Ecological and biogeochemical change in an early Paleogene peat-forming environment: Linking biomarkers and palynology

Gordon N. Inglis a,b,⁎, Margaret E. Collinson c, Walter Riegel d,e, Volker Wilde e, Brittany E. Robson c, Olaf K. Lenz f, Richard D. Pancost a,b

a Organic Geochemistry Unit, School of Chemistry, University of Bristol, Cantock’s Close, Bristol BS8 1TS, UK
b Cabot Institute, University of Bristol, Bristol BS8 1JF, UK
c Department of Earth Sciences, Royal Holloway University of London, Egham, Surrey TW20 0EX, UK
d Geowissenschaftliches Zentrum Göttingen, Geobiologie, Goldschmidtstrasse 3, D-37077 Göttingen, Germany
e Senckenberg Forschungsinstutit und Naturmuseum, Senckenberganlage 25, D-60325 Frankfurt am Main, Germany
f Geowissenschaftliches Zentrum Göttingen, Geobiologie, Goldschmidtstrasse 3, D-37077 Göttingen, Germany

⁎ Corresponding author at: Organic Geochemistry Unit, School of Chemistry, University of Bristol, Cantock’s Close, Bristol BS8 1TS, UK. Tel.: +44 117 9546395.
E-mail address: gordon.inglis@bristol.ac.uk (G.N. Inglis).

ARTICLE INFO

Article history:
Received 28 January 2015
Received in revised form 27 July 2015
Accepted 1 August 2015
Available online 8 August 2015

Editor: T. Corrège

Keywords:
Paleocene
Eocene
Bryophyte
Sphagnum bog

ABSTRACT

Sphagnum moss is the dominant plant type in modern boreal and (sub)arctic ombrotrophic bogs and is of particular interest due to its sensitivity to climate and its important role in wetland biogeochemistry. Here we reconstruct the occurrence of Sphagnum moss – and associated biogeochemical change – within a thermally immature, early Paleogene (~55 Ma) lignite from Schöningen, NW Germany using a high-resolution, multi-proxy approach. Changes in the abundance of Sphagnum-type spores and the C23/C31 n-alkane ratio indicate the expansion of Sphagnum moss within the top of the lignite seam. This Sphagnum moss expansion is associated with the development of waterlogged conditions, analogous to what has been observed within modern ombrotrophic bogs. The similarity between biomarkers and palynology also indicates that the C23/C31 n-alkane ratio may be a reliable chemotaxonomic indicator for Sphagnum during the early Paleogene. The δ13C value of bacterial hopanes and mid-chain n-alkanes indicates that a rise in water table is not associated with a substantial increase in aerobic methanotrophy. The absence of very low δ13C values within the top of the seam could reflect either less methanogenesis or less efficient methane oxidation under waterlogged sulphate-rich conditions.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

The early Paleogene (66–34 Ma) is characterised by high atmospheric carbon dioxide (pCO2) concentrations (Pearson and Palmer, 2000; Pagani et al., 2005; Lowenstein and Dimicco, 2006; Pearson et al., 2009), high sea surface temperatures (SST) (Pearson et al., 2007; Bijl et al., 2009; Hollis et al., 2012), high land temperatures (Huber and Caballero, 2011; Pancost et al., 2013) and intensification of the hydrological cycle (Pieperhumbert, 2002; Pagani et al., 2006; Krishnan et al., 2014). As a result, early Paleogene wetland environments may have had up to ~3 times more abundant than today (Sloan et al., 1992; DeConto et al., 2012).

Modern wetlands are the largest natural source of atmospheric methane (CH4) with estimates ranging between 80 and 280 Tg CH4 yr−1 (Bridgman et al., 2013). As a result, the ecology and biogeochemistry of wetlands are increasingly recognised as central to understanding Paleogene biogeochemical feedbacks. Although there are no proxy methods for reconstructing ancient CH4 emissions, the carbon isotope value of bacterial hopanes has been used to infer relative changes in terrestrial methane cycling (e.g., Pancost et al., 2007). For example, a decrease in the carbon isotope value of bacterial hopanes during the onset of the Paleocene-Eocene Thermal Maximum (PETM; ~56 Ma) indicates enhanced CH4 production within an ancient peat-forming environment (Pancost et al., 2007). Over longer timescales, modelling studies suggest a ~6- to 7-fold increase in wetland CH4 emissions during the early Paleogene (Bee cling et al., 2011). Enhanced CH4 emissions and changes in other biogenic trace gases (i.e., N2O and O3) may have acted to increase global temperature by 2.7 °C during the early Paleogene (Bee cling et al., 2011) and could have been an important mechanism for maintaining high-latitude warmth (Sloan et al., 1992).

A particularly important topic of interest in palaeoclimatic investigations has been tracing the occurrence and distribution of Sphagnum moss in wetland environments. Sphagnum moss is the dominant plant type in modern ombrotrophic bogs (Clymo, 1984) and plays an important role in terrestrial methane cycling (Raghoebarsing et al., 2005; Kip et al., 2010). Under anoxic, waterlogged conditions, anaerobic degradation of Sphagnum produces significant quantities of CH4 that contribute to the total atmospheric CH4 flux (Clymo, 1984). However, Sphagnum can also
limit CH₄ emissions by consuming CH₄ symbiotically with aerobic methane-oxidising bacteria (Raghoebarsing et al., 2005; Kip et al., 2010).

A variety of organic geochemical proxies can be used to track changes in peat-forming vegetation, specifically the input of Sphagnum moss (Nott et al., 2000; Pancost et al., 2002; Xie et al., 2004; Bingham et al., 2010). Sphagnum species are typically dominated by mid-chain C₂₃ and C₂₅ n-alkanes (Baas et al., 2000; Nott et al., 2000), whereas terrestrial, peat-forming higher-plants, such as Ericaceae or Carex, are dominated by long-chain C₂₉ and C₃₁ n-alkanes (Eglinton and Hamilton, 1967).

