Available online at www.sciencedirect.com

SCIENCE DIRECT®

Organic Geochemistry 37 (2006) 610–625

Organic Geochemistry

www.elsevier.com/locate/orggeochem

Vascular plant biomarkers as proxies for palaeoflora and palaeoclimatic changes at the Dogger/Malm transition of the Paris Basin (France)

Yann Hautevelle [a,b,*], Raymond Michels [a], Fabrice Malartre [c], Alain Trouiller [b]

[a] UMR 7566 CNRS G2R, Université Henri Poincaré, Nancy 1, BP 239, 54506 Vandoeuvre-lès-Nancy cedex, France
[b] ANDRA, 1-7 rue Jean Monnet, 92268 Châtenay-Malabry, France
[c] UMR 7566 CNRS G2R, Ecole Nationale Supérieure de Géologie, BP 40, 54501 Vandoeuvre-lès-Nancy cedex, France

Received 31 May 2005; received in revised form 18 November 2005; accepted 7 December 2005
Available online 6 March 2006

Abstract

Vascular plant biomarkers are used here as a chemostratigraphic tool for tracing both palaeoflora and palaeoclimatic changes during the Callovian and Oxfordian in the Paris Basin. The retene/cadalene ratio shows low values in claystones from the Middle Callovian to the end of the Lower Oxfordian, then increases drastically from the end of the Lower Oxfordian (*cordatum* Zone) synchronously with the progressive development of the Oxfordian carbonate platform. The relative proportion of retene, a conifer biomarker, is strongly correlated with the abundance of some of its diagenetic precursors and with saturated diterpanes. Some of these are very common and abundant in the Pinaceae family while specific markers for non-Pinaceae conifers are not detected. Thus, the increase in the retene/cadalene ratio around the *cordatum* Zone reflects the rising proportion of Pinaceae on the London-Brabant Massif, which was the nearest land from the locations studied. As Pinaceae show many morphological adaptations to dry climate compared to the other plants reported in the Jurassic taphofloras of the Paris basin, their increasing proportion indicates an increasing aridity. This climatic change is also supported by published geochemical, palaeobiogeographical, palynological, palaeobotanical and mineralogical data. A comparable increase in the relative proportion of retene was also described for the Oxfordian of Western Australia, which could be an argument for a worldwide increase in aridity at the end of the Lower Oxfordian.

1. Introduction

Terrestrial plants are major producers of biological components which are thereafter transported within various kinds of particles (soot, resin grains, phytoclasts...) from land to sedimentary basins both by wind and rivers. During transport, sedimentation and diagenesis, most of these compounds are mineralised but some are converted into biomarkers and preserved within sediments. Vascular plant biomarkers are now well recognised molecular compounds classically used in organic geochemistry to

---

[*] Corresponding author.
E-mail address: yann.hautevelle@g2r.uhp-nancy.fr (Y. Hautevelle).

0146-6380/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.orggeochem.2005.12.010

reconstruct palaeoenvironments (e.g. Fleck et al., 2001, 2002; Bechtel et al., 2002). These land plant biomarkers are mainly:

1. *n*-Alkanes with more than 24 carbon atoms, characterised by an odd-over-even carbon number predominance and a mode at C_{29} or C_{31} typical of cuticular waxes (Caldicott and Eglinton, 1973).
2. Non-alkylated PAHs (polycyclic aromatic hydrocarbons) produced by incomplete biomass burning during ancient vegetation fires (Killops and Massoud, 1992; Jiang et al., 1998).
3. Geoterpenoids derived from diagenesis of bioterpenoids common in vascular plant tissues and resins. Terpenoid analysis of extant plants (Swain, 1965; Otto and Wilde, 2001) in well identified plant fossils and sometimes in the surrounding sediment (Otto et al., 1999, 2002b; Otto and Simoneit, 2001, 2002; Staccioli et al., 2002), of fossil resins and ambers still associated with their well identified biological producers (Simoneit et al., 1986; Otto and Simoneit, 2002; Otto et al., 2002a) and of organic aerosols produced by biomass burning (Simoneit, 2002 and references therein) yields valuable information on the specific plant sources of geoterpenoids.

These studies indicate that certain sesqui-, di- and triterpenoids have a chemosystematic or a chemotaxonomic value and can be linked to specific plant taxa. Thus, diterpenoids originate mainly from gymnosperms and can provide useful chemotaxonomic information on fossil and extant coniferales families (Otto and Wilde, 2001; Otto and Simoneit, 2001), while triterpenoids of the oleanane, ursane and lupane classes derive essentially from angiosperms (Woolhouse et al., 1992).

Consequently, the nature and relative proportions of geoterpenoids preserved in sediments are potentially useful proxies for ancient flora and reflect the plant palaeobiodiversity on emerged land close to sedimentary basins at the time of deposition. Therefore, vascular plant biomarkers can be used as a chemostratigraphic tool in order to trace palaeoflora changes on emerged land (Fig. 1). As palaeoflora changes are under climatic control and forced by seasonality, temperature and humidity variations (Barale, 1990; Vakhrameev, 1991), the precise determination of which plant families appear/disappear or become more/less predominant can theoretically allow us to specify the nature of climatic variations if the favourable temperature and/or humidity requirements of the families are known (Fig. 1).

Molecular and isotopic tracers of palaeoflora and palaeoclimatic changes have been reviewed recently by Pancost and Boot (2004) who point out that palaeoflora reconstructions remain a largely unexplored field and a great challenge in organic geochemistry applied to palaeoenvironmental research: van Aarssen et al. (2000) provide the most convincingly evidence of a palaeovegetation change recorded by sesqui- and diterpenoids, suggesting that large forests of conifers developed during the Oxfordian on the Australian hinterland. However, an increase in conifer forest area cannot be interpreted in terms of climatic change because conifers live under all

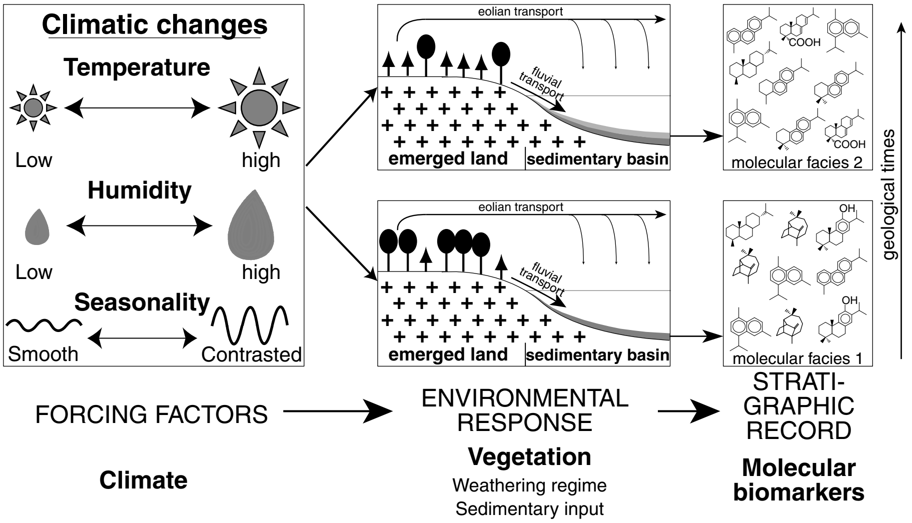


Fig. 1. Main factors implied in the stratigraphic record for palaeoclimatic and palaeoflora changes by molecular biomarkers.

climates. Thus, it is absolutely necessary to define a palaeoflora change with more precision in order to specify the nature of the climatic change.

This paper concerns Callovo-Oxfordian sedimentary series located at the North and East of the Paris Basin, in which a major change vascular plant biomarker distribution is recorded and described. For the first time, a change in the plant biomarker distribution is interpreted in terms of palaeoflora change and of palaeoclimatic evolution.

2. Geological setting and palaeoflora on emerged land

2.1. Geological setting

The Paris Basin (France) is an intracratonic flexural basin initiated by the post-hercynian breakdown of Pangea since the Triassic and has accumulated sediments during Meso-Cenozoic times (Guillocheau et al., 2000; Le Solleuz et al., 2004). During the Jurassic, its tropical position (between 20 and 35°N in latitude, Fig. 2), a globally warm greenhouse climate (Hallam, 1994) and a low to moderate bathymetry (Guillocheau et al., 2000) were favourable for the development of large carbonate platforms. This carbonate sedimentation was periodically interrupted by argillaceous deposits during platform drowning, which correspond to second order maximum flooding events (Jacquin et al., 1998; Guillocheau et al., 2000). The studied Callovian and Oxfordian series have successively recorded the drowning of the carbonate Bathonian–Callovian platform, the deposition of the Argiles de la Woëvre Formation from the Middle Callovian to the Lower Oxfordian, a progressive transition to carbonate facies at the end of the Lower Oxfordian and finally the development of the Middle Oxfordian carbonate platform. Major changes in clay mineralogy in the sedimentary record have previously been described in the sedimentary series (Debrabant et al., 1992; Pellenard, 2003). During the Callovian and Oxfordian, the Paris Basin was covered by a shallow epicontinental sea limited by shoals at the South and East, the Channel Basin towards England and two areas of emerged land, the Armorican and London-Brabant Massifs (Fig. 2). The London-Brabant Massif is the nearest land from the five wells investigated in the present study (cf. Section 4.1) and is probably the main source of detrital clays and organic matter deposited in this area.

