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THE MOLECULAR COMPOSITION OF SPOROPOLLENIN FROM FOSSIL MEGASPORES AS REVEALED BY MICRO-FTIR AND PYROLYSIS-GC-MS

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Sporopollenin represents the naturally occurring macromolecules that constitute the chemically resistant component of the outer wall (exine) of spores and pollens. The actual chemistry of sporopollenin has been a topic of debate for years (Dutta 2006; de Leeuw et al., 2006 and references therein). Fossil sporopollenins are of particular interest as they make up the maceral sporinite, an important component of some coals. To investigate the chemical composition of fossil sporopollenin, megaspores of Lower Tertiary (*Azolla* sp.), Lower Cretaceous (*Dijkstraiporites helios, Paxillitriletes midas*, *Cabochonicus carbunculus*) and Upper Carboniferous (*Tuberculatisporites* sp., *Laevigatisporites reinschii*, *Calamospora laevigata*, *Zonalessporites* sp.) age have been investigated. Following kerogen isolation, about 10-50 individual megaspore specimens have been handpicked, cleaned by dichloromethane to remove soluble organic matter, and analysed by micro-FTIR and Curie-point pyrolysis-GC-MS.

Both spectroscopic and pyrolytic investigations clearly indicate that fossil sporopollenin is composed of aliphatic and aromatic moieties. The micro-FTIR spectra of the walls of all spores are characterised by aliphatic CH_x (3000-2800 and 1460-1450 cm^{-1}) and CH_3 (1375 cm^{-1}) absorptions, aromatic C=C (1560-1610 cm^{-1}) and CH (700-900 cm^{-1}) absorptions and various C=O group absorptions at 1740-1700 cm^{-1}. Alkylbenzenes and alkylphenols are the major aromatic pyrolysates. A homologous series of *n*-alkene/*n*-alkane doublets were detected in all fossil sporopollenin. Oxygenated aromatic compounds like benzaldehyde, acetophenone and 4-vinylphenol were found in the pyrolysates of all megaspores of Lower Cretaceous and Lower Tertiary periods. However, they are absent or occur below detection limit in the pyrolysates of Upper Carboniferous megaspores. The present investigations show that the aliphatic building blocks became selectively abundant, and oxygenated aromatic compounds selectively degraded with diagenesis and increasing thermal maturity and time of burial. 4-Vinylphenol is the pyrolytic decarboxylation product of *p*-coumaric acid which is believed to protect the spore from UV-B radiation (Blokker et al., 2006 and references therein). If oxygenated aromatic compounds are selectively degraded during burial and diagenesis,

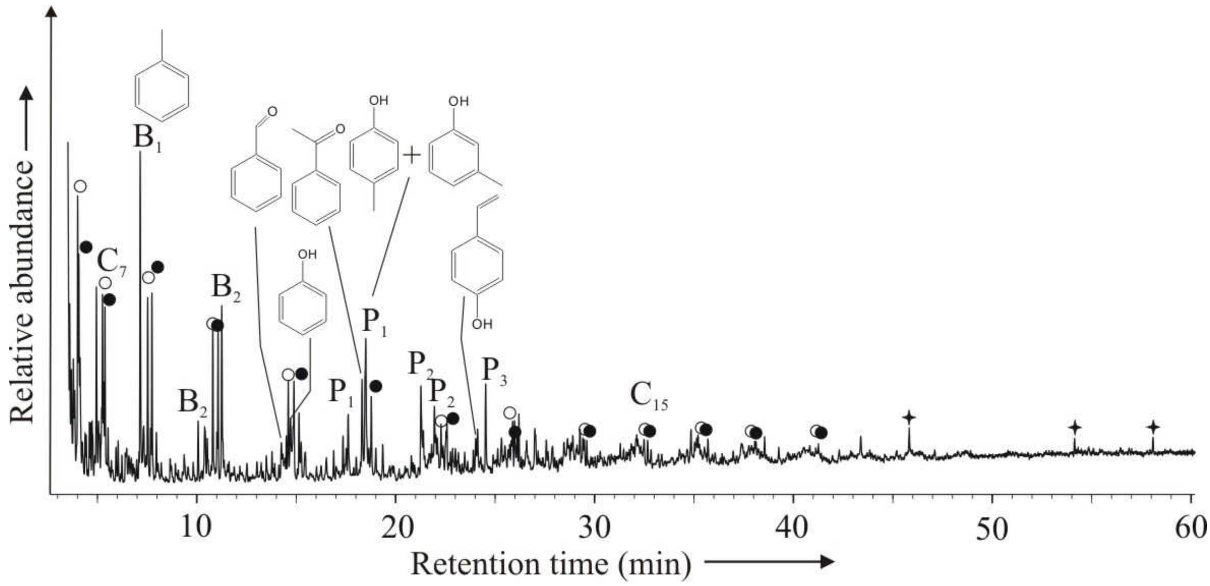

Figure 1. Total ion chromatogram resulting from the Curie point pyrolysis-GC-MS of Cretaceous megaspore *Dijkstraiporites helios*. Each doublet corresponds to an alkene (○) and alkane (●); selected C-numbers are indicated. B and P indicate alkylbenzenes and alkylphenols, respectively and their subscript indicate total number of methyl groups. ✦ indicates contaminant.

then the presence of *p*-coumaric acid in spore wall holds little promise for assisting the reconstruction of past UV-B radiation. Within the realm of our present investigation, it is suggested that all megaspore walls had the same chemical composition prior to fossilization. The subsequent differences in chemical composition of fossil sporopollenin are likely due to the influence of different diagenetic processes and thermal history.

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