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A 1.16 Ma record of carbon accumulation in western European peatland during the Oligocene from the Ballymoney lignite, Northern Ireland

DAVID J. LARGE

School of Chemical Environmental and Mining Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK (e-mail: david.large@nottingham.ac.uk)

Abstract: The Oligocene Ballymoney lignite in Northern Ireland is one of the thickest lignites in Europe and provides the potential for comparing Holocene and pre-Holocene peatland evolution and its response to long-term climate change on time scales much greater than 10 ka. Samples were collected from 50 m of lignite and analysed for $\delta^{13}C$. Spectral analysis of the $\delta^{13}C$ record reveals that the record contains significant frequencies at 0.21 m^{-1} and 1.12 m^{-1}. These cycles are interpreted as the *c*. 100 ka eccentricity and 20 ka precession cycles, respectively. These cycles were then tuned and the duration was determined as 1.16 Ma with a carbon accumulation rate of 27 g C m^{-2} a^{-1}. If long-term changes in lignite $\delta^{13}C$ are related to changes in the $\delta^{13}C$ of the exogenic carbon reservoir, and if the lignite Chattian age is accepted, then the lignite probably formed between 24.6 and 25.8 Ma. Comparison of the estimated carbon accumulation rate with other Cenozoic peatland carbon accumulation rates indicates that this rate appears to be insensitive to changes in the concentration of atmospheric CO_2.

Peatland is a significant carbon reservoir containing *c*. 455 Gt of carbon (Gorham 1991), one-third of the total world soil carbon pool. As peatland contains 88–97% water (Charman 2002), peatland dynamics are extremely sensitive to changes in the hydrological cycle, which in turn respond to variations in climate and the carbon cycle. As most peatland carbon is contained within postglacial, boreal and subarctic peat (Gorham 1991) this tends to restrict much of our understanding of peatland evolution to high- to mid-latitude peatland on time scales of <10 ka (Vitt *et al*. 2000; Kremenetski *et al*. 2003). As the Earth's climate changes the need to understand the long-term behaviour of the peatland carbon reservoir under non-glacial conditions becomes more important, and the only historical record of this is contained in thick pre-Quaternary lignite and coal deposits, some of which may have accumulated over periods exceeding 1 Ma (Holdgate *et al*. 1995; Large *et al*. 2004). To allow pre-Quaternary lignite and coal deposits to be set in a palaeoclimatic context, one of the most important steps is the development of an internal or absolute time frame. This can be achieved by utilizing the potential for coal and lignite to contain evidence of orbitally paced environmental change (Jones *et al*. 1997; Large *et al*. 2003, 2004). From this evidence it is then possible to estimate long-term carbon accumulation rates and explore the simultaneous evolution of marine and terrestrial carbon reservoirs (Large *et al*. 2004).

One of the best areas for comparing Holocene and pre-Holocene peatland evolution is western and northern Europe, which contains some of the best studied Holocene peatland (Blackford 2000) and thick pre-Holocene lignite (Parnell *et al*. 1989; Seifert *et al*. 1993; Kolcon & Sachsenhofer 1999; Bechtel *et al*. 2002). Using samples of the late Oligocene Ballymoney lignite, the thickest lignite deposit in the UK, this study uses evidence of orbital cycles to set the lignite in a temporal and stratigraphic framework that can form a basis for future research into long-term pre-glacial peatland evolution in western Europe. Carbon accumulation rates are calculated and compared with other Holocene and Cenozoic rates to determine the influence of changes in the concentration of atmospheric CO_2. The stratigraphic position of the lignite is also considered relative to the marked decrease in atmospheric CO_2 levels during the late Oligocene (Pagani *et al*. 2005).

Methods

Sample collection

Samples were collected from the Geological Survey of Northern Ireland (GSNI) Ballymoney No. 1 core, 13/603, originally collected in 1984 from the Oligocene Lough Neagh Group sediments (national grid reference [C95132554], 55°4′5″N, 6°30′42″W, Fig. 1). Samples were collected from the thickest most continuous lignite section in the core, with only minor mudstone partings, between depths of 139 m and 190 m. Core recovery was better than 95%. Where possible, discrete samples up to 2 cm long were collected every 15 cm. In all, a total of 321 samples were collected. Rooted clay partings, enriched in organic matter, were common towards the top and base of the section and absent between 161 m and 173 m depth (Fig. 2). Occasionally small amounts of sand were associated with the mudstone partings and one mudstone was observed to contain hematite and siderite cement. Partings were mainly less than 0.2 m thick, apart from at the base of the core depth, where two partings 0.8–1 m thick were encountered (Fig. 2). The clay partings were paler than the lignite, their colour depending on the proportion of organic matter to clay. Most of the lignite was hard and uniform in colour; occasional samples contained amber and leaf remains. Wood was commonly encountered in the lignite, with a well-preserved cellular structure. Sample description and accompanying data are available online at http://www.geolsoc.org.uk/SUP18279. A hard copy can be obtained from the Society Library.

Geological background

The geological background to the Ballymoney lignite and other lignites of the Lough Neagh Group has been summarized in three publications (Wilkinson *et al*. 1980; Parnell *et al*. 1989; Mitchell 2004). The Lough Neagh Group siliciclast sediments (predominantly kaolinite-rich mudrocks) and lignites were deposited in small local inland basins, in the vicinity of Ballymoney, and around Lough Neagh (Fig. 1). In these basins the Lough Neagh Group can be up to 500 m thick with interlayered thick

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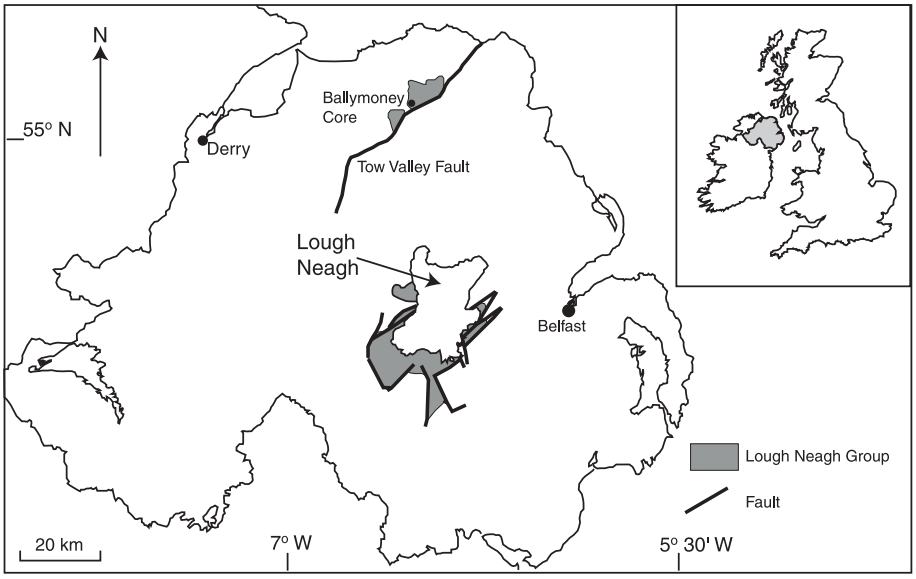


Fig. 1. Location map showing the distribution of Oligocene, Lough Neagh Group sediments in Northern Ireland. Northern Ireland is the shaded area on the inset map of the UK and Ireland. Samples analysed in this study were collected from the Ballymoney core.

