Geochemical features of altered carbonaceous mudstones from Troyanovo-3 Mine borehole (Maritsa Iztok lignite field, Bulgaria)

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Scope. Geochemical characterization of the organic-rich mudstones in a lignite - mudstone sequence from a borehole from the Troyanovo-3 Mine (Fig. 1) at the Maritsa Iztok Basin (MIB).
The main purpose of the study was to examine the features of the mudstone interlayering the coal seams and to evaluate their alteration (incl. maturation) level.

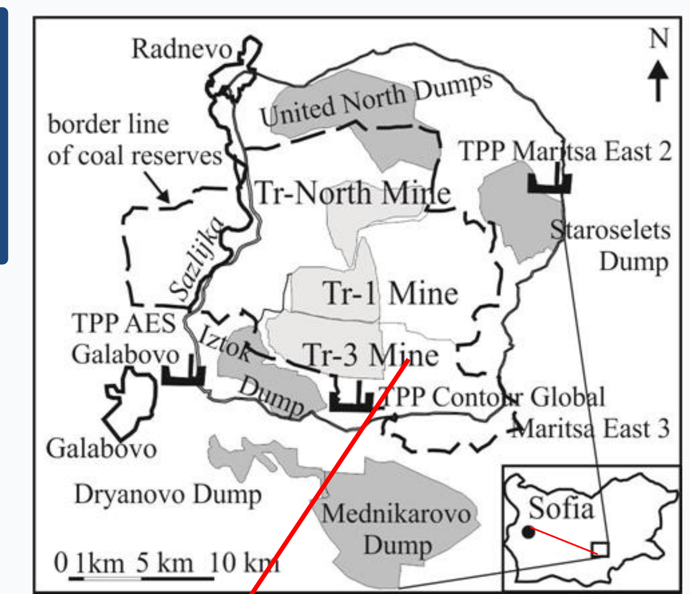

Fig. 1. Scheme of the MIB (www. marica-iztok.com)

Materials and Methods.

Total 46 Sms. were taken, roughly every meter of the log 19 - 60 m (Fig. 4). Seven mudstone Sms. were chosen and powdered (<100 µm), for Rock-Eval (RE) study.
For extraction, fractionation protocol and GC-MS identification see Stefanova *et al.*, (2016) *Organic Geochemistry*, v. 96, 1-10.

General characteristics of MIB and Troyanovo-3 Mine.
The Late Miocene lignite-bearing sequence of MIB (Fig. 2) consists of a coal basement of gray-black mudstone and sand, and three coal seams separated by black clay blended coal, coaly shale and mudstone. The sequence average thickness is 35-40 m and the depth varies from 6-10 up to 110-120 m. The coals are extremely immature (0.2% Ro), brown soft lignite (RE T_{max} ~ 380 °C); TOC_{db} = 21.3-56.7 wt%; ash_{db} = 16-45 wt%; total moisture, M_t 50-60 wt%; sulphur, S_{db} = 3-6 wt%; net calorific value = 6,485-7,322 kJ/kg) (www.marica-iztok.com). The lignite complex is covered by variegated mudstone interbedded by sandstone, limestone, and dolostone.
Troyanovo-3 Mine occupies the SE part of MIB (Fig. 3). The mine differs to the other two mines operating in the MIB in various aspects: geological position and basement; modern and ancient active tectonics and related to faults and "coal-free" zones; mud volcanoes and H_2S emission; emersion surface; hot underground waters.

