A long-term, high-latitude record of Eocene hydrological change in the Greenland region

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Abstract.

A range of proxy approaches have been used to reconstruct short-term changes to Earth’s hydrological cycle during the early Eocene hyperthermals. However, little is known about the response of Earth’s hydrological and biogeochemical systems to long-term Cenozoic cooling, which began following the Early Eocene Climatic Optimum (53.3 – 49.4 million years ago; Ma). Here, we use the molecular distribution and isotopic composition of terrestrial biomarkers preserved in marine sediments of ODP Site 913, East Greenland, to develop a long-term record of high-latitude hydrological change between 50 and 34 Ma. There is a marked decline in the concentration of conifer-derived diterpenoids and angiosperm-derived triterpenoids during the Eocene. As the input of wind-blown conifer pollen remains stable during this interval, this implies that decreasing di- and triterpenoid concentrations reflect declining influence of fluvial inputs – and perhaps terrestrial runoff – throughout the Eocene. Branched GDGTs and bacterial-derived hopanes indicate an increased input of soil- and kerogen-derived organic matter, respectively, after 38 Ma. This coincides with evidence for ice rafted debris and suggests input of organic matter via glacial processes. This also implies some continental glaciation occurred on East Greenland in the middle-to-late Eocene. Leaf wax hydrogen isotopes extending throughout this section – the first such long-term record from the Paleogene – indicate that precipitation $\delta^{2}H$ was persistently higher than that of modern coastal Greenland, consistent with warmer ocean source waters and enhanced poleward moisture transport. Non-intuitively, however, this effect appears to have been smallest during the warmest part of the record, and higher $\delta^{2}H$ values occur in the middle Eocene. Although interpretation of these hydrogen isotope trends is unclear, they clearly indicate – alongside the changes in biomarker abundances – a perturbed hydrological
cycle through the Eocene in coastal Greenland. More long-term records are required to ascertain if this represents regional or global hydrological reorganisation.

**Keywords**: biomarkers; alkanes; vegetation; Cenozoic; Palaeogene

### 1. Introduction

Past greenhouse climates can provide insights into how the Earth’s hydrological cycle differed during intervals of global warmth. Several previous studies have focused upon the Paleocene-Eocene Thermal Maximum (PETM; ~56 million years ago; Ma), a hyperthermal event characterised by surface ocean warming of between 5 - 9 °C and a rapid onset of less than 20 kyr (Hollis et al., 2019; Kennett and Stott, 1991; Sluijs et al., 2007; Sluijs et al., 2006; Tripati and Elderfield, 2005; Zachos et al., 2006; Zachos et al., 2003). During this interval, the hydrological cycle appears to have been particularly sensitive to warming (Carmichael et al., 2017; Carmichael et al., 2018). Multi-proxy records provide evidence for increased mid-to-high-latitude precipitation (Pagani et al., 2006; Sluijs et al., 2008). Proxies also indicate enhanced continental runoff, including in NW Europe (Inglis et al., 2019; Kender et al., 2012), the High Arctic (Dypvik et al., 2011) and the SW Pacific (Crouch et al., 2003). However, the sensitivity of the hydrological cycle to longer-term Eocene temperature trends remains largely unexplored.

The early Eocene (56.0 – 47.8 Ma) appears to be associated with an intensified hydrological cycle relative to preindustrial conditions (Pross et al., 2012; Eldrett et al., 2009; Wilf et al., 2005; Greenwood et al., 2010). This is consistent with high CO₂ estimates (> 1000ppm) and elevated global mean temperatures (Anagnostou et al., 2016; Hollis et al., 2019). However, a comparison between fossil leaf-derived
precipitation estimates with model simulations illustrate that models typically underestimate high-latitude precipitation (Carmichael et al., 2016). The response of the hydrological cycle to long-term middle and late Eocene cooling remains unknown. This is crucial as the hydrological cycle is likely to have been important in regulating Earth's climate over long timescales, for example, through changes in atmospheric latitudinal heat transport (Pierrehumbert, 2002) and continental weathering (Beaulieu et al., 2012). Such changes will also impact marine productivity (Kelly et al., 2005) and possibly ocean circulation via changes in the distribution of precipitation and evaporation (Bice and Marotzke, 2002). Long term, multi-proxy records are therefore critical to understanding the relative importance of these processes throughout the Cenozoic.

Here, we explore Eocene hydroclimatic changes within East Greenland by analysing lipid biomarkers preserved within the sediments of Ocean Drilling Program (ODP) Site 913B (Myhre et al., 1995). This site represents one of the best long-term high-latitude records for Eocene environmental changes, with continuous deposition having occurred from the EECO to the Eocene-Oligocene boundary (Schouten et al., 2008). This interval coincides with a significant decrease in pCO₂ (Anagnostou et al., 2016) and consequent global (Zachos et al., 2008) and regional (Bijl et al., 2009; Cramwinckel et al., 2018; Inglis et al., 2015b) cooling. Given that high-latitude sites appear to have been hydrologically sensitive to increased temperatures at the PETM (see Carmichael et al., 2017 and ref. therein), a gradual reduction in precipitation and runoff is expected to be recorded at ODP Site 913 in response to the long-term regional cooling (c.f. Eldrett et al., 2009). To test this, we analyse the distribution, concentration and isotopic composition of the diverse terrestrial biomarkers within ODP Site 913 sediments and provide insights into a range of paleoenvironmental
processes around Greenland, including changes in vegetation and fluvial, aeolian and glacial transport processes. The results are then integrated with previously published data to yield insights into the environmental changes impacting the site throughout the Eocene. The results are interpreted in the context of a suite of climate model simulations to assist in the elucidation of complex and multiple environmental controls, and to test and compare competing hypotheses.

2. Methods

2.1. Site description

Ocean Drilling Program (ODP) Leg 151 Site 913 (Myhre et al., 1995), located in the Norwegian-Greenland Sea (75° 29' N, 6° 57' W, water depth, ~3300 m), was drilled in September 1993. The site was deposited in a slope or basinal setting and offers near continuous deposition between the Early Eocene and Eocene-Oligocene boundary (Eldrett et al., 2007; Schouten et al., 2008). Based on the age model of Eldrett et al. (2009) and updated by Inglis et al. (2015), the samples studied in this paper span the interval 50 Ma to 34 Ma. During the earliest Eocene, the Norwegian Greenland Sea consisted of a series of highly restricted embayments (Figure 1), which were subject to stepwise tectonic opening throughout the Eocene (Hohbein et al., 2013). Over the course of the Eocene, the location of the Site 913 drill site likely migrated northwards, from around 65°N during the early Eocene to around 70°N by the late Eocene (Supplementary Information).

