The geochemical characteristics of the Menilite Formation in the Czech Carpathians: A short review

PETR JIRMAN[1,2], EVA GERŠLOVÁ[1] and LUJZA MEDVECKÁ[1]

[1]Department of Geological Sciences, Faculty of Science, Masaryk University, Kotlářská 2, 611 37, Brno, Czech Republic; p.jirman@seznam.cz
[2]Czech Geological Survey, branch Brno, Leitnerova 22, 602 00 Brno, Czech Republic

Abstract: The Paratethys area contains a significant number of petroleum provinces. Most of the accumulations within the Carpathians are sourced by the Oligocene organic-rich Menilite Formation and its equivalents. The vertical variations in lithology within the formation reflect different depositional environment which strongly influences the source rock potential. The Menilite Formation has mostly "good" to "very good" source rock potential based on the Rock-Eval and TOC data, respectively. The Chert Member represents the most prolific member and reaches the HI up to 725 mg HC/g TOC. Significantly lower source rock potential was evaluated within the Šitbořice and partly Subchert members. The organic matter within the Menilite Formation is based on the organic petrography observations predominantly composed by the kerogen type I, while the kerogen type III macerals are typically very rare. The Rock-Eval interpretations indicating presence of kerogen type II and III were inaccurate due to higher amount of non-pyrolyzable organic carbon portion which underestimated the HI.

Introduction

The occurrence of the Menilite Formation in the Czech Republic is described from the Ždánice, Subsilesian, Silesian and Fore-Magura Units. The Menilite Formation is there according to Stráník et al. (1974) and Stráník (1981) subdivided into the Subchert Member (NP22), Chert Member (upper NP22 to lower NP23), Dynów Marlstone (NP23) and Šitbořice Member (upper NP23 to lower NP25) and comprises non-calcareous shales, marlstones and cherts (Bubík et al. 2016). The overall thickness of the formation is up to 200 meters within the Ždánice Unit and up to about 100 m in the Silesian Unit.

Material and methods

A total of 118 samples were analysed using ELTRA S/C Elemental Analyser. A subset of 77 samples was evaluated by Rock-Eval pyrolysis. The data was previously partly published by Jirman et al. (2018, 2019).

The Rock-Eval 6 instrument was used to determine the free hydrocarbons content S_1 [mg HC/g rock], residual hydrocarbon potential S_2 [mg HC/g rock] and temperature of the maximum of the S_2 peak T_{max} [°C]. The hydrogen index (HI) was calculated following Lafargue et al. (1998) as $100 \cdot S_2/TOC$ [mg HC/ g TOC]. Determination of HI_{true} is based on the same formula but using the pyrolyzable portion (TOC_{live}) which was determined according to Dahl et al. (2004) based on the S_2 versus TOC cross-plot. Samples with oxygen index (OI) data were analysed on Rock-Eval 6 instrument (Turbo version). The OI was calculated as $100 \cdot S_3/TOC$ [mg CO_2/g TOC], where S_3 represents the amount of CO_2 [mg CO_2/g rock] generated in the pyrolytic oven during decomposition of organic matter. Contents of total carbon (TC) and total organic carbon (TOC) were analysed using ELTRA S/C Elemental Analyser. TOC was measured after de-carbonization of the samples with concentrated phosphoric acid.

An Olympus BX51 microscope including a Zeiss Photomultiplier MK3 system with fluorescence light and a lens of 40× magnification was used to quantitative maceral analysis using polished blocks. Macerals were determined following Taylor et al. (1998) and ICCP (1998, 2001).

The source rock potential

The source rock potential was evaluated by the genetic potential (Rock-Eval S_1+S_2 peaks) and the TOC according to Peters and Cassa (1994).

The Menilite Formation has mostly "good" source rock potential according to the genetic potential and "very good" potential according to the TOC

(Fig. 1). The Chert Member has the highest source rock potential among the members with the average genetic potential of 45 mg HC/g rock and TOC of 5.9 $\%_{wt}$. The lowest potential has been observed within the Šitbořice Member and partly within the Subchert Member. On the other hand, the Šitbořice Member represents most of the Menilite Formation thickness while the Chert Member is typically only several meters thin.

The thermal immaturity of the organic matter was confirmed by Rock-Eval T_{max} (up to 433 °C). Higher thermal maturity is expected below the Magura Group of Nappes due to deeper burial.