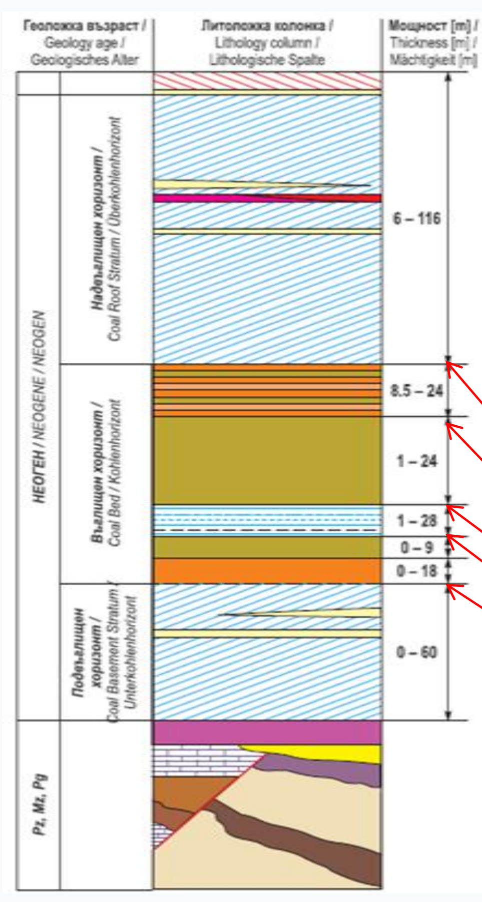

Fig. 2. Maritsa Iztok lignite field scheme of the geological sequence (www. marica-iztok.com)

Fig. 3. View of the working extracting area

Fig. 4. Field photo of the core-log

RESULTS AND DISCUSSION

The extractable OM amounts are low (0.03-2.25 %.). *n*-Alkanes (nC_{14} - nC_{33}) are abundant in the mudstones EOM. The distributions (Fig. 5A) are marked by "odd" over "even" predominance in the range nC_{21}-nC_{33}. Distributions were strongly dominated by 16α(H)-Phyllocladane (Table 1). Identified/quantified biomarkers series are present in Table 2 and some chemical structures characteristic for vegetation input are illustrated as well.

