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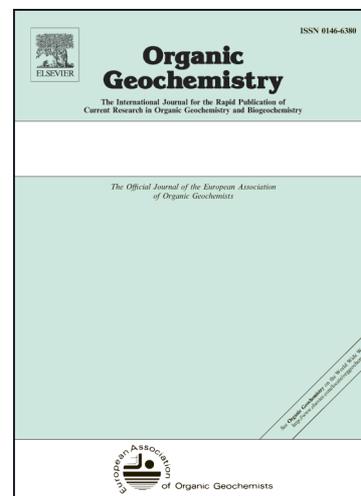
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Mid-Holocene climate change and landscape formation in  
Ireland: Evidence from a geochemical investigation of a  
coastal peat bog

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ABSTRACT

Following a period of unusually strong winds and high seas in the spring of 2014,  
a blanket peat bog formerly covered by a beach comprised of fine sand and large  
rocks was uncovered at a coastal site in Spiddal, Co. Galway, Ireland. The

surface of the bog was littered with standing tree stumps, the remnants of a Holocene forest that had succumbed to a relatively sudden drowning. A combination of inorganic and organic geochemical techniques was applied to determine the cause of this rapid submersion and to glean palaeoclimatic information from the preserved record within the peat. The study represents the first use of a multiproxy lipid biomarker approach to investigate palaeoclimate conditions from a peat bog in Ireland. The results provide evidence of climatic variation throughout a ca. 3400 yr timeframe during the mid-Holocene. Biomarker proxies displaying the relative contribution of *Sphagnum* spp. vs. higher plants were used to show changes in precipitation and temperature during peat formation. The data correlate with described events, including the 4.2 ka event and the Subboreal-Subatlantic transition and show the benefit of a lipid biomarker method for investigating Ireland's peatland resources. In particular, the indication of colder/wetter conditions coinciding with the 4.2 ka event implies the possibility that its effects were felt in Ireland, contrary to some reports. The results suggest that a combination of warm and dry conditions followed by a rapid rise in sea level led to the growth and subsequent drowning of the ancient forest landscape.

#### **Keywords**

Holocene; Palaeoclimate; Climate change; Lipid biomarkers; Compound specific stable isotope analysis; Peat; Ireland; Drowned forest

## 1. Introduction

Peat bogs are important sites for palaeoclimate investigation. They contain a natural archive of past environmental change (Chambers et al., 2012) which, in ombrotrophic mires, has a direct relationship with precipitation. Ombrotrophic or 'cloud-fed' peat bogs are not influenced by ground water and surface water, being affected solely by precipitation and evaporation (Nichols et al., 2006; Bingham et al., 2010; Zhang et al., 2014). This results in vegetation and organic matter (OM) which is well preserved in an anoxic environment and which is particularly sensitive to variation in local climate conditions (Blackford and Chambers, 1991; Pancost et al., 2002; McClymont et al., 2010).

Ireland has an abundance of ombrotrophic peat bogs representing an important resource of palaeoclimate information in Northwestern Europe. As such, the majority of Irish Holocene records derive from data from peat (Swindles et al., 2013). Researchers have applied several techniques, including testate amoebae, plant macrofossils, degree of humification and isotopic variation in cellulose to investigate fluctuation in Irish climate (e.g. Barber et al., 2000, 2003; Plunkett, 2006; Blundell et al., 2008; Swindles et al., 2010; Roland et al., 2014, 2015). Evidence for large climatic events has been reported using these approaches. For example, the Subboreal-Subatlantic transition is evidenced by widespread climatic deterioration in both hemispheres. Using data from peat bogs, a shift to wetter/cooler conditions associated with this period in Ireland

was attributed to a delayed response to solar forcing at 2800 cal. yr BP (Plunkett et al., 2004; Swindles et al., 2007).

Another such event is a period of global climatic change at ca. 4200 yr BP (4.2 ka event) which saw high temperature at lower latitudes leading to severe drought, with serious implications for human civilizations in these areas (Weiss et al., 1993). Higher latitudes are known to have experienced colder conditions during this time (Bond et al., 2001). Previous studies have obtained evidence of the impact of this event in Ireland from the peat record (Barber et al., 2003, 2007); however, more recent investigations using multiple proxies and multiple datasets have suggested that there is no compelling evidence (Swindles et al., 2013; Roland et al., 2014).

Due to the organic-rich nature of peat, lipid biomarkers offer a powerful approach for palaeoclimate investigation, particularly in settings where decomposition may hinder the use of these other techniques (Pancost et al., 2002). Analysis of lipid biomarkers provides an insight into the source of OM on a molecular level (Eganhouse, 1997; Pancost and Boot, 2004; Simoneit, 2004; Peters et al., 2005). The development and refinement of multiple biomarker proxies play an important role in the investigation of past climatic change from the peat record (Nott et al., 2000; Pancost et al., 2002; Nichols et al., 2006; Nichols and Huang, 2007; Zheng et al., 2007; Bingham et al., 2010; Zhang et al., 2014; Schellekens et al., 2015). Many of the proxies involve comparison of compounds derived from peat-forming species of *Sphagnum* and vascular plants. *Sphagnum* plants favour colder and wetter conditions and thus thrive during

periods of lower temperature and increased precipitation, which is reflected in the contribution of mid-chain *n*-alkanes (C<sub>23</sub> and C<sub>25</sub>), dominant in *Sphagnum* lipid profiles (Baas et al., 2000; Nott et al., 2000). Conversely, during times of increased temperature and drier conditions, long chain *n*-alkanes (C<sub>29</sub> and C<sub>31</sub>) dominant in vascular plants, provide increased water retention and protection from higher temperature, which is reflected in the peat record (McClymont et al., 2010; Zhang et al., 2014).

Other lipid classes and proxies can be used to study the input and relative changes in vegetation type on a broad taxonomic level. The *n*-alkanol average chain length (ACL) has been in an attempt to differentiate between relative inputs of *Ericaceae* and *Sphagnum* (Poynter and Eglinton, 1990; Pancost et al., 2002). This proxy may also provide insight into preservation state. C<sub>23</sub> to C<sub>31</sub> *n*-alkan-2-ones have been suggested as specific markers for *Sphagnum* (Nichols and Huang, 2007), whilst abundances of certain steroids and terpenoids have also been linked to change in vegetation (Pancost et al., 2002). The combination of these geochemical indicators has provided a toolkit for palaeoclimate studies in peat forming environments.

Pancost et al. (2011) investigated the use of the lipids derived from methanogenic archaea, archaeol and sn-2-hydroxyarchaeol, as potential biomarkers in ombrotrophic bogs, including Ballyduff Bog in Ireland. However, the work here represents the first comprehensive palaeoclimate study of an Irish peat bog utilizing lipid biomarker proxies. The aim was to investigate changes in local vegetation and climate over a 3400 yr period during the mid-Holocene by

providing a new Irish palaeoclimate dataset within this period, and identifying the events that led to the flooding of this forested landscape.

## 2. Material and methods

### 2.1. Sampling and location

Samples were taken from a recently exposed coastal peat bog in Spiddal, Co. Galway, Ireland (Fig. 1). The bog is characteristic of an ombrotrophic Atlantic blanket bog, in keeping with the surrounding peatland landscape (Connolly and Holden, 2009). However, due to its unique coastal setting and previous submersion it is a relatively unique site. The limestone bedrock at the base of the peat could potentially allow groundwater to penetrate the bog during times of heavy rainfall. The bog is in a tidal zone and was previously submerged beneath a layer of sand. Due to a period of stormy weather and rough sea conditions (February 2014) the sand was removed, revealing the peat bog, complete with protruding tree stumps of *Pinus* and *Quercus* origin (Williams and Doyle, 2014). The only living plant life on the peat surface was the marine alga *Cladophora rupestris*.

Sand and rock were cleared from the surface of the peat. A ca. 1 m trench was dug into the bog and samples taken from the trench wall every ca. 5 cm. The entire profile was homogenous dark brown in colour, containing yellowish-brown plant fragments throughout. There was no apparent fluctuation in colouration or

mineralogy. Material was removed with a clean stainless steel spatula washed with MeOH and dichloromethane (DCM) and stored in furnace Al foil. Samples were subsequently stored at -20 °C prior to analysis.

