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FORMATION OF AN ALIPHATIC POLYMER DURING HEATING EXPERIMENTS WITH *LYCOPODIUM* SPORES

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The main components of *Lycopodium* spores is the biopolymer sporopollenin and significant amounts of ester-bound fatty acid material. The preservation of these components in the geosphere is currently the object of investigation (De Leeuw et al. 2006). To understand the chemical transformations that occur during the diagenesis of spores, solvent extracted and saponified examples from *Lycopodium* were heated under vacuum in sealed glass tubes at a series of temperatures (100-400 °C) for 48 hours. Hydrous pyrolysis of *Lycopodium* spores was also conducted in an N_2 atmosphere. Following heating, spores were solvent extracted with toluene and methanol (9:1) and allowed to dry before analysis by FT-IR. Spores were further characterised by pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) and thermochemolysis-GC-MS using tetramethylammonium hydroxide (TMAH) as the reagent.

With increasing temperature the FT-IR analyses show a decrease in oxygen containing functional groups, a decrease in overall aromaticity and an increase in the aliphatic component. The FT-IR spectra for the heated spores closely resemble that from fossil spores.

The Py-GC-MS chromatograms also clearly demonstrate that there is an increase in the aliphatic material in the pyrolysable component with increasing temperature. Figure 1 displays the Py-GC-MS total ion chromatogram from a sample of *Lycopodium* spores heated under vacuum at 300 °C for 48 hours. The main products released upon pyrolysis are a series of alkane/alkene doublets (C_6 to C_{17}) along with benzene, toluene, ethylbenzene and xylenes (BTEXs).

FT-IR analyses reveal that the aliphatic component in the fresh *Lycopodium* spores is present as ester bound *n*-carboxylic acids (mostly *n*-$C_{16:0}$ and *n*-$C_{18:1}$) and *n*-diacids (C_8 to C_{20}). The distribution of the alkane/alkenes (i.e. predominance of *n*-C15 and *n*-C17) is consistent with their source being the ester bound organic acids. It appears that this resistant aliphatic polymer has been formed from the hydrolysable component with sporopollenin, an observation that is consistent with the recent results and interpretations (e.g. Gupta et al.; *In press*).

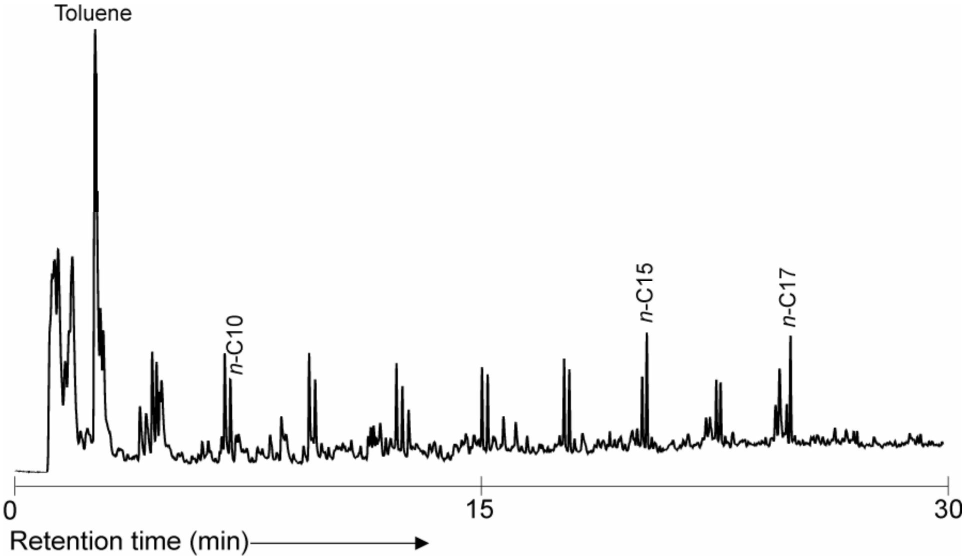

Figure 1. Py-GC-MS (at 610 °C) total ion current of *Lycopodium* after heating at 300 °C for 48 hours under vacuum.

REFERENCES

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