As such, the C₂₃/C₃₁ n-alkane ratio has been proposed as a tracer for Sphagnum input into ancient peat deposits (Nott et al., 2000; Bingham et al., 2010). A number of studies have shown the close correspondence between the C₂₃/C₃₁ n-alkane ratio and the relative abundance of Sphagnum leaves in a variety of modern ombrotrophic bogs (Nott et al., 2000; Pancost et al., 2002, 2003; Xie et al., 2004). While this has been used to reconstruct vegetation and hydrological change during the Holocene (e.g., Nott et al., 2000), it has not been applied to older peat-forming environments.

In order to investigate ecological, hydrological and biogeochemical change within an early Paleogene peat-forming setting, we reconstruct downcore variations in Sphagnum moss within a lignite seam using a high-resolution, multi-proxy approach. Samples are derived from Seam 1, a thermally immature lignite from the Schöningen Südfeld mine, northern Germany (~41°N palaeolatitude). We use the C₂₃/C₃₁ n-alkane ratio and the abundance of Sphagnum-type spores to reconstruct the occurrence of Sphagnum moss. Using this, and other palynological and petrological indicators, we elucidate hydrological change within an early Paleogene peat-forming environment. We then use bacterially-derived hopane distributions and compound-specific carbon isotopes to characterise the biogeochemical response associated with these hydrological changes in a warmer climate.

2. Methods

2.1. Site description

Samples were collected from the Schöningen Südfeld mine in northern Germany, NW Europe (Fig. 1) where the sediments were deposited in a low lying coastal setting (Riegel et al., 2012). Samples are derived from a ~2.7 m thick lignite seam (Seam 1) overlain and underlain by brackish to shallow marine, clastic sedimentary deposits (Riegel et al., 2012). Given the thickness of the seam, we focussed our high-resolution study on the lower and upper part of Seam 1. Samples were collected (c. every 5 cm) from the lower (267 to 200 cm) and upper part of Seam 1 (57 to 0 cm) as well as the overlying brackish to shallow marine interbeds (0 to 36 cm above the seam top). Peat accumulation rates in tropical and subtropical climates are 2 mm/year and 0.8 mm/year, respectively (Collinson et al., 2009 and references therein). Assuming a median peat-to-lignite compaction ratio (7:1) (Ryer and Langer, 1980), Seam 1 spans between 9.5 and 23.6 kyr. The full range, taking the material into account (i.e., woody dominated material vs parenchymatous tissues; Collinson et al., 2009) is 2.7 to 101.2 kyr.

The dinocyst zone D 5nb was recognised above Main Seam in the nearby Emmerstedt area by Ahrendt et al. (1995). If the Main seam is coeval at both sites this would indicate that Seam 1 at Schöningen is earliest Eocene. Within Interbed 2, above Seam 1, there is an abundance of the dinocyst Apectodinium (Riegel et al., 2012) which may represent the Paleocene-Eocene Thermal Maximum (PETM) as it does at other sites (Crouch et al., 2003; Sluijs et al., 2007; Sluijs and Brinkhuis, 2009). If so then Seam 1 could be latest Paleocene. However, it should be noted that there are other Apectodinium acmes in northern mid-latitude settings during the early Paleogene (see discussion in Collinson et al., 2009, p. 45–51). In summary, we conclude that Seam 1 is of latest Paleocene or earliest Eocene age. Palaeogeographically, Schöningen was located between the Harz Mountains and the Flechtingen Rise at the southern shore of the North Sea during this time interval (Riegel et al., 2012; Fig. 1) at a palaeolatitude of ~41°N (van Hinsbergen et al., 2015).

2.2. Elemental and bulk δ¹³C analyses

Total carbon (TC), total nitrogen (TN) and total hydrogen (TH) analyses were performed using a Carlo Erba EA1108 Elemental Analyser. Total sulphur (TS) analysis was performed in a similar method using a Eurovector EA3000 Analyser. Inorganic carbon (IC) analysis was performed using a Modified Coulomat 702 Analyser with a coulometric cell. Total organic carbon (TOC) content was determined by subtracting IC from TC. Bulk δ¹³C analysis was undertaken at Royal Holloway following the methods used by Pancost et al. (2007).

2.3. Organic geochemistry

Approximately 1–10 g of sediment was extracted via Soxhlet apparatus for 24 h using dichloromethane (DCM):methanol (MeOH)
Soft samples were crushed manually to a top particle size of c. 1000 μm, respectively (Dickson et al., 2009). The neutral fraction was subsequently fractionated over alumina into apolar and polar fractions using hexane:DCM (9:1 vol/vol) and DCM:MeOH (1:2 vol/vol), respectively. All fractions were analysed via gas chromatography–mass spectrometry (GC–MS) using a Thermoquest Finnigan Trace GC interfaced with a Thermoquest Finnigan Trace MS. The electron ionisation source was set at 70 eV. Scanning occurred between m/z ranges of 50 to 650 Da. The GC was fitted with a fused silica capillary column (50 m × 0.32 mm i.d.) coated with a ZB1 stationary phase (dimethylpolysiloxane equivalent, 0.12 μm film thickness). Compound specific carbon isotope analysis was performed on selected apolar fractions using a Trace GC Ultra gas chromatograph coupled to a Finnigan MAT DeltaPlus IV mass spectrometer via a Finnigan MAT Conflo IV interface. GC Conditions were as for GC–MS. Each value was measured in duplicate and is reported in standard per mil notation (‰) relative to Vienna PeeDee Belemnit (VPDB).

The average chain length (ACL) is defined for n-alkanes using the following equation (Eglinton and Hamilton, 1967);

\[
ACL = \frac{(25nC_{25}) + 27(nC_{27}) + 29(nC_{29}) + 31(nC_{31}) + 33(nC_{33})}{(nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33})}
\]

while the carbon preference index (CPI) is defined using the following equation (Bray and Evans, 1961);

\[
CPI = 0.5 \times \frac{\sum (nC_{25} + nC_{27} + nC_{29} + nC_{31})}{\sum (nC_{26} + nC_{28} + nC_{30} + nC_{32})}
\]

The pAq ratio is defined for n-alkanes using the following equation (Ficken et al., 2000);

\[
pAq = \frac{nC_{23} + nC_{25}}{nC_{23} + nC_{25} + nC_{29} + nC_{31}}
\]

2.4. Palynology

Approximately 1–2 g of lignite was boiled with 15% hydrogen peroxide (H₂O₂) followed by treatment with 2% potassium hydroxide (KOH). Samples from unconsolidated clastic interbeds were briefly boiled with 15% H₂O₂ and ultrasonicated to separate the organic and mineral matter. In some instances, 2% KOH was added to organic-matter rich clastic samples. Cold hydrofluoric acid was applied for several days in order to remove silica and silicate material from each sample. Samples were then sieved through a 10 μm mesh screen, retaining the coarser fraction. A sub-sample was mounted in glycerine jelly to produce slides and residues will finally be stored in the palaeobotanical collections of the Senckenberg Forschungsinstitut und Naturmuseum, Frankfurt am Main, Germany.