The lithology at Site 913 exhibits significant variation throughout the section (Firth et al., 1995; Myhre et al., 1996). Lithological Unit 4 (ca. 674 to 770 mbsf) deposited before 48 Ma, exhibits lamination and comprises massive silty clays and silty muds. At just below 702 mbsf (~49.1 Ma), millimetre-sized coal fragments occur.
These sediments are assumed to have been deposited close to the paleo-shoreline and under the influence of gravity flows (Myhre et al., 1995; Thiede and Myhre, 1996). Unit 3 sediments (< 674 mbsf, deposited after 48 Ma) comprise primarily clays, with biosiliceous clays dominant between ca. 462 and 500 mbsf (37 - 39 Ma). Unit 3 sediments are suggested to have been deposited under lower energy currents with a greater influence of aeolian transport (Myhre et al., 1995; Thiede and Myhre, 1996).

**Figure 1. Location of ODP Site 913 during the Early Eocene (56 to 47.8 Ma; red star).** Lighter blue shading indicates shallower water depths. Palaeographic reconstructions provided by GETECH Group Plc (as in Lunt et al 2016).

### 2.2. Organic geochemistry

A total of 32 sediments from ODP Site 913B, comprising Unit 4 and Unit 3 sediments, ranging in age from ~34 to ~50 Ma, were freeze-dried and exterior surfaces rinsed in dichloromethane (DCM):Methanol (MeOH) (2:1 v/v) to remove surface contaminants before powdering in a Retsch planetary ball mill. Between 25 and 30 g
of each sediment was subsequently extracted via Soxhlet apparatus for 24 hours using DCM:MeOH (2:1 v/v) as the organic solvent. Activated copper was added to each sample to remove elemental sulphur following the extraction. The TLE was separated by column chromatography with activated silica (230 - 400 mesh) using ammonium saturated chloroform and chloroform:acetic acid (100:1 v/v) to elute a neutral fraction and an acid fraction, respectively (modified from Dickson et al. 2009). An internal standard consisting of 10 µl 5α-androstane was added to each sample to quantify GC-amenable apolar compounds. The neutral fractions were subsequently separated into apolar and polar fractions by alumina column chromatography (activity II, 150 mesh), eluting with n-Hexane:DCM (9:1 v/v) and DCM:MeOH (1:2 v/v), respectively.

For samples with significant co-elution of other hydrocarbons between the target n-alkane compounds, urea adduction was performed to separate cyclic and acyclic compounds (Pancost et al., 2008). Urea saturated methanol (200µl) was added to each sample, followed by acetone (200µl) and n-hexane (200µl). Samples were frozen for 30 minutes to aid crystal formation and then dried under nitrogen flow. Urea crystals were washed with n-hexane to remove the non-adducted cyclic and branched compounds (e.g. terpenoids). To obtain the acyclic, unbranched compounds (e.g. n-alkanes), the urea crystals were then dissolved in MeOH:double distilled water (DDW) and extracted by washing with hexane.

2.2.1. GC-MS analysis

Apolar fractions were initially screened by gas chromatography flame ionisation detection (GC-FID) to determine appropriate concentrations for subsequent analytical analyses. Identification of biomarkers in the apolar fractions then proceeded by gas chromatography mass spectrometry GC-MS analysis, using a ThermoQuest Trace
GC-MS fitted with 50 m x 0.32 mm i.d. fused silica column with HP1 stationary phase. The GC oven program was as follows: starting temperature 70°C, rising at 20°C / min to 130°C before rising at 4°C / min for 42.5 minutes resulting in a final temperature of 300°C. The oven temperature was then held stable for 20 minutes giving a total run-time of 65.5 minutes. The electron ionisation source was set to 70 eV. Scanning occurred in the range 50 to 650 m/z. Compounds were identified primarily by mass spectra and comparison of relative retention times in existing literature.

2.2.2. LC-MS analysis

The polar fraction, containing the isoprenoidal and branched GDGTs, was dissolved in hexane/iso-propanol (99:1, v/v) and passed through 0.45 μm polytetrafluoroethylene (PTFE) filters. Fractions were analysed by high performance liquid chromatography atmospheric pressure chemical ionisation – mass spectrometry (HPLC/APCI-MS). Samples were analysed to separate 5-methyl and 6-methyl brGDGTs (Hopmans et al., 2016). Normal phase separation was achieved using two Waters Acquity UPLC BEH Hilic (2.1 x 150 mm; 1.7 μm i.d.) with a flow rate of 0.2 ml.min⁻¹. Samples were eluted isocratically with 78% A and 18% B for 25 min followed by a linear gradient to 35% B over 25 minutes, then a linear gradient to 100% B in 30 minutes, where A = hexane and B = hexane:IPA (9:1, v/v) (Hopmans et al., 2016). The injection volume was 15 μL, typically from 100 μL. Analyses were performed using selective ion monitoring mode (SIM) to increase sensitivity and reproducibility (m/z 1302, 1300, 1298, 1296, 1294, 1292, 1050, 1048, 1046, 1036, 1034, 1032, 1022, 1020, 1018, 744, and 653).

2.2.3. GC-C-IRMS analysis
Compound specific hydrogen isotopic compositions were determined for $C_{29}$ and $C_{31}$ $n$-alkanes by gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) using a ThermoFisher Trace GC Ultra coupled to a ThermoFisher Scientific Delta V Isotope Ratio MS. The GC column used was a 30 m x 0.25 mm i.d. fused silica column with ZB1 stationary phase. The H$_3$-factor was measured daily allowing isotope values to be corrected for protonation reactions occurring within the ion source of the mass spectrometer (Sessions et al., 2001). The GC program was as follows: starting temperature 70°C, rising at 10°C / min to 300°C, at which point the oven temperature was held stable for 8 minutes, giving a total analysis-time of 32 minutes. Triplicate runs of each sample were performed. The average error for a triplicate measurement was typically < 5‰ (see Supplementary Information). Each individual sample was co-injected with sacrificial compounds consisting of $n$-pentadecane and ethyl caprylate to condition the reactor. Measured isotope values were normalised by comparing the instrument's response to Schimmelmann standards consisting of a suite of 15 $n$-alkanes (Sessions et al., 1999), injected before and after each triplicate of sample runs. Normalised results are reported in standard per mil (‰) notation as $\delta^{2}H$ values relative to Vienna Standard Mean Ocean Water (VSMOW) and calculated against calibrated H$_2$ gas, introduced directly into the ion source.

2.3. Biomarker proxies

The distribution of branched glycerol dialkyl glycerol tetraethers (brGDGTs) in mineral soils is influenced by mean annual air temperature (MAAT), with the degree of methylation decreasing as temperature increases (De Jonge et al., 2014; Weijers...
et al., 2007). This is captured in the methylation of branched tetraether (MBT'SME) index (De Jonge et al., 2014; Naafs et al., 2017):

\[
MBT'SME = \frac{(Ia + Ib + Ic)}{(Ia + Ib + Ic + IIa + IIb + IIc + IIIa)}
\]

(1)

For samples dominated by 5-methyl brGDGTs, MBT'SME is translated to MAAT using a revised mineral soil calibration (Naafs et al., 2017):

\[
MAAT_{soil}' = 39.09 \times MBT'SME - 14.40 \ (n = 177, R^2 = 0.76, RMSE = 4.1 \degree C)
\]

(2)

Roman numerals refer to individual GDGT structures shown in the Supplementary Information. In brief, I, II and III represent the tetra-, penta- and hexamethylated components, respectively, and a, b and c represent the brGDGTs bearing 0, 1 or 2 cyclopentane moieties. 6-methyl brGDGTs are indicated by an apostrophe (e.g. IIa' – see equation 4).

