COMPOSITION OF LIPIDS FROM LIGNITE DEPOSITS OF THE FAR EAST: RELATIONS TO VEGETATION AND CLIMATE CHANGE DURING THE CENOZOIC

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Twenty-one samples of coal and 1 sample of carbonaceous shale have been collected from different coal seams from the open-pit and underground mines, representing the Cenozoic coal basin widely distributed in the region of Primorye and Sakhalin (Russia), and NE China (Hunchun deposit). Their degree of coalification ranges from lignite to sub-bituminous coal. Age of the studied rocks has been determined as a result of the regular geological mapping in addition to paleobotanical (including palynological) dating (Pavlyutkin and Petrenko, 2010). The paleobotanical studies were focused on the coals-hosting rocks, most often carbonaceous shale and mudstone containing abundant floral remnants. These data do not allow correlation of the coals in details, although their stratigraphic position is well defined in general. Each of the studied seams has been attributed to one of the local chronostratigraphic units, namely: Sineutesovsky (Early Miocene-latest Oligocene), Pavlovsky (Oligocene-latest Eocene), Ust-Davydovsky (Late Eocene), Uglovsky (Early Eocene), and Kivdinsky (Late Paleocene). However, relative position of the seams is uncertain inside each unit.

The molecular composition of the extracted lipids is highly variable, including leaf-wax \textit{n}-alkanes in the C\textsubscript{23} to C\textsubscript{31} range, diterpenoids, hopanoids, and angiosperm-derived triterpenoids. The polar fractions are dominated by long-chain saturated fatty acids, long-chain \textit{n}-alkanols and \textit{n}-alkan-2-ones. Source-specific terpenoid biomarkers include pimarane-, abietane-, and phyllocladane-type diterpenoids. The presence of ferruginol and dehydroferruginol testifies the contribution of Taxodiaceae to peat formation (Otto et al., 1997). The high abundances of pimarane-type diterpenoids and the presence of non-aromatic abietane-derivatives argue for the contribution of Pinaceae. Non-hopanoid triterpenoids containing the structures typical of the oleanane skeleton, the ursane skeleton, or the lupane skeleton are known as biomarkers for angiosperms (Sukh Dev, 1989). Based on the presence of lupane-type triterpenoids, including 24,25-bisnoroxyllobetula-1,3,5(10)-triene and 24,25-bisnorallolobetula-1,3,5(10)-triene (Stevanova et al., 2016) an important input of Betulaceae can be concluded. The results are in agreement with paleobotanical data highlighting abundant conifers of the Taxodiaceae and Pinaceae families, as well as \textit{Betula, Alnus, Fagus}, and \textit{Ulmus} during Cenozoic (Pavlyutkin and Petrenko, 2010).

The relative abundances of diterpenoids versus di- plus angiosperm-derived triterpenoids revealed increased contributions of angiosperms during the Oligocene, whereas, the peat-forming vegetation during Eocene and Miocene was dominated by gymnosperms. Consistent with these results, a positive relationship exists between the di-/(di- + tri)-terpenoid biomarker ratios and $\delta^{13}$C of Oligocene samples indicating the role of varying gymnosperm/angiosperm contributions on the carbon isotopic composition of lignite (Bechtel et al., 2003). Average C-isotope data of long-chain \textit{n}-alkanes, diterpenoids, and angiosperm-
derived triterpenoids of the outlined chronostratigraphic units follow the trends in isotopic composition of total organic matter. Beside the influence of changes in $\delta^{13}$C of atmospheric CO$_2$, $\delta^{13}$C values of individual compounds may be related to changes in humidity and air temperature, due to the influence of climate on stomatal closure of the peat-forming plants. This interpretation is supported by the lower $\delta$D values during the Oligocene, due to decreased temperatures during this period of coal formation. Different $\delta$D values are obtained from individual diterpenoids: pimarane-type diterpenoids are significantly depleted in deuterium. The results are in agreement with previous studies (Tuo et al., 2006) outlining different sources of hydrogen and/or different biosynthetic pathways during their formation.

References