## *2.2. Sample preparation*

All samples were freeze-dried, homogenized and passed through an 850 µm mesh sieve, yielding a single < 850 µm fraction prior to extraction. All glassware was washed thoroughly, solvent washed with MeOH and CHCl<sub>3</sub> and furnace for 8 h at 480 °C in a Lenton box furnace. All Teflon equipment was sonicated in CHCl<sub>3</sub> prior to use. Stainless steel equipment was washed with CHCl<sub>3</sub>.

## *2.3. Radiocarbon dating*

Seven samples of bulk material were dated at the Radiocarbon Dating Facility in Queens University, Belfast. Samples analysed were from 0-5, 20-25, 35-40, 55-60, 75-80, 85-90 and 105-110 cm. The results were calibrated using OxCal 4.2 software employing the IntCal13 curve (Ramsey, 2009; Reimer et al., 2013). Age values for the non-dated layers were calculated from linear interpolation.

## *2.4. X-ray fluorescence analysis (XRF)*

XRF measurements were taken using a handheld Thermo Scientific Niton XL3t device following the procedure of Radu and Diamond (2009). Samples were placed in 32 mm double open-ended sample cups, secured in place with polyester stuffing, and covered with polypropylene X-ray film (Premier Lab Supply, FL, USA). A sample cup assembly without sample was measured as a blank. All measurements were performed in triplicate using bulk mode for soil samples. An internal instrument calibration was performed prior to analysis.

#### *2.5. Total organic carbon (TOC) and total nitrogen (TN)*

Elemental analysis was performed in triplicate using a Fisons NCS 1500 NA elemental analyser. Samples were treated with 1N HCl in Ag capsules following the procedure of Verardo et al. (1990) to remove carbonate. After drying overnight, the capsules were wrapped in Sn boats and combusted in the presence of O<sub>2</sub>. The CO<sub>2</sub> evolved was measured and the TOC content (%) calculated by comparison with a certified reference standard (acetanilide), which was analysed in conjunction with the samples.

#### *2.6. Lipid extraction*

Lipids were extracted using ultrasonically assisted extraction (Otto et al., 2005). Each sample (1-3 g) was sonicated for 15 min with 10 ml MeOH and

centrifuged for 15 min at 6000 rpm. The supernatant was filtered through a Whatman GF/A glass fibre filter. The procedure was repeated with solvent of decreasing polarity (10 ml 1:1 MeOH:DCM, followed by 10 ml DCM). The combined filtrate was concentrated by way of rotary evaporation, and quantitatively transferred to a 2 ml glass vial.

Neutral lipids were separated from the total lipid extract (TLE) following the method of Pinkart et al. (1998). A custom-made Bond-Elut solid phase extraction (SPE) column packed with an aminopropylsilica solid phase (5 mm diam., PE, 500mg Ultra-Clean NH<sub>2</sub>, Agilent Technologies) was used. The cartridge was washed with 5 ml hexane, 5 ml CHCl<sub>3</sub>, 5 ml Me<sub>2</sub>CO, and 5 ml 6:1 MeOH:CHCl<sub>3</sub> prior to use. The dried TLE was suspended in 500 µl CHCl<sub>3</sub>, transferred to a cartridge, and pulled onto the stationary phase under vacuum. The neutral fraction was eluted with 5 ml CHCl<sub>3</sub>. A glycolipid fraction was eluted next with 5 ml Me<sub>2</sub>CO, followed by a polar fraction eluted with 2.5 ml 6:1 MeOH:CHCl<sub>3</sub> and 2.5 ml 6:1 MeOH:CHCl<sub>3</sub> containing 0.2 M NaOAc. All fractions were concentrated under anhydrous N<sub>2</sub> to a minimum volume and each transferred to a 2 ml glass vial. The glycolipid and polar lipid fractions were stored at -20 °C for future analysis.

The neutral lipid fraction was silylated with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) prior to gas chromatography-mass spectrometry (GC-MS) analysis. 5 $\alpha$ -Cholestane (100 µl, 100 ppm) was added to as internal standard and the solvent removed under N<sub>2</sub>. BSTFA (50 µl) was

added to the dried fraction along with 50  $\mu\text{l}$  pyridine as catalyst and the mixture heated at 70  $^{\circ}\text{C}$  for 2.5 h.

### 2.7. GC-MS

An aliquot (1  $\mu\text{l}$ ) of sample was immediately analysed in triplicate with an Agilent model 7890N gas chromatograph equipped with a 7683 autosampler according to the conditions of Otto et al. (2006). The GC instrument was coupled to an Agilent 5973N mass spectrometer operating in electron impact mode at 70 eV. The column was a 30 m HP-5MS column (0.25 mm i.d., 1  $\mu\text{m}$  film thickness). The sample (1  $\mu\text{l}$ ) was injected with a 2:1 split ratio. The GC inlet temperature was 280  $^{\circ}\text{C}$  and the oven programme: 65  $^{\circ}\text{C}$  (held 2 min) to 300  $^{\circ}\text{C}$  (held 20 min) at 6  $^{\circ}\text{C}/\text{min}$ .

Compounds were assigned from comparison with mass spectral library databases (NIST and Wiley) and comparison of MS patterns with published spectra and authentic standards. Analytes were quantified from total ion peak area using multiple-point calibration curves of representative standards (i.e. nonadecane for *n*-alkanes and *n*-alkan-2-ones, hexadecanol for *n*-alkanols, stigmasterol for sterols and -amyrin for terpenoids). Recovery (%) was measured using an internal standard added prior to extraction and was found to be > 95%. Procedural blanks were run to monitor background interference.

The odd over even preference (OEP) was determined by calculating the carbon preference index (CPI) of the *n*-alkanes from C<sub>25</sub> to C<sub>33</sub> using the following equation (Bray and Evans, 1961):

$$\text{CPI}_{25-33} = 0.5 \times [(\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}) / (\text{C}_{24} + \text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32})] + [(\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}) / (\text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32} + \text{C}_{34})]$$

Values > 1 denote an OEP whereas values < 1 indicate an even over odd (EOP) predominance.

The P-aquatic (P<sub>aq</sub>) ratio (Ficken et al., 2000), originally proposed to examine the input of algae to lake sediments, has been applied to measure the input of *Sphagnum* species to peat deposits (Nichols et al., 2006; Zhang et al., 2014; Inglis et al., 2015). It involves comparison of medium to long chain *n*-alkanes, as the former are predominant in both *Sphagnum* and aquatic macrophytes:

$$\text{P}_{aq} = (\text{C}_{23} + \text{C}_{25}) / (\text{C}_{23} + \text{C}_{25} + \text{C}_{29} + \text{C}_{31})$$

The average chain length (ACL; Eglinton and Hamilton, 1967; Poynter and Eglinton, 1990) for the *n*-alkanes from C<sub>23</sub> to C<sub>33</sub> was calculated for each sample.

$$ACL_{23-33} = ((23(C_{23}) + 25(C_{25}) + 27(C_{27}) + 29(C_{29}) + 31(C_{31}) + 33(C_{33}))/C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33})$$

ACL for *n*-alkanols was calculated from the even homologues from C<sub>22</sub> to C<sub>30</sub>. The *n*-alkanol to *n*-alkane ratio (Poynter and Eglinton, 1990) was employed as a measure of degradation due to the assumed higher degradation rate for *n*-alkanols due to the presence of the OH group.

$$(alc/alc+alk) = (C_{24} + C_{26} + C_{28}n\text{-alkanols})/(C_{24} + C_{26} + C_{28}n\text{-alkanols}) + (C_{27} + C_{29} + C_{31}n\text{-alkanes})$$

### 2.8. GC – isotope ratio MS (GC-IRMS)

All samples were analysed in triplicate using continuous flow IRMS and the same GC conditions as above. The GC instrument was coupled to an IsoPrime IRMS instrument (IsoPrime100) via a combustion furnace (GC5, CuO, Pt 650). The <sup>13</sup>C values were measured against a CO<sub>2</sub> reference gas of known <sup>13</sup>C value and are reported vs. a stable isotope reference standard (*n*-alkanes mixture B2, Indiana University, USA). Reproducibility was better than ± 0.5‰. The results were corrected for the addition of carbon during derivatization and only well resolved major analytes are reported.

