An organic geochemical perspective on terrestrialization

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Abstract: The colonization of land required new strategies for safe gamete/diaspore dispersal, and to cope with desiccation, harmful radiation, fire and gravity. Accordingly, the morphology, behaviour and physiology of the organisms changed. Here, we explore to what extent physiological adaptations, reflected in the molecular content of the sediments, add to our understanding of the terrestrialization. Many compounds considered characteristic of land organisms do not provide valuable information from the fossil record since (1) they were not preserved; (2) they occur or correspond to substances that evolved prior to the terrestrialization (e.g. cutin vs. algaenan, cellulose); or (3) they have been changed diagenetically and/or catagenetically. The latter leads to geo(macro)molecules without a chemical fingerprint relating them to their original bio(macro)molecules despite, sometimes, excellent morphological preservation of the organic remains. Nevertheless, some molecular markers and their stable isotopes provide independent information on the terrestrialization process. The odd predominance of n-alkane surface waxes is a feature already apparent in early land plants and could, with caution, be used as such. Furthermore, fossil terpenoids and their derivatives are valuable for reconstructing the evolution of major plant groups. The radiation of the phenylpropanoid pathway with for example, sporopollenin and lignin seems to be closely related to the evolution of land plants.

As for other disciplines occupied with unravelling past life and environment, organic geochemistry relies heavily on the paradigm that the present provides a key to the past. For organic geochemistry, the biosynthetic pathways of living organisms provide such a key. The biosynthetic differences between organisms provide insight into the evolution of biosynthetic pathways and this can be applied to, and calibrated against, the fossil record. Evolution also implies adaptation and, by linking species ecology to their biochemistry, the adaptive value of the biosynthetic pathways and the biomolecules produced may be resolved.

This biosynthetic link to environment can also be applied to the past. For instance, the notion that oxygen is required in steroid and non-hopanoid triterpenoid synthesis implies that analysis of steroids in ancient sediments may help to unravel the early evolution of the atmosphere (Summons et al. 2006). Analogous to the oxygenation of the Earth’s atmosphere, terrestrialization also required major adaptations of the terrestrializing organisms to the living conditions on land. The conquest of land required the development or strengthening of supportive structures such as skeletons, stems and roots to withstand Earth’s gravity without the support of water and to resist wind. It also demanded water-saving strategies such as arthropod and plant cuticles, vertebrate skin and cork to survive low humidity environments and sometimes fire, as well as the development of water-conducting tissues in plants (roots, tracheids). Finally, the higher exposure to harmful radiation required sunscreens such as pigments, aromatic and other substances as UV filters. Whereas the endo- and exoskeletal adaptations are intrinsically based on the formation of large biopolymers, water saving and UV protection may be also realized by means of smaller molecules.

Our working hypothesis is that the major changes in biosynthetic pathways which accompanied the terrestrialization of organisms are reflected in the molecular composition of the organic matter present in Palaeozoic sedimentary rocks. For instance, a minor change in the biosynthesis of sporopollenin may have led to lignin. In return, we can expect the changes in composition of the organic matter (OM) in Palaeozoic rocks to help determine following evolutionary trends. The question being asked is to what extent is our working hypothesis valid and what does this provide us with to understand terrestrialization? We restrict ourselves to primary producers and arthropods since they have a rich fossil record, both organic geochemically and as micro- and macroscopic remains. We exclude other terrestrial (heterotrophic) life forms (worms, snails, vertebrates, etc.) since they do not usually leave a chemically characteristic signature in the sediments.
Organic matter analysis: lipids and macromolecules

From an analytical point of view, bio- and geomolecules can be subdivided into two types of organic substances. The first type consists of relatively small molecules which dissolve in common organic solvents and form the lipids. These lipids can be analysed relatively easily using for example, gas or liquid chromatography. Examples are archaeal membrane lipids, higher plant cuticular waxes, long-chain alkenones from Haptophyta and steroids such as dinosterol from dinoflagellates. Those lipids that have a relatively low biodegradability may fossilize as such and can be applied to reconstruct past environments and the (early) evolution of life (e.g. Brocks & Summons 2003).

Apart from this, lipids and lipid ratios can be used to reconstruct the environment such as for long chain alkenones (Marlowe 1984; Brassell et al. 1986; Prahl & Wakeham 1987; Conte et al. 2006) and of archaeal glycerol dibiphytanyl glycerol tetraether membrane lipids (De Rosa & Gambacorta 1988; Schouten et al. 2003; Kim et al. 2008). These biomolecules can also become diagenetically or thermally modified but, as long as the resulting products can be reliably related to their source organisms, they may still provide important clues on past life and environment. For example, triaromatic dinosteroids are derived from the thermal modification of the dinoflagellate steroid dinosterol. Their presence in Palaeozoic sediments has been used as an argument for a Palaeozoic rather than Mesozoic origin of the dinoflagellates (Moldowan & Talyzina 1998; Empt 2004).

The second type of molecules is of macromolecular nature and therefore insoluble in most solvents. In living organisms, the most abundant macromolecules are proteins and polysaccharides. The insoluble organic matter in the sediments, also termed ‘kerogen’, is poorly understood despite being by far the largest organic carbon pool on Earth (Berner 1989; Vandenbroucke & Largeau 2007) including all the particulate organic matter we see with the naked eye and through microscopes such as leaf and arthropod cuticles and palynomorphs.

This kind of material provides considerable analytical problems with respect to structural elucidation and quantification. Non-destructive methods provide important structural information on the atomic level such as nuclear magnetic resonance (NMR) (Deshmukh et al. 2005) and at the level of functional groups such as (micro) Fourier transform infra-red (FTIR) spectroscopy (Marshall et al. 2005; Versteegh et al. 2007). Destructive methods fragment the macromolecules and these fragments also provide vital information needed to reconstruct the original macromolecule. Of these, chemical degradation applies a series of chemical treatments whereby each successive treatment is able to break stronger chemical bonds than the previous treatment (Hunt et al. 1986; Gelin 1996; Blokker et al. 1998). Pyrolysis breaks down the molecule thermally in an inert atmosphere (Maters et al. 1977; Nip et al. 1987), however. For the characterization of fossil macromolecular organic matter and its preservation pathways, it is essential to combine several of these techniques. Despite these problems, studying this material is worthwhile (e.g. Briggs et al. 2000).

The biochemical signal from terrestrialization

Desiccation management – long-chain aliphatics

Simple lipids-waxes. Protection against a lack of water is of prime importance for land organisms. This can be achieved by resisting desiccation to keep a positive water balance, for example, by erecting an evaporative barrier at the organism surface and/or by developing desiccation tolerance. It seems reasonable to assume that adaptations to desiccation developed prior to the terrestrialization of plants and algae. It might be an important adaptation for freshwater species or species that live in smaller enclosed and coastal habitats to enable them to resist periods of dryness and allowing spreading from one watershed to another (e.g. by wind and animals).

The earliest photosynthetic organisms on land were probably cyanobacteria possibly colonizing land as early as 2.6 Ga ago (Watanabe et al. 2000). They may have been present as single cells or filaments and, with time, colonized a variety of environments such as tidal zones, soils and desert crusts. Although emerging much later, this also accounts for photosynthetic microalgae such as Chlorophyta, Streptophyta, Bacillariophyta (diatoms), Eustigmatophyta, and Dinoflagellata. Generally, these taxa survive dryness by tolerating dehydration as such, or by producing resting cysts (e.g. Zygnemataceae). Mostly they use sugars, lipids or proteins to stabilize the cell contents upon desiccation (Cardon et al. 2008). To our knowledge, there is no chemical fingerprint known of upon which this strategy may be reconstructed from the fossil record. Stable carbon and hydrogen isotopes of lipids can perhaps help here.

The sister group of the Chlorophyta, the Streptophyta, gave rise to the Embryophytes (land plants), the only group which developed into macroscopic organisms with strategies to cope with the uneven and erratic water supply on land. The very first
evidence of land plants is indirectly documented by cryptospores (Strother 2000). Taylor & Strother (2008) describe Middle Cambrian palynomorphs which morphologically and ultrastructurally resemble cryptospores in many ways. However, their affinity with terrestrial or algal organisms is still under discussion; the earliest accepted occurrence of cryptospores is of Llanvirn age (middle Ordovician) (Strother et al. 1996).

The earliest ‘megafossils’ are documented in the late Llandovery (Lower Silurian) (Wellman & Gray 2000; Edwards 2001) (Fig. 1). These plants were probably small (Wellman et al. 2003) and had no water conducting organs such as trachea or roots. In this respect, they were like the modern Bryophyta which are the most primitive land plants living today. According to Proctor (2000), many of the Bryophyta have three water components: symplast water (in the cells), apoplasm water (in the ‘free space’ of the cell walls) and external capillary water which, for much of the time, exceeds the symplast water by a large but variable quantity. For these species, water and nutrient transport is therefore largely via the outside of the plant. This implies that for these very primitive plants, resistance to desiccation is mostly achieved by drought tolerance (although this seems not to be the case for their spores).

However, not all bryophytes rely on external capillary water. Most thallloid liverworts and some erect growing mosses with waxy water repellent surfaces (e.g. many Polytrichaceae and Mnaceae) rely predominantly on internal water conduction (Proctor 2000), so that these organisms develop external coverings which function as water barriers. With few exceptions, lipids associated with external coverings are the principal water barrier component of land plants and animals (Hadley 1989). For plants, these lipids consist primarily of unbranched fully saturated linear hydrocarbon backbones with chain lengths of 20–40 carbon atoms. Typically these lipids are n-alkanes, n-kenetones and secondary alcohols with a predominance of odd-numbered chain lengths and primary n-alkdehydes, n-alcohols and n-fatty acids with a predominance of even-numbered chain lengths. Furthermore, a wide variety of C_{36}–C_{60} wax-esters has been detected. These aliphatic coatings are responsible for >99% of the water barrier efficiency in plants (Schönherr 1976; Mérida et al. 1981; Jetter et al. 2006). It is therefore no surprise that pollen are also covered with surface waxes (Piffanelli et al. 1998; Schulz et al. 2000).

For arthropods (earliest evidence: late Cambrian; McNaughton et al. 2002) the strategy towards desiccation is similar to that of plants. Cuticular lipids are to a large extent identical but mono- and di-methyl alkanes also occur and may even dominate; for these organisms, they are also the primary passive barrier to evaporative water loss (e.g. Ramsay 1935; Hadley 1989; Gibbs 1998, 2002). Long-chain lipids are also synthesized by various algal such as long-chain mid-chain diols by Eustigmatophyta and diatoms (de Leeuw et al. 1981; Versteegh et al. 2000; Sinninghe Damsté et al. 2003) long chain alkenones and alkanoates by Haptophyta (de Leeuw et al. 1980; Volkman et al. 1980; Rontani et al. 2007) or long-chain polyunsaturated alkenes by dinoflagellates (Mansour et al. 1999). However, the odd predominance of n-alkanes is a typical feature of land plants, though some microalgae such as Tetrahedron (Chlorophyta) or Nannochloropsis (Eustigmatophyta) also produce long-chain n-alkanes with a strong odd predominance (Gelpi et al. 1970; Gelin et al. 1997). Other algae also produce long-chain n-alkanes with odd predominance (Gelpi et al. 1970; see also Volkman et al. 1998) and it has been suggested that such alkadienes from the green alga Botryococcus braunii have given rise to an n-alkane odd-predominance in sediments (Lichtfouse et al. 1994; Riboulleau et al. 2007).

Since the odd predominance of long chain n-alkanes already occurs in the cuticular waxes of primitive plants such as liverworts (Matsuo et al. 1974) and mosses (Nissinen & Sewon 1994), it is interesting to investigate how this feature developed through the Palaeozoic. A marked odd predominance of n-alkanes with a maximum in C_{23} or C_{25} is observed in the extracts of early mature to mature coals of Permian age from Brazil and Australia (Casareo et al. 1996; Silva & Kalkreuth 2005). Contrarily, the n-alkane distribution in the extracts of many coals of Carboniferous age is not characterized by a strong predominance of odd-numbered compounds; this feature can be ascribed to the maturity of the studied coal samples. However, even early mature coal samples only show a moderate odd predominance in the C_{25}–C_{31} range (e.g. Powell et al. 1976; Christiansen et al. 1989; Dzou et al. 1995; Fleck et al. 2001; Armstroff 2004).

An exception is the marked predominance in the C_{25}–C_{31} range observed in the extracts of very immature early Carboniferous coals from the Moscow Basin (Armstroff 2004). The long-chain predominance is also visible in some Devonian samples, in particular when (mio)spores are present in significant amounts: C_{25}–C_{31} (max C_{35}) in the immature Fammenian marls from Poland (Marynowski & Filipiak 2007); C_{23}–C_{31} (max C_{27}) in the middle-late Frasnian early mature cannel coals from Melville Island, Arctic Canada (Fowler et al. 1991); C_{23}–C_{29} (max C_{25}) in early mature Middle Devonian cutinite-rich humic coals from China containing Zosterophyllum remains (Sheng et al. 1992). These observations indicate that the characteristic signature of epicuticular
Fig. 1. Currently documented earliest occurrences of fossil plant remains (in italics) and of characteristic terrestrial biomarkers (roman). Earliest occurrences of cryptospores and trilete spores indicated in grey from Strother (2000) and in black from Strother et al. (1996) and Steemans et al. (1996). Occurrence of plant megafossils from Wellman & Gray (2000) and Edwards (2001). See text for further references and explanations. Figure created with TS Creator (www.stratigraphy.org).
waxes was already acquired in the Middle Devonian. However, if we do not consider maturity problems, there seems to be a temporal evolution in the maximum of the n-alkane distribution which could be related to plant evolution: around C\textsubscript{25} in the Devonian to C\textsubscript{29} in the Carboniferous and C\textsubscript{32} during the Permian. Present-day higher plants are characterized by a maximum in C\textsubscript{29}–C\textsubscript{31}.

