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Biomarkers as proxies for plant inputs to peats: an example from a sub-boreal ombrotrophic bog

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Abstract

Lipid distributions in modern peat-forming plants were determined and compared to biomarkers recovered from a ca. 2800 year old peat deposited in a Dutch ombrotrophic bog. The peat section spans a well-constrained shift in local hydrology and vegetation, and potential molecular proxies for plant inputs were directly tested against the macrofossil record. Based on the analyses of modern plants, low-molecular-weight (LMW) *n*-alkanes (C_{23}, C_{25}) and high-molecular-weight *n*-alkanes (C_{33}) are proposed as potential biomarkers for *Sphagnum* and non-*Sphagnum* inputs, respectively. Consistent with this, in the Bargerveen peat core, LMW *n*-alkane abundances increase and HMW *n*-alkane abundances decrease coincident with the shift to *Sphagnum* dominated peat. Additional potential proxies include the abundances of C_{22} α,ω-alkanedioic acid and phytenyl phytenoate as *Sphagnum* indicators and the abundances of the triterpenoids taraxer-14-ene and taraxast-20-ene as biomarkers for Ericaceae rootlets. © 2002 Published by Elsevier Science Ltd.

1. Introduction

The hydrology of ombrotrophic mires is governed by precipitation and evaporation (Barber, 1993), such that the prevailing vegetation reflects the local climatic conditions. Moreover, sediment accumulation rates in mires are high, allowing the development of high-resolution climatic records (e.g., Barber et al., 1994). Because plant macrofossils reflect the abundances of climatically sensitive bog vegetation, they have been used to infer past hydrological changes in bogs and, by extension, the regional climatic record (e.g., Barber et al., 1998, 1999; Mauquoy et al., 2002). However, macrofossil analyses are restricted to those deposits and time intervals in which they are sufficiently well preserved, and this has prompted the development of supplemental proxies for vegetation change.

Potentially powerful proxies for past changes in bog vegetation are lipids derived from and diagnostic for peat-forming plants. Unlike bulk vegetation, which is largely composed of readily degradable components such as carbohydrates, lipid biomarkers can be preserved in a relatively unaltered state. Biomarkers have been widely applied to marine settings as proxies for organic matter inputs (e.g., Brassell et al., 1986; Kenig et al., 1995; Pancost et al., 1998; Werne et al., 2000); however, molecular-based studies of terrestrial settings, and peat deposits in particular, are limited (Dehmer, 1993; Farrimond and Flanagan, 1995; Ficken et al., 1998; Nott et al., 2000). Several investigations have attempted to characterize the lipid constituents of peat-forming plants and identified profound variations that could be reflected in the sedimentary record (Lehtonen and

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Ketola, 1993; Ficken et al., 1998; Nott et al., 2000; Baas et al., 2000). In some cases, biomarker proxies have been shown to reflect the dominant vegetation, illustrating their potential for vegetation reconstruction; for example, Nott et al. (2000) showed that the relative abundances of *n*-alkanes and macrofossil distributions covaried. However, efforts by other workers revealed less clear relationships between alkyl lipid distributions and macrofossil abundance (Farrimond and Flanagan, 1995; Ficken et al., 1998).

The goal of this work is to expand on these previous studies by testing established proxies (i.e., *n*-alkane distributions) in a new setting and determining whether relatively unexplored compound classes (e.g., triterpenoids, wax esters) can be useful in identifying plant inputs. Thus, a peat profile from a late Sub-boreal climatic and vegetation transition was collected from the Bargerveen bog. This climatic transition is related to the regional shift from relatively warm and dry to relatively cold and wet climatic conditions that has been recorded in other peat deposits and is believed to have influenced human migration patterns (van Geel et al., 1996). At this sample site, the climatic shift affected the local vegetation such that the deposit records three dominant vegetation types: a basal unit composed predominantly of highly degraded Ericaceae rootlets; a middle unit, containing *Sphagnum cuspidatum* macrofossils; and an upper post-transition unit dominated by *Sphagnum imbricatum* (Fig. 1). Radiocarbon records developed for several Dutch peats (Kilian et al., 1995; van Geel et al., 1996, 1998) and an Irish peat (Carbury bog; van Geel et al., 1998) indicate that this transition occurred about 2800 years ago. However, pollen distributions—specifically relatively low contributions from *Fagus* (ca. 2%) and relatively high contributions from *Corylus* (ca. 20%)—indicate that the transition occurred slightly earlier at our sample site in the Bargerveen bog. This is likely a consequence of the heterogeneous nature of bog settings, such that different sites responded to the ongoing climatic evolution at different times.

Nonetheless, the Bargerveen peat profile is marked by a dramatic vegetation shift, providing an ideal stratigraphic context for testing the validity of biomarker proxies for vegetation changes. The plant species represented by the shift were sampled from modern bogs and their free lipid components determined. Compounds analyzed include *n*-alkanes, alkanols, and alkanoic acids, ω-hydroxyalkanoic acids, triterpenoids, and steroids. The observed compound distributions are compared to lipid profiles developed in a peat core spanning the vegetation shifts, and the capability of biomarkers to predict vegetation changes is evaluated.

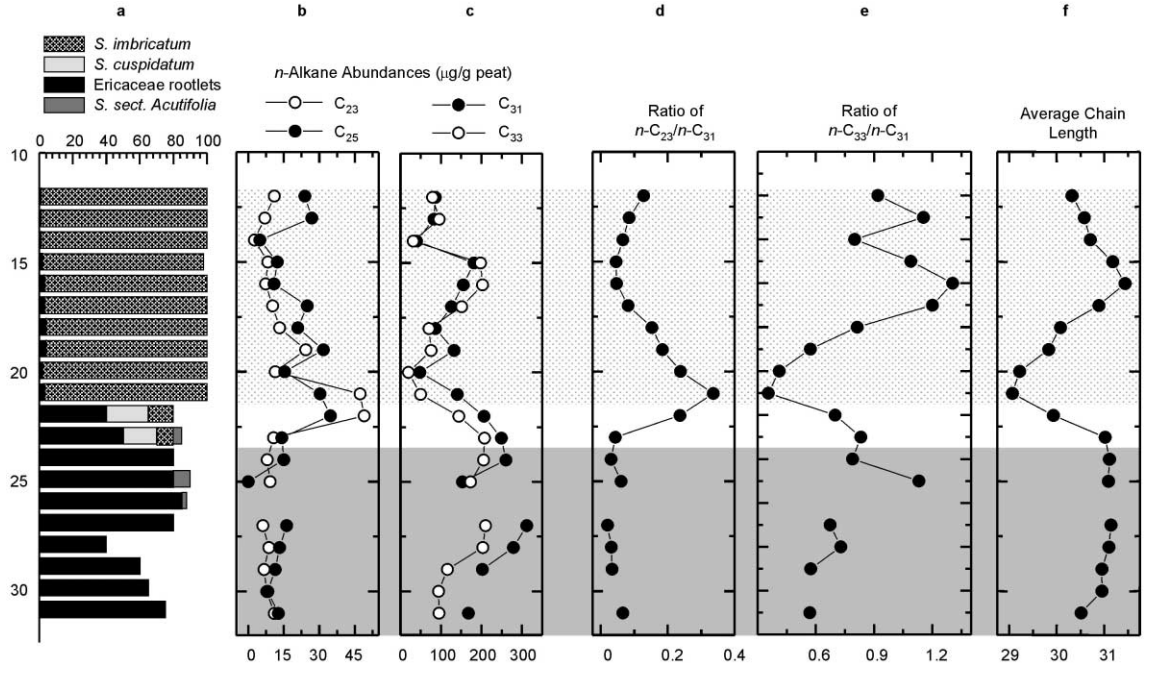

Fig. 1. Depth profiles showing (a) the macrofossil distributions and (b–f) *n*-alkane distributions in the Bargerveen peat core. The macrofossil distributions show a shift from degraded Ericaceae rootlet-dominated peat (represented by dark shading in this and subsequent figures) to a *Sphagnum*-dominated peat (light shading); two *Sphagnum* species, *S. cuspidatum* and *S. imbricatum,* are predominant. Also shown are the absolute abundances of *n*-alkanes (b,c); the ratio of *n*-C_{23} to *n*-C_{31} (d); the ratio of *n*-C_{33} to *n*-C_{31} (e); and the average *n*-alkane chain length (f).

2. Methods

2.1. Plant selection and analyses

Field specimens of *Sphagnum* species and other peat-forming plants were obtained from the Bargerveen raised bog (Zwartemeer, southeast-Drenthe, The Netherlands) and the Irish Curraghmore Bog near Galway (*S. imbricatum* only). Plants were washed, identified by both field observation and subsequent light microscopy, and stored at −20 °C until chemically analysed. Lipids were extracted, fractionated, identified by gas chromatography–mass spectrometry (GC–MS), and quantified by GC according to the methods previously described in Baas et al. (2000).

2.2. Peat collection and storage

The peat core was collected from the Bargerveen raised bog, where drainage and mining of the peat had created an outcrop, exposing the vegetation transition. The Bargerveen peat bog reserve represents one of the last remnants of a much larger raised bog, the Bourtangerveen, which extended along the northern Dutch–German border prior to drainage and exploitation during medieval and later times. A core was collected by pushing a metal box horizontally into a cleaned profile spanning the vegetation shift. The core was archived at Hugo de Vries-Laboratory of the University of Amsterdam, where it was sliced into 1 cm intervals. The intervals from 12 to 31 cm were chosen for pollen, macrofossil, and lipid biomarker analyses. In all cases, samples were collected from the center of the core to minimize complications associated with the oxidation of peat material where exposed to air.