### 2.9. Statistical analysis

Elemental, biomarker proxy,  $\delta^{13}\text{C}$  measurements, and individual sterol and terpenoid compound data were tested for any statistically significant correlation (Table A1) by calculating Pearson correlation coefficients ( $r$ ) using PAST 3.10 software (Hammer et al., 2001).  $P$  values  $< 0.05$  were considered to be statistically significant.

### 3. Results

#### 3.1. Chronology of peat profile

$^{14}\text{C}$  age values obtained for the seven bulk samples are shown in Fig. 3. Calculated age values from linear interpolation for the dated and non-dated samples are listed in Table 1. These are the dates referred to throughout. The total timespan of the peat profile is ca. 3377 yr.

#### 3.2. Elemental composition

##### 3.2.1. TOC and TN

TOC ranged from 17.5% to 39.9% (avg. 31.7%; Fig. 4). The highest value was at ca. 3205 cal. yr BP and the lowest at ca. 2240 cal. yr BP. The top two layers, spanning ca. 2079 cal. yr BP to 2240 cal. yr BP, contained the lowest

amount of TOC, with a sharp increase occurring at 2561 cal. yr BP. From this sample to the bottom of the profile, values fluctuated relatively less and displayed a gentle decreasing trend.

The profile had an average TN value of 1.3%. The minimum of 0.7% was at ca. 5456 cal. yr. BP. Values increased over time to a maximum of 1.9% at ca. 3526 cal. yr. BP. This was followed by a steady decrease to 0.8% at ca. 2240 cal. yr. BP and a slight increase to 1.1% in the most recent material dated to ca. 2079 cal. yr. BP.

Average C/N values were 24.4, with a maximum of 39.7 and a minimum of 17.6. Overall, the results followed a similar trend to TOC (Fig. 4). There was, however, a sharp increase to the maximum in the deepest layer, which was opposite to the decrease in TOC in this sample, indicating a lower N input.

### *3.2.2. Total sulfur (TS)*

TS displayed an overall average value of 5.5% (Fig. 4). Similar values of 3.6 and 4.6% were observed for the bottom and top samples of the 1 m profile respectively. Levels remained around 6.5% between 4813 and 2722 cal. yr BP and were followed by a decrease to 4.3 and 3.4% at 3848 and 3526 cal. yr BP respectively. Values returned to ca. 6.5% for the next three samples dated from 3205 to 2722 cal. yr BP, and increased to a maximum value of 8.8% at 2561 cal. yr BP. A shift to the minimum value of 1.5% occurred at 2240 cal. yr BP.

### *3.3.3. Neutral compounds*

Total *n*-alkane concentration varied between 9.2 and 73.1  $\mu\text{g/g}$  OC. All samples across the ca. 3377 yr period recorded similar *n*-alkane distributions dominated by long chain ( $\text{C}_{29}$ - $\text{C}_{33}$ ) compounds with an OEP typical of a terrigenous plant input to (Table 1). All the samples had CPI values  $> 1$ , with a minimum of 4.40 and a maximum of 31.48.

Throughout the profile there were periods of increased input from mid-chain *n*-alkanes ( $\text{C}_{23}$ - $\text{C}_{25}$ ), indicative of a contribution from *Sphagnum* (Baas et al., 2000; Ficken et al., 2000; Nichols et al., 2006). The relative contribution from *Sphagnum* vs. other higher plants was assessed (Fig. 5) using the  $\text{C}_{23}/\text{C}_{31}$  ratio (Baas et al., 2000; Nott et al., 2000). The values ranged from a minimum of 0.1 at ca. 4491 cal yr BP to a maximum of 0.6 at ca. 2240 cal yr BP. There appeared to be a decreased  $\text{C}_{23}$  input from ca. 4600 to 4300 cal yr BP, ca. 3900 to 3700 cal yr BP and in the surface sample at ca. 2079 cal yr BP. A predominance of  $\text{C}_{23}$  occurred at ca. 5000 to 4700 cal yr BP and ca. 4300 to 4000 cal yr BP, with the largest increase from ca. 2300 to 2100 cal yr BP.  $\text{C}_{31}$  is also in relatively high abundance in *Sphagnum*, whereas  $\text{C}_{29}$  is relatively rare (Baas et al., 2000; Nott et al., 2000). As such, it has been suggested that the  $\text{C}_{23}/\text{C}_{29}$  ratio may be preferable for reconstructing *Sphagnum* vs. non-*Sphagnum* contribution to peat (Nichols et al., 2006). Our results showed minimal variation between the trends for both proxies (Fig. 5).

The maximum value for  $P_{aq}$  (0.3) was at ca. 2240 cal yr BP, and the minimum (0.1) at ca. 4491 cal yr BP. Overall,  $P_{aq}$  displayed a similar trend to

that of the  $C_{23}/C_{29}$  and  $C_{23}/C_{31}$  proxies. The ACL ranged from 28.4 to 29.9 following the same trend (Fig. 5).

*n*-Alkanol total concentration ranged from 7.2 to 171.1  $\mu\text{g/g}$  OC. The ACL for *n*-alkanols provided an overall average of 24.7, with little variation along the profile. However, marked increases in values were observed for ca. 4550 to 4350 cal yr BP and ca. 2550 to 2400 cal yr BP (Fig. 6). *n*-Alkane to *n*-alkanol ratio values remained relatively constant from ca. 5456 to 2722 cal yr BP, with a minimum of 0.7 and a maximum of 0.8. At ca. 2561 cal yr BP there was a drop to 0, suggesting a period of reduced degradation. The rates increased to 0.5 at ca. 2240 cal yr BP and 0.6 at ca. 2079 cal yr BP at the surface (Fig. 6).

Long chain *n*-alkan-2-ones in ombrotrophic peat bogs have been proposed to be specific biomarkers for *Sphagnum* (Nichols and Huang, 2007) and were present in all the samples. Total concentration varied between 22.1 and 144.5  $\mu\text{g/g}$  OC.

Nichols and Huang (2007) proposed that heptacosan-2-one could be used as a *Sphagnum*-specific biomarker. We compared its concentration with that of the  $C_{31}$  *n*-alkane higher plant marker, to further investigate OM composition throughout the peat section ( $C_{27\text{-one}}/C_{31\text{-ane}}$ ). A maximum value of 4.28 was observed at 4813 cal yr BP, whilst a minimum of 0.50 occurred at 4491 cal yr BP. The overall trend in the ratio was similar to that of the  $C_{23}/C_{31}$  *n*-alkane proxy (Fig. 6).

Sterols, the most abundant lipid class in the profile, consisted predominantly of  $C_{29}$  homologues with a minor input from  $C_{27}$  and  $C_{28}$  compounds (Table 1). This is a typical distribution in peatlands and indicative of a mainly

higher plant contribution (Pancost et al., 2002). Overall, the distributions of sterols showed little variation throughout the profile.

Pancost et al. (2002) suggested that the triterpenoid taraxer-4-one may be of use as a biomarker for *Ericaceae* (heather) in ombrotrophic peat bogs. This is because it was only found in the extract of *Calluna vulgaris* roots and not in any of the *Sphagnum* tissue samples that were examined. Taraxer-4-one ranged from 0 to 41  $\mu\text{g/g}$  OC, with a general decreasing trend over time. The maximum value was at 4813 cal yr BP and was at least 5x greater than that for any other sample. Its input decreased continuously until ca. 3848 cal yr BP, where it was not detected.

