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Biomarker and micropetrographic investigations of coal from the Krepoljin Brown Coal Basin Serbia

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ABSTRACT

We investigated early diagenetic processes of the extractable organic matter from the Miocene freshwater sequence, which consists of coal fragments in clays, sandstones and shales alternating with continuous brown coal layers.
We examined eight coals, thirteen sediments and three non-coaly underground layers.
The molecular assemblages of the identified aliphatic hydrocarbons in the Krepoljin Basin reflect the abundance of plant taxa as precursors or participants in the early diagenetic stage. The data provide insight into the conditions prevailing in the lakes and bogs during early diagenesis. The dominance of diterpanes indicates that the prevalent of the organic matter was of gymnosperous origin. The hopanoid contents are considered to reflect microbial activity. That the organic matter in the Miocene Krepoljin Coal Basin is immature was confirmed by the presence of biolipids such as ββ-hopanes, C_{27} 17 β (*H*)-trisnorhopane. Saturated and aromatized abietanes, pimaranes and phyllocladanes, the most abundant compounds in all samples, indicate a predominantly higher plant input related to the Coniferous group, but identification of the individual plant families was not possible. β-Amyrin and other triterpenoid-derived triaromatic and triaromatic C-ring cleaved hydrocarbons with triterpenoid structures are thought to be characteristic for angiosperms. Unsaturated compounds, Δ^2-triterpanes, early intermediaries in the diagenetic transformation of angiosperms also indicate a low degree of sediment maturity.

1. Introduction

There were numerous large or small, occasionally mutually connected lake basins on the territory of Serbia during the Miocene. The studied area belongs to Carpatho–Balkan metallogenic province in the eastern part of Serbia. In many of them coal was mined in small, usually local coal-pits (Ercegovac et al., 2006), especially during the fast growth of the coal-mining industry and the emergence of large numbers of coal mines. The Krepoljin Brown Coal Basin is one of the smaller Miocene freshwater basins in Serbia. It is located in the Homolje Mountains, 170 km south-east of Belgrade (Fig. 1a). The sediments of the coal-bearing series of the Krepoljin Basin were formed under complex tectonic conditions of freshwater bogs during the Lower Miocene (Ercegovac et al., 2006). Older stratigraphic elements form the base, i.e. they are underlayered by Palegene and Neogene deposits, which can be divided into two distinct structural complexes:

a) the complex that is the base and bedrock for the Palegene and Neogene coal-bearing sediments, and
b) the synchronous Mesozoic complex developed over the coal beds.

The coal-bearing segment of a bed covers an extremely small area of 0.5 km^2 and is cleaved, with the occurrence of karstified Mesozoic sediments over the coal-bearing series (Ercegovac et al., 2006).

The Krepoljin Brown Coal Basin is particularly interesting for its geochemical characteristics because: a) the basin was covered by thick Mesozoic formations thus becoming protected from subsequent external influences and b) coal fragments were dispersed in the sediment series, considered as mixed sediments. Previous investigations of these coals were provided by Mihajlović (1977), Anđelković et al. (1988), Ercegovac et al. (2006), Devic et al. (2006), Devic and Jovancicevic (2008), and Devic and Popovic (2011).

The aim of this paper is to provide a better reconstruction of the precursor plant associations of the coals and sediments in the Krepoljin Basin.

2. Geological setting

The area of the Krepoljin Coal Basin consists of Paleozoic, Mesozoic and Cenozoic rocks (Fig. 1 b and 2). The basement of the basin consists of Permian sandstone Triassic and Jurassic limestone and Paleogene and Neogene dacite–andesite.