2.3. Pollen and macrofossil analyses

For macrofossil analyses, a 4.9 cm^3 portion of the core was treated with 5% aqueous KOH solution and subsequently warmed to facilitate disintegration. The peat was then washed and sieved over a 150 mm mesh screen and macrofossil fragments were quantified by light microscopy. To confirm the age of the vegetation transition, pollen and spores from additional subsamples were isolated by adding a 10% aqueous KOH solution and gently warming to 100 °C. The material was sieved (215 mm mesh) into tubes in which Lycopodium tablets had been dissolved in 10% aqueous HCl. The samples were washed with water and 96% acetic acid. A mixture of 97% H_2SO_4 and acetic anhydride (1:9 v:v) was added for acetolysis and the sample was rinsed repeatedly with water and then ethanol. Finally, glycerin was added, the samples were allowed to dry for ca. 16 h at 40 °C and then mounted on slides with glycerin gelatin. Pollen was counted using traditional light microscopy methods.

2.4. Extraction and derivatisation

The total lipid extracts of samples of freeze-dried peat (ca. 5 g) were obtained by sonication with a progressively less polar mix of solvents (MeOH/CH_2Cl_2 1:0, 3:1, 1:1, 1:3, and 0:1). After addition of a standard [10–40 μg of 2,3-dimethyl-5-(1,1-D_2-hexadecyl)thiophene], an aliquot of the total extract was methylated with diazomethane, eluted with ethyl acetate through a short column packed with silica 60 (Merck 60, 0.063–0.2 mm, 70–230 mesh) to remove highly polar, non-GC amenable compounds, and silylated with a 1:1 mixture of BSTFA (1% TMS) and pyridine at 60 °C for 20 min. A second aliquot of the total lipid extract was separated into apolar and polar fractions by eluting with hexane:CH_2Cl_2 (9:1 v:v) and MeOH, respectively, from a column packed with silica 60.

2.5. Gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS)

Derivatised total lipid extracts and apolar fractions were analyzed by GC and GC–MS. GC–MS was conducted using a Hewlett-Packard 5890 gas chromatograph interfaced to a VG Autospec Ultima Q mass spectrometer operated at 70 eV with a mass range of m/z 50–800 and a cycle time of 1.8 s (resolution 1000). Compound identifications were based on comparison with the mass spectra and retention times of authentic standards. A fused silica CP-Sil 5 capillary column (25 m × 0.32 mm, $d_f = 0.12$ μm) was used with helium as the carrier gas. Samples were injected at 70 °C and the temperature was programmed to increase at 20 °C/min to 130 °C, at 4 °C/min to 320 °C, and held at 320 °C for 15 min. Abundances of apolar compounds were determined by integration of GC peak areas from a flame ionization detector and the same analytical conditions as described above. Abundances of polar compounds were determined by integration of peak areas of diagnostic ions generated during GC–MS analyses. Quantification for both apolar fractions and total extracts was based on comparison of peak areas to a standard [2,3-dimethyl-5-(1,1-D_2-hexadecyl)thiophene] added to the sample after extraction but prior to additional treatment. Recovery of this standard is ca. 100%, but it clearly does not have chemical properties similar to all of the analysed components; thus, errors for abundance determinations are reported as ±15%—a conservative first order estimate based on comparisons of several analyses.

3. Results and discussion

3.1. Modern plant studies

The primary plant inputs to the Bargerveen peat are the leaves and stems of *Sphagnum* species and Ericaceae

rootlets, which are preferentially preserved relative to Ericaceae leaves and stems; the lipid distributions of the predominant species of each are discussed below.

3.1.1. *Sphagnum* species

Previously, we reported the lipid distributions of twelve different *Sphagnum* species (Baas et al., 2000), and the results of that work are summarized in Table 1. The dominant *Sphagnum* species in the fossil Bargerveen peat are *S. cuspidatum*, *S. imbricatum*, and species of the group Acutifolia. Although multiple *Sphagnum* species are members of the group Acutifolia, the most likely peat-former is *S. rubellum*, and the lipids present in that species are included in Table 1. The lipid distributions of each of the three peat-forming *Sphagnum* species are characterized by relatively high abundances of $C_{22–30}$

Table 1
Abundances (in ug/g dry plant) of lipids in peat-forming *Sphagnum* species and the leaves, stems, and roots of *Calluna vulgaris* and *Erica tetralix* (after Baas et al., 2000)[a]

Compound	*S. imbricatum*	*S. cuspidatum*	*S. rubellum*	*Erica tetralix*			*Calluna vulgaris*		
				Fine roots	Coarse roots	Stems	Leaves	Roots	Stems + leaves[b]
Sterols									
24-Methylcholesta-5,22-dien-3β-ol **(XVII)**	70	270	82	8	0	0	0	0	0
24-Methylcholest-5-en-3β-ol **(XVIII)**	67	330	90	10	9	1	0	0	0
24-Ethylcholesta-5,22-dien-3β-ol **(XIX)**	180	730	240	16	15	0	0	0	0
24-Ethylcholest-5-en-3β-ol **(XX)**	300	190	110	3800	3000	920	0	440	1600
Triterpenoids									
α-Amyrin **(II)**	0	30	76	3100	1800	620	35 000	370	3900
β-Amyrin **(VI)**	0	9	16	910	710	1800	13 000	550	5700
Lupeol **(XIV)**	0	33	21	780	600	120	19 000	0	0
Oleanoic Acid **(V)**	34	71	100	1800	1000	600	11 000	55	14 000
Taraxerol **(VIII)**	0	0	0	0	0	0	0	610	0
Taraxer-4-one **(IX)**	0	0	0	0	0	0	0	490	0
Ursolic Acid **(I)**	110	360	430	12 000	2900	2400	52 000	130	34 000
Unsaturated ursolic acid	23	100	61	1700	1300	600	26 000	20	7500
n-*Alkanoic acids*									
C22:0	30	9	9	11	26	9	11	2	38
C24:0	110	37	46	33	62	40	22	7	95
C26:0	140	23	26	63	100	79	47	10	69
C28:0	27	5	8	85	120	18	71	23	67
C30:0	3	5	7	130	130	6	85	6	55
n-*Alkanols*									
C22:0	7	4	8	7	11	2	2	1	34
C24:0	62	13	34	9	36	6	11	4	500
C26:0	140	16	23	10	51	8	20	1	120
C28:0	80	20	20	25	110	21	43	4	85
C30:0	7	3	3	35	10	8	30	1	59
n-*Alkanes*									
C21:0	48	11	11	0	5	1	0	1	21
C23:0	86	44	23	4	6	3	0	1	13
C25:0	40	8	27	4	5	3	0	1	16
C27:0	8	2	4	2	4	2	26	1	28
C29:0	7	3	29	12	14	6	50	2	160
C31:0[c]	3	4	58	89	52	18	270	17	700
C33:0	0	0	30	95	0	0	1043	8	3500
Wax esters									
Phytenyl phytenoate **(XXI)**	0	150	29	0	0	0	0	0	0

[a] See Appendix for structures represented by Roman numerals.
[b] Amount of internal standard is very low compared to most abundant lipids.
[c] Co-elutes with tocopherol; corrected by quantifying using fragment ions generated during GC–MS.

n-alkanoic acids, $C_{22–30}$ *n*-alkanols, C_{28} and C_{29} sterols, and triterpenoids dominated by ursolic acid (**I**; see Appendix for structures), oleanoic acid (**V**), and a tentatively identified unsaturated ursolic acid. *S. cuspidatum* and *S. imbricatum* are also characterized by relatively high abundances of low-molecular-weight (LMW) *n*-alkanes (C_{21}, C_{23}, C_{25}) and low abundances of high-molecular-weight (HMW) *n*-alkanes (C_{29}, C_{31}, C_{33}). In fact, *n*-C_{33} is absent in both of these *Sphagnum* species, while *n*-C_{23} is the most abundant *n*-alkane. We also observed an isoprenoid wax ester, tentatively identified as phytenyl phytenoate (**XXI**), which appears to be unique to certain *Sphagnum* species including *S. rubellum* and *S. cuspidatum*.

3.1.2. Ericaceae

The exact species of Ericaceae that were predominant during deposition of the Bargerveen peat cannot be ascertained from root macrofossils; nonetheless, high abundances of leaves and stems from *Calluna vulgaris* and *Erica tetralix* suggest that these species were dominant and the primary source of the roots. However, it is unclear whether Ericaceae roots would be the dominant source of lipids to ancient peats and, thus, the lipid distributions were determined for distinct plant tissue types: the fine roots, thick roots, stems and leaves of *E. tetralix* and the stems and roots of *C. vulgaris* (Table 1). In contrast, the previous *Sphagnum* analyses were based only on combined leaf/stem plant tissues, because these plants do not have roots.

Compounds present in Ericaceae plants are similar to those found in *Sphagna*, and include *n*-alkanes, *n*-alkanols, *n*-alkanoic acids, triterpenoids, and steroids. However, the total absolute abundances of individual lipids are often an order of magnitude higher in all tissue types of Ericaceae species than in *Sphagna*. In addition, there are significant compositional variations among the different tissue types of the Ericaceae. In all Ericaceae tissue types, LMW *n*-alkanes are either absent or present in trace quantities, whereas HMW *n*-alkanes are relatively more abundant (over 5000 μg of total *n*-alkanes per g of plant material in the leaves of *C. vulgaris*). The distributions of cyclic compounds are also variable; triterpenoids are much more abundant than steroids in Ericaceae leaves and stems, are present in similar abundances to 24-ethylcholest-5-en-3β-ol (sitosterol; **XX**) in Ericaceae roots, and are less abundant than steroids in *Sphagnum*. Also, certain triterpenoids, such as α-amyrin (**II**), β-amyrin (**VI**), taraxerol (**VIII**), and taraxer-4-one (**IX**), that are absent or present in low concentrations in *Sphagna*, are abundant in certain Ericaceae tissues. The last two compounds appear to be have diagnostic value, being identified only in the roots of *C. vulgaris*. Compared to *Sphagna*, *n*-alkanols in Ericaceae are present in low abundances relative to cyclic compounds whilst HMW *n*-alkanes in Ericaceae are present in relatively higher abundances.