Most coals older than the Devonian are liptinite-rich coals, which may derive from spores or from algae. Their n-alkane signature may therefore be not terrestrial derived. Due to the occurrence of odd-numbered n-alkanes in some algae, the n-alkane distributions must be interpreted with care. This is particularly true for samples older than Devonian where terrestrial debris is scarce. An odd-number n-alkane predominance has been previously observed in several Botryococcus rich-torbanite of Permian age and was mainly attributed to a higher plant contribution (Araujo et al. 2003; Dawson 2006). These odd-numbered n-alkanes could also derive from the saturation of Botryococcus lipids, however (for an overview on Botryococcus lipids see Metzger et al. 2007).

Slight odd predominances in the range C\textsubscript{25}–C\textsubscript{31} were also observed in the extracts of a Cambrian sediment from Tarim Basin (China) (Zhang et al. 2000) as well as in the extracts of several Proterozoic, Cambrian and Ordovician sediments from different basins in East China (Li et al. 2002). In the case of East China, this distribution was assigned to a contribution from cyanobacteria of the Spirula type (Li et al. 2002). Considering the stratigraphic distribution of microscopic higher plant remains (Fig. 1), a contribution from higher plant lipids is somehow questionable in the Cambrian and Ordovician samples. Since land-plant derived n-alkanes are (as far as C\textsubscript{3} plants are considered) usually more enriched in \textsuperscript{12}C relative to \textsuperscript{13}C than their algal counterparts, comparison of the stable carbon isotopic composition of these alkanes with the isotopic composition of typical marine/aquatic biomarkers may aid in the identification of a land-plant signal.

**Macromolecules.** In addition to simple lipids, protection against desiccation could also be offered by resistant biomacromolecules made of long-chain lipids (see also reviews by van Bergen et al. 2004; de Leeuw et al. 2006), although the exact role of these macromolecules is not entirely clear. Mono to tetra-functionalized long-chain alcohols and acids form the building blocks of cutin, a biopolymer present in the cuticles of most land plants (Kolattukudy 1981; Deshmukh et al. 2003). Pyrolysis shows that aliphatic lipids are also major building blocks of cutan (Tegelaar et al. 1989a; Boom et al. 2005) a macromolecule which occurs in the cuticles of plants with grassulacean acid metabolism (CAM), where it may be an evolutionary solution to severe drought stress (Boom et al. 2005). Nuclear magnetic resonance (NMR) analysis suggests that this aliphatic biopolymer also contains aromatic units (Deshmukh et al. 2005). Cutin and cutan should therefore be considered ‘terrestrial markers’ of higher plants. The preservation potential of cutin is, however, very low; the building blocks are cross-linked with relatively weak esters while stronger ether-bridges connect the cutan building blocks, which is more resistant.

The production of aliphatic biopolymers was not invented by land plants but evolved much earlier. The analysis of the cell walls of a wide range of algae shows that some algae produce a resistant aliphatic biopolymer made of cross-linked long-carbon chains called algaenan (see review by Versteegh & Blokker 2004; Metzger et al. 2007). Algaenans resist harsh chemical treatment and they have a relatively high preservation potential which may account for the long fossil record of the Chlorophyta (Batten 1996; Batten & Grenfell 1996; Colbath 1996; Guy-Ohlsen 1996; van Geel & Grenfell 1996; Wicander et al. 1996). Even although the exact biological role of algaenan is not known, it has been suggested that the highly aliphatic (plastic-like) algaenan may function as a relatively waterproof layer; it is interesting to note that apart from the marine eustigmatophyte *Nannochloropsis*, the development of algaenan mostly occurs in freshwater algae, notably Chlorophyta (e.g. *Tetraedron, Scenedesmus, Pediasstrum*) which probably have the largest risk of desiccation.

The similarities in structure and function between algaenan and cutin and cutan of land plants (all aliphatic biopolymers, which are both based on ether- or ester-linked long-chain fatty acids; van Bergen et al. 2004) may imply that they represent subsequent stages in the evolution of the same biosynthetic pathway. This could constitute an argument in favour of the freshwater algal origin of terrestrial plants. In sediments, cutan is difficult to discriminate from algaenan or from a highly aliphatic cutan-like geopolymer. The latter can be formed from common lipids by oxidative polymerization during early diagenesis discussed below (Boom et al. 2005; Gupta et al. 2006a, 2007a; de Leeuw 2007). This implies that fossil aliphatic biopolymers do not provide evidence for a land-plant (cuticular) origin of the organic matter perse. In this case, stable carbon isotopic analysis of the aliphatic constituents may also be needed to obtain a conclusive answer.

**UV protection, radiation damage**

Terrestrialization also involved an increased exposure to harmful radiation. Ultraviolet-B
(UVB) rapidly attenuates in water (penetration depth is of the order of millimetres) so protection to UVB had to increase considerably. The optical properties of plants (especially the effects of UV radiation on plants) have been intensively studied, partly in reaction to the recognition of the polar ozone holes in the atmosphere (Rozema et al. 2002a; de Bakker et al. 2005; Pfundel et al. 2006). In land plants, UV absorption is achieved by aromatic compounds such as the flavonoids and their derivatives (I–V) and other compounds produced via the phenylpropanoid pathway such as hydroxycinnamic acid (VI) and lignin. A wide diversity of flavonoids are already present in the Bryophyta. Flavonoids are absent in Hornworts (Stafford 1991; Rausher 2006) and have been found in one alga, the Charophyte Nitella (Markham & Porter 1969; Iwashina 2009). Flavonoids, or their derivatives in sediments, are of potential interest to elucidate the early terrestrialization of the embryophytes.

Flavonoids were widely used during the 1970s for plant systematic as well as evolutionary studies, in particular for angiosperms, based on the distinction of ‘advanced’ v. ‘primitive’ characters (Crawford 1978; Giannasi 1978; Stuessy & Crawford 1983) (Fig. 2). However, it appeared that the advanced v. primitive distinction in flavonoids composition was not straightforward, and that one given compound could be synthesized via different pathways. Flavonoids may therefore not be fully reliable indicators for phylogenetic studies at higher taxonomic levels (Crawford 1978; Giannasi 1978). Flavonoids are known from Tertiary sediments such as Kaempferol (III) (Niklas & Giannasi 1977a, b) and their earliest record is of the biflavonoid 5-O-Methylginkgetin (II) from Cretaceous Ginkgo fossils (Zhau et al. 2006). Accordingly, despite their potential interest for the terrestrialization process, it seems that they are not preserved long enough in sediments to provide further insight into the early embryophyte evolution.

Suberin

Suberin (Tegelaar et al. 1995) is another ether-based macromolecule produced by plants. It seems to be primarily used to form barriers between compartments or with the exterior. Depending on the place of deposition in the plant it protects against fire, desiccation and pathogens and limits ion transport and gas diffusion. It occurs in roots and tubers, bundle sheet cells of C4 plants and as cork in woody species that have secondary thickening (Enstone et al. 2002; Franke & Schreiber 2007).

The biopolymer suberin consists of an aromatic domain. Aromatic building blocks are generated via the phenylpropanoid pathway such as p-coumaric, ferulic and sinapic acids (VII–IX) also found in sporopollenin and as alcohols in lignin (see below), as well as an aliphatic domain with aliphatic building blocks similar to those of the plant cuticle (discussed above). The aliphatic component is considered to reduce transport whereas the aromatic part has been suggested to inhibit pathogen invasion (Kolattukudy 2001; Bernards 2002; Franke & Schreiber 2007). Like lignin, suberin is not known from the most primitive embryophytes. Being ester cross-linked, suberin

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Fig. 2. Evolutionary scheme of the biosynthesis of the major subgroups of flavonoids with a 5,7-dihydroxy A-ring. Four levels, A, B, C, and D are shown. Levels A, B are found in bryophytes, C in ferns and fern allies and D in gymnosperms and angiosperms. PA: proanthocyanidin (modified after Stafford 1991). See supplementary information for molecular structures (structures I–V).
probably has a low preservation potential. Due to its mixture of aliphatic and aromatic monomers it may be difficult, if not even impossible, to deduce a specific suberin fingerprint from the fossil record.

Suberan is a rather enigmatic highly aliphatic non-hydrolysable biopolymer. It has been described from bark (Tegelaar et al. 1995). Possibly, this polymer originates from oxidative polymerization of unsaturated lipids.

Signalling and warfare

Living on land also required a new way of transmitting signals between organisms. Previously, signalling was restricted to water soluble compounds; on land, volatile compounds had to be developed. Here, nature has expanded in a myriad of molecules such as repellents, odours and pheromones. To be effective, these molecules need to provoke a reaction by the receiver, implying that the compounds must be biologically active. Often such compounds are already active at low concentrations. For warfare this is different; the toxins may remain on the organism outside or in the cells and tend to be lipid or water soluble. They need not be transportable by air. In this case, however, the compounds are also constructed to be biologically active and interfere with the physiology of the attacking organism.

Many of these compounds are produced via the phenylpropanoid pathway which experienced a huge radiation with the adaptation of plants to land (Cooper-Driver & Bhattacharya 1998; Lewis & Davin 1999). Compounds produced via this pathway function for example, as antioxidants, have antifungal or antimicrobial properties or are insecticides, nematocides, antifeedants and poisons. These include the flavonoids mentioned above (I, III, IV) and their dimer (II) to polymers [the proanthocyanidins or condensed tannins (V) (He et al. 2008). In addition, these all have a strong influence on soil structure and composition by retarding organic matter breakdown and capturing nutrients and, through this, substantially modifying the global carbon cycle (Kraus et al. 2009).

Condensed tannins appear much later in evolution than the flavonoids (Fig. 2). They occur only in leptosporangiate ferns, gymnosperms and angiosperms (Popper & Fry 2004; Popper 2008), leaving a much smaller impact on the carbon budget for the early evolution of land plants. Such fossil tannins are only unequivocally known from brown coal (Wilson & Hatcher 1988).

Two other groups of tannins exist; neither are derived from flavonoids (de Leeuw & Largeau 1993). These are the hydrolysable tannins typical for angiosperms (Okuda et al. 2000) but which also occur in the filamentous green algae Spirogyra (Nishizawa et al. 1985) and the phlorotannins occurring in brown algae. Since neither group has direct relevance for the terrestrialization they will not be considered further.

Another common and diverse group of products produced via the phenylpropanoid pathway are lignans (phenylpropanoid dimers), nor-lignans (with diphenylpentane carbon skeletons) and lignan oligomers which, in contrast to lignin (a polymer of monolignols), are non-structural components (Lewis & Davin 1999; Suzuki & Umezawa 2007). Lignans are known from bryophytes such as liverworts and hornworts (Lewis & Davin 1999) and are not known from algae (see also the lignin section below). Lignan remains may therefore have been preserved in the earliest land plants and could be used as tracers.

Another protective strategy is the production of resins. Plant resins are used typically for protection (Langenheim 1995). Resin can be exuded passively (when a plant is wounded) or actively. Often resin emerges from canals or resin cells. Resin provides a mechanical and chemical protection against pathogens. When present on leaves, resin also acts as a barrier against desiccation and UV damage.

Resins contain a complex mixture of non-volatile compounds mainly consisting of di- or tri-terpenoids. In addition, resins contain volatile compounds, including mono- and sesqui-terpenoids, which can be dominant in fresh resins. These volatile compounds tend to disappear with time but a fraction can remain entrapped when the matrix polymerizes and becomes hard (Anderson & Cregling 1995). Resin- (and amber-) producing trees are present both among gymnosperms (e.g. conifers, cycads) and angiosperms. The most prolific genera all live in the tropical to subtropical region (Langenheim 1995).

Plant resins have a rich fossil record in the form of amber or resinite. Amber and resinite are more or less synonymous terms describing geological material evolved from plant resin. The main difference lies in the fact that amber generally describes macroscopic remains, while resinite describes microscopic remains observed petrographically (Anderson & Cregling 1995). This may explain why ‘true’ amber is rarely described before the Cretaceous while resinite has been described in coal samples as old as Carboniferous (and maybe older). Among the oldest recognized ambers are Late Triassic ambers from Italy (Roghi et al. 2006), although some reports of Carboniferous amber exist (Smith 1896). This observation fits well with anatomical evidence that the earliest plants showing resin channels or resin-filled cells in their anatomy are members of the earliest but now extinct gymnosperm group, the Pteridospermopsida (Rothwell & Taylor
et al. 1994), eudesmane was also observed in Palaeozoic coals from Spain. These are the earliest reports of eudesmane in geological samples to our knowledge (Fig. 1), although we might expect an earlier appearance since this compound is present in some liverworts (Toyota & Asakawa 1990). The abundance of eudesmane in coal extracts decreases as maturity increases (Dzou et al. 1995), which might explain the rarity of reports of this compound in Palaeozoic sediments so far.
Cadinane (XVII) is thought to derive from cadinanes and cadinols which are ubiquitous in plants, bryophytes and fungi (Bordoloi et al. 1989) and from fragmentation of polycadinene resins (class II) produced by angiosperms (van Aarssen et al. 1990). Cadinane is particularly present in gymnosperm (class I) resins (Simonet 1986; Grimalt et al. 1988). The dimers of cadinane, bicadinanes, are often observed in oils. They are generated by maturation of angiosperm (class II) resins (van Aarssen et al. 1990; Stout 1995). Cadinanes are therefore well-characterized higher plant biomarkers which are often observed in Cretaceous or younger sediments (van Aarssen et al. 1990). So far, fully saturated cadinanes have not been observed in Palaeozoic sediments.

However, their aromatic counterparts –Cadalenes (XVII) – have been found in the extracts of different coalis of Carboniferous age (del Río et al. 1994; Stefanova et al. 1995; Armstroff et al. 2006). Its earliest occurrence reported so far is Visean (Armstroff et al. 2006) (Fig. 1).

Diterpenoids. Particularly abundant among conifers and their ambers are diterpenoids with abietane, pimarane, kaurane and podocarpane (XVIII–XX) skeletons. They are mostly produced by higher plants, though some marine algae also synthesize these compounds in a much functionalized form (Simonet 1986). According to the review of Alexander (1987a), the different land plants can be recognized from their specific diterpenoids contribution. Bryophytes and pteridophytes differ from gymnosperms by their absence of abietane, beyerane and phyllocladane (XVIII, XXII, XXIII) skeletons. The appearance of these latter compounds in the sedimentary record could therefore document the transition from ‘horizontal’ to ‘vertical’ land plants. Phyllocladane, in particular, would be a specific biomarker for conifers.