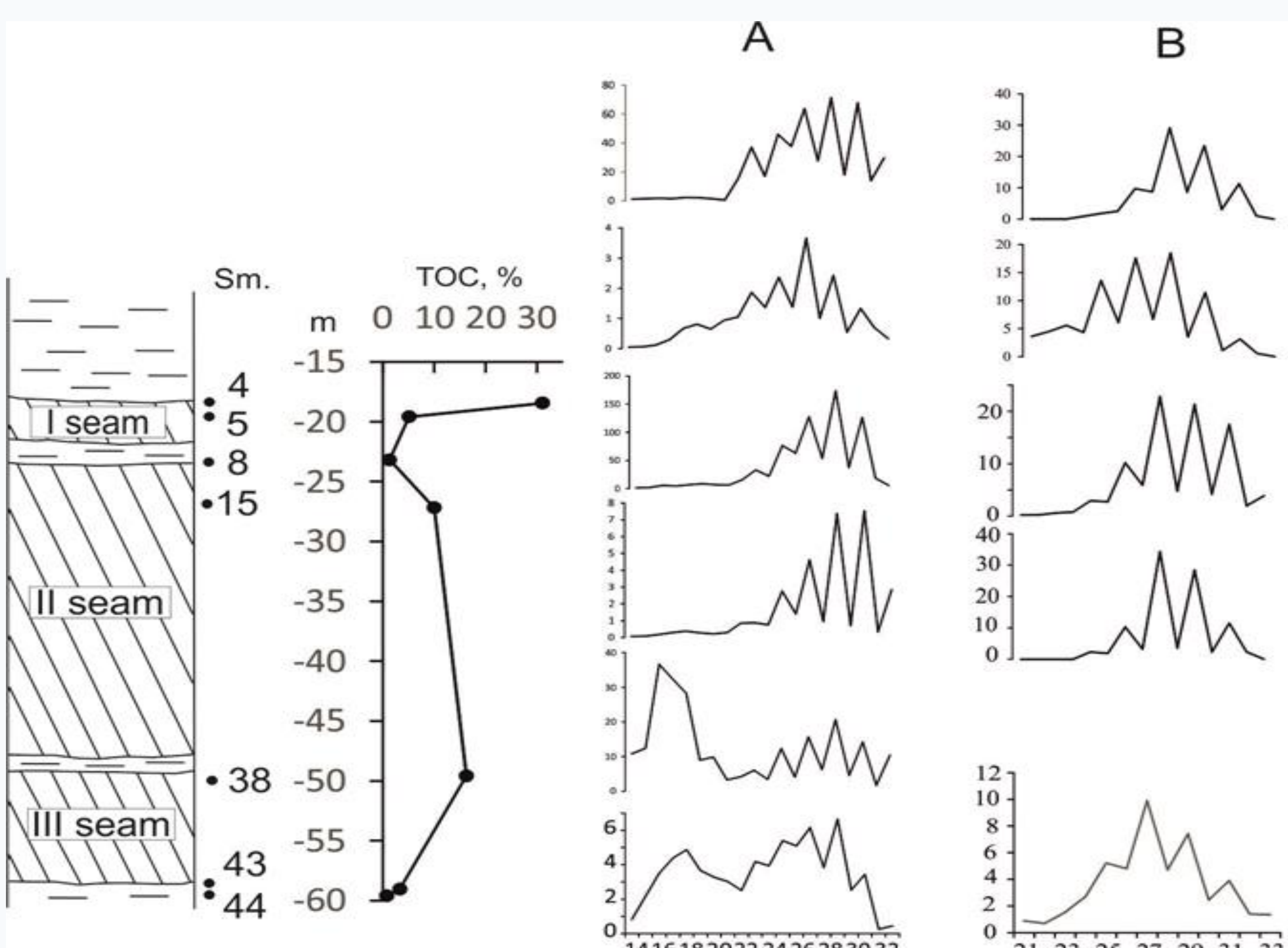

Fig.5. The core-log with samples positions and numbers, TOC and *n*-alkanes **(A)**, and *n*-alkan-2-ones **(B)** distributions