Differences among the Ericaceae tissue types are also significant. *n*-Alkanes are two to five times more abundant in leaves and stems than in roots, whilst sitosterol is absent in the leaves. This presents additional complications, because it is unclear whether Ericaceae leaves and stems, while not the dominant macrofossils, could be significant sources for lipids in peat.

3.2. Potentially diagnostic biomarkers or biomarker distributions

Although there are several biomarkers or lipid classes that could be diagnostic for certain peat-forming plant species, our work reveals three potential complications with the use of lipids to reconstruct plant inputs to peats. First, most of the compounds commonly observed in peats have multiple sources. Some compounds such as phytenyl phytenoate and LMW *n*-alkanes are much more abundant in some plants than others, but the isoprenoid wax ester was the only diagnostic biomarker observed (for certain *Sphagna*). Second, lipid distributions vary significantly amongst different tissue types of an individual plant. This is particularly important when trying to evaluate the input of Ericaceous species, which typically form peat from their complex root systems but which could also contribute lipids via other plant tissue types. Finally, the yields of most lipids from Ericaceous species are much higher than those of *Sphagnum*; thus, even in *Sphagnum*-rich intervals, lipids from Ericaceae could also be abundant.

Nonetheless, these lipid analyses combined with previous efforts (Nott et al., 2000; Baas et al., 2000) reveal the potential for some lipids in reconstructing plant inputs to ancient peats. The *n*-C_{23} alkane, and to a lesser degree *n*-C_{25}, is relatively uncommon in terrestrial settings (Eglinton and Hamilton, 1967) but abundant in seven *Sphagnum* species collected from the UK (Nott et al., 2000), eleven *Sphagnum* species collected from the Netherlands (Baas et al., 2000), and four species of *Sphagnum* examined by Corrigan et al. (1973). In contrast, in 13 species of peat-forming plants other than *Sphagna*, *n*-C_{23} and *n*-C_{25} are present in low abundances and higher molecular weight *n*-alkanes are predominant (Nott et al., 2000; Table 1, this work). Thus, *n*-C_{23} can be used as a rather diagnostic *Sphagnum* biomarker in peat deposits where these plants are typically abundant. Similarly, HMW *n*-alkanes, and especially *n*-C_{33}, which is either absent or present in low abundances in all investigated *Sphagnum* species, can be used as tracers for the input of other peat-forming vegetation such as Ericaceae. The applicability of such *n*-alkane based biomarker proxies in peats was shown by correlative shifts in *n*-alkane distributions and macrofossil abundances in a 200 year old peat core from Bolton Fell Moss, Cumbria (Nott et al., 2000).

Analyses of modern plants also reveal that the tentatively identified isoprenoid wax ester could serve as a

biomarker proxy for certain *Sphagnum* species. This compound was not found in any of the *E. tetralix* or *C. vulgaris* tissues for which data are reported here; nor was it found in any of the following peat-forming plants: *Aulacomnium palustre, Dicranum scoparium, Andromeda polifolia, Empetrum nigrum* (leaves, stems, and roots), *Oxycoccus palustris*, *Eriophorum vaginatum, Eriophorum angustifolium,* and *Rhynchospora alba* (stems and roots). In contrast, this ester was found in several *Sphagnum* species and among the peat-forming Sphagna was particularly abundant in *S. cuspidatum*. Thus, the isoprenoid wax ester could serve as a useful proxy for sedimentary contributions from *S. cuspidatum* and the relatively wet conditions that are favorable for its growth.

Other potential biomarkers could be triterpenoids derived from taraxerol and taraxerone, which were identified only in the roots of *C. vulgaris*. Studies of triterpenoid diagenesis in marine sediments (ten Haven and Rullkötter, 1988) suggest that such compounds will ultimately be transformed into the more thermally stable oleanane and oleanene isomers. Because β-amyrin and oleanoic acid are abundant in the modern peat-forming plants, such products will be less diagnostic. However, in the relatively immature peats, more specific markers such as taraxerol and taraxer-14-ene (**X**) might still be preserved.

Although no other diagnostic biomarkers were identified, the distributions of the major compound classes differ significantly between *Sphagnum* and Ericaceae species. For example, Ericaceae are characterised by higher triterpenoid to steroid and triterpenoid to *n*-alkanoic acids ratios than *Sphagnum*—although these ratios do vary significantly amongst different plant tissue types in the Ericaceae species. Thus, the proportional abundances of these compounds, although they are not diagnostic biomarkers for either Ericaceae or *Sphagna*, could perhaps also serve as predictors of ancient plant inputs providing they undergo diagenetic alteration at the same rate.

3.3. Application to ancient peat deposits

To test whether plant lipids can be used either qualitatively or quantitatively to reconstruct plant inputs to ancient peats, we determined the abundances of lipids in the Bargerveen peat profile. Particular attention was devoted to those compounds that had previously been identified in modern-peat forming vegetation, including: *n*-alkanes, *n*-alkanoic acids, *n*-alkanols, wax esters, triterpenoids, and steroids. In addition, we observed diacids in our peat samples; although we did not find these compounds in modern peat-forming plants, they could derive from higher plants and provide additional proxies as discussed below.

3.3.1. n-Alkanes

The distributions and absolute abundances of extracted *n*-alkanes vary throughout the Bargerveen core. LMW (C_{23} and C_{25}) *n*-alkane abundances vary from <5–45 μg/g of peat while HMW (C_{31} and C_{33}) *n*-alkane abundances range from 20 to 300 μg/g (Fig. 1b and c). At all depths, distributions are dominated by the HMW homologues such that the average chain length vary from 29 to 31 (Fig. 1f); correspondingly, the ratio of *n*-C_{23} to *n*-C_{31} is below 0.1 in most samples (Fig. 1d). However, the average chain length shifts to lower values (from 31 to 29) and the C_{23}/C_{31} ratio increases sharply to 0.35 at approximately the same depth as the transition from Ericaceae rootlet-dominated to *Sphagnum*-dominated peat. The shift is apparently caused by both an increase in the absolute abundance of LMW *n*-alkanes to a maximum of 45 μg/g and a decrease in the absolute abundance of HMW *n*-alkanes to a minimum of 20 μg/g (although not in the same sample). These observations are consistent with previously reported results suggesting that *n*-C_{23} could serve as a biomarker for *Sphagnum* inputs (Nott et al., 2000).

However, several aspects of the *n*-alkane distributions are inconsistent with predictions based on macrofossil distributions and modern plant analyses. Foremost among these is the fact that although the ratio of *n*-C_{23} to *n*-C_{31} does increase markedly at the Ericaceae-*Sphagnum* transition, in no sample does the value exceed 0.35. Based on the modern samples and previous peat-based studies (Nott et al., 2000; Baas et al., 2000), LMW homologues are expected to dominate the distributions of *n*-alkanes if they are derived predominantly from *Sphagnum*. Also, in the upper part of the section, the ratios of *n*-C_{23} to *n*-C_{31} and the absolute abundances of *n*-C_{23} are low and variable despite no apparent change in macrofossil inputs. The higher-than-expected relative abundances of HMW *n*-alkanes could reflect an important aeolian contribution; because the turnover rate of leaf waxes can be particularly high, aeolian inputs could dominate the molecular distributions even in a peat composed largely of plant material. Alternatively, the unexpected distributions could indicate that some plant species or tissues are more important sources of *n*-alkanes than others, such that they dominate *n*-alkane distributions even when their macrofossil remains are not abundant. Indeed, the abundances of *n*-alkanes in Ericaceae species and particularly *E. tetralix* leaves are more than an order of magnitude greater than in *Sphagnum* species.

The ratio of *n*-C_{33} to *n*-C_{31} exhibits similarly unexpected behaviour (Fig. 1e). Because the former compound is more abundant than *n*-C_{31} only in the leaves of *E. tetralix* and *C. vulgaris* and is absent from *S. imbricatum*, its abundance relative to *n*-C_{31} is expected to decrease up the section. Instead, the absolute abundances of *n*-C_{31} and *n*-C_{33} roughly parallel each other, and the ratio of *n*-C_{33} to *n*-C_{31} actually increases in the upper part of the *Sphagnum*-rich interval, suggesting that the predominant source of HMW *n*-alkanes are the

leaves of *E. tetralix*, the only plant or plant tissue examined with such a distribution. Thus, the unexpected ratios of both n-C_{23} to n-C_{31} and n-C_{33} to n-C_{31} could result from Ericaceae leaf lipid inputs that are particularly dominant in the *Sphagnum*-rich interval. This does not necessarily mean that Ericaceae were more abundant during that time. A constant input of Ericaceae leaf lipids co-occurring with a shift in the dominant peat-forming vegetation from Ericaceae rootlets with high *n*-alkane abundances to *Sphagnum* plants with low *n*-alkane abundances (Table 1) could result in the observed profiles. Indeed, leaf, seed, and pollen counts suggest that Ericaceae leaf inputs to the peat varied minimally in this interval.