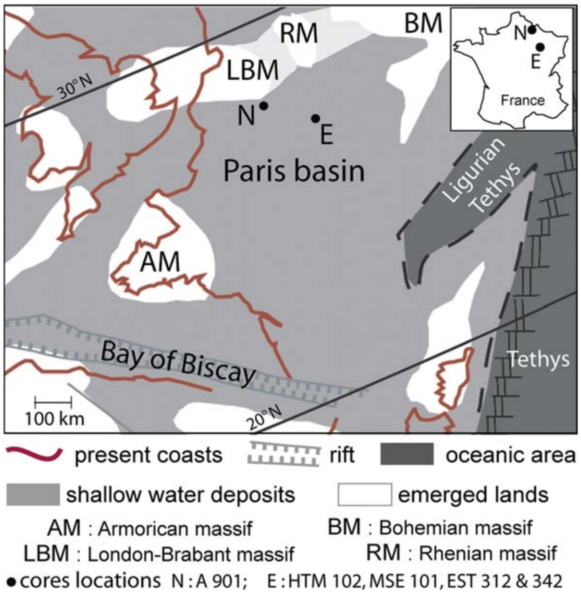


Fig. 2. Palaeogeographic map of Western Europe at the Dogger/Malm boundary (modified from Dercourt et al., 2000).

2.2. Palaeoflora on emerged land

The palaeobotanical classification used in this study is summarized in Table 1. Vascular plants (Tracheophyta) are classically divided into two phylums, Pteridophyta and Spermatophyta (seed plants). The Spermatophyta phylum is divided into two sub-phylums, Gymnospermae and Angiospermae. Gymnosperms were very abundant during the Jurassic, which is sometimes called the "Age of Gymnosperms" while angiosperms appeared during the Early Cretaceous (Crane et al., 1995) and do not concern this study. The term gymnosperm is used *s.l.* in the present paper and includes numerous Jurassic-living orders as Ginkgoales, Cycadales, Bennettitales, Caytoniales and the most diversified Coniferales. Conifers were also abundant and were represented by various extant families like Araucariaceae, Cupressaceae, Pinaceae, Podocarpaceae, Taxodiaceae and the extinct Cheirolepidiaceae (Lemoigne, 1988).

Predominant plants in the Middle Floristic Province defined by Lemoigne (1988), in which the studied area occurs, are Pteridophyta, Bennettitales, Cycadales, Ginkgoales and Caytoniales. Barale (1981) reported the presence of Filicales (ferns), Cycadales, Bennettitales, Coniferales and more particularly Araucariaceae in the Upper Jurassic of Jura (France). Lemoigne and Thierry (1968) reported the presence of Pteridophyta, Bennetti-

Table 1
Palaeobotanical classification followed in this work

	Phylum	Sub-phylum	Orders
Tracheophyta presence of a structured and lignified vascular system	**Spermatophyta or Phanerogams** seed plants	Angiospermae	Not represented in this study
		Gymnospermae s.l. non-flowering plants	Ginkgoales, Cycadales, Caytoniales, Bennettitales, Coniferales (conifers[a])
	Pteridophyta plants without seeds		Psilophytales, Lycopodiales, Equisetales, Filicales (ferns)
Thallophyta absence of a structured and lignified vascular system	**Bryophyta** (mosses, liverworts...)		
	Fungi, Algae		

[a] Conifers are divided into many families (Araucariaceae, Cupressaceae, Pinaceae, Podocarpaceae, Taxodiaceae, Cheirolepidiaceae).

tales, Araucariaceae and Cupressaceae in Callovo-Oxfordian series from Burgundy (France).

Care must be taken with these palaeobotanical reports because they are based on uncommon and exceptional deposits, leading to a low spatial-temporal resolution of the palaeobotanical stratigraphic record. Many palaeoxylology studies on Jurassic fossil woods of France also provide information on ancient floras (Philippe and Thévenard, 1996; Philippe et al., 1998; Garcia et al., 1998). These studies indicate the presence of Taxodiaceae as well as of a conifer mangal in the Middle Bathonian and the Middle Oxfordian of Franche-Comté (Eastern France). Palynology was essentially used for biostratigraphy and less for palaeobotany studies because, as xylomorphs, palynomorphs do not necessarily correspond to well-identified botanical taxa. Also, the presence of conifer pollen and the increase in spore pollen abundance in the East of the Paris Basin during the Oxfordian were reported (e.g. Rauscher and Schmitt, 1990; Huault et al., 1995, 2003).

Palaeoflora described on emerged land bordering the Paris Basin during the Jurassic is quite consistent with typical Jurassic vegetation. Indeed, Pteridophyta (notably Filicales), Cycadales, Ginkgoales, Bennettitales, Caytoniales and Coniferales are reported in Jurassic taphofloras all over the world (Vakhrameev, 1991; Stewart and Rothwell, 1993; Taylor and Taylor, 1993).

3. Major Jurassic vascular plant biomarkers and their palaeochemotaxonomic significance

3.1. Sesquiterpenoids

Sesquiterpenoid biomarkers derived from vascular plants occur frequently in sediments and crude oils. Some are non-specific, like dihydro-*ar*-curcumene ($C_{15}H_{24}$, **I**), isodihydro-*ar*-curcumene ($C_{15}H_{24}$, **II**) and their enantiomers because they derive from bisabolanes which are widespread in vascular plants (Bastow et al., 1997). On the other hand, others are very specific, like the cedranes as α-cedrene ($C_{15}H_{24}$, **III**) and cuparanes as cuparene ($C_{15}H_{22}$, **IV**), which have a Cupressaceae or a Taxodiaceae origin (Grantham and Douglas, 1980; Otto et al., 1999; Otto and Wilde, 2001).

Cadinenes and cadinols occur in most of the vascular plants and are degraded during diagenesis into cadalene ($C_{15}H_{28}$, **V**) via the formation of monoaromatic cadinanes and cadinenes (Simoneit, 1986; Simoneit et al., 1986). Furthermore, it is not excluded that cadalene can partly derive from cadinane class sesquiterpenoids also present in some Bryophyta, Fungi and Algae (Simoneit et al., 1986; Bordoloi et al., 1989; Elias et al., 1997). During catagenesis, cadalene can also be produced from polycadinene, a component of dammar resin synthesized by a few angiosperms like Dipterocarpaceae (van Aarssen et al., 1994). However, such an origin can be ruled out since the studied series is of pre-angiosperm age and is thermally immature (Landais and Elie, 1999).

3.2. Diterpenoids

Diterpenoids are excellent biomarkers for terrestrial plants because they are major compounds in gymnosperm tissues (Simoneit et al., 1986). Bioditerpenoids are very diversified and essentially comprise unsaturated hydrocarbons, resin acids and phenolic compounds.

Diterpenoids with a kaurane (**VI**), phyllocladane (**VII**), beyerane (**VIII**) or totarane (**IX**) skeleton derive from all conifer families except Pinaceae. Labdane (**X**) and pimarane (**XI**) diterpenoids are generic conifer biomarkers (Noble et al., 1985, 1986; Otto et al., 1997; Otto and Wilde, 2001). Abietane-class diterpenoids constitute an important class in palaeochemotaxonomy; although they are also widespread among conifers. Indeed, abietanoic acids such as abietic acid ($C_{20}H_{30}O_2$, **XII**) are major compounds of ancient and modern Pinaceae resins (Otto and Wilde, 2001; Otto and Simoneit, 2001, 2002; Rezzi et al., 2005). Many diagenetic pathways for abietic acid have been proposed and all lead to the formation of retene ($C_{18}H_{18}$, **XIII**) via intermediate compounds such as dehydroabietic acid ($C_{20}H_{28}O_2$, **XIV**), dehydroabietins (18-norabieta-8,11,13-triene, $C_{19}H_{28}$, **XV** and 19-norabieta-8,11,13-triene, $C_{19}H_{28}$, **XVI**), simonellite ($C_{19}H_{24}$, **XVII**) and tetrahydroretene ($C_{18}H_{22}$, **XVIII**; e.g. Simoneit, 1986; Otto and Simoneit, 2001, 2002; Marchand-Geneste and Carpy, 2003). Also, 2- and 9-methylretenes ($C_{19}H_{21}$, **XIX**) are often associated with these aromatic abietanes (Bastow et al., 2001). Dehydroabietane ($C_{20}H_{30}$, **XX**) is a biediterpenoid synthesized by conifers but can also derive from the diagenesis of abietic acid. Norabietatetraenes ($C_{19}H_{26}$, **XXI**) can also be formed during the diagenesis of abietic acid. Under more reducing conditions, norabietanes such as fichtelite ($C_{19}H_{34}$, **XXII**) can be formed instead of retene (Simoneit, 1986; Otto and Simoneit, 2001).

