THE PRESERVATION OF CELLULOSE IN FOSSIL WOOD – IMPLICATIONS FROM ORGANIC GEOCHEMICAL STUDY OF FOSSIL AND MODERN WOOD

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Fossil wood with well-preserved cellulose is detected in Piskowitz (Pis), Meuro, and Welzow-Süd (WS) open-cast mines of the Miocene Lusatia (Lausitz) lignite-mining district in eastern Germany. The fossil wood samples are represented by *Taxodioxylon cryptomerioides* collected from the WS open-cast mine, *Sciadopityoxylon wettsteinii* from the Meuro open-cast mine, and *Quasisequoioxylon piskowitzense* from the Pis open-cast mine. Aimed to explain the preservation of cellulose, an organic geochemical study was performed on the above mentioned fossil wood samples and intact heartwood tissues of the respective modern woody species: *Cryptomeria japonica* D.Don, *Sciadopitys verticillata* Siebold & Zucc., *and Sequoiadendron giganteum* (Lindl.) J.Buchholz.

The results of semi-quantitative Micro Fourier transform infrared (micro-FTIR) spectroscopy, as well as of holocellulose content (determined by the chlorite holocellulose assay) of fossil wood samples are summarized in Table 1. They reveal: good (*Quasisequoioxylon piskowitzense and Sciadopityoxylon wettsteinii*) to excellent (*Taxodioxylon cryptomerioides*) preservation of cellulose; distinct aliphatic hydrogen as indicated by aliphatic stretching bands in the 2800-3000 cm^{-1} region; and well preserved oxygenated groups (1700-1800 cm^{-1}) that imply limited microbial degradation of organic matter (OM) and its low maturity.

Table 1 *Semiquantitative micro-FTIR analysis of fossil wood and content of holocellulose*

Sample	2800-3000 cm^{-1}	1700-1800 cm^{-1}	1650-1550 cm^{-1}	(2800-3000)/ 1740	(2800-3000)/ 1592	Cellulose/ Lignin	Holocellu-lose (%)
Quasisequoioxylon piskowitzense	40.8	4.2	5.7	9.7	7.2	4.1	15.56
Taxodioxylon cryptomerioides	40.1	6.5	5.9	6.2	6.8	6.9	37.59
Sciadopityoxylon wettsteinii	39.7	7.2	5.4	5.5	7.3	3.2	19.96

The content of total organic carbon (TOC) is comparable between *Sciadopityoxylon wettsteinii* and *Taxodioxylon cryptomerioides* (≈51.5%), with lower yield in *Quasisequoioxylon piskowitzense* of 38.7%. TOC contents in modern wood samples are very similar (44–46 %). The content of extractable organic matter (EOM) of fossil wood samples varied from 215 to 330 mg/g TOC, whereas modern wood samples have considerably lower

amounts (22–74 mg/g TOC). The EOM of all samples is dominated by polar fraction and asphaltenes.

Modern wood samples have a lower content of hydrocarbon biomarkers than the fossil counterparts. In all studied samples, biomarker hydrocarbon classes (in aliphatic and aromatic fraction of EOM) are represented by diterpenoids, sesquiterpenoids, and *n*-alkanes. Very low amounts of steroids and hopanoids are detected in fossil wood only. Biomarker assemblages of all samples are characterized by notable prevalence of diterpenoids and the presence of conifer derived sesquiterpenoids, thus clearly confirming gymnosperm sources. Diterpenoids in both fossil and modern wood consist of compounds with isopimarane, pimarane, abietane phyllocladane, hibaene, and kaurane skeletons. Aliphatic diterpenoids sharply prevail over aromatic counterparts, which are detected as minor components in *Quasisequoioxylon piskowitzense*, *Taxodioxylon cryptomerioides*, *Cryptomeria japonica*, and *Sequoiadendron giganteum*. Sesquiterpenoid distributions in fossil wood samples are represented by longifolane, cedrane, cadinene isomers, drimane, cuparene, and cadalene. Sesquiterpenoids in modern wood comprise muurolene isomers, α-cedrene, longipinene, bisabolene, cuparene, and cadalaene. Normal fatty acids (FAs) are detected in the range from C_8 to C_{28}, with notable prevalence of even homologues. C_{16} FA and monoenoic C_{18} FA dominate in all samples. Distributions of diterpenoids and sesquterpenoids in fossil and modern wood samples are similar. The main difference is reflected through the higher ratio of saturated to unsaturated aliphatic diterpenoids with pimarane and abietane skeletons in fossil wood (5.02–8.35) than in modern one (0.42–4.10). This result can be attributed to hydrogenation reactions and implies reducing conditions. Regarding FA distributions, the main differences between fossil and modern wood are reflected through significantly higher ratio of saturated C_{18} FA to dienoic C_{18} FA in fossil wood compared to modern wood, slightly elevated proportions of even C_8-C_{12} FA homologues in modern wood, and slightly elevated proportions of even C_{24}-C_{28} FA homologues in fossil wood.

The $\delta^{13}C$ values of wood fossils: -24.6‰ (*Quasisequoioxylon piskowitzense*), -21.9‰ (*Taxodioxylon cryptomerioides*), and -20.3‰ (*Sciadopityoxylon wettsteinii*) are consistent with Neogene gymnosperm trees. Slightly elevated $\delta^{13}C$ values (particularly in later samples) compared to the majority of preserved wood fossils in coal and lignite deposits from the early Miocene through Pliocene in central Europe (Lukens et al., 2019) are also indicative of good preservation of cellulose, since its decomposition is usually associated with the progressive depletion of ^{13}C in wood (Bechtel et al., 2008).

Biomarker assemblages suggest that the preservation of cellulose in fossil wood samples was governed by reducing conditions. Furthermore, it can be also attributed to weathering of the surrounding tuff- and rhyolite-dominated acidic volcanic rock that might have caused lowering of pH. All fossil wood samples contain minor hopanoids (0.05-0.70 μg/g TOC), implying negligible post-depositional microbial degradation of OM. Limited microbial degradation of OM could be also caused by protection of the wood by conifer resins. For example, fossil Cupressaceae *sensu lato*, as confirmed by detection of hibaene, totarane, and cuparene, was more resinous than the modern forms. The absence of perylene in fossil wood indicates the limited degradation of wood by fungi.

References

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