Comparison to the Jurassic Mikulov Marls

The Upper Jurassic Mikulov Marls have been identified as the major source rock in the Vienna Basin (e.g., Blížkovský et al. 1994; Geršlová et al. 2015). The Menilite Formation evaluated by Jirman et al. (2018, 2019) has higher source rock potential (Fig. 1) according to the genetic potential (average 15 versus 4.6 mg HC/g rock) and TOC (average 3.6 versus 1.4 $\%_{wt.}$) compared to the Mikulov Marls.

However, the key factors affecting the amount of the oil generation are thermal maturity, strata thickness and facial stability. These parameters are much favourable for the Mikulov Marls compared to the Menilite Formation.

The Menilite Formation kerogen genetic type

The kerogen genetic type was evaluated based on the (1) Rock-Eval pyrolysis data represented by the HI, T_{max} and OI and (2) maceral analysis.

The Rock-Eval interpretations

Based on the Rock-Eval data (Fig. 2), the organic matter within the Menilite Formation represents mostly kerogen type II with high amount of kerogen type III. Rare type I admixtures occurs in the Chert Member. The HI versus OI data generally confirms described kerogen distribution even the type III within the Šitbořice Member was not observed.

The organic petrography interpretations

The organic matter of all Menilite Formation samples is based on the organic petrography dominated by liptinite macerals representing the kerogen type I. In contrast, vitrinite and inertinite macerals (kerogen type III) are typically very rare or virtually absent, respectively.

The Subchert Member contains abundant liptodetrinite accompanied by bituminite and alginite all belonging to the kerogen type I. The organic matter within the Chert Member is characterized by prevailing alginite macerals (kerogen type I). The dominant maceral within the Dynów Marlstone is liptodetrinite and rare bituminite

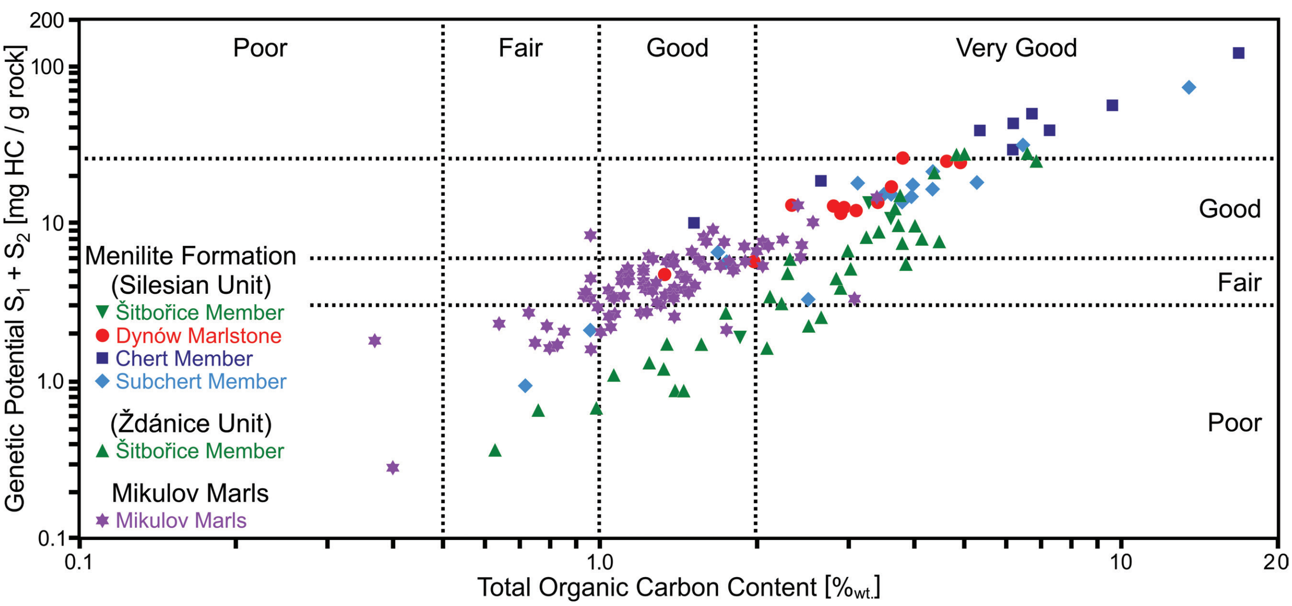

Fig. 1. Comparison of the source rock potential of the Menilite Formation from Silesian and Ždánice units and the Mikulov Marls. The data after Jirman et al. (2018, 2019) and Geršlová et al. (2015).

