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Geochemical study of the organic matter from the southern part of the Maritsa Iztok Basin

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Геохимични изследвания на органичното вещество от южната част на Източномаришкия басейн

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Abstract. A sequence of carbonaceous mudstones interlayering three lignite seams is characterized by geochemical proxies. The core samples studied came from a borehole drilled in Trojanovo-3 Mine of Maritsa Iztok Basin. The *n*-alkane molecular composition is dominated by the > C_{29} long-chain homologues, with a strong “odd” over “even” homologue predominance. In addition to, the prevailing smooth signature of *n*-alkane distribution attests for one major organic matter source – land-derived higher plants. The sesqui- and di-terpenoid assemblage specifies the prevalence of Cupressaceae, Taxodiaceae, and Podocarpaceae species in the coal-forming mire. The lupane-type triterpenoids registered are a sign for Betulaceae family presence. Biomarkers for herb, macrophyte and algal/bacterial contribution are also recognizable.

Keywords: organic matter origin, geochemical study, Maritsa Iztok Basin.

Introduction

The geochemical properties of organic matter (OM) preserved in the geological sequences provide a wealth of information. The bulk geochemical data reflect a mixture of allochthonous and autochthonous inputs. The study of OM at the molecular level reveals contributions from the three domains of life: archaea, eukarya and bacteria. The individual compounds, or compound classes, that can be traced to a particular source organism/group of organisms, biomarkers, are of interest as at the molecular levels allow for (i) the separation of terrestrial, aquatic and sedimentary components; (ii) the examination of certain groups of algae and microorganisms that lack hard silica/carbonate shell and are absent from the fossil record (Meyers, 2003).

Studies on the organic geochemistry of coal-mudstone sequences from Maritsa Iztok Basin (MIB) by Bechtel et al. (2005) and Milakovska et al. (2021) showed clear distinction in the biomarker community and also in their relations in the sequences from the different basin locations. In a previous investigation on samples from a borehole from Trojanovo-3 Mine of Maritsa Iztok Basin Milakovska et al. (2022) found variations in the geochemical features of the carbonaceous mudstones induced by OM transformation and alteration processes. In the present paper, the stratigraphic occurrence of biomarkers is presented for

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the same core samples. The main goal was to provide information on the molecular proxies that can be used to reconstruct the OM sources developed in the lacustrine deposit.

Geological Framework

MIB is located in Zagore Depression that occupies the eastern part of the East Thrace Depression. The Zagore Depression was formed as a result of Late Oligocene–Late Miocene North-south extension in Aegean extensional province (Burchfiel et al., 2000). The Maritsa Iztok Basin structure is composed by pre-Miocene basement (fragment of Mezo-Alpine collisional orogen) and simply structured Miocene–Pliocene cover. Maritsa Iztok Basin is considered as Neogene superimposed depression as the Paleogene deposits are lacking.

The Late Miocene lignite-bearing complex (Maritsa Formation) comprises: coal basement of grey-black mudstone and fine to coarse sand; three lignite seams separated by black clay-blended coal, coaly shale and mudstone. The lignite-bearing complex is 35–40 m thick and lies at various depths (6–10 up to 110–120 m). Mammalian remnants of genus *Anancus* were found in the very top level of Maritsa Fm. (Nedjalkov, Rachev, 1990). First data for fish vertebrae and pharyngeal teeth, small and big specimens of gastropods (*Planorbarius corneus*, *Linnaeus*, and *Galba* sp.) and ostracod valves reported Milakovska et al. (2021). The fossils were found in core samples of mudstones interlayering the coal seams in Trojanovo-1 Mine of Maritsa Iztok Basin. Ochreous, gray and green mudstone and silty claystone interbedded by layers or lenses of sandstone, limestone, and dolostone comprise the Gledachevo Formation (Upper Miocene–Pliocene, Nedjalkov, Kojumdjieva, 1983; Nedjalkov, Rachev, 1990) covering the lignite-bearing complex. The fossils occasionally found in Gledachevo Fm. are: freshwater molluscs (*Theodoxus crenulatus crenulatus*, Klein; *Brotia esheri esheri*, Brogniart; *Unio sp*. ind.) in a sandy lens, ostracods of *Candona* and *Darvinula* genus in a limestone layer, and a *Stegotetrabelodon* skull in clays. A formation of dispersion clays (Pliocene, Nedjalkov, Kojumdjieva, 1983) lies on the top of the sequence and is composed of fine and silty clay with mammalian (*Zygolophodon borsoni* Hays) remnants.

