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Molecular and isotopic stratigraphy in an ombrotrophic mire for paleoclimate reconstruction

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Abstract—A 40 cm deep *Sphagnum*-dominated peat monolith from Bolton Fell Moss in Northern England was systematically investigated by lipid molecular stratigraphy and compound-specific $\delta^{13}C$ and δD analysis using gas chromatography (GC), GC-mass spectrometry (GC-MS), GC-combustion-isotope ratio-MS (GC-C-IRMS) and GC-thermal conversion-IRMS (GC-TC-IRMS) techniques. ^{210}Pb dating showed the monolith accumulated during the last ca. 220 yr, a period encompassing the second part of Little Ice Age. While the distributions of lipids, including *n*-alkan-1-ols, *n*-alkan-2-ones, wax esters, sterols, *n*-alkanoic acids, α,ω-alkandioic acids and ω-hydroxy acids, display relatively minor changes with depth, the cooler climate event was recorded in the concentrations of *n*-alkanes and organic carbon, CPI values of *n*-alkanes and *n*-alkanoic acids, and the ratio of 5-*n*-alkylresorcinols/sterols. Superimposed on the fossil fuel effect, the relatively cooler climate event was also recorded by $\delta^{13}C$ values of individual hydrocarbons, especially the C_{23} *n*-alkane, a major compound in certain *Sphagnum* spp. The δD values of the C_{29} and C_{33} *n*-alkanes correlated mainly with plant composition and were relatively insensitive to climatic change. In contrast the C_{23} *n*-alkane displayed variation that correlated strongly with recorded temperature for the period represented by the monolith, agreeing with previously reported deuterium records in tree ring cellulose spanning the same period in Scotland, Germany and the USA, with more negative values occurring during the second part of Little Ice Age. These biomarker characteristics, including the compound-specific $\delta^{13}C$ and δD records, provide a new set of proxies of climatic change, potentially independent of preserved macrofossils which will be of value in deeper sections of the bog where the documentary records of climate are unavailable and humification is well advanced. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

The preservation qualities of peat bogs make them unique in retaining plant fossils. The stratigraphic records that these fossils produce contain valuable information about past climate. Changes in the surface wetness of a bog arising through differences in precipitation and evaporation can influence species of plant thriving there. Therefore, the plant fossil records that are retained in the peat can be used as a proxy for climate (Barber, 1985). Ombrotrophic mires, whose only water source is from direct precipitation, have been shown to be particularly responsive to climatic change (Barber et al., 1994). The high accumulation rate characteristic of ombrotrophic mires and their preservation qualities allow exceptional high resolution records of past climates to be retained.

Techniques used for paleoclimate reconstruction from peat deposits have included macrofossil analysis (Barber, 1994), humification indices (Blackford and Chambers, 1993), stable isotopic records (White et al., 1994; Figge and White, 1995), testate amoebae (Hendon et al., 2001) and ^{14}C (Mauquoy et al., 2002). Recent research has significantly improved our understanding of the climate signals reflected in the above proxies. For example, they have been shown to be replicable within and between sites (Barber et al., 1998; Mauquoy and Barber, 1999; Hendon et al., 2001) with the records being cyclic, with periodicities reflecting links with oceanic cycles (Chapman and Shackleton, 2000) and solar variability (Mauquoy et al., 2002, and references therein). Successful applications include the use of $\delta^{13}C$ values of isolated macrofossils from peat bogs to reconstruct past atmospheric CO_2 concentrations (White et al., 1994; Figge and White, 1995). Variations in δD values of bulk peat and isolated peat cellulose have been shown to correlate with plant community compositions, as judged from macrofossil analyses and, hence, climate (Schiegl, 1972; Dupont and Mook, 1987; van Geel and Middeldorp, 1988).

Just as peat bogs are exceptional environments for preserving fossil organisms the potential also exists for them to preserve the original biochemical components of those organisms. In common with marine (Brassell et al., 1986; Prahl and Wakeham, 1987) and lacustrine (Huang et al., 1999) sediments, lipid biomarkers preserved in peat may provide additional molecular and/or stable isotopic stratigraphic records of past climate. Previous work has shown that lipids do indeed survive in peats in appreciable concentrations. For example, an investigation of lipid subfractions of *Sphagnum* and *Carex* peats of various degrees of humification identified long-chain acyclic methyl ketones (Lehtonen and Ketola, 1990) which may derive from peat-forming mosses and sedges, or via bacterial oxidation of *n*-alkanes and/or β-oxidation and decarboxylation of *n*-fatty acids. In a further study (Lehtonen and Ketola, 1993) the diagenetic changes to peat lipids in 4 different peat types,

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Sphagnum, *Carex*, *Bryales* and *Carex*/*Bryales* was explored; hydrocarbon, ketone, alcohol, sterol and acidic fractions were investigated. Although no specific humification effects were detectable in the *n*-alkanol distributions of *Sphagnum* and *Bryales* peats, the sterol fraction was found to consist of 4 major components i.e., β-sitosterol, stigmasterol, campesterol and stigmastanol, together with lower abundances of stanols that were most likely to be products of microbial reduction of the corresponding sterols. The acidic lipid fraction comprised *n*-alkanoic acids and ω-hydroxy acids, with the longer chain homologues ($>C_{22}$) of the former increasing in abundance with increased humification. In common with the *n*-alkanoic acids the longer chain hydroxy acids ($>C_{22}$) increased in relative abundance with increased humification. Overall, the peat lipid components were attributed to moss and higher plant source with changes in alkyl lipid distributions becoming more exaggerated with increased humification and ascribed as a microbial diagenetic effect.

Studies of lipids from peat deposits other than raised bogs have included the comparison of peats from tropical, subtropical, temperate and cool temperate climates (Dehmer, 1995). It was suggested that the odd numbered *n*-alkanes (C_{25}, C_{27} and C_{29}) derived from higher plant waxes and that those with chain lengths less than C_{23} may be due to bacterial activity. The presence of hopanoids [17β, 21β(H)-22*R*-homohopane the main componentin peats was attributed to microbial activity. Several nonhopanoid aromatic triterpenoids were identified in peats from subtropical regions, including 1,2,9- and 2,2,9-trimethyl-1,2,3,4-tetrahydropicene, the formation of which was attributed to bacterially mediated aromatization of α- and β-amyrin.

One of the few attempts to relate the lipid composition of peat to changing plant contribution during the accumulation of a peat bed was that of Farrimond and Flanagan (1996). In this study the *n*-alkane, *n*-alcohol, sterol and hopanoid contents of 18 samples from a 93 cm thick continuous section of peat were determined and the lipid distributions compared with pollen assemblages. Overall, it was found that although lipid and pollen data show comparable trends in plant input, they did not correlate well in detail and this was attributed to the lipids being derived from allochthonous plant debris and pollen, transported in from surrounding areas.

A more recent investigation of lipids in peat employed a compound specific $\delta^{13}C$ approach to derive a record of climatic changes over the last 2000 yr (Ficken et al., 1998). $\delta^{13}C$ values of *n*-alkanes were compared with lipid and macrofossil stratigraphies, in an effort to provide information about atmospheric CO_2 concentration and the changing plant inputs. The lipid distributions of subsamples of a section of peat (54 cm profile) and 12 identified plant species growing on the bog, were determined and compared to establish the origin of the peat lipids. It was discovered that apart from the $\delta^{13}C$ values of *n*-alkanes in the top 6 cm there was very little variation down the core and the depletion of ^{13}C seen in the topmost samples (average $\delta^{13}C$ for C_{29+31}, -31.5 to -30.7‰) was attributed to burning of fossil fuels lowering the atmospheric ^{13}C content. $\delta^{13}C$ values of *n*-alkanes from deeper peat samples (average $\delta^{13}C$ for C_{29+31}, -30.1 to -29.7‰) however, did not reveal variations that would be readily exploitable for paleoclimate reconstruction. Overall, the study appeared to be hampered by a lack of biomarkers specific to the peat inputs.

We report herein the results of an investigation aimed at building on the studies outlined above, with our overall objective being to establish a firmer basis for the use of peat based lipid biomarker and isotope records of climate change. To achieve this we have focussed on ombrotrophic mires since these peat deposits: (i) are known to be highly responsive to climate change due to nutrient and water inputs that are entirely of atmospheric origin. Macrofossil analyses have demonstrated that peat-forming plant communities respond more or less synchronously to shifts to wetter and/or cooler climates (Aaby, 1976; Barber, 1981; Svensson, 1988; Barber et al., 2000; Hughes et al., 2000); (ii) display high accumulation rates and thus can provide high resolution records (decadal timescales), and (iii) allochthonous organic inputs are minimal. In addition, we have attempted to identify biomarkers that can be more precisely used to track inputs from specific peat-forming plants, e.g., sedges and mosses. We target initially an upper section of peat close to the bog surface representing accumulation during the recent past, a period for which an accurate dating model based on ^{210}Pb could be established, and documentary meteorological records exist for the region over the past 300 yr (Manley, 1974; Parker et al., 1992; Jones and Hulme, 1997; Jones et al., 1997; Barber et al., 2000). The latter provide the basis for comparison with lipid and stable isotopic stratigraphic and macrofossil records as an essential step in the development of biomarker based climate proxies from peat.

2. EXPERIMENTAL

2.1. Site and Sampling

Bolton Fell Moss, situated in Cumbria (National Grid Reference NY 495695), was a large ombrotrophic mire covering an area of around 400 ha in northern England and at present is dominated by *Sphagnum* mosses with an area of some 30 ha. Previous detailed analyses of the macrofossil assemblages have demonstrated the peat-forming plant communities at Bolton Fell respond more or less synchronously to shifts to wetter and/or cooler climates and that these wet shifts correlate with climatic changes known from independent proxy and documentary records (Barber et al., 1994, 1998). A 40 cm peat monolith was taken from the centre of Bolton Fell Moss using a monolith tin and stored in a freezer (-20°C) in the dark until required for analysis. After discarding the outer peat to avoid introduction of contaminants the monolith was subsampled by slicing into 1 cm sections. Macrofossil analyses in an adjacent core were performed according to the methods of Barber et al. (1994).

2.2. Dating

The top 30 cm of the monolith was dated by ^{210}Pb (Fig. 1).^{210}Pb (half-life = 22.3 yr) is a naturally occurring radionuclide that has been extensively used in the dating of recent sediments. Dating is based on determination of the vertical distribution of ^{210}Pb derived from atmospheric fallout (termed unsupported ^{210}Pb, or $^{210}Pb_{excess}$), and the known decay rate of ^{210}Pb (Appleby and Oldfield, 1992). ^{210}Pb activity was determined by a proxy method through alpha spectrometric measurement of its granddaughter nuclide ^{210}Po. The method employed is based on Flynn (1968), using double acid leaching of the sediment with ^{209}Po as an isotopic tracer followed by autodeposition of the Po isotopes in the leachate on to silver discs. Discs were counted for a minimum of 100,000 s, and detection limits are 0.1 Bq kg^{-1}. The $^{210}Pb_{excess}$ activity was estimated by subtraction of the value of ^{210}Pb activity in deeper samples (0.001 Bq g^{-1}, 28–29 cm).

