

The Subchert Member reaches the highest average TOC of 3.6 wt. % (range 0.46–6.3 wt. %) of all Menilite Formation members. TOC contents are higher in the carbonate-poor upper part and lower in the carbonate-rich lower part. The brown-grey calcareous claystone to marlstone (9 samples) has an average TOC of 4.24 wt. %. The GP of the Subchert Member is high with the average of 16.6 mg HC/g rock (range 0.29–32.3 mg HC/g rock). The average HI is 389 mg HC/g TOC (range 59–505 mg HC/g TOC). In both parameters, the brown-grey calcareous claystone to marlstone has the highest average values of 20.2 mg HC/g rock or 454 mg HC/g TOC, respectively, compared to other lithotypes.

TOC contents of the exposed part of the Chert Member vary widely from 0.72 to 3.5 wt. % (average 2.21 wt. %). The GP and HI reach average values of 18.0 mg HC/g rock (range 5.1–29.3 mg HC/g rock) and 746 mg HC/g TOC (range 667–790 mg HC/g TOC), respectively. The small thickness of the exposed part of the Chert Member prevents the recognition of depth trends.

The Dynów Marlstone has relatively uniform TOC contents (1.59–2.08 wt. %; average 1.79 wt. %). The GP and HI values reach average values of 11.0 mg HC/g rock (range 10.0–12.4 mg HC/g rock) or 595 mg HC/G TOC (range 563–614 mg HC/g TOC), respectively. Generally all parameters are rather uniform and do not display significant vertical depth trends (Fig. 4).

The Šitbořice Member has TOC contents in the range of 0.20 to 5.2 wt. % (average 2.25 wt. %) without apparent depth trend. The average TOC content of brown-grey calcareous claystone to marlstone (17 samples) is 3.33 wt. %, while that of light grey clay to claystone (5 samples) and Jasło Limestone or grey pelocarbonate (6 samples) is significantly lower (0.58 wt. %). The average GP of the Šitbořice Member is 7.2 mg HC/g rock (range 0.08–16.7 mg HC/g rock), while the average HI is 242 mg HC/g TOC (range 36–395 mg HC/g TOC) and lower than in underlying units. The brown-grey calcareous claystone to marlstone of the Šitbořice Member reaches higher average values of GP (11.3 mg HC/g rock) and HI (322 mg HC/g TOC).

T_{max} values typically range from 416 to 437 °C (average 421 °C). A single pelocarbonate sample from the Šitbořice Member (sample "Š03") with very low TOC (0.26 wt. %), but high PI (0.28) has a T_{max} of 361 °C. Therefore, this value is considered an artefact caused by bitumen contamination. Apart from sample "Š03", PI values range from 0.02 to 0.14 (average: 0.05).

TS contents typically range from 0.24 to 4.2 wt. % and are positively related to TOC contents. Only sample "SCH09" from the Subchert Member has a low TOC (0.46 wt. %), but a very high TS (8.96 wt. %) content. TOC/TS ratios are generally < 2.8 (average 1.42). Higher TOC/TS ratios are restricted to Dynów Marlstone (average 2.99) and some samples from the base of the Subchert Member.

Organic petrography

The organic matter of all studied samples is dominated by macerals of the liptinite group (Fig. 5). The most abundant macerals are alginite, bituminite and liptodetrinite. Pyrite is found as single or framboidal crystals and small aggregates in all samples very often associated with alginite macerals.

The microscopically visible organic matter in the Subchert Member consists mainly of alginite derived from small unicellular or thin-walled algae followed by liptodetrinite. Bituminite and resinite occur in a very small amount. The amount of huminite and inertinite macerals reaches up to 15 and 2 vol. %,

Table 1: Geochemical proxies and Rock-Eval data of the individual member and whole Menilite Formation including uppermost part of the underlying Frýdlant Formation.

Parameter Member	**TOC [wt. %]**	**GP [mg HC/g rock]**	**HI [mg HC/g TOC]**	**Kerogen Type (based on HI)**	**T_{max} [°C]**
Šitbořice Mb.	0.20−5.2 (28) 2.25	0.08−16.7 (28) 7.2	36−395 (28) 242	Type II and III	416−437 (28) 423
Dynów Mrst.	1.59−2.08 (3) 1.79	10.0−12.4 (3) 11.0	563−614 (3) 595	Type II-I	424−426 (3) 424
Chert Mb.	0.72−3.5 (3) 2.21	5.1−29.3 (3) 18.0	667−790 (3) 746	Type I	424−426 (3) 425
Subchert Mb.	0.46−6.3 (11) 3.6	0.29−32.3 (11) 16.6	59−505 (11) 389	Type II, admix. of type III	418−426 (11) 420
Menilite Fm. (Σ)	0.20−6.3 (45) 2.54	0.08−32.3 (45) 10.5	36−790 (45) 335	Mostly type II	416−437 (45) 421
Frýdlant Fm. (Σ)	0.17−0.50 (3) 0.30	0.04−0.40 (3) 0.19	23−78 (3) 50	Strictly type III	416−422 (3) 420

TOC=total organic carbon; GP=genetic potential (Rock-Eval S_1+S_2 values); HI=hydrogen index; T_{max}=temperature of maximum of S_2 peak. Range of selected parameters is given as numerator (number of evaluated samples in parentheses); average values in denominator.

respectively. The size of the huminite can be up to 100 µm and some particles of huminite have been observed as mineralized.

The Chert Member contains predominantly bituminite the size of which can exceed 500 µm. The alginite and liptodetrinite macerals are less common. Huminite and inertinite macerals are rare and mainly small in size (<20 µm) with some exception of mineralized huminite bands/layers that can reach up to 800 µm in length and 50 µm in thickness. The Chert Member samples show a distinct layering and fish remnants. The sample "CH03" contains a thick pyrite layer.