The distribution of isoprenoidal glycerol dialkyl glycerol tetraethers (isoGDGTs) in marine sediments is influenced by sea surface temperature (SST), with the degree of cyclisation increasing as temperature increases (Schouten et al., 2002). This is captured in the tetraether index of 86 carbon atoms (TEX86) index:

\[
TEX_{86} = \frac{(GDGT-2 + GDGT-3 + Crenarchaeol regioisomer)}{(GDGT-1 + GDGT-2 + GDGT-3 + Crenarchaeol regioisomer)}
\]

(3)

The numbers refer to individual GDGT structures shown in the Supplementary Information. Here we correlate TEX86 values to SST using a Bayesian Regression model (BAYSPAR) (Tierney and Tingley, 2014b, 2015). This calibration assumes a linear relationship with temperature. This approach does not suffer from regression dilution bias (c.f. TEX86H; Kim et al., 2010) and provides a more robust statistical
framework for constraining uncertainty than the standard error estimates of previous linear calibrations (Hollis et al., 2019; Tierney and Tingley, 2014a).

The ratio of branched GDGTs to crenarchaeol in marine sediments is a function of organic matter input and is expressed as the Branched versus Isoprenoid Tetraether (BIT) index (Hopmans et al., 2004):

$$\text{BIT} = \frac{(\text{brGDGT-}Ia + \text{brGDGT-IIa}') + \text{brGDGT-IIIa}'}{(\text{brGDGT-}Ia + \text{brGDGT-IIa}')} + \text{brGDGT-IIIa} + \text{Crenarchaeol)}$$ (4)

The numbers refer to individual GDGT structures shown in the Supplementary Information.

The average chain length (ACL) expresses the average number of carbon atoms per molecule for the long-chain odd-carbon numbered n-alkanes (Pancost and Boot, 2004). The ACL is defined for n-alkanes using the following equation (Eglinton and Hamilton, 1967):

$$\text{ACL} = \frac{(25 \times C_{25}) + (27 \times C_{27}) + (29 \times C_{29}) + (31 \times C_{31}) + (33 \times C_{33})}{(25 + 27 + 29 + 31 + 33)}$$ (5)

The carbon preference index (CPI) reflects the dominance of odd-carbon-numbered relative to even-carbon-numbered n-alkane homologues (Bray and Evans, 1961). The CPI is defined using the following equation (Bray and Evans, 1961):

$$\text{CPI} = 0.5 \times \frac{(C_{25} + C_{27} + C_{29} + C_{31}) / C_{26} + C_{28} + C_{30} + C_{32}) + (C_{27} + C_{29} + C_{31} + C_{33}) / C_{26} + C_{28} + C_{30} + C_{32})}{2}$$ (6)

Submerged and floating macrophyte plants, as well as many mosses, exhibit a maximum in n-alkane distribution at C23 or C25, with a particularly high concentration
of these homologues occurring in peat bog-dwelling *Sphagnum* moss. The dominance of mid-chain vs long-chain \( n \)-alkanes is captured in the \( P_{\text{aq}} \) index and defined for \( n \)-alkanes using the following equation (Ficken et al., 2000):

\[
P_{\text{aq}} = \frac{C_{23} + C_{25}}{C_{23} + C_{25} + C_{29} + C_{31}}
\]

(7)

The terrestrial-aquatic ratio reflects the dominance of short- vs long-chain \( n \)-alkanes and is defined for \( n \)-alkanes using the following equation (Pancost and Boot, 2004):

\[
\text{TAR} = \frac{C_{17} + C_{19} + C_{21}}{C_{29} + C_{31} + C_{33}}
\]

(8)

### 2.4. Climate model simulations

The climate simulations described in this paper were carried out using the coupled atmosphere-ocean climate model HadCM3L. Simulations were performed at \( \times 2 \) and \( \times 4 \) preindustrial atmospheric \( \text{CO}_2 \) concentrations (i.e. 560 and 1120 ppmv, respectively; Farnsworth et al. 2019) for each stratigraphic stage of the Eocene (Ypresian, 56.0 - 47.8 Ma; Lutetian, 47.8 - 41.2 Ma; Bartonian, 41.2 - 37.8 Ma and Priabonian, 37.8 – 34.0 Ma). \( \text{CO}_2 \) concentrations (\( \times 2 \) and \( \times 4 \) PI \( \text{CO}_2 \)) were selected to represent a range of possible Eocene climate states (Anagnostou et al., 2016). The climate model simulations are identical to those described in detail in Farnsworth et al (2019). For the \( \times 2 \) and \( \times 4 \) PI \( \text{CO}_2 \) simulations, the only difference between each stage is the prescribed paleogeography (see Figure S1 in Supp Info of Lunt et al., 2016) and the solar constant (see Figure 2 of Lunt et al., 2016). The paleogeographies were developed from geological reconstructions by Getech Plc. These simulations indicate gradual restriction of the Tethys Ocean and gradual opening of Southern Ocean gateways during the Eocene (see Inglis et al., 2015 for more details). The climate
model used for the simulations is very similar to the HadCMB3LM2.1aD model
described and evaluated in Valdes et al. (2017), except that we include a modification
to the ozone profile to ensure that the model does not develop a runaway warming at
×4 CO2, as discussed in Lunt et al. (2016).

3. Results

3.1. Biomarker distributions and their interpretation

3.1.1. n-alkanes

Long chain n-alkanes with a strong odd-over-even predominance (C_{27} - C_{35}) are
typically attributed to epicuticular waxes synthesised by vascular plants (Eglington and
Hamilton, 1967). At ODP Site 913, sediments exhibit varying n-alkane distributions
(Figure 2), indicative of changing plant inputs. The terrestrial aquatic ratio (TAR), the
ratio between long chain n-alkanes and shorter chain homologues, is commonly used
as a proxy for the input of terrestrial plant matter relative to marine algae and
phytoplankton (Cranwell, 1982). Decreasing TARs at Site 913 indicate an increasing
proportion of terrestrial inputs in the younger sediments (Figure 3a).

Carbon preference indices (CPIs) in plant leaves are generally > 5 and
decrease during transport, degradation and thermal maturation (Diefendorf and
Freimuth, 2017). At Site 913, indices are typically > 2 throughout the section (Figure
3b), indicating thermally immature sediments which have retained the biological odd-
over-even predominance, consistent with a leaf wax origin. CPIs increase from ~2
during the early Eocene (~50 Ma) to ~3.5 during middle Eocene (~40 Ma), followed by
a further increase to higher, more variable values after 40 Ma (Figure 3b). TAR is
relatively high (ca. 0.9) during the early Eocene (> 48 Ma) indicating that n-alkanes
are derived from leaf wax and bacterial/algal inputs (Pancost and Boot, 2004). During
the middle and late Eocene (34 to 48 Ma), the TAR is very low (ca. 0.2) indicating that
n-alkanes are mostly derived from leaf wax input. Combined, TARs (Fig. 3a) and CPIs
(Fig. 3b) indicate a persistent but increasing input of minimally degraded leaf waxes
during the middle and late Eocene.