2.5. Petrology

Petrological study was undertaken only on the lignites of Seam 1 (not on the overlying or underlying siliclastic interbeds). Polished blocks of crushed lignite were prepared to industry standard by Jim Hower and colleagues at the Centre for Applied Energy Research, University of Kentucky using approximately 1–5 g of lignite. Where possible samples were crushed to the standard 20 mesh size, ≤840 μm, using a grinder. Soft samples were crushed manually to a top particle size of c. 1000 μm. A subsample was embedded in epoxy resin. Once dry, the block was polished using 60-, 240-, 400-, and 600-grit SiC papers followed by 0.3-micron alumina on Buehler Texmet paper and 0.05-micron alumina on silk. The finished polished blocks were viewed in reflected light under immersion oil (Cargille type A, density 0.923 g/cc at 23 °C, RI of 1.514) using a Leica reflected light microscope and a ×20 oil immersion objective. Lignite components (maceral groups), huminite, liptinite and inertinite, were classified according to the International Committee for Coal and Organic Petrology (ICCP) standard. Inertinite, recognised by its high reflectance and cellular preservation (ICCP, 2001), is a product of wildfire (Scott, 2002). Huminite, characterised by low reflectance and varied cellular preservation (Sýkorová et al., 2005) indicates how wet or dry the conditions of peat formation were. The huminite maceral ulminite is defined by highly gelified plant material (with homogenous cell walls, no visible internal structures and obscured cell lumina) that indicates formation under wet conditions (Sýkorová et al., 2005). Non-gelified huminite macerals attribute (cemented detrital material) and textinite (cell walls not gelified, open or open but infilled cell lumina) indicate drier conditions during peat formation (Sýkorová et al., 2005). Macerals were quantified following the method outlined in Robson et al. (2015).

3. Results

3.1. Elemental analysis

Total organic carbon (TOC) content within Seam 1 is generally high (>50–60 wt.%; Fig. 2a) with a gradual decrease in the bioturbated upper 15 cm (15–40 wt.%). TOC values in the overlying marine interbeds are relatively low (3–9 wt.%). C/N ratios are high throughout Seam 1 (50–95; Fig. 2b) with lower values in the overlying marine interbeds (21–37). This is consistent with a terrestrial organic matter source throughout (Boutton, 1991). Total sulphur (TS) content is high throughout Seam 1 (3.9–7.6 wt.%) with lowest values in the overlying marine interbeds (2.1–4.1 wt.%; Fig. 2c). High sulphur contents (e.g., >3 wt.% S) in peat horizons are generally attributed to the incorporation of seawater sulphate into the peat-forming environment (Chou, 2012).
3.2. Bulk δ13Corg

Bulk δ13Corg values (Fig. 9a, diamonds) were determined for the top of Seam 1 (57–0 cm) and the overlying marine interbeds (0–36 cm). Within the lignite, values range from −25.9‰ to −27.9‰. Within the marine interbeds, values range from −26.5‰ to −27.0‰. Between 57 and 0 cm in Seam 1, bulk δ13Corg values exhibit a gradual upwards decrease in δ13C by −1‰.

3.3. Plant-derived biomarkers

Plant biomarkers, including a range of n-alkyl and terpenoid components, dominate all of the lipid fractions analysed. The apolar fraction is characterised by a homologous series of n-alkanes with a strong odd-over-even predominance (Figs. 3, 4a). Long-chain (C27–C31) homologues, typically derived from the epicuticular wax of higher plants, are the most abundant (2 to 65 μg/g dry sediment). A terrestrial plant origin is confirmed by the n-alkane carbon preference index (CPI), which on average is 5.9 (Bray and Evans, 1961; Eglinton and Hamilton, 1967). The average n-alkane chain length (ACL) ranges from 26.8 to 29.6 within Seam 1 and is typical for modern tree species (Diefendorf et al., 2011). Mid-chain homologues (C22–C25), derived from submerged and floating macrophytes (Ficken et al., 2000) and/or Sphagnum moss (Baas et al., 2000; Nott et al., 2000), are also relatively abundant (1 to 32 μg/g dry sediment; Figs. 3–4). The C23/C31 n-alkane ratio (Fig. 7a), which is commonly used to trace the input of Sphagnum moss to Holocene peat (e.g., Nott et al., 2000), ranges from 0.1 to 0.6 within Seam 1. Short-chain (C17–C21) homologues, typically derived from marine algae, are of low abundance throughout (<1 to 14 μg/g dry sediment; Figs. 3–4).

The apolar fraction also contains a variety of di- and triterpenoids. Diterpanes of the abietane and pimarane class are abundant within Seam 1 between 57 and 43 cm, especially fichtelite, norisopimarane and retene. These compounds are non-specific conifer biomarkers (Otto and Simonetti, 2001). Tetracyclic triterpanes, which are derived from angiosperms and/or gymnosperms (Diefendorf et al., 2014), were identified but are in low abundance. Pentacyclic triterpanes derived from angiosperms (Simonetti et al., 1986; Otto et al., 2005) are abundant throughout, especially ring-A monoaromatic triterpenoids (Jacob et al., 2007; Fig. 3).

