COMPARATIVE PETROGRAPHICAL AND ORGANIC GEOCHEMICAL STUDY OF EOCENE AND OLIGOCENE COAL BASINS FROM SW BULGARIA

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Combination of various factors, like hydrological regime, nutrient supply, microbial activity, pH, redox conditions, climatic settings, all together exert profound control on the development of different plant groups and hence, result in the formation of peats with distinct characteristics. The influence of many of these factors can successfully been determined by organic petrology and organic geochemical analysis. In the current study formation of coal in the Suhostrel (Early-Mid Eocene) and the Bobov Dol (Late Oligocene) basins located in the SW Bulgaria was evaluated using organic petrographic characteristics and biomarker patterns. Furthermore, the potential of biomarkers to indicate climate cooling trend in the late Oligocene, which was less pronounced in Bulgaria compared to the global one (Bozukov et al., 2009), was examined.

Studied coals significantly differ in their coalification degree. Suhostrel coal is of high volatile A to medium volatile bituminous rank (vitrinite reflectance, Ro ~ 1.10%), whereas Bobov Dol coal is at sub-bituminous B–A rank (huminite reflectance Ro ~ 0.45–0.50%). Samples from both basins are humic coals, which are characterized by prevalence of huminite/vitrinite macerals (>80%, based on mineral matter-free, MMF), followed by liptinite (8-13% MMF) and very low abundance of inertinite (up to 4%, MMF).
Biomarker assemblages of Bobov Dol coal reveal notable predominance of gymnosperm-derived sesquiterpenoids and diterpenoids in both aliphatic and aromatic fractions (up to 5500 µg/g TOC). *n*-Alkanes in the range from C_{21} to C_{33} with prevalence of odd-long chain homologues are present in low quantity (5–67 µg/g TOC), whereas contents of non-hopanoid triterpenoids, typical for angiosperm palaeovegetation, and hopanoids are very low (0–30 µg/g TOC and 0.8–11.7 µg/g TOC, respectively). The ratios of di-/(di-+tri-)-terpenoids calculated for the aliphatic and aromatic compounds fall in the range 0.8–1.0 and 0.9–1.0, respectively. Therefore, it can be concluded that the main OM source of coal in the Bobov Dol Basin were gymnosperms. Furthermore, the composition of the individual diterpenoid compounds (cuparene, cedrane, pimarane and phyllocladane) indicates that mixed *Pinaceae/Cupressaceae* plant communities were the most responsible for the accumulation of OM (Otto and Wilde, 2001). Considering uniform conifer-dominant OM source, values of Tissue Preservation Index (TPI; 0.3–2.6) associated with Gelification Index (GI; 1.9–14.8) indicate plant deposition under water-logged conditions, with temporal infiltration of oxygen-rich water that enhanced the destruction of plant remains (associated also with increase of detrohuminite and ash contents) and/or reduced burial rate, which supported more prolonged exposure to oxic conditions. Very low abundance of hopanoids can be attributed to antiseptic effect of conifer resins and acidic to mild acidic conditions (pH = 4.8–6.3, calculated from the C_{31} ββ/(ββ+αβ) hopane ratio, Inglis et al., 2018) during peat formation.
The compositions of aliphatic and aromatic fractions clearly indicate significantly higher maturity of Suhostrel compared to Bobov Dol coal. The aliphatic fraction of Suhostrel coal is

dominated by *n*-alkanes, showing exceptionally high concentrations (~10000 – 43000 µg/g TOC). The main constituents of aromatic fractions are methylated naphthalenes, phenanthrene, dibenzofuran, dibenzothiophene and their methylated counterparts. Despite the maturity influence, unimodal *n*-alkane distributions with prevalence of C_{24}-C_{27} homologues indicate mixed hydrophytic and woody vegetation, with the predominance of the former. All samples contain non-hopanoid triterpenoid oleanane. The Oleanane Index (OI = Oleanane/(Oleanane + C_{30} αβ-hopane)) ranges from 0.23 to 0.27, implying relatively significant impact of angiosperm derived OM in difference to Bobov Dol coal. Conversely, absence of any typical gymnosperm derived sesquiterpenoid and diterpenoid, with exception of sub-ordinate amounts of 1-methylphenanthrene and 1,7-dimethylphenanthrene (Jiang and George, 2019) in coal's aromatic fraction, which can also be formed by aromatization of other non-diterpenoid precursors, suggests lower impact of gymnosperm vegetation to Suhostrel coal OM compared to Bobov Dol. The abundance of oleanane in Suhostrel samples is further indicative for OM deposition under reducing conditions, since oxic environments favor the progressive diagenetic aromatization of the parent amyrine skeleton. This is consistent with the low concentration of inertinite macerals. The relatively high content of dibenzothiophene derivatives suggests occasional marine ingressions into the paleomire, as result of the changes of the land-sea distribution during Eocene (Rögl, 1999).

Studied coals significantly differ in their coalification degree: Suhostrel (Ro ~ 1.10%), Bobov Dol (Ro ~ 0.45–0.50%). The obtained results show that main OM sources of Bobov Dol coal were mixed *Pinaceae/Cupressaceae* conifer communities from moderately wet oligo- to mesotrophic swamps. OM of Suhostrel coal is mainly derived from mixed angiosperm hydrophytic and woody vegetation, with the predominance of the former. The peatification was performed under reducing conditions with occasional marine ingressions into the paleomire. Although comparison of biomarker patterns at different OM maturity levels is complicated, some relevant indication can be observed from the compositions of non-hopanoid terpenoids, which showed that mild late Oligocene climate cooling in Bulgaria was associated with change from hydrophytic angiosperm- to gymnosperm-dominated peatlands. This is consistent with the results of investigation of the Bulgarian Paleogene flora (Bozukov et al., 2009).

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