To test this possibility, we attempted to predict the n-C_{33} to n-C_{31} ratio using the absolute abundances of *n*-alkanes in modern samples and the proportional abundances of *E. tetralix* leaves, *E. tetralix* roots, and *S. imbricatum* in the macrofossil record (Fig. 2; similar results are obtained if *C. vulgaris* leaves and roots are used). For the last two, proportional abundances were determined directly from macrofossil distributions. However, exposed Ericaceae plant tissues such as stems and leaves are not well preserved and we cannot directly account for their proportional inputs using the macrofossil record. Thus, for *E. tetralix* leaf contributions, we chose an arbitrary value of 20% and assigned that to the interval with the highest n-C_{31} abundances (27 cm); percentage leaf inputs to all other intervals were calculated by normalizing that 20% value on the basis of relative n-C_{31} abundances (i.e samples in which n-C_{31} are half as abundant as in sample 27 are assumed to have a 10% leaf input). Clearly, there are limitations to this approach; first, the value of 20% is arbitrary and could be much lower, and second, n-C_{31} abundances are used to calculate the modeled ratio of n-C_{33} to n-C_{31}. However, similar results are obtained if we assign the maximum leaf inputs as any value in the range of 5–25%, and models using either *Erica* seeds or pollen as a proxy for leaf inputs reveal similar trends, albeit with greater scatter in the data. Although the model curve does not predict absolute C_{33} to C_{31} ratios accurately, it does reproduce the observed general trends as well as some of the smaller-scale variation in the profile (such as samples at 14 and 28 cm). An exception is the dramatic shift to lower n-C_{33} to n-C_{31} ratios that occurs during the period of inferred wettest local conditions. This could reflect the limitations in the model or it could be due to effects for which the model does not account, such as climate-induced shifts in plant *n*-alkane distributions. These possibilities will be discussed in a later paper, and here we simply use the model to illustrate the fact that plant tissue types not preserved in the macrofossil record could be lipid-rich and significantly influence lipid distributions.

Unfortunately, a similar model does not reproduce the observed n-C_{23} to n-C_{31} ratios (Fig. 3). The model clearly overestimates the LMW *n*-alkane abundances throughout the *Sphagnum*-rich interval. The model and actual data do exhibit similar trends—C_{23} to C_{31} ratios are low in the Ericaceae-rich interval, increase at 22 cm, then decrease due to elevated leaf inputs from 20 to 15

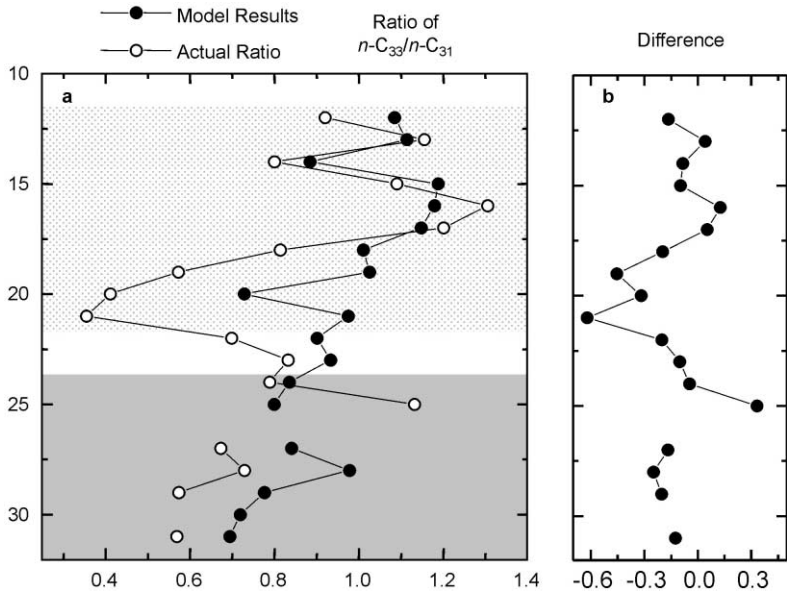

Fig. 2. Depth profile of measured and predicted n-C_{33} to n-C_{31} alkane ratios in the Bargerveen peat (a) and the difference between the measured and predicted ratios (b). Predicted values are based on the abundance of *n*-alkanes in modern plants and the inferred or measured abundances of those plants in the peat core.

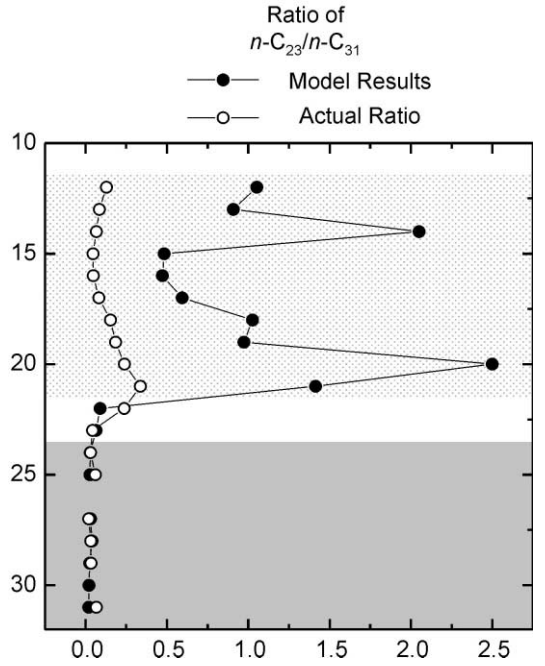

Fig. 3. Depth profile of measured and predicted n-C_{23} to n-C_{31} alkane ratios in the Bargerveen peat. Predicted values are based on the abundance of n-alkanes in modern plants and the inferred or measured abundances of those plants in the peat core.

cm, and finally increase again in the uppermost part of the section. Thus, it seems that n-alkanes can serve as a qualitative indicator of plant inputs but do not always provide quantitative assessment of plant inputs, compared to the macrofossil data. The inability of C_{23} to C_{31} ratios to accurately reproduce macrofossil records could reflect inaccuracies associated with either lipid or macrofossil records of plant input; for example, many of the biomarkers could derive from amorphous material. However, the greatest discrepancy occurs in the *Sphagnum* interval, where nearly 100% of the plant material could be identified, and it is suggested the reconstruction of plant contributions to sediments using only biomarker data be done with caution.

3.3.2. n-*Alkanoic acids and* n-*alkanols*

In the Bargerveen peat samples, n-alkanols are relatively abundant (up to 600 μg/g peat) and typically dominated by either the C_{24} or C_{26} homologue (Fig. 4). Absolute abundances are variable, but exhibit no clear changes associated with the climatic and vegetation shift. In contrast, the n-alkanol average chain length changes significantly through the section, increasing from lowest values of 24 at the base of the section to a maximum value of 26.3 at 18 cm before decreasing to values of 24.5 throughout the rest of the section. This positive shift is largely due to an increase in the absolute abundances of the C_{26} and C_{28} homologues (Fig. 4d), and is opposite to that observed for the n-alkanes. Abundances of n-alkanoic acids exhibit significantly lower variation (Fig. 5), with elevated abundances found only in two samples (at 21 and 17 cm). The average chain length (ACL) is similarly invariant except for the interval from 14 to 12 cm, in which the ACL decreases from ca. 24 to ca. 22.

Both n-alkanoic acids and n-alkanols are abundant in all investigated Ericaceae and *Sphagnum* species. Of n-alkanols in modern plants, the C_{28} homologue was most abundant in *E. tetralix* coarse roots, leaves, and stems and *S. cuspidatum*, the C_{26} homologue was dominant in *S. imbricatum*, and the C_{24} homologue was most abundant in *C. vulgaris* and *S. rubellum*. Thus, the shift in n-alkanol ACL from ca. 24 in the Ericaceae horizon to 26 in the interval from 24 to 18 cm is consistent with a shift in the predominant source of lipids from *C. vulgaris* to *Sphagnum* species but not a shift from *E. tetralix* to *Sphagnum*. The decrease back to ACL values of ca. 24.5 in the uppermost part of the section (17–12 cm) could reflect additional leaf inputs from *C. vulgaris* leaves as discussed above for n-alkanes. However, the overall differences in n-alkanol abundances in peat-forming plants are relatively minor, consistent with previous studies of peat-forming plants (Ficken et al., 1998), and interpretations should be made cautiously. Distributions of n-alkanoic acids are essentially similar in all of the modern peat-forming plants (Karunen and Salin, 1980; Ficken et al., 1998; Table 1), and, thus, the lack of variability in the peat profile is not unexpected.

3.3.3.. α,ω-*Diacids*

α,ω-Alkanedioic acids ranging from C_{22} to C_{26} (with predominantly even carbon numbers) are also present in most of the Bargerveen peat samples (Fig. 6). Although absolute abundances of diacids were not determined, their relative abundances (Fig. 6b) decrease up section to trace levels in the lower *Sphagnum* interval before increasing to their highest values in the uppermost part of the section. This increase is expressed by the C_{22} and C_{24} but not the C_{26} homologue, such that the ratio of C_{22} to C_{26} is three to six times higher in the upper part of the section than in the Ericaceae interval.

Despite extensive analyses, we failed to detect diacids in the free lipid extract of any modern plant samples, suggesting that in peats these compounds derive from macromolecular components. Previous work (Karunen and Ekman, 1982) identified C_{22} and C_{24} ω-OH n-alkanoic acids as significant constituents of hydrolysable biomacromolecules in peat comprised of *Sphagnum fuscum*. Diacids were also present but in very low abundances (Karunen and Ekman, 1982), and in our study, no diacids were released by base hydrolysis of *S. imbricatum* (residue after solvent extraction). Because the most abundant ω-hydroxyalkanoic acids released by hydrolysis of *Sphagnum* are the C_{22} and C_{24} homologues, it is