2.3. Lipid Extraction and Fractionation

The freeze-dried peat was ground to pass through a 0.5 mm sieve. Small aliquots of powdered peat were submitted to elemental analyses for total organic carbon determinations. About 0.5 g peat was Soxhlet-

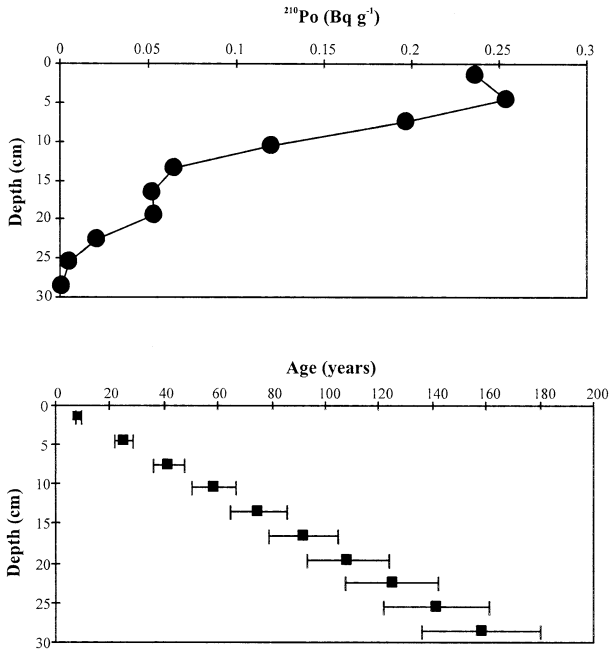

Fig. 1. ^{210}Pb activity as determined from measurement of the granddaughter nuclide ^{210}Po (top) and the calculated ages (bottom) for the top 30 cm in the peat monolith.

extracted with dichloromethane/acetone (9:1, v/v) for 24 h after adding a mixture of standards. The total lipid extracts were separated into neutral and acid fractions by solid phase extraction using aminopropyl Bond Elut cartridges (Varian Chromatography) by sequential elution with dichloromethane/isopropanol (2:1, v/v) and 2% acetic acid in diethylether. The neutral fraction was further separated into hydrocarbon, aromatic, ketone/wax ester, alcohol/sterol and polar fractions using column chromatography (silica gel 60) by sequential elution with hexane, hexane/dichloromethane (9:1, v/v), dichloromethane, dichloromethane/methanol (1:1, v/v) and methanol. The alcohol/sterol fraction was adducted with saturated urea in methanol solution to separate *n*-alkanols from cyclic compounds.

2.4. Instrumental Analysis

Before GC and GC-MS analysis, the acid fraction was first methylated with BF_3/methanol. The methylated acid fraction, alcohol/sterol fraction and ketone/wax ester fraction were heated (70°C, 1.5 h) with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) to yield the corresponding trimethylsilyl ester/ether derivatives. GC analyses of hydrocarbons, alcohols, sterols and acids (1 μL sample injection) were undertaken using a Hewlett Packard 5890 series II gas chromatograph equipped with an on-column injection port and a flame ionization detector (FID). Separation of compounds was achieved using a fused silica CPSil-5CB capillary column (50 m $\times$ 0.32 mm i.d.; film thickness 0.12 μm). Hydrogen was used as the carrier gas and the GC oven temperature was programmed as follows: 40°C (1 min), 40–200°C at 10°C min^{-1}, 200–300°C at 3°C min^{-1}, 300°C (20 min). GC-MS analysis of the fractions were performed on a Carlo Erba 5160 Mega gas chromatograph (on-column injection) interfaced directly with a Finnigan MAT 4500 quadrupole mass spectrometer (EI, 70 eV). The GC column and oven temperature program were identical to those used for GC analyses. Helium was used as the carrier gas. Identification and quantification of ketones and wax esters was performed by HT-GC and HT-GC/MS using capillary columns coated with a thin film of high temperature-stable stationary phase (DB-1, 15 m $\times$ 0.32 m; 0.12 μm film thickness). The GC temperature program was 50°C (1 min), 50–350°C at 10°C min^{-1}, 350°C (20 min).

Stable carbon-isotope compositions of the hydrocarbon fractions were determined using a Varian 3400 GC attached to a Finnigan MAT Delta-S isotope ratio mass spectrometer via a combustion interface consisting of an alumina reactor (0.5 mm i.d.) containing copper and platinum wires (0.1 mm o.d.). The column, carrier gas and temperature program were the same as for the GC and GC-MS analyses. Reproducibility of δ^{13}C values of specific compounds is better than $\pm$0.5‰ based on triplicate analyses and an internal laboratory standard. Results are reported in the standard delta notation relative to the Pee Dee Belemnite (PDB) standard.

Determination of δD values in individual *n*-alkanes was achieved using a Hewlett Packard GC attached to a Finnigan MAT Delta-plus IRMS via a thermal conversion system. The high temperature conversion system (up to 1500°C) based on the GC combustion II system from Finnigan MAT could quantitatively converts the hydrogen bound in organic compounds after GC separation into H_2 gas before analysis in the IRMS. The IRMS has a dispersion of 180 mm, a wide simultaneous detection focal plane for the detection of masses 2 and 3, and a gridless retardation lens with close to 100% transmission, incorporated into the Faraday cup design for the *m/z* 3 channel. An additional contribution to the mass 3 signal, originating from the formation of H_3^+ ions from ion molecule reactions between H_2^+ and neutral H_2 in the ion source, was corrected for through a small and stable H_3-factor measured every day. All values of δD reported here are relative to VSMOW. A laboratory standard was used to determine the H_3^+ factor for the day, normalize δD values to the VSMOW scale, and monitor the stability of the system. Another standard of *n*-alkane mixture containing 6 homologues (C_{20}-C_{30}, even) varying in δD by 250‰ was analyzed at least twice a day, to assess analytical accuracy. The mean precision of δD measurement for these alkanes over the whole analysis of this study was $\pm$5‰.

3. RESULTS AND DISCUSSIONS

3.1. Peat Dating

Peat accumulation rates were determined using the simple model of ^{210}Pb dating (Robbins, 1978), where the accumulation ratio is given by the slope of the least squares fit for the natural log of the $^{210}Pb_{excess}$ activity versus depth. The peat accumulation rate for the top 30 cm of this monolith was calculated to be 1.8 mm a^{-1}, standard error range 1.6–2.1 mm a^{-1}, 2 standard deviation (2σ) ranges 1.3–2.8 mm a^{-1}. This rate was extrapolated to the bottom 10 cm of this profile to give an estimated date for the bottom most section (39–40 cm) of the monolith of 220 aBP. Similar anomalously young dates to that observed in the top section of the profile (i.e., 0–40 cm) have been reported previously in ^{210}Pb-dated *Sphagnum* hummocks (El-Daoushy et al., 1982) and other ^{14}C-dated peat bogs (van Geel and Middeldorp, 1988).

3.2. Macrofossils

The macrofossil profile (Fig. 2) from an immediately adjacent peat core shows the dominance of *Sphagnum*, especially at the depth of 8–9 to 30–31 cm. *Sphagnum* accumulated in the top 40 cm includes *S. magellanicum*, the most abundant species, *S. s. acutifolia* mainly dominating at 23–24 to 32–33 cm and *S. s. cuspidata*. Monocotyledons occur primarily between 4–5 to 8–9 cm and 30–31 to 37–38 cm. A low abundance (less than 10%) of *Ericaceae* is seen to occur between 13–14 and 22–23 cm. As much as 20% of plant debris at 6 cm depth is attributed to unidentifiable (humified) organic matter, which is taken to indicate relatively dry conditions prevailed at the bog surface at the time of peat formation (Barber et al., 1994).

3.3. Lipid Fractions

3.3.1. Hydrocarbons

The gas chromatograms of the hydrocarbon fractions show a dominance of *n*-alkanes ranging mainly from C_{21}-C_{35}, having

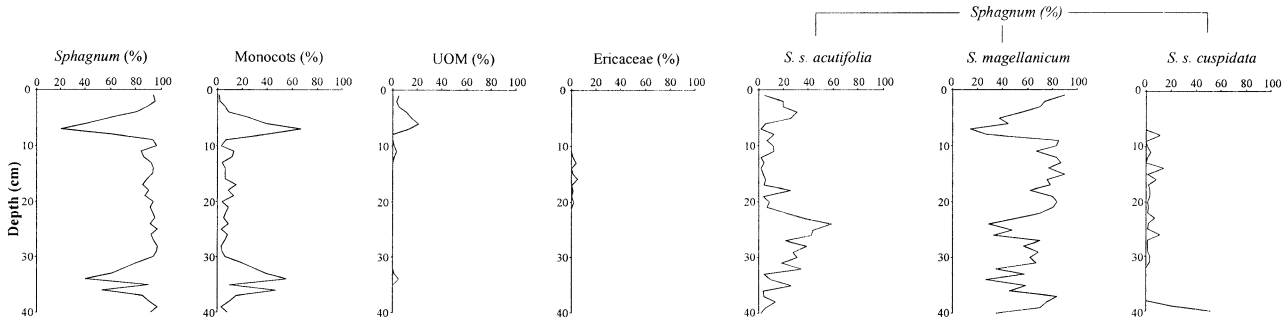

Fig. 2. Macrofossil compositions of an adjacent monolith, including total *Sphagnum*, Monocotyledons (predominantly sedges), with composition of "dry" (unidentified organic matter [UOM]) through to "wet" indicating (*S. s. Cuspidata*) peat-forming species.

a maximum at C_{23} and/or C_{31} (Fig. 3) and displaying a distinct odd-over-even carbon number predominance (Table 1). This type of carbon number distribution is believed to originate mainly from epicuticular waxes of peat-forming plants (Baas et al., 2000; Nott et al., 2000). The most striking feature of the carbon number distribution is the progressive shift in the carbon number maximum from C_{31} to C_{23} then back to C_{31} down the profile (Fig. 3). Shorter chain homologues (C_{14}-C_{20}) comprised no more than 3% of the total *n*-alkanes. These low molecular weight *n*-alkanes may be of bacterial origin (Otto et al., 1994) while the presence of C_{17} and C_{19} components points to a contribution from algae (Blumer et al., 1971).

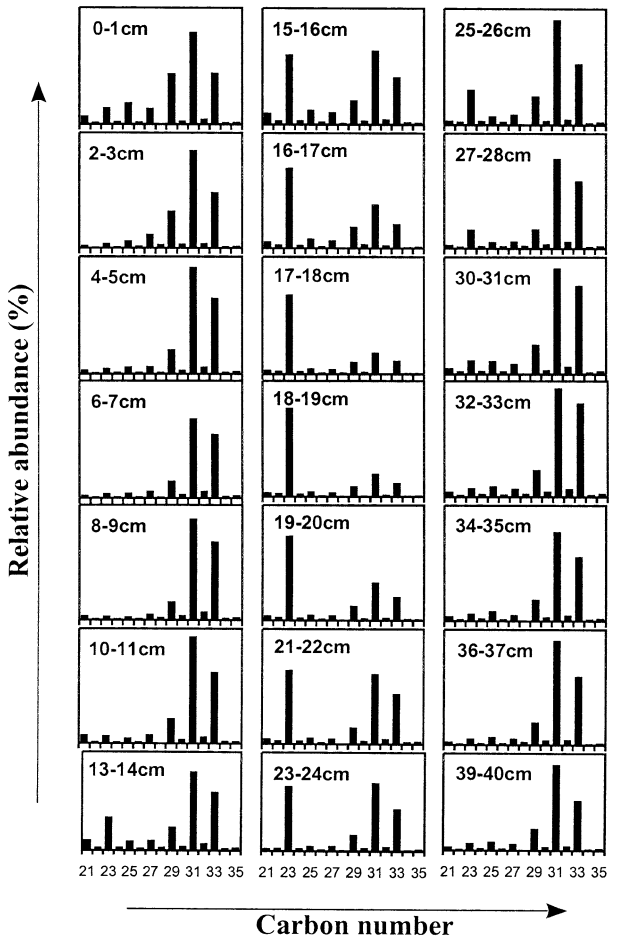

Fig. 3. Carbon number distributions of *n*-alkanes down profile in the 40 cm peat monolith.

A small proportion of *n*-alkenes from C_{19} to C_{29} were detected along with the long chain *n*-alkanes. The occurrence of long chain *n*-alkenes has been seen previously in eutrophic lake sediments (Giger and Schaffner, 1977), Antarctic soils (Matsumoto et al., 1990) and oligotrophic peat (Dehmer, 1995). It has been proposed that these alkenes derive from vascular plants, microalgae and cyanobacteria (Dehmer, 1995).