Figure 2: Diverse terrestrial biomarker distributions in ODP Site 913 sediments. Representative total ion current gas chromatograms shown for the (a) early Eocene (~49.2 Ma; 703.83 mbsf) and (b) late Eocene (~35.2 Ma; 464.31 mbsf). The structures of the principal plant-derived diterpenoids and triterpenoids and steroidal biomarkers are shown in (a). Numbers accompanied with Greek letters signify the carbon number and stereochemistry of hopanoids (a). Plant-derived n-alkanes are numbered according to the number of carbon atoms (a and b).
Other aspects of the $n$-alkane distribution can reveal insights into changing vegetation sources. For example, the ACL (Figure 3c) exhibits values (ca. 28.5 to 29.5) that are typical for terrestrial higher plants (ca. 27 to 30; Bush and McInerney, 2013; Diefendorf et al., 2011; Diefendorf and Freimuth, 2017). The $P_{aq}$ index – which has previously been used to infer input of *Sphagnum* moss and/or aquatic plant species to Eocene-aged sediments (Inglis et al., 2015a) - declines from values of ~0.5 in the Early Eocene to values <0.1 in the late Eocene (Figure 3d), indicating a decline in moss or aquatic plant species or an increase in terrestrial higher plants between the early Eocene (47.8 to 56 Ma) and latest Eocene (ca. 34 Ma).

### 3.1.2. Diterpenoids

Diterpenoids are principal constituents of higher plant resins and support tissues, particularly in gymnosperms (Diefendorf et al., 2012; Simoneit et al., 1986). A range of aromatic diterpenoid hydrocarbons occur in the oldest ODP Site 913 sediments (Fig. 2a), including retene (m/z 219), simonellite (m/z 237), 18- and 19-norabieta-8,11,13-triene (m/z 241), tetrohydroretene isomers (m/z 223), and dehydroabietane and methyl-dehydroabietane (m/z 255). These biomarkers have been widely attributed to conifers in previous studies (e.g. Otto and Simoneit, 2001). Although minor concentrations can be present within marine organisms (e.g. Lin and Chang, 2000), such a source seems unlikely here where they dominate over algal biomarkers. The concentrations and relative abundances of retene and simonellite decline markedly between 49 Ma and 46 Ma and remain low throughout the middle to late Eocene (Figure 4a - note that the scale is logarithmic).

### 3.1.3. Triterpenoids
Figure 3: Input of plant-derived organic matter at ODP Site 913 during the Eocene: (a) terrestrial aquatic ratio (TAR), (b) carbon preference index (CPI), (c) average chain length (ACL), d) $P_{aq}$ ratio, (e) $C_{27-33}$ $n$-alkanes ($μg/g$ dry sediment). Also shown are the occurrences of dropstones (stars; Eldrett et al., 2004) and the changes in lithology (Myhrre et al., 1995). All data are updated to GTS2012.

Oleanoids, ursanoids and lupanoids are common triterpenoids in higher plants and can trace terrestrial inputs within marginal marine settings (Rullkötter et al., 1994). Site ODP 913 sediments, especially those from the middle Eocene, contain abundant unsaturated oleanoids, including 18-$α$-(H)-olean-12-ene (Fig. 4c), olean-18-ene and olean-13(18)-ene. The early and middle Eocene intervals also contain a variety of degraded and aromatised triterpenoids, including C-ring cleaved aromatic triterpenoids (Fig. 4b; de Las Heras et al., 1991) and des-A-triterpenoids (Jacob et al.,
2007; Fig. 2). All of these compounds are derived from the oleanane and lupane families, which are biomarkers of angiosperm plants and are diagenetic products of oleanic acids and β-amyrin (Rullkötter et al., 1994).

Given the differing principal origins of higher plant di- and triterpenoids, their relative contributions have been used to assess changes in the composition of the source vegetation (Bechtel et al., 2003; e.g. Fig. 4d). Whilst these changes are non-
quantitative - due to differences in lipid production between angiosperms and gymnosperms (Diefendorf et al., 2014) and differing effects of diagenesis on different compounds (Nakamura et al., 2010) - they suggest a relative decline in the input of diterpenoids relative to triterpenoids at Site 913, with a marked change at about 48 Ma (Fig. 4d). A similar result is obtained when normalising diterpenoids to long-chain n-alkanes (Fig. 4d). Overall, the high abundances of a range of higher plant biomarkers indicate a strong but changing terrestrial organic matter signal during the Eocene (ca. 34 to 50 Ma).

3.1.4. Hopanoids

The apolar fractions contain a range of C$_{27}$ - C$_{35}$ hopanoids, including regular hopanes, hopenones, benzohopanones and neohopenones (Figure 2a). These triterpenoids, especially those > C$_{30}$, generally derive from bacteriohopanepolyols, which function as membrane lipids in Bacteria (Sáenz et al., 2015; Talbot and Farrimond, 2007). Changes in hopane stereochemistry occur during diagenesis. With increasing maturation, the 17β,21β(H) configuration is transformed to the more stable 17β,21α(H) and 17α,21β(H) configuration, although there are exceptions (Inglis et al., 2018). In the extended C$_{31}$ - C$_{35}$ hopanes, a chiral centre also exists at the C22 position, which racemizes during thermal maturation to form a mixture of 22S and 22R isomers (Mackenzie et al., 1980). Such changes have been widely used to reconstruct the thermal history of sediments, where decreasing ββ/(αβ + ββ) indices and increasing 22S/(22R + 22S) values indicate increasing thermal maturity. However, low ββ/(αβ + ββ) indices and high 22S/(22R + 22S) can also represent input of ancient organic matter eroded from sedimentary rocks (e.g. Handley et al., 2012; Lyons et al., 2018). In general, both indices at ODP Site 913 show the same trend: input of
thermally immature OM between 50 and 40 Ma and an unexpected input of thermally mature OM between 34 and 40 Ma (Fig. 5a-b).

Figure 5: Input of soil- and kerogen-derived organic matter at ODP Site 913. a) C\textsubscript{30} hopane $\beta\beta/(\alpha\beta + \beta\beta)$ indices, (b) C\textsubscript{31} hopane 22s/(22s + 22R) indices, (c) BIT index (Schouten et al. 2008, Liu et al. 2009, Inglis et al., 2015). Also shown are the occurrences of dropstones (stars; Eldrett et al., 2004), the changes in lithology (Myhrre et al., 1995) and approximate onset of IRD in ODP Site 913 sediments (Eldrett et al., 2007).