The polar fraction contains mid- and long-chain n-alkanols (C20–C32) with a strong even-over-odd predominance (Fig. 4b). The average chain length ranges from 24.7 to 27.1 and the dominant n-alkanol is C26 or C28. This is consistent with a mixed contribution from Sphagnum moss and peat-forming plants such as Ericaceae (Ficken et al., 2000; Pancost et al., 2002). This presence of peat-forming plants other than Sphagnum is consistent with the identification of amyrenone, a triterpenoid ketone frequently found in angiosperms. An unknown compound with M + 438 and m/z 203 was identified and is also likely derived from angiosperms (Stefanova et al., 2008). The fatty acid fraction contains mid- and long-chain n-alkanoic acids (C24–C32) with a strong even-over-odd predominance (Fig. 4c). The average chain length ranges from 25.6 to 28.0 and the dominant n-alkanoic acid is C28. This is consistent with terrestrial plant source (Eglinton and Hamilton, 1967). The fatty acid fraction contains trace quantities of short-chain n-alkanoic acids (C16–C18) which can have a bacterial or plant-derived source (Baas et al., 2000).

![Fig. 3. Partial gas chromatogram of a typical lignite-derived apolar fraction. a) TIC. Roman numerals denote plant-derived diterpane and triterpene derivatives (Jacob et al., 2007); I: Retene. II and III: Unknown Ring-A monoaromatic triterpenoid. IV: Dinor-oleana(ursa)-1,3,5(10),13(18)-tetraene. V, VI and VII: Unknown Ring-A monoaromatic triterpenoid. VIII Dinor-oleana(ursa)-1,3,5(10),12-tetraene. IX: Lanosta(eupha)pentane. X: Dinor-oleana(ursa)-1,3,5(10)-triene. XI: Dinor-oleana(ursa)-1,3,5(10),13(18)-tetraene. XII: Tetranor-oleana(ursa)-1,3,5(10),6,8,11,13-heptatetraene. XIII: Tetranor-oleana(ursa)-1,3,5(10),6,8,11,13-heptaene. XIV: Tetranor-lupa-1,3,5(10),6,8,11,13-heptaene. Numbers accompanied with Greek letters signify the carbon number and the C-17 and C-21 stereochemistry of bacterial hopanes. b) m/z 57 trace showing isoprenoids (open circles) and n-alkanes (closed circles).](image-url)
Compound specific carbon isotope (δ13C) analysis was performed upon a selection of apolar, plant-derived biomarkers from the top of Seam 1 and the overlying marine interbeds (n = 18). In some samples, co-elution of other compounds prevents the determination of δ13C values. The δ13C value of long-chain (C27–C29) n-alkanes within Seam 1 (Figs. 5 and 9a) ranges from −29.4 to −32.5‰, consistent with a C3 higher-plant origin (Collister et al., 1994) and values typically observed in ombrotrophic bogs (Pancost et al., 2000). The δ13C value of mid-chain (C23–C25) n-alkanes (Figs. 5 and 9a) is slightly heavier, ranging from −27.9 to −30.5‰ and is consistent with a contribution from a partially submerged source (Ficken et al., 2000). The δ13C values are summarised in Fig. 5.

3.5. Palynology

Within Seam 1, the dominant plant types represented by palynomorphs are Sphagnum moss as indicated by the abundance of Sphagnum-type spores (Fig. 6) (especially Tripectinopsis, originally used as a subgenus of the widely used but invalid genus Stereisporites), ferns (e.g., Laevigatosporites – Fig. 7b), swamp-dwelling conifers (e.g., Inaperturopolipollenites – Fig. 7a) and mixed mesopctic forest vegetation (e.g., Tricolporopollenites cingulum). Seam 1 is traceable over a few kilometres and the relative abundance of Sphagnum-type spores exhibits a similar change in relative abundance through the seam in all three sections studied (Hanner-Schiemann, 1998). In this section, consistently low values occur in the lower part of the seam between 200 and 267 cm (0–10%) with a large increase in abundance in the upper part between 0 and 57 cm (7–48%) (Fig. 7b). During the latter interval, Sphagnum-type spores comprise, on average, ∼21% of the entire palynological assemblage. Sphagnum-type spores are absent or in very low abundance within the overlying marine interbeds (∼0.3%). Ferns, specifically Laevigatosporites (Fig. 8b) are abundant between 57 and 43 cm (∼10.6%) while Inaperturopolipollenites (Fig. 8a) proliferates within the overlying interbeds (∼32%).

The dinoflagellate cyst Apectodinium (Fig. 8f) tentatively identified as A. homomorphum (Riegel et al., 2012), is abundant just above the base of marine interbed 2 where it comprises 13–45% of the entire palynomorph assemblage. Within Seam 1, small quantities of Apectodinium occur between 12 and 2 cm (∼2%), likely as a result of bioturbation penetrating down into the seam from the overlying interbed. Resting cysts of the freshwater green-algal family Zygnemataceae (Fig. 8f) are present between 21 and 2 cm (∼2%), but absent within the overlying marine interbeds and the rest of Seam 1.

3.6. Petrology

Lignite is composed of macerals that are microscopically recognisable fragments of organic matter. Of the three main maceral groups, huminite was the most abundant group within Seam 1 (69.3%), ranging from 53 to 87%. Liptinite was the second most abundant (20.9%), ranging from 9.9 to 30.8% while inertinite (Fig. 8g) was the least abundant (9.8%), ranging from 0.8 to 23.8%. Within the huminite maceral group, three macerals were quantified: attrinite, textinite and ulminite. Attrinite was the most abundant (33.7%), ranging from 15.4 to 48.8%. Textinite was the second most abundant (27.1%), ranging from 12.5 to 60.7% while ulminite

**Fig. 4.** The average fractional abundance of a) n-alkanes, b) n-alkanols and c) n-alkanoic acids within Seam 1 (n = 30). Error bars reflect one standard deviation.

**Fig. 5.** δ13C value of plant-derived (dark grey) and microbial-derived (light grey) biomarkers within the top of Seam 1 (0–54 cm) and the overlying marine interbeds (0–36 cm).
(Fig. 7c) was the least abundant (8.3%), ranging from 0.8 to 21.4%. On a macroscopic scale, lignites in both the upper and lower parts of Seam 1 are composed of a mix of matrix and tissue lithotypes, but recognisable plant tissue (uncharred) is more common in the lower part of the sequence and charcoal is more common in the upper part. Lithotypes in which charcoal was visible in the field contain higher inertinite percentages in the related polished block containing a crushed sample, in comparison to samples in which no field charcoal was visible.