Triterpenoids have not been widely reported in lipid extracts of peat and, when documented they are generally unsaturated components in immature peat deposits (Dehmer, 1995). Non-hopanoid triterpenes identified from this peat monolith are dominated by taraxer-14-ene and taraxast-20-ene, with lower abundances of olean-12-ene and urs-12-ene. The presence of taraxer-14-ene has been reported previously in peats, brown coals and marine sediments (Brassell et al., 1980; Pancost et al., 2002). Possible precursors, such as taraxer-14-en-3-ol and taraxer-14-en-3-one, have been found in several marine sediments (Brassell et al., 1980; Brassell and Eglinton, 1983; Brassell et al., 1986; Volkman et al., 1987). These nonhopanoid triterpenes in the peat are derived predominately from the peat-forming plants and their likely biogenic precursors, such as taraxerol and β-amyrin (Pancost et al., 2002), are widespread in the plant kingdom, in particular taraxerol, the C_{30}-alcohol, has been demonstrated to be a common triterpenoid present in *Sphagnum* spp. (Karrer, 1958).

The major triterpane identified in this peat is C_{31} $\alpha\beta$-29-methylhopane together with a low abundance of C_{31} $\beta\beta$-29-methylhopane. Hopanes with a 17β(H), 21β(H) configuration are normally regarded as being bacterially derived (Ourisson et al., 1979), formed through the reduction of hopanoid acids and polyols. The geohopanes of the $\alpha\beta$-type are suggested to form through the isomeric transformation of the biohopanes of the $\beta\beta$-type during diagenesis, but an explanation for their occurrence without implicating thermal maturation is unclear (Seifert and Moldowan, 1980). The dominance of the C_{31} $\alpha\beta$ hopane in peat has been reported previously (van Dorsselaer et al., 1977; Quirk et al., 1984) and shown to appear at the very earliest stage of moss decay. This compound even appears in the surface sample in the peat subject of this investigation. It has been proposed that the formation of 17α(H), 21β(H)-homoho-

Table 1. CPI values of *n*-alkanes, *n*-alkanols, *n*-alkanoic acids, α,ω-alkandioic acids and ω-hydroxy acids.

Depth (cm)	*n*-Alkanes	*n*-Alkanols	*n*-Alkanoic acids	α, ω-Alkandioic acids	ω-Hydroxy acids
0–1	17.5	7.9	7.2	3.2	6.5
2–3	14.1	8.2	5.5	5.8	4.3
4–5	14.6	13.4	5.4	9.7	4.2
6–7	12.3	8.6	5.2	10.7	6.4
8–9	12.0	8.1	5.2	10.3	6.0
10–11	14.7	6.7	5.7	10.1	12.4
13–14	9.7	11.3	8.0	11.8	10.4
15–16	12.0	12.6	7.3	12.7	7.1
16–17	13.3	8.6	7.7	7.9	12.7
17–18	14.1	9.8	9.4	12.3	8.6
18–19	18.5	10.6	8.5	9.5	12.0
19–20	16.6	12.9	8.5	13.1	7.8
21–22	14.2	10.5	7.7	16.9	8.3
23–24	14.7	8.9	6.7	8.6	8.1
25–26	12.9	11.0	5.9	11.7	9.3
27–28	10.8	12.0	6.9	12.9	10.7
30–31	13.1	6.0	7.6	8.2	15.6
32–33	11.8	11.5	7.7	10.2	14.9
34–35	14.1	9.6	8.1	11.7	13.6
36–37	14.3	7.8	7.5	12.1	10.0
39–40	16.0	8.7	8.4	9.1	13.5

pane is due to the oxidative and subsequent decarboxylation reactions of bacteriohopantetrol with microbially mediated (rather than chemically mediated; Rohmer et al., 1980) epimerization at position C-17 catalyzed by the acidic environment in the mire (van Dorsselaer et al., 1977; Reis-Kautt and Albrecht, 1989). The proposed microbial origin for this compound is supported by compound-specific $\delta^{13}C$ values as discussed below.

3.3.2. Ketones/Wax Esters

n-Alkan-2-ones identified in the peat, range from C_{25} to C_{35} and have a maximum at either C_{29} or C_{31} and exhibit a strong odd-over-even carbon number predominance. Long-chain ketones have been widely reported as components of the epicuticular waxes of higher plants (Kolattukudy, 1976; Walton, 1990). Triterpenoids identified in this fraction include taraxerone and olean-13(18)-en-3-one.

Morrison and Bick (1967) reported a series of *n*-alkan-2-ones in the peat wax fraction extending over the carbon number range C_{17}-C_{35}, with the distribution possessing a high odd-over-even carbon number predominance, and the most abundant homologues being C_{25} and C_{27}. In a *Sphagnum* peat studied by Lehtonen and Ketola (1990) methyl ketones were also found to range from C_{17}-C_{35} but maximized at C_{17}, with the shorter chain C_{17}-C_{23} homologues greatly increasing in abundance with increasing degree of humification. The peat monolith subject of this investigation lacks the shorter chain C_{17}-C_{23} homologues, probably indicating a relatively lower state of humification due to the shallow depth of burial.

Several possible origins are suggested for the *n*-alkan-2-ones: (i) epicuticular waxes of peat-forming plants, (ii) microbial oxidation of *n*-alkanes, (iii) β-oxidation and decarboxylation of *n*-fatty acids, and/or (iv) microbial cracking of longer-chain *n*-alkan-2-ones to yield the shorter chain components. The high abundance of C_{29} and C_{31} ketones in Bolton Fell Moss peat may indicate the microbial oxidation of *n*-alkanes, with possible contributions from the epicuticular waxes of peat-forming plants. The oxidative decarboxylation of the dominant C_{24} and C_{26} *n*-fatty acids would yield C_{23} and C_{25} methyl ketones, which are only minor components throughout the peat profile. Therefore *n*-fatty acids appear not to be in the main precursors for the methyl ketone formation in the Bolton Fell peat.

Wax esters (Fig. 4) bearing a C_{16} fatty acyl moiety mainly ranged from C_{38} to C_{52}, maximizing either at C_{40} and C_{42} (dominating below 15–16 cm) or C_{48} and C_{50} (dominating above 15–16 cm) with obvious even-over-odd carbon number predominances; only 2 samples (2–3 and 4–5 cm) show dominant C_{44} and C_{46} homologues.

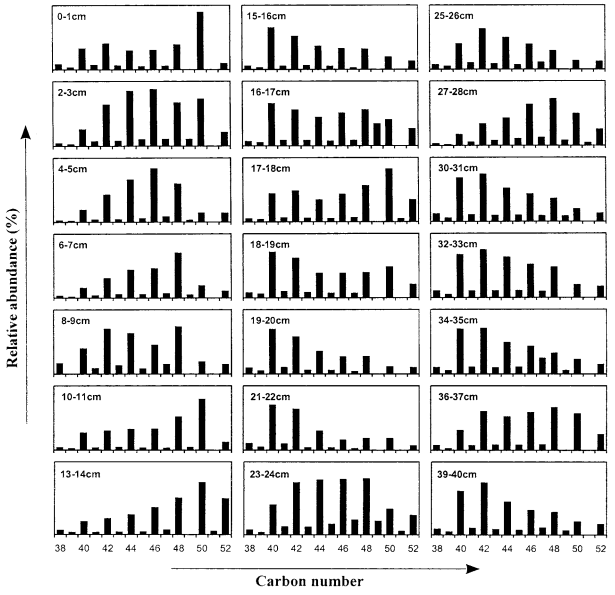

Fig. 4. Carbon number distributions of wax esters down profile in the 40 cm peat monolith.

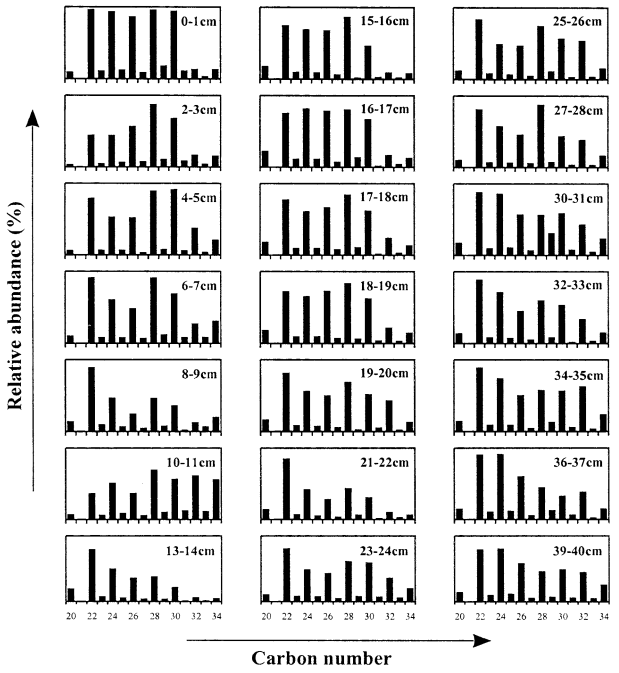

Fig. 5. Carbon number distributions of *n*-alkanols down profile in the 40 cm peat monolith.

3.3.3. Alcohols/Sterols

The major sterols and stanols occurring in the monolith are 24-ethylcholest-5-en-3β-ol (β-sitosterol), 24-ethyl-5α-cholestan-3β-ol (stigmastanol), 24-ethylcholesta-5,22-dien-3β-ol (stigmasterol), 24-ethyl-5α-cholest-22-en-3β-ol, 24-methylcholest-5-en-3β-ol (campesterol) and 24-methyl-5α-cholestan-3β-ol (campestanol). This distribution is entirely consistent with higher plant dominated nature of the peat. The ratio of stigmastanol/β-sitosterol shows an increase with depth, especially below 30 cm. As only trace amounts of stigmastanol have been identified in the stanol fractions of various sphagna (Karunen et al., 1983), Lehtonen and Ketola (1993) attributed the stanols of peat to the microbial reduction of the corresponding stenols (Δ^5-sterols). In lacustrine sediments the increase in stanol/Δ^5-sterol ratio with increasing depth has also been considered to be indicative of such a microbial reduction (Gaskell and Eglinton, 1976; Mermoud et al., 1985; Cranwell, 1986).

The principal triterpenoids include α-amyrin, 17α(H), 21β(H)-bishomohopan-32-ol and 17β(H), 21β(H)-bishomohopan-32-ol. C_{32} hopanols are generally ascribed to bacterial inputs (Ourisson et al., 1979) and have been reported previously in decayed *Sphagnum* (Quirk et al., 1984).

n-Alkanols extracted from the peat ranged from C_{20} to C_{34} (Fig. 5) with an obvious even-over-odd carbon number predominance (Table 1), with the C_{22} homologue generally predominating; the 0–1 and 15–19 cm depth horizons displayed a similar abundance of C_{22}, C_{24}, C_{26}, C_{28} and C_{30} homologues. Although these functionalized compounds are expected to be at least as bio-available as the *n*-alkanes (Ficken et al., 1998), the variation in the distributions of *n*-alkanols does not correlate with the macrofossil data; likely complicating factors include the hydrolysis of wax esters thereby contributing *n*-alkanols to the free lipid fraction.

5-*n*-Alkyl-resorcinols with alkyl side chains of C_{19}, C_{21}, C_{23} and C_{25} were identified at all depths, maximizing at C_{21} (e.g., 1–2 to 7–8 cm) or C_{19} (e.g., 10–11 to 26–27 cm) homologues (Avsejs et al., 2002).

