# MATURATION AND ISOTOPIC CHANGES OF INDIVIDUAL HYDROCARBONS IN LIGNITE LITHOTYPES THROUGH DIAGENESIS AND EARLY CATAGENESIS

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Maturity changes of biomarkers and aromatic hydrocarbons, as well as changes in their isotopic compositions were studied through diagenesis and early catagenesis. Lignite samples (huminite reflectance, Rr = 0.30±0.03) from the Kostolac Basin, Serbia were used as substrates. In order to investigate the influence of lignite lithotype on maturity changes of organic matter, the study was carried using mineral-rich coal, matrix coal and xylite-rich coal. Simulation of maturity was performed by mild open system pyrolysis during 4 hours at the temperatures of 400 °C (Pyr400), 450 °C (Pyr450) and 500 °C (Pyr500). This temperature range was chosen according to data from thermogravimetric analysis which indicate that the first significant mass loss (after releasing of moisture) occurs between 400 °C and 500 °C. Aliphatic and aromatic fractions isolated from lignite extracts and liquid pyrolysis products were analyzed by gas chromatography-mass spectrometry. Carbon isotope determinations ($\delta^{13}C$) of individual compounds in these fractions were also performed.

Compositions of aliphatic and aromatic fractions of lignite extracts and liquid pyrolysis products remarkably differ (Fig. 1). Extracts of lignite are characterized by a distinctive domination of odd long-chain homologues. On the other hand, all liquid pyrolysates have similar distributions of *n*-alkanes with the prevalence of mid-chain homologues ($C_{21}$-$C_{25}$) and the equal abundance of odd and even numbered *n*-alkanes (Carbon Preference Index, CPI ~ 1). In lignite extracts $\delta^{13}C$ was measured only on $C_{25}$-$C_{31}$ odd *n*-alkanes, whereas in the pyrolysis products it was determined in the range from $C_{17}$ to $C_{28}$, showing decreasing trend with chain length in all samples. *n*-$C_{25}$ and *n*-$C_{27}$ have very close values in pyrolysates and lignite extracts, confirming that isotopic signatures are useful tracers for alteration products of biological molecules. Long-chain homologues exhibit slight enrichment in $^{12}C$ from Pyr400 to Pyr500, whereas almost no change is detected in $\delta^{13}C$ of short-chain *n*-alkanes. Pristane/phytane (Pr/Ph) ratio clearly increased from Pyr400 to Pyr500.

In all samples the most abundant compound in hopanoid distributions is $C_{27}$17β(H)-hopane. Hopanoids with biological 17β(H)21β(H)-configuration are present in all pyrolysates, whereas unsaturated 17(21)- and 13(18)-hopenes, identified in lignite extracts, were not detected. The ratios of $C_{27}$, $C_{29}$ and $C_{30}$17β(H)21β(H)-hopanes to 17α(H)21β(H)-hopanes obviously decrease from Pyr400 to Pyr 500. The same is related to $C_{30}$17β(H)21α(H)/$C_{30}$17α(H)21β(H)-hopane and $C_{31}$17α(H)21β(H)22(S)/22(R)-hopane ratios, although they show less pronounced changes than above mentioned hopane parameters. Steroid distributions in lignite extracts comprise exclusively unsaturated $\Delta^2$, $\Delta^4$ and $\Delta^5$ sterenes with sharp predominance of $C_{29}$ homologues. In pyrolysates sterenes are absent and steroid distributions dominated by $C_{27}$-$C_{29}$ 5α(H)14α(H)17α20(R)-steranes. Prevalence of $C_{29}$ homologue is apparent in all pyrolysates, however it slightly decreases from Pyr400 to Pyr500. Thermodynamically more stable ααα(S)-steranes are absent in Pyr400, which suggests their formation in late diagenesis. $C_{29}$ααα(S)/$C_{29}$ααα(R) sterane ratio increases from Pyr450 to Pyr500. It should be mentioned that intensity of observed changes of hopane and sterane maturity ratios decreases in the following order: mineral-rich coal >

matrix coal > xylite-rich coal. This result implies that mineral matter, which is dominated by clays in all lithotypes, plays an important role in the isomerisation of polycyclic biomarkers.

