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THE POTENTIAL OF BIOMARKERS TO DISTINGUISH LOWER AND MIDDLE MIOCENE LIGNITES FROM THE COAL-MINING DISTRICT OF LUSATIA

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The organic geochemical study of Lower and Middle Miocene lignites from the coal-mining district of Lusatia (Lausitz) in eastern Germany has been performed. Since the samples showed a uniform and low degree of thermal maturity (huminite reflectance 0.32–0.37 %Rr), it can be considered that maturity has no significant impact on biomarker distributions. Therefore, the objective of the study is to examine the potential of biomarkers to distinguish Lower and Middle Miocene lignites in relation to sources and depositional environment of organic matter (OM). Lignite samples were collected from the 2nd Miocene Seam Horizon or its equivalent of Piskowitz (Lower Miocene) and Welzow-Süd (Middle Miocene) open-cast mines (Kus et al., 2020). The contents of moisture, ash, sulphur, and total organic carbon (TOC) were determined. The biomarker compositions were evaluated using gas chromatography-mass spectrometry.

TOC contents (48.17 – 57.20 %) associated with ash contents < 11.5 % indicate relatively stable water-level during peat formation and moderate supply of mineral matter. Total sulphur content ranges from 0.67 to 0.80% and from 0.90 to 1.24 % in Lower and Middle Miocene samples, respectively, implying peatification in the freshwater environment.

In aliphatic fractions of all samples, *n*-alkanes prevail, followed by hopanoids and diterpenoids, while steroids, non-hopanoid triterpenoids, fernenes, sesquiterpenoids, and isoprenoids are present in low concentrations. An exception is Middle Miocene sample, which is characterized by a higher abundance of hopanoids than *n*-alkanes. This is consistent with low Tissue Preservation Index (TPI) and high Gelification Index (GI) (Kus et al., 2020), signifying an elevated pH in the mire with intense microbial activity that favours decomposition of wood tissues. In all samples long-chain *n*-alkanes (C_{26}–C_{33}) are the most abundant, exhibiting notable odd- over even predominance. The elevated contents of mid-chain, C_{23} and C_{25} *n*-alkanes, resulting in higher Paq index, are observed in Lower Miocene samples. The most abundant diterpenoid in aliphatic fraction of Lower Miocene lignites is 16α(H)-phyllocladane, whereas in Middle Miocene samples it is isopimarane or norabietane. The hopanoid distributions of all samples dominated by C_{31}17α(H)21β(H)22(R)-hopane, but Lower- and Middle Miocene lignites notably differ according to abundance of hopenes that is order of magnitude higher in later. This is associated with higher content of fernenes in Middle Miocene samples, which are absent in most of the Lower Miocene lignites.

Although non-hopanoid triterpenoids played a subordinate role in the aliphatic fractions, they prevail in aromatic fractions of lignites. The result is consistent with the rapid aromatization of their amyrin precursors during diagenesis in comparison to diterpenoids. The abundance of other biomarker classes in aromatic fraction decreases in the following order: diterpenoids > hopanoids > sesquiterpenoids > steroids > polycyclic aromatic hydrocarbons, PAHs (fluorene, naphthalene, phenanthrene, fluoranthene, pyrene, chrysene, and their alkylated derivatives, benzo[k]fluoranthene, benz[a]anthracene). Exceptions are Middle Miocene sample, which has greater content of hopanoids than diterpenoids (in accordance to the

dominance of these biomarkers in the aliphatic fraction, low TPI and high GI) and another one, also Middle Miocene lignite, where PAHs prevail over steroids, being order of magnitude more abundant than in other samples. Among aromatic non-hopanoid terpenoids, 24,25-dinorlupa-1,3,5(10)-triene dominates in all samples, with the exception of Middle Miocene lignite enriched in PAHs, where 1,2,9-trimethyltetrahydropicene prevails. Among aromatic diterpenoids, dehydroabietane or simonellite prevail in Lower Miocene samples, whereas in Middle Miocene lignites, simonellite or retene are the most abundant. Aromatic hopanoids are represented by series of orphan aromatic hopanoids (bearing an ethyl group at C-21), with one to four aromatic rings.

The presence of diterpenoids (Di) and non-hopanoid triterpenoids (Tri) in relatively high concentrations in all samples shows that both gymnosperms and angiosperms contributed to the precursor OM. However, the Di/(Di+Tri) ratio < 0.5 (Bechtel et al., 2003) suggests a greater contribution of angiosperms. The contents of C_{27} and C_{29} n-alkanes in relation to C_{31} and C_{33} homologues imply similar impact of forested and reed-mire vegetation. The presence of tricyclic (abietane, pimarane, isopimarane) and tetracyclic (phyllocladane, bayerane, kaurane) diterpenoids indicates the contribution of the following families of gymnosperms to the precursor OM: Pinaceae, Taxodiaceae, Cupressaceae and Phyllocladaceae, whereas cuparene and dehydroicetexane are specific for Cupressaceae (Nytoft et al., 2019). Slight input of aquatic macrophytes and ferns is also evident. The degrees of aromatization of diterpenoids and non-hopanoid pentacyclic triterpenoids (Stojanović and Životić, 2013) are generally low in all samples consistent with stable water-level during peatification, signifying reducing conditions in the palaeomire. Good correlation between content of hopanoids and degree of aromatization of diterpenoids and non-hopanoid triterpenoids implies that diagenetic aromatization of the OM was governed by bacterial activity, rather than thermal alteration. The exception is middle Miocene sample that characterizes by notably higher degree of terpenoids' aromatization associated with distinctively elevated amount of PAHs. The result can be attributed to palaeo-wildfires.

The biomarker patterns show relatively similar compositions in studied lignites, indicating no significant change in palaeclimate from Lower to Middle Miocene. Middle Miocene lignites are characterized by more pronounced variations of biomarker signatures than Lower Miocene samples, most probably due to the more pronounced fluctuation of water-level and/or palaeo-wildfires. The main differences between Middle and Lower Miocene coals are expressed by higher dehydroicetexane content, Paq index, the tetracyclic/tricyclic diterpanes ratio and non-hopanoid triterpenoids content, as well as by lower content of total hopenes (particularly those with double bond at 13(18)-position) and fernenes in the latter one. Mentioned results indicate decreasing contribution of Cupressaceae and emergent macrophytes, associated with increased input of Pinaceae, angiosperms and ferns to the precursor OM of Middle Miocene samples in comparison to Lower Miocene samples.

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