The occurrence of the fully saturated diterpenoids in Permian and Carboniferous coals is relatively frequent (e.g. Noble et al. 1985; Schulze & Michaelis 1990; Fleck et al. 2001; Fabianska et al. 2003; Piedad-Sánchez et al. 2004; Izart et al. 2006); phyllocladane, ent-beyerane and ent-kaurane (XX–XXV) are often reported in particular. The presence of phyllocladane and ent-beyerane in these samples is consistent with the evolved flora which existed in the Late Carboniferous.

The study of Schulze & Michaelis (1990) on Carboniferous coals from Germany showed that ent-kaurane is more abundant in the Westphalian samples from the Ruhr, while ent-beyerane and phyllocladane are more abundant in the Westphalian and Stephanian coals from the Saar. The authors proposed that this change might be due to different inputs of higher plants, possibly related to the different sedimentary settings (limnic in the Ruhr v. paralic in the Saar). Changes in the pentacyclic terpenoids were also documented in these coals (Vliex et al. 1994; Auras et al. 2006) (see below). The presence of ent-beyerane, ent-kaurane and phyllocladane in Lower Carboniferous sediments has led to the suggestion that a precursor of the conifers already produced these compounds at that time (Disnar & Harouna 1994). Since these compounds do not occur in the Pinaceae, it has been suggested that the Pinaceae separated early from the other conifers (Armstroff et al. 2006), implying that conifers had already evolved in the Early Carboniferous.

Sheng et al. (1992) described an abundance of tetracyclic diterpanes in Middle Devonian humic coals from China. Among the identified compounds are 17-norphylocladanes, ent-beyerane and ent-kaurane. This corresponds to the earliest reported occurrence of ent-kaurane and ent-beyerane (Fig. 1). Palaeobotanical data indicate that these Middle Devonian coals mainly derive from pteridophytes (Sheng et al. 1992). These are plants which, according to the review of Alexander et al. (1987a), should neither contain phyllocladane nor beyerane. The absence of phyllocladane from the Middle Devonian coals therefore appears consistent with the absence of conifers during this period, while the presence of ent-beyerane questions either the origin of this compound in the Devonian coals or its absence from pteridophytes (Sheng et al. 1992). As far as we know, the oldest reported occurrence of phyllocladane is Serpukhovian that is, late Early Carboniferous (Fabianska et al. 2003; Izart et al. 2006) (Fig. 1).

Totally or partially aromatized compounds deriving from the tricyclic terpenoids are also frequently reported in sediments. The most common compounds are retene and simonellite (XXVI–XXVII) which are thought to derive from the aromatization of abietane. However, Alexander et al. (1987b) demonstrated in Miocene coals that retene and simonellite are more likely derived from phyllocladane and kaurane. Retene has been described in the extracts of numerous Carboniferous coals (del Río et al. 1994; Stefanova et al. 1995; Fabianska et al. 2003; Armstroff et al. 2006; Izart et al. 2006). Armstroff (2004) also describes the presence of retene in Frasnian cannel coals from Russia. To our knowledge, this is the earliest reported occurrence of retene which can be confidently associated with a terrestrial origin (Fig. 1). If, as proposed by Alexander et al. (1987b), retene from land plants derives from aromatization of kaurane, its presence in Devonian coals has no strong significance as kaurane is mostly associated with Bryophyta and Pteridophyta. Conversely, if it is demonstrated that retene only derives from abietane or from
phyllocladane, its presence in Devonian sediments would document that at least the biosynthesis of abietic acid (if not conifers) already existed in the Fammenian.

Retene, however, has also been observed in the extracts of several Lower Palaeozoic to Precambrian carbonates, where inputs from terrestrial plants are not likely (Jiang et al. 1995; Zhang et al. 1999). An algal and/or bacterial source was proposed by these authors. Consistent with this conclusion, retene was also observed (although in low amounts) in the pyrolsates of a green alga and cyanobacterium cultures (Wen et al. 2000). Care is therefore recommended in the interpretation of the presence of retene in sediments where inputs from higher plants are low and, most particularly, in Ordovician–Silurian sediments.

**Triterpenoids.** The triterpenoids are a very large family which comprises the well-known group of bacterial biomarkers, the hopanoids, as well as the hypersalinity biomarker gammacerane (XXVIII) (Simoneit 1986). Several higher plant biomarkers also belong to this family, the most famous compound being oleanane (XXIX) (Simoneit 1986).

According to a recent review of the distribution of pentacyclic triterpenes by Jacob (2003), some skeletons are particularly widespread among angiosperms such as oleanane, lupane, friedelane and ursane (XXIX–XXXII). At least one skeleton, the serratane (XXXIII), would be characteristic of gymnosperms, mosses, ferns, lycopodiophytes and bryophytes. Although it has been observed in several angiosperms (and in particular Poaceae), fernane (XXXIV) is in particular present among ferns (Jacob 2003). In relation to their abundance in angiosperms, the occurrence of oleane, lupane, ursane and their derived compounds is mostly restricted to Cretaceous or younger oils and sediments (Peters et al. 2005). The presence of oleane in Carboniferous sediments has however been described by Moldovan et al. (1994). This was followed by a long investigation in order to identify the source of this compound in Palaeozoic sediments. Recent studies identified Gigantopterids as the source of oleane in Palaeozoic sediments which, added to morphological arguments, would place the appearance of the angiosperm lineage before the Permian (Taylor et al. 2006).

Apart from the rare reports of oleane, the terrestrial triterpenoids more often described in Palaeozoic sediments are aromatic compounds belonging to the arborane/fernane family which have been recently named MATH (5-methyl-10(4-methylpentyl)des-A-25-norarbora(ferna)-5,7,9-triene), MAPH (25-norarbora(ferna)-5,7,9-triene), DAPH1 (24,25-dinorarbora(ferna)-1,3,5,7,9-pentaene) and DAPH2 (iso-25-norarbora(ferna)-1,3,5,7,9-pentaene) (Vliex et al. 1994; Borrego et al. 1997; Izart et al. 2006) (XXXV–XXXVII; Fig. 1). The fact that only aromatic compounds are reported may be due to maturity as Paull et al. (1998) observed fernenes in very immature sediments of Triassic age. The aromatic arborane/fernane derivatives were observed to be present in Stephanian coals from Germany, but almost absent from the underlying Westphalian coals (Vliex et al. 1994; Auras et al. 2006). Vliex (1994) related this feature to the increase of Gymnospermopsida (Coniferales) in the vegetation, linked to a transition to a drier climate. Due to the imprecision on the exact structure of the molecules, arborane or fernane derivatives could either originate from higher plant fernenes or from isoorborinol (XXXIX). The latter is a compound present in a few angiosperms but which has been assigned a mostly bacterial origin (Hauke et al. 1992, 1995; Jaffé & Hausmann 1995).

As a matter of fact, aromatic arborane/fernane derivatives have also been observed in several sediments where terrestrial inputs are seemingly inexistent (Hauke et al. 1992). According to Hauke et al. (1995), however, the compounds identified by Vliex et al. (1994) are true fernane derivatives. Recently, a detailed geochemical and botanical study of these Stephanian coals allowed Cordaites to be identified as the source of these fernane derivatives (Auras et al. 2006).

**Skeletal materials**

Organisms living on land lack the support of water to overcome gravity and therefore have to strengthen or develop supportive tissues. If we consider the present-day skeletal biopolymers, which are potentially stable enough to survive in the fossil record on a regular basis and thus potentially leave a fingerprint of the terrestrialization process, we often observe these at the boundary between the cell/organism inside and its outside and combine their structural function with protection, for example, cuticles. They consist of only four basic building blocks produced by ancient biosynthetic pathways common to Archaea, Bacteria and Eukarya (Kandler & König 1998). These building blocks are sugars, amino acids, long-chain lipids and aromatics.

**Sugars, amino acids and their polymers – chitin.** Among the earliest such structures are probably the peptidoglycans (amino acid–sugar polymers) found in the cell walls of Bacteria and Archaea. Peptidoglycans are known to be resistant to degradation compared to proteins and are observed in recent sedimentary organic matter (Grutters et al. 2002; Nagata et al. 2003). However, they do not account for an important part of the organic matter
(Veuger et al. 2006). Although sugars and amino acids may severely crosslink and form degradation-resistant polymers (Maillard 1912), they have not been used for evolutionary or environmental reconstruction. Probably, they are too omnipresent and taxon-unspecific for these purposes.

Polysaccharide synthesis is also ancient. Cellulose is produced by cyanobacteria and proteobacteria. It has been suggested that the ability of vastly unrelated eukaryotic species to produce cellulose has been acquired via endosymbiosis with these bacteria and lateral gene transfer (Niklas 2004). Despite a large chemical diversity in peptidoglycans and polysaccharides among organisms, most are degraded. This explains why there is so little evidence of fossil bacterial polymeric products, despite the bacterial omnipresence. Only cellulose and chitin appear to be relatively resistant to biodegradation and form a considerable fossil record. The refractory character of these macromolecules is clearly related to the exact composition of the monomers and their stereoconfiguration in the polymer. This is demonstrated by comparing the extremely low fossilization potential of starch (poly 1 → 4 α-D-Glucose) with that of cellulose (poly 1 → 4 β-D-Glucose) (Fig. 3).

The polysaccharide chitin (N-acetyl-D-glucosamine; Fig. 4) which is so abundant in arthropods and oomycetes today is not known from prokaryotes (Niklas 2004). The capability to synthesize chitin is therefore considered to have arisen much later in evolution compared to cellulose synthesis. Its presence in many marine organisms such as arthropods, molluscs and annelids places its evolution well before the evolution of land-adapted organisms, however.

Studies on chitin preservation provide another argument as to why this substance is not suitable for unravelling the terrestrialization process. Laboratory experiments show that chitin belongs to the most degradation-resistant parts of arthropods (Baas et al. 1995; Briggs et al. 1995). At first sight, this is not surprising since arthropod cuticles are also abundant in the fossil record. But are these cuticles still made of chitin?

The oldest known traces of the chitin marker D-glucosamine (XXXX) occur in extremely well-preserved weevil cuticles (up to 0.6% of the organic matter) present in the 25 Ma lacustrine sediments from Enspel (Stankiewicz et al. 1997; Flannery et al. 2001). Less well-preserved or older arthropod cuticles show no such traces of chitin (Stankiewicz et al. 1998; Gupta et al. 2007). This alone probably explains why chitin could not be detected in chitinozoans (Voss-Foucart & Jeuniaux 1972; Jacob et al. 2007); the biological affinity of the chitinozoa therefore remains unresolved. This also implies that a reassessment of the presence of chitin in Palaeocene dinoflagellate cysts (Belayouni & Trichet 1980) is called for. Mostly, chitin-barren
fossil cuticles release series of alkanes and alkenes upon pyrolysis, suggesting that the chitin has been replaced and/or transformed by an aliphatic geopolymer. Experimental evidence suggests that these aliphatic compounds may in fact be lipids that have become attached to the biomacromolecule. These lipids are likely to originate from the closest source available, the organism itself (Gupta et al. 2006, 2007; de Leeuw 2007).

Aromatics and their polymers – lignin. Aromatic polymers are lignin (Fig. 5) as are at least some sporopollenins (Boom 2004). There are some enigmatic algal biomacromolecules with high preservation potential such as the wall material of dinoflagellate cysts. The wall material is currently referred to by the cryptic name ‘dinosporin’. Although dinosporin has been suggested to be aromatic with the isoprenoid tocopherol as an aromatic building block (Kokinos et al. 1998), this view has been challenged by others (de Leeuw et al. 2006). The position of dinosporin in the scheme presented above therefore remains unclear. Apart from this single report of a possible aromatic signature in dinosporin and the increase of phenolic moieties in the algaenan of the Ordovician freshwater acritarch Gloeocapsamorpha prisca in relation to salinity increase (Derenne et al. 1992), the presence of aromatic moieties seems to be a feature of terrestrial biomacromolecular organic matter.

Lignin is a macromolecule resulting from the polymerization of three phenolic units synthesized via the phenylpropanoid pathway, namely the monolignols p-coumaryl, coniferyl and sinapyl alcohols (XXXI–XXXIII) (de Leeuw & Largeau 1993; Raven 2000) (Fig. 4). The polymerization reaction has long been considered to be a random process but this concept appears to be wrong (see reviews of both Lewis 1999; Davin & Lewis 2005). The corresponding degradation products are coumaryl, guaiacyl (or vanillyl) and syringyl moieties (XXXIV–XXXVI), respectively (Hedges & Mann 1979).

Differences in the abundance of the structural lignin compounds are observed among higher plants: guaiacyl units dominate in gymnosperms wood, syringyl and guaiacyl units are dominant in woody tissues of dicotyledonous angiosperms, p-coumaryl and guaiacyl dominate in woody tissues of monocotyledonous angiosperms and non-woody tissues are generally dominated by p-coumaryl units (Hedges & Mann 1979; Logan & Thomas 1985). Pteridophyte lignins are derived from sinapyl alcohol (Barcelo et al. 2007).

From these observations, the respective abundance of the three units in sedimentary organic matter should change in parallel with the evolution of land plants (Logan & Thomas 1987). Although structural motifs of syringyl peroxidases (an enzyme in lignin synthesis) have been identified in Bryophytes (Ros et al. 2007), lignin is absent in these plants (Lewis & Yamamoto 1990). Lignin has also been reported from a red algae which is considered a case of parallel evolution of lignin synthesis (Martone et al. 

![Fig. 4. Example structure of chitin.](image)

![Fig. 5. Example structure of lignin (based on Holtman et al. 2003).](image)
2009). The results obtained by Logan & Thomas (1987) on different Carboniferous plants were consistent with this idea: guaiacyl oxidation products were mostly detected from Sigillaria ovata, a plant which contained woody tissues, while no guaiacyl units were obtained from Lepidodendron and Lepidophloios which were mostly non-woody plants. However, these results should be regarded with care since monolignols also are building blocks of lignans (Lewis & Davin 1999). As discussed above, these latter compounds are widespread among tracheophytes and are also present in bryophytes (Lewis & Davin 1999; Raven 2000). Consistently, the three lignin phenols were observed (although in low amounts) in the oxidation products of different bryophytes (Logan & Thomas 1985).