both again representing the kerogen type I. Within the Šitbořice Member, the organic matter is represented by the liptinite group (kerogen type I) with admixtures of vitrinite group (kerogen type III). However, the prevailing kerogen type may be classified as type II due to the admixtures of spores, pollens and plant particles (type III).

Kerogen genetic type interpretations comparison

As evident from the kerogen genetic type interpretations of both the Rock-Eval and Organic petrography data, the results are not in agreement. The kerogen genetic type evaluation based on raw HI versus T_{max} and/or versus OI data (Fig. 2) generally underestimate the kerogen type towards the type III.

However, the HI can be according to Dahl et al. (2004) simply re-calculated to the so-called HI_{true}. The HI_{true} as a HI based on the pyrolyzable portion of the organic carbon only rectifies errors caused by the non-pyrolyzable organic carbon content which is determined by the TOC versus S_2 cross-plot (Fig. 3). The HI_{true} reaches ~570 mg HC/g TOC in the Subchert Member, ~750 in the Chert Member, ~730 in the Dynów Marlstone and ~590 mg HC/g TOC in the Šitbořice Member. The kerogen genetic type evaluation based on the HI_{true} is in agreement to the maceral analysis in this study.

Conclusions

The Menilite Formation has "good" to "very good" source rock potential based on the Rock-Eval and TOC data. Both the parameters reach higher values within the Menilite Formation compared to the Mikulov Marls. The hydrocarbon potential of the Menilite Formation strongly reflects changing conditions during its deposition and diagenesis.

The Menilite Formation contains predominantly kerogen type I even the HI values indicate kerogen type II and III. This is caused by the presence of non-pyrolyzable organic carbon portion within the overall TOC which underestimates the HI.