4. Discussion

4.1. Evidence for the occurrence of Sphagnum in Seam 1, Schöningen

The C_{23}/C_{31} n-alkane ratio is used as a chemotaxonomic proxy for Sphagnum input in modern peat-forming environments (Baas et al., 2000; Nott et al., 2000; Pancost et al., 2002; Bingham et al., 2010) and is often supplemented with other proxies (e.g., pollen or leaf assemblages)
to reconstruct vegetation change during the Holocene (e.g., Nott et al., 2000). Here we compare biomarker and palynological downcore trends in order to investigate the distribution and occurrence of Sphagnum moss within an early Paleogene, peat-forming environment.

Spores assigned to Sphagnum moss are present in most seams of the early Eocene Schöningen Formation (Riegel et al., 2012). They are most commonly represented by Tripunctisporis, a former subgenus of the invalid genus Stereisporites; however, at least three to four morphotypes of Sphagnum-type spores can be distinguished (i.e., Tripunctisporis and Distancoraesporis plus a number of forms more closely resembling modern Sphagnum spores; Fig. 6). Tripunctisporis differs slightly from spores of modern Sphagnum, but its co-occurrence with charred remains of Sphagnum-leaves in a thin lignite seam within interbed 4 (Riegel et al., 2012) confirms a likely Sphagnum origin as originally suggested by Döring et al. (1966). The proportion in which Sphagnum-type spores contribute to the frequency curve (Fig. 7) varies without any obvious pattern to it. However, Tripunctisporis and Distancoraesporis dominate in most of the samples. Sphagnum-type spores are low or absent within the base of Seam 1 (200–267 cm; < 10%). This is consistent with low C_{29}/C_{31} n-alkane values (<0.4) which indicate that Sphagnum moss was probably not an important component of the peat-forming vegetation within this interval (Fig. 7). The pAq ratio (Fig. 7d), which can also be used to detect changes in Sphagnum occurrence and local hydrology (Nichols et al., 2006), averages 0.27 and ranges from 0.13 to 0.50 within the base of Seam 1 (200–267 cm). This suggests mixed input from terrestrial higher plants, dominated by C_{29} and C_{31} n-alkanes, and Sphagnum moss, dominated by C_{33} and C_{35} n-alkanes. Submerged and/or floating freshwater aquatic macrophytes can also produce mid-chain n-alkanes and may contribute towards the observed pAq values (Ficken et al., 2000).

Within the top of Seam 1 (0–57 cm), Sphagnum-type spores increase significantly and comprise 20 to 50% of the entire palynological assemblage. During the same interval, the C_{29}/C_{31} n-alkane ratio increases (~1.6) and yields values that are typical of a modern, Sphagnum-dominated bog (Nott et al., 2000; Pancost et al., 2002; Xie et al., 2004; Bingham et al., 2010). The similarity between biomarkers and palynology (Fig. 7) provides compelling evidence that Sphagnum moss was an important peat-forming plant within the top of Seam 1 (0–57 cm) and that the C_{29}/C_{31} n-alkane ratio is a reliable chemotaxonomic indicator for Sphagnum input during the early Paleogene. Sphagnum expansion coincides with an increase in the pAq ratio (0.52 to 0.79; Fig. 7d) and a decrease in the n-alkane average chain length (ACL; Fig. 8e). The latter is consistent with modern studies which exhibit a similar decrease during the transition from Ericaceae to Sphagnum-dominated peat (Pancost et al., 2003).

Sphagnum-type spores are typically absent (Collinson et al., 2009) or rare (Wilson and Webster, 1946; Nichols and Traverse, 1971; Jardine and Harrington, 2008) within early Paleogene peat-forming environments. However, the similarity between Sphagnum biomarkers and Sphagnum-type spores within Seam 1, suggests a deeper evolutionary origin for Sphagnum moss. This is supported by the identification of Sphagnum leaves and/or spores in other Cenozoic (Jie and Xiuyi, 1986) and Mesozoic (Lacey, 1969) terrestrial settings.

4.2. Environmental controls on Sphagnum occurrence within Seam 1, Schöningen

In modern settings, Sphagnum is adapted to acidic, waterlogged and nutrient-limited environments and its occurrence is largely controlled by changes in local hydrology (van Breemen, 1995). To assess the role of hydrological change upon ancient Sphagnum occurrence, we use biomarkers, palynology and petrological evidence to constrain hydrological and environmental change within Seam 1. While the low abundance of Sphagnum-type spores and biomarkers within the base of Seam 1 (200–267 cm; Fig. 7) suggests relatively dry conditions (Clymo, 1984), lignite macerals can provide further insights into local hydrological change. Attrinite, which forms in relatively dry conditions at the mire surface (Sýkorová et al., 2005), is the most abundant maceral within the base of Seam 1 (~34%) and suggests relatively dry conditions. Textinite, which also forms in relatively dry, possibly low pH environments within forested peatlands and/or raised bogs (Sýkorová et al., 2005), is similarly abundant within the base of Seam 1 (~27%) and indicates a relatively dry environment.
Within the top of Seam 1, between 57 and 46 cm, there is a transient increase in conifer biomarkers (e.g., fichtelite: Fig. 8c) and fern spores (e.g., Laevigatosporites spp.; Fig. 8b), likely indicating the expansion of conifer forests with a fern understory. This is associated with an increase in the relative abundance of inertinite (i.e., fossil charcoal), suggesting increased wildfire activity. Between 46 and 20 cm, there is an increase in the relative abundance of Sphagnum-type spores (~20%) and C32/C31 n-alkane ratios (>1) (Fig. 7a, b) indicating the development of waterlogged, nutrient-limited conditions. This is consistent with other early Paleogene, peat-forming environments where Sphagnum-type spores proliferate following changes in basin subsidence and drainage (Pocknall, 1987). Ulminite, which forms in wet, low pH conditions within forested peatlands or raised bogs (Sýkorová et al., 2005), correlates with the relative abundance of Sphagnum-type spores throughout the top of Seam 1 (Fig. 7bc) and provides additional evidence that Sphagnum occurrence was driven by the expansion of waterlogged conditions. Although some Sphagnum taxa can thrive in more mesotrophic, low-lying swamps (e.g., Sphagnum russowii or Sphagnum riparium), the abundance of ulminite and the distribution of bacterial hopenoids is more consistent with an acidic, oligotrophic peat-forming environment (see later). Inertinite relative abundance remains high throughout this upper part of the seam (Fig. 8d). This suggests that fire activity may have played a role in maintaining Sphagnum relative abundance by impeding the spread of taller, hence more vulnerable, vascular plants across the bog surface.