A second problem with lignin phenols is that, during diagenesis, all three units degrade differently. The general order of resistance is p-coumaryl > guaiacyl > syringyl (Hedges et al. 1985; Logan & Thomas 1985; Orem et al. 1996). Among diagenetic/catagenetic transformations of wood are demethoxylations which also naturally lead to the diminution of syringyl and guaiacyl units, favouring p-coumaryl units in the remaining tissues (Orem et al. 1996; Hatcher & Clifford 1997). A significant contribution of p-coumaryl units was obtained by Logan & Thomas (1987) in the oxidation products of Carboniferous Sigillaria ovata. This feature could reflect both the diagenetic increase of these units due to decarboxylation of lignin units and the contribution of lignan from bryophytes.

Several aliphatic phenols were observed in the flash pyrolsates of the Lower Devonian plants Renalia, Zosterophyllum and Psilophyton (Ewbank et al. 1996). Although these compounds may correspond to lignin pyrolysis products, in particular after diagenetic demethoxylation of lignin, their presence in the pyrolsates of Lower Devonian plants does not unequivocally attest for the presence of lignin in these early plants; they could also derive from the pyrolysis of condensed tannins (Ewbank et al. 1996). Despite its interest, the study of Ewbank et al. (1996) mostly demonstrated that, since pyrolysis products are poorly characteristic, flash pyrolysis is not suited to molecularly characterize the material of early land plants.

The development of spores (and pollen) is an important requisite for terrestrialization since it enables dispersion of gametophytes through air. The effective UVB absorbance of aromatic rings (Pfündel et al. 2006) may play a role in protecting airborne pollen; variations in the aromatic content of fossil pollen have been proposed as a UVB proxy (Rozema et al. 2001, 2002b). However, this proxy is based on pyrolysis of the (fossil) pollen. The coumaric and ferulic moieties produced in this way are probably derived from sporopollenin-type biopolymers in the pollen wall and not derived from compounds believed to regulate UV damage (de Leeuw et al. 2006).

The structure of sporopollenin, the wall polymer of pollen and spores, has long been a matter of debate and it seems likely that both aliphatic and aromatic sporopollenins occur (de Leeuw et al. 2006). Although the structure of the aliphatic sporopollenins is unclear, the aromatic sporopollenin consists of coumaric, ferrulic and sinapic acids (VII–IX) as building blocks. These are the same building blocks for lignin but with propyl-acids in stead of propyl-alcohols (Boom et al. 2005). Biosynthetically, the lignols are formed from these carboxylic acids by reduction and it is interesting to note that, prior to the evolution of lignin synthesis, plants already were able to produce the biopolymer sporopollenin.

Recently, it has been demonstrated that one of the key enzymes in the phenylpropanoid pathway needed to convert the phenylpropanoid acids into their alcohols, 4-coumarate:CoA ligase (4CL) (Ferrer et al. 2008) already occurs in the Bryophyte Physcomitrella patens (Silber et al. 2008). The presence of a similar enzyme cinnamate:CoA ligase (ScCCL) in the bacterium Streptomyces coelicolor (Kaneko et al. 2003) suggests that this part of the pathway has a much longer history than previously expected. It would be interesting to know to what extent the phenylpropanoid pathway had to evolve in order to arrive at sporopollenin synthesis and further to lignin biosynthesis.

Another open question is why, later in evolution, lignin and not sporopollenin became a major structural element in vascular plants. Although apparently the earliest land plants already produced spores, it is not known where in evolution the synthesis of sporopollenin started. Sporopollenin has been claimed to be produced by Coleochaete (Delwiche et al. 1989), a member of the Characeae which is a sister group of Embryophytes (Waters 2003). However, due to a lack of insight in the nature of sporopollenin in the past and despite increasing insight into the nature of acid- (and acetolysis-) resistant algal walls (e.g. de Leeuw et al. 2006) this has not yet been resolved. One method of shedding light on sporopollenin evolution could be a systematic analysis of the structural diversity (if any) of sporopollenins of primitive land plants and their closest relatives.

**Organic matter transformation**

**Composition and preservation**

An important step in investigating the relation between fossil organic matter and its source organisms from a chemical point of view is assessing
the extent to which the biomolecules survive taphonomic processes. Knowledge of present degradative pathways also provides a key to the past, enabling the sedimentary organic molecules to be linked to their biological sources. Through this, the evolution of past life and environment can be reconstructed.

Biological tissues are made of different types of molecules which can be broadly classified according to their chemical functions into carbohydrates (simple sugars and polymers among which cellulose), lipids, peptides (simple amino acids and their polymers, the proteins) and lignin, the principal component of wood. Although different from peptides, nucleic acids (which are the building blocks of DNA) have a fate which is similar to that of peptides during burial, and therefore can be assimilated to peptides.

After organism death and during burial in sediments, the organic matter is bio- or chemically degraded. This results in an important loss of the organic material, but also to chemical modifications of the biomolecules. After this stage, the original material can be either totally unrecognizable or recognizable to a certain degree. During this transformation of biomolecules to geomolecules (the diagenesis), the fate of the different classes of compounds is very different: simple sugars and peptides are generally rapidly mineralized while lipids, complex sugars, sporopollenin and lignin are less easily degraded and therefore have a higher chance of being buried in sediments.

The sedimentary environment is clearly of prime importance. Burial rates, primary productivity, oxygen availability, water depth, organic matter concentration and mineral composition all influence organic matter preservation (Tyson 2001; Burdige 2007; Rothman & Forney 2007). In addition, the initial chemistry of the organic matter is also important (Middelburg 1989; Sinninghe Damsté et al. 2002; Versteegh & Zonneveld 2002; Prahl et al. 2003).

From the study of the organic matter deriving from a wide variety of sedimentary and diagenetic environments, a series of preservation pathways has been proposed (de Leeuw & Largeau 1993; de Leeuw et al. 2006; de Leeuw 2007). The degradation–recondensation pathway (Tissot & Welte 1984) is based on the formation of macromolecular organic matter by random, post-mortem polymerization reactions of degradation residues. Because the organic matter involved in this pathway is generally highly degraded, the deduction of the biological affinities of the fossil organic matter preserved along this pathway is somehow complicated.

In contrast to this, the selective preservation pathway (Philp & Calvin 1976; Tegelaar et al. 1989b) assumes that the biomolecules preserve as they have been synthesized. This pathway concerns many lipids and a few specific biomacromolecules including lignin. Selective preservation of macromolecules is generally associated with the preservation of the morphology (Largeau et al. 1986) although the opposite, excellent morphological preservation, does not imply excellent chemical preservation (see review of de Leeuw et al. 2006; de Leeuw 2007; Gupta et al. 2007b). Biomolecules preserved through this pathway are highly recognizable, even after millions of years of burial (Derenne et al. 1988).

The natural sulphurization (Sinninghe Damsté & de Leeuw 1990) and oxidative polymerization pathways (Harvey et al. 1983; Versteegh et al. 2004; de Leeuw 2007; Gupta et al. 2007b) stress that free sulphur species and oxidizing agents cause condensation and crosslinking, respectively, of both lipids and macromolecules. This reduces the bioavailability of the material so that labile compounds that otherwise would have been mineralized may escape into the fossil record (Kok et al. 2000). Molecules preserved through this pathway can retain most of their original specificity, even after long periods of time (Koopmans et al. 1997; Versteegh et al. 2007). Clearly, due to the much higher availability of oxygen in air and much longer oxygen exposure times, the oxidative polymerization pathway is particularly likely to happen on land.

Burial to important depth, or for long periods of time will also lead to the thermal modification of the organic matter (OM). This process, termed cracking, is the base of petroleum and natural gas formation. The particular organic matter becomes increasingly aromatic and cyclic by selective removal of the aliphatic components and by aromatization and cyclization of the residue. The more the compound is thermally degraded, the less will its original structure will recognizable.

Although maturation of organic matter may play an important role in relatively young sediments (provided temperature is sufficiently high), this is a clear issue on Palaeozoic and older material (Roberts et al. 1995; Yule et al. 2000) where slow transformation at mild temperature conditions is compensated for by long periods of time. The same is true for changes in the composition of stable carbon and hydrogen in the organic matter. This results in a δ13C depletion of the released compounds and a 14C enrichment of the kerogen (Schimmelmann et al. 2001). For hydrogen, changes are larger and depend on the compounds considered. In particular, hydrogen on tertiary carbons (e.g. in isoprenoids) is subject to exchange with the surrounding water (Pedentchouk et al. 2006). Nevertheless, shifts are minor compared to the natural variations in the distributions of these stable isotopes in organic matter (Schimmelmann et al. 2001; Pedentchouk et al. 2006).
Aliphatization and related problems

Studies on the macromolecular nature of Palaeozoic and older acritarchs have shown both aliphatic and aromatic wall compositions (Kjellström 1968; Collinson et al. 1994; Arouri et al. 1999, 2000; Foster et al. 2002; Dutta et al. 2006). Others have concentrated on the biomarker lipids associated with the acritarchs (Moldovan & Talyzina 1998; Talyzina et al. 2000) and the host sediments (Meng et al. 2005), and have drawn conclusions on the biological affinities of the acritarchs. What are the consequences for the application of organic geochemistry to elucidating the terrestrialization of life? Considering both the diagenetic and catagenetic processes, attributing an aromatic or aliphatic contribution to an original biomacromolecular structure remains problematic. As long as the lipids which have become incorporated in the macromolecular matrix post mortem have been derived from the source organisms themselves, the approach of carefully releasing and analysing these lipids seems to be the more successful approach.

Analogous to the transformation of chitinous biomolecules into aliphatic geomolecules (see above), sporopollenin and other biomacromolecules seem to transform chemically over time. Whereas fresh megaspores of Isoetes and Salvinia are purely aromatic, the fossil material consists of a mixture of aliphatic and aromatic moieties, again suggesting addition of long-chain aliphatic compounds (van Bergen et al. 1993; Boom 2004). Furthermore, the cyst walls of the recent dinoflagellate Lingulodinium polyedrum seem to be non-aliphatic (Kokinos et al. 1998) whereas fossil dinoflagellate cysts have been reported to contain mixed aromatic and aliphatic moieties (de Leeuw et al. 2006).

An extreme case of aliphatization by condensation of aliphatic lipids has been described for ‘dinocasts’ from the Eocene of Pakistan: the relatively solid to spongy dinoflagellate-shaped structures occurring in the sediments are believed to represent the oxidatively polymerized cell contents of motile dinoflagellates (Versteegh et al. 2004). Although addition of aliphatic components modifies the signature of several aromatic biomacromolecules (chitin, sporopollenin) such processes seem to be absent for fossil lignin. This may result from the fact that, in most cases, the membrane lipids are very closely located to the biomacromolecule; in lignin there are no lipids around. As such, this may be an indirect and circumstantial piece of evidence for the oxidative polymerization pathway.

It is not only aliphatics which are subject to oxidative polymerization. This process also applies to the terpenoids in resins, leading to resin hardening and amber formation. One may wonder to what extent the oldest amberbs, which are dominated by aliphatic moieties (van Bergen et al. 1995), were originally aliphatic or have become so by aliphatization.

For initially aliphatic biomacromolecules such as cutin, cutan and algaenan, the post mortem aliphatization is intrinsically much more difficult to detect. The incorporation of free lipids to the naturally resistant algaenan of Botryococcus race A by oxidative cross-linking has been clearly demonstrated in coorongite (Gatellier et al. 1993), a rubbery material derived from the accumulation of algal remains on the shores of lakes. As Botryococcus free lipids and algaenans were both aliphatic, the aliphaticity of coorongite was very similar to that of the algaenan; however, the signature upon pyrolysis was significantly different (Gatellier et al. 1993). For Botryococcus braunii race B, the algaenan walls also incorporate polycetals of polymethylnolanes. This may provide a clear marker for the presence of cell walls of this taxon in sediments (Metzger et al. 2007). However, in this case assessment of the degree of change of the original biopolymer by the post mortem oxidative polymerization of membrane and other associated free lipids also remains problematic.

One of the classical examples of the selective preservation pathway is the algaenan of fossil Tetraedron envelopes from the Messel Oil Shale. Apart from being strikingly well-preserved morphologically, the chemical fingerprint of these cuticles upon flash pyrolysis closely resembles its modern counterpart (Goth et al. 1988). But what difference would a contribution of aliphatic lipids from the organism have made? Similarly, oxidative polymerization of aliphatic lipids has been suggested to have played a role in the formation of the aliphatic algaenan of the Ordovician alga Gloeosaccasamorpha priscia (Blokker et al. 2001), but it is difficult to ascertain to what extent this aliphatic material corresponds to the original cell walls.

An analogous problem is illustrated on cutin and cutan. The ether cross-linked cutan of CAM plants is, chemically speaking, more stable than ester cross-linked cutin of most other higher plants: cutin is broken down into its original monomers upon base hydrolysis while cutan resists this treatment. Since the fossil plant cuticles also survive base hydrolysis, they have been considered to represent selectively preserved cutan (Tegelaar et al. 1989c). However, fossil non-hydrolysable cuticles are known from plants that do not produce cutan (Gupta et al. 2006b, 2007b; de Leeuw 2007). In fact, the depositional environment of CAM plants does not at all favour cutan preservation whereas several cutin-producing plants occur in or near excellent preservational environments. Laboratory experiments using elevated temperature and pressure have recently demonstrated that, similar
to chitin, lipids may become incorporated in cutin in due course (Gupta et al. 2006a). It finally appears that most of the previously observed fossil cutans in fact correspond to cuticle lipids which were oxidatively linked during diagenesis (van Bergen et al. 2004).