#### 3.3.4. $\delta^{13}\text{C}$ values

$\delta^{13}\text{C}$  measurements were analysed for representative compounds from each lipid class, namely  $\text{C}_{29}$  and  $\text{C}_{31}$  *n*-alkanes,  $\text{C}_{24}$  and  $\text{C}_{28}$  *n*-alkanols,  $\text{C}_{27}$  *n*-alkan-2-one and  $\beta$ -sitosterol. No low molecular weight *n*-alkanes were within our detection range, nor were any terpenoids. The  $\text{C}_{29}$  *n*-alkane values displayed an increasing trend over time, with a maximum of -30.5‰ at 2240 cal yr BP and a minimum of -34.3‰ at 4491 cal yr BP. There was less variation in the  $\text{C}_{31}$  *n*-alkane values, with a maximum of -33.9‰ and a minimum of -35.8‰ at 4170 and 4813 cal yr BP respectively. Overall there was a gradual trend of depletion for this compound.

The  $\text{C}_{24}$  *n*-alkanol values ranged from -34.0 to -32.0‰ with an average of -32.9‰.  $\text{C}_{28}$  *n*-alkanol values were gradually depleted over time, with a maximum

of  $-32.7\text{‰}$  and a minimum of  $-34.8\text{‰}$ . The  $C_{28}$  *n*-alkanol values followed a similar trend.

$C_{27}$  *n*-alkan-2-one values ranged from  $-33.3$  to  $-31.4\text{‰}$  at 4491 and 2240 cal yr BP respectively, becoming enriched over time. Values for  $\beta$ -sitosterol showed the greatest variation for all investigated compounds, with a minimum of  $-32.1\text{‰}$  at 2561 cal yr BP and a maximum of  $-25.0\text{‰}$  at 4813 cal yr BP.

## 4. Discussion

### 4.1. Origin of OM in the Spiddal ombrotrophic peat bog

The OM at the site appears to be primarily of terrestrial origin. This is indicated by the predominance of lipid biomarkers of higher plant origin including the high molecular weight (HMW) *n*-alkanes with a strong OEP, the HMW *n*-alkanols with an EOP, long chain *n*-alkan-2-ones, as well as the abundance of vascular plant steroids and terpenoids. A significant contribution from *Sphagnum* moss is highlighted by the occurrence of low molecular weight (LMW) *n*-alkyl compounds throughout the peat profile. The  $\delta^{13}\text{C}$  values of individual biomarkers, with a minimum of ca.  $-35\text{‰}$  and maximum of ca.  $-25\text{‰}$  across the whole range, indicate a predominant contribution from  $C_3$  plants (Ficken et al., 1998). López-Días et al. (2013) suggested a bacterial source for *n*-alkan-2-ones in a peat bog in Roñanzas, Northern Spain. However, the  $\delta^{13}\text{C}$

values for these compounds in the Spiddal peat are consistent with a terrestrial plant origin.

In contrast, the high TS values suggest an input of sulfate from seawater, with values > 3% in peat seen as indicative of a marine setting (Chou, 2012; Inglis et al., 2015). All but one of the samples (2152 cal yr BP) were above this limit. TS correlated with TOC (Table A1) in these samples ( $r = 0.66$ ,  $P < 0.01$ ) and similar trends can be observed for both sets of data (Fig. 4). This could indicate a significant contribution of organic S to the TS. S can be transported from the ocean to the atmosphere and the land through sea spray aerosols (Mahowald et al., 2011). It is possible that a proportion of the S at the site was deposited by this mechanism due to the close proximity to the ocean. S from seawater in the form of  $\text{SO}_4^{2-}$  or  $\text{H}_2\text{S}$  could also potentially have diffused into the peat while it was submerged. S isotopic analysis in future work would help determine the influence of these sources. Although the peat bog was influenced by seawater at varying levels over time, the amount of marine OM input was negligible in comparison with the strong higher plant input during peat formation. Although some of the LMW *n*-alkyl compounds may originate from marine organisms, the lack of marine-specific sterols such as dinosterol or spongesterol (Lee et al., 1979; Volkman et al., 1993) could suggest that this influence is minor. Therefore, it would appear that the OM deposited during peat formation was predominantly of terrestrial origin, suggesting that the peat record at this site remains a relatively reliable indicator of palaeoenvironmental change, despite its coastal

setting. Further analysis such as of bulk  $\delta^{13}\text{C}$  could provide more evidence to test this hypothesis.

#### 4.2. Climate change in Ireland during the mid-Holocene

Using a combination of the lipid classes analysed, it was possible to retrace variation in climatic conditions over time due to the response of the peat OM to change in precipitation. Pearson correlation show that there is good correlation between all the biomarker proxies (Table A1); however,  $\text{C}_{23}/\text{C}_{29}$  shows the widest variation. The  $\delta^{13}\text{C}$  values for  $\text{C}_{31}$  *n*-alkane were 2.5‰ more positive on average than for the  $\text{C}_{29}$  *n*-alkane. Variation in carbon isotope values of up to 6‰ has been observed between *n*-alkanes within the same plant tissue (Rieley et al., 1993; Collister et al., 1994). However, there is a statistically significant correlation between the  $\delta^{13}\text{C}$  values of the  $\text{C}_{27}$  *n*-alkan-2-one attributed to *Sphagnum* input, and that of the  $\text{C}_{29}$  *n*-alkane ( $r = 0.70$ ,  $P < 0.02$ ). Neither of these shows a correlation with the  $\delta^{13}\text{C}$  value for the  $\text{C}_{31}$  *n*-alkane. The correlation over a ca. 3400 yr period could suggest that some of the  $\text{C}_{29}$  *n*-alkane input is derived from the species of *Sphagnum* contributing to peat formation at this site, implying that in this case the  $\text{C}_{23}/\text{C}_{31}$  and the  $\text{C}_{27\text{-one}}/\text{C}_{31\text{-ane}}$  ratios are more reliable than the  $\text{C}_{23}/\text{C}_{29}$  ratio. Pancost et al. (2002) recommend that lipid biomarker data be used cautiously without the support of macrofossil analysis. Compound specific isotope analysis enables more robust biomarker data interpretation for peat samples where such additional data is not available.

The high  $C_{23}/C_{29}$  *n*-alkane ratio at ca. 5456 cal yr BP is indicative of increased contribution from *Sphagnum* plants, which suggests colder, wetter conditions during this interval. However, all other proxies disagree with this, displaying values close to their respective averages. There is a conflict here between the  $C_{23}/C_{29}$  and  $C_{23}/C_{31}$  *n*-alkane proxies. At ca. 4813 cal. yr BP all the ratios point to an increase in cold and wet conditions, with most indicating that this was one of the coldest and wettest periods throughout the timeframe. The results agree somewhat with the idea of dry conditions becoming gradually wetter from ca. 5800 to 4800 cal. yr BP as outlined by Caseldine et al. (2005). However, no evidence of an extreme climatic event between 5200 and 5100 cal. yr BP as described by Caseldine et al. (2005) was observed at the Spiddal site.

Conditions shifted dramatically at ca. 4491 cal yr BP, providing the warmest and driest period in the record. All the biomarker proxies are in agreement with this, showing an increased relative contribution from higher plants to the lipid record. Later, at ca. 4170 cal yr BP, all indicators depict a return towards a colder, wetter climate, yet some proxies suggest that the shift is stronger than from other proxies. The  $C_{23}/C_{29}$  *n*-alkane and  $P_{aq}$  ratios suggest a distinct return to conditions similar to those at ca. 4813 cal yr BP, whilst the  $C_{23}/C_{31}$  *n*-alkane and the  $C_{27}$  *n*-alkan-2-one proxies suggest a less severe retraction. This date coincides with that of the 4.2 ka event. The identification of colder/wetter conditions at this time in our study would suggest that the effect of the event in Ireland is not yet clear. Also, the site here and that of Barber et al. (2003) are located in central Ireland, whereas Roland et al. (2014) investigated

locations in the north of Ireland. Thus, regional differences in local conditions may explain discrepancies between studies. These contradictions show a need for further investigations of the palaeoclimate of Ireland around 4200 yr BP.

All the proxies provide evidence of a warmer and drier climate at ca. 3848 cal yr BP. The trends in the  $C_{23}/C_{29}$  *n*-alkane ratio and  $C_{27}$  *n*-alkan-2-one suggest that these conditions continue with little fluctuation for the next ca. 1300 yr, until ca. 2561 cal yr BP, where colder conditions return. The  $C_{23}/C_{31}$  *n*-alkane, and  $P_{aq}$  ratios may reflect change towards colder and wetter conditions at ca. 3205 cal yr BP, with a subsequent shift to relatively warmer conditions at ca. 2883 cal yr BP. The  $C_{27}$  *n*-alkan-2-one trend indicates the coldest/wettest conditions from all proxies at ca. 2561 cal yr BP.

