

PYRO-GC×GC-TOFMS/FID FOR THE STUDY OF ORGANIC MATTER IN UNCONVENTIONAL HYDROCARBON RESERVOIRS

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Introduction

The work is devoted to analysis of organic matter in core samples from source rock formation. The objective is to evaluate hydrocarbon generation potential of the rocks based on current organic matter content and composition and reconstruction of sedimentation conditions that controlled organic matter accumulation.

Source rocks contain different forms of organic matter: gas and liquid hydrocarbons, heavy compounds and insoluble organic matter-kerogen. Content of each component may vary depending on formation and type of the rock. In this study, we applied Rock-Eval pyrolysis for bulk geochemical characterization of rocks and Pyro-GC×GC-TOFMS/FID at 350°C and 500°C for detailed analysis of organic matter composition [1]–[4]. To evaluate genesis of the organic matter and paleo-redox environment during marine sedimentation process we applied biomarker analysis of thermal extracts. The data were integrated to estimate organic matter genesis and perform productivity assessment.

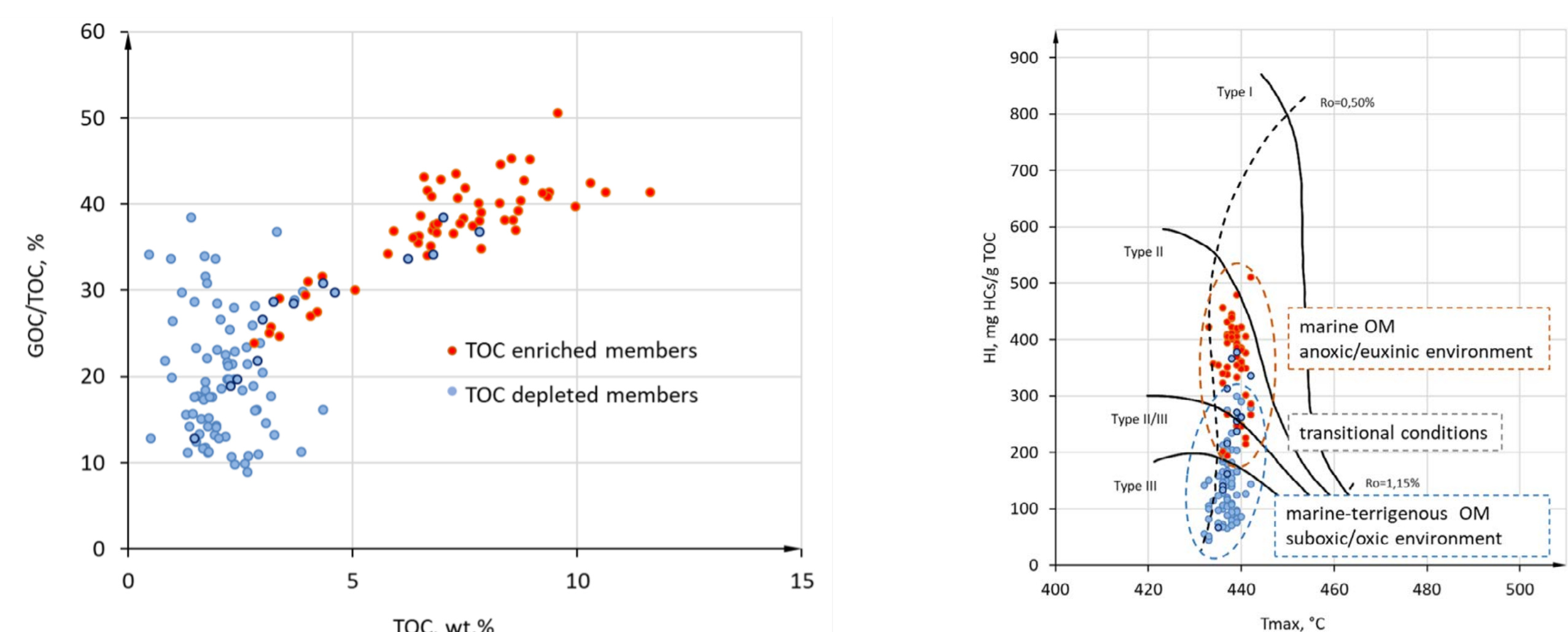
Geological object

The object of the study is unconventional hydrocarbon reservoir (shale) with layered structure: there are TOC enriched and depleted intervals within the cross-section. Based on TOC and U content, in total 19 m of the core we distinguished 7 lithological members with thickness varying from 1 to 3.7 m and 5.9 m of underlying deposits.

Instruments and methods

TOC measurements and Rock-Eval pyrolysis were performed using HAWK RW (Wildcat Technologies); U content measurements – elemental gamma logger (Coretest Systems); Pyro-GC×GC-TOFMS/FID – Pegasus 4D (LECO) with thermal desorption and pyrolysis injection units (Gerstel).

We used TOC and U content for 150 samples (19 m of core) in combination with biomarker analysis of thermal extracts for one sample per member to characterize the quantity and quality of organic matter and estimate paleo sedimentation conditions.



