CAPABILITY OF $\delta^{13}C$ AND δ^2D ISOTOPE ANALYSES OF OIL FRACTIONS FOR OIL-OIL CORRELATION (SE PANNONIAN BASIN, SERBIA)

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Oil samples originating from different oil fields and local depressions of the Serbian part of the Pannonian Basin were studied (Fig. 1a). Detailed analysis of biomarkers indicated mixed terrestrial aquatic organic matter (OM) deposited in reducing to suboxic conditions. In almost all samples marine C_{30} steranes (4-desmethylsteranes) were present in low concentration, showing OM deposition under restricted saline lagoonal conditions or brackish environment. On the other hand presence of oleanane in majority of the samples proved input from angiosperm land plants. Pristane/phytane and $C_{35}\alpha\beta(S)/C_{34}\alpha\beta(S)$-hopane ratios suggested that Zrenjanin (ZR), Jermenovci (JR) and Gaj (GJ) oils were formed in reducing environment, Kelebija (KE), Turija (TU), Elemir (EL), Rusanda (RS) and Kikinda (KI) in alternate environment, whereas for Čoka (CO), Palić (PL), Majdan (MA), Mokrin (MK) and Bradarac-Maljurevac (BM) oils suboxic conditions were observed. Age-specific nordiacholestane (NDR) ratio indicated Tertiary age of studied oils. Total ion chromatogram (TIC) of the saturated fraction in the majority of the oils is characterized by notable predominance of n-alkanes (showing maxima in n-C_{16} − n-C_{18} range), without any observable unresolved complex mixtures, indicating that oils were not exposed to biodegradation. Exceptions in that sense represent Velebit (VE), KE, JR and GJ samples, which are characterized by very low concentration of n-alkanes in TIC of the saturated fraction. However, the presence of bicyclic sesquiterpanes in all of these biodegraded oils indicated 3rd-4th degree of biodegradation (Peters et al., 2005). The maturity assessment of oils was done using $C_{29}\alpha\alpha(S)/C_{29}\alpha\alpha(S+R)$-steranes, $C_{29}\beta\beta(R)/C_{29}(\beta\beta(R)+\alpha\alpha(R))$-steranes, $C_{31}\alpha\beta(S)/C_{31}\alpha\beta(S+R)$-hopanes, $C_{30}\beta\alpha$-moretane/$C_{30}\alpha\beta$-hopane, as well as by methylphenanthrene index (MPI 1) and methyldibenzothiophene ratio (MDR). These parameters indicated low maturity for TU, ZR, Boka (BK), JR and GJ oils, corresponding to calculated vitrinite reflectance, Rc of 0.60-0.70 %, moderate for EL, RS, MA, MK and Vojvoda Stepa (VST) oils corresponding to Rc of 0.70-0.80 % and Rc > 0.80 % for KE, PL, CO and VE. C_9-C_{20} regular acyclic isoprenoids were also used for characterization of facies, maturity and migration assessment, they worked moderately in the case of biodegraded oils.

$\delta^{13}C$ saturated vs. delta $\delta^{13}C$ aromatic relation (Sofer, 1984) confirmed mixed OM origin. However, it showed more contribution of marine OM to VE, KE, ZR, PL and KI oils. This result indicates that samples from North Bačka (Fig. 1a), VE, KE and PL differ according to sourced OM from other samples. Also, observed result suggests that ZR and KI samples originated from different sources than other Banat oils. Principal component analysis (PSA) performed using stable $\delta^{13}C$ and δ^2D isotopic compositions of saturated, aromatic, NSO fractions and asphaltenes resulted in two statistically important principal components, F1 based on $\delta^{13}C$ of fractions (55.38 % of variance) and F2 based on δ^2D of fractions (40.84 % of variance). Comparison of results of PCA with map of oil deposits indicates that F1 vs. F2 plot well represents the locations of studied sites (Fig. 1a). However, it provides some additional data that ZR oils differ from other Central Banat oils from RS and EL oil fields, which was also assumed based on biomarker ratios (more marine influence, more reducing conditions and lower maturity). Also this diagram suggests that RS oils from deposit I and II