The Dynów Marlstone is very homogeneous with dominant alginite macerals from liptinite group. The presence of fish remnants has been confirmed. The huminite and inertinite macerals are rare and small in size.

The Šitbořice Member is characterized mostly by alginite and liptodetrinite. Huminite particles are more abundant than in the Dynów Marlstone.

Discussion

Thermal maturity

The studied succession is thermally immature. The low thermal maturity is indicated by both the Rock-Eval temperature T_{max} (average 421 °C) and low PI (average 0.05). Trends in thermal maturity cannot be expected because of the small thickness of the studied section. Thus, slight T_{max} variations are presumably related to different lithological composition. Based on the observed low thermal maturity, the TOC and HI values are considered as original.

Kerogen type

Based on the organic petrography, the predominance of macerals of liptinite group assigns organic matter from Menilite Formation to kerogen type I and II (Pickel et al. 2017). Slightly higher content of huminite and inertinite, which are considered as typical kerogen type III macerals, was remarked within Subchert and Šitbořice members. The enriched content of terrestrial derived macerals within the Šitbořice Member may reflect changing depositional conditions from predominantly hemipelagic conditions towards the turbiditic ones.

The cross-plot of HI versus T_{max} (Fig. 6) indicates prevailing kerogen type II within the Subchert and Šitbořice members, type II-I within the Dynów Marlstone and type I in the Chert Member, respectively. The low HI samples (13 samples with HI<250 mg HC/g TOC) of the Menilite Formation indicating kerogen type III belong to the light grey clay to claystone and Jasło Limestone (or grey pelocarbonate) within the Šitbořice Member and light grey clay to claystone and greenish calcareous sandstone of the Subchert Member. Those samples contain almost exclusively low TOC contents (average of 0.63 wt. %) which may cause imprecise kerogen type interpretation (Peters & Cassa 1994). This applies also for the uppermost Frýdlant Formation, where kerogen type III is indicated.

A refined kerogen type evaluation within the Šitbořice and Subchert members based on the HI can be gained by applying a method suggested by Dahl et al. (2004). The method determines HI_{true} calculated based on the pyrolysable kerogen (TOC_{live}) only. The TOC_{live} can be calculated as $TOC-TOC_{inert}$, where TOC_{inert} is determined from TOC versus S_2 cross-plot (Fig. 7, Dahl et al. 2004). The TOC_{inert} represents ~0.55 wt. % (~15 %) of overall TOC within the Subchert Member and ~0.61 wt. % (~27 %) in the Šitbořice Member. Thus, the HI_{true} is higher for corresponding ratio which differs a little according to different statistical evaluation (Dahl et al. 2004), but indicates presence of kerogen type II within both the Šitbořice and Subchert members. The method cannot be used for other members due to insufficient number of samples for statistical evaluation. In any case, the low-TOC samples negatively influencing the kerogen type evaluation were not observed within the Chert Member nor the Dynów Marlstone. Thus, the classical kerogen type evaluation based on HI values (Fig. 6) is relevant for both the Chert Member and Dynów Marlstone.

