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Petrographical and organic geochemical study of the Kovin lignite deposit, Serbia

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ABSTRACT

The origin of the organic matter (OM) and the characteristics of the depositional environment of lignites from the Upper Miocene Kovin deposit (hosting three coal seams) of Serbia were evaluated based on petrographic data, bulk organic geochemical parameters, biomarker analysis and stable isotope geochemistry ($\delta^{13}C$ of individual biomarkers). Samples were collected from four boreholes, GD-601 and GD-603 (the "A" field), and KB-79 and KB-91 (the "B" field), representing different parts of coal seams I, II, and III.

Investigated lignites are typical humic coals. The OM of lignites is derived from woody vegetation and herbaceous peat-forming plants, with prevalence of the former in most samples. Peat-forming vegetation is characterized by abundant decay resistant gymnosperm (coniferous) plants, followed by a low amount of angiosperms. Lignite forming plants mostly belonged to the gymnosperm families Cupressaceae, Taxodiaceae, Phyllocladaceae and Pinaceae. Slight input of ferns, fungi and aquatic macrophyta to lignite OM is also evident. Distributions of hopanoids and isotopic compositions of these biomarkers reflect the activity of various microbial populations represented by methanotrophic-, chemoautotrophic- and heterotrophic bacteria during diagenesis. Prominent C_{28} 28,30-bisnorneohop-13(18)-ene was observed for the first time in the lignite extracts. According to the $\delta^{13}C$ value it was probably derived from chemoautotrophic bacteria. C_{28} 28,30-bisnorneohop-13(18)-ene could be one of the possible precursors of a series of orphan aromatic hopanoids bearing an ethyl group at C-21, via progressive aromatization.

Peatification proceeded in a fresh water environment under variable redox conditions, from anoxic to slightly oxic. All three coal seams are heterogeneous. The lower parts of the coal seams represent a topogenous fresh water peat mire with open water areas, which was subjected to inundations. The upper parts of coal seams represent a wet forest swamp with relatively stable conditions. Despite the observed variations in all three coal seams, the mean values of petrographic and organic geochemical parameters suggest general increasing of wetness and establishment of more stable conditions from seam III to seam I. Maceral and biomarker data indicate that rapid flooding of the bogs stopped peat growth in all three coal seams.

Relatively frequent variations in all three coal seams, followed by repetition of lignite characteristics depict well the pronounced seasonality e.g. short term cycles of the climate during Late Miocene in investigated area.

1. Introduction

Concerning the significance of various fossil fuel resources of Serbia, brown coals, particularly lignites, are of great economic importance as they represent the main source for energy production (http://www.smeits.rs/include/data/docs0066.doc). A significant number of coal-bearing basins with significant coal reserves were formed during the Miocene in the territory of Serbia, as a result of favourable peat-forming conditions (Jelenković et al., 2008; Magyar et al., 1999). The economically most important Upper Miocene coal basins are Kolubara, Kostolac and Kovin deposits. Lignite deposits have large resources, and relatively uncomplicated geology resulting in simple exploitation conditions. Most of lignite produced (90%) is used for

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electricity generation in thermal power plants (TPP; http://www.smeits.rs/include/data/docs0066.doc). Apart to the economical significance, lignites can be regarded as an important fossil archive of terrestrial organic matter (OM) reflecting changes in palaeoclimatic and palaeoenvironmental conditions over geological times.

Maceral composition and petrography-based parameters were used in many studies on coal deposits for the characterisation of the depositional environment and the peatification of land plant material (Bechtel et al., 2003, 2014; Calder et al., 1991; Diessel, 1986; Kalkreuth et al., 1991; Karayiğit et al., 2015; Markic and Sachsenhofer, 1997; Petersen and Ratanasthien, 2011; Stock et al., 2015). In the past few decades organic geochemical analysis of biomarkers in coal extracts has been used as a promising tool for assessment of the reconstruction of vegetation assemblage and palaeoenvironmental conditions in peatlands during the formation of coal-bearing strata (Bechtel et al., 2003, 2007; Stefanova et al., 2002, 2005, 2013; Zdravkov et al., 2011; Životić et al., 2010).

Although analysis of biological markers in sediments represents a powerful technique for assessing the sources and depositional environments of the OM, the interpretation is often complicated by multiple geneses (Volkman, 1986; Otto and Wilde, 2001; Peters et al., 2005). Compound-specific carbon isotopic measurements can be used to establish the relationship between biological precursors and their diagenetic products via both chemical structural inheritance and the carbon isotopic compositions of individual compounds (Bechtel et al., 2008, 2012; Duan et al., 2004; Murray et al., 1998; Sinninghe Damsté et al., 2014; Strobl et al., 2014; Tuo et al., 2003). Therefore, the combination of molecular and isotopic composition of OM extends the ability to trace inputs of organic material and carbon flows in ancient environments and to retrieve information about ancient biogeochemical processes and depositional environments.

In this paper, the petrographic characteristics, biomarker patterns and isotopic composition of individual biomarkers of lignites from the Kovin coal deposit are presented in detail. Based on a comprehensive study, the origin of the organic matter and characteristics of the depositional environment of the Kovin deposit have been reconstructed.