At ca. 2240 cal yr BP all proxies indicate cold and wet conditions, one of the coldest and wettest periods of the entire profile. The shift towards colder/wetter conditions from ca. 2883 to 2240 cal. yr BP corresponds (Fig. 7) to the Subboreal-Subatlantic transition. There is a sharp shift back to a warmer and drier climate in the shallowest sample representing ca. 2079 cal yr BP. This was one of the radiocarbon dated samples and was assigned as  $2068 \pm 51$  cal yr BP, a similar date to that obtained by Williams and Doyle (2014) for a birch branch from the same site (2110 - 2084 cal yr BP).

The warmer and drier climate would have provided favourable conditions for the growth of a forest, which would ultimately become the 'drowned' forest that remains at the site today in the form of standing tree stumps. The cessation of peat formation, coupled with the deposition of a sand layer covering the

acrotelm and the embedded tree stumps, implies that there was a rapid rise in sea level at this time that engulfed the forest. Increasing TS also supports the influx of a marine influence. This was likely the only time in ca. 3400 yr that the site was submerged beneath the ocean, supported by the lack of any sand layers throughout the 1 m peat profile. There is a paucity of evidence providing relative sea level (RSL) data for the west coast of Ireland, with the majority of estimates being given for north, south and east coasts (Brooks and Edwards, 2006). A period of elevated RSL, followed by a downward trend towards present day levels has been observed at these other locations (Brooks et al., 2008). Recent evidence from other 'drowned' forest sites along the west coast suggest that this trend did not occur on that side of the island (Williams and Doyle 2014). The rapid increase in sea level observed at this site supports this evidence, and warrants further investigation, which may provide valuable data for reconstruction of Holocene sea level in the area.

## 5. Conclusions

A geochemical approach was used to investigate a peat bog profile from Spiddal, Co. Galway, Ireland. A suite of terrestrial plant derived lipid biomarkers and published proxies revealed clear changes in vegetation type. This likely reflects high latitude changes in climate, and resulting changes in local environmental conditions during this mid-Holocene interval, some of which may have led to the rapid submersion of a forest at this location. Three distinct

periods of cold and wet conditions were identified at ca. 4813, 4170 and 2240 cal. yr BP, along with four periods of warmer and drier conditions at 4491, 3848, 2883 and 2079 cal. yr BP. These climatic extremes show some correlation with published records from Ireland attributed to climatic events, namely the 4.2 ka event and the Subboreal-Subatlantic transition. However, evidence of other climatic events such as the 5.2 ka event and the Roman Warm Period was not obtained. Our study found evidence of a 4.2 ka event with colder/wetter conditions, similar to other peatland sites from central Ireland. This is contrary to the absence of evidence from peatland sites in the north of the island. This could suggest the possibility that this climatic event may not be absent from Ireland, but may not have affected all parts of the country. It would, however, be unusual for an event of this global magnitude to have such a localised impact, so further investigation of this incident is needed. Future work should involve a combination of multidisciplinary analytical techniques including geochemical methods in conjunction with analysis of testate amoebae, pollen and plant macrofossils. Work of this nature should also use multiple sampling locations to determine any spatial variability in the effect of the event. The results emphasise the importance of Ireland's peat resources as a record of palaeoenvironmental change. The organic geochemical approach has potential to provide a new dataset for Irish palaeoclimate research and should be utilised in future studies of ombrotrophic peat bogs, as well as the investigation of sites providing a greater spatial variability on the island. Here we show that a period of warm and dry conditions encouraged the growth of the forest at this location

around 2100 cal. yr BP and that a rapid rise in sea level in the following years is most likely responsible for its drowning.

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### **References**

- Baas, M., Pancost, R., Van Geel, B., Sinninghe Damsté, J.S., 2000. A comparative study of lipids in Sphagnum species. *Organic Geochemistry* 31, 535–541. doi:10.1016/S0146-6380(00)00037-1
- Barber, K.E., 2007. Peatland records of Holocene climate change. In: Elias, S. (Ed.), *Encyclopedia of Quaternary Science*. Elsevier, Oxford, pp. 1884–1895.
- Barber, K.E., Chambers, F.M., Maddy, D., 2003. Holocene palaeoclimates from peat stratigraphy: Macrofossil proxy climate records from three oceanic raised bogs in England and Ireland. *Quaternary Science Reviews* 22, 521–539. doi:10.1016/S0277-3791(02)00185-3
- Barber, K.E., Maddy, D., Rose, N., Stevenson, A. C., Stoneman, R., Thompson, R., 2000. Replicated proxy-climate signals over the last 2000 yr from two

distant UK peat bogs: New evidence for regional palaeoclimate teleconnections. *Quaternary Science Reviews* 19, 481–487.

doi:10.1016/S0277-3791(99)00102-X

Bingham, E.M., McClymont, E.L., Väliranta, M., Mauquoy, 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. *Organic Geochemistry* 41, 214–220. doi:10.1016/j.orggeochem.2009.06.010

Blackford, J.J., Chambers, F.M., 1991. Proxy records of climate from blanket mires: evidence for a Dark Age (1400 BP) climatic deterioration in the British Isles. *The Holocene* 1, 63–67. doi:10.1177/095968369100100108

Blundell, A., Charman, D.J., Barber, K., 2008. Multiproxy late Holocene peat records from Ireland: towards a regional palaeoclimate curve. *Journal of Quaternary Science* 23, 59–71.

Bond, G., Kromer, B., Beer, J., Muscheler, R., Evans, M.N., Showers, W., Hoffmann, S., Lotti-Bond, R., Hajdas, I., Bonani, G., 2001. Persistent solar influence on North Atlantic climate during the Holocene. *Science* 294, 2130–2136. doi:10.1126/science.1065680

Bray, E.E., Evans, E.D., 1961. Distribution of *n*-paraffins as a clue to recognition of source beds. *Geochimica et Cosmochimica Acta* 22, 2–15. doi:10.1016/0016-7037(61)90069-2

Brooks, A., Edwards, R., 2006. The development of a sea-level database for Ireland. *Irish Journal of Earth Science* 24, 13–27.

- Brooks, A.J., Bradley, S.L., Edwards, R.J., Milne, G.A., Horton, B., Shennan, I., 2008. Postglacial relative sea-level observations from Ireland and their role in glacial rebound modelling. *Journal of Quaternary Science* 23, 175–192. doi:10.1002/jqs.1119
- Caseldine, C., Thompson, G., Langdon, C., Hendon, D., 2005. Evidence for an extreme climatic event on Achill Island, Co. Mayo, Ireland around 5200-5100 cal. yr BP. *Journal of Quaternary Science* 20, 169–178. doi:10.1002/jqs.901
- Chambers, F.M., Booth, R.K., De Vleeschouwer, F., Lamentowicz, M., Le Roux, G., Mauquoy, D., Nichols, J.E., van Geel, B., 2012. Development and refinement of proxy-climate indicators from peats. *Quaternary International* 268, 21–33. doi:10.1016/j.quaint.2011.04.039
- Chou, C.L., 2012. Sulfur in coals: A review of geochemistry and origins. *International Journal of Coal Geology* 100, 1–13. doi:10.1016/j.coal.2012.05.009
- Collister, J.W., Rieley, G., Stern, B., Eglinton, G., Fry, B., 1994. Compound-specific  $^{13}\text{C}$  analyses of leaf lipids from plants with differing carbon dioxide metabolisms. *Organic Geochemistry* 21, 619–627. doi:10.1016/0146-6380(94)90008-6
- Connolly, J., Holden, N.M., 2009. Mapping peat soils in Ireland: updating the derived Irish peat map. *Irish Geography* 42, 343–352. doi:10.1080/00750770903407989
- Eganhouse, R.P., 1997. Molecular markers and environmental organic geochemistry: An overview. In: Eganhouse, R.P. (Ed.), *Molecular Markers in*