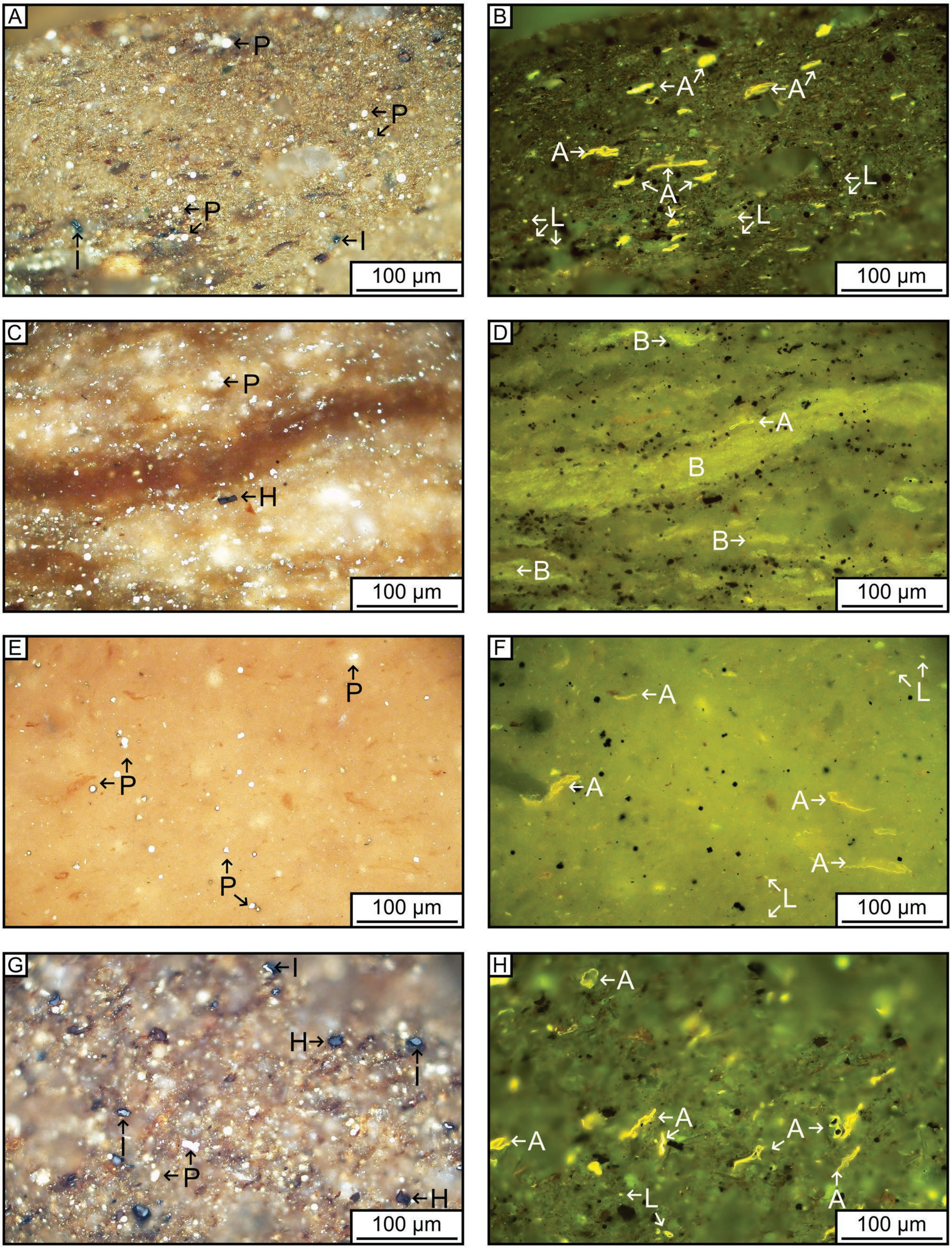

Fig. 5. Reflected white light (left) and fluorescence mode (right) photographs sorted according to depth: Subchert Member (SCH10, A–B), Chert Member (sample CH01, C–D), Dynów Marlstone (sample D02, E–F) and Šitbořice Member (sample Š24, G–H). P=pyrite, H=huminite, I=inertinite, A=alginite, B=bituminite, L=liptodetrinite.

Indications for salinity conditions

The TOC/TS ratio can be used as an indicator for salinity and redox conditions (Berner 1984; Berner & Raiswell 1984). While TOC/TS ratios ~2.8 indicates normal marine conditions, values >2.8 are typical for sulphate-limited brackish water conditions. Significantly lower TOC/TS ratios may indicate sulphate reduction and euxinic conditions.

It is generally accepted that the Chert Member and the Dynów Marlstone were deposited in environments with significantly reduced salinity (Krhovský 1981; Jirman et al. 2019). Low TOC/TS values prevail in the studied rocks (Fig. 4). This could indicate sedimentation in oxygen-depleted environment. There is significantly higher content of TS in the Chert Member and Dynów Marlstone samples in the Bystřice nad Olší section (average TS=1.04 wt. %) in comparison with the Loučka section in the Silesian Unit (average TS=0.26 wt. %; Jirman et al. 2019). With the same type of organic matter and environmental conditions, one explanation can be increased salinity. However, biomarkers are needed for verification. Nevertheless, it becomes evident that Dynów and Chert samples are characterized by higher TOC/TS ratios than most other samples. Strongly varying and some increased values of TOC/TS ratios in the Subchert Member may indicate significant salinity variations. Additional paleontological data are needed to confirm salinity variations in the Bystřice nad Olší section.

Source rock potential

The source rock potential (Fig. 8) was evaluated based on the cross-plot of GP (Rock-Eval S_1+S_2 values) versus TOC according to Peters & Cassa (1994). The Menilite Formation encountered within the Bystřice nad Olší section has mostly “good” source rock potential according to GP, even though the TOC indicates “very good” potential. Surprisingly, the source rock potential of the Subchert and Chert members is almost equal (16.6 versus 18.0 mg HC/g rock). Based on previous research, much better source potential was expected within the Chert Member (e.g., Jirman et al. 2019, average GP 45.1 mg HC/g rock). Considering the presence of type I kerogen, the relatively low source potential of the Chert Member in the Bystřice nad Olší section is caused by TOC contents, which are significantly lower than in other locations (e.g., Jirman et al. 2019). Within this context, the insufficient number of Chert Member samples has to be emphasized. Samples with low source rock potential (“poor” to “fair” classification in Fig. 8) represent the light grey clay to claystone and Jasło Limestone (or grey pelocarbonate) within the Šitbořice Member and light grey clay to claystone and greenish calcareous sandstone of the Subchert Member. “Good” source rock potential is also indicated for the Dynów Marlstone, which includes high quality type I and II kerogen. The underlying uppermost part of the Frýdlant Formation has negligible source rock potential compared to the Menilite Formation (Fig. 8).

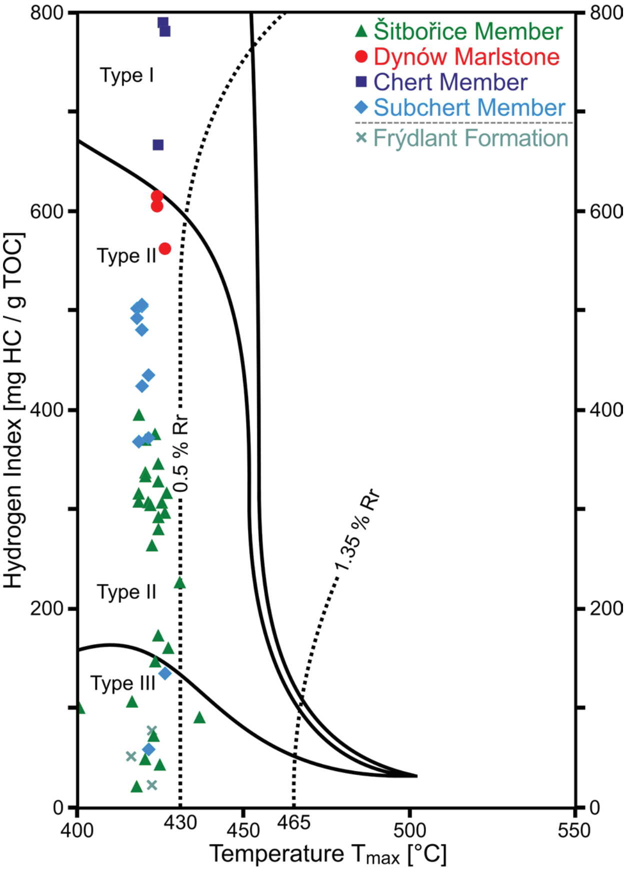

Fig. 6. Cross-plot of HI versus Rock-Eval temperature T_{max} (Pseudo van Krevelen diagram) indicating prevailing kerogen type and thermal maturity of the Menilite Formation including the uppermost part of the underlying Frýdlant Formation. Kerogen type maturation paths according to Espitalié et al. (1985).