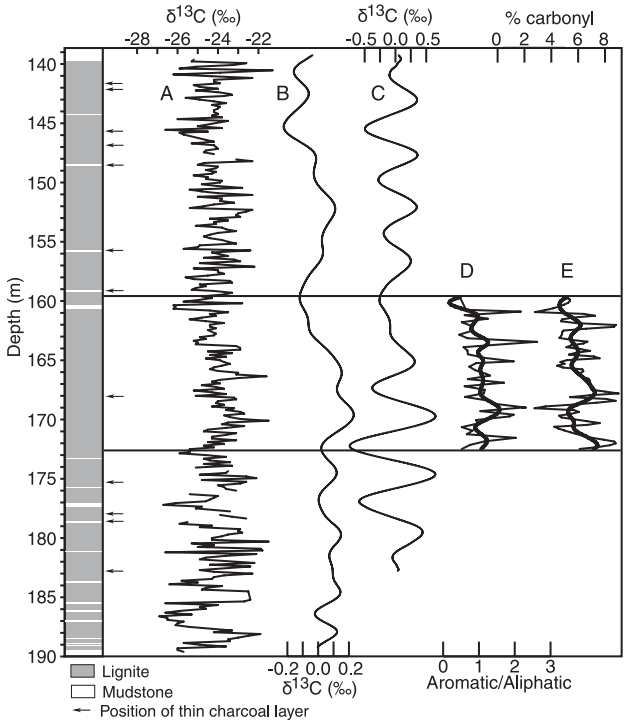


Fig. 2. Stratigraphic log of the Ballymoney lignite (grey) from 139 m to 190 m depth, showing the distribution of clay-rich (white) and charcoal-rich (black) layers compared with: A, the bulk $\delta^{13}C$ record; B, the trend in $\delta^{13}C$ identified using the SSA technique; C, the inferred eccentricity signal identified using the MTM techniques and reconstructed using SSA; D, the ratio of aromatic to aliphatic carbon; E, the percentage of carbonyl carbon. Trends in the aromatic/aliphatic ratio and percentage of carbonyl carbon, identified by SSA, are shown as bold lines.

lignite seams and mudstones occurring in the upper part of the Ballymoney Formation (Mitchell 2004). In the vicinity of Ballymoney the Lough Neagh group lies adjacent to the Tow Valley Fault (Fig. 1) and may have accumulated in small transtensional basins adjacent to this fault (Parnell *et al*. 1989). Studies of pollen (Wilkinson *et al*. 1980) indicate that the Lough Neagh group was deposited during the mid- to late Oligocene probably during the Chattian (28.3–23 Ma; Gradstein *et al*. 2004), and accumulated in a low-lying frost-free environment. Vertical changes in the spore pollen assemblage around Lough Neagh indicate that the environment may have become drier towards the top of the group (Parnell *et al*. 1989). The lignite occurs in seams up to 105 m thick and is a low-rank lignite B with a total moisture content of 30–40% (Mitchell 2004).

Analytical methods

Total organic carbon (TOC) was measured on 16 lignite samples and density on 10 samples. These data are used to calculate the carbon concentration per unit volume, which is then used to estimate the long-term carbon accumulation rate. To be consistent, both density and TOC were measured on an as-received basis. Hence, the main source of uncertainty when calculating the carbon concentration per unit volume arises from lack of knowledge of the shrinkage of the material during partial drying in storage. There are no reported shrinkage values for Lough Neagh Group lignite in the literature and as fresh samples are not available this could not be quantified. However, in Australian lignite the volumetric shrinkage at 50–60% moisture content ranges from 19 to 44% and decreases with moisture content (George & Mackay 1991). Reported moisture contents for the Lough Neagh group lignite (Mitchell 2004) range from 36.2% for Ballymoney lignite to 51% near Lough Neagh, so it is unlikely that shrinkage in the Ballymoney lignite would exceed 20%, and it is probably much less. In addition, the lignite was stored under ambient conditions, which would not have been conducive to excessive drying.

TOC was measured using a Thermo-Electron Corporation Flash Elemental Analyser. Powdered sample (0.2 g) was placed in a tin capsule and then combusted at a temperature of 900 °C. Density was measured using a specific gravity bottle and deionized water.

$\delta^{13}C$ analysis was performed on 0.2 mg of sample by elemental analyser isotope ratio mass spectrometer (EA-IRMS). Results were reported relative to V-PDB. Calculated standard deviation of duplicate lignite analysis was generally better than 0.15‰. Accuracy was checked using the standard reference material IAEA-CH-7 polyethylene ($\delta^{13}C$ of −31.8‰).

Solid-state ^{13}C nuclear magnetic resonance (NMR) was used to explore the proportion of aromatic to aliphatic carbon and the decay state of lignin. A total of 43 samples were analysed between the depths of 160 m and 170 m. None of the samples analysed contained macroscopic charcoal. NMR spectra were obtained using a Bruker DSX200 system equipped with double-bearing probes for cross-polarization (CP) and magic angle spinning. The resonance frequency for ^{13}C was 50 MHz, and the sample was spun at the magic angle with a speed of 5 kHz. The contact time and relaxation delay for the CP techniques were 3.0 ms and

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1.5 s, respectively, with 7000 scans accumulated for high-power ^{1}H decoupling. All spectra were obtained at ambient temperature and processed with a line-broadening factor of 50 Hz. Chemical shifts were calibrated using an external sample of tetrakis(trimethylsilyl)silane. The CP method, although sensitive, tends to overestimate the proportion of aliphatic carbon (Snape *et al*. 1997). To account for this, 10 replicate samples were analysed using the much longer single pulse excitation (SPE) technique. This technique collected 1800 scans using a ^{13}C pulse width of 4.5 μs with a recycle delay of 30 s between successive 90° pulses. The relationship between SPE and CP determinations of the ratio of aromatic to aliphatic carbon is linear ($r = 0.98$) and a correction was applied prior to considering the effect of aromatic to aliphatic ratio on the isotope composition.

