



Workshop “Organic matter transformations in Maritsa Iztok dump materials: view by geochemical proxies”

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ABSTRACT BOOK

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PETROGRAPHICAL AND BIOMARKER STUDY OF LIGNITE LITHOTYPES AND SUBLITHOTYPES OF XYLITE-RICH COAL (KOLUBARA BASIN, SERBIA)

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Maceral and biomarker composition of different lignite lithotypes, matrix-coal, mineral-rich coal, charcoal-rich coal and xylite-rich coal represented by 5 sublithotypes: pale yellow, dark yellow, dark yellow-fibrous, brown and black was studied in detail. Samples were taken from the Upper Miocene ("Pontian") Tamnava-Zapad field of the Kolubara Basin (Serbia). The objective was to establish the sources of organic matter (OM) and to determine palaeoenvironmental conditions. Moreover, grindability properties have also been assessed.

Content of total organic carbon (TOC) is relatively high and uniform in all sublithotypes of xylite-rich coal, being slightly elevated in yellow compared to brown and black xylite. Matrix, charcoal and particularly, mineral-rich coal have lower amount of TOC. Content of mineral matter varied in wide range (from < 1 % in pale yellow xylite to > 35 % in mineral-rich coal). Therefore, petrographic composition is considered based on mineral matter-free.

Huminite is apparently prevailing maceral group in all samples (> 83 %), with exception of charcoal which is characterised by prevalence of inertinite group macerals. Yellow xylite sublithotypes are sharply dominated by textinite (> 88 %), whereas in both aliphatic and aromatic fractions of extracted OM, diterpenoids (in total up to 5790 µg/g TOC) prevailed notably over other biomarker classes which are present in traces (with exception of gymnosperm derived sesquiterpenoids). In brown and black xylite, telohuminite is more abundant than detrohuminite. In these xylite sublithotypes content of ulminite is higher than in yellow counterparts. Content of diterpenoids is lower than in yellow xylites, which is associated with higher amounts of all other biomarker classes (*n*-alkanes, steroids, hopanoids, sesquiterpenoids and non-hopanoid triterpenoids). However, diterpenoids (up to 900 µg/g TOC) prevailed notably over other biomarkers. Matrix and mineral-rich coal is characterised by higher content of detrohuminite than telohumite. This is followed by decrease in content of total diterpenoids (up to 573 µg/g TOC) and increase in content of all other biomarkers in comparison to xylite-rich coal. However, diterpenoids also represent the most abundant biomarkers. Charcoal displayed almost identical abundance of detrohuminite and telohumite. Charcoal has the lowest abundance of diterpenoids (191 µg/g TOC), although these biomarkers prevailed over other biomarker classes implying significant impact of conifers to precursor OM. Content of steroids and hopanoids in charcoal is low and similar to their abundance in yellow xylites, whereas content of *n*-alkanes is higher than in yellow xylites and lower than in other samples. Content of liptinite was very low in yellow xylites (< 2 %), showing increasing trend through charcoal, black and brown xylite, being the highest in matrix (11.3 %) and mineral-rich coal (13.2 %). Resinite prevailed in yellow xylite sublithotypes, suberinite in brown and black xylite, whereas liptodetrinite was dominant liptinite maceral in matrix and mineral-rich coal. Charcoal is characterised by prevalence of liptodetrinite and suberinite. Content of inertinite (dominated by inertodetrinite) is generally low, the highest being in mineral-rich coal (5.5 %). The exception is charcoal, where inertinite group macerals dominate (54.0 %) and is characterised by prevalence of fusinite (35.5 %).

The most prominent diterpenoids in aliphatic fraction of all samples are pimarane and 16 α (H)-phyllocladane, whereas the most abundant aromatic diterpenoids are simonellite, dehydroabietane and *cis*-dehydroicetexane. The *cis*-dehydroicetexane/dehydroabietane ratio gradually increased from pale yellow via dark yellow, brown and black xylite, matrix and mineral rich-coal, the highest being in charcoal. Since recent investigation showed that *cis*-dehydroicetexane is indicative for Cupressoideae [1], it can be supposed that impact of this conifer family to precursor OM increased in mentioned order. Sesquiterpenoids in aliphatic fractions are represented by cadinenes which prevailed over patchoulane and eudesmanes. Cadalene was most prominent aromatic sesquiterpenoid. Angiosperm derived non-hopanoid triterpenoids are present in very low concentrations (as des-A-degraded compounds only) in aliphatic fraction, whereas in aromatic fraction both pentacyclic and des-A-degraded tetracyclic compounds with oleanane, ursane and lupane skeleton were identified.

Distribution of individual *n*-alkanes is characterised by predominance of odd long-chain homologues (C₂₇-C₃₁) and maximum at C₂₉. Pale yellow and dark yellow xylites display elevated contents of mid- (C₂₁-C₂₅) and short-chain (C₁₅-C₂₀) *n*-alkanes, followed also by the lowest Carbon Preference Index values. This result could be attributed to the lower input of fatty acids from epicuticular waxes [2]. Furthermore, elevated content of C₂₃ *n*-alkane in yellow xylite sublithotypes can be indicative for contribution of *Sphagnum* mosses [3]. The result coincides with higher C₃₀ hop-17(21)-ene/C₃₁ $\alpha\beta$ (R)-hopane ratio in yellow xylites, whereas other samples showed similar values of this ratio.

Biomarker characteristics suggest that main precursors of OM were conifers. Based on identified sesqui- and diterpenoids, a dominant role of the conifer families Cupressaceae, Taxodiaceae and Pinaceae could be concluded in all lithotypes [4]. This indicates no significant climatic change during Pontian. However, observed differences in maceral and biomarker composition imply changes in palaeoenvironment which resulted in different degree of degradation of decay resistant conifers and changeable, but relatively small input of angiosperms and herbaceous plants to precursor OM. Mineral-rich coal was formed in topogenous fresh water peat mire with open water areas. Formation of matrix coal was performed in reed marsh. The peatification of pale yellow and dark yellow xylites proceeded in dry forest swamp. Ombrogenous mire (sharply dominated by conifers) prohibited inundation and deposition of siliciclastics. Brown and black xylite was formed in wet forest swamp, whereas formation of charcoal is associated with wildfire. Relatively high content of mineral matter in charcoal indicates an allochthonous origin, i.e. large quantities of fusinite were brought into the deepest parts of the mire by wind and water.

Hardgrove Grindability Index (HGI) shows increasing trend in the following order: black xylite < brown xylite < matrix coal < mineral-rich coal < charcoal. Attempt to determine HGI for yellow xylites failed, resulting in extremely high, non-reliable values, indicating that standard method for bituminous coals cannot be applied to these sublithotypes.

References

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