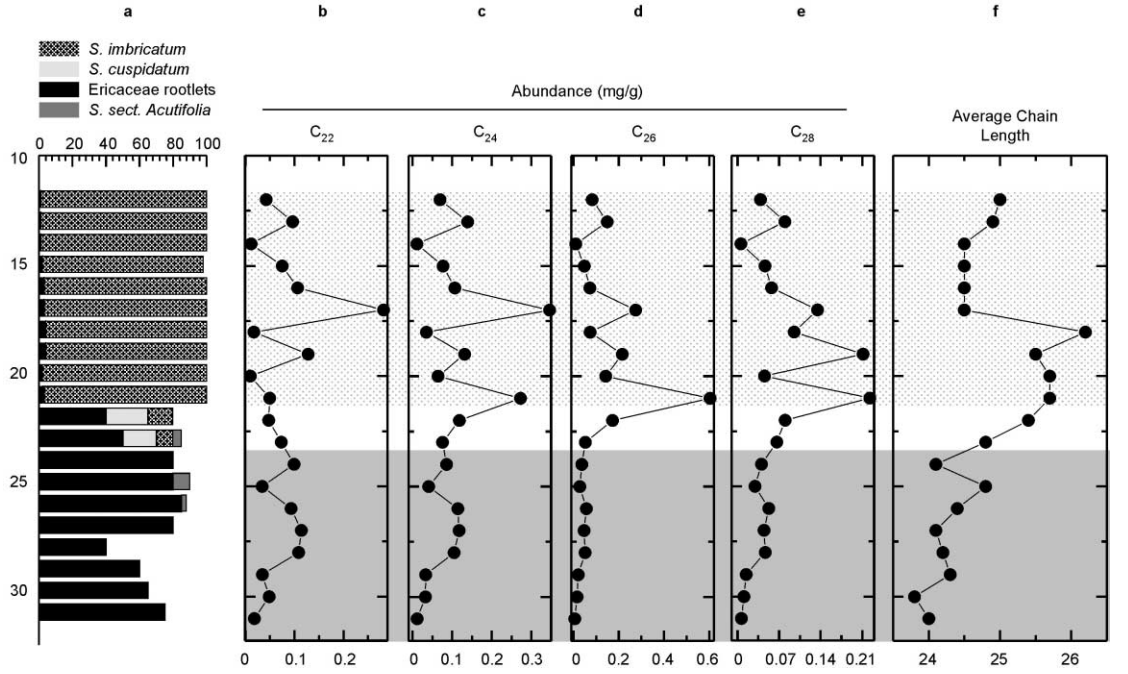

Fig. 4. Depth profiles showing the macrofossil distributions (a), *n*-alkanol abundances ($C_{22:0}$ to $C_{28:0}$ shown in b–e), and *n*-alkanol average chain lengths (f) in the Bargerveen peat core.

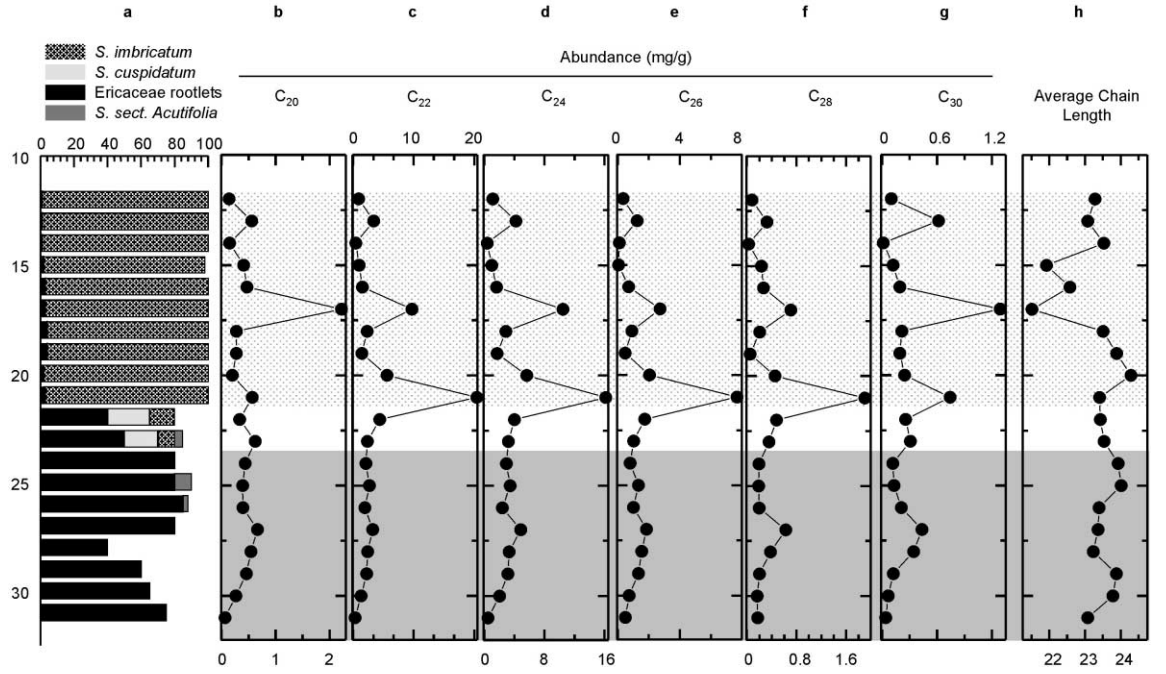

Fig. 5. Depth profiles showing the macrofossil distributions (a), *n*-alkanoic acid abundances ($C_{20:0}$ to $C_{30:0}$ shown in b–g), and *n*-alkanoic acid average chain lengths (h) in the Bargerveen peat core.

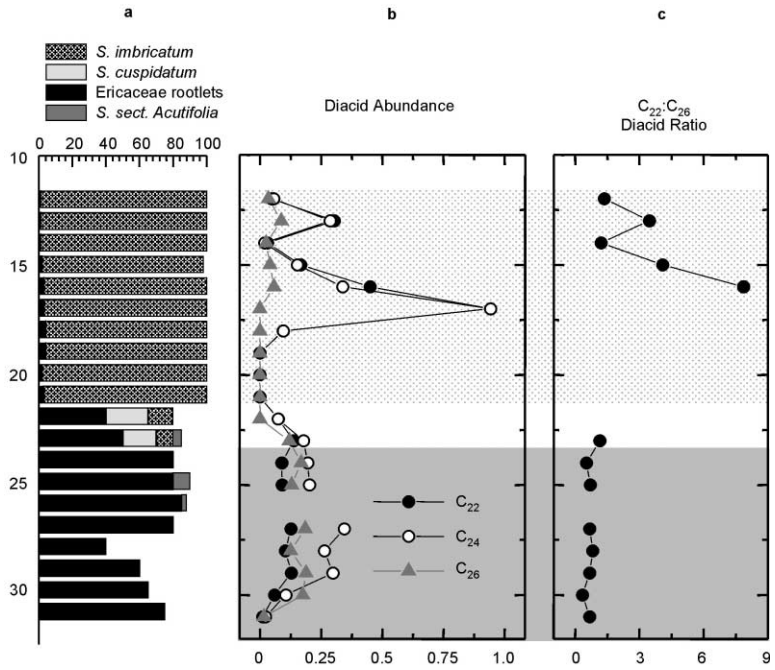

Fig. 6. Depth profiles showing the macrofossil distributions (a), relative α,ω-alkanedioic acid abundances normalized to 1 as explained in the text (b), and the ratio of C_{22} to C_{26} alkanedioic acid abundances (c) in the Bargerveen peat core.

possible that oxidation of ω-hydroxyalkanoic acids released from macromolecules is the source of C_{22} and C_{24} diacids in the *Sphagnum* interval of the Bargerveen peat core. Thus, the absolute abundances of diacids likely reflect diagenetic processes—particularly oxidation reactions in shallow peats. However, the abundance of LMW homologues, which are predominant in *Sphagnum* species, relative to HMW homologues of unknown source could serve as a proxy for *Sphagnum* inputs. Indeed, C_{22} to C_{26} diacid ratios are low (<1) in the Ericaceae interval and, where these compounds are present, significantly higher (1.5–7.5) in the *Sphagnum* interval. Although confirmation of the sources of these compounds is required, the trends revealed in Fig. 6 suggest that diacids could be useful in reconstructing plant inputs.

3.3.4. Wax esters

Wax esters are present in all investigated plants, and their absolute abundances and distributions are similar in all investigated peat samples (data not shown). Consequently, it seems that wax esters have little utility in plant input reconstruction. In contrast, the tentatively identified isoprenoid wax ester, phytenyl phytenoate, is present only in certain *Sphagnum* species (Table 1); of the species represented by macrofossils in the peat core, *S. rubellum* and *S. cuspidatum* lipid extracts contain it but extracts of *S. imbricatum* do not. In general, phytenyl phytenoate is either absent or present in only trace abundances in the peat profile (Fig. 7). However, elevated abundances occur in samples from the 22 to 20 cm depth interval. Although this does not correspond exactly to the interval containing *S. cuspidatum* fossils (23–21 cm), the similarity between the lipid and macrofossil profiles suggest that phytenyl phytenoate could be used to track inputs of *S. cuspidatum*. It is unclear if other *Sphagnum* species could also be important sources of this compound in peat deposits. Elevated abundances of the isoprenoid wax ester are not apparently associated with *S. rubellum* macrofossils in deeper sections of the core, although this could reflect the fact that these plant remains are much less abundant than S. *cuspidatum* macrofossils. Phytenyl phytenoate is also abundant in *S. fimbriatum* and is present in lesser abundances in several other *Sphagnum* species (Baas et al., 2000); thus, this compound's occurrence in other peats might not be explicitly indicative of *S. cuspidatum*. Nonetheless, the Bargerveen peat profile suggests that phytenyl phytenoate abundances could be useful in evaluating ancient bog vegetation.

3.3.5. Triterpenoids

In all of the peat intervals and modern plants, triterpenoids with ursane, oleanane, and lupane carbon skeletons are present. In modern plants, the most abundant triterpenoids are typically those in which a carboxyl group is attached to the C_{17} position (oleanoic acid and ursolic acid), but the equivalent non-carboxylated alcohols

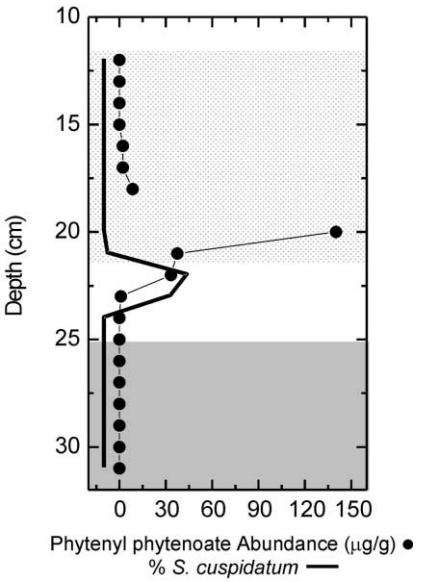

Fig. 7. Depth profile showing the abundance of the tentatively identified phytenyl phytenoate in the Bargerveen peat core. The solid black line shows the proportional abundance of *S. cuspidatum* macrofossils.