The first paleoflora data are based on petrographic study of Minčev et al. (1967) performed mainly on Seam II coal samples from Troyanovo-1 Mine of MIB. The results imply for high coniferous input in the upper levels, and high angiosperm input – in the middle ones. The biomarker assemblage of lignite from Maritsa Iztok Basin by Stefanova et al. (1995) proves Cupressaceae, Taxodiaceae and Podocarpaceae, but not Pinaceae presence by a strong dominance of 16α(H)-Phyllocladane in neutrals and phenols/ketophenols (ferruginol, sugiol, hinokione, etc.) in slightly polars (Stefanova et al., 2002). The paleoflora features derived from lignite-mudstone sequences of Maritsa Iztok Basin by Bechtel et al. (2005) and Milakovska et al. (2021) showed that swamps were surrounded by forests mainly of Cupressaceae/Taxodiaceae, Podocarpaceae and Betulaceae-Myricaceae-Cyrillaceae trees, and inhabited by Sphagnum species.

Samples and scheme of study

The six samples studied represent mudstones of a lignite-mudstone succession from a borehole of Troyanovo-3 Mine, located in the SE area of MIB. The mudstone samples were collected from different levels – underlaying, interlayering and covering the coal seams. All samples numbering and bulk characteristics were reported in our previous investigation (Milakovska et al., 2022). Detailed analytical information on schemes of isolation and fractionation is described in the article cited. The TOC content of the samples varies strongly, from 0.77 to 31.13 wt % classifying them as mudstone, carbonaceous mudstone, and coaly mudstone. The extractable organic matter (EOM) yield is in the range 0.03–13.3%. The maltene fractional compositions, *n*-alkane and *n*-alkan-2-one distributions, isoprenoid ratios, and 16α(H)-phyllolcadane amount of the samples were reported and interpreted in attempts to disentangle the potential OM transformation processes in the borehole. Therein OM source and depositional environment were not discussed and presently we focused on this topic.

Results and discussion

The experimental results and discussion are divided into sections by individual compound classes.

Linear alkanes

The *n*-alkane distributions showed similar patterns for five samples and different - for one sample. The *n*-alkane distributions are smooth for the coal seam samples (Sm. 4, 5, 15, 38) and Sm. 43, and bimodal – only for Sm. 44, underlaying Seam III. Long-chain *n*-alkanes prevail in all samples and short/long (S/L) ratio varies from 0.03 to 0.67. Differences appear at maximizing homologue(s) depending on depth and vegetation cover variations.

In *n*-alkane signatures the dominant is nC_{29} (Sm. 4, 15, 43, 44), nC_{27} (Sm. 5), and nC_{29} and nC_{31} (Sm.

38). Samples are characterized by "odd"/"even" *n*-alkane ratio (Carbon Preference Index) >1, up to 5.81. The long-chain prevalence with maximum at nC_{29} is typical for MIB lignite that points to a dominant land higher plant input composed mainly of plant wax, especially dominant in needle leaved evergreen trees. The nC_{27} abundance is a hint for deciduous plant presence. In immature coals the dominance of long-chain *n*-alkanes compared to short-chain ones is additionally interpreted as forming from terrestrial plants at higher altitudes.

Further characterization of long-chain homologues helps for vegetation recognition. Namely, nC_{31} is generally attributed to a higher plant wax origin (Andersson et al., 2011), but despite the disputable interpretation can be derived from grasses or some Sphagnum species as well. On the other hand, nC_{27} and nC_{29} are more often related to shrubs and trees (Meyers, 2003). The *n*-alkanes of Sm. 4 (Seam I), Sm. 15 (Seam II), Sm. 43, and Sm. 44 (Seam III undercoal mudstone) maximize at nC_{29} that suggests main terrestrial plants contribution. Linear *n*-alkane separation for Sm. 5 (on the top of Seam I) maximizes at nC_{27} inducing deciduous plant prevalence in more humid and temperate conditions. Based on nC_{31} abundance in values very close to the maximum for Sm. 38 (laying on the top of Seam III) herb presence in the palaeomire could be also admitted. The linear *n*-alkanes distributions for Sm.43 and 44 (occupying the Seam III undercoal levels) show second maximum at nC_{18} pointing to algal/microbial contribution. Three nC_{23}/nC_{31} maximal values (Sm. 5, 43, 44) combined with elevated short- and mid-chain hydrocarbon content argues for Sphagnum species and/or grasses. The suggestion is strengthen by the lack of geochemical proves for Pinacea presence in the MIB lignite that also admits grasses input.

