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Organic geochemical characteristics of Bulgarian jet

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ABSTRACT

The paper presents the results of the organic geochemical studies of Bulgarian jet samples of early Jurassic and early Cretaceous age from two deposits located within the Moesian platform and the Balkan tectonic zone. Total organic carbon contents (71 and 78% daf) indicate sub-bituminous coalification rank. Moderately high to high sulfur contents (0.8–1.7% daf) support activity of sulfate reducing bacteria. High amounts of volatile matter (53–59% daf) and slightly enhanced HI values (185–249 mg HC/g TOC) argue for organic matter bituminization. The latter is also confirmed by the very low T_{max} values (~400 °C), which are interpreted as a result of the release of bituminous substances during the early stages of pyrolysis.

Extractable organic matter is consistent with the low maturity and is characterized by high portions of NSO compounds and asphaltenes (> 80%). Hydrocarbons constitute about 10% and are characterized by the predominance of the saturated over the aromatics. The strongly short-chain homologs dominated *n*-alkanes distributions, with expressed maxima at n-C_{17} and n-C_{18}, and CPI in the range 1–2, is consistent with the woody origin of the jet. In addition, the low C_{29}/C_{27} (~1) sterane ratios denote possible impregnation of the drift woods with phytoplankton-derived lipids from the host rocks. Low Pr/Ph (0.42–0.65) and Pr/n-C_{17} (0.28–0.43) ratios, as well as high Ph/n-C_{18} (0.4–0.78) ratio outline anoxic conditions of jet formation. Furthermore, the absence of chromans in the jet extracts from the Moesian platform suggests depositional environment with reduced salinity, whereas low di-MTTC/tri-MTTS (0.32) in the sample from the Balkan tectonic zone points to normal marine conditions.

The occurrence of pimaranes and α-phyllocladane in the extracts from Nikolaevo jet points to *Taxodiaceae* or *Araucariaceae* conifers as possible precursors, whereas the presence of α-cedrane and cuparene in the sample from Lesidren deposit argues for *Cupressaceae* origin. In addition, triterpenoid biomarkers with lupane and ursane skeletal structures in the Lesidren jet is tentatively interpreted as an impregnation of the conifer drift wood with lipids from pre-angiosperm plants.

Results from the bulk and molecular analyses revealed that Bulgarian jet originates from conifer drift wood, deposited under anoxic environmental settings, and subsequently subjected to hydrogenation and biodegradation.

1. Introduction

Jet originates from drift wood deposited under anoxic conditions. Its formation is related to the impregnation of the drift wood with bituminous substances, which might be generated within resin-impregnated woods during maturation (Suárez-Ruiz et al., 1994b; Bechtel et al., 2001), or could be derived from external sources (Suárez-Ruiz et al., 1994a). Because of the bituminization, jet is typically characterized by high content of bituminous matter and significantly reduced vitrinite reflectance in comparison to coals of same maturity degree (Petrova et al., 1985; Suárez-Ruiz et al., 1994a,b). In addition, the molecular composition of the jet could be influenced by bituminous matter of microbial origin (Bechtel et al., 2001). In marine environment, the bacterial degradation of the wood fragments may start during their drifting, or could occur after their deposition in the sediment.

In Bulgaria, jet is rarely found and is present either as single inclusions in sedimentary rocks or associate with coals in coal-bearing strata (Minčev, 1982). The findings are mainly concentrated in Central Northern Bulgaria and fall within the Moesian platform and the Balkan Tectonic Zone (Fig. 1; Minčev, 1980, 1978; Minčev and Nikolov, 1979).

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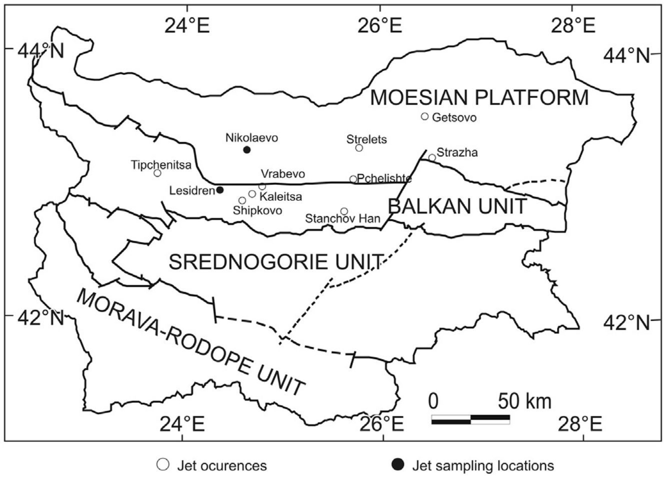

Fig. 1. Schematic diagram of the main tectonic units in Bulgaria (modified after Dabovski et al., 2002) with locations of jet occurrences (after Minčev, 1978).

The jet-bearing sedimentary rocks are of early Jurassic (deposit Lesidren) and Cretaceous age (Hauterivian – deposits Kaleitsa, Pchelishte, Vrabevo; Aptian – deposits Nikolaevo, Tipchenitsa, Strelets; and Cenomanian – deposit Stanchov Han). Since the discovery in the early sixties of the 20th century, Bulgarian jet was subjected to investigations focused on determination of microhardness, coalification rank, ultimate (C, H, N, S, O) and proximate (moisture, ash yield, volatile matter) characteristics. In addition, the petrographic composition and the influence of the oxidative processes were also extensively studied (Minčev, 1978, 1980; Minčev and Nikolov, 1979; Markova and Minčev, 1983; Markova et al., 1989; Markova, 1991).