The source potential index (SPI) known also as cumulative hydrocarbon potential (Tissot et al. 1980) expresses the maximum quantity of hydrocarbons that can be generated beneath 1 m^2 of source rock surface area (Demaison & Huizinga, 1991). The SPI represents a rough estimate only as it presumes completely mature source rock and does not distinguish between oil- and gas- generation capacity. For better characterization, the Šitbořice Member was subdivided into two parts based on its different lithological composition and prolificness.

Input parameters for the SPI calculation are shown in Table 2. A constant rock density of 2.5 t/m^3 was used as proposed by Demaison & Huizinga (1991) in cases where that parameter is not known. Because the Menilite Formation is not fully exposed within the Bystřice nad Olší section, thickness values were taken from Jirman et al. (2019), who studied the Loučka section (Silesian Unit; see Fig. 1) where part of the Subchert Member, whole Chert Member and Dynów Marlstone are exposed.

Based on the calculation, the Šitbořice Member has the highest SPI of 0.59 t HC/m^2, which is mainly a result of its greater thickness. The SPI of 0.25 and 0.13 t HC/m^2 was calculated for the Subchert and Chert members, respectively. Interestingly, the Dynów Marlstone has a higher SPI (0.19 t HC/m^2) than the Chert Member, which is characterized by the highest GP values. The SPI of the entire succession is ~1.15 t HC/m^2 which is comparable to SPI of 1.25 t HC/m^2 calculated by Jirman et al. (2019) for the Silesian Unit based on the Loučka section. Both calculations are significantly lower than SPI calculated by Sachsenhofer et al. (2018a, b) and Rauball et al. (2019) for Polish and Ukrainian Carpathians. Mainly this is as a consequence of the lesser thickness and limited stratigraphic range of the Menilite Formation in the Western Carpathians.

Comparison to previous studies

Czech Republic

Few data was published on the Menilite Formation from the territory of the Czech Republic. Up to now the Menilite Formation was studied exclusively in the Ždánice (Franců & Feyzullayev 2010; Jirman et al. 2018) and Silesian units (Jirman et al. 2019; Fig. 1). Jirman et al. (2019) emphasized the lithological similarities between the Loučka section in the Silesian Unit and time-equivalent sediments in the Waschberg Zone and the Austrian Molasse basin, despite of ~350 km distance.

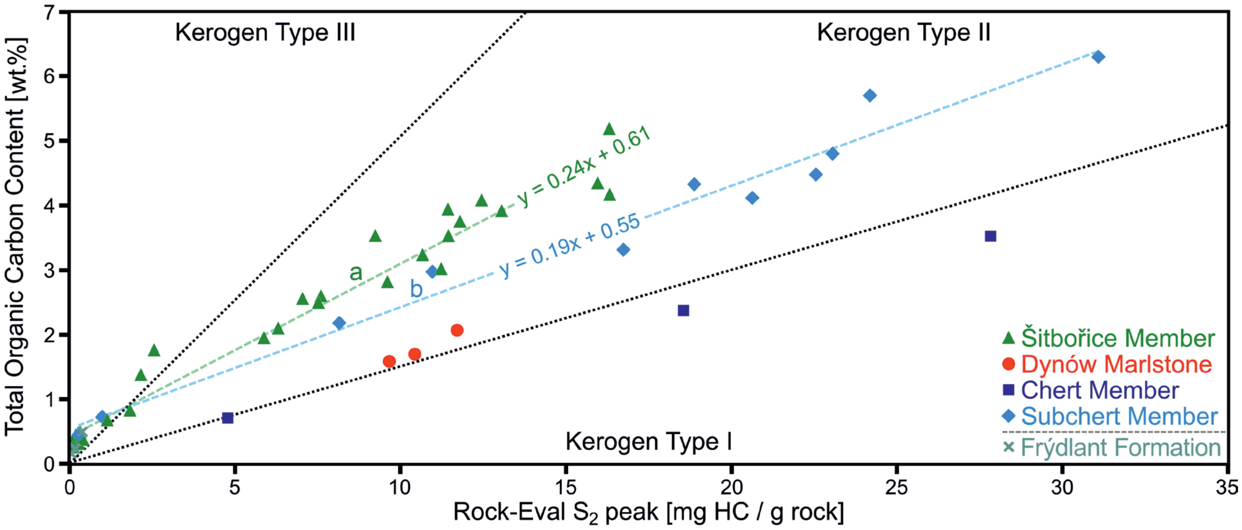

Fig. 7. Cross-plot of TOC versus remaining hydrocarbon potential S2 indicating the prevailing kerogen type and regression curves for TOCinert determination. Modified according to Dahl et al. (2004), kerogen genetic boundaries according to Langford & Blanc-Valleron (1990). Line “a” represents Subchert Member regression line; line “b” represents Šitbořice Member regression line.