- Environmental Chemistry. American Chemical Society, 426 pp.
- Eglinton, G., Hamilton, R.J., 1967. Leaf Epicuticular Waxes. *Science* 156, 1322–1335. doi:10.1126/science.156.3780.1322
- Ficken, K., Li, B., Swain, D., Eglinton, G., 2000. An *n*-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. *Organic Geochemistry* 31, 745–749. doi:10.1016/S0146-6380(00)00081-4
- Ficken, K.J., Barber, K.E., Eglinton, G., 1998. Lipid biomarker,  $\delta^{13}\text{C}$  and plant macrofossil stratigraphy of a Scottish montane peat bog over the last two millennia. *Organic Geochemistry* 28, 217–237. doi:10.1016/S0146-6380(97)00126-5
- Hammer, Ø., Harper, D.A.T., Ryan, P.D., 2001. PAST: Paleontological Statistics Software Package for education and data analysis. *Palaeontologia Electronica* 4, page spread?.
- Inglis, G.N., Collinson, M.E., Riegel, W., Wilde, V., Robson, B.E., Lenz, O.K., Pancost, R.D., 2015. Ecological and biogeochemical change in an early Paleogene peat-forming environment: Linking biomarkers and palynology. *Palaeogeography Palaeoclimatology Palaeoecology* 438, 245–255. doi:10.1016/j.palaeo.2015.08.001
- Killops, S., Killops, V., 2005. *Introduction to Organic Geochemistry*, 2nd ed. Blackwell Science Ltd., Oxford.
- Lee, C., Farrington, J.W., Gagosian, R.B., 1979. Sterol geochemistry of sediments from the western North Atlantic Ocean and adjacent coastal areas. *Geochimica et Cosmochimica Acta* 43, 35–46. doi:10.1016/0016-

7037(79)90044-9

López-Días, V., Blanco, C.G., Bechtel, A., Püttmann, W., Borrego, A.G., 2013.

Different source of *n*-alkanes and *n*-alkan-2-ones in a 6000 cal. yr BP

Sphagnum-rich temperate peat bog (Roñanzas, N Spain). *Organic*

*Geochemistry* 57, 7–10.

doi:<http://dx.doi.org/10.1016/j.orggeochem.2013.01.006>

Mahowald, N., Ward, D.S., Kloster, S., Flanner, M.G., Heald, C.L., Heavens,

N.G., Hess, P.G., Lamarque, J.-F., Chuang, P.Y., 2011. Aerosol impacts on  
climate and biogeochemistry. *Annual Review of Environmental Resources*

36, 45–74. doi:10.1146/annurev-environ-042009-094507

McClymont, E.L., Pendall, E., Nichols, J., 2010. Stable isotopes and organic  
geochemistry in peat: tools to investigate past hydrology, temperature and  
biogeochemistry. doi:10.1002/jqs.1295.Mitchell

Nichols, J.E., Booth, R.K., Jackson, S.T., Pendall, E.G., Huang, Y., 2006.

Paleohydrologic reconstruction based on *n*-alkane distributions in  
ombrotrophic peat. *Organic Geochemistry* 37, 1505–1513.

doi:10.1016/j.orggeochem.2006.06.020

Nichols, J.E., Huang, Y., 2007. C<sub>23</sub>-C<sub>31</sub> *n*-alkan-2-ones are biomarkers for the  
genus *Sphagnum* in freshwater peatlands. *Organic Geochemistry* 38, 1972–  
1976. doi:10.1016/j.orggeochem.2007.07.002

doi:10.1016/j.orggeochem.2007.07.002

Nott, C.J., Xie, S., Avsejs, L. a., Maddy, D., Chambers, F.M., Evershed, R.P.,

2000. *n*-Alkane distributions in ombrotrophic mires as indicators of

- vegetation change related to climatic variation. *Organic Geochemistry* 31, 231–235. doi:10.1016/S0146-6380(99)00153-9
- Otto, A., Shunthirasingham, C., Simpson, M.J., 2005. A comparison of plant and microbial biomarkers in grassland soils from the Prairie Ecozone of Canada. *Organic Geochemistry* 36, 425–448. doi:10.1016/j.orggeochem.2004.09.008
- Pancost, R.D., Baas, M., Van Geel, B., Sinninghe Damsté, J.S., 2002. Biomarkers as proxies for plant inputs to peats: An example from a sub-boreal ombrotrophic bog. *Organic Geochem.* doi:10.1016/S0146-6380(02)00048-7
- Pancost, R.D., Boot, C.S., 2004. The palaeoclimatic utility of terrestrial biomarkers in marine sediments. *New Approaches. Marine Organic Biogeochemistry A Tribute to Life Science John I. Hedges* 92, 239–261. doi:DOI: 10.1016/j.marchem.2004.06.029
- Pancost, R.D., McClymont, E.L., Bingham, E.M., Roberts, Z., Charman, D.J., Hornibrook, E.R.C., Blundell, A., Chambers, F.M., Lim, K.L.H., Evershed, R.P., 2011. Archaeol as a methanogen biomarker in ombrotrophic bogs. *Organic Geochemistry* 42, 1279–1287. doi:10.1016/j.orggeochem.2011.07.003
- Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. *The Biomarker Guide*. Cambridge University Press, Cambridge, UK.
- Pinkart, H.C., Devereux, R., Chapman, P.J., 1998. Rapid separation of microbial lipids using solid phase extraction columns. *Journal of Microbiological Methods* 34, 9–15. doi:10.1016/S0167-7012(98)00060-8
- Plunkett, G.M., 2006. Tephra-linked peat humification records from Irish ombrotrophic bogs question nature of solar forcing at 850 cal. yr BC. *Journal*

of Quaternary Science 21, 9–16. doi:10.1002/jqs.951

Plunkett, G.M., Pilcher, J.R., McCormac, F.G., Hall, V.A., 2004. New dates for first millennium BC tephra isochrones in Ireland. *The Holocene* 14, 780–786. doi:10.1191/0959683604hl757rr

Poynter, J., Eglinton, G., 1990. Molecular composition of three sediments from Hole 717C: 116, 155–161.

Radu, T., Diamond, D., 2009. Comparison of soil pollution concentrations determined using AAS and portable XRF techniques. *Journal of Hazardous Materials* 171, 1168–71. doi:10.1016/j.jhazmat.2009.06.062

Ramsey, C.B., 2009. Bayesian analysis of radiocarbon dates. *Radiocarbon* 51, 337–360.

Reimer, P., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P.G., Ramsey, C.B., Buck, C.E., Cheng, H., Edwards, R.L., Friedrich, M., Grootes, P.M., Guilderson, T.P., Haflidason, H., Hajdas, I., Hatté, C., Heaton, T.J., Hoffmann, D.L., Hogg, A.G., Hughen, K.A., Kaiser, K.F., Kromer, B., Manning, S.W., Niu, M., Reimer, R.W., Richards, D.A., Scott, E.M., Southon, J.R., Staff, R.A., Turney, C.S.M., Plicht, J. van der, 2013. IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 Years cal BP. *Radiocarbon* 55, 1869–1887. doi:10.2458/azu\_js\_rc.55.16947

Rieley, G., Collister, J.W., Stern, B., Eglinton, G., 1993. Gas chromatography/isotope ratio mass spectrometry of leaf wax *n*-alkanes from plants of differing carbon dioxide metabolisms. *Rapid Communicationa in Mass Spectrometry* 7, 488–491.

Roland, T.P., Caseldine, C.J., Charman, D.J., Turney, C.S.M., Amesbury, M.J.,

2014. Was there a “4.2ka event” in Great Britain and Ireland? Evidence

from the peatland record. *Quaternary Science Reviews* 83, 11–27.

doi:10.1016/j.quascirev.2013.10.024

Roland, T.P., Daley, T.J., Caseldine, C.J., Charman, D.J., Turney, C.S.M.,

Amesbury, M.J., Thompson, G.J., Woodley, E.J., 2015. The 5.2 ka climate

event: Evidence from stable isotope and multi-proxy palaeoecological

peatland records in Ireland. *Quaternary Science Reviews* 124, 209–223.

doi:10.1016/j.quascirev.2015.07.026

Schellekens, J., Bindler, R., Martínez-Cortizas, A., McClymont, E.L., Abbott,

G.D., Biester, H., Pontevedra-Pombal, X., Buurman, P., 2015. Preferential

degradation of polyphenols from Sphagnum – 4-isopropenylphenol as a

proxy for past hydrological conditions in Sphagnum-dominated peat.