3.3.4. Carboxylic Acids

The acid fractions from the peat monolith were complex but dominated by *n*-alkanoic acids, α,ω-alkandioic acids and ω-hydroxy acids. *n*-Alkanoic acids displayed carbon number distribution ranging from C_{16} to C_{34}, maximizing at C_{24} or C_{26} (Fig. 6) and displaying a strong even-over-odd carbon number predominance (Table 1). A bimodal distribution of *n*-alkanoic acids centering at C_{16} and C_{24} is seen at the shallowest depths with palmitic acid (C_{16}) rapidly decreasing in abundance down core. Generally, the fatty acid distribution does not vary greatly throughout the monolith, a trend which was also observed in a Scottish blanket peat investigated by Ficken et al. (1998). Slight variations in the carbon distributions are seen in the 2–3 to 10–11 cm sections where the longer-chain acids ($>C_{30}$) are more abundant.

α,ω-Alkandioic acids distributions ranged from C_{20} to C_{28} with a maximum at C_{22} (Fig. 7) and displayed a high even-over-odd carbon number predominance (Table 1). The distributions of α,ω-alkandioic acids remained almost constant throughout the whole monolith with the exception 16–18 cm section where C_{22}, C_{24} and C_{26} homologues exhibited similar abundances.

ω-Hydroxy acids ranged (Fig. 8) from C_{20} to C_{28}, maximizing at C_{22} (0–1 to 16–17 cm, 21–22 cm, 27–28 cm and 36–37 cm), or C_{26} (16–17 to 20–21 cm, 23–24 to 25–26 cm, 30–31 to 35–36 cm and 39–40 cm), and displayed a high even-over-odd carbon number predominance (Table 1). A feature of the distribution of ω-hydroxy acids is that the longer chain components, the C_{26} in particular, increased in relative abundance below 13–14 cm depth. A similar increase in the abundance of the C_{26} ω-hydroxy acid has been reported previously in highly decomposed *Sphagnum* peat (Lehtonen and Ketola, 1993).

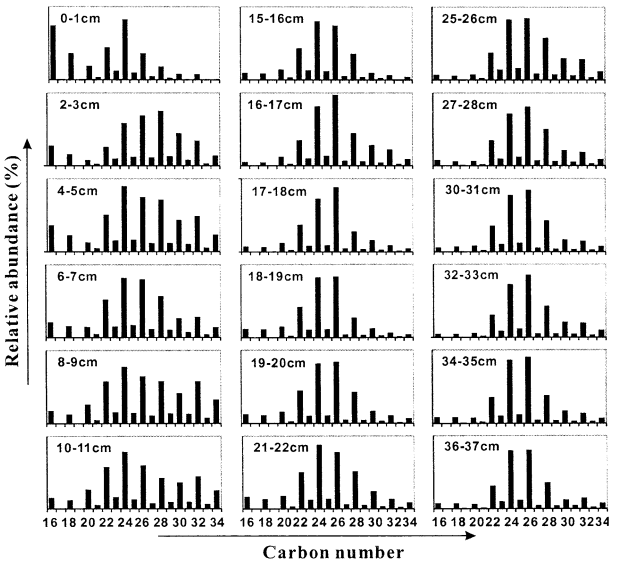

Fig. 6. Carbon number distributions of *n*-alkanoic acids down profile in the 40 cm peat monolith.

Fatty acids are ubiquitous in living organisms fulfilling a variety of roles. Hydroxy acids are the most common functionalized fatty acids in higher plants but appear to be relatively uncommon in fungi. Long chain ω-hydroxy acids ($>C_{20}$) are characteristic higher plant biomarkers, deriving from the polyesters cutin and suberin (Walton, 1990). The α,ω-diacids probably also originate mainly from the higher plants and mosses where they also occur as polymer ester constituents of the peat-forming vegetation (Eglinton and Hamilton, 1967; Karunen et al., 1983; Lehtonen and Ketola, 1993). However, fatty acids can be altered by microbial oxidation in sedimentary environments, e.g., oxidation of ω-hydroxy acids to α,ω-diacids by yeast and bacteria, thus care must be exercised when using such components as source indicators. The similar carbon distributions of the α,ω-diacids and ω-hydroxy acids and the relatively low carbon preference index (CPI) values of α,ω-diacids (Table 1) in the shallowest samples, indicate that at least a portion of the α,ω-diacids may be produced by microbial oxidation of long chain ω-hydroxy acids.

3.4. Bulk and Compound-Specific $\delta^{13}C$ and δD Values

3.4.1. $\delta^{13}C$ Values of Bulk Peat

The $\delta^{13}C$ values of the bulk peat subsampled from the monolith ranged from -24.6 to -28.0‰ (Table 2), consistent with a C_3 plant source (Galimov, 1985). A general trend toward more depleted values (-24.6 to -28.0‰) is seen above 22–23 cm (^{210}Pb-dated at ca. A.D. 1870). It has been demonstrated that the burning of fossil fuels since the industrial revolution (last 130 yr) has resulted in the $\delta^{13}C$ value of the atmosphere becoming more depleted in ^{13}C by ca. 1.3‰. Hence, the $\delta^{13}C$ value of the preindustrial atmosphere has shifted from -6.5 to the -7.8‰ recorded in the present day (Friedli et al., 1986). The factors contributing to the additional 2.2‰ variation, believed to reflect the influence of temperature, are discussed later.

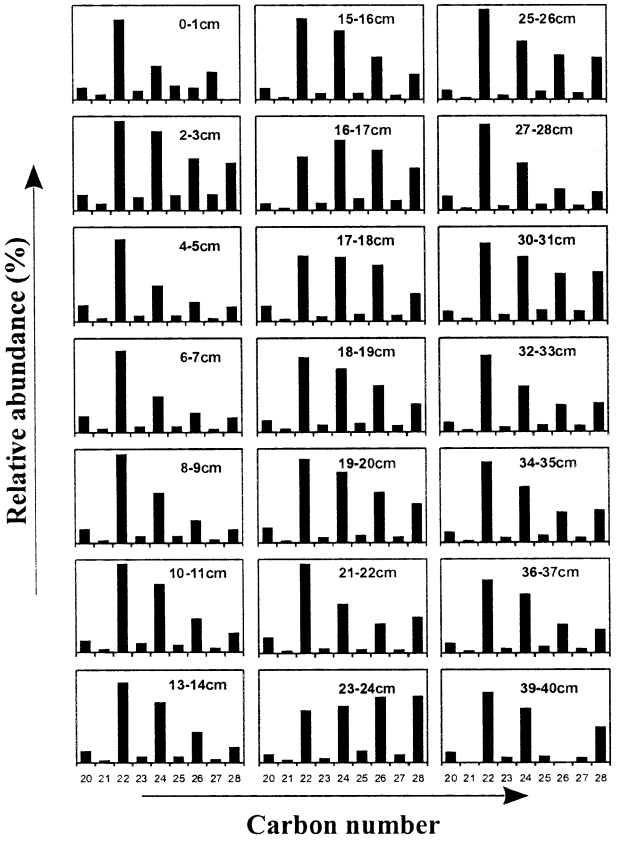

Fig. 7. Carbon number distributions of α,ω-alkandioic acids down profile in the 40 cm peat monolith.

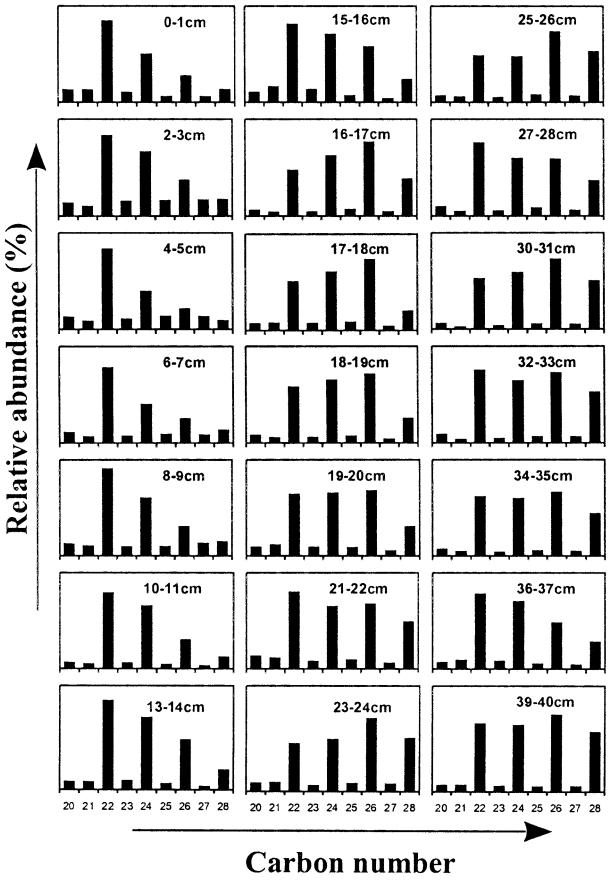

Fig. 8. Carbon number distributions of ω-hydroxy acids down profile in the 40 cm peat monolith.

3.4.2. $\delta^{13}C$ Values of Specific Hydrocarbons

Table 2 presents the $\delta^{13}C$ values of a range of lipid components of the peat monolith. All the listed compounds display relatively depleted $\delta^{13}C$ values compared with the bulk peat. This is consistent with previously reported differences between the $\delta^{13}C$ values of lipid components and bulk tissues of C_3 plants where *n*-alkanes (and most other straight chain compounds) are derived via the acetate-malonate biosynthetic pathway resulting in increased carbon isotope fractionation between lipids and plant tissues (Rieley et al., 1993; Collister et al., 1994). The carbon isotopic compositions of C_{23} and C_{29} *n*-alkanes vary from -35.6 to -31.7‰, and -33.5 to -29.3‰, respectively. The C_{29} *n*-alkane is more enriched (2.1‰) in ^{13}C than the C_{23} *n*-alkane, which is consistent with values determined for modern *Sphagnum* plants (Ficken et al., 1998; Nott, 2000). All *n*-alkanes are generally more depleted in ^{13}C than the nonhopanoid triterpenes including taraxer-14-ene, olean-

Table 2. Vertical distribution of $\delta^{13}C$ values (‰) in bulk peat and specific compounds in the 40-cm monolith.[a]

		n-Alkanes						Triterpenes			
Depth (cm)	Bulk peat	C_{23}	C_{25}	C_{27}	C_{29}	C_{31}	C_{33}	tax-20	tax-14	oln-12	$C_{31}\alpha\beta$
0–1	−27.0	−35.6	−35.9	−34.4	−31.9		−32.7	−29.6	−28.4	−29.6	−25.2
2–3	−27.4	−34.4	−34.5	−34.0	−31.5		−31.4		−28.6	−31.1	−26.4
4–5	−27.5	−33.9	−34.5	−33.0	−33.0			−31.5	−29.3	−31.4	
6–7	−27.8	−33.7			−33.5				−29.8	−32.1	−27.0
8–9	−28.0	−34.4	−34.2	−32.9	−32.7	−34.4			−29.1	−34.9	
10–11	−27.2	−33.8	−33.7	−33.5	−32.8	−32.4		−33.0	−28.7	−32.4	
13–14	−26.4	−32.9	−32.9	−31.7	−32.3	−31.9	−32.9	−29.9	−29.2	−29.5	
15–16	−25.9	−33.4	−33.5	−33.1	−30.4	−32.7	−32.1	−28.9	−28.4	−26.9	
16–17	−25.5	−32.6				−29.9		−28.9	−28.1		
17–18	−25.4	−32.6			−30.0	−32.0		−27.8	−27.1	−26.4	
18–19	−25.4	−32.5				−30.4		−28.0			
19–20	−25.3	−32.5			−29.9	−31.5		−27.7	−26.8	−26.9	
21–22	−24.6	−33.4			−29.3	−32.6		−28.6	−27.8	−25.3	−25.5
23–24	−24.7	−31.9			−29.8	−30.5				−25.7	
25–26	−25.0	−31.7	−31.9	−31.4	−30.9	−31.0	−30.9	−29.6	−27.8	−29.5	−24.3
27–28	−26.2	−31.9	−33.7	−31.2	−31.2	−31.2	−31.3	−29.3	−26.7	−30.8	−24.0
30–31	−26.0	−32.5	−34.4	−31.1	−30.7	−31.6	−30.4	−30.2	−26.9	−27.7	−25.4
32–33	−26.4	−32.9	−34.5	−30.9	−30.7	−31.7		−30.7	−27.7	−28.3	−24.4
34–35	−26.2	−33.6	−35.0		−30.7		−30.9	−30.0	−27.1	−28.4	
36–37	−25.5	−32.9		−31.1	−29.8			−32.9	−28.0	−28.6	
39–40	−25.7	−33.1	−33.8	−29.8	−30.0		−29.4	−29.6	−26.7	−28.3	
Mean (‰)	−26.1	−33.2	−34.0	−32.2	−31.1	−31.7	−31.3	−29.6	−28.0	−29.1	−25.3
Variation (‰)	3.4	3.9	4.0	4.6	4.2	4.5	3.3	5.3	3.1	9.6	3.0

[a] tax-20: taraxast-20-ene; tax-14: taraxer-14-ene; oln-12: olean-12-ene; $C_{31}\alpha\beta$: $C_{31}\alpha\beta$-hopane.