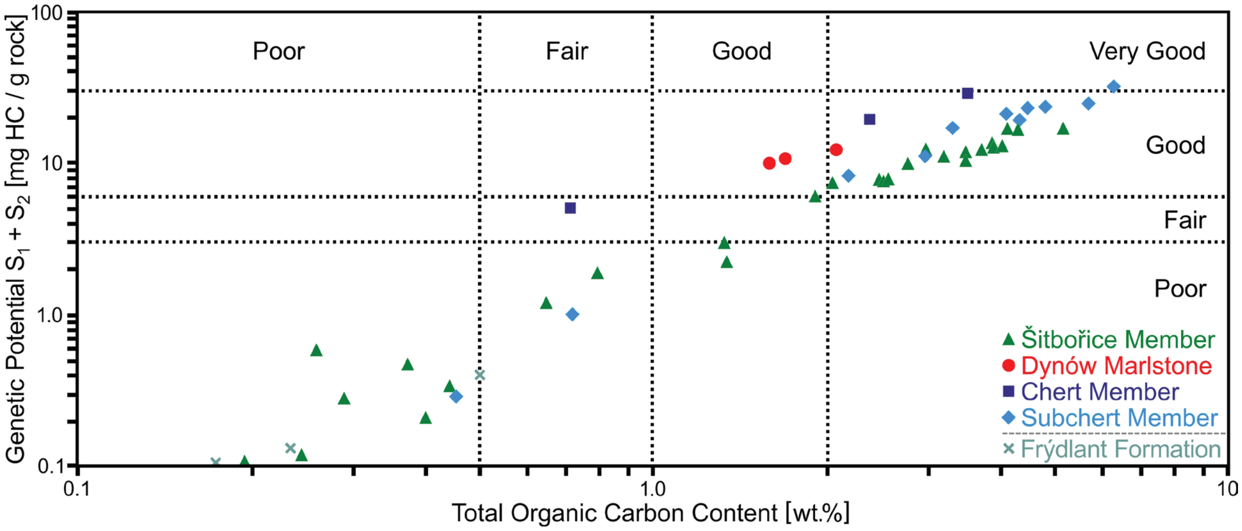

Fig. 8. Source rock potential of the Menilite Formation and uppermost part of the underlying Frýdlant Formation of the Bystřice nad Olší section. The classification according to Peters & Cassa (1994).

Table 2: The source potential index (SPI; Demaison & Huizinga 1991) estimations of the Menilite Formation in the Czech sector of the Subsilesian Unit.

Member	**Lithology**	**Thickness* [m]**	**GP (S_1+S_2) [mg HC/g rock]**	**SPI [t HC/m^2]**
Šitbořice Mb. (prolific lithotypes)	brown-grey calcareous claystone to marlstone	20	11.27	0.56
Šitbořice Mb. (non-prolific lithotypes)	other including Jasło Lm.	10	0.93	0.02
Dynów Mrst.	dull yellow-orange laminated nannofossil marlstone	6.8	11.05	0.19
Chert Mb.	brown laminated silicified claystone and menilite chert	2.9	17.97	0.13
Subchert Mb.	mostly brown-grey calcareous claystone to marlstone	6.0	16.63	0.25
Menilite Fm. (Σ)	–	45.7	–	1.15

* thickness used for the SPI calculation were partly adopted from Jirman et al. (2019).

Based on the study of Jirman et al. (2019), the most prolific part of the Menilite Formation is the Chert Member (TOC 1.5–16.5 wt. %, average HI 640 mg HC/g TOC). The Bystřice nad Olší section confirms the highest prolificness of the Chert Member despite of lower TOC contents. The Subchert Member and the Dynów Marlstone within the Loučka section have similar average TOC and HI values (3.5 wt. %, 372 mg HC/g TOC vs. 3.2 wt. %, 447 mg HC/g TOC), but whereas both parameters increase upwards within the Subchert Member, they are rather uniform in the Dynów Marlstone. The Subchert Member in both the Loučka (Jirman et al. 2019) and Bystřice nad Olší sections has almost identical TOC and HI (average values of 3.5 wt. %, 372 mg HC/g TOC vs. 3.6 wt. % 389 mg HC/g TOC) and show similar depth trends. The Dynów Marlstone in Bystřice nad Olší section has lower TOC but higher HI compared to Loučka section. However, only 3 samples were evaluated in this study compared to 12 from Loučka section. Based on the study of Franců & Feyzullayev (2010), TOC contents (2.5–5.9 wt. %) and HI values (250–680 mg HC/g TOC) in Křepice-5 borehole (Fig. 1) are much higher in the lower part of the Menilite Formation (Subchert Member to Dynów Marlstone) compared to the Šitbořice Member (TOC ~1.5 wt. %; HI ~70 mg HC/g TOC). In contrast, the Šitbořice Member in borehole cores of Mouchnice-1 and -2 and Nevojice-1 wells (Fig. 1) contains higher TOC (0.6–6.9 wt. %; average: 2.9 wt. %) and strongly varying, but often high HI values (53–541 mg HC/g TOC; Jirman et al. 2018). The TOC and HI of the Šitbořice Member in the Bystřice nad Olší section are little bit lower than those of Mouchnice-1 and -2 and Nevojice-1 (Jirman et al. 2018), but much higher compared to Křepice-5 (Franců & Feyzullayev 2010). The SPI estimate of the Menilite Formation in Bystřice nad Olší and Loučka sections is similar (~1.15 vs. ~1.25 t HC/m^2) but lower compared to ~1.5 t HC/m^2 calculated by Sachsenhofer et al. (2018a, b) for the Křepice-5 borehole (Franců & Feyzullayev 2010), where the Menilite Formation is 90 m thick. Table 3 provides information on Menilite Formation in the Czech Republic, based on data from Jirman et al. (2018, 2019) and this study.

Austria

In Austria, time equivalent sections of the Menilite Formation are known from the Waschberg Zone and the Austrian Molasse Basin (Figs. 1 and 2).