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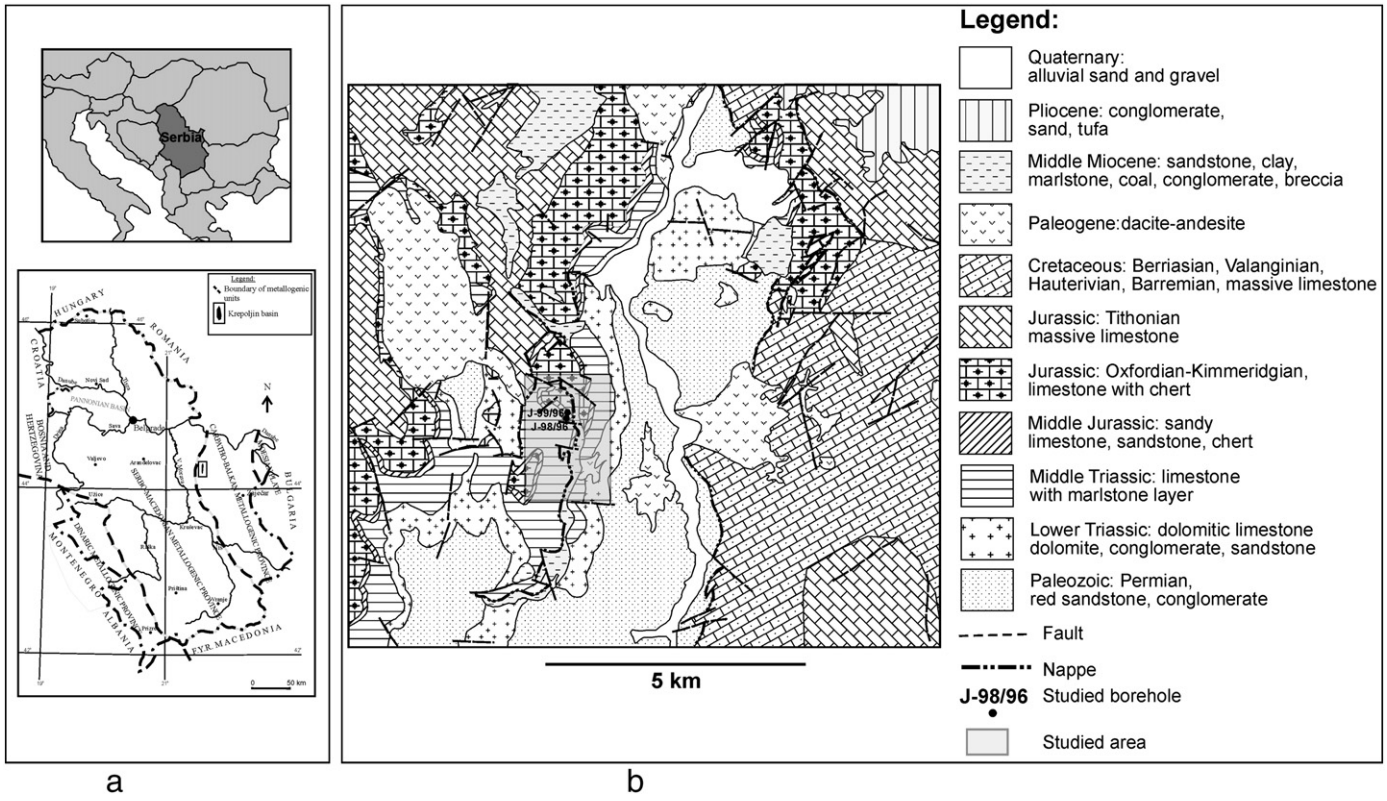

Fig. 1. Map of Europe with position of study area (a), and simplified geological map of the Krepoljin basin (b).

The Middle Miocene fresh water coal-bearing sequence (Anđelković et al., 1988; Mihajlović, 1977) is composed of underlying series, coal layer and overlying series (Fig. 3):

i. *The underlying series* has a variable grain size distribution and consists of predominant clay-bearing weakly bound soft sandstone and sand of greenish colour. The thickness of underlying sediments varies due to the degree of preservation and erosion. In central areas of the basin, where coal seam is preserved, the thickness of underlying series is greater than 70 m.
ii. *Main coal seam* of the Krepoljin Basin is made of two coal layers, markedly different in characteristics regarding the regularity of the areal extension, thickness and the presence of in-seam waste. The lower coal layer, in which the majority of coal reserves are concentrated, has a regular distribution, with a maximum thickness of 20 m. The upper coal layer has limited areal extent and smaller thickness of up to 10 m. In contrast to the lower coal layer, the upper one is interbedded with sandy–clayey sediments which make up to 40% of the coal layer. The maximum thickness of the Main coal seam is 29 m.
iii. *The overlying series* consists of marlstone, marly clay and shale with thin layers of sandstone and sand. Total thickness of that series is up to 30 m. In some parts of the basin, overlying series has been destroyed due to the overthrusting of Permian sandstone and Mesozoic limestone over coal-bearing Miocene sediments.

Overburden sediments in central and western part of the Krepoljin Basin consist of Mesozoic limestone with maximum thickness of 297 m.

The Krepoljin Basin has very complicated tectonic setting with numerous faults (Fig. 1b) as a result of eastward overthrusting of Mesozoic sediments over Miocene.

3. Samples and analytical methods

Twenty four fresh core samples were collected from two boreholes (J-98/96 and J-99/96) from the Krepoljin basin (Fig. 1), representing different parts of the Main coal seam, overlaying and underlying sediments. The sampling interval was determined on the basis of lithological changes. The relative sampling positions is given in Fig. 3.

In the examined Miocene sequence of coals and sediments formed in freshwater environments, four hydrochemically different sedimentation environments could be distinguished considering the assemblages of the prevalently sedimentary minerals: (i) Illite-montmorillonitic (IM); (ii) calcitic (Ct); (iii) an environment in which non-coaly underlayers were formed (NC) and (iv) an environment in which continuous coal layers were formed (Figs. 2, 3 and Table 1). Twenty-four samples from two boreholes were investigated, comprising eight coals, thirteen mixed sediments (IM and Ct) and three non-coaly underlying sediments (NC).

3.1. Mineralogical composition

The approximate abundance of the main minerals in the mixed and the non-coaly sediments was estimated by qualitative X-ray diffraction analysis using a Philips RW1710 diffractometer and software APD processing (Table 2).

3.2. Total organic carbon content (TOC)

The TOC determination was performed with a Vario EL III CHNOS Elemental Analyzer on samples previously treated with dilute HCl in order to remove carbonates (Table 3).

3.3. Soluble organic matter

The bitumen was extracted by Soxhlet extraction with CH_2Cl_2, for 36h. The extracts were separated into three fractions using column chromatography (diameter 1.5 cm, length 49 cm) through silica gel and aluminium oxide ($SiO_2/Al_2O_3 = 225/165$). The saturated hydrocarbon fraction was eluted with petroleum ether, the aromatic hydrocarbons with