Trends in the $\delta^{13}C$ and NMR derived records were identified using singular spectrum analysis (Ghil *et al*. 2002). $\delta^{13}C$ and NMR data are included in the Supplementary Publication (see p. 1233).

Results

TOC and density

The average TOC was measured at 55.3% with a standard deviation of 8%. The average density of the lignite was measured at 1.16 g cm^{-3} with a standard deviation of 0.17 g cm^{-3}.

δ^{13}C

The $\delta^{13}C$ record (Fig. 2) has a mean value of −24.2‰ with a standard deviation of 1.1‰, with values ranging from −21.3‰ to −26.9‰. These values are typical of vegetation utilizing the C3 photosynthetic pathway that was dominant during the Oligocene. Long-term trends identified using singular spectrum analysis display a slight rise from 189 to 170 m depth and then a fall from 170 m depth to the top of the seam. The data appear to contain evidence of long-term and short-term oscillations, with distinct long-term oscillations with a period of about 5 m occurring between depths of 177 m and 145 m (Fig. 2).

C-NMR

The NMR-derived distribution of carbon in the lignite is given in the Supplementary Publication (see p. 1233). The carbon is predominantly a mixture of aliphatic carbon derived from cell walls, resins and waxes, and aromatic carbon primarily derived from lignin. As expected, the two forms of carbon display a strong inverse correlation ($r = 0.97$, $P < 0.001$). Aromatic concentrations vary from 39 to 61% and aliphatic carbon concentrations from 19 to 49%. Carbohydrate concentrations are minimal, do not exceed 3% and are unlikely to have significantly influenced the chemistry of the coal. The ratio of aromatic to aliphatic carbon displays some correlation with $\delta^{13}C$ ($r = 0.62$, $P < 0.001$). Oscillations in carbonyl carbon, a potential indicator of fungal decay (Vane *et al*. 2001), tend to oppose oscillations in the aromatic/aliphatic ratio and this is most obvious when the underlying trends are examined (Fig. 2). This indicates that carbonyl carbon tends to be more abundant in lignite, which is enriched in aliphatic carbon; such enrichment in aliphatic carbon indicates enhanced aerobic decay.

Spectral analysis

Method

Spectral analysis was undertaken to determine whether significant periodic or quasi-periodic oscillations occur in the isotope record, and whether or not these can be attributed to orbital climate forcing. In undertaking spectral analysis it is assumed that there is no significant hiatus in the peatland record and minor hiatuses, if present, are insufficient to disrupt periodicities.

The absence of major hiatuses is supported by the lack of evidence for unconformities within the Lough Neagh Group. Theoretical considerations also indicate that thick peatland is unlikely to experience major breaks in deposition. This is due to the peatland being a self-accommodating system in which the volume in which peat can accumulate is created by continuing decay within the bulk of the peat (Clymo *et al*. 1998) and the unlikely situation that the surface of the peatland will be devoid of vegetation for any significant period of time. Even if the surface becomes drier, it is more likely that different plant species would colonize the peat surface, as is observed in drained peatland today (Charman 2002). Furthermore, if the rate of input to the peatland is reduced because of drying and increased aerobic decay, then the balance between input and decay should start to favour subsidence of the peat surface, reduction of hydraulic gradients and hence shift the hydrological balance in favour of peat preservation. Additional uncertainty comes from the presence of thin clay layers, which may have accumulated at markedly different rates. However, these are generally rich in organic matter and account for only 5% of the total lignite thickness.

To place limits on the possible range in which orbital frequencies may be found it is necessary to assume that rates of carbon accumulation in mid-latitude late Oligocene peatland will fall within the global range observed in peatland today. This is a reasonable assumption for two reasons. First, comparison of modelled latitudinal variation in Holocene net primary production (NPP) (Beerling & Woodward 2001) with the latitudinal variation in carbon accumulation rates in peatland (Fig. 3, derived from (Diessel *et al*. 2000)) demonstrates that peatland carbon accumulation rates decline in line with decreasing NPP from low to high latitudes and that at 45–55°N most estimated peatland carbon accumulation rates are less than 20% of the modelled NPP. Second, the carbon stored in the vegetation biomass in NW Europe even under elevated concentrations of atmospheric CO_2 typical of the early Palaeogene is estimated (Beerling 2000; Beerling & Woodward 2001) to lie within the present global range of 0–20 kg C m^{-2} (White *et al*. 2000). As CO_2

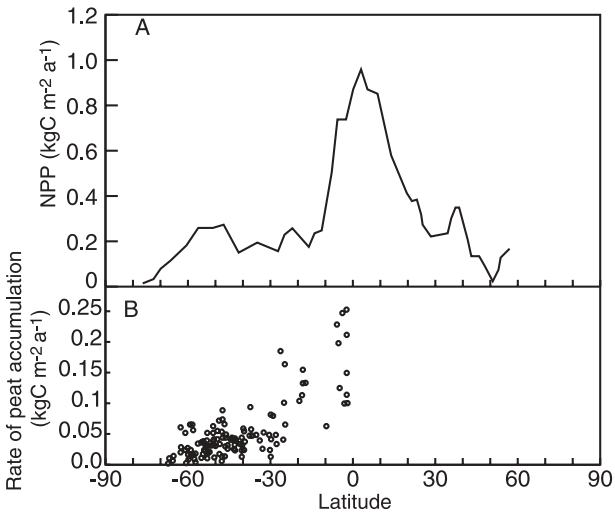


Fig. 3. Comparison of (**a**) the latitudinal distribution of Holocene net primary production (NPP) calculated by Beerling & Woodward (2001) with (**b**) the latitudinal variation in the rate of carbon accumulation in peatland derived from the composite peat accumulation data of Diessel *et al*. (2000). Peat accumulation rates were converted into carbon accumulation rates by assuming a dry bulk density of 0.1 g cm^{-3} and a carbon concentration in dry peat of 50%. It should be noted that this compilation of peat accumulation data includes both long- and short-term accumulation rates, which will result in higher estimates than would be expected for long-term accumulation rates only.

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levels during the Chattian are estimated (Pagani *et al*. 2005) to be in the range of 250–800 ppm, between Eocene levels (1000–2000 ppm) and Holocene levels (250–375 ppm), it is unlikely that the terrestrial net primary production and long-term rates of peat accumulation would lie outside the present global range.