(α-amyrin, β-amyrin, and lupeol [**XIV**]) are also abundant. This is especially true for the Ericaceae plants, for which α-amyrin and β-amyrin are among the most abundant free lipids. In all peat samples, ursolic acid is the most abundant triterpenoid and commonly the most abundant free lipid, at concentrations typically greater than 4 mg/g peat (Fig. 8). Similarly, concentrations of oleanoic acid and unsaturated ursolic acid are typically greater than 1 and 0.5 mg/g peat, respectively. Concentrations of all three compounds increase slightly up section and are particularly high in the 17 and 19 cm intervals (up to 35 mg/g peat for ursolic acid). Absolute concentrations of 1,2,9 - trimethyl - 1,2,3,4 - tetrahydropicene (**IV**; Spyckerelle, 1975), friedelanone (**XVI**), and lupenone (**XV**) were not determined; the relative concentration profile (normalised such that the sample with the highest abundance has a value of 1.0 in Fig. 8) of 1,2,9-trimethyl-1,2,3,4-tetrahydropicene is similar to those of the other triterpenoids, but the friedelanone and lupenone depth profiles are distinct in that they lack a maximum at 19 cm. 1,2,9-Trimethyl-1,2,3,4-tetrahydropicene is an aromatic triterpenoid that is absent in living plants and almost certainly the product of aromatisation of higher plant triterpenoids (Dehmer, 1995). Likely, the aromatisation proceeds via progressive dehydrogenation of 3-hydroxy triterpenoids from ring A to ring D, possibly mediated by bacterial activity (Wakeham et al., 1980). Consequently, ursolic acid or other α-amyrin-type compounds are likely sources in the Bargerveen peat. The depth profiles of ursolic acid and 1,2,9-trimethyl-1,2,3,4-tetrahydropicene are similar, which is the opposite of the simple inverse relationship expected for a product-precursor pair; however, such a relationship is expected if the abundances of both product and precursor are dictated by other variables (i.e. a high abundance of each associated with certain vegetation types). α-Amyrin and β-amyrin were not observed in significant abundances in any of the investigated peat samples, including the Ericaceae interval, where such compounds might have been expected to be abundant.

In addition to these polar compounds, taraxer-14-ene (**X**) and taraxast-20-ene (**XIII**) are also present in the apolar fractions. Abundances of these compounds are similar and decrease from ca. 200 μg/g in the Ericaceae interval to <50 μg/g in the *Sphagnum* interval (Fig. 9). These shifts parallel proportional Ericaceae root abundances. Clearly, the correlation is not precise: peats from 27 cm and 28 cm have similar concentrations of taraxer-14-ene and taraxast-20-ene but quite different proportional Ericaceae root abundances. However, this could reflect contributions of triterpenoids from degraded and, thus, unidentified roots in some intervals, and overall, the similarity of the taraxer-14-ene, taraxast-20-ene, and Ericaceae root abundance depth profiles is quite remarkable. However, the source(s) of these compounds is unclear. Although neither taraxer-14-ene nor taraxast-20-ene is present in the lipid extracts of Ericaceae roots, taraxerol and taraxer-4-one are abundant in the roots of *C. vulgaris*. It is likely that the corresponding taraxasterol (**XI**) and taraxast-4-one (**XII**) are also present, albeit in lower abundances and difficult to identify due to coelution. Thus, it is likely that taraxer-14-ene and taraxast-20-ene are derived from functionalised precursors present in the *C. vulgaris* roots. However, this origin implies that taraxer-14-ene and taraxast-20-ene derive from a) dehydration of the alcohol followed by b) reduction of the resulting Δ^2 double bond (Fig. 10; ten Haven et al., 1992). If such a process occurred, it should have also affected α-amyrin and β-amyrin (which have identical carbon skeletons but Δ^{12} rather than Δ^{14} or Δ^{20} unsaturation) as has been reported for triterpenoids in mangrove swamps (Killops and Frewin, 1994). However, the cyclic alkenes expected from such dehydration reactions, olean-12-ene (**VII**) and urs-12-ene (**III**), were not observed in the apolar fraction.

An alternative origin, given the particularly high abundances of α-amyrin and β-amyrin in Ericaceae roots, is dehydration of these compounds forming urs-2,12-diene and olean-2,12-diene, respectively; taraxer-14-ene and taraxast-20-ene could then be formed by reduction of the Δ^2 bond and rearrangement of the Δ^{12} unsaturation. For taraxer-14-ene, this last step would be associated with a methyl shift from position 14 to position 13 (Fig. 11). However, the Δ^{12} unsaturation is particularly stable (McQuillin, 1963) and such a rearrangement seems unlikely (Steps 3–5 in Fig. 11). Moreover, previous

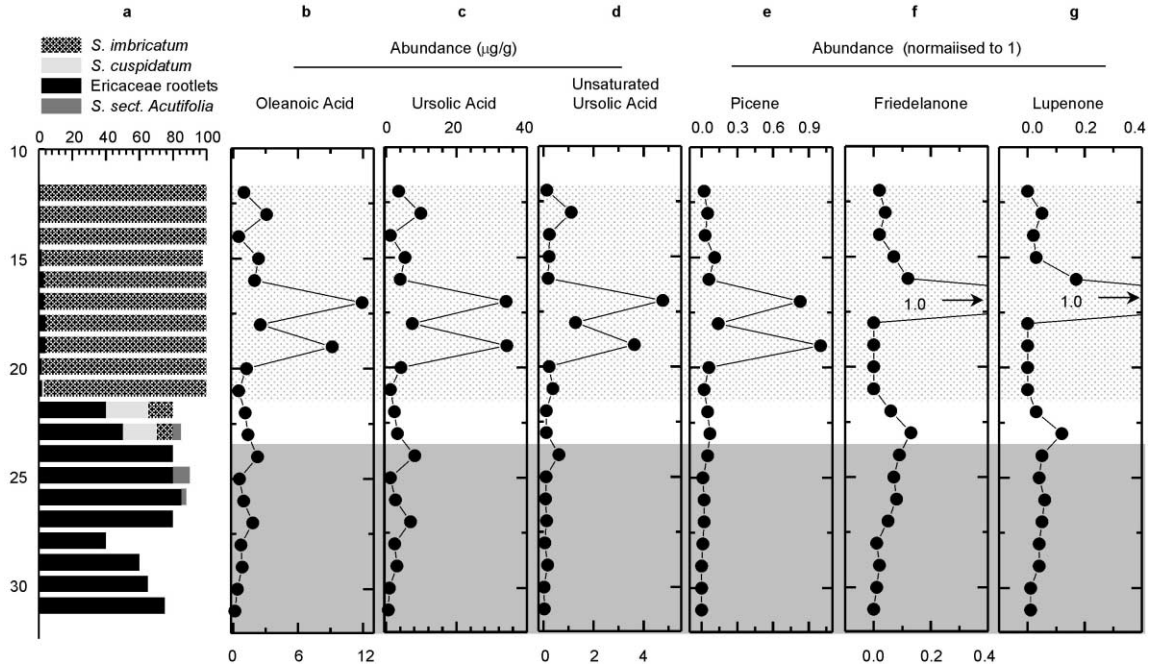

Fig. 8. Depth profiles showing the macrofossil distributions (a), absolute abundances in mg/g of peat of oleanoic acid (b), ursolic acid (c), and tentatively identified unsaturated ursolic acid (d), and the relative abundances (normalised to 1.0 as explained in the text) of 1,2,9-trimethyl-1,2,3,4-tetrahydropicene (e), friedelanone (f), and lupenone (g) in the Bargerveen peat core.

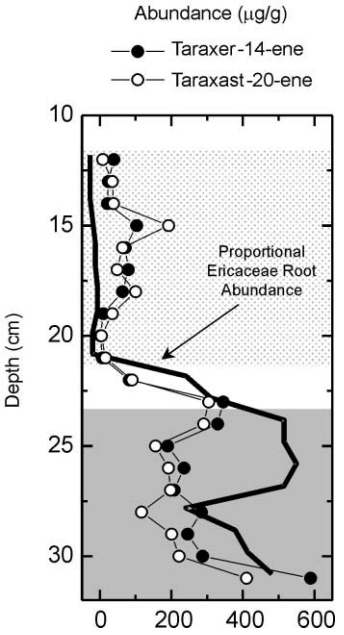

Fig. 9. Depth profile showing the absolute abundances of taraxer-14-ene and taraxast-20-ene in the Bargerveen peat core. The solid line shows the proportional abundance of Ericaceae root macrofossils.

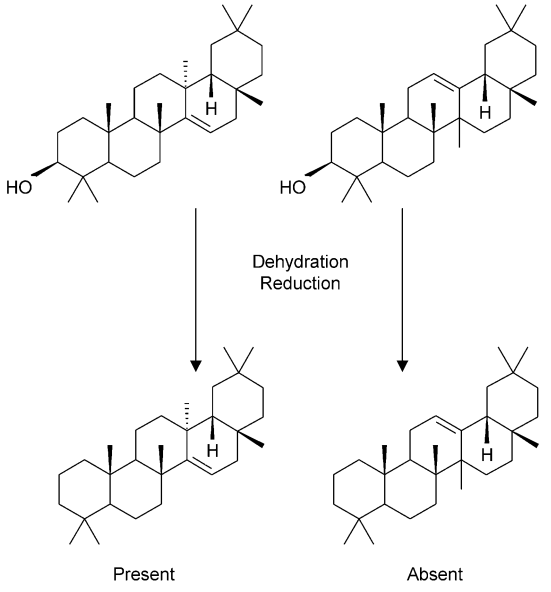

Fig. 10. Possible diagenetic pathway resulting in the formation of taraxer-14-ene from the dehydration of tarax-14-en-3β-ol. Also shown is the same reaction for β-amyrin, but the resulting olean-12-ene was not observed in our samples.

workers (ten Haven and Rullkotter, 1988 and references therein) showed that during diagenesis and thermal maturation taraxer-14-ene is actually converted to the more stable olean-12-ene. Thus, we conclude that the most likely origin for these hydrocarbons in the Bargerveen sediments is indeed dehydration of the corresponding triterpenoid alcohols. If so, then these biomarkers indicate that *C. vulgaris* rather than *E. tetralix* is the predominant source of the Ericaceae remains in the Bargerveen core, consistent with the trends in *n*-alkanol ACL.