Furthermore, as pointed by Otto et al. (1997), Otto and Simoneit (2001), and Stephanova et al. (2002), abietanoic acids are not the only possible precursors for retene. Actually, all abietane class bioditerpenoids, such as phenolic and ketophenolic abietanes (e.g. ferruginol, $C_{20}H_{30}O$, **XXIII**; hinokiol, $C_{20}H_{30}O_2$, **XXIV**; hinokione, $C_{20}H_{28}O_2$, **XXV**; taxodone, $C_{20}H_{28}O_3$, **XXVI** and sugiol, $C_{20}H_{28}O_2$, **XXVII**), which occur in non-Pinaceae conifer families, may be degraded to produce retene (Fig. 3). While the early diagenesis of abietanoic acids leads to the formation of dehydroabietic acid, phenolic and ketophenolic abietanes are transformed into diagenetic phenolic abietanes like 6,7-dehydroferruginol ($C_{20}H_{28}O_2$, **XXVIII**), 12-hydroxysimonellite ($C_{19}H_{24}O_2$, **XXIX**), 18-norferruginol ($C_{19}H_{28}O_2$, **XXX**) and 3-oxo-12-hydroxysimonellite ($C_{19}H_{22}O_2$, **XXXI**; Otto and Simoneit, 2001; Stephanova et al., 2002); 6,7-dehydroferruginol, 12-hydroxysimonellite and 3-oxo-12-hydroxysimonellite are degraded to simonellite while 18-norferruginol is converted to 18-norabieta-8,11,13-triene. Thus, retene is a semi-specific biomarker of conifers, which cannot be used to distinguish between their different families, while some of its less altered precursors can. Therefore, this study focusses on precursors and reaction intermediates of retene in order to determine which

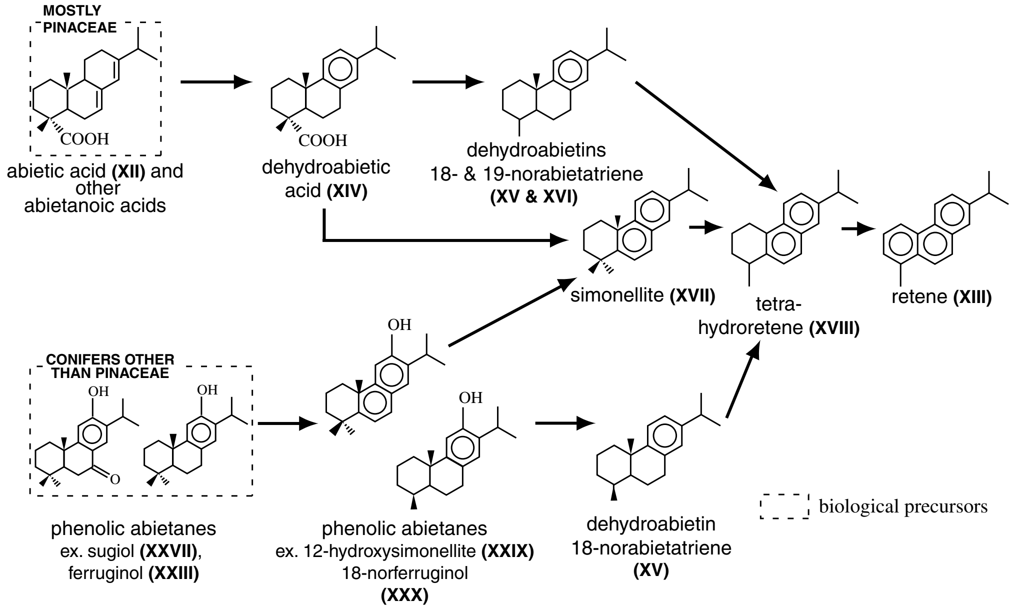


Fig. 3. Simplified diagenetic pathway for the degradation of abietane class bioditerpenoids (synthesized from Simoneit, 1986; Simoneit et al., 1986; Otto and Simoneit, 2001; Stephanova et al., 2002).

precise conifer families contribute to sedimentary organic matter.

Table 2 summarizes the occurrence of these structural classes among conifer families. Even if Table 2 appears to be a useful tool for palaeochemotaxonomy, some limitations must be pointed out:

1. Chemical intra-family variability is not taken into account. Indeed, the terpenoid distribution is not rigorously identical among all species of a family and can vary slightly within the same species as a function of habitat.
2. Only few fossil and modern genera have been analysed within each family.
3. Major compounds detected in most of the representatives of the same family have been taken into account, but it cannot be excluded that varying proportions of markers specific to other families occur in some species.
4. To our knowledge, the biomarkers from fossil Cheirolepidiaceae, an extinct Mesozoic family of conifers, have never been examined.

3.3. *Dimethoxyalkylcoumarins*

Recent studies on extant and fossil ginkgolean plants show the chemotaxonomic value of two dimethoxyalkylcoumarins with $C_{14:1}$ and $C_{16:1}$ alkenyl (**XXXII**) chains, which occur, however, in low amounts (Nguyen Tu et al., 2003).

4. Experimental

4.1. *Samples*

Thick argillaceous series and their surrounding carbonate platforms deposited during the Callovian and Oxfordian (Middle/Upper Jurassic) were investigated for the presence of vascular plant biomarkers. About 150 core and cuttings samples distributed through five wells drilled for Andra (French National Radioactive Waste Management Agency) in the North-East Paris Basin were studied. Four (MSE 101, HTM 102, EST 312 and EST 342) are located in the Eastern part of the basin (Meuse and Haute-Marne) and form two transects orientated

Table 2
Occurrence of sesqui- and diterpenoids in different families of conifers

Vascular plant biomarkers	Compound numbers referring to appendix	Examples of compound	Conifer families				
			Araucariaceae	Cupressaceae	Pinaceae	Podocarpaceae	Taxodiaceae
Sesquiterpenoids							
Bisabolane class	I.–II.	Dihydro-*ar*-curcumene	X	X	X	X	X
Cedrane class	III.	α-Cedrene		X			X
Cuparane class	IV.	Cuparene		X			
Cadinane class	V.	Cadalene	X	X	X	X	X
Diterpenoids							
Kaurane class	VI.	*ent*-Kauranes	X	X		X	X
Phyllocladane class	VII.	Phyllocladanes	X	X		X	X
Beyerane class	VIII.	*ent*-Beyeranes	X	X		X	X
Totarane class	IX	Diaromatic totarane		X		X	X
Labdane class	X.	Labdanes	X	X	X	X	X
Pimarane class	XI.	Pimarane	X	X	X	X	X
Abietane-type							
Abietanoic acids	XII., XIV.	Abietic acid, dehydroabietic acid	(x)	(x)	X	(x)	(x)
Retene	XIII		X	X	X	X	X
Dehydroabietins	XV, XVI.	18- & 19-norabieta-8,11,13-trienes	X	X	X	X	X
Simonellite	XVII.		X	X	X	X	X
Tetrahydroretene	XVIII.		X	X	X	X	X
Methylretenes	XIX.		X	X	X	X	X
Dehydroabietane	XX.		X	X	X	X	X
Saturated abietanes	XXII.	Norabietanes, abietane	X	X	X	X	X
(Keto-)Phenolic abietanes	XXIII.–XXXI.	Ferruginol	X	X		X	X

Roman numbers refer to appendix. References and explanations are in the text.
X: reported in this family.
(x): Reported in this family associated with higher proportion of totaranes and/or (keto)phenolic abietanes.

NNW-SSE (15 km long) and NE-SW (30 km long). The core A 901 was drilled at Montcornet (Aisne), located in the North of the basin (Fig. 2).

4.2. Analytical procedure

Samples were crushed and then powdered to <300 μm. Soluble organic matter was extracted with dichloromethane at 100 bar and 80°C from 80 to 120 g of rock powder using an accelerated solvent extractor (DIONEX ASE 200). Steel cells filled with pulverised samples were carefully solvent-prewashed in the ASE 200. The purge gas was nitrogen. The heating phase and the static extraction times were both 5 min. Two extraction cycles were performed to ensure that the lipid fraction was completely extracted. Elemental sulfur was removed by introduction of HCl-activated copper chips in vials containing the solvent and the extract. Dichloromethane was evaporated using a Zymark TurboVap LV and the extract was left to dry overnight and weighed. The hydrocarbon fraction was separated from the polar fraction using column chromatography on alumina, eluting successively with dichloromethane and methanol/dichloromethane (50/50 v/v). Hydrocarbons were fractionated using silica gel column chromatography to recover aliphatic, aromatic and a more polar fraction by successive elution with pentane, pentane/dichloromethane (65/35 v/v) and methanol/dichloromethane (50/50 v/v). The two polar fractions were both recovered in the same vial. An aliquot of the combined polar fractions was methylated using TMAH. Aliphatic, aromatic, and polar fractions were analysed using gas chromatography–mass spectrometry (GC–MS; a HP 5890 Series II GC coupled to a HP 5971 MS; full scan and SIM modes used, with an ionising voltage of 70 eV). The column was a DB-5 J&W capillary (60 m × 0.25 mm i.d., 0.1 μm film thickness). The temperature programme was 70–315 °C at 15 °C/min to 130 °C, then 3 °C/min followed by an isothermal stage at 315 °C for 15 min. Helium was the carrier gas (1 ml/min). All fractions were diluted in hexane (4 mg/ml for aliphatic and 8 mg/ml for aromatic and polar fractions) and 1 μl of solution was injected for GC-MS analysis. Identification of compounds was made using published mass spectra and relative retention times. The cadalene to retene ratio was calculated by measuring the respective peak areas using the characteristic fragments at *m*/*z* 219 for retene and *m*/*z* 183 for cadalene.