This assumption allows a window to be defined in which orbital frequencies (100 ka eccentricity, 40 ka obliquity and 21 ka precession) may be expected to lie (Fig. 4). Periodicities lying outside this window will result in unreasonable long-term carbon accumulation rates. Average long-term Holocene carbon accumulation rates vary from 19.9 g C m^{-2} a^{-1} in boreal peatland (Korhola *et al*. 1995) to 100 g C m^{-2} a^{-1} in tropical peatland (Page *et al*. 2004). Using these limiting carbon accumulation rates in conjunction with the measured average density and carbon concentration of the lignite, it is possible to place limits on the likely period of deposition for 50 m of the Ballymoney lignite. The limiting period of deposition ranges from 0.28 to 1.41 Ma. As the palaeolatitude of the Ballymoney lignite is similar to its present-day latitude it is expected that the period of deposition of the Ballymoney lignite should lie closer to the boreal end of this range. Based on these calculations, the intervals in which eccentricity, obliquity and precession frequencies may be expected can be defined (Fig. 4). For example, if the lignite formed over 0.28 Ma, then it could contain 2.8 eccentricity cycles, seven obliquity cycles and 14 precession cycles per 50 m of lignite with frequencies of 0.056 m^{-1}, 0.14 m^{-1} and 0.28 m^{-1}, respectively.

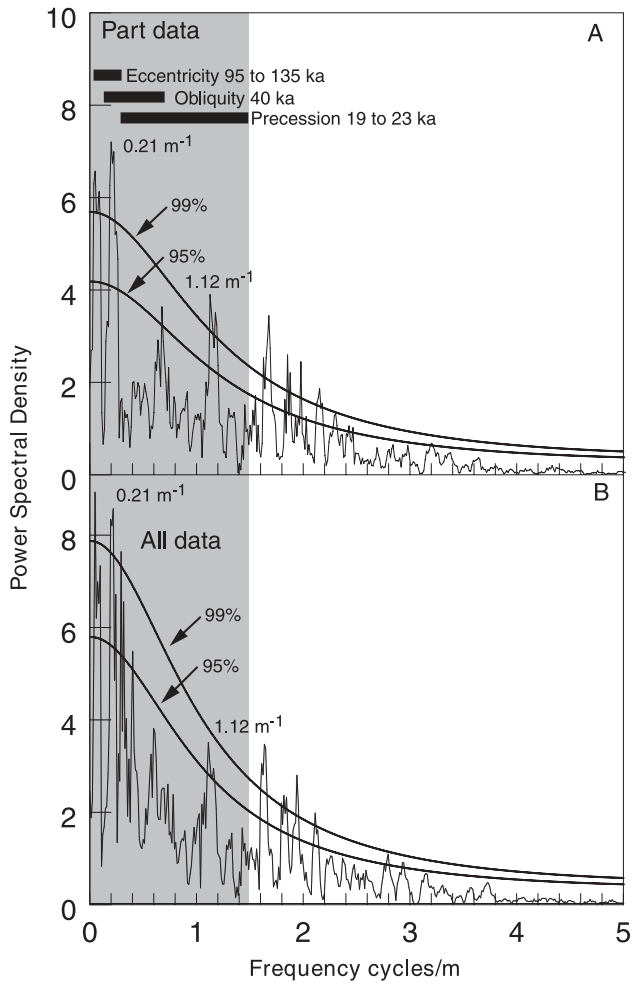


Fig. 4. Power spectra of the Ballymoney lignite showing (**a**) the power spectrum for the upper 43 m of the lignite and (**b**) the whole lignite record including the clay-rich basal 7 m. The shaded region is the zone in which orbital frequencies are expected to occur. Within this zone the possible frequency ranges for eccentricity, obliquity and precession are indicated at the top of (**a**).

Spectral analysis was performed using the SSA-MTM toolkit (Ghil *et al*. 2002) on both the whole dataset and the upper 43 m of the seam, omitting the 7 m clay-rich base, to see if the clay layers influence the frequency spectrum. Prior to spectral analysis the datasets were re-sampled every 0.08 cm using a constrained cubic spline. Spectral analysis was undertaken using combined singular spectrum analysis (SSA) and the multitaper taper method of Fourier analysis (MTM). SSA was used to identify and remove underlying trends containing low-frequency components from the data using the methods of (Ghil *et al*. 2002) and to provide a non-linear reconstruction of significant frequencies identified by both the SSA and MTM technique. The MTM method was used to identify significant frequencies in the proposed orbital range. The technique was applied using three tapers and a resolution of two with robust estimate of background noise using the linear misfit criterion. Up to five tapers with a resolution of four were also applied, and this did not affect the significance of peaks considered to represent orbital frequencies.

The most significant spectral component in the frequency domain occurs at 0.21 cycles m^{-1} in both datasets. This frequency is too low to be attributed to precession (19–23 ka) and could either be obliquity (40 ka) or eccentricity (95–130 ka). A second significant peak within the orbital range occurs at 1.12 cycles m^{-1} and if due to orbital forcing could only be caused by precession. If this is a precession signal then the peak at 0.21 cycles m^{-1} would correspond to a period of between 100 and 130 ka, exactly within the 95–130 ka eccentricity band. This is also consistent with large 18–20 m cycles that are visible in the long-term trend corresponding to the 400 ka eccentricity signal. If the 0.21 cycles m^{-1} frequency is obliquity then neither the inferred precession frequency nor the 400 ka eccentricity cycles would fit with an orbital model and the inferred carbon accumulation rate of about 70 g C m^{-2} a^{-1} is on the high side of what would be expected for a mire at 45–55°N.

Tuning

Based on the above arguments, the peak at 0.21 cycles m^{-1} is interpreted as eccentricity, on the basis that it provides the best orbital interpretation of the data. This signal is used for converting depth to time. In the absence of any radiometric dates for the sequence, this assumption will remain speculative.

To convert depth to time the filtered 0.21 cycles m^{-1} signal was tuned to an arbitrary section of the Oligocene theoretical eccentricity curve (Laskar *et al*. 2004). The tuned $\delta^{13}C$ data are included in the Supplementary Publication (see p. 1233). Comparison with a theoretical curve was preferred over tuning to a 100 ka sinusoid as the theoretical curve captures more the natural variation encountered in the eccentricity signal. During tuning the clay-rich top and base of the seam were slightly stretched relative to the central lignite section and this may indicate that the clay-bearing sections are more compressed as a result of either slower accumulation rates or greater compaction in the clay than the lignite. After tuning to eccentricity, spectral analysis was performed again and significant power observed in the precession and obliquity bands (Fig. 5).