3.1.5. Branched GDGTs

Branched GDGTs derive predominantly from as-yet undetermined soil bacteria (although acidobacteria are a likely source; Sinninghe Damsté et al., 2018). At ODP Site 913, their distribution is dominated by tetramethylated brGDGTs (~54% of total brGDGT distribution) and the abundance of 6-methyl brGDGT isomers is low to moderate (~13% of the total brGDGT distribution). The low fractional abundance of 6-
methyl isomers can be attributed to 1) the dominance of tetramethylated brGDGTs (which do not have a methyl group at the C-5 or C-6 position) and/or 2) a relatively acidic depositional environment.

BIT indices have been previously reported for Site 913 from 40 - 31 Ma (Schouten et al., 2008). That record exhibits no clear secular trend but does have great variability, ranging between 0.17 (marine signal) to 0.98 (terrestrial signal) and spanning nearly the entire range of the index (0 to 1; Hopmans et al., 2004; Weijers et al., 2006). This is interpreted to reflect variable inputs of biospheric soil organic carbon. Our new late Eocene data (Figure 5c) are consistent with those of Schouten et al. (2008); where adjacent sediment samples from the same core have been analysed, reproducibility of the BIT index is generally strong (Supplementary Information). We also extend the existing BIT record to sediments from the early-middle Eocene (Figure 5c), revealing a change in BIT indices between 44 to 40 Ma. As reported by Schouten et al. (2008), younger sediments (34 to 40 Ma), have high and highly variable BIT indices, from ~0.2 to greater than 0.9 (Fig. 5c). However, sediments older than 44 Ma have markedly lower BIT values and less variability, between 0.2 and 0.5 (Fig. 5c).

3.2. Hydrogen isotopic composition of n-alkanes

Further insight into the hydrological controls influencing ODP Site 913 sediments can be obtained via compound specific hydrogen isotope analysis (δ²H). The δ²H value of biomarkers (especially leaf waxes) have been used extensively to reconstruct the δ²H value of precipitation, especially in marine sediments where they represent a catchment-integrated climate signal (Schefuß et al., 2005; Tierney et al., 2008; Tipple and Pagani, 2010; c.f. Tipple and Pagani, 2013; Hou et al., 2007). There can be a time lag (ca. 1-10 kyr) between leaf wax synthesis and their subsequent
deposition in shallow marine sediments (e.g. Douglas et al. 2014); however, the input of pre-aged leaf wax biomarkers is unlikely to be problematic over longer timescales. Leaf wax biomarkers are particularly useful because hydrogen atoms are covalently bound to carbon atoms, preventing isotopic exchange at temperatures below 100°C (Sachse et al., 2012). The isotopic composition established during biosynthesis can therefore be preserved over geological timescales, especially if they have experienced minimal diagenetic or catagenetic alteration, as indicated for Site 913 n-alkanes by the relatively high CPIs.

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**Figure 6:** Leaf wax $\delta^{2}H$ values indicate a perturbed hydrological cycle on East Greenland during Eocene (a) $\delta^{2}H$ value of C$_{29}$ (red) and C$_{31}$ (blue) n-alkanes. Also shown are the occurrences of dropstones (stars; Eldrett et al., 2004) and the changes in lithology (Myhrre et al., 1995). Error bars represent ±1 standard deviation of triplicate measurements.

Changes in the hydrogen isotopic composition of C$_{29}$ and C$_{31}$ n-alkanes ($\delta^{2}H_{wax}$) at ODP Site 913 are shown in Figure 6. The C$_{29}$ n-alkane is generally the most abundant throughout the section and its $\delta^{2}H$ values range between -229‰ and -154‰. The oldest samples, from the later stages of the EECO, have the most $^{2}H$-depleted values in the sequence, ca. -225‰. Between 48 and 46 Ma, progressive deuterium
enrichment occurs with decreasing age, reaching a maximum enrichment at 45.5 Ma.

In the middle Eocene, between 46 Ma and 42 Ma, $\delta^2$H values remain generally high, although there is some variability. From around 41 Ma to 33 Ma, $\delta^2$H values are relatively stable, varying between -185‰ and -205‰. The C$_{35}$ n-alkanes generally occur in lower abundances, but reproducibility in their $\delta^2$H values is robust (Figure 6; Supplementary Information) and the n-C$_{35}$ $\delta^2$H record is similar to that of n-C$_{29}$, especially in the early and late Eocene. Intriguingly, between 46 Ma and 40 Ma, the $\delta^2$H values of n-C$_{29}$ and n-C$_{31}$ are offset (ca. 20‰ but up to 40‰) with the latter failing to record the excursion to particularly high $\delta^2$H values recorded by the former. This could arise from changes in leaf wax sources, and this is discussed below.

4. Discussion

4.1 High-latitude temperature change during the Eocene

To investigate the influence of temperature change upon our terrestrial biomarker distributions, we have compiled and developed new temperature estimates from ODP Site 913 during the Eocene. Previously published branched GDGT-derived mean annual air temperature (MAAT) estimates – assumed to reflect soil-derived GDGTs delivered from Greenland – range between 12 and 18°C throughout the late Eocene (39 to 34 Ma) with no obvious long-term trends (Schouten et al. 2008). However, that study pre-dates the recent advances in analytical techniques that allow for the separation of 5- and 6-methyl brGDGTs (Hopmans et al., 2016), and it did not utilise the most recent calibrations (De Jonge et al., 2014; Naafs et al., 2017). Applying those approaches, we have developed new branched GDGT-derived MAAT estimates in ODP Site 913. Our results yield slightly lower MAAT estimates, ranging between ~12
and 16°C, throughout the middle and late Eocene (43 to 34 Ma; Fig. 7b); we could not determine brGDGT-derived MAATs for the early Eocene due to the low abundance of our target compounds. Our values are consistent with bioclimatic analyses (using the Nearest Living Relative approach; Fig. 7b), which suggest relatively constant mean air temperatures of around 14±3 °C throughout the middle and late Eocene (Eldrett et al., 2009). Such bioclimatic analyses extend into the early Eocene, where they indicate warm but surprisingly similar temperatures of ~14°C (Fig. 7b). Both GDGT and pollen-derived temperature estimates (ca. 12 to 18°C) are higher than obtained via modelling simulations (ca. 8 to 10°C for each x4 CO2 simulation; see Supplementary Information). However, HadCM3L (and also other models) typically struggle to replicate high-latitude proxy-derived temperature estimates (e.g., Lunt et al., 2012 and references therein).

Relatively stable terrestrial temperatures through the Eocene, especially into the early Eocene (see Eldrett et al., 2009), are inconsistent with a changing vegetation fossil pollen assemblage that indicates the presence of freshwater swamps, palms and cycads during the early Eocene giving way to extensive coniferous forests during the middle Eocene (Eldrett et al., 2009), under the influence of presumed long-term cooling. To explore this mismatch, we compared our results alongside SST estimates obtained from ODP Site 913 using TEX86. Note that we have recalculated TEX86-derived SSTs from Inglis et al. (2015) using a spatially varying Bayesian calibration (Tierney and Tingley, 2015). This approach indicates decreasing SSTs (ca. 6 to 8°C) between 47 Ma and 34 Ma (Fig. 7c), consistent with the changing vegetation assemblage (and global records) but contrasting with the stable temperatures reconstructed using spore- and pollen-derived bioclimatic analysis.
Figure 7: Temperature and hydrology on East Greenland during the Eocene; a) MAP inferred from palynomorphs (Eldrett et al. 2009), b) MAAT inferred from palynomorphs (Eldrett et al. 2009; red) and brGDGTs (blue), c) TEX$^{86}$-derived SSTs. All data are updated to GTS2012.