slightly differ. RS I oils are very similar to EL oils, whereas RS II is more correlative with North Banat oils. F1 vs. F2 diagram showed that stable $\delta^{13}C$ and $\delta^{2}D$ isotopic compositions of individual fractions are not capable to distinguish biodegraded oils, maybe due to the low biodegradation level of several biodegraded samples. It suggests that $\delta^{13}C$ and $\delta^{2}D$ isotopic compositions of individual fractions could be used for correlation purposes up to 3rd-4th degree of biodegradation. In such case $\delta^{2}D$ of saturated and aromatic fractions allowed us to distinguish oils from different redox environments (Fig. 1b). $\delta^{2}D$ values increase with rise of Eh, following by decrease of line slope. Although biodegraded oils were not separated by F1 vs. F2 plot (Fig. 1a), our data showed that $\delta^{2}D$ of saturated fraction vs. $\delta^{2}D$ of aromatic fraction diagram (Fig. 1b) could not be used for oils exposed to biodegradation. This result suggests that $\delta^{2}D$ values are more sensitive to biodegradation than $\delta^{13}C$ values.
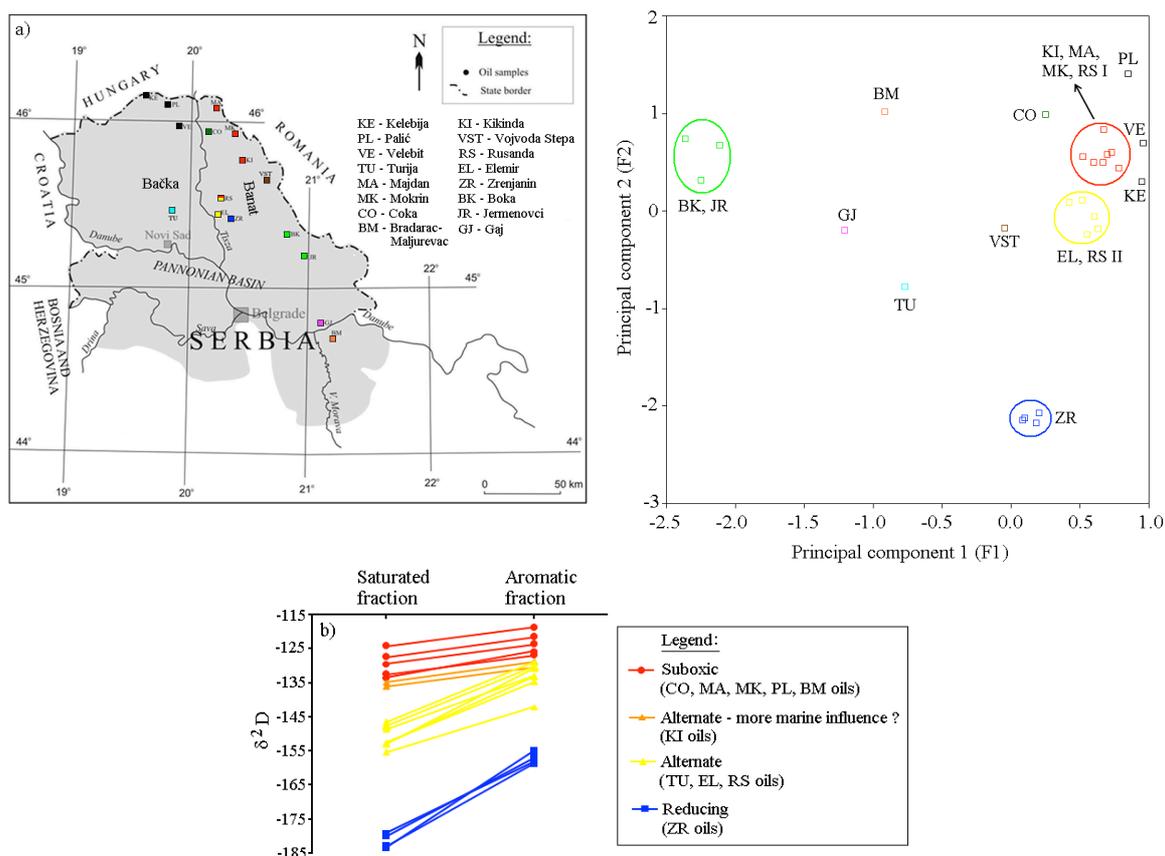
Figure 1. *Map showing locations of investigated oils and results of PSA analysis (a); $\delta^{2}D$ isotopic composition of saturated and aromatic fraction indicating redox conditions (b).*

References

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