Interpretation

Period of accumulation and carbon accumulation rates

Based on the orbital tuning, the 50 m of Ballymoney lignite accumulated over *c*. 1.16 Ma. Using this estimated period of accumulation in conjunction with the measured average density and average carbon concentration allows calculation of a long-term average carbon accumulation rate for the lignite of 27.6 g C m^{-2} a^{-1}. This rate is likely to be on the high side, as shrinkage, which results in the true dry density being less than the density estimated, was not accounted for. It can also be inferred that long-term carbon accumulation rates tend to be

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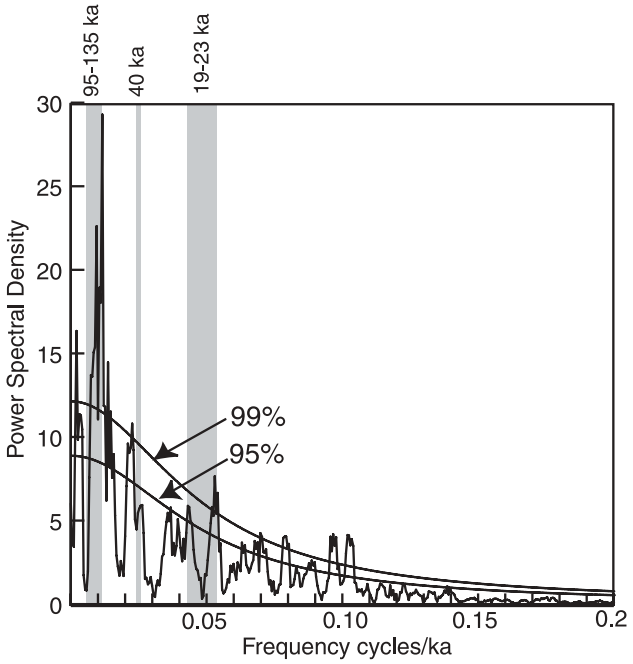


Fig. 5. MTM power spectrum for the tuned lignite record showing the distribution of power relative to the orbital frequencies. The 99% and 95% significance levels are indicated.

constant. This does not mean that short-term carbon accumulation rates were constant or that rates were constant within one cycle but that over several cycles the average rate of carbon accumulation tends to be constant. Even if the rate of carbon accumulation varied from almost zero at the start of a cycle to a maximum in the middle and back to almost zero this would produce a detectable but noisy signal in the power spectrum as long as each cycle is approximately the same length.

Origin of $\delta^{13}C$ signal

Both the duration of the seam and the estimated carbon accumulation rate are essentially independent of the origin of the $\delta^{13}C$ signal as long as the orbital signal is due to the influence of environmental variables close to the time of deposition. However, if comparison is to be made with the marine record then the origin of this signal needs to be considered. The $\delta^{13}C$ of atmospheric CO_2 is in equilibrium with the marine carbon reservoir and this provides a direct link between the terrestrial and marine records. In principle, long-term changes in the $\delta^{13}C$ of marine carbon should be recorded in the terrestrial record (Gröcke 2002). However, identification of this global signal may be confounded by other factors that influence the bulk isotopic composition of the lignite. The primary additional influences on lignite bulk $\delta^{13}C$ composition are vegetation type, hydrological stress in the environment of deposition (Arens *et al*. 2000) and preferential decay of different components (Gröcke 2002), all of which are potentially linked to environmental change at the time of deposition.

Different components of the original biomass (e.g. lignin, cellulose and aliphatic carbon) have different $\delta^{13}C$ values and decay at different rates. Consequently, differential decay of these compounds can alter the residual bulk $\delta^{13}C$ value. To avoid the influence of decay, the isotope analysis of either specific compounds or specific plant remains such as leaf cuticle is a much better way of obtaining an interpretable record (Poole *et al*. 2004). However, both of these techniques were beyond the scope of this study. Instead, the distribution of carbon between aliphatic, aromatic and carbohydrate fractions, the main components of plant matter with markedly different decay potentials and $\delta^{13}C$, was used to assess the influence of decay. Typically, the less decay resistant cellulose is 5‰ enriched in ^{13}C relative to the more decay resistant aromatic lignin (Poole *et al*. 2004), which in turn is 4–5‰ enriched in ^{13}C relative to decay resistant aliphatic, lipid-associated carbon (Gröcke 2002), so preferential decay of these components is likely to influence the bulk $\delta^{13}C$. ^{13}C NMR indicates that cellulose concentrations are negligible. The correlation between the aromatic/aliphatic ratio and bulk $\delta^{13}C$ indicates that decay has probably influenced the $\delta^{13}C$ as aliphatic carbon concentrations of up to 50% are unlikely to occur in the primary terrestrial plant input, particularly bearing in mind that each centimetre of analysed core represents the integrated plant input over a period of *c*. 0.2 ka. This is also supported by the tendency for carbonyl carbon, a product of aerobic fungal decay (Vane *et al*. 2001) to increase when the aromatic/aliphatic ratio decreases.

By assuming that the aromatic/aliphatic ratio is the overriding influence on $\delta^{13}C$ it is possible to estimate the average aliphatic and aromatic $\delta^{13}C$ values that produce a best fit to the data and whether or not these can account for the long-term and short-term variability. Comparing multiple models with an average $\delta^{13}C$ of −24‰ indicates that the best fit that minimizes the difference between modelled and measured $\delta^{13}C$ values is an average aliphatic $\delta^{13}C$ of −28‰ and an average aromatic $\delta^{13}C$ of −21‰ (Fig. 6). Comparing the difference between the measured and modelled data (Fig. 6) with the measured data demonstrates that the longer-term trends are still apparent. Changes in the proportion of aromatic to aliphatic carbon may therefore account for some of the short-term changes in $\delta^{13}C$ but cannot account for the long-term variability. It is therefore concluded that the long-term variability must be due to factors other than decay.

These long-term trends must arise from changes in the $\delta^{13}C$ of atmospheric CO_2, environmental stress or vegetation change. Given the water-saturated nature of most peat-forming environments, environmental water stress may be deemed unlikely. However, seasonal water stress is possible and could vary, particularly if the peatland was primarily rain fed. Vegetation type may change but the biomarker studies that would allow this to be distinguished were beyond the scope of this study. However, changes in vegetation type in response to even drastic climatic change are generally slow under non-glacial conditions (Wing & Harrington 2001) and it is unlikely that the vegetation would have changed significantly even over long time scales. This is confirmed by the lack of change in pollen within the Lough Neagh Group (Wilkinson *et al*. 1980).