In this paper, bulk geochemical data together with the molecular composition of the hexane-soluble non-polar extract fractions from Bulgarian jet samples from the Lesidren and Nikolaevo deposits, are presented. The main purpose of the study is to supplement the existing knowledge of jet with data on the geochemical composition of the organic matter and to determine the origin and possible diagenetic transformations of Bulgarian jet.

2. Geological settings

The occurrences of jet on the territory of Bulgaria are restricted to the Central and Northern part of the country and fall within the Moesian platform and the Balkan tectonic zone (Balkan orogen and its foreland – the Fore-Balkan; Fig. 1). The jet-bearing sedimentary rocks are of Early Jurassic and Early Cretaceous age and formed within epicontinental seas (Nachev and Nachev, 2003), which developed on the southern edge of the Moesian platform. During the Mesozoic the latter represented the active continental margin of Eurasia. According to Bojanov et al. (1989) its evolution is associated with episodic subduction and collision of continental fragments detached from the African plate and the formation of the Balkan orogenic belt.

Near the Nikolaevo village (Moesian platform; Fig. 1) the Aptian jet-bearing Svishtovska Fm. is composed of mid- to coarse-grained loose sandstones with massive structure and grain supported texture. These are locally interbedded by calcareous sandstone to sandy limestone interbeds, often containing orbitolina shells and ooliths (Khrischev et al., 1995), suggesting deposition in shallow marine (wave- or tide-dominated) environment. Jet represent trunk fragments (5–85 cm) distributed irregularly within the siliciclastic rocks (Minčev, 1980). Most jet pieces show zonal structure, comprised of up to three zones. The internal zone “A” represents the non-oxidized vascular tissue with well-defined growth rings. The external zone “B” represents the peripheral slightly weathered zone of the wood fragment, which is typically characterized by the occurrence of radial cracks, partly infilled by siliciclastic and/or clayey material. Some pieces also contain a third zone “C” (1 to 4 mm thick), representing the outermost and highly weathered part of the wood.

The actual geological settings of the Lesidren jet deposit (Balkan tectonic zone; Fig. 1) are unknown. Minčev (1978) has reported that the jet fragment was recovered from coal-bearing early Jurassic sedimentary rocks. Based on this description we here tentatively identify the Haetangian Bachiishtenska Fm. as the possible jet-bearing formation. It is represented by alternating continental and marine sedimentary rocks (Sapunov and Tchoumatchenco, 1995). These are mainly dark grey to black shales interbedded by quartzitic sandstones. Locally, some of the interbeds are represented by bioclastic limestones. At places, the shales are enriched in plant detritus and grade into carbonaceous shales or even into coal beds. Coal is of bituminous rank (1.3% R_r); Minčev (1978).

The physical and petrographic characteristics of the Bulgarian jet were provided by Minčev (1978, 1980). The drift wood fragments are composed almost exclusively of ulminite and resinite, partially infilling cell openings. Minor amounts of corpohuminite and suberinite are also observed in some of the pieces. Low vitrinite reflectance (R_r = 0.21–0.39%) argues for low coalification rank (lignite). However, vitrinite reflectance of jet is significantly reduced in comparison with the associated coals, therefore indicating that it is of limited utility as maturity indicator (Suárez-Ruiz et al., 1994a).

3. Material and methods

For the purpose of the present study, two jet samples from the Lesidren and Nikolaevo deposits, recovered from their host rocks in the early sixties of the 20th century, were chosen (Fig. 1). Two additional samples, representing zones “A” and “B” of a Nikolaevo jet fragment, were also studied in order to examine the effects of weathering and the differences in the organic geochemical parameters.

The analytical procedure includes ultimate (C, H, O, N, S; ISO 17247:2013, 2013) and proximate analysis (moisture, ash yield, volatile matter; ISO 17246:2010, 2010). Rock-Eval pyrolysis was performed using a Rock-Eval 6 instrument. The value of S_2 (mg HC/g rock) was used to calculate the hydrogen index (HI = 100 x S_2 / TOC [mg HC/g TOC]; Espitalié et al., 1977). The temperature of maximum hydrocarbon generation (T_{max}) was recorded as a maturity parameter.

For organic geochemical investigations about 5 g of each sample were mixed with a standard inert material and homogenized. Extraction was performed by a Dionex ASR 200 equipment using dichloromethane for 1 h at 75 °C and 75 bar. The extract was concentrated using a Zymark Turbo Vap 500 device. Extracts were dissolved in a solvent mixture of hexane:dichloromethane (80:1) and asphaltenes were subsequently separated by centrifugation. The hexane-soluble organic compounds (maltenes) were subdivided into saturated and aromatic hydrocarbons and NSO components using a Köhnen-Willsch MPLC (medium pressure liquid chromatography) instrument (Radke et al., 1980).

The fractions of saturated and aromatic hydrocarbons were analyzed by a gas chromatograph-mass spectrometer (GC–MS) Thermo-Fisher Trace GC Ultra, equipped with a 30 m silica capillary column (DB-5MS). Oven temperature was programmed from 70 to 300 °C with steps of 4 °C/min, followed by isothermal period of 15 min. Helium was used as carrier gas. The device was set in electron impact mode with a scan rate of 50–650 Da (0.7 s/scan). The results were processed with the software Thermo-Fisher Xcalibur v.2.0. Identification of biomarkers is based on retention time and comparison of mass spectra with published data. The determination of absolute concentrations of biomarkers was done using internal standards (deuterated *n*-tetracosane for the aliphatic fraction and 1,1-binaphthyl for the aromatic fraction) and values were normalized against the total organic carbon contents.