5. Results

Dimethoxyalkylcoumarins, which seem to be specific compounds for the Ginkgoales order, are absent from our samples. This is not surprising because of their low abundance in living Ginkgos and their low preservation potential over geological time (Nguyen Tu et al., 2003).

In this study, the cadalene/retene ratio is used first because retene and cadalene are the final degradation products of the cadinane and abietane classes of compounds.

Evolution of the ratio with depth is shown in Fig. 4 for the five wells. Most of the samples located at the top of the Bathonian–Callovian platform are characterised by a greater abundance of cadalene over retene, while others show a higher proportion of retene. The ratio is very low, close to 0, in Callovo–Oxfordian claystones in the four wells from the East of the basin and relatively low in the claystones from the A 901 well.

The relative proportion of retene increases significantly and simultaneously in EST 312, HTM 102 and MSE 101 for the *cordatum* Zone. In well A 901 the retene/cadalene curve displays high frequency variations which may be due to its proximity to the London-Brabant Massif. In order to smooth these high frequency variations, we calculated a moving average for each sample, taking into account the value for the sample and those of the four surrounding samples (two below and two above). The resulting curve is relatively stable during the Callovian, then increases slightly during the *mariae* Zone and finally increases more intensively from the *cordatum* Zone. This increase in the relative proportion of retene in these wells is synchronous with the appearance of the first carbonate layers announcing the installation of the Oxfordian carbonate platform. The ratio remains high during the Middle Oxfordian and retene, almost absent beneath the *cordatum* Zone, is now one of the most predominant compounds in the aromatic fraction. However, a few samples dated from the *cordatum* Zone and the Middle Oxfordian show a lower proportion of retene.

Cadalene is associated with minor amounts of monoaromatic cadinane class sesquiterpenoids. Cuparane class and cedrane class sesquiterpenoids are not significantly present and were barely observed in low amount in a few samples. The abundance of retene is associated with other tricyclic aromatic diterpenoids with an abietane class

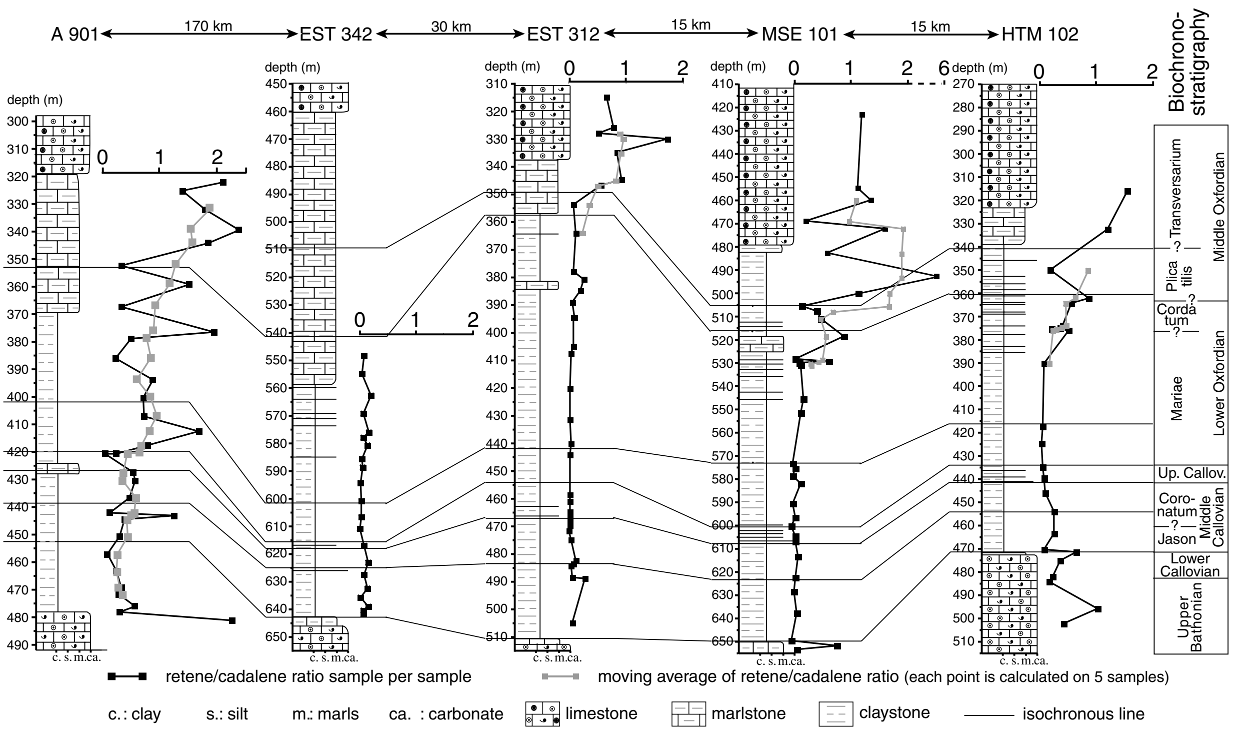


Fig. 4. Evolution of the retene/cadalene ratio from Callovian to Oxfordian in the studied wells. Values calculated by a moving average of 5 samples are represented by the grey plot lines. Correlations are made after biostratigraphic data (Thierry et al., 2006) and well log study.

skeleton, like dehydroabietane, dehydroabietins (18- and 19-norabieta-8,11,13-trienes), 1,2,3,4-tetrahydroretene, simonellite and methylretenes. These compounds were identified by comparison of their mass spectra with those published by Simoneit (1977), Philp (1985) and Bastow et al. (2001). Their abundance is strongly positively correlated with the relative abundance of retene (Fig. 5a and b).

The abundance of diterpanes, classically monitored using *m*/*z* 123 and 109 in the aliphatic fraction, is also strongly correlated with the presence of retene in the corresponding aromatic fraction. Diterpanes are almost absent from samples characterized by low retene/cadalene values and are very abundant in samples associated with high retene/cadalene values (Fig. 5c and d). Their distribution is similar in all samples in which they are significantly present. These compounds are tentatively assigned from interpretation of MS fragmentation patterns and comparison with published spectra. The compound corresponding to peak **1** (Fig. 5d) shows a short retention GC time and a mass spectrum with a molecular ion at *m*/*z* 278 ($C_{20}H_{38}$) consistent with 8β(H)-labdane (Noble et al., 1986). Compounds corresponding to the doublet of peaks **3** and **4** also have MS fragmentations similar to that of labdane and it seems likely that one of these peak corresponds to 8α(H)-labdane, whereas the second compound may be another, unknown, saturated labdane derivative. Compounds corresponding to peaks **2**, **5**–**11** all have identical spectra characterized by a molecular fragment at *m*/*z* 262, which indicates that they are $C_{19}H_{34}$ tricyclic diterpenoids. Their spectra match very well with published mass spectra of norabietane, fichtelite and their isomers (Philp, 1985; Dzou et al., 1999). The low intensity of peak **12** does not allow us to have a good quality spectrum for this compound, but its molecular ion at *m*/*z* 276 corresponds to a $C_{20}H_{36}$ tricyclic diterpane which could be abietane. These diterpanes occur in very low amounts in the A 901 samples, whatever the value of the retene/cadalene ratio. If present, tetracyclic diterpanes such as beyeranes, kauranes and phyllocladanes are below the detection limit. Fig. 6 shows the distribution of other compounds, termed **13** and **14**, using the fragment at *m*/*z* 163. These compounds display similar mass spectra, with a molecular ion at *m*/*z* 260 and an intense $M^+–CH_3$ fragment at *m*/*z* 245. They have not, to our knowledge, been described before and