1. Rock-Eval pyrolysis data for the studied cross-section: total organic carbon content (TOC), pyrolyzable organic carbon vs TOC (GOC/TOC), temperature of maximum hydrocarbon generation (Tmax), total hydrocarbons derived from TOC (HI)

Results and discussion

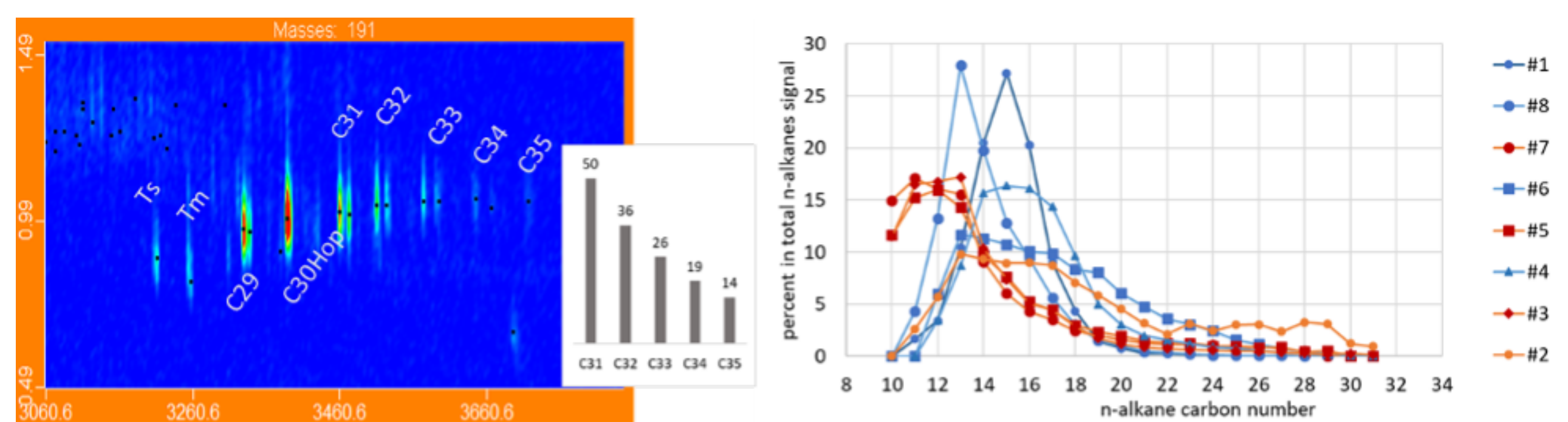
Benchmark of 5 wt.% TOC was set to discriminate members in the cross-section (Fig.2). Thus, there are four members, that are TOC depleted (<5 wt.%), and there are four TOC enriched members (>5 wt.%). Organic matter maturity level is at the beginning of the oil window for the studied rocks.

Member	Thickness, m	Lithology	TOC average, wt %	U average, ppm	Main product of kerogen decomposition
#8	3.7	Siliceous claystone with pyrite, bioturbated	2.0	2.7	Gas
#7	1.4	Kerogen containing siliceous claystone	7.6	19.1	Oil
#6	1.0	Siliceous claystone with pyrite, bioturbated	1.9	1.8	Gas and condensate
#5	1.2	Kerogen containing siliceous claystone with pyrite	7.1	20.6	Oil
#4	1.5	Kerogen containing siliceous claystone with pyrite	4.3	12.5	Gas and condensate
#3	1.2	Kerogen containing siliceous laminated claystone	8.8	25.6	Oil
#2	2.6	Kerogen containing carbonate-siliceous claystone	5.5	4.8	Oil
#1	5.9	Siliceous silty claystone	2.2	1.1	Gas

