Ancient insects

Stone centipede

The tough external skeleton of insects, centipedes, shrimps and spiders is made largely of chitin, the second most abundant organic chemical on earth (after cellulose – the protective coat of plant cells). A remarkable one billion (1,000,000,000) tonnes of chitin are produced every year, mainly by tiny zooplankton floating in the oceans.

We wanted to find out what happens to all this chitin after the animals die. Does any of it survive into the fossil record?

When we left shrimps and crickets to decay in the laboratory for several weeks or even months, we found that chitin survives much longer than the other components of the cuticle (the animals' protective coat). Proteins in the cuticle decayed much faster.

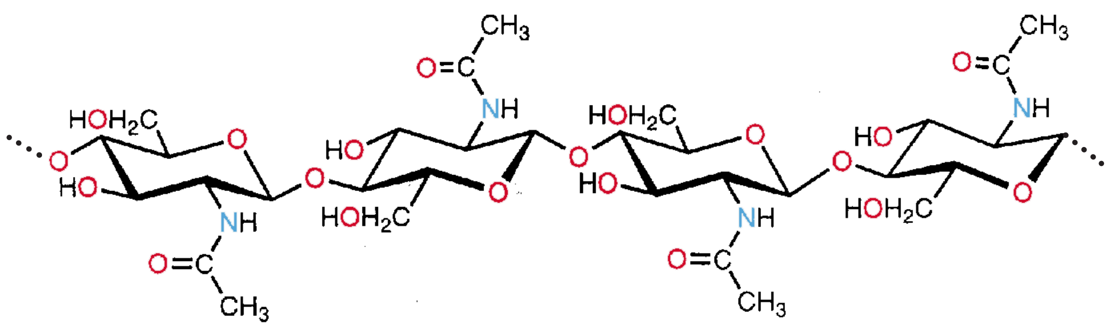
We discovered chitin in some fossils that were millions of years old. Our first evidence came from the cuticle of beetles preserved in the 20,000 year old tar pits at La Brea, California - and then from 25 million-year-old fossil insects entombed in an ancient lake bed at Enspel, Germany.

The cuticles of much older fossils (more than 500 million years) can still be picked off the surface of rocks and analysed, but they showed no trace of either chitin or protein. We can analyse the cuticle by vaporising it at very high temperatures (more than 600°C) and identifying individual components in the vapour. This method showed us that the cuticle is drastically altered over 500 million years, and now contains hydrocarbon-like material, similar to that in oil source rocks.

This is rather surprising: oil forms over millions of years from the decaying remains of plants, but up until now we did not think that much of it came from animals.

We still do not understand how the chemical components of cuticle could be transformed into macromolecular hydrocarbon-like matter. It is this chemical transformation that we are now trying to understand.

Chitin: The cuticles of invertebrates are built up of strings of this type of molecule: thousands of units are linked together like the four shown here.



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

Ancient insects: the science in detail

This project is investigating how the cuticles of invertebrate animals, particularly arthropods (such as insects, shrimps and spiders), are preserved in the fossil record.

We analysed three main types of sample:

1. living organisms and their decay products

2. Quaternary fossils (1.6-80 thousand years old) in well dated sequences (eg peat and lake sediments)

3. older fossils ranging from the Tertiary to the Palaeozoic era (3-450 million years old).

The primary target of our work has been chitin, the constituent of many invertebrate cuticles that is most resistant to bacterial degradation. We have also detected traces of the other major components of the cuticle, catechols and proteins, showing that all the main building blocks of arthropod cuticles can be detected easily by this method.

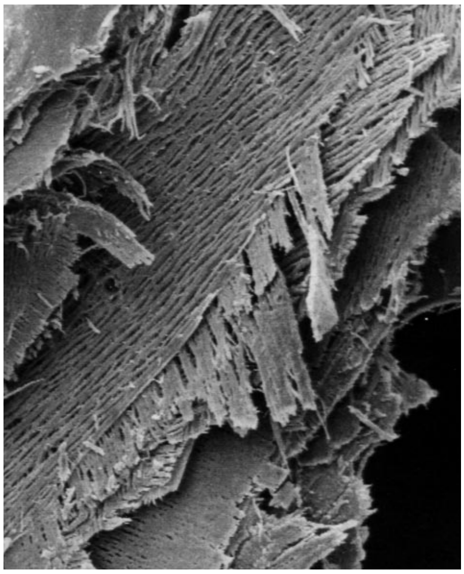
What happens to cuticles when they decay naturally over a period of weeks to years? We measured changes in the abundance of chitin and proteins in the cuticle of the mantis shrimp *Neogonodactylus*, as they decayed in laboratory experiments. We found that the chitin polymer is very resistant to decay, while the protein components of the cuticle break down rapidly. When we examined the shrimp's cuticle using a scanning electron microscope, we could see that, as the protein decays, the cuticle deteriorates from a solid sheet to a mesh of criss-crossing fibres of chitin.

