

Ancient plant material provides direct evidence of former climates and environments. **Christopher Vane** describes how new techniques are helping us to understand the natural climate cycle.

Big molecules — clues to the past

Natural organic matter within alluvial sediments — such as leaves, wood, pollen and spores — can provide an understanding of past environmental conditions. Climatic changes, from intense cold to even warmer conditions than are experienced today, can be deduced in Quaternary sediments by recognising chemical ‘fossils’, changes in stable carbon isotope values, and the floral assemblages. By comparing these to modern-day equivalents we can infer the local palaeoenvironment and climate in which the plants grew. Multidisciplinary studies of alluvial organic matter using bulk and molecular chemistry and stable carbon isotopes have recently been gathering momentum at the BGS. These have included investigations of river alluvium in Swaledale and cores of Holocene age (covering the past 11 000 years) in estuarine sediments from the Humber and the Thames.

One new approach to reconstructing past environments is to examine the chemical structure of plant-derived organic matter. Land plants are composed of three main chemical structural components, cellulose, hemicellulose and lignin. Cellulose and hemicellulose are easily decayed in sediments by microbes because only a few simple enzymes are required to break the repeating sugar structures. In contrast the apparently random linkage pattern, large size and aromatic structure of lignin inhibits microbial attack and aids selective preservation in soils and sediments.

At the BGS, we use two methods to break up large biopolymers such as lignin into individual compounds small enough to be measured (that is, small enough to fit down a gas chromatograph), these are pyrolysis and chemolysis. In pyrolysis chemical bonds present in plant-derived organic matter are broken using thermal energy which turns the chemicals into gases, which can

be swept on to a gas chromatograph column in a stream of inert helium gas. Pyrolysis differs from burning because oxygen is excluded from the system. Chemolysis is more precise in that only lignin-derived compounds linked by ether bonds (carbon-oxygen-carbon) are produced. Consequently, we use both chemolysis and pyrolysis in a complementary manner. Gas chromatography separates out the many hundreds of different products. Imagine a huge pile of different sized balls being blown by a leaf blower down a corridor. The different balls interact not only with each other but also with the floor and walls causing them to move at different speeds thus they exit at different times. The mass spectrometer determines at what time the molecules exited and what they are composed of and, if suitable standards were added, how much there is of an individual component.

Three broad vegetation groups can be easily distinguished, based on the

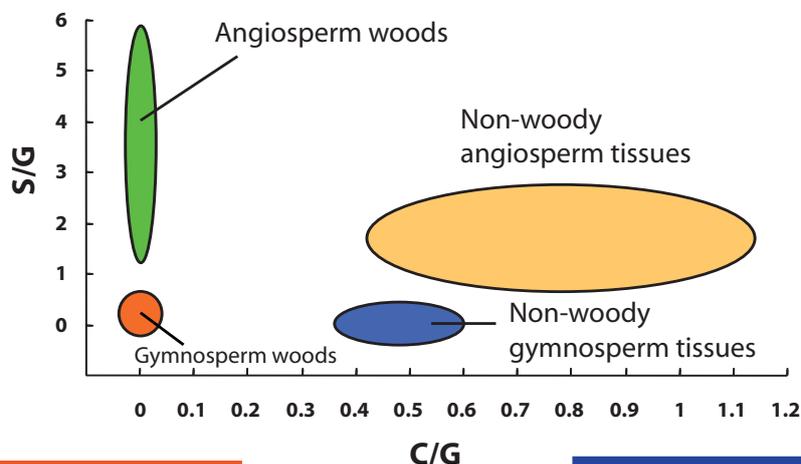
proportions of individual lignin compounds: gymnosperm woods such as spruce and pine, angiosperm such as oak and beech and monocotyledons such as grasses. Additional information from cinnamic acids which link lignin to hemicellulose in vascular plants can also be used in combination with the three lignin phenolic units to further characterise plant materials in sediments. In many cases, plants can be identified at the species level — vital information for reconstructing the palaeoenvironment and palaeoclimate. As well as providing a wealth of information on vegetation source, characterising organic matter at a