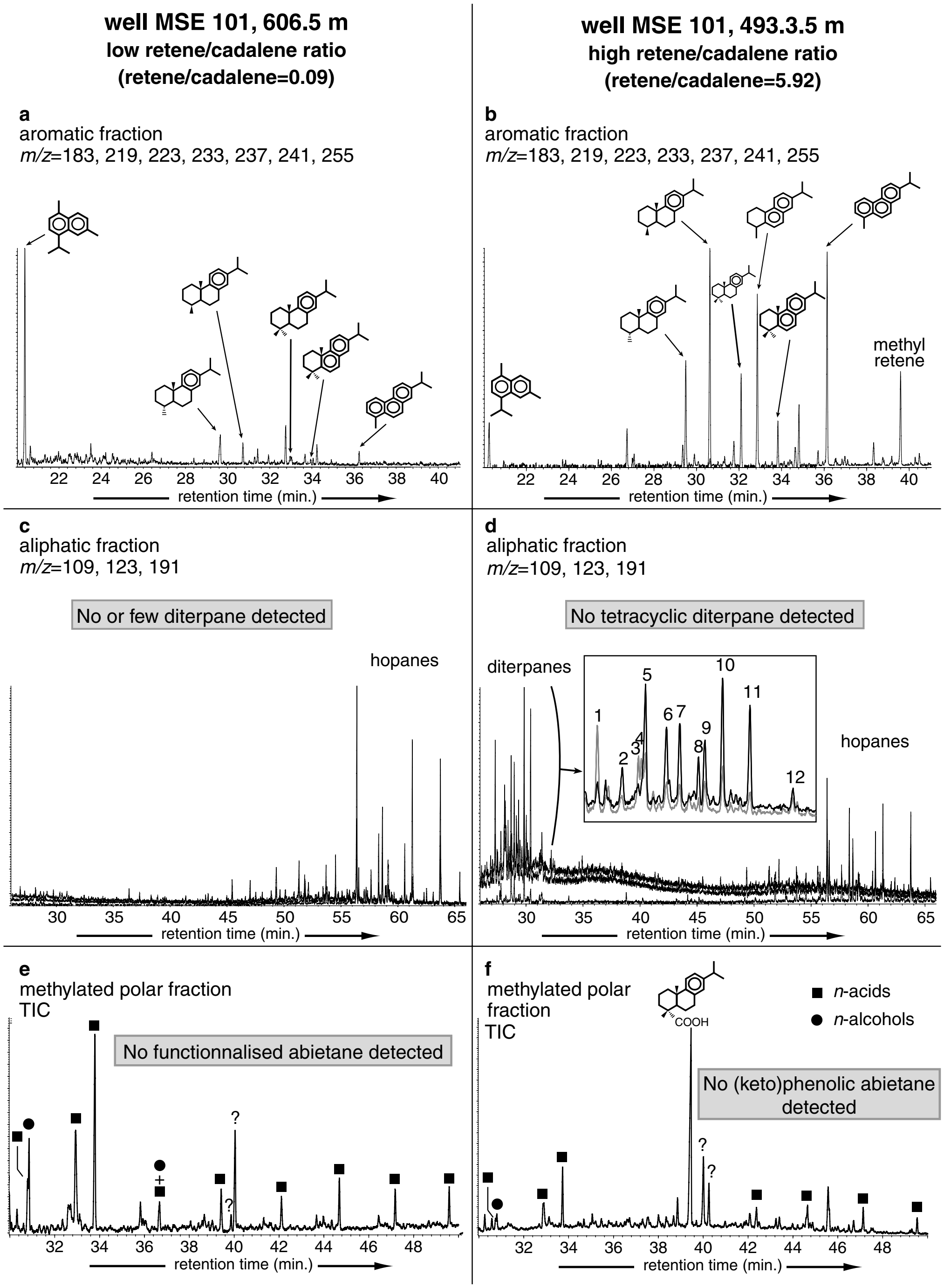


Fig. 5. GC-MS traces of the aromatic (a, b), aliphatic (c, d) and methylated polar (e, f) fractions of two samples respectively characterized by a low and a high retene/cadalene ratio.

their abundance also correlates with that of retene. Fig. 6 points out the similarities in their partial mass spectra with those of dehydroabietins. Fragments generated by these unknown compounds have 4 m/z units fewer than, and relative intensities close to, fragments for dehydroabietins. This suggests the dehydrogenation of two of the three double bonds located in ring C of dehydroabietins. Furthermore, the molecular ion at m/z 260 is also consistent with a norabietane structure with one double

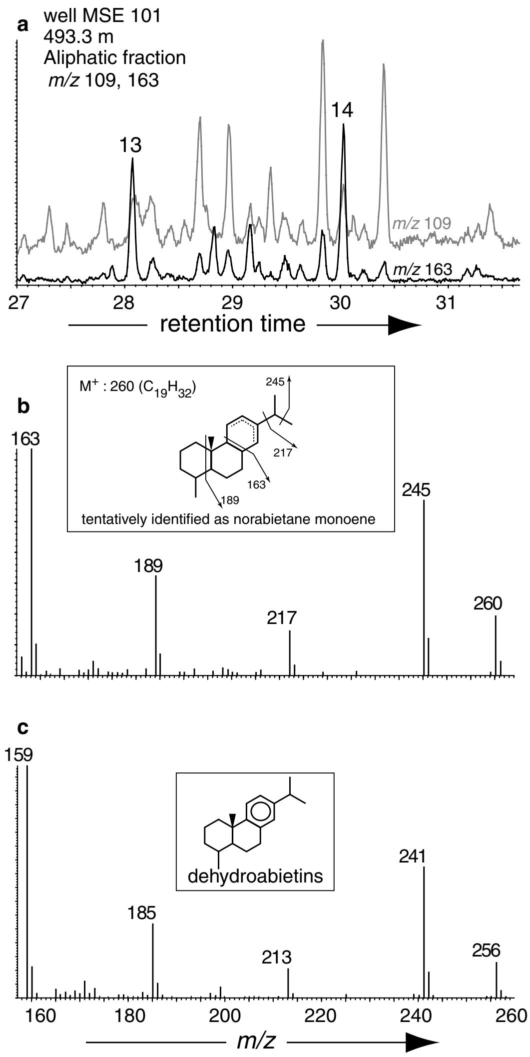


Fig. 6. Partial chromatogram of the aliphatic fraction of a sample characterized by a high retene/cadalene ratio showing two compounds **13** and **14** tentatively assigned as isomers of norabietane monoene (a). Mass spectrum of the compounds (b) compared to that of 19-norabieta-8,11,13-triene (c).

bond, so the fragmentation pattern shown in Fig. 6 can be proposed. Hence, these two compounds are tentatively assigned as two isomers of norabietane monoenes. The occurrence of diterpenes is not surprising because the studied sedimentary series also contain unsaturated terpenoids such as sesquiterpenes, diasterenes and hopenes. Norpimaranes and pimaranes, which are often found in association with abietanes and norabietanes, are not found in these extracts.

Dehydroabietic acid methyl ester (identification confirmed by co-injection with a standard) is only found in the polar fraction of the samples in which retene is detected in significant proportion (Fig. 5e and f) while (keto)phenolic abietanes and other abietanoic acids (e.g. abietic acid) are never found.

Therefore, the increase in the retene/cadalene ratio from the *cordatum* Zone does not only represent an increasing abundance of retene over cadalene but also reflects a significant change in the distribution of many vascular plant biomarkers.

6. Discussion

6.1. Significance of the change in the land plant biomarker distribution

The increase in the relative proportion of retene dated from the *cordatum* Zone takes place in conjunction with a progressive lithological transition from offshore claystone deposits to shallow-water carbonate platform, expressing a palaeobathymetric drop, as sedimentological data suggest. A possible diagenetic control for the increase in the retene/cadalene ratio due to these palaeoenvironmental and sedimentological changes can be ruled out since cadalene and retene are aromatic hydrocarbons with precursors having similar sensitivity to depositional and diagenetic conditions. In other words, any chemical factor leading to an enrichment of one of these compounds also leads to an enrichment of the other. This means that the retene/cadalene ratio is not affected by depositional and diagenetic conditions and its variation must reflect palaeoflora changes on proximal emerged land.

Therefore, the increase in retene from the *cordatum* Zone indicates a higher relative input of retene and its precursors in the sedimentary environment, in direct relationship to a major change in the palaeoflora on the London-Brabant Massif.

6.2. Nature of the palaeoflora change

Cadalene derives from cadinenes and cadinols synthesized by most land plants, like some Bryophyta, Coniferales and Ginkgoales (Bordoloi et al., 1989; Otto and Wilde, 2001; Nguyen Tu et al., 2003) and cannot be used, like its precursors, to determine the nature of the palaeoflora change.

Retene derives from abietane class bioditerpenoids which occur in conifer resins and is thus classically used as a generic biomarker for conifers. However, if some retene precursors can be used to determine which conifer family or families were present on the hinterland at the time of deposition, others, like simonellite and tetrahydroretene, are not more specific than retene since diagenetic degradation of all abietane class biditerpenoids leads to their formation (Fig. 3). However, the occurrence or absence of certain specific diterpenoids associated with retene in our samples provides useful information on the precise origin of these compounds. The high abundance of dehydroabietic acid, together with the lack of phenolic and ketophenolic abietanes, strongly suggests that these diterpenoids originate mainly from the Pinaceae family alone. Indeed, the chemical composition of Pinaceae is characterized by the abundance of abietanoic acids and the absence of (keto)phenolic abietanes. In contrast, other conifers show a lower abundance of abietanoic acids and the presence of (keto)phenolic abietanes.

Saturated diterpanes also have chemosystematic value (Noble et al., 1985, 1986; Otto and Simoneit, 2001). The presence of labdane and abietane class diterpanes, together with the absence of tetracyclic diterpanes, is also in agreement with a Pinaceae origin for diterpenoids associated with retene. Indeed, fossil Pinaceae do not contain significant proportions of kaurane, phyllocladane and beyerane, unlike other conifer families, but contain high amounts of labdane and abietane class diterpenoids (Otto et al., 1997; Otto and Simoneit, 2001; Otto and Wilde, 2001). The very low proportions of sesquiterpenoids with cuparene or cedrane structures in our samples also supports the idea that Cupressaceae and Taxodiaceae were poor contributors to the organic matter of the Callovo–Oxfordian sedimentary series; this is in agreement with fossil wood data (M. Philippe, personal communication). Thus, retene, which classically derives from a wide range of biditerpenoids produced by all conifer families, has the particularity in the Callovo-Oxfordian deposits of the North-East of Paris Basin to derive almost exclusively from abietanoic acids synthesized by Pinaceae or their forerunners. Therefore, the increase in its relative proportion vs. cadalene reflects a major palaeoflora change and more precisely an increase in the proportion of Pinaceae, or of their forerunners, on the London-Brabant Massif.

