

## CARBON ISOTOPIC COMPOSITIONS OF BIOMARKERS AND THEIR CHANGES BY DIAGENETIC ALTERATION (KOVIN LIGNITE DEPOSIT, SERBIA)

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Carbon isotopic compositions and influence of diagenetic alteration on isotopic signatures of biomarkers were investigated on samples from the Upper Miocene lignite (random huminite reflectance  $0.30 \pm 0.03$  %) from the Kovin deposit (Serbia). Diterpenoids were the most abundant compound in extractable organic matter of all samples, prevailing over *n*-alkanes, hopanoids, non-hopanoid triterpenoids and steroids.

The  $\delta^{13}\text{C}$  values of beyerane, pimarane and  $16\alpha(\text{H})$ -phylocladane ranged from -27.3 to -25.1 ‰, -27.5 to -25.5 ‰ and -27.8 to -26.0 ‰, averaging at -26.0 ‰, -26.4 ‰ and -26.8 ‰, respectively, indicating similar sources from conifer families Cupressaceae, Taxodiaceae, Phyllocladaceae, Araucariaceae and/or Pinaceae. However, slightly lower standard deviation of  $\delta^{13}\text{C}$  for  $16\alpha(\text{H})$ -phylocladane than for beyerane and pimarane is consistent with the fact that the phyllocladanes have fewer precursors compared to the tricyclic diterpanes and beyerane. The  $\delta^{13}\text{C}$  values of aromatic diterpenoids, dehydroabietane and simonellite in range from -27.6 to -25.2 ‰ (average 26.7 ‰) and -28.4 to -25.2 ‰ (average -27.1 ‰) are close to  $\delta^{13}\text{C}$  values of saturated diterpenoids, indicating the source from the same conifer families. The  $\delta^{13}\text{C}$  value of retene in the range from -27.5 to -30.8 ‰ (average -28.6 ‰) is lower than  $\delta^{13}\text{C}$  values of dehydroabietane and simonellite, indicating that aromatisation of diterpenoids may cause a depletion in  $^{13}\text{C}$  up to 2 ‰. Interestingly, isopimaradiene shows lower  $\delta^{13}\text{C}$  values (-26.9 – -28.9 ‰) than other diterpenoids, which might indicate an association with “leaf” rather than heartwood resins (Murray et al., 1998).

Due to the low concentration of non-hopanoid triterpenoids,  $\delta^{13}\text{C}$  was measured only for 4 aromatic compounds: 24,25-dinoroleana-1,3,5(10),12-tetraene (-31.4 – -29.3 ‰, average -29.9 ‰); 24,25-dinorlupa-1,3,5(10)-triene (-30.3 – -27.4 ‰, average -28.7); 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydronicene (-30.7 – -27.8 ‰, average -29.4 ‰) and 3,3,7-1,2,3,4-tetrahydrochrysene (-31.4 – -28.6 ‰, average -30.3 ‰). These results showed that aromatic non-hopanoid triterpenoids are 2-3 ‰ depleted in  $^{13}\text{C}$  compared to the aromatic diterpenoids. A-ring monoaromatic oleanane is up to 1.5 ‰ depleted in  $^{13}\text{C}$  than corresponding A-ring monoaromatic lupane, suggesting certain differences in precursor angiosperm families. 2,2,4a,9-Tetramethyl-1,2,3,4,4a,5,6,14b-octahydronicene is product of progressive aromatisation of  $\beta$ -amyrin, whereas 3,3,7-1,2,3,4-tetrahydrochrysene is formed by ring-A-degradation of  $\beta$ -amyrin, followed by aromatisation. The  $\delta^{13}\text{C}$  values of these two compounds indicate that A-ring-degradation of precursor molecule followed by aromatisation resulted in slightly higher  $^{13}\text{C}$  depletion than progressive aromatisation.