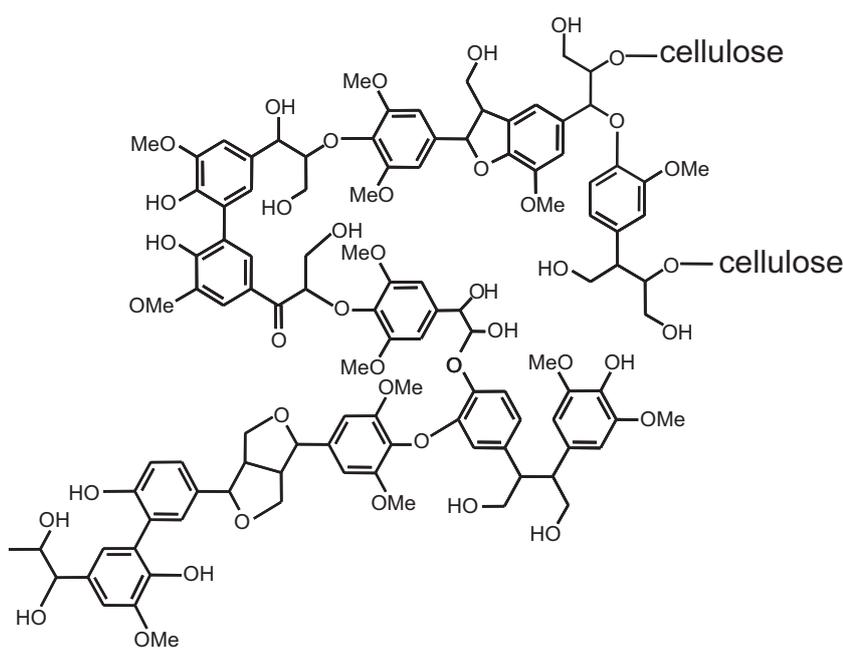
Sampling on the banks of the River Swale, Swaledale, Yorkshire, where deforestation is indicated by changes in bulk and molecular chemistry from alluvial sediments.

molecular level also provides information on the environment of deposition, for example vegetation buried in an aerobic environment has higher levels of phenolic compounds with carboxylic acid groups, compared with the same vegetation buried in an anaerobic environment.

The measurement of bulk chemical parameters such as elemental carbon to nitrogen ratios (C/N) and stable carbon isotopes ($\delta^{13}\text{C}$) is a cost-effective way of complementing the use of molecular environmental indicators such as lignin. For example, marine-derived organic matter can be distinguished from terrestrial (peat) using stable carbon isotopes. Scientists from the BGS and NERC Isotope Geosciences Laboratory are currently investigating the variations in molecular and stable isotope chemistry along a transect of a modern salt marsh at Welwick on the Humber Estuary. This work will help to verify reconstructions of past environments and sea-level changes in estuarine settings.



Woody and non-woody angiosperm and gymnosperm tissues are easily distinguished using the relative intensity ratio of lignin products separated and quantified using pyrolysis, gas chromatography/mass spectrometry (GC/MS), or chemolysis GC/MS. These methods require only 0.5 mg of organic matter allowing palaeoenvironmental reconstructions on tiny sediment samples.



Lignin, a super-sized biopolymer, which is the chemical scaffold of all land plants.

Future work will focus on four Thames cores collected from Swanscombe, Tilbury, Cliffe and Grain. Molecular data provided by chemolysis and pyrolysis, together with stable carbon isotopes, will be used to identify and classify vegetation type and depositional environments. This geochemical information will be coupled with palynology (the study of fossil spores) and radiocarbon dating of the fresh-water peats to provide a detailed picture of the changing climate and environment conditions of the Thames Estuary over the past 11 000 years.

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