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Molecular signatures of kerogens and bitumens from the Lower Devonian Rhynie chert: Insights into the botanical affinity of the earliest land plants

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The Lower Devonian Rhynie chert of Scotland is an iconic geological formation that preserves the earliest known terrestrial ecosystem. This assemblage contains key evidence of earliest lineages of land plants, e.g., protracheophytes and paratracheophytes (former Rhyniaceae), together with animals, fungi, algae, and bacteria (Edwards et al., 2017). The exquisite preservation of this early biota provides an ideal scenario to explore the basal evolution of the land biosphere.

The Rhynie chert has been vastly studied from multiple viewpoints, however, the biomolecular composition, i.e., “molecular signature”, of the Rhynie flora, including the early detection of fossil lignin, remains clearly unresolved. Lignin biosynthesis has been considered as one of the crucial influences behind the survival and proliferation of land plants in terrestrial ecosystems. Here, we characterize the molecular fossils to help decipher the botanical affinities of the Rhynie flora.

Kerogens were isolated by the standard HF/HCl extraction procedure, and bitumens were extracted from the kerogens using organic solvents. The bitumens were studied with GC-MS, and the kerogens were analysed using Py-GC-MS and Py-GC×GC-TOFMS in the presence of TMAH reagent. The bitumens are characterized mainly by some aliphatic compounds such as a series of *n*-alkanes, pristane, phytane, and a series of diterpanes in very low abundance, as well as a set of aromatic compounds such as naphthalene and methylnaphthalenes, phenanthrene and methylphenanthenes and retene. The pyrolysates, obtained using Py-GC-MS are dominated by benzene and methyl benzenes, phenol and methylphenols, Polycyclic Aromatic Hydrocarbons (PAHs) like naphthalene and methylnaphthalenes, phenanthrene and methylphenanthenes, anthracene and methylanthracene, fluoranthene, pyrene, etc. Series of fatty acid methyl esters (FAME) and of *n*-alkane/alkene doublets were also detected. The thermochemolysates acquired from Py-GC×GC-TOFMS include the same compounds; additional methoxybenzene derivatives, methoxy toluene, methoxy benzaldehydes, and benzoic acid methyl esters, generated by reaction with TMAH, were also identified. Phenols and methoxybenzenes in the pyrolysates and thermochemolysates originate from lignin, and this is the first time that lignin monomers are formally identified from Rhynie chert samples.

References:

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