*Geochimica et Cosmochimica Acta* 150, 74–89. doi:10.1016/j.gca.2014.12.003

Simoneit, B.R.T., 2004. Biomarkers (molecular fossils) as geochemical indicators

of life. *Adv. Sp. Res.* 33, 1255–1261. doi:10.1016/j.asr.2003.04.045

Swindles, G.T., Blundell, a., Roe, H.M., Hall, V. A., 2010. A 4500-year proxy

climate record from peatlands in the North of Ireland: the identification of

widespread summer “drought phases”? *Quaternary Science Reviews* 29,

1577–1589. doi:10.1016/j.quascirev.2009.01.003

Swindles, G.T., Lawson, I.T., Matthews, I.P., Blaauw, M., Daley, T.J., Charman,

D.J., Roland, T.P., Plunkett, G., Schettler, G., Gearey, B.R., Turner, T.E.,

Rea, H. a., Roe, H.M., Amesbury, M.J., Chambers, F.M., Holmes, J.,

- Mitchell, F.J.G., Blackford, J., Blundell, A., Branch, N., Holmes, J.,  
Langdon, P., McCarroll, J., McDermott, F., Oksanen, P.O., Pritchard, O.,  
Stastney, P., Stefanini, B., Young, D., Wheeler, J., Becker, K., Armit, I.,  
2013. Centennial-scale climate change in Ireland during the Holocene.  
*Earth-Science Rev.* 126, 300–320. doi:10.1016/j.earscirev.2013.08.012
- Swindles, G.T., Plunkett, G., Roe, H.M., 2007. A delayed climatic response to  
solar forcing at 2800 cal. BP: multiproxy evidence from three Irish  
peatlands. *The Holocene* 17, 177–182. doi:10.1177/0959683607075830
- Verardo, D.J., Froelich, P.N., McIntyre, A., 1990. Determination of organic  
carbon and nitrogen in marine sediments using the Carlo Erba NA-1500  
analyzer. *Deep Sea Research Part A. Oceanography Research Papers* 37,  
157–165. doi:10.1016/0198-0149(90)90034-S
- Volkman, J.K., Barrett, S.M., Dunstan, G.A., Jeffrey, S.W., 1993. Geochemical  
significance of the occurrence of dinosterol and other 4-methyl sterols in a  
marine diatom. *Organic Geochemistry* 20, 7–15. doi:10.1016/0146-  
6380(93)90076-N
- Weiss, H., Courty, M.A., Wetterstrom, W., Guichard, F., Senior, L., Meadow, R.,  
Curnow, A., 1993. The genesis and collapse of third millennium north  
mesopotamian civilization. *Science* 261, 995–1004.
- Williams, D.M., Doyle, E., 2014. Dates from drowned Mid-Holocene landscapes  
on the Central Western Irish Seaboard. *Irish Journal of Earth Science* 32,  
23–27.
- Zhang, Y., Liu, X., Lin, Q., Gao, C., Wang, J., Wang, G., 2014. Vegetation and

climate change over the past 800 years in the monsoon margin of northeastern China reconstructed from n-alkanes from the Great Hinggan Mountain ombrotrophic peat bog. *Organic Geochemistry* 76, 128–135.

doi:10.1016/j.orggeochem.2014.07.013

Zheng, Y., Zhou, W., Meyers, P.A., Xie, S., 2007. Lipid biomarkers in the Zoigê-Hongyuan peat deposit: Indicators of Holocene climate changes in West China. *Organic Geochemistry* 38, 1927–1940.

doi:10.1016/j.orggeochem.2007.06.012

**Table 1**

Total organic carbon (TOC), total sulfur (TS), total nitrogen (TN) and C/N ratio as well as abundances of lipid compounds at each depth. Also shown are  $^{13}\text{C}$  values for specific biomarkers.

Depth (cm)	0-5	5-10	15-20	20-25	25-30	35-40	45-50	55-60	65-70	75-80	85-90	105-110
Age (cal yr BP) <sup>a</sup>	2079	2240	2561	2722	2883	3205	3526	3848	4170	4491	4813	5456
TOC (%)	22.4	17.5	34.2	37.4	36.3	39.9	33.5	32.9	34.1	30.6	34	27.8
TN (%)	1.1	0.8	1.3	1.4	1.6	1.6	1.9	1.4	1.5	1.5	1.3	0.7
C/N	20.4	21.9	26.3	26.7	22.7	24.9	17.6	23.5	22.7	20.4	26.2	39.7
TS (%)	4.6	1.5	8.8	5.9	6.0	6.4	4.3	3.4	6.9	6.8	7.3	3.6
<i>n</i> -Alkanes ( $\mu\text{g/g}$ OC)												
C <sub>22</sub>	1.5	0.3	0.3	0.5	0.4	0.3	0.3	0.4	0.7	0.3	0.8	1.0
C <sub>23</sub>	3.1	0.7	0.7	1.1	1.1	1.1	1.3	1.3	2.2	0.9	2.1	5.3
C <sub>24</sub>	3.8	0.9	0.7	1.2	0.9	0.7	0.7	0.9	2.3	0.7	2.6	2.8
C <sub>25</sub>	2.5	0.4	0.6	1.2	0.9	0.9	1.3	1.4	1.7	0.9	1.3	2.1
C <sub>26</sub>	1.8	0.4	0.6	0.7	0.6	0.6	0.7	0.7	0.8	0.5	0.7	1.2
C <sub>27</sub>	5.4	0.7	1.1	1.8	1.4	1.3	1.6	2.6	2.6	2.5	2.6	4.4
C <sub>28</sub>	2.2	0.3	0.3	0.8	0.6	0.4	0.6	0.9	1.0	0.9	0.6	1.4
C <sub>29</sub>	13.9	1.4	2.5	5.0	5.5	4.1	5.3	6.4	4.7	5.6	4.1	9.3
C <sub>30</sub>	1.9	0.4	0.5	1.1	0.8	0.5	0.6	0.9	0.8	1.0	0.7	2.4

C <sub>31</sub>	14.1	1.2	1.7	3.3	3.8	2.8	4.4	6.8	5.0	7.7	3.9	15.3
C <sub>32</sub>	2.2	0.1	0	0	0	0	0	1.5	1.6	0	0.5	5.4
C <sub>33</sub>	8.2	1.3	2.5	2.6	4.0	2.3	3.8	4.9	4.5	6.7	4.1	17.8
@	60.5	8.1	11.4	19.2	19.9	15.0	20.6	28.6	27.9	27.6	24.0	68.3
<i>n</i> -Alkanols (µg/g OC)												
C <sub>22</sub>	26	1.0	0	22.2	22.5	9.2	21.5	16.8	14.6	15.8	16.3	28.7
C <sub>23</sub>	4.7	7.6	0.2	0.8	1.6	0.7	1.1	2.1	1.1	1.6	1.3	3.7
C <sub>24</sub>	30.3	1.9	0	30.6	31.7	12.1	31.1	26.6	24.7	24.0	21.8	53.1
C <sub>25</sub>	2.7	0.2	2.4	1.0	1.0	0.5	0.9	0.9	1.1	1.4	1.4	3.7
C <sub>26</sub>	12.8	0.5	0.1	10.2	8.9	4.3	8.2	6.4	7.7	7.2	9.0	17.4
C <sub>27</sub>	1.4	0	3.3	0.6	0.5	0.3	0.5	0.6	0.7	1.1	0.8	2.2
C <sub>28</sub>	14.2	0.4	0.1	8.0	7.0	3.0	4.8	7.2	6.9	18.2	10.3	23.4
C <sub>29</sub>	1.5	0	0.7	0.6	0.5	0.3	0.5	0.7	0.7	1.3	0.8	3.3
C <sub>30</sub>	4.6	0	0	2.5	1.0	1.5	1.9	2.3	2.7	5.9	3.3	10.0
C <sub>31</sub>	2.5	0	0.4	0.8	0	0.7	0	0.6	0.7	1.1	0.6	3.0
C <sub>32</sub>	3.6	0	0	1.5	1.6	1.1	1.2	1.0	1.7	2.1	1.8	6.3
C <sub>33</sub>	2.0	0	0	0.7	0	0.7	0	0.8	1.1	0	0.6	3.0
C <sub>34</sub>	2.8	0	0	1.5	1.3	1.3	1.8	1.5	2.3	2.1	2.2	2.5
@	109.1	11.5	7.2	80.9	77.5	35.6	73.5	67.5	65.9	81.8	70.2	160.4
<i>n</i> -Alkan-2-ones (µg/g OC)												
C <sub>22</sub>	0.4	0.1	0.1	0.1	0	0.2	0	0.1	0.1	0.2	0.2	0.6
C <sub>23</sub>	6.6	3.8	6.3	6.7	5.9	4.2	11.4	7.5	8.4	2.5	5.8	58.8