Even relatively simple lipids are not always easy to relate to their source. Although structural modification such as loss of functional groups or changes in stereochemistry do not usually prevent assignment to their source organisms (e.g. Sinninghe Damsté et al. 1997; Moldowan & Talyzina 1998) they may disappear from the analytical window. The corollary of aliphatization is that free lipids may become part of larger macromolecular structures so that extra analytical steps are required for their detection and identification (e.g. Adam et al. 2006).

For the particular organic matter, we may have visual information on the biological affinities of the fossils at hand, but to what extent is this matched by the chemical composition of the fossils? It seems that much of the aliphatization is brought about by lipids from the immediate surroundings of the original biomacromolecule, that is, derived from the source organism. Moreover, our present understanding of the natural sulphurization and oxidative polymerization pathways imply that these added substances survived relatively undamaged structurally and isotopically. This means that there should still be a fair chance of obtaining information on the nature of the source organisms, provided the individual products released upon chemical degradation or (offline) pyrolysis can be related to a single source and metabolic pathway (van Dongen et al. 2002; van Bergen & Poole 2002; Poole et al. 2004).

Aliphatization of macromolecular material from plants and animals therefore seems to be ineluctable, which complicates the identification of the molecular characteristics (and therefore the biosynthetic pathways) of very old organic matter.

**Conclusion**

Organic geochemistry plays an important role in the elucidation of the history of early life (Brocks et al. 1999; Brocks & Summons 2003; Summons et al. 2006). Similarly, it should play a role in understanding the terrestrialization process, in particular for plants. Numerous molecular biomarkers of terrestrial plants, derived either from structural tissues such as lignin phenols, from epicuticular waxes or from the large class of terpenoids exist, and they are widely used in Tertiary and recent sediments.

The study of the terrestrialization process with organic geochemistry is associated with numerous difficulties, however, in particular in assigning Palaeozoic fossil organic matter to its source. Apart from the fact that the samples have often suffered from thermal alteration, the difficulties mostly arise from a lack of taxonomic precision of the molecular biomarkers. Other difficulties arise from the frequent chemical modification of the material, despite excellent morphological preservation (e.g. aliphatization).

All these difficulties easily explain the relatively large temporal gap which currently exists between the earliest microscopic plant remains documented in Middle Ordovician (Strother et al. 1996) and the earliest unambiguously documented terrestrial biomarkers in Middle Devonian (Sheng et al. 1992). Despite this, the set of currently identified molecules of terrestrial origin is already sufficiently good to discriminate changes in plant associations during the Carboniferous, revealing further information on the terrestrialization process.

It is additionally hoped that condensation processes, which remove lipids from the pool of bioavailable products, may conversely facilitate the survival of specific lipids over long periods of time and, as such, record the biochemical evolution related to the terrestrialization in the sediments. Advancement of the assessment of the stable carbon and hydrogen isotopic compositions on lipids or (offline) pyrolysis products increasingly contributes to unravelling the evolution of biosynthetic pathways and diagenetic overprints. Great advances will also be made with the development of micro-scale techniques (microsampling, micro extractions and nano-SIMS). These techniques will allow the study of fossils present in very low amounts such as very early spores and cuticles, or the study of monospecific fossil associations. Another rapidly developing approach to resolving terrestrialization involves genomics: tracing the evolution of enzymes critical to the biosynthetic pathways involved in the terrestrialization process.

Terrestrialization and earliest plants had previously failed to attract many organic geochemists. However, this is changing as demonstrated by several recent studies and review papers (van Bergen et al. 2004; Armstrong et al. 2006; Auras et al. 2006). It is therefore likely that the right compounds have not been looked at in the right place and with the right techniques – yet.

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Appendix

Structural formulae of the compounds mentioned in the text.

**Flavanone:** R1, H; R2, C=O

**3-OH-Flavanone:** R1, OH; R2, C=O

**Flavan-3-ol:** R1, OH; R2, H

**Flavone:** C=C=C, R1, H; R2, C=O

**Flavonol:** C=C=C, R1, OH; R2, C=O

**Anthocyanidin:** O=C=C; C=C; R2, H or OH; positive charge on C-ring

**Isoflavanone:** Aryl migration to C=3; R2, C=O

**5-O-Methylginkgetin** (a biflavonoid)

**Hydrocynnamic acid**

**p-Coumaric acid**

**Ferulic acid**

**Sinapic acid**

**Labdanoid backbone**

**Cadinane**

**Borneol**

**Isoborneol**

**Camphene**

**Eudesmane**

**Drimane**

**Cadalene**

**Abietane**

**Pimarane**

**Kaurane**

**Podocarpene**

**Beyerane**

**Phyllocladane**

**ent-Beyerane**

**ent-Kaurane**

**Retene**

**Simonellite**
References

ADAM, P., SCHAEFFER, P., & ALBRECHT, P. 2006. C40 monoaromatic lycopane derivatives as indicators of the contribution of the alga Botryococcus braunii race L to the organic matter of Messel oil shale (Eocene, Germany). *Organic Geochemistry*, **37**, 584–596.

ALEXANDER, R., KAGI, R. I., NOBLE, R. A., & VOLKMAN, J. K. 1984. Identification of some bicyclic alkanes in petroleum. *Organic Geochemistry*, **6**, 63–72.

ALEXANDER, G., HAZAI, I., GRIMALT, J. & ALBARGÉS, J. 1987a. Occurrence and transformation of phyllocladanes in brown coals from Nograd Basin, Hungary. *Geochemica et Cosmochimica Acta*, **51**, 2065–2073.

ALEXANDER, R., NOBLE, R. A. & KAGI, R. I. 1987b. Fossil resin biomarkers and their application in oil to source rock correlation, Gippsland basin, Australia. *Australian Petroleum Exploration Association Journal*, **27**, 63–72.

ANDERSON, K. B. & BOTTO, R. E. 1993. The nature and fate of natural resins in the geosphere—III. Re-evaluation of the structure and composition of Highgate Copalite and Glessite. *Organic Geochemistry*, **20**, 1027–1038.

ANDERSON, K. B. & CRESHING, I. C. 1995. *Amber Resinite and Fossil Resins*. American Chemical Society, Washington.

ANDERSON, K. B., WINANS, R. E. & BOTTO, R. E. 1992. The nature and fate of natural resins in the
geosphere—II. Identification, classification and nomenclature of resinites. *Organic Geochemistry*, 18, 829–841.

Araujo, C. V., Barranti, S. M. *et al.* 2003. ICCP—Thermal Indices Working Group: Summary of the 2002 Round Robin Exercise. *ICCP News*, 29, 5–12.

Armstroff, A. 2004. Geochemical significance of biomarkers in Palaeozoic coals. Ph.D. Der Fakultät VI–Bauingenieurwesen und Angewandte Geowissenschaften, Technischen Universität Berlin.

Armstroff, A., Wilkes, H., Schwarzauer, J., Littke, R. & Horsfield, B. 2006. Aromatic hydrocarbon biomarkers in terrestrial organic matter of Devonian to Permian age. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 240, 253–274.

Armstrong, D. W., Zhou, E. Y., Zukowski, J. & Kosmowska-Ceranowicz, B. 1996. Enantiomeric composition and prevalence of some bicyclic monoterpenoids in chirality. *Chirality*, 8, 39–48.

Abouri, K., Greenwood, P. F. & Walter, M. R. 1999. A possible chlorophycean affinity of some Neoproterozoic acritarchs. *Organic Geochemistry*, 30, 1323–1337.

Abouri, K. R., Greenwood, P. F. & Walter, M. R. 2000. Biological affinities of Neoproterozoic acritarchs from Australia: microscopic and chemical characterisation. *Organic Geochemistry*, 31, 75–89.

Auras, S., Wilde, V., Hoernes, S., Scheffler, K. & Püttmann, W. 2006. Biomarker composition of higher plant macrofossils from Late Palaeozoic sediments. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 240, 305–317.

Baas, M., Briggs, D. E. G., van Heemst, J. D. H., Kear, A. J. & de Leeuw, J. W. 1995. Selective preservation of chitin during the decay of shrimp. *Geochemical et Cosmochimica Acta*, 59, 945–951.

Barcelo, A. R., Ros, L. V. G. & Carrasco, A. E. 2007. Looking for syringyl peroxidaes. *Trends in Plant Science*, 12, 486–491.

Batten, D. J. 1996. Green and blue-green algae. Colonial Chlorococcales. *In: Jansonius, J. & McGregor, D. C.* (eds) Palynology: Principles and Applications. Vol. 1. AASP Foundation, Salt Lake City, 191–203.

Batten, D. J. & Grenfell, H. R. 1996. Green and blue-green algae. *Botryococcus*. *In: Jansonius, J. & McGregor, D. C.* (eds) Palynology: principles and applications. Vol. 1. AASP Foundation, Salt Lake City, 205–214.

Belavyouni, H. & Trichet, J. 1980. Glucosamine as a biochemical marker for Dinoflagellates in phosphatised sediments. *Physics and Chemistry of the Earth*, 12, 205–210.

Bernards, M. A. 2002. Demystifying suberin. *Canadian Journal of Botany*, 80, 227–240.

Bernier, R. A. 1989. Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over palaeozoic time. *Global and Planetary Change*, 1, 97–122.

Blokker, P., Schouten, S., van den Ende, H., de Leeuw, J. W., Hatcher, P. G. & Sinninghe Damsté, J. S. 1998. Chemical structure of algaenans from the fresh water algae *Tetraedron minimum*, *Scenedesmus communis* and *Pediastrum boryanum*. *Organic Geochemistry*, 29, 1453–1468.

Blokker, P., van Bergen, P., Pancost, R., Collinson, M. E., de Leeuw, J. W. & Sinninghe Damsté, J. S. 2001. The chemical structure of *Gloeocapsamorpha prisca* microfossils: Implications for their origin. *Geochemica et Cosmochimica Acta*, 65, 885–900.

Boom, A. 2004. A geochemical study of lacustrine sediments: towards palaeo-climatic reconstructions of high Andean biomes in Colombia. PhD thesis. University of Amsterdam, Amsterdam.

Boom, A., Sinninghe Damsté, J. S. & de Leeuw, J. W. 2005. Cutan, a common aliphatic biopolymer in cuticles of drought-adapted plants. *Organic Geochemistry*, 36, 595–601.

Bordoloi, M., Shukla, V. S., Nath, S. C. & Sharma, R. P. 1989. Naturally occurring cadinenes. *Phytochemistry*, 28, 2007–2037.

Borrego, A. G., Blanco, C. G. & Püttermann, W. 1997. Geochemical significance of the aromatic hydrocarbon distribution in the bitumens of the Puertollano oil shales, Spain. *Organic Geochemistry*, 26, 219–228.

Borrego, A. G., Bernard, P. & Blanco, C. G. 1999. Aliphatic hydrocarbons in the bitumens of the Puertollano oil shales. *Applied Geochemistry*, 14, 1049–1062.

Brasell, S. C., Eglinton, G., Marlowe, I. T., Pflaumann, U. & Sarnthein, M. 1986. Molecular stratigraphy: a new tool for climatic assessment. *Nature*, 320, 139–133.

Briggs, D. E. G., Kear, A. J., Baas, M., de Leeuw, J. W. & Rigby, S. 1995. Decay and composition of the hemichordate *Rhabdocoele*: implications for the taphonomy of graptolites. *Lethaia*, 28, 15–23.

Briggs, D. E. G., Evershed, R. P. & Lockeart, M. J. 2000. The biomolecular paleontology of continental fossils. *Paleobiology*, 26, 169–193.

Brooks, J. J. & Summons, R. E. 2003. Sedimentary hydrocarbons, biomarkers for early life. *In: Schlesinger, W. & Turekian, K.* (eds) *Biogeochemistry*. Vol. 8. Elsevier, Amsterdam, 63–115.

Brooks, J. J., Logan, G. A., Buck, R. & Summons, R. E. 1999. Archean molecular fossils and the early rise of eukaryotes. *Science*, 285, 1033–1036.

Burdige, D. J. 2007. Preservation of organic matter in marine sediments: controls, mechanisms, and an imbalance in sediment organic carbon budgets? *Chemical Reviews*, 107, 467–485.

Cardon, Z. G., Gray, D. W. & Lewis, L. A. 2008. The green algal underground: evolutionary secrets of desert cells. *BiScience*, 58, 114–122.

Casadevall, F. E., George, S. C., Batts, B. D. & Conaghan, P. J. 1996. The effects of varying tissue preservation on the aliphatic hydrocarbons within a high-volatile bituminous coal. *Organic Geochemistry*, 24, 785–800.

Christiansen, F. G., Olsen, H., Piasecki, S. & Stemmerik, L. 1989. Organic geochemistry of upper palaeozoic lacustrine shales in the East Greenland basin. *Organic Geochemistry*, 16, 287–294.

Colbath, G. K. 1996. Green and blue-green algae. *Introduction. In: Jansonius, J. & McGregor, D. C.* (eds) *Palynology: Principles and Applications*. Vol. 1. AASP Foundation, Salt Lake City, 171–172.

Collinson, M. E., van Bergen, P. F., Scott, A. C. & de Leeuw, J. W. 1994. The oil-generating potential of plants from coal and coal-bearing strata through
time: a review with new evidence from Carboniferous plants. In: SCOTT, A. C. & FLEET, A. J. (eds) Coal and Coal-bearing Strata as Oil-prone Source Rocks. Geological Society, London, Special Publications, 77, 31–70.

CONTE, M. H., SICRE, M.-A. ET AL. 2006. Global temperature calibration of the alkenone unsaturation index (UK’37) in surface waters and comparison with surface sediments. Geochemistry Geophysics Geosystems, 7, doi: 10.1029/2005GC001054.

COOPER-DRIVER, G. A. & BHATTACHARYA, M. 1998. Role of phenolics in plant evolution. Phytochemistry, 49, 1165–1174.

CRAWFORD, D. 1978. Flavonoid chemistry and angiosperm evolution. The Botanical Review, 44, 431–456.

creiling, j. c. & kruge, m. a. 1998. Petrographic and chemical properties of carboniferous resinite from the Herrn No. 6 coal seam. International Journal of Coal Geology, 37, 55–71.

Czechowski, F., Simonett, B. R. T., Sachanbinski, M., CHOJCA, J. & WOLONIEC, S. 1996. Physicochemical structural characterization of ambers from deposits in Poland. Applied Geochemistry, 11, 811–834.