Within the Waschberg Zone, the Ottenthal Formation (NP21 to NP23) is regarded as an equivalent of the Subchert Member, Chert Member and Dynów Marlstone, while the Thomasl Formation (NP23 to NP24 or NP25) represents the Šitbořice Member equivalent (Fig. 2). Pupp et al. (2018) observed low TOC (~1.13 wt. %) and HI values (up to 252 mg HC/g TOC), typical for kerogen type III, within the Ottenthal and Thomasl formations. Thus, the source rock potential was evaluated as “poor”. However, an effect of weathering of the studied Waldweg section near Ottenthal cannot be excluded and the true source rock potential may be higher (Pupp et al. 2018). This is supported by borehole cuttings of Thomasl Formation from Thomasl and Poysdorf boreholes, where higher TOC (~2.2– 2.5 wt. %), HI (up to 416 mg HC/g TOC) and “fair” to “good” source rock potential were confirmed (Pupp et al. 2018). The estimated SPI (0.9–1.6 t HC/m^2) is a little bit higher than in the Bystřice nad Olší section, but mainly due to higher thickness of encountered Thomasl Formation Otherwise, the TOC and HI values are in the same order as in Šitbořice Member in Bystřice nad Olší section. Thermal immaturity of organic matter was observed in both studies.

Further west in the Austrian Molasse Basin (Figs. 1 and 2), the middle and upper parts of the Schöneck Formation (NP21 to lowermost NP23) are regarded as an analogical sequence to the Subchert and Chert members. The Dynów Formation (NP23) has been distinguished separately, while the Eggerding and Zupfing formations (upper NP23 to lower NP25) are time-equivalent to the Šitbořice Member (Fig. 2). Higher TOC (up to 12 wt. %) and HI were analysed within the Schöneck Formation (Schulz et al. 2002, 2005) compared to Subchert and Chert members in Bystřice nad Olší section. The Schöneck Formation buried beneath the Alpine nappes is the proven source rock (Gratzer et al. 2011; Bechtel et al. 2013), while it remains immature north of the Alpine thrust front. The Dynów

Table 3: Compilation of geochemical proxies and Rock-Eval data of individual members and the whole Menilite Formation in the Czech part of the Western Carpathians. Data according to this study and Jirman et al. (2018, 2019).

Parameter **Member**	**TOC** **[wt. %]**	**GP** **[mg HC/g rock]**	**HI** **[mg HC/g TOC]**	**T_{max}** **[°C]**
Šitbořice Mb.	0.20–6.9 (68) 2.64	0.08–27.7 (68) 7.4	36–541 (68) 217	400–437 (68) 417
Dynów Mrst.	1.33–4.9 (26) 3.04	4.72–25.8 (15) 14.0	286–670 (15) 477	413–426 (15) 421
Chert Mb.	0.72–16.5 (17) 5.25	5.1–122.8 (12) 38.3	467–790 (12) 667	412–428 (12) 419
Subchert Mb.	0.46–13.5 (52) 3.5	0.29–72.7 (27) 16.9	59–565 (27) 379	406–426 (27) 416
Menilite Fm. (Σ)	0.20–16.5 (163) 3.25	0.08–122.8 (122) 13.3	36–790 (122) 329	400–437 (122) 418

TOC=total organic carbon; GP=genetic potential (Rock-Eval S_1+S_2 values); HI=hydrogen index; T_{max}=temperature of maximum of S_2 peak. Range of selected parameters is given as numerator (number of evaluated samples in parentheses); average values in denominator.

Marlstone within the Austrian Molasse basin is characterized by high TOC (from 0.5 to 3.0 wt. %; Schultz et al. 2004, Sachsenhofer & Schulz 2006) and HI (from 500 to 600 mg HC/g TOC), same as in the Bystřice nad Olší section. The Eggerding Formation has TOC contents in the range of 0.6 – 6 wt. % and HI between 105 and 600 mg HC/g TOC (Schulz et al. 2005; Sachsenhofer et al. 2010, 2018a, b). Both parameters are higher than in the Šitbořice Member in the Bystřice nad Olší section.

Poland and Ukraine

In the Polish and Ukrainian Carpathians, the Menilite Formation is known from the Boryslav–Pokuttya, Skole (Skyba), Subsilesian, Silesian (Krosno) and Dukla units. The formation also occurs in tectonic windows of the Magura Unit. However, it is often difficult to attribute data and correlate specific stratigraphic units within the Menilite Formation due to intricate lithostratigraphic subdivision (e.g., Skole and Boryslav–Pokuttya units in Fig. 2). In contrast to the Western Carpathians, the Menilite Formation in the Eastern Carpathians in Ukraine may reach into Lower Miocene levels (Andreyeva-Grigorovich et al. 1986). Generally, the TOC ranges between 4 and 8 wt. % (Sachsenhofer & Koltun 2012; Kosakowski 2013; Kosakowski et al. 2018 cum. lit.) but locally exceeds 20 wt. % (e.g. Kosakowski 2013, Kosakowski et al. 2009, 2018, Rauball et al. 2019), which is significantly higher compared to TOC values observed in the Czech Republic (Table 3) and Austria. Based on the HI, oil-prone kerogen type II prevails in all units (Koltun et al. 1998; Sachsenhofer & Koltun 2012; Kosakowski 2013; Kotarba et al. 2013, 2014, 2017, Rauball et al. 2019) same as in the Czech Republic and Austria. Admixtures of kerogen type I and II/III or III were observed in Boryslav–Pokuttya, Skole (Skyba), Silesian (Krosno) and Dukla units (Kosakowski 2013; Kotarba et al. 2013, 2014, 2017). The Menilite Formation has mostly "good" to "very good" source rock potential (Kosakowski et al. 2018) in Poland and Ukraine. The highest potential was observed within Skole (Skyba) and Boryslav–Pokuttya units (Kosakowski et al. 2009; Sachsenhofer & Koltun 2012, Kotarba et al. 2019). The SPI reaches 2.1–5.5 t HC/m^2 in Poland and up to >74.5 t HC/m^2 in Ukraine (Sachsenhofer et al. 2018b, Rauball et al. 2019) which is much higher compared to SPI calculated for the Czech Republic or Austria but mainly as a consequence of wider stratigraphic range and of multiply greater thickness. The Menilite Formation is immature to early mature in the Boryslav–Pokuttya and Skole (Skyba) Unit (Koltun et al. 1998; Kotarba et al. 2014; Kosakowski 2013). Oil window maturity has been reported from the Silesian (Krosno) Unit, while the initial to main stages of the oil window and locally even overmaturity in the Dukla Unit have been observed (Kosakowski 2013; Kotarba et al. 2013, 2014). In general, an increasing trend of maturity towards the internal units has been observed (e.g., Sachsenhofer & Koltun 2012; Kosakowski et al. 2018).

