Cuticles of fossil plants

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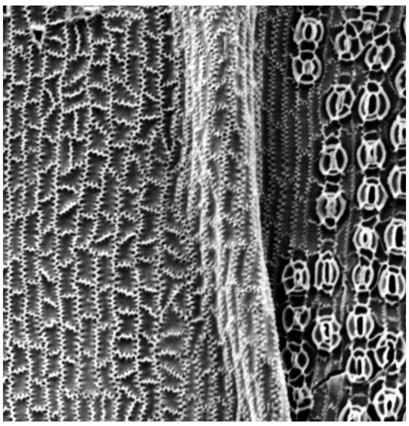
Green surfaces of land plants all over the Earth are covered by a protective 'skin', the cuticle. When leaves fall off the plant the leaf litter decays. In swampy settings it becomes peat and eventually coal. Other leaves are washed into lakes and rivers, settle in sediments, and form fossils. Some leaf particles ultimately reach the sea. The fossil fuels (coal, oil and gas) upon which modern civilisation depends are the result of alteration of plant organic matter over millions of years.

Insets: Fossils of Gingko (top) look remarkably similar to modern leaves (bottom), both superficially and in their detailed structure. But their chemical composition is very different.

We wanted to find out if the chemical composition of the protective cuticle controls the preservation of leaves. Is the cuticle altered in fossils and can leaf fossils be seen as stages in fossil fuel generation? Can we trace the fate of cuticle organic matter using chemical analysis of fossils or sediments?

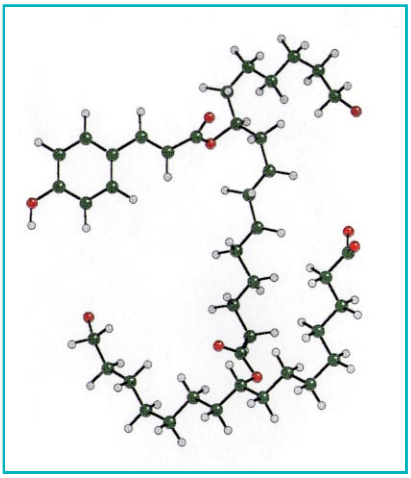
A cuticle like this covers the surface of all land plants (scanning electron micrograph).



In order to answer these questions, we have studied leaves of modern and fossil maiden hair trees (Ginkgo) and conifers from the swamp cypress, monkey puzzle and pine as well as extinct plant groups. We have used several methods of chemical analysis combined with electron microscopy to study the morphology and structure of the cuticles. Our samples range from modern to over 300-million-year-old fossils from a variety of rock types.

A portion of the molecular structure of cutin, the major constituent of plant cuticles; it is a cross-linked network of hydrocarbon-like chains.

key: ● carbon, ● oxygen, ● hydrogen.



We have discovered that:

- **Fossil leaf cuticles often show unaltered overall morphology and fine detailed internal structure. Nevertheless, their chemical character has been altered.**
- **The chemical alteration of molecules in the cuticle always gives a hydrocarbon-rich 'oily' pattern of chemical fragments on analysis. These altered fossil plant cuticles have the potential to yield oil and gas.**
- **The chemical composition of the cuticle does not control the preservation of leaves as fossils.**

The Ancient Biomolecules Initiative is a five-year programme to understand the fate of biological molecules in archaeological and fossil materials, and to explore the applications of this new knowledge. The Initiative is funded by the Natural Environment Research Council.

Natural Environment Research Council

Cuticles of fossil plants: the science in detail

Ginkgo (the maiden hair tree) has an excellent fossil record from the Mesozoic onwards. The modern cuticle (like those of 12 modern conifers we have studied) does not yield a highly resistant residue following selective chemical extraction. It consists predominantly of the natural polyester cutin. Fossils which retain the morphology and ultrastructure of modern plants still show major changes in chemical character (especially an increased predominance of hydrocarbon fragments up to C_{30}). However, fossils also retain distinctive chemical signatures (eg phenols).

Methods

Cuticles from modern plants were subjected to selective chemical extraction to distinguish specific components. At all stages modern and fossil cuticles were monitored by scanning and transmission electron microscopy so that chemical changes could be related directly to alteration in morphology and ultrastructure.

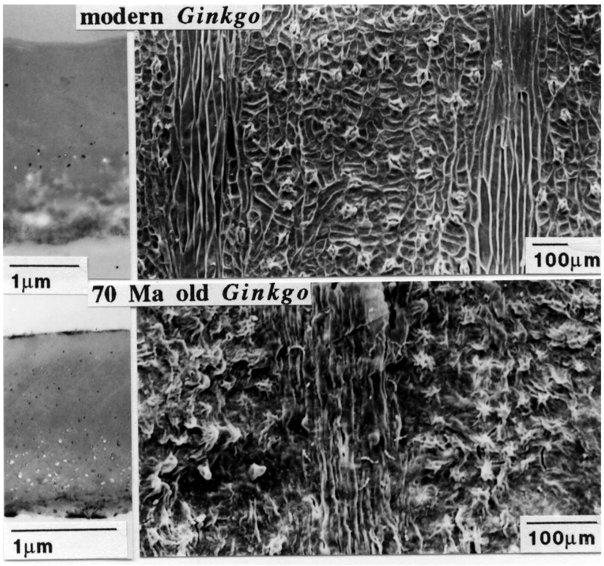
All of the fossil cuticles we have studied show the same fundamental alteration to their chemical character irrespective of their age, the nature of the enclosing rock, the type of plant or the morphology and ultrastructure of the cuticle. However, all fossil cuticles also reveal some individually distinctive chemical signatures.