DAVIN, L. B. & LEWIS, N. G. 2005. Lignin primary structures and dirigent sites. Current Opinion in Biotechnology, 16, 407–415.

Dawson, D. 2006. Stable hydrogen isotope ratios of individual hydrocarbons in sediments and petroleum. PhD thesis. Curtin University of Technology.

de Bakker, N. V. J., van Bodegom, P. M. ET AL. 2005. Is UV-B radiation affecting charophycean algae in shallow freshwater systems? The New Phytologist, 166, 957–966.

de Leeuw, J. W. 2007. On the origin of sedimentary aliphatic macromolecules: a comment on recent publications by Gupta et al. Organic Geochemistry, 38, 1585–1587.

de Leeuw, J. W. & Largeau, C. 1993. A review of macromolecular compounds that comprise living organisms and their role in kerogen, coal and petroleum formation. In: Engeser, M. H. & Macio, S. A. (eds) Organic Geochemistry. Principles and Applications. Plenum Press, New York, 23–72.

de Leeuw, J. W., van der Meer, F. W., Riptstra, W. I. C. & Schenck, P. A. 1980. On the occurrence and structural identification of long chain unsaturated ketones and hydrocarbons in sediments. In: DOUGLAS, A. G. & MAXWELL, J. R. (eds) Advances in Organic Geochemistry, 1979. Pergamon, Oxford, 211–217.

de Leeuw, J. W., Riptstra, W. I. C. & Schenck, P. A. 1981. The occurrence and identification of C_{50}, C_{11}, and C_{12} alkan-1,15-diols and alkan-15-on-1-ols in Unit I and Unit II Black Sea sediments. Geochimica et Cosmochimica Acta, 45, 2281–2285.

de Leeuw, J. W., Versteegh, G. J. M. & van Bergen, P. F. 2006. Biomacromolecules of plants and algae and their fossil analogues. Plant Ecology, 189, 209–233.

de Rosa, M. & Gambacorta, A. 1988. The lipids of Archaeabacteria. Progress in Lipid Research, 27, 153–175.

del Río, J. C., García-Molla, J., González-Vila, F. J. & Martin, F. 1994. Composition and origin of the aliphatic extractable hydrocarbons in the Puertollano (Spain) oil shale. Organic Geochemistry, 21, 897–909.

Delwiche, C. F., Graham, L. E. & Thomson, N. 1989. Lignin-like compounds and sporopollenin in Coleo-chaete, an algal model for land plant ancestry. Science, 245, 399–401.

Derenne, S., Largeau, C., Casadevall, E. & Connan, J. 1988. Comparison of torbanites of various origins and evolutionary stages. Bacterial contribution to their formation. Causes of the lack of botryococcane in bitumens. Organic Geochemistry, 12, 43–59.

Derenne, S., Metzger, P. E. ET AL. 1992. Similar morphological and chemical variations of Gloeocapsomorpha prisca in Ordovician sediments and cultured Botryococcus braunii as a response to changes in salinity. Organic Geochemistry, 19, 299–313.

Deshmukh, A. P., Simpson, A. J. & Hatcher, P. G. 2003. Evidence for cross-linking in tomato cutin using HR-MAS NMR spectroscopy. Phytochemistry, 64, 1163–1170.

Deshmukh, A. P., Simpson, A. J., Hadad, C. M. & Hatcher, P. G. 2005. Insights into the structure of cutin and cutan from Agave americana leaf cuticle using HRMAS NMR spectroscopy. Organic Geochemistry, 36, 1072–1085.

Dinsar, J. R. & Harouna, M. 1994. Biological origin of tetracyclic dipteranes, n-alkanes and other biomarkers found in lower Carboniferous Gondwana coals (Niger). Organic Geochemistry, 21, 143–1532.

Dunn, M. T., Rothwell, G. W. & Mapes, G. 2003. On Paleozoic plants from marine strata: Trivena arkansana (Lignoerididaeae) gen. et sp. nov., a lignoerid from the Fayetteville Formation (middle Chesterian/Upper Mississippian) of Arkansas, USA. American Journal of Botany, 90, 1239–1259.

Dutkiewicz, A., George, S. C., Mossman, D. J., Ridley, J. & Volk, H. 2007. Oil and its biomarkers associated with the Palaeoproterozoic Oklo natural fission reactors, Gabon. Chemical Geology, 244, 130–154.

Dutta, S., Greenwood, P. F., Brocke, R., Schaeffer, R. G. & Mann, U. 2006. New insights into the relationship between Tasmanites and tricyclic terpenoids. Organic Geochemistry, 37, 117–127.

Dzou, L. I. P., Noble, R. A. & Senftle, J. T. 1995. Maturation effects on absolute biomarker concentration in a suite of coals and associated vitrinite concentrates. Organic Geochemistry, 23, 681–697.

Edwards, D. 2001. Early land plants. In: BRIGGS, D. E. G. & CROWTHER, P. R. (eds) Palaeobiology II. Chap. 1.3.4, Blackwell, Oxford, 63–66.

Empt, P. 2004. Steroidbiomarker als Indikatoren der Entstehung mariner Algen im Paläozoitum (Ordovizium bis Perm). PhD thesis. Universität Köln.

Enstone, D. E., Peterson, C. A. & Ma, F. S. 2002. Root endoderms and exoderms: Structure, function, and responses to the environment. Journal of Plant Growth Regulation, 21, 335–351.

Ewbank, G., Edwards, D. & Abbott, G. D. 1996. Chemical characterization of Lower Devonian vascular plants. Organic Geochemistry, 25, 461–473.

Fabianska, M. J., Bzowska, G., Matuszevska, A., Racka, A. & Skret, U. 2003. Gas chromatography-mass spectrometry in geochemical investigation of organic matter of the Grodzicz beds (Upper
Carboniferous), Upper Silesian coal basin, Poland. *Geochemistry*, 63, 63–91.

Ferrar, J.-L., Austrin, M. B., Steward, C., Jr. & Noel, J. P. 2008. Structure and function of enzymes involved in the biosynthesis of phenylpropanoids. *Plant Physiology and Biochemistry*, 46, 356–370.

Flannery, M. B., Stott, A. W., Briggs, D. E. G. & Evershed, R. P. 2001. Chitin in the fossil record: identification and quantification of D-glucosamine. *Organic Geochemistry*, 32, 745–754.

Fleck, S., Michels, R., Izart, A., Elie, M. & Landais, P. 2001. Palaeoenvironmental assessment of Westphalian fluvio-lacustrine deposits of Lorraine (France) using a combination of organic geochemistry and sedimentology. *International Journal of Coal Geology*, 65–88.

Foster, C. B., Stephenson, M. H., Marshall, C., Logan, G. A. & Greenwood, P. F. 2002. A revision of *Rediuvisporonites* Wilson 1962: description, illustration, comparison and biological affinities. *Palynology*, 26, 35–58.

Fowler, M. G., Goodarzi, F., Gentzis, T. & Brooks, P. W. 1991. Hydrocarbon potential of Middle and Upper Devonian coals from Melville Island, Arctic Canada. *Organic Geochemistry*, 17, 681–694.

Franke, R. & Schreiber, L. 2007. Suberin—a biopolyester forming apoplastic plant interfaces. *Current Opinion in Plant Biology*, 10, 252–259.

Gatellier, J.-P. L. A., de Leeuw, J. W., Sinninghe Damsté, J. S., Derenne, S., Largeau, C. & Metzger, P. 1993. A comparative study of macromolecular substances of a Coorongite and cell walls of the extant alga *Botryococcus braunii*. *Geochimica et Cosmochimica Acta*, 57, 2053–2068.

Gelin, F. 1996. Isolation and chemical characterisation of resistant macromolecular constituents in microalgae and marine sediments. *Geologica Ultraejectina*, 139, 1–147.

Gelin, F., Boogers, I., Noodeloos, A. A. M., Sinninghe Damsté, J. S., Rieggman, R. & de Leeuw, J. W. 1997. Resistant biomacromolecules in marine microalgae of the classes Eustigmatophyceae and Chlorophyceae: Geochemical applications. *Organic Geochemistry*, 26, 659–675.

Gelpl, E., Schneider, H., Mann, J. & Oró, J. 1970. Hydrocarbons of geochemical significance in microscopic algae. *Phytochemistry*, 9, 603–612.

Giannasi, D. E. 1978. Systematic aspects of flavonoid biosynthesis and evolution. *The Botanical Review*, 44, 399–294.

Gibbs, A. G. 1998. Water-proofing properties of cuticular lipids. *American Zoologist*, 38, 471–482.

Gibbs, A. G. 2002. Lipid melting and cuticular permeability: new insights into an old problem. *Journal of Insect Physiology*, 48, 391–400.

Goth, K., de Leeuw, J. W., Pütthmann, W. & Tegelaar, E. W. 1988. Origin of Messel Oil Shale kerogen. *Nature*, 336, 759–761.

Grimalt, J. O., Simoneit, B. R. T., Hatcher, P. G. & Nissenbaum, A. 1988. The molecular composition of ambers. *Organic Geochemistry*, 13, 677–690.

Gross, H. & König, G. M. 2006. Terpenoids from marine organisms: unique structures and their pharmacological potential. *Phytochemistry Reviews*, 5, 115–141.

Grutters, M., van Raaphorst, W., Epping, E., Helder, W., de Leeuw, J. W., glavin, D. P. & Bada, J. 2002. Preservation of amino acids from in situ-produced bacterial cell wall peptidoglycans in northeastern Atlantic continental margin sediments. *Limnology and Oceanography*, 47, 1521–1524.

Gupta, N. S., Colliinson, M. E., Briggs, D. E. G. & Evershed, R. P. 2004a. Reinvestigation of the occurrence of cutan in plants: implications for the leaf fossil record. *Paleobiology*, 32, 432–449.

Gupta, N. S., Michels, R., Briggs, D. E. G., Evershed, R. P. & Pancost, R. D. 2006b. The organic preservation of fossil arthropods: an experimental study. *Proceedings of the Royal Society of London*, 273, 2777–2783.

Gupta, N. S., Briggs, D. E. G. & Colliinson, M. E. 2003. A Reply: de Leeuw comment “on the origin of sedimentary aliphatic macromolecules.” *Organic Geochemistry*, 38, 1588–1591.

Gupta, N. S., Briggs, D. E. G., Colliinson, M. E., Evershed, R. P., Michels, R. & Pancost, R. D. 2007b. Molecular preservation of plant and insect cuticles from the Oligocene Etsepl Formation, Germany: Evidence against derivation of aliphatic polymer from sediment. *Organic Geochemistry*, 38, 404–418.

Guy-Odhson, D. 1996. Green and blue-green algae. Prasiphycncean algae. In: Jansonius, J. & McGregor, D. C. (eds) *Palynology: Principles and Applications*. Vol. 1. AASP Foundation, Salt Lake City, 181–189.

Hadley, N. F. 1989. Lipid water barriers in biological systems. *Progress in Lipid Research*, 28, 1–33.

Harvey, G. R., Boran, D. A., Chesal, L. A. & Tokar, J. M. 1983. The structure of marine fulvic and humic acid. *Marine Chemistry*, 12, 119–132.

Hatcher, P. G. & Clifford, D. J. 1997. The organic geochemistry of coal: from plant materials to coal. *Organic Geochemistry*, 27, 251–274.

Hauke, V., Graff, R. et al. 1992. Novel triterpene- derived hydrocarbons of the arborane/fernan series in sediments: Part II. *Geochimica et Cosmochimica Acta*, 56, 3595–3602.

Hauke, V., Adam, P. et al. 1995. Isoarborinol through geological times: Evidence for its presence in the Permian and Triassic. *Organic Geochemistry*, 23, 91–93.

He, F., Pan, Q. H., Shi, Y. & Duan, C. Q. 2008. Biosynthesis and genetic regulation of proanthocyanidins in plants. *Molecules*, 13, 2674–2703.

Hedges, J. I. & Mann, D. C. 1979. The lignin geochemistry of marine sediments from the southern Washington coast. *Geochimica et Cosmochimica Acta*, 43, 1809–1818.

Hedges, J. I., Cowie, G. L., Ertel, J. R., Barbour, R. J. & Hatcher, P. G. 1985. Degradation of carbohydrates and lignins in buried woods. *Geochimica et Cosmochimica Acta*, 49, 701–711.

Holtman, K. M., Chang, H.-M., Jameel, H. & Kadla, J. F. 2003. Elucidation of lignin structure through degradative methods: comparison of modified DFRC and thioacidolysis. *Journal of Agricultural and Food Chemistry*, 51, 3535–3540.

Hunt, D. F., Sharanowitiz, J., Winston, S. & Hauer, C. R. 1986. Protein sequencing by tandem mass
spectrometry. Proceedings of the National Academy of Science of the USA, 83, 6233–6237.

Iwashina, T. 2009. The structure and the distribution of the flavonoids in plants. Journal of Plant Research, 113, 287–299.

Izart, A., Sachschnofer, R. F. et al. 2006. Stratigraphic distribution of macerals and biomarkers in the Donets Basin: implications for paleoecology, paleoecology and eustasy. International Journal of Coal Geology, 66, 69–107.

Jacob, J. 2003. Enregistrement des variations paléoenvironnementales depuis 20000 ans dans le Nord Est du Brésil (Lac Caço) par les trétrerpênes et autres marqueurs organiques. PhD thesis. Institut des Sciences de la Terre d’Orléans (ISTO), Université d’Orléans.

Jacor, J., Paris, F., Monod, O., Miller, M. A., Tang, P., George, S. C. & Bény, J. M. 2007. New insights into the chemical composition of chitinocoza. Organic Geochemistry, 38, 1782–1788.

Jaffé, R. & Hausmann, K. B. 1995. Origin and early diagenesis of arborineone/isoarborinol in sediments of a highly productive freshwater lake. Organic Geochemistry, 22, 231–235.

Jetter, R., Kunst, L. & Samuels, A. L. 2006. Composition of plant cuticular waxes. In: Riederer, M. & Müller, C. (eds) Biology of the Plant Cuticle. Chap. 4, Blackwell, Oxford, 144–178.