In our search for the oldest surviving chitin, we analysed Pleistocene and Tertiary beetles. 20,000 year-old insects from the tar pits La Brea in California gave us the first evidence for the exceptional preservation of chitin in this unique environment. Although the protein in these samples was severely degraded, we were able to detect some intact amino acids (tyrosine, tryptophan and phenylalanine) which appear to be resistant to decay.

Fossil insects from the shales of an ancient lake bed in Enspel, Germany, contained chemically detectable remains of chitin, extending the record for preserved chitin to 25 million years. We could not find any chitin in the cuticles of older fossil arthropods from about 30 sites. These ancient cuticles seemed to have been chemically transformed into two distinct types of molecule: the first were highly aliphatic hydrocarbons, and the second contained aromatic molecules such as alkyl benzenes.

Future work

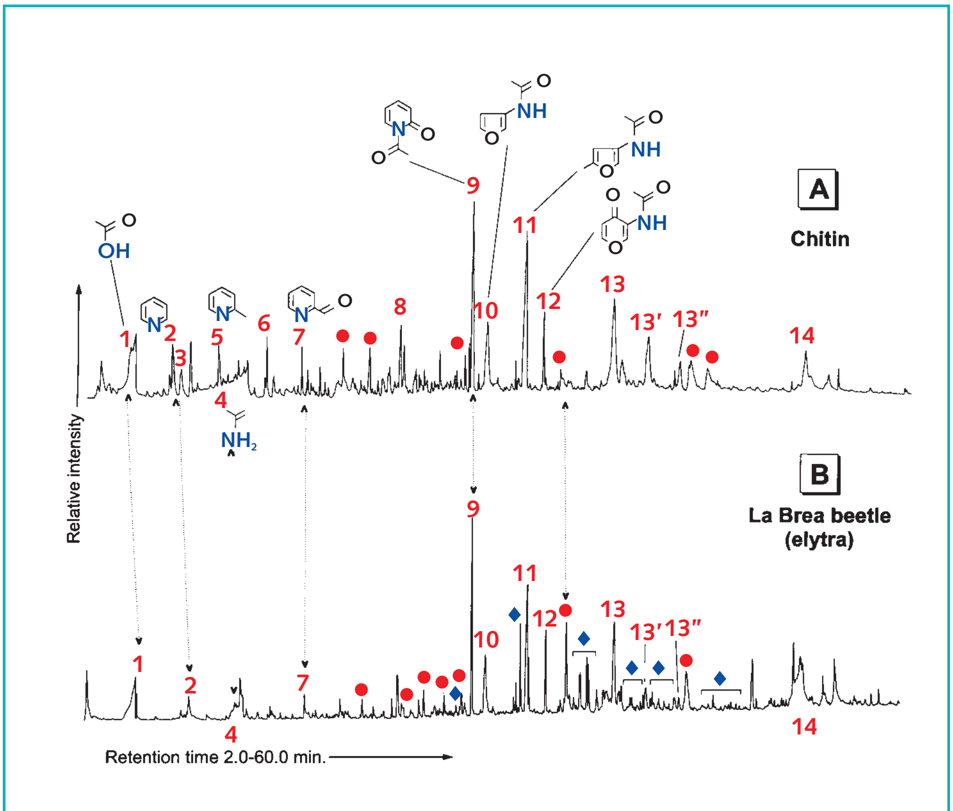
There is no obvious chemical process that would convert cuticle components into aliphatic and aromatic hydrocarbons. Our major goal now is to explain the origin of these molecules. We are collaborating with colleagues in Nancy, France, to solve this problem. Could it be that the amorphous organic matter abundant in some oil-prone sediments contains significant quantities of degraded debris from marine arthropods and other zooplankton? If this is so, some oils may be at least partly of animal origin!



Scanning electron photomicrograph of the cuticle of a beetle removed from the Pleistocene asphalt desposit at Rancho La Brea, California. The overlapping layers of chitin fibrils are obvious in this fossil specimen, where the protein matrix has largely decayed.

Methods

In order to identify the organic molecules present in fossils and decayed animals, we used a powerful analytical method called flash pyrolysis, which involves vapourising the material at very high temperatures (more than 600ºC). The vapourised molecules are then identified by gas chromatography and/or mass spectrometry. This method is particularly good at identifying large molecules (such as proteins and polysaccharides) in very small samples (around 100μg).



Pyrolysis (610° C/10 sec) gas chromatographic-mass spectrometric total ion traces for: A Purified chitin, and B A piece (0.1 mg) of wing case from a fossil beetle at La Brea. Numbers and ● indicate major pyrolysis products derived from chitin and amino acids. ◆ indicates products from the asphalt enclosing the fossil beetle.

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