With our Bristol colleagues we have also studied co-occurring fossil animal and plant cuticles. Although these have distinctive chemical signatures, both show a predominance of hydrocarbon fragments in pyrolysis traces. This is not the result of transfer of material from plant to animal, as the detailed hydrocarbon patterns are distinct.

We conclude that the presence of a resistant macromolecule (such as cutan) is not a prerequisite for preservation of cuticle in fossil leaves of conifers and their relatives. We deduce that preservation results from formation of a macromolecular residue by diagenetic stabilisation of normally labile aliphatic constituents. Therefore, leaves lacking a resistant macromolecule in their cuticles need not have low preservation potential.

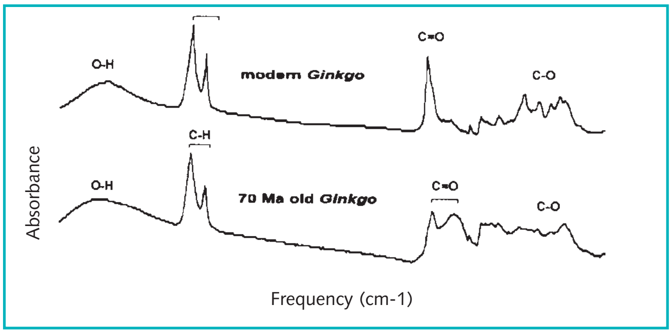
Future work

We would like to understand the preservation processes using flowering plant leaves, which can be obtained in large numbers and high diversity throughout the Cainozoic. Analysis of fossil specimens spanning 65 million years would be coupled with chemical studies of cuticle constituents of their living relatives in order to model the diagenetic changes.

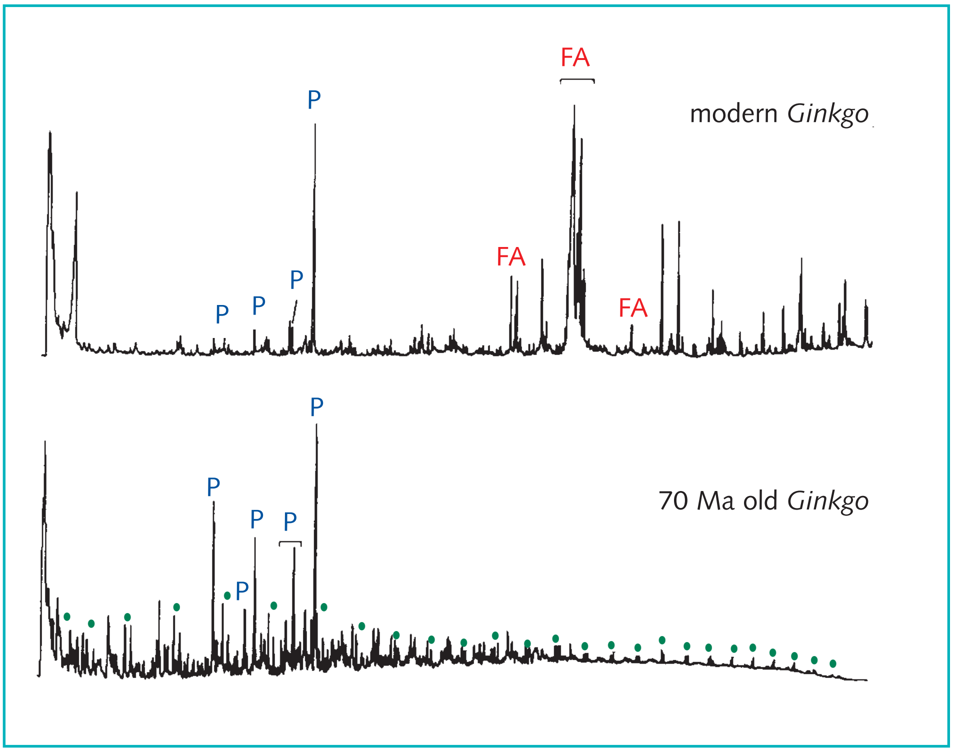


Left: Electron microscopy (EM) shows that fossil cuticles can look apparently unaltered, retaining characteristic morphology and ultrastructure. Modern and fossil cuticles are sheets, the scanning EMs on the right show the surface with vein (elongate) and intervein areas, whilst the transmission EMs on left show vertical sections with an outer amorphous and inner structured 'porous' layer.

Below: We also used Fourier transform infrared spectroscopy to see chemical bonds in intact material. Infra red spectra of cuticle fragments (obtained by Reg Wilson, IFR Norwich) show retention of major chemical bonds in fossils but clear changes. The chemical environment of the C=O bond has partly changed from an ester link to a terminal carboxylic acid group.



Below: We used flash pyrolysis which involves chemically fragmenting cuticles at very high temperatures (>600ºC). Volatile molecules are then identified by gas chromatography and mass spectrometry. This method is particularly appropriate for the study of large molecules in small samples. The pyrogram of the fossil shows retention of phenols (P) but reveals major changes. The cutin fatty acids (FA) are absent and there is now a series of straight chain aliphatic hydrocarbons ('oily' components, • in figure).



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