Such information is not available from macrofossil studies and illustrates how a combination of molecular and macrofossil characterization approaches can refine reconstruction of past bog vegetation. However, it also clearly illustrates the importance of considering diagenetic alteration of lipids. Although the peat studied is less than 3000 years old, significant and apparently differential alteration of plant lipids—reflected by the presence of taraxer-14-ene and taraxast-20-ene and the absence of olean-12-ene and urs-12-ene—has occurred. Moreover, although most peat-based investigations focus on the Holocene, in older tropical peat deposits, rearrangement of biological lipids to more stable compounds could completely obscure some signals (e.g. conversion of taraxer-14-ene to olean-12-ene).

3.3.6. Steroids

Absolute abundances of steroids in the Bargerveen peat profile were not determined due to co-elution with triterpenoids (abundances of 24-ethylcholesta-5,22-dien-3β-ol [**XIX**] normalised to 1.0 as above are shown in Fig. 12b). With the exception of the sample from the 17 cm interval, 24-ethylcholesta-5,22-dien-3β-ol abundances decrease slightly up-section from values of ca. 0.2 to ca. 0.1. More striking are the abundances of 24-ethylcholesta-5,22-dien-3β-ol relative to ursolic acid (Fig. 12c; again normalised to the maximum value), which decrease from 0.4 to 0.9 in the Ericaceae dominated interval to 0.1 in the *Sphagnum* dominated interval. This was unexpected, because sterols, and particularly 24-ethylcholesta-5,22-dien-3β-ol, are more abundant than triterpenoids in the investigated *Sphagnum* species but less abundant than triterpenoids in the Ericaceae species. Possibly, this trend reflects preferential preservation of steroids relative to triterpenoids during the extensive degradation of the lower, Ericaceae-rich interval. Alternatively, the trend could reflect unaccounted Ericaceae plant remains in a manner analogous to that used to partially explain *n*-alkane distributions. Indeed, the 24-ethylcholesta-5,22-dien-3β-ol to ursolic acid ratio is much lower in Ericaceae stems and leaves than in Ericaceae roots (Table 1). Also, triterpenoid concentrations in Ericaceae leaves are much higher than in *Sphagnum*, suggesting that Ericaceae leaf-derived triterpenoids could swamp *Sphagnum*-sourced sterols in the upper interval. Thus, a constant contribution of Ericaceae leaves with high ursolic acid abundances relative to sterols could have caused the observed trend.

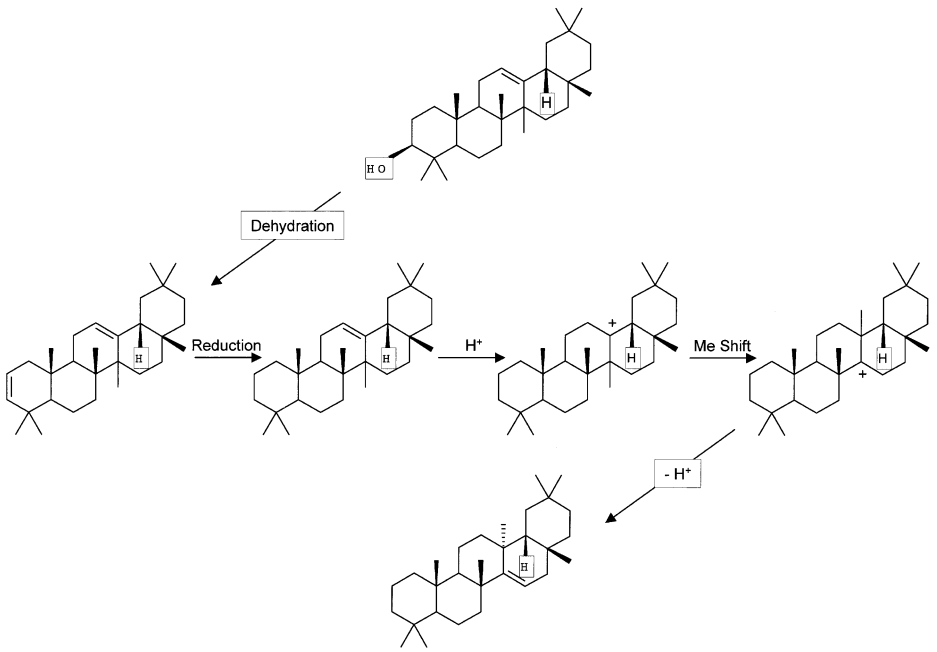

Fig. 11. Possible diagenetic pathway resulting in the formation of taraxer-14-ene from the dehydration and subsequent rearrangement of β-amyrin. However, steps 3–5 in the scheme are considered unlikely given the relative stability of the Δ^{12} intermediate.

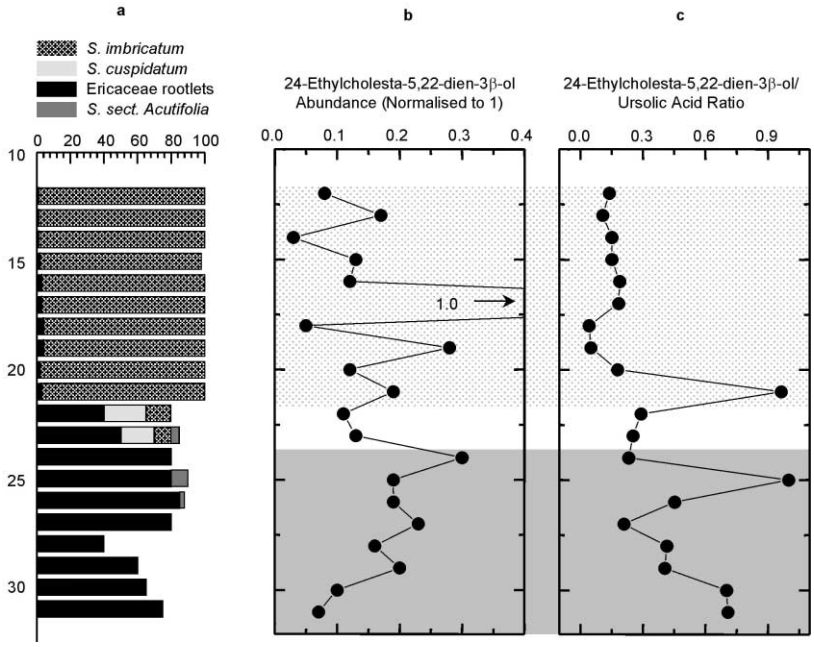

Fig. 12. Depth profiles showing the macrofossil distributions (a), relative abundances (normalized to 1.0 as explained in the text) of 24-ethylcholesta-5,22-dien-3β-ol (b), and ratios (normalized to 1.0) of 24-ethylcholesta-5,22-dien-3β-ol to ursolic acid (c) in the Bargerveen peat core.

4. Conclusions

Biomarkers preserved in ancient peats could have some utility in the reconstruction of palaeovegetation. *n*-C_{23} and *n*-C_{25} alkanes qualitatively track *Sphagnum* inputs, and the tentatively identified isoprenoid wax ester could serve as a proxy for certain *Sphagnum* species such as *S. cuspidatum*. *n*-C_{31} and *n*-C_{33} alkanes appear to be useful, albeit not diagnostic, proxies for Ericaceae leaf inputs, and the triterpenoids taraxer-14-ene and taraxast-20-ene closely track Ericaceae root abundances, likely reflecting a contribution from *C. vulgaris*. Similarly, ratios based on the relative abundances of different compound classes—*n*-C_{31} to *n*-C_{33} alkanes, *n*-alkanol distributions, triterpenoids to *n*-alkanes, and steroids to triterpenoids—exhibit shifts coincident with vegetation changes suggesting that they also could be used to reconstruct past vegetation changes.

However, none of these lipids or lipid distributions appears useful as a quantitative proxy. For example, although the ratio of *n*-C_{23} to *n*-C_{31} does increase in the *Sphagnum* interval, as expected, it is much lower than expected from ratios in modern plants. Moreover, ratios as high as 10—nearly 30 times the maximum value we observe—have been reported for other peats (Nott et al., 2000). Clearly, the proportional *Sphagnum* inputs to those peats are not thirty times greater than for the *Sphagnum*-rich interval examined here. Thus, the increase in the *n*-C_{23} to *n*-C_{31} ratio provides a qualitative record of the shift to *Sphagnum*-dominated peat, but the absolute values do not accurately record the proportional abundances of *Sphagnum*. This and other discrepancies could reflect numerous controls on lipid abundances other than the prevailing bog vegetation, including variable abundances of lipids in different plant tissues and selective preservation of certain lipids. The former concern seems to be particularly important in explaining variations in *n*-alkane distributions and it is cautioned that future workers take into account the varying preservation potential of different plant tissues.

As a result, we suggest that the most constructive use of plant-derived biomarkers in peats is to supplement macrofossil analyses (e.g. use of *n*-alkanols, taraxer-14-ene and taraxast-20-ene to predict that *C. vulgaris* is the predominant source of Ericaceae roots). Where macrofossils are absent, lipid biomarkers provide an alternative method for evaluating plant inputs, but must be used cautiously.