Jiang, N., Tong, Z. et al. 1995. The discovery of retene in Precambrian and Lower Paleozoic marine formations. Chinese Journal of Geochemistry, 14, 41–51.

Kandler, O. & König, H. 1998. Cell wall polymers in Archaea (Archaeobacteria). Cellular and Molecular Life Sciences, 54, 305–308.

Kaneko, M., Ohnishi, Y. & Horinouchi, S. 2003. Cinnamate: Coenzyme A Ligase from the Filamentous Bacterium Streptomyces coelicolor A3(2). Journal of Bacteriology, 185, 20–27.

Kim, J.-H., Schouten, S., Hopmans, E. C., Donner, B. & Sinninghe Damsté, J. S. 2008. Global sediment core-top calibration of the TEX86 palaeothermometer in the oceans. Geochimica et Cosmochimica Acta, 72, 1154–1173.

Kjellström, G. 1968. Remarks on the chemistry and ultrastructure of the cell wall of some Palaeozoic lioospheres. Geologiska Föreningens i Stockholm Förhandlingar, 90, 221–228.

Kok, M. D., Schouten, S. & Sinninghe Damsté, J. S. 2000. Formation of insoluble, nonhydrolyzable, sulfur-rich macromolecules via incorporation of inorganic sulfur species into algal carbohydrate. Geochimica et Cosmochimica Acta, 64, 2689–2699.

Kokinos, J. P., Eglinton, T. I., Goñi, M. A., Boon, J. J., Martoglio, P. A. & Anderson, D. M. 1998. Characterisation of a highly resistant biocommacromolecular material in the cell wall of a marine dinoflagellate resting cyst. Organic Geochemistry, 28, 265–288.

Kolattukudy, P. E. 1981. Structure, biosynthesis and biodegradation of cutin and suberin. Annual Reviews in Plant Physiology, 32, 539–576.

Kolattukudy, P. E. 2001. Structure, biosynthesis and biodegradation of cutin and suberin. In: Babel, W. & Steinbüchel, A. (eds) Biopolymesters. Springer, Heidelberg, 1–49.

Koops, M. P., Schaeffer-Reiss, C. et al. 1997. Sulphur and oxygen sequestration of n-C_{37} and n-C_{34} unsaturated ketones in an immature kerogen and the release of their carbon skeletons during early stages of thermal maturation. Geochimica et Cosmochimica Acta, 61, 2397–2408.

Kraus, T. E. C., Dahlgren, R. A. & Zasoski, R. J. 2009. Tannins in nutrient dynamics of forest ecosystems - a review. Plant and Soil, 256, 41–66.

Langenheim, J. H. 1995. Biology of amber producing trees: focus on case studies of Hymenaea and Agathis. In: Anderson, K. B. & Crelling, J. C. (eds) Amber, Resinite and Fossil Resins. American Chemical Society, Washington, 1–31.

Largeau, C., Derenne, S., Casadevall, E., Kadouri, A. & Sellier, N. 1986. Pyrolysis of immature torbanite and of the resistant biopolymer (PRB A) isolated from extant alga Botryococcus braunii. Mechanism of formation and structure of torbanite. Organic Geochemistry, 10, 1023–1032.

Lewis, N. G. 1999. A 20th century roller coaster ride: a short account of lignification. Current Opinion in Plant Biology, 2, 153–162.

Lewis, N. G. & Yamamoto, E. 1990. Lignins: occurrence, biogenesis and biodegradation. Annual Reviews in Plant Physiology and Plant Molecular Biology, 41, 455–496.

Lewis, N. G. & Davin, L. B. 1999. Lignans: biosynthesis and function. In: Barton, D. H. R., Nakashiki, K. & Meth-Cohn, O. (eds) Comprehensive Natural Products Chemistry. Vol. 1. Elsevier, London, 639–712.

Li, J. G., Philp, R. P. & Cui, M. Z. 2002. Unusual n-alkane distributions in extracts from marine carbonate rocks at high levels of maturity and overmaturity. Chinese Journal of Geochemistry, 21, 322–333.

Lichtfouse, E., Derenne, S., Mariotti, A. & Largeau, C. 1994. Possible algal origin of long chain odd n-alkanes in immature sediments as revealed by distributions and carbon isotope ratios. Organic Geochemistry, 22, 1023–1027.

Logan, K. J. & Thomas, B. A. 1985. Distribution of lignin derivatives in plants. The New Phytologist, 99, 571–585.

Logan, K. J. & Thomas, B. A. 1987. The distribution of lignin derivatives in fossil plants. The New Phytologist, 105, 157–173.

McNaughton, R. B., Cole, J. M., Dalrymple, R. W., Braddy, S. J., Briggs, D. E. G. & Lukie, T. D. 2002. First steps on land: Arthropod trackways in Cambrian–Ordovician eolian sandstone, southeastern Ontario, Canada. Geology, 30, 391–394.

Maillard, L.-C. 1912. Action des acides aminés sur les sucres; formation des mélanoidines par voie méthodique. Comptes Rendus Hebdomadaires des Séances de l’Académie des Sciences Paris, 154, 66–68.

Mansour, M. P., Volkman, J. K., Holdsworth, D. G., Jackson, A. E. & Blackburn, S. I. 1999. Very-long-chain (C_{37}) highly unsaturated fatty acids in marine dinoflagellates. Phytochemistry, 50, 541–548.

Markham, K. R. & Porter, L. J. 1969. Flavenoids in the algae (Chlorophyta). Phytochemistry, 8, 1777–1781.

Marlowe, I. T. 1984. Lipids as palaeoclimatic indicators. PhD thesis. University of Bristol.
MARSHALL, C. P., JAVAUX, E. J., KNOLL, A. H. & WALTER, M. R. 2005. Combined micro-Fourier transform infrared (FTIR) spectroscopy and micro-Raman spectroscopy of Proterozoic acritarchs: a new approach to palaeobiology. Precambrian Research, 138, 208–224.

MARTONE, P. T., ESTEVES, J. M., LU, F. C., RUEL, K., Denny, M. W., SOMERVILLE, C. & RALPH, J. 2009. Discovery of lignin in seaweed reveals convergent evolution of cell-wall architecture. Current Biology, 19, 169–175.

MARYNOWSKI, L. & FILIPIAK, P. 2007. Water column euxinia and wildfire evidence during deposition of the Upper Famennian Hangenberg event horizon from the Holy Cross Mountains (central Poland). Geologcal Magazine, 144, 569–595.

MATER, W. L., VAN DE MEENT, D. ET AL. 1977. Curie-point pyrolysis in organic geochemistry. In: JONES, C. E. R. & CRAMERS, C. A. (eds) Analytical Pyrolysis. Elsevier, Amsterdam, 203–216.

MATSUO, A., NAKAYAMA, M., GOTO, H., HAYASHI, S. & NISHIMOTO, S. 1974. n-Paraffin composition of some liverworts. Phytochemistry, 13, 957–959.

MENG, F. W., ZHOU, C. M., YIN, L. M., CHEN, Z. L. & YUAN, X. L. 2005. The oldest dinoflagellate: morphological and molecular evidence from Mesoproterozoic rocks at Yongji, Shanxi Province. Chinese Science Bulletin, 50, 1230–1234.

MÉRIDA, T., SCHÖNHERR, J. & SCHMIDT, H. W. 1981. Fine structure of plant cuticles in relation to water permeability: The fine structure of the cuticle of Clivia miniata teg. leaves. Planta, 152, 259–267.

MEYTER, P., RAGER, M.-N. & LARGEAU, C. 2007. Polyacetal based on polymethylsqualene diols, precursors of algaenan in Botryococcus braunii race B. Organic Geochemistry, 38, 566–581.

MIDDELBURG, J. J. 1989. A simple rate model for organic matter decomposition in marine sediments. Geochimica et Cosmochimica Acta, 53, 1577–1581.

MILLAY, M. A. & TAYLOR, T. N. 1977. Ferrusoxtha gen. n., a lyginopterid pollen organ from the Pennsylvanian mica et Cosmochimica Acta, 49, 1577–1581.

MOLLER, L. M., TAYLOR, M. T. & TAYLOR, D. W. 1994. The molecular fossil record of oleanane and its relation to angiosperms. Science, 265, 768–771.

NAGATA, T., MEON, B. & KIRCHMAN, D. L. 2003. Microbial degradation of peptidoglycan in seawater. Limnology and Oceanography, 48, 745–754.

NIKLAS, K. J. 2004. The cell walls that bind the tree of life. BioScience, 54, 831–841.

NIKLAS, K. J. & GIANNASI, D. E. 1977a. Flavonoids and other chemical constituents of fossil Miocene Zelkova (Ulmaceae). Science, 196, 877–878.

NIKLAS, K. J. & GIANNASI, D. E. 1977b. Geochemistry and thermolysis of flavonoids. Science, 197, 767–769.

NIK, M., GENUIT, W. ET AL. 1987. Chemical characterization of Hungarian brown coals by Curie-point pyrolysis-low-energy electron impact mass spectrometry and multivariate analysis and by Curie-point pyrolysis-gas chromatography-photoionization mass spectrometry. Journal of Analytical and Applied Pyrolysis, 11, 125–147.

NIJ Vinyl, D. L., RES, J. H. E. & MURPHY, D. J. 1998. Biogenesis and function of the lipidic structures of pollen grains. Sexual Plant Reproduction, 11, 65–80.

POOLE, I., VAN BERGEN, P. F., KOOL, J., SCHOUTEN, S. & CANTRILL, D. J. 2004. Molecular isotopic heterogeneity of fossil organic matter: implications for 13C biomass and 13C palaeoatmosphere proxies. Organic Geochemistry, 35, 1261–1274.
Popper, Z. A. 2008. Evolution and diversity of green plant cell walls. *Current Opinion in Plant Biology*, **11**, 286–292.

Popper, Z. A. & Fry, S. C. 2004. Primary cell wall composition of pteridophytes and spermatophytes. *The New Phytologist*, **164**, 165–174.

Powell, T. G., Douglas, A. G. & Allen, J. 1976. Variations in the type and distribution of organic matter in some Carboniferous sediments from northern England. *Chemical Geology*, **18**, 137–148.

Prahl, F. G. & Wakeham, S. G. 1987. Calibration of unsaturation patterns in long-chain ketone compositions for palaeotemperature assessment. *Nature*, **330**, 367–369.

Prahl, F. G., Cowie, G. L., de Lange, G. J. & Sparrow, M. A. 2003. Selective organic matter preservation in “burn-down” turbidites on the Madeira Abyssal Plain. *Paleogeography*, **18**, 1052, doi: 10.1029/2002PA000853.

Proctor, M. C. F. 2000. The bryophyte paradox: tolerance of desiccation, evasion of drought. *Plant Ecology*, **151**, 40–49.

Ramsay, J. A. 1935. The evaporation of water from the cockroach. *Journal of Experimental Biology*, **12**, 373–383.

Rausher, M. D. 2006. The evolution of flavonoids and their genes. *In: Grotewold, E. (ed.) The Science of Flavonoids*. Chap. 7, Springer, New York, USA, 175–211.

Raven, J. A. 2000. Land plant biochemistry. *Philosophical Transactions of the Royal Society of London, B*, **355**, 833–846.

Riboulleau, A., Schnyder, J., Riquer, L., Leefbvre, S., Baudin, F. & Deconinck, J.-F. 2007. Environmental change during the Early Cretaceous in the Purbeck-type Durlston Bay section (Dorset, Southern England): a biomarker approach. *Organic Geochemistry*, **38**, 1804–1823.

Roberts, S., Tricker, P. M. & Marshall, J. E. A. 1995. Raman spectroscopy of chitinozoans as a maturation indicator. *Organic Geochemistry*, **23**, 223–228.

Roghi, G., Ragazzi, E. & Gianolla, P. 2006. Triassic Amber of the Southern Alps (Italy). *Palaios*, **21**, 143–154.

Rontani, J.-F., Prahl, F. G. & Volkman, J. K. 2007. Re-examination of the double bond positions in alkenones and derivatives: biosynthetic implications. *Journal of Physiology*, **42**, 800–813.

Ros, L. V. G., Garaladín, C., Pomar, F., Merino, F., Pedreño, M. A. & Ros Barceló, A. 2007. Structural motifs of syringyl peroxidases predate not only the gymnosperm-angiosperm divergence but also the radiation of tracheophytes. *The New Phytologist*, **173**, 63–78.

Rothman, D. H. & Forney, D. C. 2007. Physical model for the decay and preservation of marine organic carbon. *Science*, **316**, 1325–1328.

Rothwell, G. W. & Taylor, T. N. 1972. Carboniferous pteridosperm studies: morphology and anatomy of *Schopfiastrum decussatum*. *Canadian Journal of Botany*, **50**, 2649–2658.

Rozema, J., Broekman, R. A. *et al.* 2001. UV-B absorbance and UV-B absorbing compounds (*para*-cumaric acid) in pollen and sporopollenin: the perspective to track historic UV-B levels. *Journal of Photochemistry and Photobiology, B*, **62**, 108–117.

Rozema, J., Björn, L. O. *et al.* 2002a. The role of UV-B radiation in aquatic and terrestrial ecosystems—an experimental and functional analysis of the evolution of UV-absorbing compounds. *Journal of Photochemistry and Photobiology, B*, **66**, 2–12.

Rozema, J., van Geel, B., Björn, L. O., Lean, J. & Madronich, S. 2002b. Toward solving the UV puzzle. *Science*, **296**, 1621–1622.

Schimmelmann, A., Boudou, J.-P., Lewan, M. D. & Wintsch, R. P. 2001. Experimental controls on D/H and 13C/12C ratios of kerogen, bitumen and oil during hydrolysis pyrolysis. *Organic Geochemistry*, **32**, 1009–1018.

Schönherr, J. 1976. Water permeability of isolated cuticular membranes: the effect of cuticular waxes on diffusion of water. *Planta*, **131**, 159–164.