The remaining possibility is that the long-term changes in lignite $\delta^{13}C$ reflect changes in the exogenic carbon reservoir. In support of this, analysis of marine $\delta^{13}C$ records indicates that they contain significant oscillations on 400 and 100 ka time scales throughout the Chattian (Wade & Pälike 2004). Thus the long-term changes in lignite $\delta^{13}C$ on time scales $\geqslant$100 ka are consistent with the expected scale of change in the $\delta^{13}C$ of the exogenic carbon reservoir. Furthermore, if the full range of vegetation and environmental change is encompassed within the 100 ka cycles, then the longer-term trends must reflect longer-

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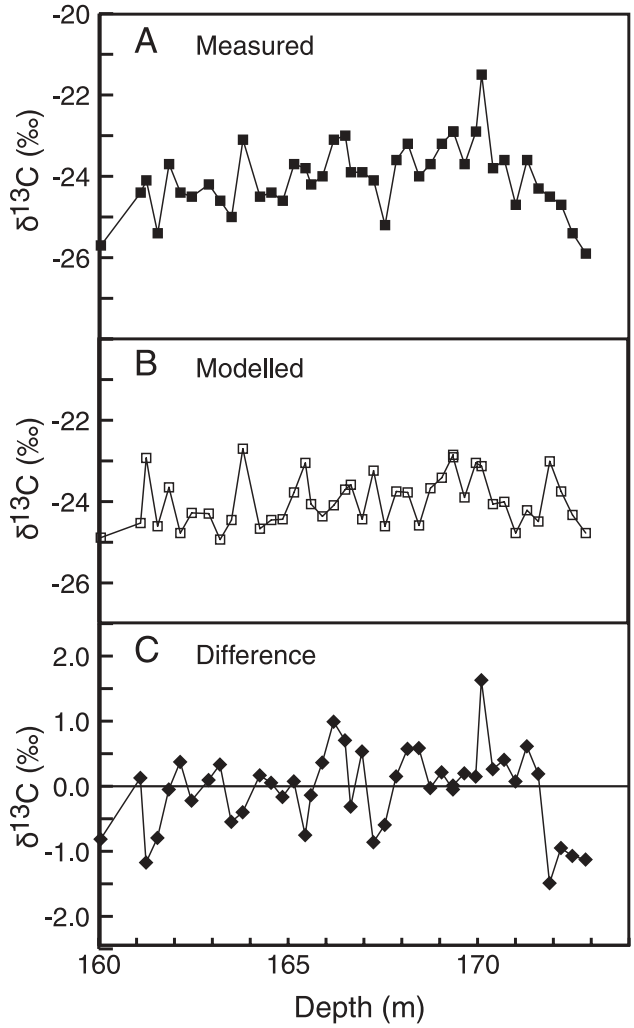


Fig. 6. (**a**) Measured $\delta^{13}C$ values compared with (**b**) modelled $\delta^{13}C$ values compared to (**c**) the difference between the modelled and measured values. The modelled values were calculated using the percentage of aromatic and aliphatic carbon measured by ^{13}C NMR and by allocating an average $\delta^{13}C$ of 21‰ and 28‰ to the aromatic and aliphatic carbon, respectively. These best-fit values were determined by minimizing the difference between the modelled and measured values.

term changes in the isotopic composition of the exogenic carbon reservoir.

In summary, the interpretation of the $\delta^{13}C$ signal remains uncertain but evidence of long-term changes in the $\delta^{13}C$ of the exogenic carbon reservoir would be expected and these may be recorded in the lignite on time scales exceeding 100 ka.

Period of deposition

If we accept that the long-term trend in the lignite may reflect changes in the exogenic carbon reservoir, then it is possible to compare this long-term trend with the marine record and determine the possible stratigraphic position of the Ballymoney lignite. Two constraints are that the long-term trend must display a slight increase in average $\delta^{13}C$ values followed by a marked decline, and this event should occur within the Chattian. In the composite marine record (Zachos *et al*. 2001) there two intervals in the Chattian that display distinct rise and fall on a scale comparable with the estimated depositional period of the Ballymoney lignite (Fig. 7). Of these two intervals, only the one from 25.8 to 24.6 Ma provides a particularly good fit. Alternatively, if the spore pollen biostratigraphy is moderately uncertain, an additional interval within the Rupelian from 30.9 to 29.7 Ma also provides a reasonable fit to the long-term trend (Fig. 7). Bearing in mind that the entire Lough Neagh Group and its equivalents have been classified as Chattian, and that the main lignite occurs towards the top of the group, it seems unlikely that the uppermost lignite-bearing sediments would have a pre-Chattian age, so the favoured interval is from 25.8 to 24.6 Ma. This timing occurs towards the end of the period of crustal sagging along the NW European continental margin, which occurred between 35 and 25 Ma (Praeg *et al*. 2005). This may indicate that thick peat started to accumulate as the rate of subsidence diminished.

Discussion

Based on the interpretation above it is possible to compare the inferred rates of carbon accumulation with those calculated for the Holocene and other periods within the Cenozoic. Average long-term carbon accumulation rates in boreal and arctic peatland range from 6 to 26 g C m^{-2} a^{-1} (Turunen *et al*. 2001, 2002, 2004; Anderson 2002; Worrall *et al*. 2003) and the boreal average is estimated at 19.9 g C m^{-2} a^{-1} (Korhola *et al*. 1995). Reported long-term carbon accumulation rates for peatland

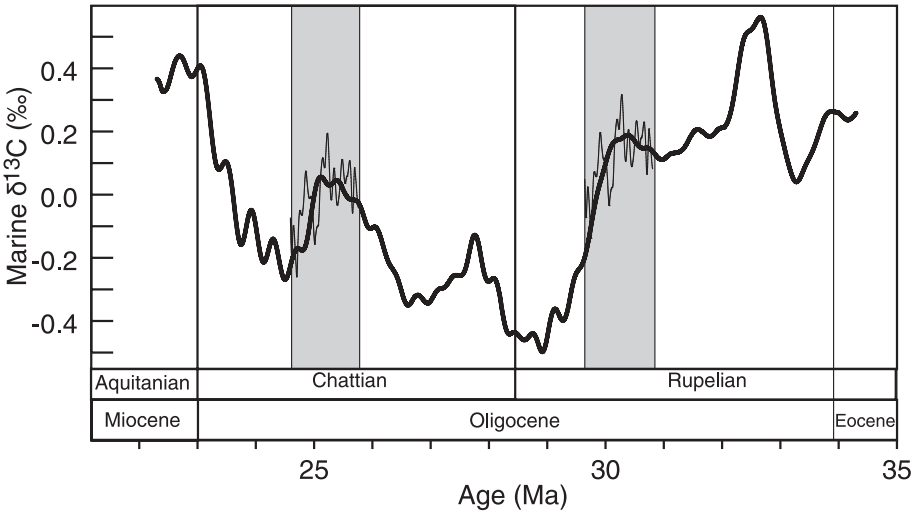


Fig. 7. Comparison of the tuned long-term trend in the lignite $\delta^{13}C$ record with the composite marine benthic Foraminifera $\delta^{13}C$ record of Zachos *et al*. (2001). Best-fit intervals are highlighted and within these intervals the long-term trend in lignite $\delta^{13}C$ (plotted with the same vertical scaling) is superimposed on the marine record.