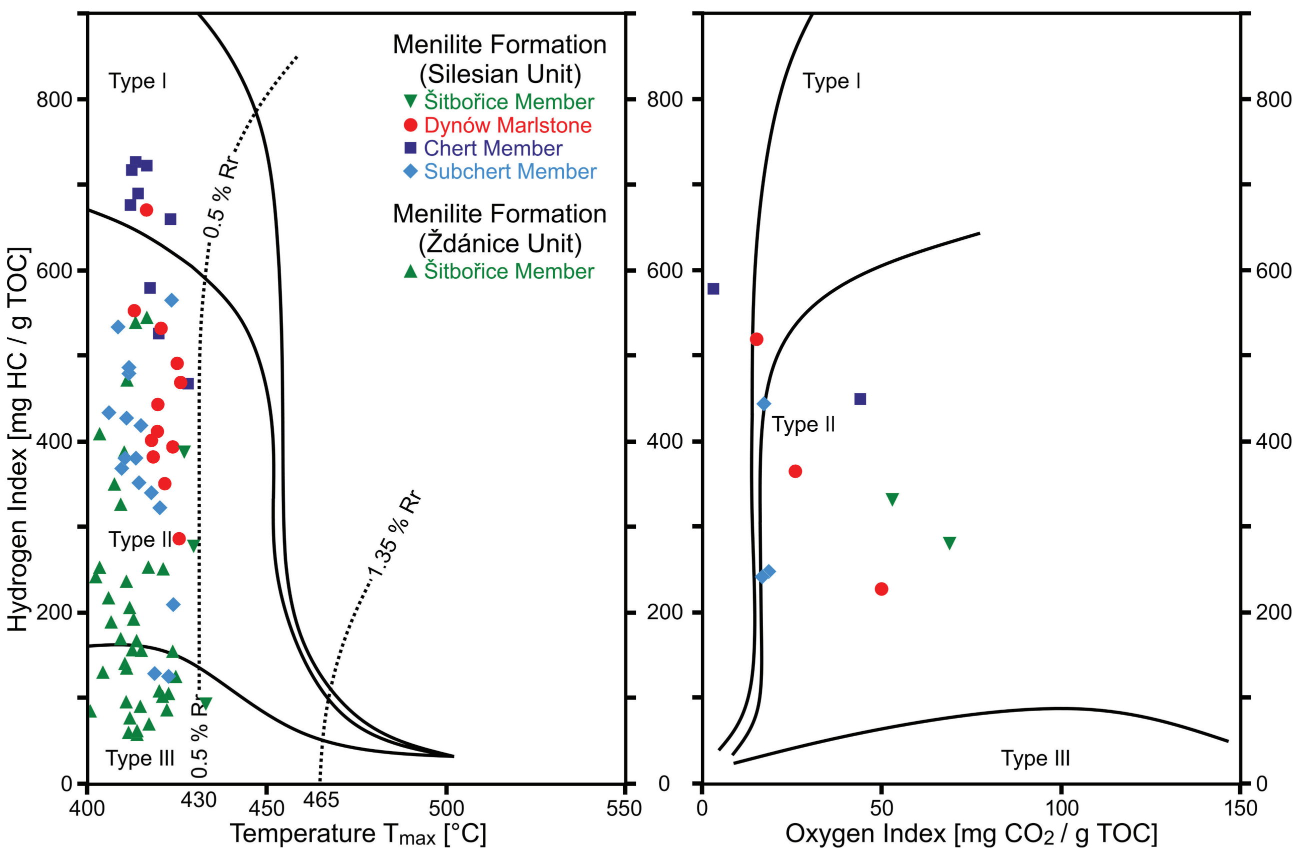

Fig. 2. Comparison of the Menilite Formation from Silesian and Ždánice units with respect to the prevailing kerogen type based on the HI versus T_{max} or OI, respectively. Kerogen type maturation paths according to Espitalié et al. (1985). The data after Jirman et al. (2018, 2019).

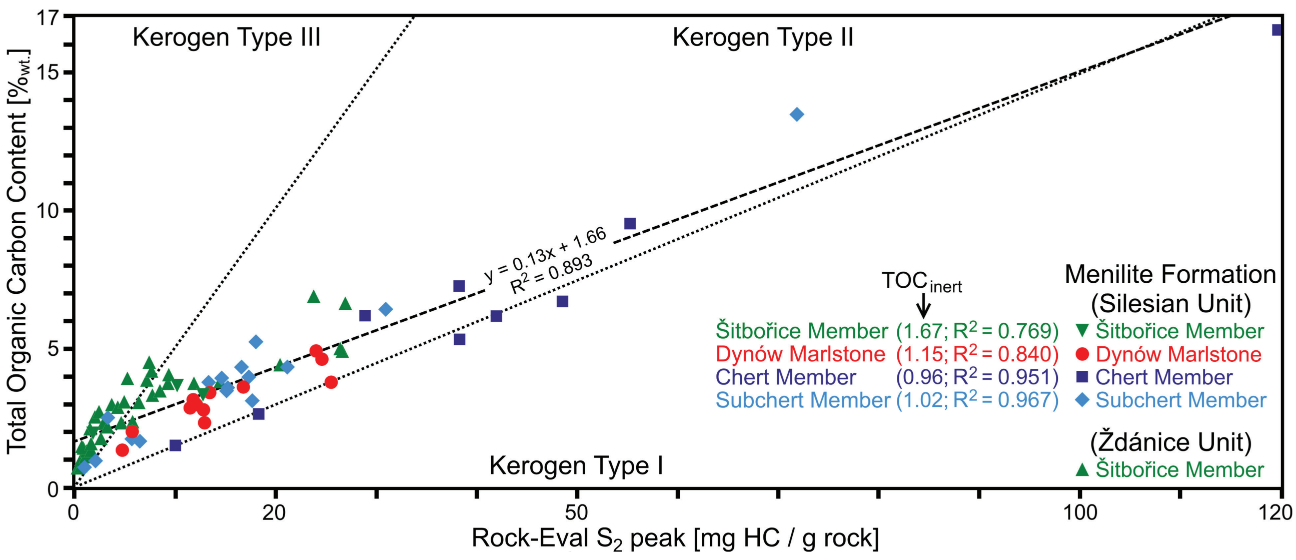

Fig. 3. Cross-plot of TOC versus residual hydrocarbon potential (Rock-Eval S_2 peak). The amount of non-pyrolyzable organic carbon necessary for the HI_{true} calculation was determined based on this diagram. Modified according to Dahl et al. (2004); genetic boundaries of kerogen types according to Langford and Blanc-Valleron (1990). The data after Jirman et al. (2018, 2019).