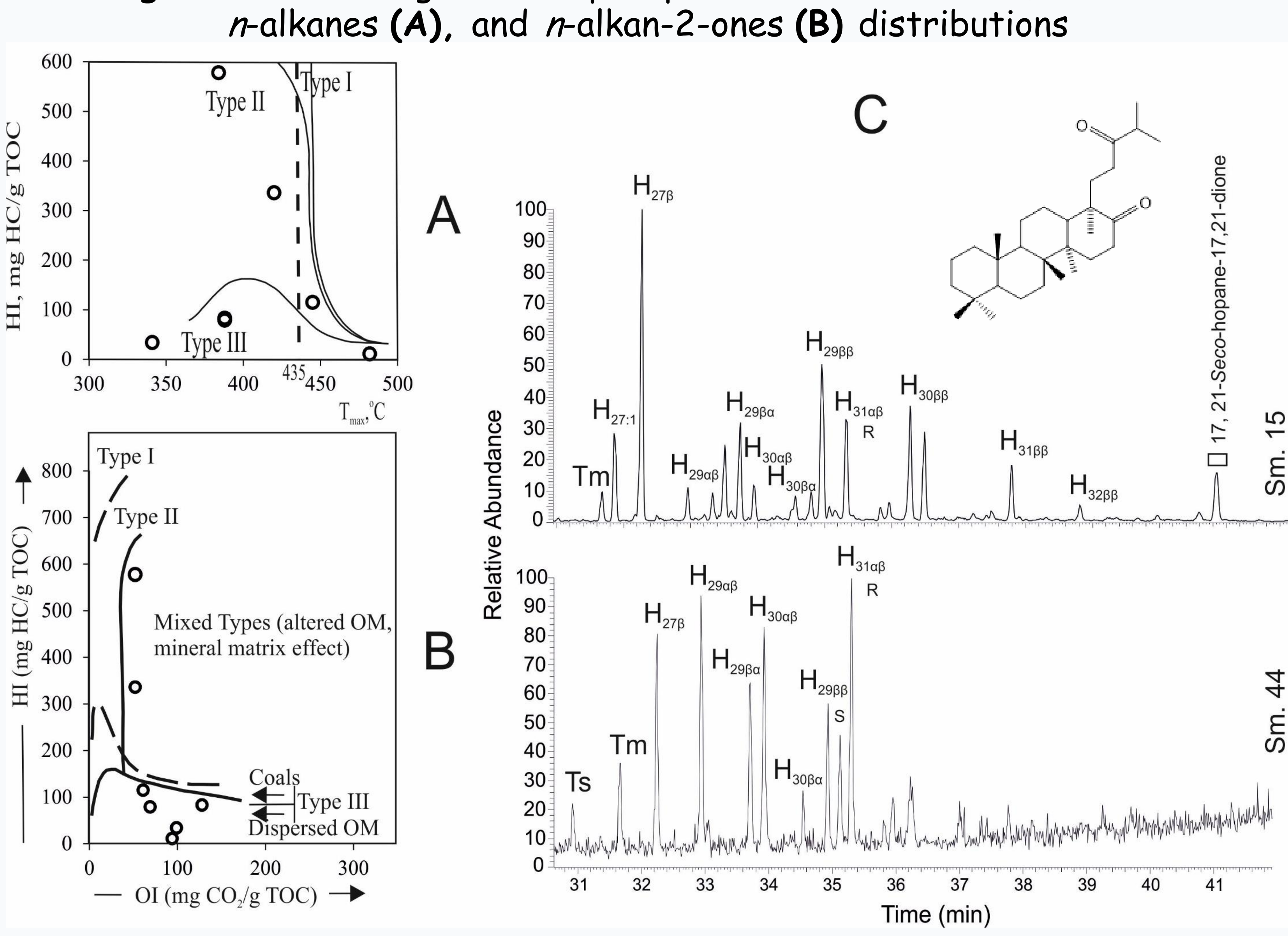

Fig. 6. HI *vs.* T_{max} **(A)**, HI *vs.* OI **(B)** plots for the mudstone samples; **(C)** Hopane (H) distribution for Sms. **15** and **44**.