Conclusions

The present paper represents one of a few studies focused to the source rock potential and geochemical characteristics of the Menilite Formation in the Czech Republic, where the formation was described by Glocker (1844) for the first time. The Bystřice nad Olší section is located in the Subsilesian Unit near the Polish border.

The Menilite Formation in the Bystřice nad Olší section is thermally immature. The thermal immaturity is indicated by both the Rock-Eval temperature T_{max} and low PI. Hence, the observed TOC and HI are considered as original.

The organic matter in the Menilite Formation is classified as kerogen type II–I based on HI and organic petrography. The most abundant macerals are alginite, bituminite and liptodetrinite. Huminite and inertinite macerals representing the terrestrial kerogen type III are present in low amount within the Subchert Member and the Šitbořice Member, where it may reflect changing depositional conditions from predominantly hemipelagic conditions towards turbiditic ones. Indications of kerogen type III admixtures based strictly on the HI occur almost exclusively in low-TOC samples which may negatively influence the kerogen type interpretation.

The Menilite Formation in the Bystřice nad Olší section has generally a “good” source rock potential, even though the TOC indicates “very good” potential. Surprisingly, the potential of the Subchert and Chert members is almost equal. The underlying uppermost part of the Frýdlant Formation has negligible source rock potential.

The source potential index (SPI) of the Menilite Formation indicating the amount of hydrocarbons, which can be generated beneath 1 m^2 of surface area was estimated as ~1.15 t HC/m^2. This SPI is comparable to SPI estimates from the Ždánice and Silesian units in the Czech Republic and the Waschberg Zone in Austria. However, it is significantly lower to SPI estimated for the Menilite Formation in Poland and especially Ukraine. This is mainly because of the relatively low thickness of the Menilite Formation in the Western Carpathians.

As expected TOC/TS ratios reach maximum values in the brackish Chert Member and the Dynów Marlstone. However, the absolute values are surprisingly low (~3.0). This may indicate slightly increased salinity during deposition of the Bystřice nad Olší section or more strictly anoxic conditions.