6.3. Interpretation in terms of palaeoclimatic change

Vegetation change dynamics are essentially controlled by climate (Fig. 1) but in some cases they could be ruled by tectonic events or significant palaeogeographical evolutions (Bruch and Mosbrugger, 2002). These last forcing factors are excluded in our study because neither a major tectonic event nor a palaeogeographical change is reported for the Callovian and Oxfordian in the Paris Basin (Jacquin et al., 1998; Guillocheau et al., 2000; Dercourt et al., 2000). Furthermore, as the palaeolatitude of the London-Brabant Massif did not change significantly from the Callovian to the Oxfordian (Dercourt et al., 2000), the palaeoflora change cannot be due to plate tectonic displacement of the massif through climatic zones, but rather is more convincingly due to a climatic change. Pinaceae have acquired many xeromorphic adaptations, meaning morphological adaptations to dry climate. Indeed, Pinaceae differ from other conifer families by their more or less flat needle-like leaves covered by a thick layer of epicuticular waxes with stomata sunk in wells or furrows below the leaf surface. These xeromorphic adaptations reduce considerably evapo-transpiration and allow them to colonize arid regions. Furthermore, other conifer families, which do not show morphological adaptation to dry climate, preferentially settle in humid environments in which Pinaceae are absent or poorly represented. Indeed, Meso-Cenozoic swamps and peat have been intensively studied by palaeobotanists, palynologists and organic geochemists who report the abundance of Podocarpaceae, Cupressaceae, Araucariaceae and Taxodiaceae fossils, pollens and biomarkers while those of Pinaceae are seldom mentioned (e.g. Bechtel et al., 2002; Stephanova et al., 2002). Extant Cycadales live under equatorial and tropical climates without important climatic fluctuations (Jones, 1993). Ferns preferentially colonize humid zones (Van Konijnenburg-Van Cittert, 2002) and their spores and fossils are often reported in ancient swamps and peat (e.g. Wang, 2002; Eble et al., 2003). Bennettitales are also excellent climatic markers because they are restricted to tropical and subtropical regions (Vakhrameev, 1991).

Consequently, the increasing proportion of Pinaceae within flora rather adapted to a tropical, then humid, climate indicates undoubtedly an increase in aridity.

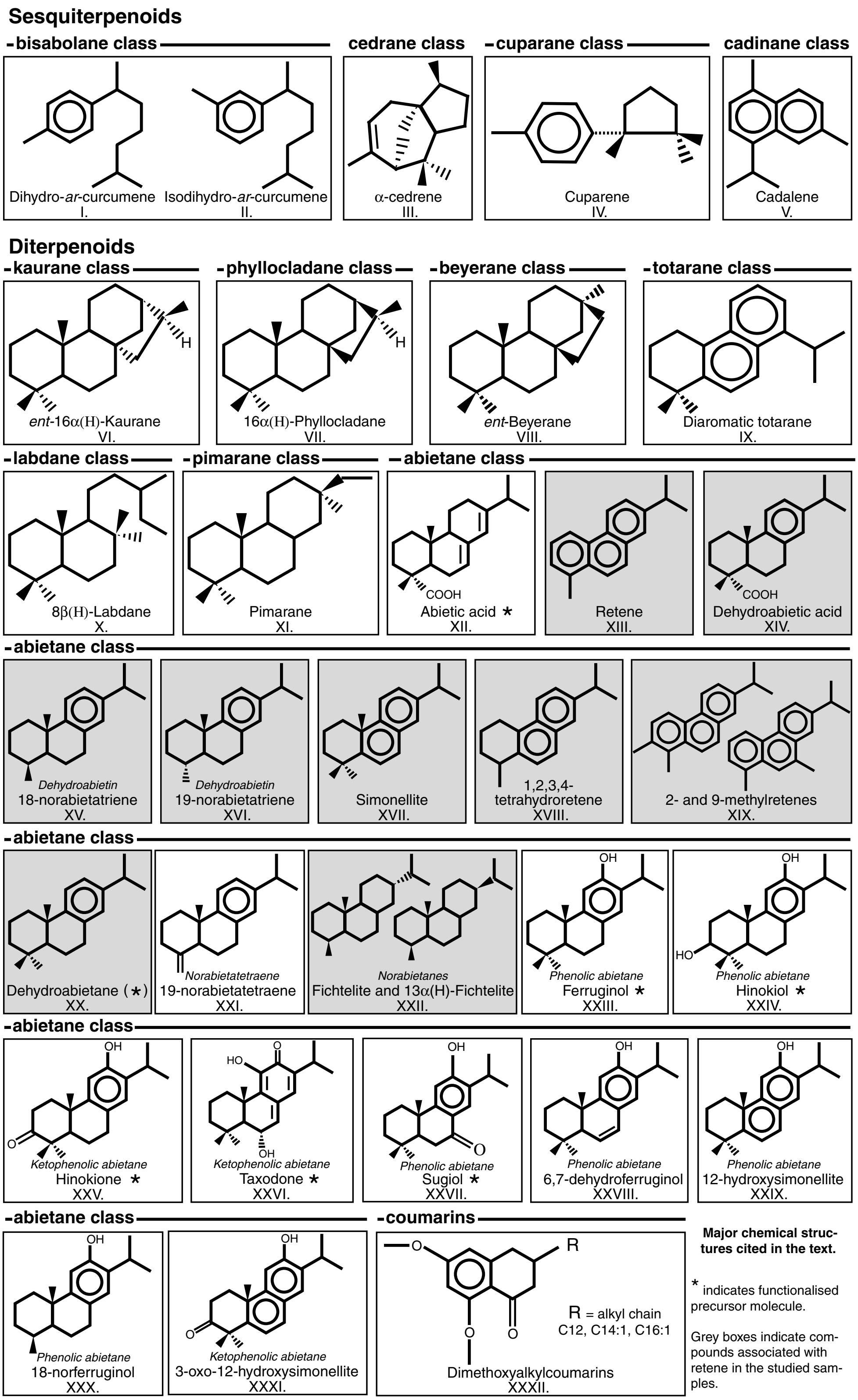
Many studies have pointed out a climatic change at the end of Early Oxfordian. Palaeothermometric data indicate a warming of oceanic water at the European scale (Riboulleau et al., 1998 and references therein) which explains diverse shifting of biogeographical boundaries toward the North either for reefs and corals or for cephalopods (Martin-Garin, 2005; Cecca et al., 2005). Abbink et al. (2001) also highlight a sharp warming associated with an increase in aridity on land just after the end of the *cordatum* Zone (*plicatilis* Zone), using palynological studies of cores drilled in England. Kaolinite is a clay mineral produced by the intense hydrolysis of soils under a wet climate (Chamley, 1989). At the British and Paris Basins scale, the relative proportion of kaolinite compared to other clay minerals largely decreases, and sometimes disappears, between the *mariae* and *transversarium* Zones in many localities. This change in clay mineralogy is also interpreted as a progressive drying from the Lower to Middle Oxfordian (Pellenard, 2003). Worldwide palaeoclimatic maps drawn by Rees et al. (2000) using foliar morphologies observed worldwide in fossil plants show that the London-Brabant Massif was in the Warm Temperate Zone during the Middle Jurassic and in the Winterwet Zone during the Late Jurassic.

This means that through the Dogger/Malm boundary, the climate of the London-Brabant Massif, initially warm and moderately humid, became globally dryer with one humid season.

A similar increase in the retene proportion, quantified by the "higher plant parameter (HPP), has been described by van Aarssen et al. (2000) for Oxfordian sedimentary rocks from three wells located in Carnarvon Basin (Western Australia) and at least 1500 km apart. During the Middle and Late Jurassic, this basin was positioned at a similar longitude to the Paris Basin but at latitude 40–50 °S (after maps of Rees et al., 2000). This evolution was also interpreted as a palaeovegetation and palaeoclimatic global change by the authors. Moreover, it took place during a well recognized climatic change in Australia. Such evolution in vascular plant biomarkers, occurring during the same time interval in two regions thousands of kilometres apart, strongly suggests a worldwide drying event. Furthermore, these same authors (i.e. van Aarssen et al., 2000) showed that the HPP evolves cyclically from the Toarcian to the Barriasian and that this cyclicity is of a second-order sensu Vail (periods of 10–45 Ma). This type of cyclicity is under the control of global scale forcing factors (Vail et al., 1991). This is the second argument in favour of a worldwide drying event during the Oxfordian.