4.2 Controls on biomarker transport

4.2.1. Disentangling vegetation change and fluvial/aeolian mechanisms of organic matter input

Declining temperatures between the EECO and late Eocene are expected to impact the hydrological cycle (Held and Soden, 2006). Previous interpretations, inferred from ODP Site 913 pollen assemblages indicate constant regional precipitation (Eldrett et al., 2009), but we note that this approach failed to identify declining SSTs (Inglis et al., 2015b) or regional vegetation change (Eldrett et al.,
To probe environmental conditions further, we utilise a range of biomarker ratios (e.g. TAR, $P_{aq}$, diterpenoid to triterpenoid ratios) to reconstruct changes in the sources of organic matter and disentangle underlying transport mechanisms.

It is likely that decreasing terrestrial-to-aquatic ratios (TAR) during the middle and late Eocene are driven by increasing aeolian and/or fluvial input of terrestrial-derived higher plant leaf wax. This is consistent with the increase in long-chain $n$-alkane concentrations, especially from 38 to 36 Ma (Fig. 3e) and decreasing $P_{aq}$ values (Fig. 3d). Intriguingly, the abundance of conifer-sourced diterpenoids decreases markedly between the early and middle Eocene. These compounds – which can be derived from leaves, resin and bark - are typically transported via river systems (Medeiros et al., 2012; Medeiros and Simoneit, 2008), such that the trend suggests decreasing fluvial inputs through time. Decreasing fluvial input is also consistent with the long-term decrease in concentrations of angiosperm-derived triterpenoid biomarkers (although that record is more complex; see below) and lower C/N ratios in the middle and late Eocene (Andreasson et al., 1996). It is also consistent with changes in lithology, which indicate fluvially-influenced sediments during the EECO and more aeolian-deposited sediments in the middle Eocene (Myhre et al., 1995; Thiede and Myhre, 1996). Seemingly in contradiction to this interpretation are the long-term increase in BIT indices and the shift to more thermally mature hopane distributions, and these are discussed below (see Section 4.2.2).

The difference between diterpenoid and $n$-alkane derived records, therefore, likely arises from different transport processes governing their inputs, with the marked decline in di- and triterpenoid concentrations (Figure 4a) reflecting weakening fluvial inputs throughout the Eocene, and $n$-alkane abundances (Fig. 3e) and distributions reflecting either stable or increasing aeolian inputs. The latter is consistent with the
persistent input of wind-blown conifer pollen throughout this interval (Eldrett et al., 2009). Such an explanation also accounts for the secular increase in CPIs, with n-alkanes in early Eocene sediments likely reflecting greater degradation during storage and fluvial transport with a subsequent decrease during the middle-to-late Eocene (Fig. 3b). However, the qualitative interpretation of such organic matter source secular trends is complicated by the multiple controls on fluvial and aeolian inputs (Pancost and Boot, 2004). The most important control is geography: in shelf and sometimes slope settings and especially where close to river outflows, fluvial inputs dominate, whereas in the open ocean beyond the influence of fluvial runoff, aeolian processes dominate (Eglinton et al., 2002; Simoneit, 1977; Vogts et al., 2012). The magnitude of fluvial inputs is also governed by intensity and nature of runoff, catchment dynamics, and vegetation (Pancost and Boot, 2004), whereas aeolian inputs are governed by wind strength and direction (i.e. see above papers).

Therefore, it is difficult to deconvolute the tectonic and climatic controls on the decline in fluvial inputs. Below 550 m (prior to ~42.1 Ma), sediments are barren of diatoms and the “common/abundant” classification is assigned only between 35 and 39 Ma (Scherer and Koç, 1996). Furthermore, the oldest diatoms at ODP Site 913 (ca. 41.8 Ma), although subjected to pyritisation, have been identified as *Paralia sulcate* and *Stephanopyxis turris*, the former common in coastal environments (McQuoid and Nordberg, 2003) and the latter recognised as a shallow water coastal taxon (Mitlehner and Hart, 2010). Thus, a more coastal and fluvially influenced depocentre for Site 913 before 39 Ma cannot be ruled out. Anomalously low fish apatite δ¹⁸O values also suggest that Site 913 was influenced by freshwater outflow, at least in the early Eocene (Andreasson and Schmitz, 1996; Waddell and Moore, 2008). As such, the high organic matter inputs of inferred fluvial origin in older sediments could have been
due to a wetter climate but also could reflect a more proximal location and depositional
environment related to the evolution of the basin. By extension, relatively low organic
matter inputs in younger sediments could be attributed to reduced precipitation and/or
a more distal depositional environment.

4.2.2. Glacial processes: an additional control on biomarker transport?

As discussed above, not all biomarker secular trends can be readily explained
by a decrease in fluvial input or constant/increasing aeolian inputs. In particular,
increasing BIT indices during the middle and late Eocene (~40 Ma onwards) are
incompatible with an inferred decrease in fluvial organic matter input. Very high BIT
values observed in some intervals (> 0.9) are inconsistent with aeolian input or in situ
production of brGDGTs (Peterse et al., 2009; Weijers et al., 2014). Instead we suggest
that high but variable BIT indices reflect the delivery of contemporaneous, soil-derived
OC via periodic ice rafting (as proposed by Schouten et al. 2008). The large and
unexpected input of thermally mature hopanoids after 40 Ma also suggests delivery of
ancient, reworked sedimentary organic matter via ice rafting, as invoked within the
Quaternary (Heffter et al., 2017; Parnell et al., 2007), Neogene (Duncan et al., 2019)
and late Paleogene (Duncan et al., 2019) marine sediments. Collectively, these results
indicate varying contributions of contemporaneous and reworked organic matter
during the (late) Eocene.

Although the regional glacial history of the Northern Hemisphere during the
Eocene is the subject of considerable debate (Spray et al., 2018), there is other
evidence for cryospheric development in the middle Eocene (~38 Ma onwards). This
includes the presence of ice rafted debris at ODP Site 913 (Eldrett et al., 2007) and
sea ice diatoms in the Arctic (Moran et al., 2006; Stickley et al., 2009). Input of IRD at
ODP Site 913 also coincides with a minimum in TEX$^{86}$ SST estimates. This strengthens the case for a possible intermittent glaciation restricted to the eastern coast, either as a small ice-cap or as isolated glaciers (Spray et al., 2019).