2. Geological settings

The Late Miocene (Pontian, according to the local stratigraphic scale, Rögl, 1996) Kovin lignite deposit is located about 50 km east from Belgrade (Fig. 1a). The Kovin deposit and the Kostolac basin form a single coal basin, with the Danube River as a natural boundary (Fig. 1b). The Kovin deposit is divided into two fields: western – field “A”, and eastern – field “B”, whose areas are 16.3 km^2 and 23.7 km^2, respectively. According to the Geological Survey of the Kovin deposit, the lignite resources are currently estimated at 275 Mt. (http://www.rudnikkovin.rs/wp; http://www.smeits.rs/include/data/docs0066.doc). Subaqual (under the water) exploitation of lignite in the offshore zone of the “A” field, named “Experimental exploitation field” (EEF; Fig. 1b) was started in 1991, and is still active. Since 1991, within the Kovin deposit about 5 Mt. in total of lignite has been produced. The Kovin mine produces about 300.000 t of lignite per year (http://www.rudnikkovin.rs/wp; http://www.smeits.rs/include/data/docs0066.doc).

Geological exploration began at the eastern part of the basin during the late 19th century. Late Miocene (Pontian) age of the coal-bearing sediments was confirmed in paleontological studies carried out by Pavlović (1959); Spajić-Miletić (1960, 1969) and Stevanović (1951).

The Kovin deposit together with the Kostolac basin was formed in the Pannonian Basin System in shallow lacustrine, delta plain and fluvial environments. The Pannonian Basin was formed around 20 Ma ago as large continental back-arc basin in response to the rapid roll-back of a lithospheric slab that was situated at the exterior of the Carpathian Mountains (Cloetingh et al., 2006; Horváth et al., 2006; Sclater et al., 1980; Tari et al., 1992). The oldest extensional *syn*-kinematic deposits are usually considered to be Early Miocene in age (Rögl, 1998; Pavelić, 2001), but recent studies show that they may have formed as early as the Late Oligocene (Toljić et al., 2013). They consist of fluvial, lacustrine, continental and a limited amount of marine deposits. During Middle and Late Miocene times syn-kinematic deposition continued in a predominantly marine environment (Fodor et al., 1999; Horváth et al., 2006; Kováč et al., 1998; Tari et al., 1999; ter Borgh et al., 2013 and references therein), while the distribution and amounts of vertical movements varied across the basin and resulted in highly heterogeneous water depths (Matenco and Radivojević, 2012; Pigott and Radivojević, 2010; ter Borgh et al., 2013). In the period from the Middle to the Late Miocene three important events occurred in the evolution of the Central Paratethys (ter Borgh et al., 2015 and references therein):

1) Extension in the Pannonian Basin area gradually ceased which led to a decrease of accommodation space,
2) Formation of the paleo-Danube as result of drainage reorganization in the Alps which led to major increase of sediment influx and
3) Isolation of the Central Paratethys from the marine realm and formation of Lake Pannon by the uplift of the Carpathian Mountains.

Lake Pannon was subsequently filled in by progradation from the northern and eastern margins (Magyar et al., 2013; Sztanó et al., 2013). Progradation from the southern and western basin margins occurred as well, while the bodies from the two basin margins met in the SE part of the Pannonian Basin (ter Borgh et al., 2015), around 60 km north of Belgrade. The aquatic environments in the Lake Pannon gradually changed from marine to brackish, then to caspibrackish (8–16 g of salt/l, similar as salinity in Caspian Sea, approximately 12 g/l) and finally to freshwater, followed by development of lakes, mires and alluvial plains. During the warm early Late Miocene (ca. 10 Ma) increasing humidity with high summer precipitation (Bruch et al., 2007; Utescher et al., 2007) caused a reorganization of the coastal-deltaic faunas (Harzhauser and Mandic, 2008). Continuous decline of salinity of Lake Pannon caused a slightly alkaline environment (Harzhauser et al., 2007).

The area of the Kovin deposit consists of Palaeozoic schist, Tertiary, and Quaternary sediments (Figs. 1, 2). The basement of the Kovin deposit is formed of Devonian low grade schist overlain by Neogene sediments. The total thickness of Neogene sediments is estimated to be 1000 m. Neogene of the Kovin deposit consists of the following units (Fig. 2a):

1. **Sarmatian** (Middle Miocene) consists of clayey and sandy marlstone, marly clay, marly and clayey sandstone, subordinately of gravel and quartz sand, in shallow brackish-marine environment, with total thickness over 100 m;
2. **Pannonian** (Late Miocene) contains caspibrackish grey and white marlstone with rare thin layers of clay and silt with two lignite seams, the lower up to 6 m in thickness, and the upper maximum 1 m in thickness (Stojanović et al., 2012). Total thickness of the Pannonian sediments is over 200 m;
3. **Pontian** (Late Miocene) consists of shallow, caspibrackish to freshwater clastic sediments (sand and silt with thin clay, carbonation clay and gravel layers), with three lignite seams: oldest III seam, middle II, and the youngest I seam, having maximal thickness of 48.7 m, 7.6 m, and 15.2 m, respectively. The total thickness of the Pontian series is over 300 m;
4. **Lower Pliocene** consists of fresh water clay and sandy clay with total thickness of 20 m;
5. **Quaternary** formed of fluvial gravel, sand, clay and sandy-clayey sediments with total thickness of 40.3 m.

The Kovin deposit hosts all the three coal seams (III, II and I; Fig. 2a). The oldest III coal seam is detected locally in the eastern part of the B field, although the extent of this seam is not completely explored. The seam thickness varies generally from a few to 48.7 m (including interbedded rocks). It splits into two coal layers, upper and lower with maximal thickness of the run of mine coal of 2.6 m and 2.5 m

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