The relative abundance of Sphagnum-type spores (~30%) and the C32/C31 n-alkane ratio (~2) decreases within the very top of Seam 1 (20–0 cm). This interval coincides with a decrease in the n-alkane ACL and the incorporation of green algae (Zyg nephataceae — Fig. 8f) associated with standing freshwater environments. This suggests that freshwater flooding restricted the growth of higher plants and, to a lesser extent, mosses. Peat-deposition is eventually terminated by a brackish, shallow-marine environment, with sea level inundation either driven by changes in local basin subsidence (i.e., an increase in accommodation space) associated with regional passive salt withdrawal towards the Helmsdtdt-Stassfurt Salt Wall during the early and middle Eocene (Brandes et al., 2012), changes in terrestrial runoff associated with a warmer climate (Slotnick et al., 2012) and/or eustatic sea level rise (Riegel et al., 2012).

4.3. Insights into the biogeochemistry of Paleogene ombrotrophic bogs

Modern ombrotrophic bogs are characterised by a distinct microbial assemblage that is associated with the unusual dominance of the C31, 17α,21β([H] homohopane (Quirk et al., 1984; Dehmer, 1993, 1995; Pancost and Sinninghe Damsté, 2003). This isomer is common in high maturity sediments (Seifert and Moldowan, 1980) and, with the exception of the soil bacterium Frankia spp. (Rosa-Putra et al., 2001), is not synthesised by living organisms. Its occurrence within modern peat deposits has therefore been attributed to rapid isomeric catalysis at the C-17 position as a result of acidic conditions (van Dorselaer et al., 1995; Dehmer, 1993, 1995; Pancost et al., 2003), although a biological origin remains possible. The ratio of the C31, 17β,21β([H] homohopane to total homohopanes (=[ββ/αβ]+[ββ]) in modern peats ranges from <0.01 to 0.8 and averages ~0.1 (Pancost et al., 2003; Inglis, G. unpublished). Within Seam 1, Schöningen, the C31, 17α,21β([H] homohopane is the dominant hopane (Fig. 3) and the [ββ]/[αβ]+[ββ]+ ratio ranges from 0.16 to 0.27, averaging 0.27. The C31, 17α,21β([H] homohopane is also a major constituent of other thermally immature Cenozoic lignites (Dehmer, 1988; Pancost et al., 2007). This suggests that diagenetic reactions and/or bacterial communities within Seam 1 and other ancient peat-forming environments are similar to those of Holocene wetlands. By extension, in relatively immature, marginal marine sediments, low [ββ/αβ]+[ββ] ratios could also serve as a useful new proxy for the input of peat (or eroded lignite).

The δ13C values of bacterial hopenoids can also provide insights into microbial methane cycling. The carbon isotopic composition (δ13C) of the C31, 17α,21β([H] homohopane in modern Sphagnum-dominated bogs is typically enriched in 13C (~22 to ~26‰) relative to bulk organic matter and plant-derived n-alkanes (Pancost et al., 2000; Inglis, G. unpublished). This likely indicates a heterotrophic bacterial population consuming 13C-enriched carbohydrates (Pancost et al., 2000; Xie et al., 2004). In the same setting, the δ13C value of C31, 17β,21β([H] bishomohopan-214olefin is lower, ranging from ~27‰ to ~30‰, perhaps suggesting a mixed suite of bacterial sources consuming both 13C-enriched carbohydrates and 13C-depleted, methane-derived CO2 (Pancost et al., 2000). In some cases, however, the δ13C value of extended hopenoids can be depleted in 13C; in particular, van Winden et al. (2010) reported δ13C values of C22/ββ bishomohopan-214olefin in extant Sphagnum species ranging from ~34‰ to ~37‰, suggesting that they partially derive from symbiotic methanotrophs. The lowest modern δ13C values are derived from diploptene (C30, 17β, 21β ([H]-hop-22(29)-ene) within a Carex-dominated bog where δ13C values range between 31.6‰ and ~50.3‰ (Zheng et al., 2014).

In another Paleogene wetland deposit, the Cobham Lignite (~56 Myr ago), the δ13C values of the C25- and C31-17(3)[H],21β([H] hopane decrease dramatically (to values as low as ~76‰ and ~42‰, respectively) in response to freshwater flooding and indicates the consumption of isotopically light methane by aerobic methanotrophs (Pancost et al., 2007). Such values have yet to be observed in a modern or Holocene peat deposit, but they are consistent with modelled wetland methane emissions, which suggest a 6– to 7-fold increase during Paleogene warm climates (Beerling et al., 2011). To investigate this further, we generate hopenane δ13C values within the top of Seam 1 and use this to reconstruct the relative amount of aerobic methanotrophy within an early Paleogene, peat-forming environment.

Within the top of Seam 1 the δ13C value of the C31, 17α,21β([H] hopenane ranges between ~24.9‰ and ~28.3‰ (Fig. 9b). These values are similar
to those observed in modern ombrotrophic bogs (−22% vs. −26%; Pancost et al., 2000) and suggest a similar source organism and ecology. The δ13C value of the C30− and C31−17β,21β(H) hopane ranges between −28 and −32‰ (Figs. 5 and 9b). These values are persistently 2–10% lighter than modern C31 17α,21β(H) hopane δ13C values and are more consistent with modern C23 ββ bishomohopanol δ13C values (−27% to −30%; Pancost et al., 2000). This suggests that the C30− and C31−17β,21β(H) hopanes are derived from a mixture of methanotrophic and heterotrophic bacterial populations (van Winden et al., 2012). Such relatively low values persist through the top 54 cm of Seam 1—that likely reflects 1.8 to 4.7 kyr—and could indicate a somewhat more intense methane cycling regime than observed in boreal Holocene bogs (cf. Pancost et al., 2000). However, unlike the Cobham Lignite (Pancost et al., 2007) or even some Holocene studies (Zheng et al., 2014), very low 13C hopane values were not observed suggesting that the top of Seam 1 was not characterised by extensive aerobic methanotrophy. Hopane δ13C values are relatively invariant throughout the top of Seam 1, despite an increase in Sphagnum abundance and waterlogged conditions (see Section 4.1). This could potentially be attributed to the absence of symbiotic methane-oxidising bacteria (Raghoebarsing et al., 2005; Kip et al., 2010). Alternatively, the incursion of sulphate-rich marine waters may suppress the rate of methanogenesis (Whiticar, 1999). This hypothesis is consistent with the presence of Apectodium within the overlying marine interbeds and high elemental sulphur concentrations throughout the seam (3.9–7.6 wt%; Fig. 2c) (Chou, 2012). Recent work has also shown that low δ13C hopane values are not necessarily associated with an increase in waterlogged conditions (cf. Van Winden et al., 2012). For example, Zheng et al. (2014) show that low 13C hopane values (−42% to −50%) are associated with a pronounced dry interval during the mid-Holocene. This likely reflects changes in methane flux pathways and more efficient methane oxidation under drier conditions (Zheng et al., 2014). By extension, the absence of very low 13C hopane values at Schöningen could reflect less efficient methane oxidation under wetter conditions (cf. Zheng et al., 2014).