Schouten, S., Hopmans, E. C., Forster, A., van Breugel, Y., Kuypers, M. M. M. & Sinninghe Damsté, J. S. 2003. Extremely high sea-surface temperatures at low latitudes during the middle Cretaceous as revealed by archaeal membrane lipids. *Geology*, **31**, 1069–1072.

Schulz, S., Arsene, C., Tauer, M. & McNeill, J. 2000. Composition of lipids from sunflower pollen (*Helianthus annuus*). *Phytochemistry*, **54**, 325–336.

Schulze, T. & Michaelis, W. 1990. Structure and origin of terpenoid hydrocarbons in some German coals. *Organic Geochemistry*, **16**, 1051–1058.

Sheng, G., Simonet, B. R. T., Leif, R. N., Chen, X. & Fu, J. 1992. Tetracyclic terpenes enriched in Devonian cuticle humic coals. *Fuel*, **71**, 523–532.

Silber, M. V., Meiberg, H. & Ebel, J. 2008. Identification of 4-coumarate:CoA ligase gene family in the moss, *Physcomitrella patens*. *Phytochemistry*, **69**, 2449–2456.

Silva, M. B. & Kalkreuth, W. 2005. Petrological and geochemical characterization of Candiota coal seams, Brazil–Implication for coal facies interpretations and coal rank. *International Journal of Coal Geology*, **64**, 217–238.

Simoneit, B. R. T. 1986. Cyclic terpenoids in the geosphere. *In: Johns, R. B. (ed.) Biological Markers in the Sedimentary Record*. Elsevier, Amsterdam, 41–99.

Sinninghe Damsté, J. S. & de Leeuw, J. W. 1990. Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere: State of the art and future research. *Organic Geochemistry*, **16**, 1077–1101.

Sinninghe Damsté, J. S., Baas, M., Koopmans, M. P. & Geenensaven, A. J. J. 1997. Cyclisation, aromatisation and expulsion reactions of β-carotene during sediment diagenesis. *Tetrahedron Letters*, **38**, 2347–2350.

Sinninghe Damsté, J. S., Ripsstra, W. I. C. & Reichart, G. J. 2002. The influence of oxic degradation on the sedimentary biomarker record II. Evidence from Arabian Sea Sediments. *Geochimica et Cosmochimica Acta*, **66**, 2737–2754.

Sinninghe Damsté, J. S., Rampen, S., Ripsstra, W. I. C., Abbas, B., Muyzer, G. & Schouten, S. 2003. A diatomaceous origin for long-chain diols and mid-chain
hydroxy methyl alkanotes widely occurring in Quaternary marine sediments: indicators for high-nutrient conditions. Geochimica et Cosmochimica Acta, 67, 1339–1348.

Smith, J. 1896. On the discovery of fossil microscopic plants in the amber of the Ayrshire coal-field. Transactions of the Geological Society of Glasgow, 10, 318–322.

Stafford, H. A. 1991. Flavonoid evolution: an enzymic approach. Plant Physiology, 96, 680–685.

Stankiewicz, B. A., Briggs, D. E. G., Evershed, R. P., Flannery, M. B. & Wittke, M. 1997. Preservation of chitin in 25-million-year-old fossils. Science, 276, 1541–1543.

Stankiewicz, B. A., Scott, A. C., Collinson, M. E., Finch, P., Mösle, B., Briggs, D. E. G. & Evershed, R. P. 1998. Molecular taphonomy of arthropod and plant cuticles from the Carboniferous of North America: implications for the origin of kerogen. Journal of the Geological Society, London, 155, 453–462.

Steemans, P., Le Hêrisse, A. & Bozdogan, N. 1996. Ordovician and Silurian cryptospores and miospores from southeastern Turkey. Review of Palaeobotany and Palynology, 93, 35–76.

Stefanova, M., Simotej, B. R. T., Stojanova, G., Nosyrev, I. E. & Goranova, M. 1995. Composition of the extract of a Carboniferous bituminous coal: 1. Bulk and molecular constitution. Fuel, 74, 768–778.

Stout, S. A. 1995. Resin-derived hydrocarbons in fresh and fossil dammar resins and miocene rocks and oils in the Mahakam delta, Indonesia. In: Anderson, K. B. & Crelling, J. C. (eds) Amber, Resinites and Fossil Resins. American Chemical Society, Washington, 43–75.

Strother, P. K. 2000. Cryptospores: the origin and early evolution of the terrestrial flora. The Palaeontological Society Papers, 6, 3–19.

Strother, P. K., Al-Hadri, S. & Traverse, A. 1996. New evidence for the lower Middle Ordovician of Saudi Arabia. Geology, 24, 55–58.

Stuessy, T. F. & Crawford, D. J. 1983. Flavonoids and phylogenetic reconstruction. Plant Systematics and Evolution, 143, 83–107.

Summons, R. E., Bradley, A. S., Jahnke, L. L. & Waldbauer, J. R. 2006. Steroids, triterpenoids and molecular oxygen. Philosophical Transactions of the Royal Society of London, B, 361, 951–968.

Suzuki, S. & Umezawa, Z. 2007. Biosynthesis of lignans and norlignans. Journal of Wood Science, 53, 273–284.

Talyzina, N. M., Moldowan, J. M., Johannsson, A. & Fago, F. J. 2000. Affinities of Early Cambrian acri-tarchs studied by using microscopy, fluorescence flow cytometry and biomarkers, Review of Palaeobotany and Palynology, 108, 37–53.

Taylor, D. W., Li, H., Dahl, J., Fago, F. J., Zinniker, D. & Moldowan, J. M. 2006. Biogeochemical evidence for the presence of the angiosperm molecular fossil oleane in Paleozoic and Mesozoic non-angiospermous fossils. Paleobiology, 32, 179–190.

Taylor, W. A. & Strother, P. K. 2008. Ultrastructure of some Cambrian palynomorphs from the Bright Angel Shale, Arizona, USA. Review of Palaeobotany and Palynology, 151, 41–50.

Tegelaar, E. W., de Leeuw, J. W., Derenne, S. & Largeau, C. 1989a. A reappraisal of kerogen formation. Geochimica et Cosmochimica Acta, 53, 3103–3106.

Tegelaar, E. W., de Leeuw, J. W. et al. 1989b. Scope and limitations of several pyrolysis methods in the structural elucidation of a macromolecular plant constituent in the leaf cuticle of Agave americana L. Journal of Analytical and Applied Pyrolysis, 15, 29–54.

Tegelaar, E. W., Matthezing, R. M., Jansen, J. B. H., Horsfield, B. & de Leeuw, J. W. 1989c. Possible origin of n-alkanes in high-wax crude oils. Nature, 342, 529–531.

Tegelaar, E. W., Hollman, G., Van der Vegt, P., de Leeuw, J. W. & Holoway, P. J. 1995. Chemical characterization of the periderm tissue of some angiosperm species: recognition of an insoluble, non-hydrolyzable, aliphatic biomacromolecule (Suberin). Organic Geochemistry, 23, 239–250.

Tissot, B. P. & Welte, D. H. 1984. Petroleum Formation and Occurrence. Springer. Berlin, 1–699.

Toyota, M. & Aşakawa, Y. 1990. An eudesmane-type sesquiterpene alcohol from the liverwort Frullania tamariscii. Phytochemistry, 29, 3664–3665.

Tyson, R. V. 2001. Sedimentation rate, dilution, preservation and total organic carbon: some results of a modeling study. Organic Geochemistry, 32, 333–339.

Van Aarsen, B. G. K. & de Leeuw, J. W. 1992. High-molecular-mass substances in resinites as possible precursors of specific hydrocarbons in fossil fuels. Organic Geochemistry, 19, 315–326.

Van Aarsen, B. G. K., Cox, H. C., Hoogenboom, P. & de Leeuw, J. W. 1990. A cadinene biopolymer in fossil and extant dammar resins as a source for cadinanes and bicaladanes in crude oils from South East Asia. Geochimica et Cosmochimica Acta, 54, 3021–3031.

Van Bergen, P. F. & Pool, J. 2002. Stable carbon isotopes of wood: a clue to palaeoclimate? Palaeoecology, Palaeoclimatology, Palaeoecology, 182, 31–45.

Van Bergen, P. F., Collinson, M. E. & de Leeuw, J. W. 1993. Chemical composition and ultrastructure of fossil and extant salvinialean microspore massule and megaspores. Grana Supplement, I, 18–30.

Van Bergen, P. F., Collinson, M. E., Scott, A. C. & de Leeuw, J. W. 1995. Unusual resin chemistry from Upper Carboniferous pteridosperm resin rodlets. In: Anderson, K. B. & Crelling, J. C. (eds) Amber, Resinite and Fossil Resin. American Chemical Society, Washington, 149–169.

Van Bergen, P. F., Blokker, P. et al. 2004. Structural biomacromolecules in plants: What can be learnt from the fossil record? In: Hemsley, A. R. & Pool, J. (eds) Evolution of Plant Physiology. Chap. 8, Elsevier, Amsterdam, 133–154.

Van Dongen, B. E., Schouten, S. & Sinninghe Damsté, J. S. 2002. Carbon isotope variability in monosaccharides and lipids of aquatic algae and terrestrial plants. Marine Ecology Progress Series, 232, 83–92.
van Geel, B. & Grenfell, H. R. 1996. Green and blue-green algae. Spores of Zygnemataceae. In: Jansonius, J. & McGregor, D. C. (eds) Palynology: principles and applications. Vol. 1. AASP Foundation, Salt Lake City, 173–179.

Vandenhove, M. & Largeau, C. 2007. Kerogen origin, evolution and structure. Organic Geochemistry, 38, 719–833.

Versteegh, G. J. M. & Zonneveld, K. A. F. 2002. Use of selective degradation to separate preservation from productivity. Geology, 30, 615–618.

Versteegh, G. J. M. & Blokker, P. 2004. Resistant macromolecules of extant and fossil microalgae. Phycological Research, 52, 325–339.

Versteegh, G. J. M., Jansen, J. H. F., de Leeuw, J. W. & Schneider, R. R. 2000. Mid-chain diols and keto-ols in sediments. A new tool for tracing past sea surface water masses? Geochemistry et Cosmochimica Acta, 64, 1879–1892.

Versteegh, G. J. M., Blokker, P., Wood, G., Collinson, M. E., Sinninghe Damsté, J. S. & de Leeuw, J. W. 2004. Oxidative polymerization of unsaturated fatty acids as a preservation pathway for micro-algal organic matter. Organic Geochemistry, 35, 1129–1139.

Versteegh, G. J. M., Blokker, P., Marshall, C. R. & Pross, J. 2007. Macromolecular composition of the dinoflagellate cyst Thalassiosira pelagica (Oligocene, SW Germany). Organic Geochemistry, 38, 1643–1656.

Veuger, B., van Oevelen, D., Boschker, H. T. S. & Middelburg, J. J. 2006. Fate of peptidoglycan in an intertidal sediment: an in situ 13C-labeling study. Limnology and Oceanography, 51, 1572–1580.

Vliek, M., Hagemann, H. W. & Püttmann, W. 1994. Aromatized arborane/fermane hydrocarbons as molecular indicators of floral changes in Upper Carboniferous/Lower Permian strata of the Saar-Nahe Basin, southwestern Germany. Geochimica et Cosmochimica Acta, 58, 4689–4702.

Wolman, J. K., Eglinton, G., Corner, E. D. & Sargent, J. R. 1980. Novel unsaturated straight-chain C27-C30 methyl and ethyl ketones in marine sediments and a coccolithophore Emiliana huxleyi. In: Douglas, A. G. & Maxwell, J. R. (eds) Advances in Organic Geochemistry, 1979. Pergamon, Oxford, 219–227.

Volkman, J. K., Barrett, S. M., Blackburn, S. I., Mansour, M. P., Sikes, E. L. & Gelin, F. 1998. Microalgal biomarkers: a review of recent research developments. Organic Geochemistry, 29, 1163–1179.

Voss-Foucart, M. F. & Jeauniaux, C. 1972. Lack of chitin in a sample of Ordovician chitinozoa. Journal of Paleontology, 46, 769–770.

Watanabe, Y., Martini, J. E. & Ohmoto, H. 2000. Geochemical evidence for terrestrial ecosystems 2.6 billion years ago. Nature, 408, 574–578.

Waters, E. R. 2003. Molecular adaptation and the origin of land plants. Molecular Phylogenetics and Evolution, 29, 456–463.

Wellman, C. H. & Gray, J. 2000. The microfossil record of early land plants. Philosophical Transactions of the Royal Society of London, B, 355, 717–732.

Wellman, C. H., Osterloff, P. L. & Mohiuddin, U. 2003. Fragments of the earliest land plants. Nature, 425, 282–285.

Wen, Z., Ruiyoung, W., Radke, M., Qingyu, W., Guoying, S. & Zhihui, L. 2000. Retene in pyrolysates of algal and bacterial organic matter. Organic Geochemistry, 31, 757–762.

Wicander, R., Foster, C. B. & Reed, J. D. 1996. Green and blue-green algae Gloeocapsomorpha. In: Jansonius, J. & McGregor, D. C. (eds) Palynology: principles and applications. Vol. 1. AASP Foundation, Salt Lake City, 215–225.

Wilson, M. A. & Hatcher, P. G. 1988. Detection of tannins in modern and fossil barks and in plant residues by high-resolution solid-state 13C nuclear magnetic resonance. Organic Geochemistry, 12, 593–546.

Yule, B. L., Roberts, S. & Marchall, J. E. A. 2000. The thermal evolution of sporopollenin. Organic Geochemistry, 31, 859–870.

Zhang, L., Huang, D. & Liao, Z. 1999. High concentration retene and methylretene in Silurian carbonate of Michigan Basin. Chinese Science Bulletin, 44, 2083–2086.

Zhang, S. C., Hansson, A. D. et al. 2000. Paleozoic oil-source rock correlations in the Tarim basin, NW China. Organic Geochemistry, 31, 273–286.

Zhou, Y.-X., Li, C.-S., Luo, X.-D., Wang, Y.-F. & Zhou, J. 2006. Palaeophytochemical constituents of Cretaceous Ginkgo coriacea Florin leaves. Journal of Integrative Plant Biology, 48, 983–990.