The Menilite Formation is one of the potential source rocks with less yield in the Czech Republic. Therefore, oil can be expected to have mixed geochemical features.

Acknowledgements: The authors thank to MND, a.s. for the samples and ERASMUS+ programme for supporting the Ph.D. student Petr Jirman. Special thanks go to M. Bubík and R.F. Sachsenhofer. The research has been financially supported by the institutional funds of Masaryk University.

References

Blížkovský M., Kocák A., Mořkovský M., Novotný A., Gaža B., Kostelníček P., Hlavatý V., Lunga S., Vass D., Franců J. & Müller P. 1994: Exploration History, Geology and Hydrocarbon Potential in the Czech Republic and Slovakia. In: Popescu B.M. (Ed.): Hydrocarbons of Eastern Central Europe, Habitat. Exploration and Production History. *Springer-Verlag*, Berlin, 71–117.

Bubík M., Franců J., Gilíková H., Otava J. & Švábenická L. 2016: Upper Cretaceous to lower Miocene of the Subsilesian Unit (western Carpathians, Czech Republic): stratotypes of formations revised. *Geol. Carpath.* 67, 3, 239–256.

Dahl B., Bojesen-Koefoed J., Holm A., Justwan H., Rasmussen E. & Thomsen E. 2004: A new approach to interpreting Rock-Eval S_2 and TOC data for kerogen quality assessment. *Organic Geochemistry* 35, 1461–1477.

Espitalié J., Deroo G. & Marquis F. 1985: La pyrolyse Rock-Eval et ses applications. Premiere partie. *Revue de l'Institut Français du Pétrole* 40, 563–579.

Geršlová E., Opletal V., Sýkorová I., Sedláková I. & Geršl M. 2015: A geochemical and petrographical characterization of organic matter in the Jurassic Mikulov Marls from the Czech Republic. *International Journal of Coal Geology* 141–142, 42–50.

International Committee for Coal and Organic Petrology 1998: The new vitrinite classification (ICCP system 1994). *Fuel* 77, 349–358.

International Committee for Coal and Organic Petrology 2001: The new inertinite classification (ICCP system 1994). *Fuel* 80, 459–471.

Jirman P., Geršlová E., Pupp M. & Bubík M. 2018: Geochemical characteristic, thermal maturity and source rock potential of the Oligocene Šitbořice member of the Menilite Formation in the Ždánice Unit (Czech Republic). *Geol. Quarterly* 62, 858–872.

Jirman P., Geršlová E., Bubík M., Sachsenhofer R.F., Bechtel A. & Więcław D. 2019: Depositional environment and hydrocarbon potential of the Oligocene Menilite Formation in the Western Carpathians: A case study from the Loučka section (Czech Republic). *Mar. Petrol. Geol.* 107, 334–350.

Lafargue E., Marquis F. & Pillot D. 1998: Rock-Eval 6 applications in hydrocarbon exploration, production, and soil contamination studies. *Revue de l'Institut Français du Pétrole* 53, 421–437.

Langford F.F. & Blanc-Valleron M.M. 1990: Interpreting Rock-Eval pyrolysis data using graphs of pyrolizable hydrocarbons vs. total organic carbon. *AAPG Bulletin* 74, 799–804.

Peters K.E. & Cassa M.R. 1994: Applied source rock geochemistry. *AAPG Memoir* 60, 93–102.

Stráník Z. 1981: Lithofacies and correlation of the Menilitic Formation in the Carpathian Flysch belt of Moravia. *Zemní Plyn a Nafta* 26, 9–18 (in Czech with English summary).

Stráník Z., Benešová E., Cicha I., Gabriel M., Kolářová M. & Žůrková I. 1974: Vysvětlující text k základní geologické mapě 1:25 000 M-33-106-D-c (Šitbořice). MS, *Ústřední Ústav Geologický*, Brno (in Czech).

Taylor G.H., Teichmüller M., Davis A., Diessel C.F.K., Littke R. & Robert P. 1998: Organic Petrology. *Gebrüder Borntraeger*, Berlin, 1–704.