In modern, ombrotrophic, Sphagnum-dominated bogs, the carbon isotopic composition of the C23 n-alkane can also provide insights into the amount of aerobic methanotrophy. In modern bogs, the C23 n-alkane can be depleted in 13C (−5–10‰) relative to high molecular weight (C29−C33) n-alkanes (Brader et al., 2010; van Winden et al., 2010; Huang et al., 2014), suggesting incorporation of 13C-depleted, CH4-derived CO2 associated with aerobic methanotrophy (Kip et al., 2010; van Winden et al., 2010). However, in other ombrotrophic bogs, the C23 n-alkane does not exhibit 13C-depleted values (−30% to −33‰; Pancost et al., 2003). In the same study, mid-chain n-alkanoïds, which can also be derived from Sphagnum, did not exhibit 13C-depleted values, ranging from −30% to −33% (e.g., Pancost et al., 2003). Within the top of Seam 1, the δ13C value of the C23 n-alkane ranges from −28.7‰ to −30.6‰. These values are 13C-enriched (1–2‰) relative to HMW n-alkanes (−30.1‰ to −32.5‰) and are consistent with a partially submerged source (Ficken et al., 2000; Pancost et al., 2003). This indicates relatively low rates of aerobic methanotrophy within Seam 1 despite overall wetter conditions. Both mid- and long-chain n-alkanes exhibit gradual 13C-depletion towards the top of Seam 1, consistent with bulk δ13C values (Fig. 9a). During the same interval, hopane δ13C values remain relatively invariant. This suggests that mid- and long-chain n-alkane 13C-depletion cannot be attributed to a rise in the water table but instead may be the consequence of some other mechanism (e.g., changes in CO2p, plant growth rate and/or temperature). Collectively, both hopanes and mid-chain n-alkanes do not indicate significantly enhanced methanotrophy in this early Paleogene, peat-forming environment, in contrast to the Cobham lignite (Pancost et al., 2007). The reason for this remains unclear but may be related to site-specific differences. For example, the top of Seam 1, Schöningen suggests the presence of intermittent marine conditions. This is based upon high elemental sulphur concentrations (>4% wt.) and the presence of silt and/or sand lenses (Figs. 2c and 7). In contrast, the Cobham lignite sequence was deposited under a freshwater environment as indicated by the absence of dinoflagellate cysts and Ophiomorpha burrows and the presence of freshwater wetland flora (Collinson et al., 2009). Despite this, the biogeochemical response associated with flooding ancient peat-forming environments remains poorly constrained and requires further investigation.

These results indicate the complexity of methane cycling within ancient peat-forming environments; however, changes in methane concentrations remain an important positive feedback mechanism during the early Eocene. For example, earth system modelling simulations indicate that early Eocene methane emissions may have been up to 6× greater than the modern. This can account for an up to −6°C of high-latitude warming (Beering et al., 2011) and has implications for numerical model studies which often fail to replicate high-latitude, proxy-derived temperature estimates (Huber and Sloan, 2001; Hollis et al., 2012; Lunt et al., 2012). Enhanced methane emissions can also promote the formation of thick, polar stratospheric clouds (Sloan and Pollard, 1998) which may account for enhanced high-latitude warmth during the early Eocene and other greenhouse intervals (Sloan et al., 1992).

5. Conclusion

Using a high-resolution, multi-proxy approach, we reconstruct the occurrence of Sphagnum moss within an early Paleogene peat-forming environment (Seam 1, Schöningen Mine, Germany). C23/ C31 n-alkane ratios (−0.4) and the relative abundance of Sphagnum-type spores (especially Tripunctisporis) are low within the base of Seam 1 (200–267 cm), indicating that Sphagnum was not an important peat-forming plant during this interval. Within the top of Seam 1 (57–0 cm), C23/C31 n-alkane ratios increase and are comparable to, or exceed, values from modern, Sphagnum-dominated ombrotrophic bogs. This coincides with an increase in the relative abundance of Sphagnum-type spores which comprise up to 45% of the entire palynological assemblage. Our results show a close association between Sphagnum biomarkers and Sphagnum-type spores within an early Paleogene peat-forming environment, analogous to what has been observed during the Holocene, and suggest that the C23/C31 n-alkane ratio may be a reliable chemotaxonomic indicator for Sphagnum input during the early Paleogene. Changes in biomarkers, palynology and petrology indicate that Sphagnum proliferation was driven by an increase in waterlogged conditions within the top of Seam 1. Increased fire activity may also have played a role in reducing re-colonisation by vascular plants. In comparison to other early Paleogene peat-forming environments, the 13C value of bacterial hopanes and plant-derived n-alkanes do not indicate significant aerobic methanotrophy. Nor do they indicate a change in methanotrophy despite a rise in the water table. The reason for this difference remains unclear but may be linked to the incursion of sulphate-rich, marine waters which might inhibit methanogenesis and/or reduce the efficiency of methane oxidation.

