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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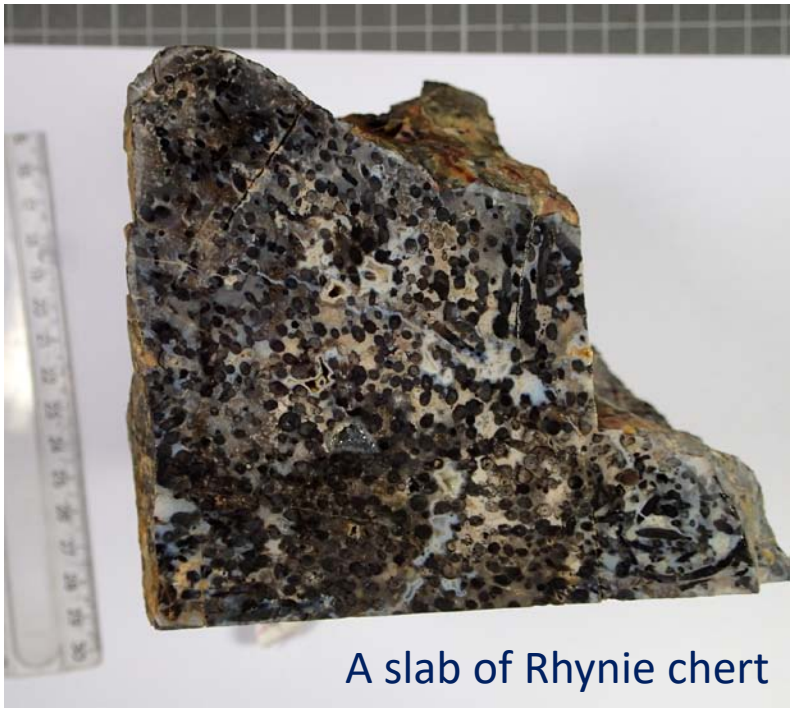
The Rhnynie cherts: the earliest terrestrial ecosystem

The assemblage contains key evidence of earliest lineages of land plants, e.g., protracheophytes and paratracheophytes (former Rhyniaceae), together with animals, fungi, algae, and bacteria all exquisitely preserved in silica matrix.



A slab of Rhynie chert

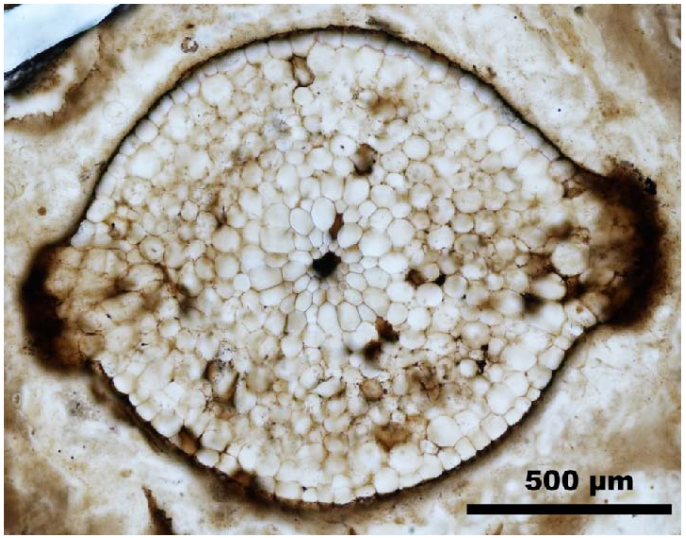
Motivation

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.

Objective

Here, we characterize the **biomolecular composition** of the **kerogens** and **bitumens** from Rhynie chert, to help decipher the botanical affinities of the Rhynie flora.

Materials and methods



Transverse section through a Rhynia stem

Maceration: HF/HCl extraction

Ultrasonication with DCM

Bitumen + **Extracted Kerogen**

Rock-Eval pyrolysis

Bulk organic geochemical information

TMAH derivatization

GC-MS

Soluble biomarkers

Py-GC-MS

Insoluble biomarkers

Py-GC×GC-ToFMS

Methylated compounds

Results

Thermal maturity

The Rock Eval pyrolysis parameters of the kerogens suggest they have reached early stage of thermal maturity.

Molecular composition of the bitumens

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 methylphenanthrenes and retene.

Molecular composition of the kerogens

The **pyrolysates** obtained form **Py-GC-MS** are dominated by benzene and methyl benzenes, phenol and methylphenols, Polycyclic Aromatic Hydrocarbons (PAHs) like naphthalene and methylnaphthalenes, phenanthrene and methylphenanthrenes, 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 found in the pyrolysates; additional methoxybenzene derivatives, methoxy toluene, methoxy benzaldehydes, and benzoic acid methyl esters, generated by reaction with TMAH, were also identified.

Inferences

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.