7. Conclusions

At the North-East of the Paris Basin, the progressive development of the Oxfordian carbonate platform above the argillaceous facies dated from the *cordatum* Zone occurs in conjunction with a major modification of the composition of vascular plant biomarkers. This change is marked by an increase in the relative proportion of certain diterpenoids compared to the proportion of cadinane class sesquiterpenoids represented in this study by the retene/cadalene ratio. Abietane class diterpenoids are characterized by the presence of dehydroabietic acid, which has abietanoic acids as precursors, while neither phenolic abietanes nor tetracyclic diterpanes were significantly detected. This molecular association strongly suggests a single Pinaceae origin for these diterpenoids. The major increase in the relative abundance of these diterpenoids from the *cordatum* Zone indicates that Pinaceae became more prevalent on the London-Brabant Massif. Because palaeoflora change dynamics are essentially under climate control and Pinaceae are more adapted to an arid climate than other taxa, as reported from palaeobotanical studies, the increasing proportion of Pinaceae must reflect a drying event at the end of the Lower Oxfordian. In addition, this climatic change is supported by isotopic palaeothermometry, palynology, palaeobiogeography, clay mineralogy and plant morphology data. The increase in the retene/cadalene ratio is finally compared to the evolution of the "higher plant fingerprint" of retene (HPF) and the "higher plant parameter (HPP), which also show an increase in the relative proportion of retene in Oxfordian sedimentary series of Western Australia. The similar increase in the relative proportion of retene during the Oxfordian at very distant locations supports the hypothesis of a global drying event. Palaeochemotaxonomy appears to be an innovative and effective stratigraphic tool for tracing palaeoflora and palaeoclimatic changes during geological time. Palynology and palaeoxylology are usually used to assess palaeoflora but, unfortunately, good preservation of fossil spores, pollens and woods is not common, so these cannot be easily linked to precise botanic taxa. This work highlights the idea that palaeochemotaxonomy is an excellent complementary tool to palaeobotany, palynology and palaeoxylology and can significantly contribute to palaeoclimatic assessment.



Major chemical structures cited in the text.

* indicates functionalised precursor molecule.

Grey boxes indicate compounds associated with retene in the studied samples.

Fig. 7.

Acknowledgements

We thank Andra (the French National Radioactive Waste Management Agency) for financial support and for providing samples, and more particularly Hervé Rebours and Patrick Landais. We are grateful to Bernard Lathuilière, Vincent Huault, Stéphanie Fleck, Marcel Elie, Pierre Faure (University Henri Poincaré, Nancy 1), Marc Philippe (Université Claude Bernard, Lyon 1), and Hervé Chamley for fruitful discussions. Angelika Otto (University of Toronto) is thanked for providing bibliography and for some comments. We are also grateful to Philippe Schaeffer for helpful comments and for provision of the dehydroabietic acid standard. The two reviewers, Ben van Aarssen and Jacques Connan are thanked for their valuable suggestions in revising the manuscript.

Appendix

See Fig. 7.

Associate Editor—**P. Schaeffer**

References

Abbink, O., Targarona, J., Brinkhuis, H., Visscher, H., 2001. Late Jurassic to earliest Cretaceous palaeoclimatic evolution of the southern North Sea. Global Planetary Change 30, 231–256.

Barale, G., 1981. La paléoflore jurassique du Jura français. Etude systématique. Aspects stratigraphiques et paléoécologiques. Documents des Laboratoires de Géologie de Lyon 81.

Barale, G., 1990. Les stratégies adaptatives chez les végétaux du Trias supérieur au Crétacé inférieur dans l'aire eurosinienne, en relation avec l'évolution du climat. Comptes Rendus de l'Académie des Sciences de Paris 311, 265–269.

Bastow, T.P., Alexander, R., Kagi, R., 1997. Identification and analysis of dihydro-*ar*-curcumene enantiomers and related compounds in petroleum. Organic Geochemistry 26, 79–83.

Bastow, T.P., Singh, R.K., van Aarssen, B.G.K., Alexander, R., Kagi, R.I., 2001. 2-Methylretene in sedimentary material: a new higher plant biomarker. Organic Geochemistry 32, 1211–1217.

Bechtel, A., Sachsenhofer, R.F., Kolcon, I., Gratzer, R., Otto, A., Püttmann, W., 2002. Organic geochemistry of the lower Miocene Oberdorf lignite (Styrian Basin, Austria): its relation to petrography, palynology and the palaeoenvironment. International Journal of Coal Geology 51, 31–57.

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

Bruch, A.A., Mosbrugger, V., 2002. Palaeoclimate versus vegetation reconstruction—palynological investigations on the Oligocene sequence of the Sava Basin, Slovenia. Review of Palaeobotany and Palynology 122, 117–141.

Caldicott, A.B., Eglinton, G., 1973. Surface waxes. In: Miller, L.P. (Ed.), Phytochemistry, Inorganic Elements and Special Groups of Chemicals, vol. 3. Van Nostrand Reinhold, New York, p. 162.

Cecca, F., Martin Garin, B., Marchand, D., Lathuilière, B., Bartolini, A., 2005. Palaeoclimatic control of biogeographic and sedimentary events in Tethyan and Peri-Tethyan areas during the Oxfordian (Late Jurassic). Palaeogeography Palaeoclimatology Palaeoecology 222, 10–32.

Chamley, H., 1989. Clay Sedimentology. Springer-Verlag, Berlin.

Crane, P.R., Friis, E.M., Pedersen, K.R., 1995. The origin and early diversification of angiosperms. Nature 374, 27–33.

Debrabant, P., Chamley, H., Deconinck, J.-F., Recourt, P., Trouiller, A., 1992. Clay sedimentology, mineralogy and chemistry of Mesozoic sediments drilled in the Northern Paris Basin. Scientific Drilling 3, 138–152.

Dercourt, J., Gaetani, M., Vrielynck, B., Barrier, E., Biju-Duval, B., Brunet, M.F., Cadet, J.P., Crasquin, S., Sandulescu, M. (Eds.), 2000. Atlas Peri–Tethys, Palaeogeographical Maps. CCGM/CGMW, 24 Maps and Explanatory Notes: I–XX.

Dzou, L.I., Holba, A.G., Ramón, J.C., Moldowan, J.M., Zinniker, D., 1999. Application of new diterpane biomarkers to source, biodegradation and mixing effects on Central Llanos Basin oils, Colombia. Organic Geochemistry 30, 515–534.

Eble, C.F., Pierce, B.S., Grady, W.C., 2003. Palynology, petrography and geochemistry of the Sewickley coal bed (Monongahela Group, Late Pennsylvanian), Northern Appalachian Basin, USA. International Journal of Coal Geology 55, 187–204.

Elias, V.O., de Barros, A.M.A., de Barros, A.B., Simoneit, B.R.T., Cardoso, J.N., 1997. Sesquiterpenoids in sediments of a hypersaline lagoon: a possible algal origin. Organic Geochemistry 26, 721–730.

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 48, 65–88.

Fleck, S., Michels, R., Ferry, S., Malartre, F., Elion, P., Landais, P., 2002. Organic geochemistry in a sequence stratigraphic framework. The siliciclastic shelf environment of Cretaceous series, SE France. Organic Geochemistry 33, 1533–1557.

Garcia, J.-P., Philippe, M., Gaumet, F., 1998. Fossil wood in Middle-Upper Jurassic marine sedimentary cycles of France: relations with climate, sea-level dynamics, and carbonate-platform environments. Palaeogeography Palaeoclimatology Palaeoecology 141, 199–214.

Grantham, P.J., Douglas, A.G., 1980. The nature and origin of sesquiterpenoids in some tertiary fossil resins. Geochimica et Cosmochimica Acta 44, 1801–1810.

Guillocheau, F., Robin, C., Allemand, P., Bourquin, S., Brault, N., Dromart, G., Friedenberg, R., Garcia, J.-P., Gaulier, J.-M., Gaumet, F., Grosdoy, B., Hanot, F., Le Strat, P., Mettraux, M., Nalpas, T., Prijac, C., Rigollet, C., Serrano, O., Grandjean, G., 2000. Meso-Cenozoic geodynamic evolution of the Paris Basin: 3D stratigraphic constraints. Geodinamica Acta 13, 189–246.

Hallam, A., 1994. Jurassic climate inferred by the sedimentary and fossil record. In: Allen, J.R.L., Hoskins, B.J., Sellwood, B.W., Spicer, R.A., Valdes, P.J. (Eds.), Paleoclimates and their Modelling. Chapman & Hall, The Royal Society, pp. 79–88.

Huault, V., Merzeraud, G., Rauscher, R., Schuler, M., 1995. Palynological variations and sedimentary cycles in the Jurassic from Paris basin. Review of Palaeobotany and Palynology 87, 27–41.

Huault, V., Elie, M., Ruck-Mosser, R., 2003. Variabilité spatiale du signal palynologique dans le bassin de Paris à la limite Dogger-Malm. Comptes Rendus Geoscience 335, 401–409.

Jacquin, T., Dardeau, G., Durlet, C., De Graciansky, P.-C., Hantzpergue, P., 1998. The North Sea cycle: an overview of 2nd order transgressive/regressive facies cycles in Western Europe. In: De Graciansky, P.-C. et al. (Eds.), Mesozoic and Cenozoic Sequence Stratigraphy of European Basins, vol. 60. SEPM Special Publication, pp. 445–466.

Jiang, C., Alexander, R., Kagi, R., Murray, A.P., 1998. Polycyclic aromatic hydrocarbons in ancient sediments and their relationship to palaeoclimate. Organic Geochemistry 29, 1721–1735.

Jones, D.L., 1993. Cycads of the World, Ancient Plants in Today's Landscape. The New York Botanical Garden, New York.