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Appendix

Analytical data

Samples Characterization				Bulk Geochemical Data						Rock-Eval Data					
Sample Name	Member / Formation	Outcrop	Relative Position	TC	TOC	TS	TOC/TS	TIC	Calc. Eq.	S_1	S_2	GP	T_{max}	HI	PI
[–]	[–]	[1–4]	[m]	[wt. %]	[wt. %]	[wt. %]	[–]	[wt. %]	[wt. %]	[mg HC/g rock]			[°C]	*	[–]
Š28	Šitbořice Mb.	4	8.51	1.69	1.34	1.94	0.69	0.34	2.87	0.04	2.16	2.20	427	161	0.02
Š27	Šitbořice Mb.	4	8.45	3.77	3.49	2.53	1.38	0.28	2.29	0.22	11.44	11.66	424	327	0.02
Š26	Šitbořice Mb.	4	6.89	6.10	4.13	4.19	0.98	1.97	16.43	0.37	16.32	16.69	418	395	0.02
Š25	Šitbořice Mb.	4	6.28	4.74	4.04	4.14	0.98	0.70	5.83	0.34	12.45	12.79	418	308	0.03
Š24	Šitbořice Mb.	4	5.98	5.70	5.16	3.79	1.36	0.53	4.45	0.39	16.31	16.70	418	316	0.02
Š23	Šitbořice Mb.	4	3.35	9.64	1.91	1.65	1.16	7.72	64.35	0.13	5.87	5.99	421	306	0.02
Š22	Šitbořice Mb.	4	3.26	7.11	3.88	2.99	1.30	3.23	26.92	0.28	13.05	13.33	420	336	0.02
Š21	Šitbořice Mb.	4	2.68	6.80	4.31	4.10	1.05	2.49	20.75	0.39	15.95	16.34	420	370	0.02
Š20	Šitbořice Mb.	4	2.62	10.93	0.29	0.24	1.21	10.64	88.68	0.01	0.27	0.28	437	91	0.04
Š19	Šitbořice Mb.	4	2.53	7.90	2.47	2.03	1.22	5.42	45.19	0.17	7.52	7.69	422	304	0.02
Š18	Šitbořice Mb.	4	2.10	11.76	0.65	0.32	2.05	11.10	92.52	0.04	1.14	1.18	424	174	0.03
Š17	Šitbořice Mb.	4	1.95	8.93	0.80	0.63	1.27	8.13	67.77	0.04	1.82	1.86	431	227	0.02
Š16	Šitbořice Mb.	4	1.68	7.59	3.20	2.59	1.24	4.39	36.56	0.22	10.67	10.89	420	334	0.02
Š15	Šitbořice Mb.	4	1.62	7.49	2.78	1.77	1.57	4.71	39.25	0.18	9.61	9.79	424	346	0.02
Š14	Šitbořice Mb.	4	1.55	3.88	0.25	1.51	0.16	3.63	30.26	0.01	0.11	0.12	425	43	0.09
Š13	Šitbořice Mb.	4	0.98	10.90	0.20	0.34	0.58	10.71	89.21	0.01	0.07	0.08	418	36	0.13
Š12	Šitbořice Mb.	4	0.82	2.83	0.44	1.43	0.31	2.38	19.86	0.01	0.32	0.33	423	72	0.03
Š11	Šitbořice Mb.	4	0.58	4.95	2.56	2.98	0.86	2.38	19.87	0.14	7.60	7.74	426	296	0.02
Š10	Šitbořice Mb.	4	0.24	2.47	0.40	1.15	0.35	2.07	17.23	0.01	0.20	0.21	420	48	0.05
Š09	Šitbořice Mb.	4	0.21	4.64	3.72	2.13	1.75	0.91	7.60	0.23	11.80	12.02	427	317	0.02
Š08	Šitbořice Mb.	3	14.36	7.74	2.52	1.64	1.53	5.22	43.48	0.53	7.04	7.57	424	280	0.07
Š07	Šitbořice Mb.	3	14.10	4.28	0.38	1.43	0.26	3.90	32.51	0.06	0.40	0.46	416	107	0.13
Š06	Šitbořice Mb.	3	9.40	11.32	1.33	1.17	1.13	9.99	83.26	0.40	2.56	2.96	423	193	0.14
Š05	Šitbořice Mb.	3	9.35	9.44	2.05	1.30	1.58	7.38	61.53	1.04	6.30	7.34	425	307	0.14
Š04	Šitbořice Mb.	3	7.28	7.77	3.91	3.65	1.07	3.85	32.12	1.24	11.43	12.67	424	292	0.10
Š03	Šitbořice Mb.	3	3.00	11.24	0.26	0.29	0.88	10.98	91.51	0.16	0.42	0.58	**361****	160	**0.28****
Š02	Šitbořice Mb.	3	1.65	7.53	2.98	2.70	1.10	4.55	37.91	0.97	11.23	12.20	423	377	0.08
Š01	Šitbořice Mb.	3	0.72	6.71	3.49	3.10	1.13	3.22	26.81	0.99	9.23	10.22	422	264	0.10
D03	Dynów Mrst.	3	0.00	9.70	2.08	0.70	2.98	7.62	63.51	0.68	11.70	12.38	426	563	0.05
D02	Dynów Mrst.	2	0.95	6.78	1.70	0.56	3.06	5.08	42.33	0.32	10.44	10.75	424	614	0.03
D01	Dynów Mrst.	2	0.50	5.62	1.59	0.54	2.95	4.03	33.59	0.36	9.66	10.02	424	606	0.04
CH03	Chert Mb.	2	0.40	0.84	0.72	1.97	0.36	0.12	1.00	0.28	4.79	5.07	424	667	0.05
CH02	Chert Mb.	2	0.30	2.54	2.38	1.27	1.87	0.16	1.35	1.01	18.55	19.56	426	781	0.05
CH01	Chert Mb.	2	0.20	3.61	3.52	1.19	2.95	0.09	0.75	1.45	27.83	29.27	426	790	0.05
SCH11	Subchert Mb.	1	7.68	7.36	5.70	2.82	2.02	1.66	13.79	0.65	24.19	24.84	419	424	0.03
SCH10	Subchert Mb.	1	6.09	7.81	6.31	3.06	2.06	1.51	12.56	1.25	31.09	32.34	418	493	0.04
SCH09	Subchert Mb.	1	5.77	3.16	0.46	8.96	0.05	2.70	22.50	0.02	0.27	0.29	421	59	0.07
SCH08	Subchert Mb.	1	5.75	8.32	3.32	1.47	2.25	5.01	41.72	0.38	16.74	17.12	419	505	0.02
SCH07	Subchert Mb.	1	5.67	10.07	4.11	1.34	3.07	5.96	49.65	0.76	20.62	21.38	418	502	0.04
SCH06	Subchert Mb.	1	5.54	10.01	4.48	1.42	3.16	5.53	46.07	0.82	22.56	23.38	419	504	0.04
SCH05	Subchert Mb.	1	5.49	10.10	4.80	1.91	2.51	5.30	44.17	0.75	23.06	23.81	419	480	0.03
SCH04	Subchert Mb.	1	5.44	10.35	2.97	1.31	2.27	7.38	61.50	0.27	10.97	11.23	418	369	0.02
SCH03	Subchert Mb.	1	5.38	9.46	2.19	1.37	1.60	7.27	60.60	0.13	8.14	8.27	421	372	0.02
SCH02	Subchert Mb.	1	5.37	7.64	0.73	1.02	0.71	6.91	57.61	0.02	0.98	1.00	426	135	0.02
SCH01	Subchert Mb.	1	5.31	9.64	4.33	1.64	2.65	5.31	44.22	0.46	18.88	19.34	421	436	0.02
SM03	Frýdlant Fm.	1	4.87	6.26	0.17	0.51	0.34	6.09	50.74	0.00	0.04	0.04	422	23	0.00
SM02	Frýdlant Fm.	1	2.44	5.79	0.50	1.25	0.40	5.29	44.12	0.01	0.39	0.40	422	78	0.03
SM01	Frýdlant Fm.	1	1.16	9.99	0.23	0.41	0.58	9.75	81.28	0.01	0.12	0.13	416	51	0.08

* the HI is expressed as mg HC/g TOC

** these values are considered an artefact caused by bitumen contamination