

## MACERAL AND BIOMARKER COMPOSITION OF LIGNITE LITHOTYPES – IMPLICATIONS ON PALAEOENVIRONMENT AND GRINDABILITY PROPERTIES

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Maceral and biomarker composition of different lignite lithotypes: matrix-coal, pale yellow xylite-rich coal, dark yellow xylite-rich coal, brown xylite-rich coal, mineral-rich coal and dopplerite originating from the Upper Miocene (“Pontian”) Kostolac Basin, Serbia was studied in detail. The objective was to establish the sources of organic matter (OM) and to determine palaeoenvironmental conditions which resulted in formation of different lignite lithotypes. Moreover, the influence of lignite lithotypes on grindability properties has also been assessed.

Lignites were manually separated into lithotypes under stereo microscope. Maceral analysis was performed in monochromatic and UV light illumination on 500 points. Elemental analysis was carried out to determine the contents of total organic carbon (TOC), sulphur and nitrogen. Quantitative biomarker composition was obtained by gas chromatography-mass spectrometry. Hardgrove Grindability Index (HGI) was determined in accordance with ISO 5074:2015.

Huminite maceral group sharply prevail over liptinites and inertinites in all samples, which have apparently elevated contents in mineral-rich coal. Textinite is the most abundant maceral in pale yellow xylite-rich coal, dark yellow xylite-rich coal and dopplerite, showing gradual decreasing trend in this order. Mineral-rich coal and brown xylite-rich coal are characterised by prevalence of ulminite, whereas in matrix coal, ulminite and densinite are present in almost equal contents.

TOC is relatively high and uniform in pale yellow xylite, dark yellow xylite and matrix coal, whereas in brown xylite, dopplerite and particularly, mineral-rich coal it is lower.

Diterpenoids are the most abundant biomarkers in all samples exhibiting gradually decreasing trend in following order: pale yellow xylite > dark yellow xylite > dopplerite > brown xylite ≈ mineral-rich > matrix coal. After diterpenoids, non-hopanoid triterpenoids and *n*-alkanes are the most abundant biomarkers in all lithotypes (although in significantly lower concentrations). Hydrocarbon patterns of pale yellow and dark yellow xylite consist almost entirely of diterpenoids and sesquiterpenoids. The elevated concentrations of non-hopanoid triterpenoids, *n*-alkanes and hopanoids are observed in matrix and mineral-rich coal. Content of steroids is generally low, the highest being in matrix and mineral-rich coal.

From identified sesqui- and diterpenoids (eudalene, cuparene, 16 $\alpha$ (H)-phyllocladane, pimarane, totarane and hibaene), a dominant role of the conifer families Cupressaceae, Taxodiaceae and Pinaceae could be concluded in all lithotypes (Otto and Wilde, 2001). Non-hopanoid triterpenoids, indicative for angiosperms, are present in extremely low concentrations in aliphatic fraction, whereas in aromatic fraction they comprise pentacyclic and des-A-degraded tetracyclic compounds with oleanane, ursane and lupane skeleton. Pentacyclic non-hopanoid triterpenoids are more abundant than tetracyclic chrysene derivatives in all samples, with exception of pale yellow and dark yellow xylite.

All samples show similar distributions of *n*-alkanes, which are characterised by predominance of odd long-chain homologues (C<sub>27</sub>-C<sub>31</sub>). However, pale yellow and dark yellow xylite display elevated contents of mid- (C<sub>21</sub>-C<sub>25</sub>) and short-chain (C<sub>15</sub>-C<sub>20</sub>) *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.

Typical feature of hopanoid distribution is relatively high abundance of unsaturated 17(21) and 13(18) hopenes. C<sub>30</sub> hop-17(21)-ene prevails in all lithotypes with exception of mineral-rich coal where C<sub>31</sub> αβ(R)-hopane is the most prominent. The latter is usually associated with activity of heterotrophic bacteria in more oxic environment, consistent with lowest TOC values in mineral-rich coal. Aromatic counterparts are represented by series of aromatic hopanoids bearing an ethyl group at C-21, with prevalence of D-ring monoaromatic hopane.

Perylene is present in all samples. Conifer Wood Degradation Index (Marynowski et al., 2013), reflecting degree of degradation of wood tissues by fungi, is order of magnitude higher in matrix, mineral-rich and brown xylite than in other lithotypes.

To the best of our knowledge HGI was measured for the first time on individual lignite lithotypes. HGI shows increasing trend in the following order: dopplerite < matrix coal < brown xylite < mineral-rich coal. Attempt to determine HGI for pale yellow xylite and dark yellow xylite was failed and resulted in extremely high, non-reliable values, indicating that standard method proposed for bituminous coals cannot be applied to yellow xylites in difference to other lithotypes studied here. Correlation analysis depicts that HGI positively correlated with contents of liptinites, inertinites, gelinite and mineral matter (MM), whereas negative correlation is observed for total huminites, telohuminite and TOC. In regards to biomarkers, HGI mostly depends on concentrations of sesquiterpenoids, hopanoids and *n*-alkanes. All of them show significant positive correlation with HGI, whereas the ratio of retene to 2-methyl, 1-(4'-methylpentyl), 6-isopropyl-naphthalene (IPN) exhibited negative impact on HGI.

Mineral-rich coal was formed in topogenous fresh water peat mire with open water areas. The peat mire was subjected to inundations and deposition of siliciclastics. The inundations and/or infiltration of oxygenated water into the mire resulted in enhanced OM degradation, e.g. low TOC. Formation of matrix coal was performed in reed march. The peatification of pale yellow- and dark yellow xylite proceeded in dry forest swamp. Ombrogenous mire (sharply dominated by conifers) prohibited inundation and deposition of siliciclastics. Brown xylite was formed in wet forest swamp, whereas dopplerite could have formed during transition of wet forest swamp into bush mire. Contents of liptinites, inertinites, gelinite, MM, sesquiterpenoids, hopanoids and *n*-alkanes have positive impact on HGI, whereas total huminites, telohuminite and TOC, as well as retene/IPN ratio exhibited negative influence on HGI. This resulted in most appropriate grindability properties of mineral-rich coal.

## References

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