12-ene and taraxast-20-ene. The mean $\delta^{13}C$ value of the 3 nonhopanoid triterpenes in the profile was determined to be −29.9‰, which is 1.5‰ less depleted than the C_{29}, C_{31} and C_{33} *n*-alkanes. This is in excellent agreement with Hayes (1993) who explains that the less depleted $\delta^{13}C$ values of terpenoids relative to *n*-alkyl lipids (by *ca*. 1.5‰) reflects isotopic differences in their respective biosynthetic precursors.

The overall variations in $\delta^{13}C$ values of *n*-alkanes, triterpenes and hopanes range from 3.0–9.6‰ (Table 2). Included in these variations is 1.3‰ resulting from the fossil fuel effect, which is reflected in the C_{23} *n*-alkane by the overall decrease of $\delta^{13}C$ values with depth spanning the industrial revolution period. However, the record of the fossil fuel effect in C_{29} *n*-alkane is much less apparent. The 2 samples taken at or near the surface (0–1 and 2–3 cm) exhibit more enriched (1.5–2‰) $\delta^{13}C$ values for the C_{29} *n*-alkane than deeper samples (4–5 and 6–7 cm). The less depleted $\delta^{13}C$ values in the surface samples might be related to the contribution of microorganisms. It has long been noted that fungi are relatively less depleted in the ^{13}C isotope, and that fungal spores generally contain C_{14}-C_{37} *n*-alkanes, often maximizing at C_{27}, C_{29} and C_{31} (Weete, 1976; Huang et al., 1996). Many nonphotosynthetic bacteria have been found to contain C_{26}-C_{30} hydrocarbons (Albro, 1976). Algae are also capable of producing C_{14}-C_{32} *n*-alkanes (Gelpi et al., 1970; Weete, 1976) with less depleted $\delta^{13}C$ values than higher plants as they fix CO_2 dissolved in water, which is relatively less depleted in ^{13}C (Farquhar et al., 1989; Huang et al., 1996). Comparisons between higher plant and bacterial *n*-alkanes have revealed 2.5–3.5‰ less depleted $\delta^{13}C$ values for bacterial *n*-alkanes (Huang et al., 1996). Thus, the less depleted $\delta^{13}C$ values for the C_{29} *n*-alkane at the peat surface is likely due to the activities of microorganisms such as bacteria, fungi and algae.

Comparisons of the $\delta^{13}C$ values in C_{23}*n*-alkane between modern *Sphagnum* spp. (−37.6‰) from this bog and the *Sphagnum*-dominated surface peat (−35.6‰) are less depleted by ~2.0‰. An enrichment of alkanes (2.5‰) in buried peat horizons compared to present-day plants has been reported previously by Ficken et al. (1998). Variations in leaf and soil *n*-alkanes (1‰) have also been reported (Lichtfouse et al., 1995). Diagenetic effects resulting in the loss of ^{13}C-depleted CO_2 and CH_4 may contribute to the observed differences. A high concentration of isotopically light carbon dioxide formed as a result of decay (mineralization) of organic remains was found to occur in the layer of air most adjacent to the ground surface (Münnich and Vogel, 1959; Keeling, 1961).

The dominance of the C_{31} $\alpha\beta$ hopane in peat has previously been reported (van Dorsselaer et al., 1977; Quirk et al., 1984) but its origin is far from clear. The stable carbon isotopic compositions of hopanoids were measured when present in sufficient concentrations. $\delta^{13}C$ values of the $C_{31}17\alpha$(H), 21β(H)-29-methylhopane in 8 samples varied from −24.0 to −27.0‰ with a mean of −25.3‰ (Table 2). Compared with the nonhopanoid triterpenes (mean $\delta^{13}C$ value of −29.9‰), this $\alpha\beta$ hopane is less depleted in ^{13}C by 4.6‰, probably indicating its microbial origin. A 4–5‰ difference in $\delta^{13}C$ values between hop-22(29)-ene or hop-13(18)-ene and higher plant *n*-alkanes was observed by Huang et al. (1996) in three types of British acid upland soils and they proposed this difference to be related to the contribution of heterotrophic bacteria and/or cyanobacteria. A notable feature is that the reported less depleted (5‰) $\delta^{13}C$ values of carbohydrates and proteins relative to lipids (Deines, 1980) is near to the 4.6‰ of the aforementioned hopane. Since the subsequent isotope fractionation in bacterial biosynthesis is small this infers that plant carbohydrates and/or proteins are the main carbon source for these peat surface dwelling microorganisms. Such carbon

Table 3. δD values of individual *n*-alkanes and total *n*-alkanes of modern peat plants.[a]

Species	δD (‰)						Relative concentration (%)						δD (‰) in total *n*-alkanes
	C_{23}	C_{25}	C_{27}	C_{29}	C_{31}	C_{33}	C_{23}	C_{25}	C_{27}	C_{29}	C_{31}	C_{33}	
S. magellanicum	−169	−175	−153	−153	−168	−170	8.5	20.2	3.8	18.0	36.0	13.5	−166
S. papillosum	−166	−159	−153	−155	−176	−166	40.6	23.4	5.2	5.1	18.1	7.6	−165
S. palustre	−170	−170	−155	−163	−171	−159	34.6	25.1	13.7	8.5	14.0	4.1	−167
S. capillifolium	−158	−165	−143	−155	−160	−155	12.4	16.4	5.6	14.9	36.9	13.8	−158
S. recurvum	−174	−158	−153	−178	−153	−154	54.7	22.8	11.6	5.7	4.4	0.8	−167
S. cuspidatum	−177	−165	−157	−169	−194	−195	29.9	6.7	3.9	9.5	35.0	15.0	−183
T. cespitosum	−144	−159	−193	−225	−225	−218	0.3	0.8	2.0	11.5	59.3	26.1	−221
E. angustifolium	−156	−142	−163	−196	−208	−200	1.2	1.8	3.3	15.4	56.7	21.6	−201
E. vaginatum	−153	−164	−183	−184	−181	−196	1.2	1.8	3.4	15.4	56.6	21.6	−184

[a] *S. = Sphagnum, T. = Trichophorum, E. = Eriophorum.*

sources for heterotrophic bacteria in soils have been proposed previously (Huang et al., 1996).

3.4.3. Variation in δD Values of n-Alkanes in Modern Peat-Forming Plants

The compound specific δD values of *n*-alkanes in modern *Sphagnum* spp. and sedges are shown in Table 3. The standard deviations of triplicate analyses typically ranged from 0.5‰ to 4.5‰. Evidently, *Sphagnum* species show relatively lower variation (16–38‰) in δD values of *n*-alkanes. In contrast, sedge species display large variations in δD values (43–81‰) with long chain *n*-alkanes (C_{29}-C_{33}) being relatively depleted compared with their short chain counterparts (C_{23}-C_{27}). Given the δD values and the relative abundance of individual *n*-alkanes in a specific plant species, we can derive the approximate δD values for the total weighted mean *n*-alkanes. The calculated values presented in Table 3 clearly indicate more discrimination against deuterium in the sedges, suggesting the different deuterium contents between mosses and sedges might result from their physiologic difference. While sedges can control water loss by regulating stomatal opening, mosses lack this ability due to the absence of functional stomata. In addition, mosses lack a waxy cuticle on the leaf epidermis so water loss occurs by simple diffusion through the cell walls of the plant, thereby reducing isotopic fractionation.

It is notable that compared with C_{29}, C_{31} and C_{33} *n*-alkanes, relatively less variation in δD values is seen amongst the shorter chain homologues from the 9 modern moss and sedge species. For example, for all the species analyzed the δD values of the C_{23} *n*-alkane range from −144 to −177‰ (variation 33‰) while δD values of the C_{31} *n*-alkane range from −153 to −225‰ (variation 72‰). Hence, the smaller variation in δD of the C_{23} *n*-alkane, though it remains unclear, makes this the more favorable compound for use in the reconstruction of past climate.

3.4.4. Variation in δD of Specific n-Alkanes

Figure 9 shows the variations in δD values of the C_{29} and C_{33} *n*-alkanes in the 40 cm monolith; less depleted values were seen at the depth interval of 6–7 cm to 32–33 cm, approximately coinciding with the distribution of dominant *Sphagnum* spp. with depth as revealed by macrofossil analyses of the adjacent core. More importantly, the mean δD value of the C_{33} *n*-alkane in this depth interval was calculated to be −163‰, which is similar to the mean value (−167‰) of 6 modern *Sphagnum* spp. collected from the bog surface. The less depleted δD values of the C_{29} and C_{33}*n*-alkanes at the depth of 6–7 cm to 32–33 cm appear to be related to the dominance of *Sphagnum* spp. The more depleted deuterium values seen at the 4–5 cm, and 36–37 cm depth intervals probably reflect the increasing growth of sedges, although there is a *c*. 2–4 cm offset in depth between the distribution of depleted deuterium in the monolith and the distribution of sedges in the adjacent core which could relate simply to minor variations in surface topography. The higher deuterium values occurring in *Sphagnum*-dominated horizons, and the lower values seen in sedge-dominated horizons in the monolith, agree with the trends seen in the δD values recorded for modern *Sphagnum* spp. and sedges as discussed above. Thus, variations in deuterium values of the long chain *n*-alkanes (C_{29} and C_{33}) relate mainly to the vegetation changes, which obscure variations in the isotopic composition of the bog water. Theoretically, the D/H ratio in the biochemical components of peat-forming plants (such as cellulose and lipids) should be a proxy for paleotemperature. However, apart from a temperature-dependent signal, this ratio is also strongly related to the physiologic characteristics affecting isotopic fractionation in the different peat-forming species. A strong correlation between δD values of cellulose and botanical composition of peat was demonstrated by Brenninkmei-

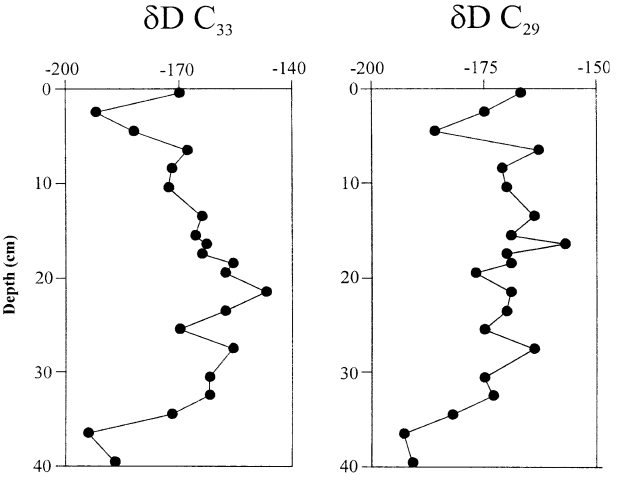

Fig. 9. Variation in δD values (‰) of C_{33} and C_{29} *n*-alkanes in the monolith.