Biomarkers for the vegetation contribution

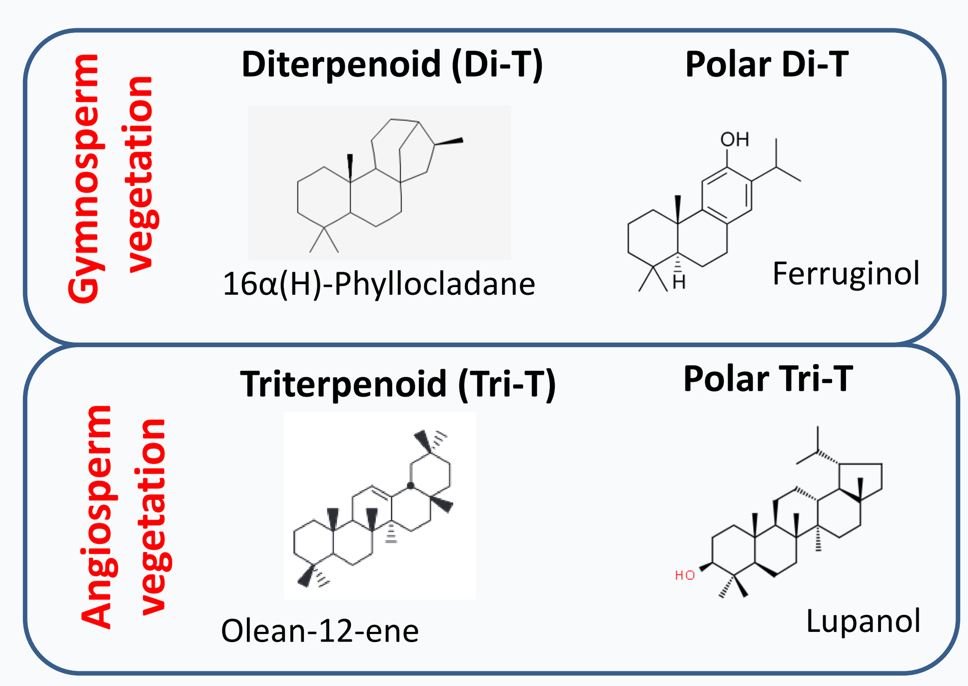

Table 1. 16α(H)-Phyllocladane content in the mudstones (µg/g) and recalculated µg/g TOC

Sm No	and depth	µg/g Sm	µg/g TOC
4	18.40-18.50	391.0	1256
5	19.20-20.10	0.3	5
15	27.10-27.30	82.5	620
38	49.50-49.70	3.1	19
43	58.90-59.20	22.4	675
44	59.50-59.70	1.0	127

Table 2. Biomarkers compositions for Sm. 4 (seam I) and Sm. 15 (seam II) in µg/gTOC, change with depth (Δ), in % and ratio Di-T/ Σ (Di-T+Tri-T)

Compounds		Sm. 4		Sm. 15		Δ
		µg/gTOC	%	µg/gTOC	%	%
Acyclic and polar compounds						
	Hydrocarbons	458.0	13	795	23.4	+ 10.4
	Ketones, i.e. symmetric/asymmetric	66.0	1.9	108	3.2	+ 0.3
	Alcohols	38.7	1.1	78	2.3	+ 2.2
Terpenoids (T)						
	Sesqui-T	112.0	3.2	64.7	1.9	- 1.3
	DiT (Σ DiT + Polar DiT)	2189.0	61.9	1985	58.5	-3.4
	TriT (Σ TriT + Polar TriT)	473.0	13.4	78	2.3	- 11.1
Steranes	Polar steranes	8.0	0.2	0	0.0	- 0.2
Tocopherols	α + β tocopherols	81.4	2.3	42.8	1.3	- 1.0
Hopanes (H)		110.0	3.1	243	7.2	+ 4.1
Total, µg/gTOC		3536		3394		
Ratio Di-T/ Σ (DiT+TriT)		0.82		0.96		+ 0.14

Table 3. Hopane biomarker parameters and seco-hopane-dione content

Sm.	Parameter				Seco-H-dione
	S/(S+R)	Hopane ratio	Ts/(Ts+Tm)	H27β/H27α	[µg/gTOC]
4	0	1.2	0	11.0	9.4
5	0	1.5	0	7.4	0.0
15	0	1.1	0	10.6	12.1
38	0	1.1	0	15.1	39.9
43	0	1.0	0	10.2	tr.
44	0.3	1.1	0.29	2.0	0.0

Ts - 18α(H)22,29,30-Trisnorneohopane; **Tm** - 17α(H)22,29,30-Trisnorhopane
Homohopane index (HomoH) = H31β **S/(S+R)**; **Hopane ratio** = H29αβ/H30αβ

Conclusions. (i) The mudstones were not buried at deeper depths, so, the OM is composed of type II-III kerogen; (ii) Multiple RE parameters and molecular biomarkers indicate that the thermal maturity of the most deep sample has attained the initial phase of "oil generation" probably as result of slightly oxidizing hot fluid circulation. The expulsion of short-chain *n*-alkanes and the migration from shallow to deeper levels have marked the shallow depth (up to 50 m) samples. Such alteration could be explained by meteoric water presence and wash out processes. (iii) The subordinate amount of angiospermous markers suggests that they were not a dominant component of the peat-forming flora, or were not able to compete with conifers. Of course, environmental factors like acidity in the mire, should not be neglected.

Outlook. The study will continue with Sms. from narrower intervals and applying techniques for structural elucidation of the polar constituents.