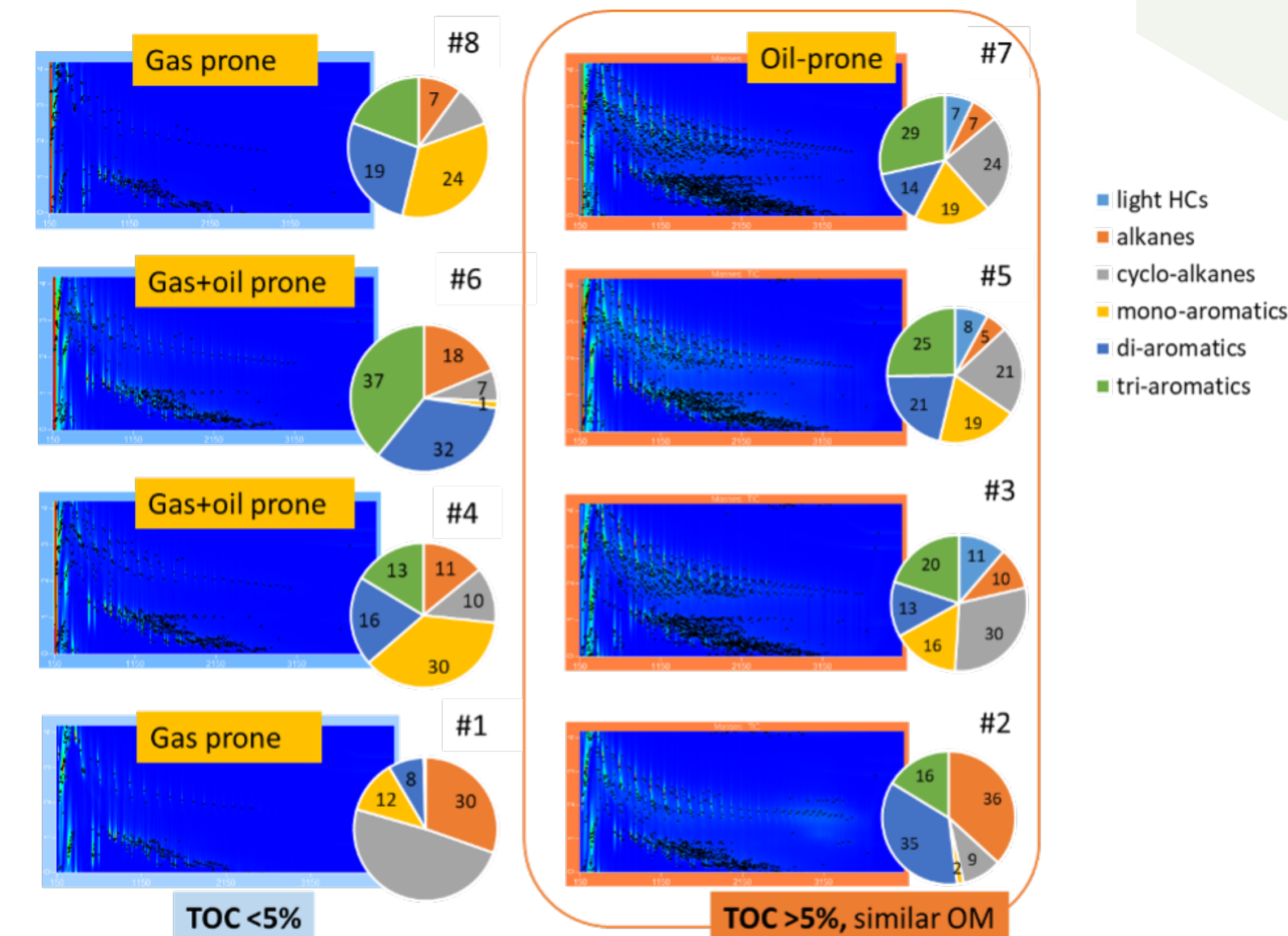
2. Cross-section averaged characteristics. 8 members are distinguished

For TOC enriched members #2, #3, #5, #7, we have found elevated U concentration and oil-prone kerogen in rocks (Fig.4), which was formed in anoxic/euxinic conditions from buried marine organic matter. On modified van Krevelen diagram (Fig. 1), these intervals correspond to organic matter type II (orange-red markers).

We have found little differences in composition of thermal extracts from samples #2, #3, #5, #7. The main features are similar: n-alkanes and hopanes fingerprint, C29/C30Hop <1, predominance of C27 regular steranes over C28 and C29 [4], and correspond to source rocks containing marine organic matter.



3. Composition of rock thermal extracts at 350°C: hopanes distribution for samples from TOC enriched members #1-2, #3, #5, #7 (left) and n-alkanes distribution (right)



4. Petroleum generation potential: composition of kerogen decomposition products at 500°C

TOC depleted members show variations in composition of organic matter and U content (blue markers on Fig.1). Organic matter in core samples from intervals #1, #6 and #8 has mixed origin with noticeable terrigenous input and accumulated under oxic environment (low U, organic matter type III). The rocks show moderate gas generation potential (Fig.4). For member #4, we estimated transitional accumulation conditions: moderate terrigenous influx and anoxic/suboxic conditions (moderate U, mixed organic matter type II-III). The resulting rocks demonstrate the potential to generate gas and gas condensate (Fig.3).

In contrast to biomarker composition of thermal extracts from TOC enriched rocks, intervals #4, #6, #8 contain only trace amounts of homohopanes C31-C35 and show elevated C29/C30 Hop ratio, which is additional evidence for terrigenous OM input resulted from river water inflow. Extract from #1 contains no hopanes, which is an indicator of lacustrine oxic conditions during sedimentation [4].

Conclusion

We have studied organic matter in core samples of source rocks (in form of petroleum and kerogen) using thermal desorption and pyrolysis unit coupled to GC×GC-TOFMS/FID. We applied this method for analysis of molecular composition of organic matter and its transformation products. The obtained data were integrated with the results of Rock-Eval pyrolysis, U content measurements, and geological information. For different intervals of the studied cross-section, we have evaluated sources of initial organic matter, sedimentation and maturation conditions.

As a result, we reconstructed the genesis of the source rock formation, identified potentially gas- and oil-prone intervals, and evaluated the productivity of the deposits.

References

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