4.3 Leaf wax δ$^{2}$H values indicate an unstable high-latitude hydrological cycle

The isotopic composition of precipitation ($\delta^{2}$H$_{\text{precip}}$; Figure 6) can be estimated by assuming a net fractionation factor ($\varepsilon_{\text{precip}}$) of 130‰, as in other Eocene studies (Pagani et al., 2006; Handley et al., 2011; Handley et al., 2012). This assumed fractionation factor – which integrates a range of variables, including evaporative enrichment (in soil and leaf), biosynthetic effects and plant type (Sachse et al. 2012) – yields an estimated Eocene $\delta^{2}$H$_{\text{precip}}$ that is enriched relative to modern day values from the coastline of Greenland (Supplementary Information). The similar $\delta^{2}$H$_{\text{precip}}$ trends obtained from the C$_{29}$ and C$_{31}$ n-alkanes during the early and late Eocene appear to indicate a climatic (rather than biosynthetic) control. However, there is a significant offset in $\delta^{2}$H$_{\text{precip}}$ values between the C$_{31}$ and C$_{29}$ n-alkanes during the middle Eocene (Fig. 6), suggesting that these compounds are sourced from different source regions and/or derived from different plant species with different net fractionation factors.

The C$_{31}$ n-alkane - which is isotopically depleted relative to the C$_{29}$ n-alkane - could derive from mountainous regions, whereas the C$_{29}$ could derive from low-lying coastal plains. This ad hoc assumption arises from the $^{2}$H-depletion of around 25‰ expected for ~2000 m in the eastern Greenland mountains relative to sea level for the modern day (based upon the Online Isotopes in Precipitation Calculator; Bowen and Revenaugh et al., 2003). This estimate likely underestimates the difference between Eocene and modern processes, because we do not correct for the absence of
extensive continental ice sheets in the Eocene; this would have caused global
seawater (and therefore precipitation source water) to be $^2\text{H}$ depleted rather than
enriched relative to modern, perhaps by $\sim 8 - 12\%$ (Tindall et al., 2010). If the different
records do reflect different source regions, then this mechanism requires an
explanation for their convergence after $\sim 40$ Ma. This could be due to a simplification
of sources arising from the shift to solely aeolian inputs (as opposed to a more complex
mixture of aeolian and fluvial inputs; see above). It could also be due to upland
 glaciation preventing vegetation cover on higher slopes, meaning that both the $C_{29}$
and $C_{31}$ n-alkanes are sourced from more lowland regions from $\sim 40$ Ma onwards. This
is consistent with evidence from biomarkers (Schouten et al., 2008; this paper) and
sedimentology (Eldrett et al., 2009) which suggests ephemeral glaciation from $\sim 40$ Ma
onwards. However, if the $C_{31}$ n-alkane is primarily sourced from plants in upland
regions, there should also be a contribution from other n-alkanes (e.g. $C_{29}$ n-alkane).

Instead, these compounds could be derived from plants growing in the same
broad location but with different net fractionation factors. To evaluate the impact of
vegetation isotope effects upon leaf wax $\delta^2\text{H}$ values, we calculate plant-specific net
fractionation factors (following Feakins 2013). We employ a four endmember mixing
model which includes $C_3$ gymnosperms, $C_3$ dicots, pteridophytes (i.e. ferns) and
bryophytes (i.e. mosses), and is defined as:

$$\epsilon_{\text{corr}} = [f_{\text{gymnosperm}} \times \epsilon_{\text{gymnosperm}}] + [f_{\text{dicot}} \times \epsilon_{\text{dicot}}] + [f_{\text{pteridophytes}} \times \epsilon_{\text{pteridophytes}}] + [f_{\text{bryophytes}} \times \epsilon_{\text{bryophytes}}]$$

where $\epsilon$ is based on the mean fractionation factor in modern plant types
(Supplementary Information; Sachse et al., 2012) and $f$ is based upon the percentage
of pollen in nearby samples (Supplementary Information; Eldrett et al., 2009). We do
not include $C_4$ plant types within our mixing model as this photosynthetic pathway had
not yet evolved. We find that the average fractionation factor (ca. -105 to -115‰) is higher than we previously assumed. However, the temporal trends remain almost identical (Figure 8), suggesting that changes in plant type are unable to explain the divergence in C_{29} and C_{31} \delta^2{H} values. As the pollen assemblage is dominated by Pinus pollen (Eldrett et al., 2009), we also calculated pollen-corrected fractionation factors for the same dataset but excluding Pinus. However, we find that the temporal trends and absolute values remain similar.

Figure 8. Pollen-corrected \(\delta^2{H}_{\text{precip}}\) values during Eocene (a) \(\delta^2{H}_{\text{precip}}\) (solid line) and \(\delta^2{H}_{\text{corrprecip}}\) (dashed line) inferred from the C_{29} n-alkane, (b) \(\delta^2{H}_{\text{precip}}\) (solid line) and \(\delta^2{H}_{\text{corrprecip}}\) (dashed line) inferred from the C_{31} n-alkane. Error bars on (a) and (b) represent \(\pm 1\) standard deviation of triplicate measurements.

Although \(\delta^2{H}_{\text{corr}}\) values represents the best estimate of precipitation, pollen-corrected \(\delta^2{H}\) reconstructions still have several limitations and determining fractionation factors between life forms and taxonomic groups remains uncertain (e.g.
Liu et al., 2016), particularly given the covariance between vegetation and climate (Sachse et al., 2012). In addition, pollen and lipids may not be sourced from the same ecosystem and could integrate different source areas.

Both traditional and pollen-corrected $\delta^2$H reconstructions (Figure 8) indicate that Eocene precipitation $\delta^2$H values at ODP Site 913 are typically enriched relative to those of modern Greenland (-80 to -130‰; see Supplementary Information). There are several reasons for this. Firstly, given the more southerly location of the drill site, at around 65°N in the early Eocene (compared to ~75°N today), the extent of Rayleigh distillation was likely lower (Dansgaard, 1964). Secondly, warmer source waters yield more $^2$H-enriched water vapour. Third, previous work on the PETM suggests that under warmer climate conditions, decreased rainout at mid-latitudes results in more $^2$H-enriched precipitation at high latitudes (Handley et al., 2011; Pagani et al., 2006).

The temporal trends, however, are more difficult to interpret and both the C$_{29}$ and C$_{31}$ n-alkanes indicate a secular shift towards higher $\delta^2$H$_{\text{precip}}$ values at a time of global and regional cooling. Superficially, this appears to document an unexpected increase in poleward moisture transport, occurring when Greenland was drifting northwards and whilst regional temperatures were declining, i.e. in contrast to the mechanisms and observations described above. Lower $\delta^2$H$_{\text{precip}}$ values during the early Eocene could potentially be explained by an `amount effect' style response (Dansgaard, 1964), whereby extensive airmass rainout results in a predominance of $^2$H-depleted precipitation. Although changes in the nature of mid-latitude precipitation to more extreme, convective style storms has been invoked at the PETM to explain geomorphological change in central US (Foreman et al., 2012) (paleolatitude ~42°N) and on the northern Tethyan margin (Schmitz and Pujalte, 2007) (paleolatitude ~38°N), whether this mechanism could be important at latitudes >60 °N remains
uncertain (e.g., Carmichael et al., 2018). However, Krishnan et al. (2014) observe a
~15‰ δ²H depletion during the onset of the ETM2 hyperthermal at Lomonosov Ridge
(Arctic Ocean), implying a larger ‘amount effect’. Refinement of the Lomonosov ridge
age model has also resulted in suggestions that the enrichment described by Pagani
et al. (2006; see above) occurred ahead of the PETM warming, with more depleted
δ²H values within the body of the PETM event. Extremely depleted δ¹⁸O values within
dinosaur tooth enamel have also been reported for the mid-Cretaceous (Suarez et al.,
2013), argued to reflect high-latitude amount effects.