Acknowledgements

We thank the NERC Life Sciences Mass Spectrometry Facility (Bristol) for analytical support and GNI thanks the NERC for supporting his PhD studentship (NE/I005714/1). RDP acknowledges the Royal Society Wolfson Research Merit Award. We gratefully acknowledge funding to Collinson and Robson from the NERC grant NE/J008565/1 and to Pancost from NERC grant NE/J008591/1. We thank Jim Hower (University of Kentucky) for production of polished blocks of crushed lignite, Karin Schmidt (Senckenberg Forschungsinstitut und Naturmuseum, Frankfurt) for extensive logistical support, especially during field work, Nathalie Grassineau (Earth Sciences, Royal Holloway) for running the bulk carbon isotope samples and David Naafs and Marcus Badger for comments on earlier versions of this manuscript. Finally, we also thank both reviewers.
for constructive comments which helped to improve the quality of this manuscript.

References

Ahrendt, H., Kühle, A., Lierzow, A., Marheine, D., Ritzkowski, S., 1995. Lithostratigraphie, Biostratigraphie und radiometrische Datierungen des Unter–Oktos von Heimstedt (SE–Niedersachsen). Z. Deutsch. Geol. Ges. 146, 450–457.

Baas, M., Pancost, R., van Geel, B., Sinninghe Damsté, J.S., 2000. A comparative study of lipids in Sphagnum species. Org. Geochem. 31 (6), 535–541.

Beerling, D.J., Fox, A., Stevenson, D.S., Valdes, P.J., 2011. Enhancing climate–feedbacks in past greenhouse worlds. Proceedings of the National Academy of Sciences.

Bil, P.K., Schouten, S., Sijis, A., Reichert, J.–G., Zachos, J.C., Brinkhuis, H., 2009. Early Palaeogene temperature evolution of the southwest Pacific Ocean. Nature 461 (7262), 771–775.

Bingham, E.M., McLemont, E.L., Valáranta, M., Maquoy, D., Roberts, Z., Chambers, F.M., Pancost, R.D., Evershed, R.P., 2010. Conservative composition of n–alkane biomarkers in Sphagnum species: implications for palaeoclimate reconstruction in ombrotrophic peat bogs. Org. Geochem. 41 (2), 214–220.

Boutton, T.W., 1991. Stable carbon isotope ratios of natural materials: II. Atmospheric, Terrestrial, Marine, and Freshwater Environments: Carbon Isotope Techniques. vol. 1 p. 171.

Brader, A.V., van Winden, J.F., Bohncke, S.J., Beets, C.J., Reichert, J.–G., de Leeuw, J.W., 2010. Fractionation of hydrogen, oxygen and carbon isotopes in n–alkanes and cellulose of three Sphagnum species. Org. Geochem. 41 (12), 1277–1284.

Brandes, C., Pollok, L., Schmidt, C., Wilde, V., Winsemann, J., 2012. Basin modelling of a lignite-bearing salt rim syncline: insights into basin syncline evolution and salt diapirism in NW Germany. Basin Res. 24 (6), 695–716.

Bry, E.E., Evans, E.D., 1961. Distribution of n–paraffins as a clue to recognition of source beds. Geochem. Cosmochim. Acta 22 (1), 2–15.

Bridgham, S.D., Caldoz–Quitoz, H., Keller, J.K., Zhang, Q., 2013. Methane emissions from wetlands: biogeochemical, microbial, and modeling perspectives from local to global scales. Glob. Chang. Biol. 19 (5), 1325–1346.

Chou, C.L., 2012. Sulfur in coals: a review of geochemistry and origins. Int. J. Coal Geol. 92–93, 1–13.

Collinson, M.E., Steart, D.C., Harrington, G.J., Hooker, J.J., Scott, A.C., Allen, L.O., Glasspool, N.V., 2007. Increased terrestrial methane cycling at the Palaeocene–Eocene thermal maximum. Nature 451 (7180), 779–782.

Clymo, R., 1984. The limits to peat bog growth. Philos. Trans. R. Soc., B 303 (1117), 605–654.

Collister, J.W., Riele, A.D., Eglinston, G., Fry, B., 1994. Compound–specific δ13C analyses of leaf lipids from plants with differing carbon dioxide metabolisms. Org. Geochem. 21 (6), 619–627.

Couch, E.M., Dickens, G.R., Brinckhuis, H., Aubey, M.–P., Hollis, C.J., Rogers, K.M., Visscher, H., 2003. The Aptianian carbon and terrestrial discharge during the Palaeocene–Eocene thermal maximum: new palynological, geochemical and calccareous nannoplankton observations at Tawauan, New Zealand. Palaeeoegr. Palaeeolatol. Palaeeoc. 194 (4), 387–400.

DeConto, R.M., Gennari, S., Morgen, H.E.G., Crampton, J.S., Gibbs, S., Pearson, P.N., Zachos, J.C., 2012. Early Pliocene warmth linked to oceanic and atmospheric changes on global and regional scales. Geology 40 (4), 291–294.

Dehmer, J., 1988. Petrographische und organischgeochemische Untersuchungen an gebändertem Braunkohle (Aachen). Z. Dtsch. Geol. Ges. 146, 450–457.

Döring, H., Krutzsch, W., Schulz, E., Timmermann, E., 1966. Uber einige neue symbiotic bacteria in peat-moss ecosystems. Nat. Geosci. 3 (9), 617–619.

Drummond, M.J., Grice, H., 1986. Sulfur in coals: a review of geochemistry and origins. Int. J. Coal Geol. 92–93, 1–13.

Dehmer, J., 1995. Petrological and organic geochemical investigation of recent peats with floating freshwater aquatic macrophytes. Org. Geochem. 20 (3), 349–362.

Diefendorf, A.F., Fox, A., Stevenson, D.S., Valdes, P.J., 2011. Enhancing climate–feedbacks in past greenhouse worlds. Proceedings of the National Academy of Sciences.

Diefendorf, A.F., Fox, A., Stevenson, D.S., Valdes, P.J., 2011. Enhancing climate–feedbacks in past greenhouse worlds. Proceedings of the National Academy of Sciences.

Diefendorf, A.F., Fox, A., Stevenson, D.S., Valdes, P.J., 2011. Enhancing climate–feedbacks in past greenhouse worlds. Proceedings of the National Academy of Sciences.