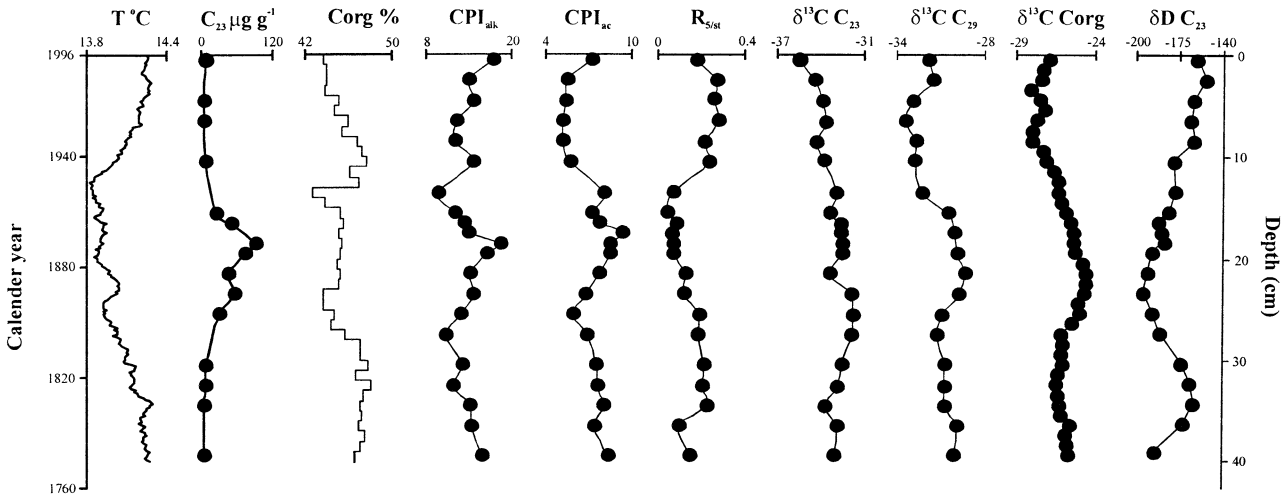

Fig. 10. Bulk, molecular and isotopic stratigraphy characteristics related to climate. T: 50-yr-running-average summer temperature in England (°C) (Manley; 1974; Parker et al., 1992; Jones and Hulme, 1997; Jones et al., 1997; Barber et al., 2000); C_{23} = concentration of C_{23} *n*-alkane (μg g^{-1}); C_{org} = organic carbon content of bulk peat (%); CPI_{alk} = carbon preference index of *n*-alkanes; CPI_{ac} = carbon preference index of *n*-alkanoic acids; $R_{5/st}$ = ratio of 5-*n*-alkyl-resorcinols to sterols; $\delta^{13}CC_{23}$ = $\delta^{13}C$ values (‰) of C_{23} *n*-alkane; $\delta^{13}CC_{29}$ = $\delta^{13}C$ values (‰) of C_{29} *n*-alkane; $\delta^{13}C$Corg = $\delta^{13}C$ values (‰) of organic carbon; δDC_{23} = δD values (‰) of C_{23} *n*-alkane.

jer et al. (1982). The climatic signal in the D/H ratio of peat cellulose in Carbury bog in Ireland was completely overwhelmed by the indirect effects of the numerous plants contributing to peat formation (van Geel and Middeldorp, 1988). It is undoubtedly the case that the deuterium content of peat is strongly influenced by climate, but that the local vegetation at the time (itself partly also a consequence of climatic conditions) is also responsible for variations of D/H. Thus, the overall fractionation is an integral of climatic and plant-physiologic factors (van Geel and Middeldorp, 1988). The latter might be considerably larger than the direct temperature-induced variation, and it might balance or even obscure the direct temperature effect. Thus, the hydrogen isotope ratios of cellulose and C_{29} and C_{33} *n*-alkanes cannot be used as precise climate proxies. Conversely, the δD values of C_{23} *n*-alkane in the peat monolith strongly relate to temperature as will be discussed later.

3.5. Climatic Anomaly Recorded by Biomarkers

Figure 10 shows that the most extreme climatic anomaly occurring during the 220 yr encompassed by the peat monolith is the cooler climate recorded between the second half of the 19th and the middle of the 20th century, known as the second part of Little Ice Age in Europe (Libby et al., 1976). Figure 10 also plots the distributional and isotopic characteristics of various biomarker components in relation to the cooler climate event.

3.5.1. C_{23} n-Alkane Indicating Exponential Biologic Growth Related to Climatic Change

In this 40 cm peat monolith the concentration of C_{23} *n*-alkane displays the following variation (Fig. 10): a progressive increase from 30–31 cm to 17–18 cm followed by a gradual decrease from 17–18 cm to 8–9 cm. Significantly, this variation coincides with the cooler temperature period (A.D. 1949–1827).

The C_{23} *n*-alkane was found to be the major *n*-alkane in some *Sphagnum* species (Ficken et al., 1998; Baas et al., 2002). (Nott et al. (2002)) demonstrated, through lipid analyses of modern plants from this bog, that a range of *Sphagnum* species, such as *S. recurvum*, *S. palustre* and *S. papillosum* also show an *n*-alkane distribution dominated by the C_{23} *n*-alkane, while in *S. magellanicum*, and *S. capillifolium* the C_{31} homologue was dominant, and *S. cuspidatum* showed a bimodal distribution with maxima at C_{23} and C_{31}. In contrast, all the sedges examined exhibit *n*-alkane distributions with the C_{31} homologue predominating. The dominance of the C_{23} *n*-alkane in the peat thus, correlates with *Sphagnum* species while the abundance of C_{31} *n*-alkane is related to both *Sphagnum* and sedges. Since the shorter chain *n*-alkanes seen in *Sphagnum* are consistent with plants growing in a relatively wetter environment (Barnes and Barnes, 1978) the concentration of the C_{23} *n*-alkane will reflect changes in the relative abundance of *Sphagnum* relative to sedges, or reflect interspecies replacement when only *Sphagnum* spp. dominates. Since the macrofossil data show that *Sphagnum* is the dominant species (~90%) at the depth intervals between 8-9 cm and 30–31 cm the variation of the C_{23} *n*-alkane concentration does indeed reflect the changing abundance of different *Sphagnum* species contributing to peat formation.

Significantly, the concentration of the C_{23} *n*-alkane at the depth interval 30–31 cm to 8–9 cm exhibits two phases of exponential variations (correlation coefficient R^2=0.99), indicating the exponential transgression and regression of C_{23} containing *Sphagnum* spp. This appears to agree with one of the fundamental biologic principles of exponential population growth (May, 1976; Odum, 1983) and the exponential growth of individuals during initial development stages (Koyama and Kira, 1956; Wilbur and Collins, 1973; Lomnicki, 1988). It has also been demonstrated ecologically that, unlike the response to

biotic factors (such as competition, parasites, pathogens, etc.), climatic factors can affect population growth in a density-independent manner (Odum, 1983) which can lead to exponential growth (May, 1976; Odum, 1983).

3.5.2. Other Biomarker Characteristics Related to Climatic Change

Besides the variation in the concentration of the C_{23} *n*-alkane, the total organic carbon, CPI values of the *n*-alkanes and *n*-alkanoic acids, and the ratio of 5-*n*-alkyl-resorcinols/sterols (Fig. 10) all show variations related to the cooler climate event. The CPI values of both the *n*-alkanes and *n*-alkanoic acids display relatively higher values in 13–14 cm to 27–28 cm depth horizon coincident with the lower mean summer temperatures (A.D. 1843–1921). The increased CPI value is probably related to reduced degradation during the cooler period consistent with the proposal of Kuder and Kruge (1998) that lower temperatures can be an important factor in reducing degradation rates in northern climates. The diagenetic decrease of CPI was also recorded at the topmost section of the peat presumably influenced by increasing mean temperature. The decrease of the ratio of 5-*n*-alkyl-resorcinols/sterols during the cooler event (Fig. 10) is related to the reduced growth of sedge species, since only these peat-forming plants appear to contain 5-*n*-alkyl-resorcinols (Avsejs et al., 2002).

3.5.3. Correlation of $\delta^{13}C$ Values with Temperature Variations

In sedimentary environments the $\delta^{13}C$ value of an individual compound is the mean of all contributing sources, including the range of different plant species, which will vary depending on their individual responses to the environmental conditions (e.g., atmospheric CO_2 concentration and its $\delta^{13}C$ value, temperature, humidity, sunlight, nutrient concentrations, etc.; Huang et al., 1996). As indicated above, the variation in $\delta^{13}C$ values of specific compounds and bulk peat in the monolith range from 3.0–9.6‰ (Table 2), which cannot be explained by anthropogenic effects alone. The relationship between the $\delta^{13}C$ values of plants and their growth temperature has been extensively investigated in cellulose from tree rings and a theoretically derived temperature coefficient of $+0.36‰\ °C^{-1}$ for cellulose $\delta^{13}C$ during photosynthesis has been proposed by Libby (1972). This is supported by an investigation in the trends in $\delta^{13}C$ values in a German oak and recorded temperature variations in western Europe (Pearman et al., 1976). However, a negative temperature coefficient of $-0.27‰\ °C^{-1}$ for mean December temperatures has been reported in tree rings of Juniperus (Leavitt and Long, 1983), while a temperature coefficient of $-0.7‰\ °C^{-1}$ was recorded for the rings of naturally grown Elm trees in Massachusetts (Farmer, 1979). In several growth chamber experiments, negative carbon isotope temperature coefficients have also been recorded in whole plants and leaves (Smith et al., 1973; Troughton and Gard, 1975; Smith et al., 1976; Schmidt et al., 1978). However, the mechanism leading to these negative coefficients remains elusive, although in an investigation of fractionation by CO_2-fixing enzymes isolated from soybean leaves revealed a negative carbon isotope temperature coefficient ($-0.22‰\ °C^{-1}$) for RuBP carboxylase (initial carboxylating enzyme in C_3 plants; Christeller et al., 1976). Thus, an explanation of the precise source of the negative correlation between compound-specific $\delta^{13}C$ values and temperature must await laboratory experiments involving peat-forming plants.

3.5.4. δD Values Related to Temperature

As discussed above, deriving climatic information from the δD value of the C_{29} and C_{33} *n*-alkanes is limited by the underlying plant composition noise. Solutions to the plant composition noise effect have been proposed in cellulose studies. One possibility proposed by van Geel and Middeldorp (1988) is to target a restricted range of taxa for δD measurements. Pendall et al. (2001) recently reported such kind of investigation, who set up a temperature-δD relationship based on the δD measurement just from modern *Sphagnum* moss cellulose and suggested this could be applied to identifiable moss fragment. Another approach would be to employ a multiple linear regression correction using δD values as the dependent and the volume percentages of floral composition as the independent variables. The residual signal after multiple linear regression is believed to correlate with climate (for detail, refer to Dupont and Mook, 1987). However, some practical problems exist in the application of these methods, and the application of multiple linear regression on Carbury Bog was unsuccessful, with the extracted residual signal failing to parallel known climatic events.

In contrast to cellulose, lipids, such as *n*-alkanes have the advantage of comprising a series of homologous components, with the different homologues having the potential to be isotopically sensitive to climatic change. Furthermore, in contrast to cellulose, which occurs in all plant taxa, lipid biomarkers related to specific plants can be targeted for isotopic analysis thereby minimizing isotopic variation arising from the plant composition noise. As mentioned above, in contrast to the long chain homologues, the short chain *n*-alkanes display relatively constant differences in δD values among *Sphagnum* spp. and even between mosses and sedges. Therefore, variation in plant-physiologic isotopic fractionation is likely to be negligible when considering these short chain compounds. Interestingly, the C_{23} *n*-alkane, the major *n*-alkane occurring in *Sphagnum* spp. (Nott et al., 2000) exhibits variation in δD values in this monolith (Fig. 10) similar to the δD records in tree ring cellulose in Germany (Schiegl, 1974), USA and Scotland (Epstein and Yapp, 1976), with more depleted deuterium values observed during cooler periods (Fig. 10). Since ombrotrophic peat bogs only receive water through direct precipitation the deuterium content of organically bound hydrogen in peat-forming plants must correlate with that of precipitation (Schiegl and Vogel, 1970). The deuterium content of precipitation has been quantitatively described and demonstrated to decrease with decreasing condensation temperature (Dansgaard, 1964; Merlivat and Jouzel, 1979; van der Straaten and Mook, 1983). It is entirely acceptable that the depleted δD values are seen both in the C_{23} *n*-alkane (this study) and tree ring cellulose records during periods of cooler climate. On this basis we have argued that the variation in the δD values of the C_{23} *n*-alkane in the monolith is strongly influenced by paleotemperature and largely independent of variation in plant species (Xie et al., 2000).