The input of reworked OC (e.g. kerogen) could also impact leaf wax δ²H values,
especially during the late Eocene (see Section 4.2.2). Previous studies suggest the
input of reworked OC can be problematic in organic-lean sedimentary settings (e.g.
Handley et al., 2012; Carmichael et al., 2017). However, the organic carbon content
within ODP Site 913 is relatively high (typically 0.5% but up to 5%; Mhyre et al., 1995)
and both the pollen assemblage and overall lipid biomarker distribution indicate
predominantly contemporaneous OC. As such, we argue the impact of reworking is
likely to be minimal in our site.

In summary, leaf wax δ²H values indicate enhanced poleward moisture
transport during the Eocene (relative to modern). This is consistent with PETM-aged
records (Carmichael et al., 2017 and ref. therein) and is attributed to enhanced
temperatures and a lower paleolatitude. However, the temporal trends are complex,
potentially reflecting changes in the source(s) of moisture associated with local
convective vs large scale circulation processes – and the magnitude of ‘rainout’ effects
associated with each. Of course, other factors such as changes in leaf wax source
(both in terms of vegetation and geography) cannot be precluded. These uncertainties
dictate caution when applying n-alkane δ²H over very long timescales (e.g. > 10⁶
years) but also in response to transient events (e.g. PETM), which are often characterised by similar or smaller perturbations.

4.4 Paleogeography and CO₂ influence the hydrological cycle on East Greenland during the Eocene

Multiple controls are likely to have influenced environmental changes on the Greenland continent during the ~16 million years studied here. Within the ODP Site 913 record, this complexity is represented by a range of sometimes contradictory climatic and environmental reconstructions. Here we apply climate model simulations (HadCM3L) to explore the relative effects of CO₂ and paleogeography on mean annual precipitation (MAP) at ODP Site 913. Simulations are performed for each geological stage of the Eocene at 2x and 4x preindustrial CO₂ (560 ppmv and 1120 ppmv respectively; Fig 8).

Model simulations from near ODP Site 913 indicate a reduction in MAP (ca. 25 and 30%) between the x4 and x2 CO₂ simulations (Figure 9). This is observed for all four stages of the Eocene and suggests that declining CO₂ during the middle and late Eocene (Anagnostou et al., 2016) can account for the inferred decrease in terrigenous organic matter at ODP Site 913. Model simulations also indicate that paleogeography can exert an important control on the hydrological cycle, with a gradual decrease in MAP (ca. 20-30%) between the Lutetian (41.2 to 47.8 Ma) and Priabonian (37.8 to 34.0 Ma) (Figure 9). This is also consistent with the inferred decrease in terrigenous organic matter inputs at Site 913 during the middle and late Eocene.

Intriguingly, the lowest MAP values are obtained for the early Eocene simulations (i.e. during an interval which appears to have been associated with an intensified hydrological cycle; e.g. Carmichael et al., 2016). This appears to be
inconsistent with leaf wax $\delta^2$H values which suggest an 'amount effect' style response and extensive airmass rainout during the early Eocene (see Section 4.3). However, recent work has shown strong decoupling between MAP and extreme rainfall events during past warm climates (e.g. the PETM; Carmichael et al., 2018; Inglis et al., 2019). This leads to an overall reduction in MAP but an increase in the size and frequency of extreme events (Carmichael et al., 2018; Inglis et al., 2019) and can potentially explaining relatively negative $\delta^2$H values during the early Eocene. Although vegetation change could also yield relatively depleted $\delta^2$H values, our pollen-corrected $\delta^2$H values do not support this hypothesis. However, a decrease in the abundance of conifer-sourced diterpenoids between the early and middle Eocene does imply changes in vegetation type. This implies that pollen and lipid biomarkers may not be sourced from the same ecosystem and could integrate different source areas.

Figure 9: Model-simulated changes in hydrological cycle at ODP Site 913 for each stage of the Eocene. Mean annual precipitation shown for 4 x preindustrial CO$_2$ (red; 1120 ppmv) and 2 x preindustrial CO$_2$ (blue; 560 ppmv).
Regardless, the model simulations suggest that both a decline in $p$CO$_2$ and paleogeography likely caused weakening of precipitation (and terrestrial organic matter inputs) during the middle and late Eocene. High-resolution atmosphere-only model simulations (e.g. HadAM3) or isotope-enabled model simulations which include hydrogen isotopes would prove useful for further interrogating the data presented within this paper.

5. Conclusions

Biomarker abundances and distributions indicate changes in the source and transport mechanisms of terrigenous organic matter from the Greenland continent to ODP Site 913 during the Eocene. In particular, a marked decline in the concentration of conifer-derived diterpenoid and angiosperm-derived triterpenoid hydrocarbons during the middle and late Eocene suggests a declining influence of fluvial inputs. Ice rafting could have been important after ~40 Ma, as indicated by a shift to more variable BIT values and more mature hopane isomerisation parameters. This is consistent with the previous identification of glacial dropstones and IRD at ~38 Ma and indicates that thermally-mature lipid biomarkers could be a useful tool to help fingerprint IRD in Paleogene marine sediments.

Although the biomarker distributions suggest weakening fluvial input from Greenland in response to declining CO$_2$ and temperatures, the $n$-alkane $\delta^{2}$H signal suggests relatively $^{2}$H-depleted values in the early Eocene. At face value, the occurrence of isotopically depleted meteoric waters during the warmest interval, apparent in both the C$_{29}$ and C$_{31}$ biomarkers, suggests that Rayleigh distillation was not the primary control on Greenland precipitation. If this were the case, fundamentally different controls on the high latitude hydrological cycle may have existed throughout
the early Eocene (e.g. high-latitude ‘amount effects’). Critically, despite the range of caveats, the new leaf wax δ²H record and dramatic changes in biomarker abundances suggest a far less stable hydrological cycle at the mid-high latitudes during the Eocene than that suggested by the pollen record alone.

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Contributions

G.N.I, M.C, D.L and R.D.P designed the study. G.N.I and M.C generated and analysed organic geochemical data. A.F and D.L performed HadCM3L model simulations. All authors contributed to data and model interpretations. G.N.I and M.C. wrote the text, with input from all authors.

Competing interests
The authors declare no competing interests.

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