The second *n*-alkane maximum at nC_{18} is in the range of the short-chain homologues (nC_{16}-nC_{18}) predominantly registered in aquatic algae and photosynthetic bacteria (Cranwell et al., 1987). The relative portions of mid-chain *n*-alkanes, maximizing at nC_{25} in all samples, are significant (8.4–35.0%) implying for considerable macrophyte input in the paleolacustrine environment.

Cyclic hydrocarbon compounds (sesquiterpenoids, diterpenoids, hopanes)

Sesquiterpenoids, i.e. cedrane, cuparane, and thujopsane, are specific chemosystematic markers identified in the studied samples. Their presence indicates an input of plant material from Cupressaceae/Taxodiaceae species (Stefanova et al., 2002) as their derivatives were reported only from modern Cupressaceae and Taxodiaceae.

Diterpenoids (C_{19}, C_{20}) with pimarane, abietane, and phyllocladane skeleton are strongly dominating compounds among the cyclic hydrocarbons in all samples, i.e. norpimarane, sandaracomirane, and phyllocladane being the most prominent. 16α(H)-Phyllocladane is maximizing in all samples reaching up to 1256 μg/g TOC for Sm. 4 (located on the top of Seam I) and that is the maximal amount ever measured for MIB samples. Phyllocladane is abundant in conifer vegetation and is a biomarker for Cupressaceae, Taxodiaceae, and Podocarpaceae (Simoneit et al, 2019).

Hopanoids are important constituents of the non-aromatic cyclic triterpenoids in the MIB mudstone-lignite sequences. Hopanes are presented by 17α,21β(H)- and 17β,21β(H)-hopanes in the range C_{27} – C_{32}, C_{28} hopane is absent. The predominant hopanoids are 17β(H)-C_{27} hop-17(21)-ene, and 17β,21β(H)-C_{29} hopane. Other notable constituents are the C_{27} and C_{29} neohop-13(18)-enes. Hopane occurrence could be related to OM intensive transformation during early diagenesis (Vu et al., 2009) by bacterial activity. However, some hopanes in the peats might be derived from mosses and ferns.

Cyclic polar compounds

Polar diterpenoids were identified in all samples, but high amounts from 123 up to 430 μg/g TOC are registered for Sm. 4, 15 and 38, located on the top of Seam I, II, and III, where ferruginol and its dehydrogenated analogue are prevailing. Polar diterpenoids are common constituents of modern species of Cupressaceae, Taxodiaceae, and Podocarpaceae (Simoneit et al., 2019). The presence of chamaecydins also confirms the existence of the Cupressaceae s.l. family in the studied borehole.

Non-hopanoid polar triterpenoids with lupane, ursane, and oleanane skeletons are markers for angiosperm contribution. In the sample set, the most abundant are lupane-type triterpenoids, e.g. cyclic ketones (lupan-3-one, lup-20(29)-en-3-one), biomarkers for trees of Betulaceae family (Stefanova et al., 1995). Oleananes are present as ketones (β-amyrone). Ursane and friedelin structures are detected in appreciable amounts.

Conclusion

The biomarker assemblage assessment by geochemical proxies in the lacustrine sequence permits to distinguish some short-term dynamics and fluctuations in the aquatic ecosystem in the SE area of Maritsa Iztok Basin. The prevailing smooth signature of *n*-alkane distributions attests for one major OM source – land-derived higher plants from higher altitudes. Sesqui- and di-terpenoid assemblage argues for Cupressaceae, Taxodiaceae, Podocarpaceae input. Lupane-type triterpenoids, biomarkers for trees of Betulaceae family, admit for angiosperm contribution. In addition to, the *n*-alkane bimodal signature for some samples attests for minor impact to the OM induced by algal/bacterial activity.

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