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geographically close to Ballymoney are 15.4 and 21.3 g C m^{-2} a^{-1} (Anderson 2002; Worrall *et al*. 2003). Values for Cenozoic peatland estimated using orbital cycles range are 27.5 g C m^{-2} a^{-1} in the Miocene (Large *et al*. 2004) and 29 g C m^{-2} a^{-1} in the Palaeocene (Large *et al*. 2003) at estimated palaeolatitudes of 40–50°.

The value reported for Ballymoney of 27.6 g C m^{-2} a^{-1} is similar to the Cenozoic values and higher than the Holocene values. If we accept that the values are correct, then the Cenozoic peatlands must have accumulated at a higher rate than the Holocene peatland. This is certainly possible, as the Cenozoic peatlands are very different from the Holocene peatland. Cenozoic lignite and coal contain a high proportion of woody material unlike the moss-dominated Holocene boreal peatland, conditions were probably warmer in the Cenozoic, and the boreal and arctic peatland estimates are generally from higher latitudes. Indeed, the estimated rates of carbon accumulation for the Cenozoic fall within the compiled overall range of Holocene values (Diessel *et al*. 2000) at latitudes of 40–55° (Fig. 3).

A problem arises when models of Holocene peatland growth are considered. These models predict that on long times scales, rates of carbon accumulation should continually decline with increasing time but at an ever decreasing rate (Clymo *et al*. 1998). The Cenozoic estimates indicate that even after periods of up to 55 Ma rates similar to those observed in the Holocene are preserved. Therefore, either the Holocene growth models cannot account for the very long-term behaviour of the peat, or carbon accumulation rates at the time of deposition may have been much higher than those calculated today.

The similarity of the Cenozoic carbon accumulation rates also raises an interesting issue: the rates of carbon accumulation appear to be relatively insensitive to the concentration of atmospheric CO_2, which is estimated to have reduced by a factor of almost 10 from the Late Palaeocene to the Early Miocene (Pagani *et al*. 2005).

This is in agreement with predictions (Bowen *et al*. 2004) that the concentration of carbon in soil is insensitive to increases in atmospheric CO_2, as the increase in soil respiration rates counterbalances the increase in NPP. However, it is not in agreement with the apparent relationship between carbon accumulation rate and NPP (Fig. 3), which indicates that NPP appears to be more important than decay in determining rates of carbon accumulation in peatland. One possible explanation for this is that peatland NPP is more limited by nutrient availability than CO_2 concentration, particularly if the peatland has been predominantly ombrotrophic. Hence ombrotrophic peatland may be insensitive to increases in CO_2. It is also possible that differences in peatland NPP are too small to be detected by the technique used.

If the comparison with the marine record is correct then this demonstrates that peatland records similar isotopic oscillations to the marine record. This potentially provides a means of testing the influence of global climate on the boreal peatlands. In the marine record increases in $\delta^{13}C$ are coupled to increases in $\delta^{18}O$ during the Oligocene, and hence cooling and ice sheet expansion (Wade & Pälike 2004). If this increase in $\delta^{13}C$ in the lignite record is related to global cooling, then better organic matter preservation and presumably higher short-term rates of carbon accumulation may have occurred in western Europe during these cooler period. Whether this is linked to a decrease in local temperatures or changes in water budget or a combination of the two cannot at this stage be determined, but it does produce a hypothesis that detailed pollen or biomarker analysis may be able to resolve.

Conclusion

Ballymoney lignite accumulated over a period of 1.16 Ma probably between 25.8 and 24.6 Ma. Estimated carbon accumulation rates are 27 g C m^{-2} a^{-1}, slightly greater than present Holocene boreal rates and similar to carbon accumulation rates estimated for late Palaeocene and Miocene coal and lignite. Carbon peatland accumulation rates at mid-latitude during the Cenozoic appear to be insensitive to changes in the concentration of atmospheric CO_2.

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References

Anderson, D.E. 2002. Carbon accumulation and C/N ratios of peat bogs in North-West Scotland. *Scottish Geographical Journal*, **118**, 323–341.

Arens, N.C., Jahren, A.H. & Amundson, R. 2000. Can C3 plants faithfully record the carbon isotopic composition of atmospheric carbon dioxide? *Paleobiology*, **26**, 137–164.

Bechtel, A., Sachsenhofer, R.F., Gratzer, R., Lucke, A. & Puttmann, W. 2002. Parameters determining the carbon isotopic composition of coal and fossil wood in the Early Miocene Oberdorf lignite seam (Styrian Basin, Austria). *Organic Geochemistry*, **33**, 1001–1024.

Beerling, D.J. 2000. Increased terrestrial carbon storage across the Palaeocene–Eocene boundary. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **161**, 395–405.

Beerling, D.J. & Woodward, F.I. 2001. *Vegetation and the Terrestrial Carbon Cycle; Modelling the First 400 Million Years*. Cambridge University Press, Cambridge.

Blackford, J. 2000. Palaeoclimatic records from peat bogs. *Trends in Ecology and Evolution*, **15**, 193–198.

Bowen, G.L., Beerling, D.J., Koch, P.L., Zachos, J.C. & Quattlebaum, T. 2004. A humid climate state during the Palaeocene/Eocene thermal maximum. *Nature*, **432**, 495–499.

Charman, D. 2002. *Peatlands and Environmental Change*. Wiley, Chichester.

Clymo, R.S., Turunen, J. & Tolonen, K. 1998. Carbon accumulation in peatland. *Oikos*, **81**, 368–388.

Diessel, C., Boyd, R., Wadsworth, J., Leckie, D. & Chalmers, G. 2000. On balanced and unbalanced accommodation/peat accumulation ratios in the Cretaceous coals from Gates Formation, Western Canada, and their sequence-stratigraphic significance. *International Journal of Coal Geology*, **43**, 143–186.

George, A.M. & Mackay, G.H. 1991. Petrology. *In:* Durie, R.A. (ed.) *The Science of Victorian Brown Coal: Structure, Properties and Consequences for Utilization*. Butterworth Heinemann, Oxford, 46–97.

Ghil, M., Allen, M.R. & Dettinger, M.D. *et al*. 2002. Advanced spectral methods for climatic time series. *Reviews of Geophysics*, **40**, 1–41.

Gorham, E. 1991. Northern peatlands: role in the carbon cycle and probable responses to climatic warming. *Ecological Applications*, **1**, 182–195.

Gradstein, F.M., Ogg, J.G., Smith, A.G., Bleeker, W. & Lourens, L.J. 2004. A new geologic time scale, with special reference to Precambrian and Neogene. *Episodes*, **27**, 83–100.