The variations seen in the δD value of the C_{23} *n*-alkane

appear to relate to variations in humidity at the bog surface. Evaporative loss of H in falling raindrops results in enrichment of deuterium that is enhanced by low humidity (Dansgaard, 1953, 1961; Ehhalt et al., 1963). Enriched δD values in tree ring cellulose resulting from low humidity have been reported by Schiegl (1974). The trend towards relatively depleted δD values for the C_{23} *n*-alkane observed during the cooler period encompassing the depth (6–7 to 32–33 cm) where *Sphagnum* spp. dominate, agrees with these latter studies. Thus, variations in δD value of the C_{23} *n*-alkane in the monolith appear to be dominated by temperature, with a further influence by humidity.

Investigation of deuterium content of modern precipitation shows, that whereas the temperature effect dominates at Northerly and Southerly regions, the amount effect accounts for the majority of the variation in tropical and subtropical regions (Dansgaard, 1964). In this peat monolith, the more depleted deuterium values observed during the cold period does not appear to result from low precipitation because negative correlations are usually observed between δD and the amount of precipitation (Dansgaard, 1964). At higher latitudes, such as in Northern England, the amount effect becomes less pronounced (Dansgaard, 1964), thus further emphasizing the temperature dependence seen for the δD values of the *n*-alkanes of the peat from Bolton Fell Moss. More data are needed to relate the deuterium contents of specific biomarkers with the origin of a particular water mass and changes in its isotope composition during the course of precipitation before reaching the location of the bog, which is under consideration of our current investigation of modern-day precipitation over a long period.

4. CONCLUSIONS

Total organic carbon content and concentrations of total lipid extracts, C_{23} *n*-alkanes and 5-*n*-alkyl-resorcinols were found to decrease during the cooler climate from the late half of the 19th to the early half of the 20th centuries as a result of reduced photosynthetic rate. The concentration of the C_{23} *n*-alkane, an abundant hydrocarbon produced predominantly by *Sphagnum* spp., clearly records the exponential growth of certain *Sphagnum* spp. related to the cooler climate event. Low temperature and the correspondingly low diagenetic rates result in increased CPI values in both *n*-alkanes and *n*-alkanoic acids.

The $\delta^{13}C$ values of bulk peat and specific compounds indicate a C_3 plant origin for most compounds in the monolith, excluding C_{31} 17α(H), 21β(H)-29-methylhopane which displays enriched $\delta^{13}C$ values, indicative of a microbial origin. The fossil fuel effect since the industrial revolution was clearly recorded by the overall depletion in ^{13}C of specific compounds, especially that of C_{23} *n*-alkane. The cooler climate during the second part of Little Ice Age was clearly seen in the less depleted $\delta^{13}C$ values of peat derived hydrocarbons.

n-Alkane homologues from modern *Sphagnum* spp. exhibit much less variation in their δD values than sedges, probably resulting from physiologic differences. Analyses of both the modern peat-forming plants and the peat comprising the contiguous subsections of the 40 cm monolith reveal that while the longer chain *n*-alkane homologues (C_{29}, C_{31} and C_{33}) display δD values mainly reflecting plant composition noise the δD values of the short chain *n*-alkanes (C_{23}, C_{25} and C_{27}) are a powerful tool for the reconstruction of past climatic change.

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REFERENCES

Aaby B. (1976) Cyclic climatic variations in climate over the past 5500 years reflected in raised bogs. *Nature* **263,** 281–284.

Albro P. W. (1976) Bacterial waxes. In *Chemistry and Biochemistry of Natural Waxes* (ed. P.E. Kolattukudy), pp. 419–445. Elsevier.

Appleby P. G. and Oldfield F. (1992) Application of ^{210}Pb to sedimentation studies. In *Uranium-Series Disequilibrium: Application to Earth, Marine and Environmental Sciences* 2nd ed (eds. M. Ivanovich and R. S. Harmon), pp. 731–778. Oxford Science.

Avsejs L. A., Nott C. J., Xie S., Maddy D., Chambers F. M., and Evershed R. P. (2002) 5-*n*-Alkylresorcinols as biomarkers of sedges in an ombrotrophic peat section. *Org. Geochem.* **33,** 861–867.

Baas M., Pancost R., van Geel B., and Sinninghe Damste J. S. (2000) A comparative study of lipids in *Sphagnum* species. *Org. Geochem* **31,** 535–541.

Barber K. E. (1981) *Peat Stratigraphy and Climatic Change: A Palaeoecological Test of the Theory of Cyclic Peat Bog Regeneration*. Balkema.

Barber K. E. (1985) Peat stratigraphy and climatic change: Some speculations. In *The Climatic Scene: Essays in Honour of Gordon Manley* (eds. M. J. Tooley and G. M. Sheail), pp. 175–185. Allen and Unwin.

Barber K. E., Chambers F. M., Maddy D., Stoneman R., and 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. E., Dumayne-Peaty L., Hughes P., Mauquoy D., and 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. *J. Quat. Sci.* **13,** 515–528.

Barber K. E., Maddy D., Rose N., Stevenson A. C., Stoneman R. E., and Thompson R. (2000) Replicated proxy-climate signals over the last 2000 years from two distant UK peat bogs: New evidence for regional palaeoclimate teleconnections. *Quat. Sci. Rev.* **18,** 471–479.

Barnes M. A. and Barnes W. C. (1978) Organic compounds in lake sediments. In *Lakes: Chemistry, Geology, Physics* (ed. A. Lerman), pp. 127–152. Springer.

Blackford J. J. and Chambers F. M. (1993) Determining the degree of peat decomposition for peat-based palaeoclimatic studies. *Int. Peat J.* **5,** 7–24.

Blumer M., Guillard R. L., and Chase T. (1971) Hydrocarbons of marine phytoplankton. *Mar. Biol.* **8,** 183–189.

Brassell S. C., Comet P. A., Eglinton G., Isaacson P. J., McEvoy J., Maxwell J. R., Thompson I. D., Tibbetts P. J. C., and Volkman J. K. (1980) The origin and fate of lipids in the Japan trench. In *Advances in Organic Geochemistry 1979* (eds. A. G. Douglas and J. R. Maxwell), pp. 375–392. Pergamon Press.

Brassell S. C. and Eglinton G. (1983) Steroids and triterpenoids as environmental and diagenetic indicators. In *Advances in Organic Geochemistry 1981* (eds. M. Bjorøy, et al.), pp. 684–697. Wiley.

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

Brenninkmeijer C. A. M., van Geel B., and Mook W. G. (1982) Variations in the D/H and $^{18}O/^{16}O$ ratios in cellulose extracted from a peat bog core. *Earth Plan. Sci. Lett* **61,** 283–290.

Chapman M. R. and Shackleton N. J. (2000) Evidence of 550-year and 1000-year cyclicities in North. Atlantic circulation patterns during the Holocene. *Holocene* **10,** 287–291.

Christeller J. T., Lang W. A., and Troughton J. H. (1976) Isotope discrimination by ribulose 1,5-diphosphate carboxylae. *Plant Phys.* **57,** 580–582.

Collister J. W., Rieley G., Stern B., Eglinton G., and Fry B. (1994) Compound specific ^{13}C analyses of leaf lipids from plants with differing carbon dioxide metabolism. *Org. Geochem.* **21,** 619–628.

Cranwell P. A. (1986) Esters of acyclic and polycyclic isoprenoid alcohols: Biochemical markers in lacustrine sediments. *Org. Geochem.* **10,** 891–896.

Dansgaard W. (1953) The abundance of ^{18}O in atmospheric water and water vapor. *Tellus* **5,** 461–469.

Dansgaard W. (1961) The isotopic composition of natural waters. *Medd. Grønland* **165,** 1–120.

Dansgaard W. (1964) Stable isotopes in precipitation. *Tellus* **16,** 436–468.

Deines P. (1980) The isotopic composition of reduced organic carbon. In *Handbook of Environmental Geochemistry: The Terrestrial Environment* Vol. 1 (eds. P. Fritz and J. C. Fontes), pp. 329–406. Elsevier.

Dehmer J. (1995) Petrological and organic geochemical investigation of recent peats with known environments of deposition. *Coal Geol.* **28,** 111–138.

Dupont L. and Mook W. G. (1987) Palaeoclimate analysis of $^{2}H/^{1}H$ ratios in peat sequences with variable plant composition. *Chem. Geol.* **66,** 323–333.

Ehhalt D., Knot K., Nagel J. F., and Vogel J. C. (1963) Deuterium and oxygen 18 in rain water. *J. Geophys. Res.* **68,** 3775–3780.

El-Daoushy F., Tolonen K., and Rosenberg R. (1982) Lead 210 and moss-increment dating of two Finnish *Sphagnum* hummocks. *Nature* **296,** 429–431.

Eglinton G. and Hamilton R. J. (1967) Leaf epicuticular waxes. *Science* **156,** 1322–1334.

Epstein S. and Yapp C. J. (1976) Climatic implications of the D/H ratio of hydrogen in C-H groups in tree cellulose. *Earth Planet. Sci. Lett.* **30,** 252–261.

Farmer J. G. (1979) Problems in interpreting tree-ring records. *Nature* **279,** 229–231.

Farquhar G. D., Hubick K. T., Condon A. G., and Richards R. A. (1989) Carbon isotope discrimination and water use efficiency. In *Stable Isotopes in Ecological Research* (eds. P. W. Rundel, J. R. Ehleringer, and K. A. Nagy), pp. 21–40. Springer Verlag.

Farrimond P. and Flanagan R. L. (1996) Lipid stratigraphy of a Flandrian peat bed (Northumberland, UK): Comparison with the pollen record. *Holocene* **6,** 69–74.

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

Figge R. A. and White W. C. (1995) High-resolution Holocene and late glacial atmospheric CO_2 record: Variability tied to changes in thermohaline circulation. *Global Biogeochemical Cycle* **9,** 391–403.

Flynn W. W. (1968) Determination of low-levels of polonium-210 in environmental materials. *Anal. Chim. Acta* **43,** 221–227.

Friedli H., Lotscher H., Oeschger H., Siegenthaler U., and Stauffer B. (1986) Ice core record of the $^{13}C/^{12}C$ ratio of atmospheric CO_2 in the past 2 centuries. *Nature* **324,** 237.

Galimov E. M. (1985) Isotopic composition of the carbon of organisms. In *The Biological Fractionation of Isotopes*, pp. 16–41. Academic Press.

Gaskell S. J. and Eglinton G. (1976) Sterols of a contemporary lacustrine sediment. *Geochim. Cosmochim. Acta* **40,** 1221–1228.

Gelpi E., Schneider H., Mann J., and Oro T. (1970) Hydrocarbons of geochemical significance in microscopic algae. *Phytochemistry* **9,** 603–612.

Giger W. and Schaffner C. (1977) Aliphatic, olenfinic and aromatic hydrocarbons in recent sediments of a highly eutrophic lake. In *Advances in Organic Geochemistry 1975* (eds. R. Campos and J. Goni), pp. 375–390. Elsevier.