Killops, S.D., Massoud, M.S., 1992. Polycyclic aromatic hydrocarbons of pyrolytic origin in ancient sediments: evidence for Jurassic vegetation fires. Organic Geochemistry 18, 1–7.

Landais, P., Elie, M., 1999. Utilisation de la géochimie organique pour la détermination du paléoenvironnement et de la paléothermicité dans le Callovo–Oxfordien du site de l'Est de la France. In : Etude de l'Est du Bassin Parisien. Actes des Journées Scientifiques CNRS/ANDRA. EDP Sciences, pp. 35–61.

Le Solleuz, A., Doin, M.-P., Robin, C., Guillocheau, F., 2004. From a mountain belt collapse to a sedimentary basin development: 2-D thermal model based on inversion of stratigraphic data in the Paris Basin. Tectonophysics 386, 1–27.

Lemoigne, Y., 1988. La Flore au Cours des Temps Géologiques. Geobios Mémoire Spécial 2 (10).

Lemoigne, Y., Thierry, J., 1968. La paléoflore du Jurassique moyen de Bourgogne. Bulletin de la Société Géologique de France 10, 323–333.

Marchand-Geneste, N., Carpy, A., 2003. Theorical study of the thermal degradation pathways of abietane skeleton diterpenoids: aromatization to retene. Journal of Molecular Structure–Theochem 635, 55–82.

Martin-Garin, B., 2005. Climatic control of Oxfordian coral reef distribution in the Tethys Ocean including a comparative survey of Recent coral communities (Indian Ocean) and a new method of coral morphometrics based on fractal dimensions. Ph.D. thesis, University of Bern.

Nguyen Tu, T.T., Derenne, S., Largeau, C., Mariotti, A., Bocherens, H., 2003. Comparison of leaf lipids from a fossil ginkgoalean plant and its extant counterpart at two degradation stages: diagenetic and chemotaxonomic implications. Review of Palaeobotany and Palynology 134, 63–78.

Noble, R.P., Alexander, R., Kagi, R.I., Knox, J., 1985. Tetracyclic diterpenoid hydrocarbons in some Australian coals, sediments and crude oils. Geochimica et Cosmochimica Acta 49, 2141–2147.

Noble, R.P., Alexander, R., Kagi, R.I., Knox, J., 1986. Identification of some diterpenoid hydrocarbons in petroleum. Organic Geochemistry 10, 825–829.

Otto, A., Simoneit, B.R.D., 2001. Chemosystematics and diagenesis of terpenoids in fossil conifer species and sediment from the Eocene Zeitz Formation, Saxony, Germany. Geochimica et Cosmochimica Acta 65, 3505–3527.

Otto, A., Wilde, V., 2001. Sesqui-, di- and triterpenoids as chemosystematic markers in extant conifers—A review. The Botanical Review 67, 141–238.

Otto, A., Simoneit, B.R.D., 2002. Biomarkers of Holocene buried conifer logs from Bella Coola and North Vancouver, British Columbia, Canada. Organic Geochemistry 33, 1241–1251.

Otto, A., Walther, H., Püttmann, W., 1997. Sesqui- and diterpenoid biomarkers preserved in *Taxodium*-rich Oligocene Oxbow Lake Clays, Weisselster basin, Germany. Organic Geochemistry 26, 105–115.

Otto, A., Kvacek, J., Goth, K., 1999. Biomarkers from the taxodiaceous conifer *Sphenolepsis pecinovensis* and isolated resin from Bohemian Cenomanian. Acta Palaeobotanica Supplement 2, 153–157.

Otto, A., Simoneit, B.R.D., Wilde, V., Kunzmann, L., Püttmann, W., 2002a. Terpenoid composition of three fossil resins from Cretaceous and Tertiary conifers. Review of Palaeobotany and Palynology 120, 203–215.

Otto, A., White, J.D., Simoneit, B.R.D., 2002b. Natural product terpenoids in Eocene and Miocene conifer fossils. Science 297, 1543–1544.

Pancost, R.D., Boot, C.S., 2004. The palaeoclimatic utility of terrestrial biomarkers in marine sediments. Marine Chemistry 92, 239–261.

Pellenard, P., 2003. Message terrigène et influences volcaniques au Callovien-Oxfordien dans les bassins de Paris et du Sud–Est de la France. Ph.D. thesis, Université de Lille. Société Géologique du Nord, Publ. 31.

Philippe, M., Thévenard, F., 1996. Distribution and palaeoecology of the Mesozoic wood genus Xenoxylon: palaeoclimatological implications for the Jurassic of Western Europe. Review of Palaeobotany and Palynology 40, 353–370.

Philippe, M., Thévenard, F., Barale, G., Ferry, S., Guignard, G., 1998. Middle Bathonian floras and phytocoenoses of France. Palaeogeography Palaeoclimatology Palaeoecology 143, 135–158.

Philp, R.P., 1985. Fossil Fuel Biomarkers. Applications and Spectra. Elsevier, Amsterdam.

Rauscher, R., Schmitt, J.-P., 1990. Recherches palynologiques dans le Jurassique d'Alsace (France). Review of Palaeobotany and Palynology 62, 145–190.

Rees, P.M., Ziegler, A.M., Valdes, P.J., 2000. Jurassic phytogeography and climates: new data and model comparisons. Available from: <http://pgap.uchicago.edu/Reesetal2000.html)>.

Rezzi, S., Bighelli, A., Castola, V., Casanova, J., 2005. Composition and chemical variability of the oleoresin of *Pinus nigra* ssp. *laricio* from Corsica. Industrial Crops and Products 21, 71–79.

Riboulleau, A., Baudin, F., Daux, V., Hantzpergue, P., Renard, M., Zakharov, V., 1998. Evolution de la paléotempérature des eaux de la plate-forme russe au cours du Jurassique supérieur. Comptes Rendus de l'Académie des Sciences de Paris 326, 239–246.

Simoneit, B.R.D., 1977. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochimica et Cosmochimica Acta 41, 463–476.

Simoneit, B.R.D., 1986. Cyclic terpenoids of the geosphere. In: Johns, R.B. (Ed.), Biological Markers in the Sedimentary Record. Elsevier, Amsterdam, pp. 43–99.

Simoneit, B.R.D., 2002. Biomass burning—a review of organic tracers for smoke from incomplete combustion. Applied Geochemistry 17, 129–162.

Simoneit, B.R.D., Grimalt, J.O., Wang, T.G., Cox, R.E., Hatcher, P.G., Nissenbaum, A., 1986. Cyclic terpenoids of contemporary resinous plant detritus and of fossil woods, ambers and coals. Organic Geochemistry 10, 877–889.

Staccioli, G., McMillian, N.J., Meli, A., Bartolini, G., 2002. Chemical characterisation of a 45 million year bark from Geodetic Hills forest, Axel Heiberg Island, Canada. Wood Science and Technology 36, 419–427.

Stephanova, M., Oros, D.R., Otto, A., Simoneit, B.R.D., 2002. Polar aromatic biomarkers in the Miocene Maritza–East lignite, Bulgaria. Organic Geochemistry 33, 1079–1091.

Stewart, W.N., Rothwell, G.W., 1993. Paleobotany and the Evolution of Plants. Cambridge University Press, Cambridge.

Swain, T., 1965. Chemical Plant Taxonomy. Academic Press, New York.

Taylor, T.N, Taylor, E.L., 1993. The Biology and Evolution of Fossil Plants. Prentice-Hall, New Jersey.

Thierry, J., Marchand, D., Fortwengler, D., Bonnot, A., 2006. Les faunes d'ammonites des sondages Andra: bio-chrono-stratigraphie des séries callovo-oxfordiennes de l'Est du Bassin de Paris. Comptes Rendus Geoscience, in press.

Vail, P.R., Audemard, F., Bowman, S.A., Eisner, P.N., Perez-Cruz, C., 1991. The stratigraphic signatures of tectonics, eustasy, and sedimentology—an overview. In: Einsele, G., Ricken, W., Seilacher, A. (Eds.), Cycles and Events in Stratigraphy. Springer Verlag, Berlin, Heidelberg, pp. 617–659.

Vakhrameev, V.A., 1991. Jurassic and Cretaceous Floras and Climates of the Earth. Cambridge University Press, Cambridge.

van Aarssen, B.G.K., de Leeuw, J.W., Collinson, J., Boon, J.J., Goth, K., 1994. Occurrence of polycadinene in fossil and recent resins. Geochimica et Cosmochimica Acta 58, 223–229.

van Aarssen, B.G.K., Alexander, R., Kagi, R., 2000. Higher plant biomarkers reflect palaeovegetation changes during Jurassic times. Geochimica et Cosmochimica Acta 64, 1417–1424.

Van Konijnenburg-Van Cittert, J.H.A., 2002. Ecology of some Late Triassic to Early Cretaceous ferns in Eurasia. Review of Palaeobotany and Palynology 119, 113–124.

Wang, Y., 2002. Fern ecological implications from the Lower Jurassic in Western Hubei, China. Review of Palaeobotany and Palynology 119, 125–141.

Woolhouse, A.D., Oung, J.N., Philp, R.P., Weston, R.J., 1992. Triterpanes and ring-A degraded triterpanes as biomarkers characteristic of Tertiary oils derived from predominantly higher plant sources. Organic Geochemistry 18, 23–31.