Geochemical characterization of organic matter in subbituminous coals from the Pernik basin, Bulgaria

Геохимична характеристика на органичното вещество в кафявите въглища от Пернишкия басейн, България

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Representative sample from Pernik coal basin was studied. The complex investigation includes determination of huminite reflectance, total organic carbon (TOC), Rock Eval parameters, extractable organic matter (EOM), and molecular composition of the hydrocarbon compounds.

Huminite reflectance (R_0) is 0.47%, which corresponds to the results reported by Valčeva (1979) and Kortenski and Zdravkov (2011). A total organic carbon (TOC) content of 54.16 wt% was measured. The obtained Rock–Eval HI values (211 mg HC/g TOC) are typical for type III kerogen. Low T_{max} values (410 °C) are in agreement with the subbituminous rank of the sample. The EOM yield of the studied sample is 66.2 mg/g TOC. The relative content of saturated hydrocarbons in EOM is low (4.5%). The extractable organic matter is mainly represented by asphaltenes (57%) and polar compounds (31%). These values are in accordance with the low maturity of the organic matter (subbituminous coal).

The obtained data show that long-chain *n*-alkanes (*n*-C_{27} to *n*-C_{31}) predominate in the saturated hydrocarbon fraction. Maximal relative intensity is determined at *n*-C_{31} (16.47 ppm). Similar *n*-alkane patterns are typical for herbaceous vegetation and mosses according to Ficken et al. (1998) and Nott et al. (2000). However, the other authors like Herbin and Robins (1968) noted that a higher concentration of the C_{31}*n*-alkane may indicates the participation of coniferous vegetations in the peat forming plants. The high carbon preference index (CPI, according to Bray and Evans, 1961) of 3.4 reflects a marked predominance of odd over even-numbered alkanes, as usually found in low rank terrigenous organic matter.

Isoprenoids are represented by the acyclic hydrocarbons pristane (Pr-1.20 ppm) and phytane (Ph-0.59 ppm). The ratio of Pr versus Ph has been used to evaluate the redox potential of the depositional environment (Didyk et al., 1978). The Pr/Ph ratio determined in the Pernik coal is 2.1, arguing for an oxic depositional environment. However, it has been shown that the pristane/phytane ratio is strongly influenced by the thermal maturity of the organic matter, which is related to the rapid formation of pristane with increasing maturity (Hughes et al., 1995; Vu et al., 2009).

The diterpenoids in the studied samples are mainly represented by hydrocarbon compounds with beyerane, abietane, pimarane and phyllocladane type skeletal structure. The following diterpanes were identified in the non-aromatic hydrocarbon fraction: norpimarane, beyerane, pimarane β-phyllocladane, abietane, and α-phyllocladane. The diterpane α-phyllocladane is usually found in coniferous vegetations except of Pinaceae (Ten Haven et al., 1992) and is regarded as a typical biomarker of Araucariaceae, Cupressaceae, and Taxodiaceae. The aromatic tri-cyclic diterpenoids norabietatriene, dehydroabietane, simonellite, retene and methylretene occur in studied samples. Simonellite is the dominant aromatic diterpenoid. The occurrence of aromatized abietane has been suggested to be mediated by microbial activity beside thermal, clay-catalysed reactions (Wakeham et al., 1980; Barnes, Barnes, 1983).

Non-hopanoid triterpenoids of the oleanane, ursane, and lupane type are present in very low concentrations. The compounds identified in the saturated and aromatic hydrocarbon fractions include ring-A degraded and pentacyclic oleanane-, ursane-, and lupane-type triterpenoids. From the relative amounts of di- versus angiosperm-derived triterpenoids, a conifer-dominated vegetation can be concluded for the Pernik coal deposit. The low contents of terpenoid

biomarkers are consistent with paleobotanical data (Otto, Wilde, 2001).

The hopanoid pattern in the studied sample is characterized by the presence of ββ and αβ type hopanes from C_{27} to C_{31}. C_{28} hopanewas not detected. Hop-17(21)-ene was detected in considerable amount, consistent with the low rank of the coal. The presence of hopanoids indicates microbial (bacterial) activity in the paleomire. However, a contribution of fungi, as well as some mosses and ferns cannot be excluded. The predominance of hopanes with ββ stereo configuration in the subbituminous sample is typical for the immature organic matter.

In the studied sample from Pernik basin, polycyclic aromatic hydrocarbons (PAHs) with three, four and five-member rings are found. Components with 5-member rings predominated over the other PAHs. Perylene is present in high amount (1.53 ppm), followed by benzo(e)pyrene, benzo(a)pyrene, 2-phenylnaphthalene, benzo(k)fluoranthene, triphenylene, and chrysene.

Alkylnaphthalenes (8.69 ppm) are found in a higher concentration than alkylphenanthrenes (3.06 ppm). The presence of alkylnaphthalenes has been used to identify the transformation process of pentacyclic triterpenoids during degradation of organic matter under reducing conditions (Philp, 1985).

The results of the present geochemical study of coal from the Pernik basin confirm the previously reported petrographic data. Coals are subbituminous with a relatively low degree of coalification. The Pernik coals probably originated mainly from conifer dominated vegetation mixed with grasses, mosses and ferns. Biomarker composition gives ground to assume microbial (bacterial) activity in the ancient peat swamps.

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