Hayes J. M. (1993) Factors controlling ^{13}C contents of sedimentary organic compounds: Principles and evidence. *Mar. Geol.* **113,** 111–125.

Hendon D., Charman D. J., and Kent M. (2001) Palaeohydrological records derived from testate amoebae analysis from peatlands in northern England: Within-site variability, between-site comparability and palaeoclimatic implications. *Holocene* **11,** 127–148.

Huang Y., Bol R., Harkness D. D., Ineson P., and Eglinton G. (1996) Post-glacial variations in distributions, ^{13}C and ^{14}C contents of aliphatic hydrocarbons and bulk organic matter in three types of Br. acid upland soils. *Org. Geochem.* **24,** 273–287.

Huang Y., Street-Perrott F. A., Perrott R. A., Metzger P., and Eglinton G. (1999) Glacial-interglacial environmental changes inferred from molecular and compound-specific $\delta^{13}C$ analyses of sediments from Sacred Lake, Mt. Kenya. *Geochim. Cosmochim. Acta* **63,** 1383–1404.

Hughes P. D. M., Mauquoy D., Baeber K. E., and Langdon P. G. (2000) Mire development pathways and palaeoclimatic records from a full Holocene peat archive at Walton Moss, Cumbria, England. *Holocene* **10,** 465–479.

Jones P. D., Conway D., and Briffa K. R. (1997) Precipitation variability and drought. In *Climates of the British Isles: Present, Past and Future* (eds. M. Hulme and E. Barrow), pp. 197–219. Routledge.

Jones P. D. and Hulme M. (1997) The changing temperature of "Central England." In *Climates of the British Isles: Present, Past and Future* (eds. M. Hulme and E. Barrow), pp. 173–196. Routledge.

Karrer R. W. (1958) *Konstitution und vorkommen der organischen pflanzenstoffe (exculsive Alkaloide)* 2nd ed. Birkhaeuser Verlag.

Karunen P., Ekman R., and Salin M. (1983) *Sphagnum* mosses as sources of sterols in peat. In *International Symposium on Peat Utilization (Proceedings)* (eds. C. H. Fuchsman and S. A. Spigarelli), pp. 487–493. Minnesota.

Keeling C. D. (1961) The concentration and isotopic abundances of carbon dioxide in rural and marine air. *Geochim. Cosmochim. Acta* **24,** 277–299.

Kolattukudy P. E. (1976) Biochemistry of plant waxes. In *Chemistry and Biochemistry of Natural Waxes* (ed. P. E. Kolattukudy), pp. 290–349. Elsevier.

Koyama H. and Kira T. (1956) Intraspecific competition among higher plants, VIII. Frequency distribution of individual plant weight as affected by interaction between plants. *J. Biol.* **7,** 73–94.

Kuder T. and Kruge M. A. (1998) Preservation of biomolecules in sub-fossil plants from raised peat bogs—A potential paleoenvironmental proxy. *Org. Geochem.* **29,** 1355–1368.

Leavitt S. W. and Long A. (1983) Possible climatic response of $\delta^{13}C$ in leaf cellulose of pinyon pine in Arizona, USA. *Isotope Geosci.* **1,** 169–180.

Lehtonen K. and Ketola M. (1990) Occurrence of long-chain acyclic methyl ketones in *Sphagnum* and *Carex* peats of various degrees of humification. *Org. Geochem.* **15,** 275–280.

Lehtonen K. and Ketola M. (1993) Solvent-extractable lipids of *Sphagnum*, *Carex*, *Bryales* and *Carex-Bryales* peats: Content and compositional features vs. peat humification. *Org. Geochem.* **20,** 363–380.

Libby L. M. (1972) Multiple thermometry in paleoclimate and historic climate. *J. Geophys. Res.* **77,** 4310–4317.

Libby L. M., Pandolfi L. J., Payton P. H., Marshall J., III, Becker B., and Giertz-Sienbenlist V. (1976) Isotopic tree thermometers. *Nature* **261,** 284–288.

Lichtfouse E., Dou S., Girardin C., Grably M., Balesdent J., Behar F., and Vanderbroucke M. (1995) Unexpected ^{13}C-enrichment of organic components from wheat crop soils: Evidence for the in situ origin of soil organic matter. *Org. Geochem.* **23,** 865–868.

Lomnicki A. (1988) *Population Ecology of Individuals.* Princeton University Press.

Manley G. (1974) Central England temperatures: Monthly means 1659 to 1973. *Q. J. R. Met. Soc.* **100,** 389–405.

Mauquoy D. and Barber K. E. (1999) Evidence for climatic deteriorations associated with the decline of *Sphagnum imbricatum* Hornsch ex Russ in six ombrotrophic mires from northern England and the Scottish borders. *Holocene* **9,** 423–427.

Mauquoy D., van Geel B., Blaauw M., and van der Plicht J. (2002) Evidence from northwest European bogs shows "Little Ice Age" climatic changes driven by variations in solar activity. *Holocene* **12,** 1–6.

Matsumoto G. I., Akiyama M., Watanuki K., and Torii T. (1990) Unusual distribution of long chain *n*-alkanes and *n*-alkenes in Antarctic soil. *Org. Geochem.* **15,** 403–412.

May R. M. (1976) *Theoretical Ecology: Principles and Applications*. Blackwell, Oxford.

Merlivat L. and Jouzel J. (1979) Global climatic interpretation of the deuterium-oxygen-18 relationship for precipitation. *J. Geophys. Res.* **84,** 5029–5033.

Mermoud F., Gulacar F. O., and Buchs A. (1985) 5α(H)-Cholestan-3α-ol in sediments: Characterization and geochemical significance. *Geochim. Cosmochim. Acta* **49,** 450–462.

Morrison R. I. and Bick W. (1967) The wax fraction of soils: Separation and determination of some components. *J. Sci. Food Agr.* **18,** 351–355.

Münnich K. O. and Vogel J. C. (1959) ^{14}C age determination of freshwater limestone deposits. *Naturwissenschaften* **46,** 168–169.

Nott C. J. (2000) Biomarkers in ombrotrophic mires as palaeoclimate indicators. PhD thesis. University of Bristol.

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

Odum E. P. (1983) *Basic Ecology*. Holt-Saunder.

Ourisson G., Albrecht P., and Rohmer M. (1979) The hopanoids palaeochemistry and biochemistry of a group of natural products. *Pure Appl. Chem.* **51,** 709–729.

Otto A., Walther H., and Püttman W. (1994) Molecular composition of a leaf- and root-bearing Oligocene oxbow lake clay in the Weisselster Basin, Germany. *Org. Geochem.* **22,** 275–286.

Pancost K. D., Baas M., van Geel B., and Sinninghe Damsté J. S. (2002) Biomarkers as proxies for plant inputs to Peats: an example from a sub-boreal embrotoropic bog. *Org. Geochem.* **33,** 675–690.

Parker D. E., Legg T. P., and Folland C. K. (1992) A new daily Central England temperature series, 1772–1991. *Int. J. Climatol.* **12,** 317–342.

Pearman G. I., Francey R. J., and Fraser P. J. B. (1976) Climatic implications of stable carbon isotopes in tree rings. *Nature* **260,** 771–773.

Pendall E., Markgraf V., White J. W. C., and Dreier M. (2001) Multiproxy record of late Pleistocene-Holocene climate and vegetation changes from a peat bog in Patagonia. *Quat. Res.* **55,** 168–178.

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

Quirk M. M., Wardroper A. M. K., Wheatley R. E., and Maxwell J. R. (1984) Extended hopanoids in peat environments. *Chem. Geol.* **42,** 25–43.

Reis-Kautt M. and Albrecht P. (1989) Hopane-derived triterpenoids in soils. *Chem. Geol.* **76,** 143–151.

Rieley G., Collister J. W., Stern B., and Eglinton G. (1993) Gas chromatography-isotope ratio mass spectrometry dioxide metabolisms. *Rapid Comm. Mass Spec.* **7,** 488–491.

Robbins J. A. (1978) Geochemical and geophysical applications of radioactive lead. In *The Biogeochemistry of Lead in the Environment*, Part A (ed. J.O. Nriagu), pp. 285–293. Elsevier/North Holland Biomedical Press.

Rohmer M., Dastillung M., and Ourisson G. (1980) Hopanoids from C_{30} to C_{35} in recent muds—Chemical markers for bacterial activity. *Naturwissenschaften* **67,** 456–458.

Schiegl W. E. (1972) Deuterium content of peat as a paleoclimatic recorder. *Science* **175,** 512–513.

Schiegl W. E. (1974) Climatic significance of deuterium abundance in growth rings of Picea. *Nature* **251,** 582–584.

Schiegl W. E. and Vogel J. C. (1970) Deuterium content of organic matter. *Earth Planet. Sci. Lett.* **7,** 307–313.

Schmidt H. L., Winkler F. J., Latzko E., and Wirth E. (1978) Carboxylation reactions and ^{13}C-kinetic isotope effects in photosynthetic ^{13}C-values of plant material. *Israel J. Chem.* **17,** 223–224.

Seifert W. K. and Moldowan J. M. (1980) The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. In *Advances in Organic Geochemistry 1979* (eds. A. G. Douglas and J. R. Maxwell), pp. 229–237. Elsevier.

Smith B. N., Herath A. M. W., and Chase J. B. (1973) Effect of growth temperature on carbon isotopic ratios in barley, pea and rape. *Plant Cell Phys.* **14,** 177–182.

Smith B. N., Oliver J., and McMillan C. (1976) Influence of carbon source, oxygen concentration, light intensity and temperature on ^{13}C/^{12}C ratios in plant tissues. *Bot. Gazette* **137,** 99–104.

Svensson G. (1988) Fossil plant communities and regeneration patterns on a raised bog in south Sweden. *J. Ecol.* **76,** 41–59.

Troughton J. H. and Gard K. A. (1975) Temperature effects on the carbon-isotope ratio of C3 and C4 and crassulacean-acid metabolism (CAM) in plants. *Planta* **123,** 185–190.

van der Straaten C. M. and Mook W. G. (1983) Stable isotopic composition of precipitation and climatic variability. In *Paleoclimates and Paleowaters*. pp. 53–64. IAEA.

van Dorsselaer A., Albrecht P. and Ourisson G. (1977) Identification of novel 17α (H)-hopanes in shales, lignites, sediments and petroleum. *Bull. Soc. Chim. France* **2,** 165–170.

van Geel B. and Middeldorp A. A. (1988) Vegetational history of Carbury Bog (Co. Kildare, Ireland) during the last 850 years and a test of the temperature indicator value of ^{2}H/^{1}H measurements of peat samples in relation to historical sources and meteorological data. *New Phytol* **109,** 377–392.

Volkman J. K., Farrington J. W., and Gagosian R. B. (1987) Marine and terrigenous lipids in coastal sediments from the Peru upwelling region at 15°S: Sterols and triterpene alcohols. *Org. Geochem.* **6,** 463–477.

Walton T. J. (1990) Waxes, cutin and suberin. In *Methods in Plant Biochemistry* (eds. J. L. Harwood and J. R. Bowyer), pp. 105–158. Academic Press.

Weete J. D. (1976) Algal and fungal waxes. In *Chemistry and Biochemistry of Natural Waxes* (ed. P. E. Kolattukudy), pp. 349–418. Elsevier.

White J. W. C., Ciais P., Figge R. A., Kenny R., and Markgraf V. (1994) A high resolution record of atmospheric CO_2 content from carbon isotopes in peat. *Nature* **367,** 153–156.

Wilbur H. M. and Collins J. P. (1973) Ecological aspects of amphibian metamorphosis. *Science* **182,** 1305–1314.

Xie S., Nott C. J., Avsejs L. A., Volders F., Maddy D., Chambers F. M., Gledhill A., Carter J. F., and Evershed R. P. (2000) Palaeoclimate records in compound-specific δD values of a lipid biomarker in ombrotrophic peat. *Org. Geochem.* **31,** 1053–1057.