Gröcke, D.R. 2002. The carbon isotope composition of ancient CO_2 based on higher-plant organic matter. *Philosophical Transactions of the Royal Society of London, Series A*, **360**, 633–658.

Holdgate, G.R., Kershaw, A.P. & Sluiter, I.R.K. 1995. Sequence stratigraphic analysis and the origins of Tertiary brown coal lithotypes, Latrobe Valley. Gippsland Basin, Australia. *International Journal of Coal Geology*, **28**, 249–275.

Jones, T.P., Fortier, S.M., Mosbrügger, V., Roessler, J., Utescher, T. & Ashraf, A.R. 1997. $^{13}C/^{12}C$ ratio double cyclicity in a Miocene browncoal: isotopic signals and orbital forcing. *Terra Nova*, **9**, 19–23.

Kolcon, I. & Sachsenhofer, R.F. 1999. Petrography, palynology and depositional environments of the early Miocene Oberdorf lignite seam (Styrian Basin, Austria). *International Journal of Coal Geology*, **41**, 275–308.

Korhola, A., Tolonen, K., Turunen, J. & Jungner, H. 1995. Estimating long-term carbon accumulation rates in boreal peatlands by radiocarbon dating. *Radiocarbon*, **37**, 575–584.

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Kremenetski, K.V., Velichko, A.A., Borisova, O.K., MacDonald, G.M., Smith, L.C., Frey, K.E. & Orlova, L.A. 2003. Peatlands of the Western Siberian lowlands: current knowledge on zonation, carbon content and Late Quaternary history. *Quaternary Science Reviews*, **22**, 703–723.

Large, D.J., Jones, T.F., Somerfield, C., Gorringe, M.C., Spiro, B., Macquaker, J.H.S. & Atkin, B.P. 2003. High-resolution terrestrial record of orbital climate forcing in coal. *Geology*, **31**, 303–306.

Large, D.J., Jones, T.F., Briggs, J., Spiro, B. & Macquaker, J.H.S. 2004. Orbital tuning and correlation of 1.7 m.y. of continuous carbon storage in an early Miocene peatland. *Geology*, **32**, 873–876.

Laskar, J., Robutel, P., Joutel, F., Gastineau, M., Correia, A.C.M. & Levrard, B. 2004. A long-term numerical solution for the insolation quantities of the Earth. *Astronomy and Astrophysics*, **428**, 261–285.

Mitchell, W.I. 2004. *The Geology of Northern Ireland—Our Natural Foundation*. Geological Survey of Northern Ireland, Belfast.

Pagani, M., Zachos, J.C., Freeman, K.H., Tipple, B. & Bohaty, S. 2005. Marked decline in atmospheric carbon dioxide concentrations during the Paleogene. *Nature*, **309**, 600–603.

Page, S.E., Wust, R.A.J., Weiss, D., Rieley, J.O., Shotyk, W. & Limin, S.H. 2004. A record of Late Pleistocene and Holocene carbon accumulation and climate change from an equatorial peat bog (Kalimantan, Indonesia): implications for past, present and future carbon dynamics. *Journal of Quaternary Science*, **19**, 625–635.

Parnell, J., Balvinder, S. & Meighan, I.G. 1989. The lignite and associated sediments of the Tertiary Lough Neagh Basin. *Irish Journal of Earth Scienes*, **10**, 67–88.

Poole, I., van Bergen, P.F., Kool, J., Schouten, S. & Cantrill, D.J. 2004. Molecular isotopic heterogeneity of fossil organic matter: implications for δ^{13}C-biomass and δ^{13}C-palaeoatmosphere proxies. *Organic Geochemistry*, **35**, 1261–1274.

Praeg, D., Stoker, M.S., Shannon, P.M., Ceramicola, S., Hjelstuen, B., Laberg, J.S. & Mathiesen, A. 2005. Episodic Cenozoic tectonism and the development of the NW European 'passive' continental margin. *Marine and Petroleum Geology*, **22**, 1007–1030.

Seifert, A., Brause, H. & Rascher, J. 1993. Geology of the Niederlausitz Lignite District, Germany. *International Journal of Coal Geology*, **23**, 263–289.

Snape, C.E., McGhee, B.J., Martin, S.C. & Andresen, J.M. 1997. Structural characterisation of catalytic coke by solid-state ^{13}C-NMR spectroscopy. *Catalysis Today*, **37**, 285–293.

Turunen, J., Tahvanainen, T., Tolonen, K. & Pitkanen, A. 2001. Carbon accumulation in West Siberian mires, Russia. *Global Biogeochemical Cycles*, **15**, 285–296.

Turunen, J., Tomppo, E., Tolonen, K. & Reinikainen, A. 2002. Estimating carbon accumulation rates of undrained mires in Finland—application to boreal and subarctic regions. *Holocene*, **12**, 69–80.

Turunen, J., Roulet, N.T., Moore, T.R. & Richard, P.J.H. 2004. Nitrogen deposition and increased carbon accumulation in ombrotrophic peatlands in eastern Canada. *Global Biogeochemical Cycles*, **18**, article number GB3002.

Vane, C.H., Martin, S.C., Snape, C.E. & Abbot, G.D. 2001. Degradation of lignin in wheat straw during growth of the oyster mushroom (*Pleurotus ostreatus*) using off-line thermochemolysis with tetramethylammonium hydroxide and solid state ^{13}C NMR. *Journal of Agricultural and Food Chemistry*, **49**, 2709–2716.

Vitt, D.H., Halsey, L.A., Bauer, I.E. & Campbell, C. 2000. Spatial and temporal trends in carbon storage of peatlands of continental western Canada through the Holocene. *Canadian Journal of Earth Sciences*, **37**, 683–693.

Wade, B.S. & Pälike, H. 2004. Oligocene climate dynamics. *Paleoceanography*, **19**, article number PA4019.

White, A., Cannell, M.G.R. & Friend, A.D. 2000. CO_2 stabilisation, climate change and the terrestrial ecosystem. *Global Change Biology*, **6**, 817–833.

Wilkinson, G.C., Bazley, R.A.B. & Boulter, M.C. 1980. The geology and palynology of the Oligocene Lough Neagh clays, Northern Ireland. *Journal of the Geological Society, London*, **137**, 65–75.

Wing, S.L. & Harrington, G.J. 2001. Floral response to rapid warming in the earliest Eocene and implications for concurrent faunal change. *Paleobiology*, **27**, 539–563.

Worrall, F., Reed, M., Warburton, J. & Burt, T. 2003. Carbon budget for a British upland peat catchment. *Science of the Total Environment*, **312**, 133–146.

Zachos, J., Pagani, M., Sloan, L., Thomas, E. & Billups, K. 2001. Trends, rhythms, and aberrations in global climate 65 Ma to present. *Science*, **292**, 686–693.

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