Acknowledgements

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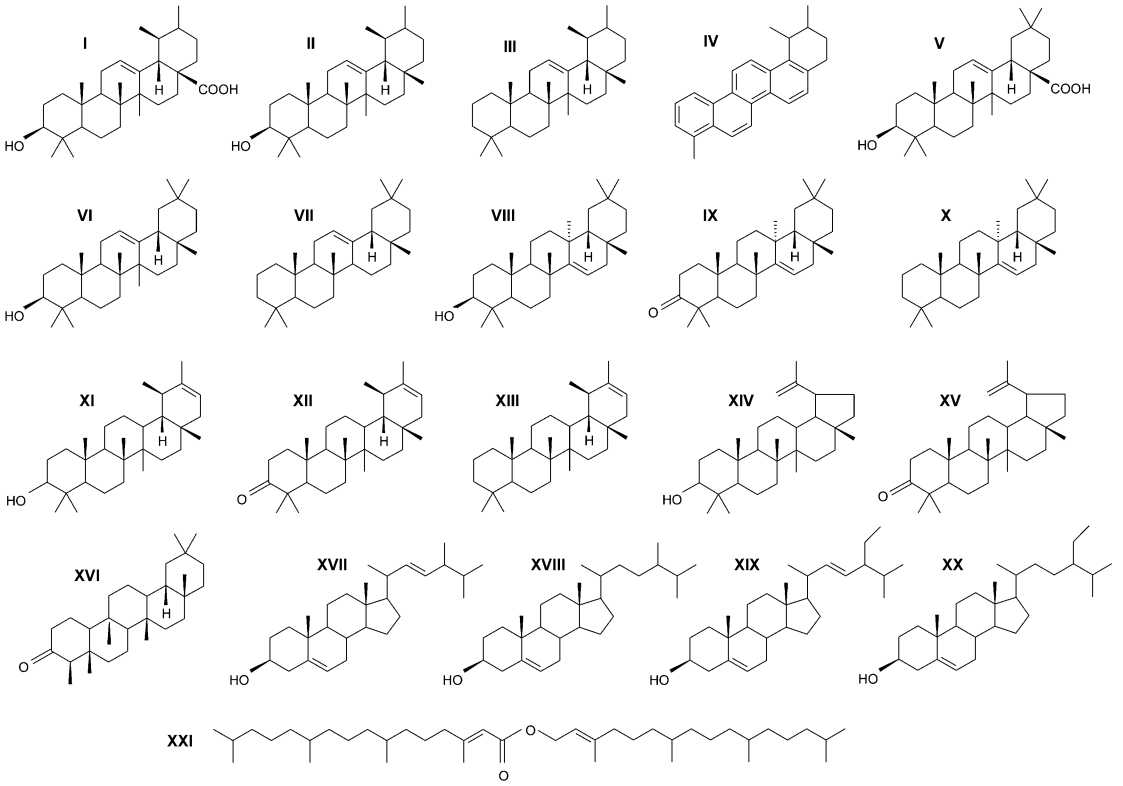
Appendix



References

Baas, M., Pancost, R.D., van, Geel, B., Sinninghe Damsté, J.S., 2000. A comparative study of lipids in *Sphagnum* species. Organic Geochemistry 31, 535–541.

Barber, K.E., 1993. Peatlands as scientific archives of past biodiversity. Biodiversity and Conservation 2, 474–489.

Barber, K.E., Chambers, F.M., Maddy, D., Stoneman, R., Brew, J.S., 1994. A sensitive, high-resolution record of Late Holocene climatic change from a raised bog in northern England. Holocene 4, 198–205.

Barber, K., Dumayne-Peaty, L., Hughes, P., Mauquoy, D., Scaife, R., 1998. Replicability and variability of the recent macrofossil and proxy-climate record from raised bogs: field stratigraphy and macrofossil data from Bolton Fell Moss and Walton Moss, Cumbria, England. Journal of Quaternary Science 13, 515–528.

Barber, K.E., Battarbee, R.W., Brooks, S.J., Eglinton, G., Haworth, E.Y., Oldfield, F., Stevenson, A.C., Thompson, R., Appleby, P.G., Austin, W.E.N., Cameron, N.G., Ficken, K.J., Golding, P., Harkness, D.D., Holmes, J.A., Hutchinson, R., Lishman, J.P., Maddy, D., Pinder, L.C.V., Rose, N.L., Stoneman, R.E., 1999. Proxy records of climate change in the UK over the last two millennia: documented change and sedimentary records from lakes and bogs. Journal of the Geological Society of London 156 (Part 2), 369–380.

Brassell, S.C., Eglinton, G., Marlowe, I.T., Pflaumann, U., Sarnthein, M., 1986. Molecular stratigraphy: a new tool for climatic assessment. Nature 320, 129–133.

Corrigan, D., Kloos, C., O'Connor, C.S., Timoney, R.F., 1973. Alkanes from four species of *Sphagnum* moss. Phytochemistry 12, 213–214.

Dehmer, J., 1993. Petrology and organic geochemistry of peat samples from a raised bog in Kalimantan (Borneo. Organic Geochemistry 20, 349–362.

Dehmer, J., 1995. Petrology and organic geochemical investigation of recent peat with known environments of deposition. Coal Geology 28, 111–138.

Eglinton, G., Hamilton, R.G., 1967. Leaf epicuticular waxes. Science 156, 1322–1335.

Farrimond, P., Flannagan, R.L., 1995. Lipid stratigraphy of a Flandrian peat bed (Northumberland, UK): Comparison with the pollen record. The Holocene 6, 69–74.

Ficken, K.J., Barber, K.E., Eglinton, G., 1998. Lipid biomarker, $\delta^{13}C$, and plant macrofossil stratigraphy of a Scottish montane peat bog over the last two millennia. Organic Geochemistry 28, 217–237.

van Geel, Buurman, B., Waterbolk, J.H.T., 1996. Archaeological and palaeoecological indications of an abrupt climate change in the Netherlands, and evidence for climatological teleconnections around 2650 BP. Journal of Quaternary Science 11, 451–460.

van Geel, B., van der Plicht, J., Kilian, M.R., Klaver, E.R., Kouwenberg, J.H.M., Renssen, H., Reynaud-Farrera, I., Waterbolk, H.T., 1998, The sharp rise of $\Delta^{14}C$ *ca* 800 cal BC. Possible causes, related climatic teleconnections and the impact on human environments, *Radiocarbon* 40, 535–550.

ten Haven, H.L., Rullkötter, J., 1988. The diagenetic fate of taraxer-14-ene and oleanene isomers. Geochmica et Cosmochimica Acta 52, 2543–2548.

ten Haven, H.L., Peakman, T.M., Rullkötter, J., 1992. Early diagenetic transformations of higher-plant triterpenoids in deep-sea sediments from Baffin Bay. Geochimica et Cosmochimica Acta 56, 2001–2024.

Karunen, P., Salin, M., 1980. Lipid composition of *Sphagnum fuscum* shoots of various ages. Finnish Chemistry 7, 500–502.

Karunen, P., Ekman, R., 1982. Age-dependent content of polymerized lipids in *Sphagnum fuscum*. Physiologia Plantarum 54, 162–166.

Kenig, F., Sinninghe, Damsté, J.S., Frewin, N.L., Hayes, J.M., de, Leeuw, J.W., 1995. Molecular indicators for paleoenvironmental change in a Messinian evaporitic sequence (Vena del Gesso, Italy) 2. High-resolution variations in abundances and C-13 contents of free and sulfur-bound carbon skeletons in a single marl bed. Organic Geochemistry 23, 485–526.

Kilian, M., van der, Plicht, J., van, Geel, B., 1995. Dating raised bogs: New aspects of ^{14}C wiggle matching, a reservoir effect and climatic change. Quaternary Science Reviews 14, 959–966.

Killops, S.D., Frewin, N.L., 1994. Triterpenoid diagenesis and cuticular preservation. Organic Geochemistry 21, 1193–1209.

Lehtonen, K., Ketola, M., 1993. Solvent-extractable lipids of Sphagnum, Carex, Bryales and Carex Bryales peats — content and compositional features vs peat humification, Organic Geochemistry 20, 363–380.

Mauquoy, D., van, Geel, B., Blaauw, M., van der, Plicht, J., 2002. Evidence from northwest European bogs show 'Little Ice Age' climatic changes driven by variations in solar activity. The Holocene 12, 1–6.

McQuillin, F.J., 1963. Reduction and hydrogenation in structural elucidation. In: Bentley, K.W. (Ed.), Technique of Organic Chemistry XI. Part One: Elucidation of Structures by Physical and Chemical Methods. Interscience, New York, pp. 497–580.

Nott, C.J., Xie, S., Avsejs, L.A., Maddy, D., Chambers, F.M., Evershed, R.P., 2000. *n*-Alkane distributions in ombrotrophic mires as indicators of vegetation change related to climatic variations. Organic Geochemistry 31, 231–235.

Pancost, R.D., Freeman, K.H., Patzkowsky, M.E., Wavrek, D., Collister, J.W., 1998. Molecular indicators of redox and marine phytoplankton composition in the late Middle Ordovician of Iowa, USA. Organic Geochemistry 29, 1649–1662.

Spyckerelle, C. (1975) Constituant Aromatiques de Sédiments. PhD Thesis, University of Strasbourg, pp. 134.

Wakeham, S.G., Schaffner, C., Giger, W., 1980. Polycyclic aromatic hydrocarbons in recent lake sediments, II: compounds derived from biogenic precursors during early diagenesis. Geochimica et Cosmochimica Acta 44, 415–429.

Werne, J.P., Hollander, D.J., Lyons, T.W., Peterson, L.C., 2000. Climate-induced variations in productivity and planktonic ecosystem structure from the Younger Dryas to Holocene in the Cariaco Basin, Venezuela. Paleoceanography 15, 19–29.