Ranges and average  $\delta^{13}\text{C}$  values for  $\text{C}_{27}$  (-33.0 – -29.1 ‰, average -30.8 ‰),  $\text{C}_{29}$  (-32.0 – -28.9 ‰, average 30.8 ‰),  $\text{C}_{31}$  (-31.8 – -29.2 ‰, average -30.9 ‰) and  $\text{C}_{33}$  (-31.5 – -29.0 ‰, average -30.4 ‰) *n*-alkanes, indicate mutual origin corresponding to lipid carbon pool of  $\text{C}_3$  higher plants. Although, marked differences between  $\delta^{13}\text{C}$  values of  $\text{C}_{27}$ - $\text{C}_{33}$  *n*-alkanes and  $\text{C}_{25}$  *n*-alkane (-30.5 – -27.2 ‰, average -29.4 ‰) were not observed, indicating that later mainly originated from vascular plants, enrichment of *n*- $\text{C}_{25}$  in  $^{13}\text{C}$  about 1 ‰ is obvious. This result can be attributed to influence of emergent aquatic macrophytes belonging to

Gramineae sp. which was observed during palynological investigation (Milivojević et al., 2014). Relatively close average carbon isotope composition of odd long-chain *n*-alkanes and angiosperm-derived triterpenoids may reflect their origin from higher plant waxes.

The  $\delta^{13}\text{C}$  values of  $\text{C}_{30}$  hop-17(21)-ene (from -51.4 to -39.0 ‰, average -43.9 ‰),  $\text{C}_{27}17\beta(\text{H})$ -hopane (from -43.9 to -36.8 ‰, average -39.6 ‰) and  $\text{C}_{29}17\beta(\text{H})$ -hopane (from -46.0 to -38.0 ‰, average -41.7 ‰) indicate contribution of chemoautotrophic- and methanotrophic- bacteria. Wide ranges of  $\delta^{13}\text{C}$  for mentioned hopanoids could be related to the multiple bacterial sources. The  $\delta^{13}\text{C}$  values of  $\text{C}_{31}17\alpha(\text{H})21\beta(\text{H})22(\text{R})$ -hopane are relatively uniform and notable distinct from  $\delta^{13}\text{C}$  of the other hopanoids, ranging from -24.2 to -27.5 ‰. This range indicates heterotrophic bacteria that consumed higher-plant-derived organic matter. The  $\delta^{13}\text{C}$  values of 28,30-bisnorhop-13(18)-ene ( $\text{C}_{28}$  neohop-13(18)-ene) range from -36.6 to -33.6 ‰, averaging at -34.9 ‰. The obtained values imply that  $\text{C}_{28}$  neohop-13(18)-ene is sourced from chemoautotrophic bacteria. D-ring monoaromatic hopane has similar  $\delta^{13}\text{C}$  values (-38.0 – -32.4 ‰, average -34.5 ‰) as  $\text{C}_{28}$  28,30-neohop13-(18)-ene indicating that later can be an important direct precursor of orphan aromatic hopanoids, via progressive aromatisation. However, greater range of  $\delta^{13}\text{C}$  values of D-ring monoaromatic hopane than of  $\text{C}_{28}$  neohop-13(18)-ene is in accordance with well known fact that former could be also formed by degradation of side chain and aromatisation of other hopanoids. ABCD-ring tetraaromatic hopane has  $\delta^{13}\text{C}$  value in range from -34.5 to -30.1 ‰ (average -32.4 ‰) which is higher than those of D-ring monoaromatic hopane. The result indicates that in difference to aromatisation of diterpenoids and non-hopanoid triterpenoids, aromatisation of hopanoids is followed by  $^{13}\text{C}$  isotopic enrichment. This is consistent with recent observation of Liao et al. (2015).

The  $\delta^{13}\text{C}$  values of perylene were in range from -30.2 to -27.6 ‰ (average -29.0 ‰) indicating diverse sources. According to the recent literature data (e.g. Marynowski et al., 2013), the most plausible source of perylene seems to be wood-degrading fungi. In studied samples range of  $\delta^{13}\text{C}$  values of perylene is similar to  $\delta^{13}\text{C}$  values of retene and aromatic non-hopanoid triterpenoids with ursane and lupane skeleton. Positive correlation observed between perylene content and contents of retene, 24,25-dinorlupa-1,3,5(10)-triene and 2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydronicene could indicate that wood degradation by fungi is followed by aromatisation of diterpenoids and triterpenoids.

## References

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