The only compounds present in aromatic fractions of lignite extracts and pyrolysis products are cadalene and retene. The maturity ratios based on trimethylnaphthalenes (TMNR) and tetramethylnaphthalenes (TeMNr) slightly increase from Pyr400 to Pyr500. The same is related to methylfluorene (MF) ratio (2-+3-MF)/(1-+4-MF) and methylphenanthrene (MP) index 3 (MPI 3). However, maturity ratios, MFI 1 and MPI 1 which contain unsubstituted aromatics (fluorene, phenanthrene) in the denominator do not show clear trends from Pyr400 to Pyr500. This can be attributed to the preferable release of unsubstituted aromatics fluorene (F) and phenanthrene compared to that of their methylated counterparts, which is documented by apparent decrease of ΣMF/F and PAI 1 ratios from Pyr400 to Pyr500. $\delta^{13}C$ values of phenanthrene in pyrolysates are very close to those observed for their possible precursors simonellite and retene in lignite extracts. Cadalene also has similar values in lignite extracts and pyrolysates. Tetramethylnaphthalenes show more negative $\delta^{13}C$ values than cadalene and phenanthrene which can be attributed to their possible formation from non-hopanoid triterpenoids which are enriched in $^{12}C$ than diterpenoids (Bechtel et al., 2008). Negligible enrichment in $^{13}C$ of aromatic compounds is observed from Pyr400 to Pyr500.

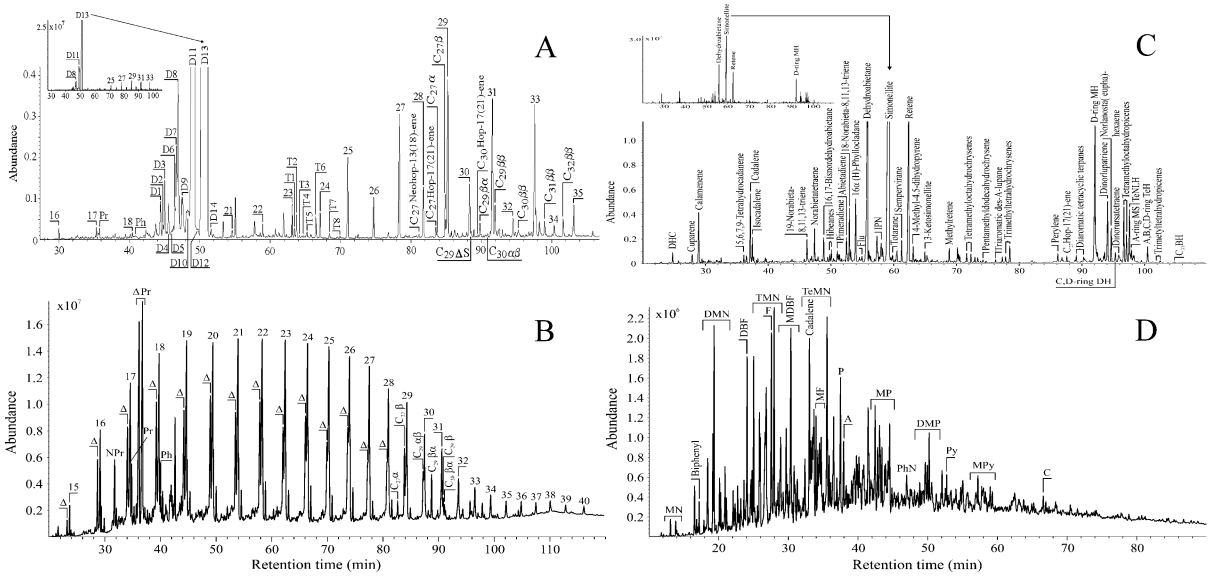


***Figure 1.*** *Total ion chromatograms of aliphatic fractions (A, B) and aromatic fractions (C, D) of matrix coal extract and corresponding liquid pyrolysate at 450 ºC.*
*n*-Alkanes are labelled according to their carbon number; Δ – 1-*n*-Alkenes with same number of carbon atoms as *n*-alkanes; D1-D14 –diterpenoids; T1-T8– des-A-degraded non-hopanoid triterpenoids. ΔS – sterene; ββ, βα and αβ designate configurations at $C_{17}$ and $C_{21}$ in hopanes;
DHC – dihydro-ar-curcumene; IPN – 2-methyl-1-(4'-methylpentyl), 6-*iso*propylnaphthalene;
MH – monoaromatic hopane; DH – diaromatic hopane; TeNLH – tetranor-lupa-1,3,5(10),6,8,11,13-heptaene; TeH – tetraaromatic hopane; BH – $C_{31}$ benzohopane; N –naphthalene; DBF – dibenzofuran; P – phenanthrene; A – anthracene; F – fluorene; Py – pyrene; C – chrysene; prefixes M, D, T and Te in figure (D) assigned methyl, dimethyl, trimethyl and tetramethyl, respectively.

## References

Bechtel, A., Gratzer, R., Sachsenhofer, R.F., Gusterhuber, J., Lücke, A., Püttmann, W., 2008. Palaeogeography, Palaeoclimatology, Palaeoecology 262, 166-175.