C <sub>24</sub>	1.9	0.5	0.7	0.7	0	0.4	0.8	0.6	1.3	0.5	1.8	1.8
C <sub>25</sub>	12.1	6.6	11.2	12.5	10.8	6.6	18.1	11.6	14.8	5.2	13.4	10.2
C <sub>26</sub>	5.2	1.3	3.1	0.6	0	0.4	7.0	2.5	3.8	1.3	6.2	4.6
C <sub>27</sub>	13	4.5	5.4	2.5	4.4	2.3	4.7	4.9	11.4	3.8	16.7	16.5
C <sub>28</sub>	3.6	0.8	1.3	1.2	1.1	0.7	0	1.7	2.0	1.4	2.7	5.3
C <sub>29</sub>	8.2	1.4	2.7	3.1	2.5	1.2	2.8	3.6	4.6	4.3	7.3	16
C <sub>30</sub>	3.5	0.4	1.2	0.6	0.8	0.7	0	1.6	1.5	0	2.1	4.4
C <sub>31</sub>	9.1	0.5	3.4	3.1	5	1.5	4.6	4.9	4.0	5.7	15.4	13.7
C <sub>32</sub>	1.6	0.3	1.1	0.5	0	0.6	0	1.5	1.9	0	0	0
C <sub>33</sub>	10.8	1.4	3.9	2.4	0	0.7	2.6	4.4	6.2	0	13.0	7.0
C <sub>34</sub>	6.1	0	3.6	1.0	0.8	1.8	0	0	0	0	0	0
C <sub>35</sub>	3.8	0.3	0.9	0.7	0.6	0.9	2.5	1.5	1.6	0	1.9	4.1
C <sub>36</sub>	1.7	0	0	0	0	0	0	0	0	0	0	0
C <sub>37</sub>	3.0	0	0.3	0	0	0.5	0	0	0	0	0	0
@	90.6	21.8	45.1	35.7	31.8	22.7	54.5	46.4	61.6	24.9	86.4	143.0
Steroids (µg/g OC)												
Cholestanol	5.3	1.0	1.4	1.8	2.3	1.2	1.6	1.5	2.1	0	1.7	4.1
24-Ethycoprostanol	8.0	2.4	3.6	4.5	4.3	2.5	3.5	2.1	3.5	1.3	0.9	2.3
Campesterol	15.7	5.1	5.7	6.3	10.0	5.1	6.7	4.5	8.3	3.7	7.4	9.8
Campestanol	15.6	2.3	2.7	4.6	5.7	3.0	5.1	3.7	5.0	3.2	3.3	8.4
Stigmasterol	15.3	3.6	4.3	5.0	6.4	3.1	4.8	3.6	5.0	2.2	4.7	12.6
-Sitosterol	86.4	23.3	25.3	30.3	41	23	36.1	23.8	40.9	18.4	56.4	41.7
Stigmastanol	70	15.9	20.2	24.8	28.4	15.7	26.2	20.1	31.2	13.8	26.3	39.4

@	216.3	53.5	63.1	77.3	98.1	53.7	83.9	59.2	96.1	42.6	100.7	118.1
Terpenoids ( $\mu\text{g/g OC}$ )												
Taraxer-4-one	0	0	0	1.4	3	1.8	3.2	0	2.7	4.4	41	7.2
$\delta^{13}\text{C}$ (‰)												
<i>n</i> -Nonacosane	-32.9	-30.5	-31	-31.6	-31.2	-31.4	-32.5	-33.1	-33.2	-34.3	-33.8	-34.1
<i>n</i> -Hentriacontane	-35.5	-	-35.3	-35.6	-35.1	-34.9	-34.1	-34.1	-33.9	-35.0	-35.8	-35.4
<i>n</i> -Heptacosan-2-one	-31.3	-30.5	-30.6	-30.9	-30.9	-31.8	-31.4	-31.7	-30.8	-33.3	-31.0	-33.2
$\beta$ -Sitosterol	-28.9	-26.6	-25.0	-25.2	-27.7	-27.1	-27.8	-28.5	-28.0	-29.3	-32.1	-28.9
1-Tetracosanol	-33.3	-33.5	-33.0	-32.9	-32.9	-32.8	-	-32.0	-32.3	-32.7	-33.0	-34.0
1-Octacosanol	-34.8	-34.7	-34.7	-34.7	-34.3	-34.4	-33.5	-33.0	-32.9	-32.7	-34.1	-33.4

<sup>a</sup> Dates shown are values obtained from linear interpolation of calibrated <sup>14</sup>C ages.

**Fig.1.** Map of Galway Bay area including study site location.

**Fig. 2.** Study location, recently exposed peatland with protruding tree stump at Spiddal, Co. Galway, Ireland.

**Fig. 3.**  $^{14}\text{C}$  age values obtained from humic substances of seven samples from the peat profile (left) as well as cal. age results calculated using OxCal 4.2 with IntCal13 calibration curve (right).

**Fig. 4.** Total organic carbon (TOC, %), total nitrogen (TN, %), C/N and total sulphur (TS, %) trends.

**Fig. 5.** *n*-Alkane proxies assessing the relative amounts of *Sphagnum* contribution at each depth. From left to right;  $\text{C}_{23}/\text{C}_{29}$ ,  $\text{C}_{23}/\text{C}_{31}$ ,  $\text{P}_{\text{aq}}$ , P-wax, CPI from  $\text{C}_{25} - \text{C}_{33}$  and ACL from  $\text{C}_{23} - \text{C}_{33}$ .

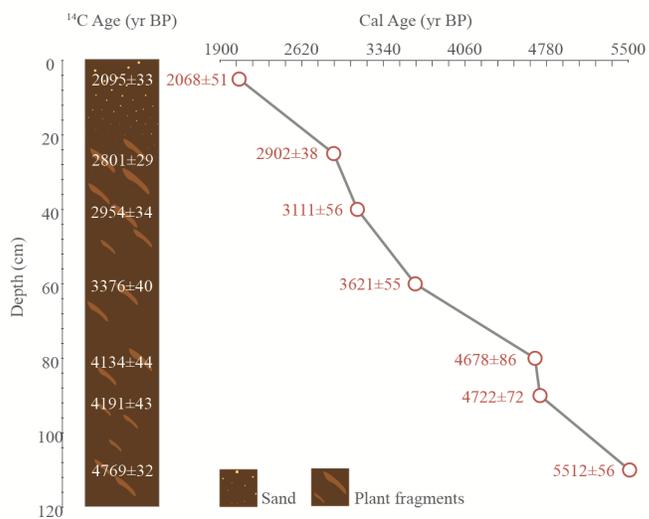
**Fig. 6.** From left to right; ratio of  $C_{27}$  *n*-alkan-2-one/ $C_{31}$  *n*-alkane ( $C_{27\text{-one}}/C_{31\text{-ane}}$ ), *n*-alkanol ACL from  $C_{22} - C_{30}$ , and alc/alc+alk (measure of diagenesis) ratio.

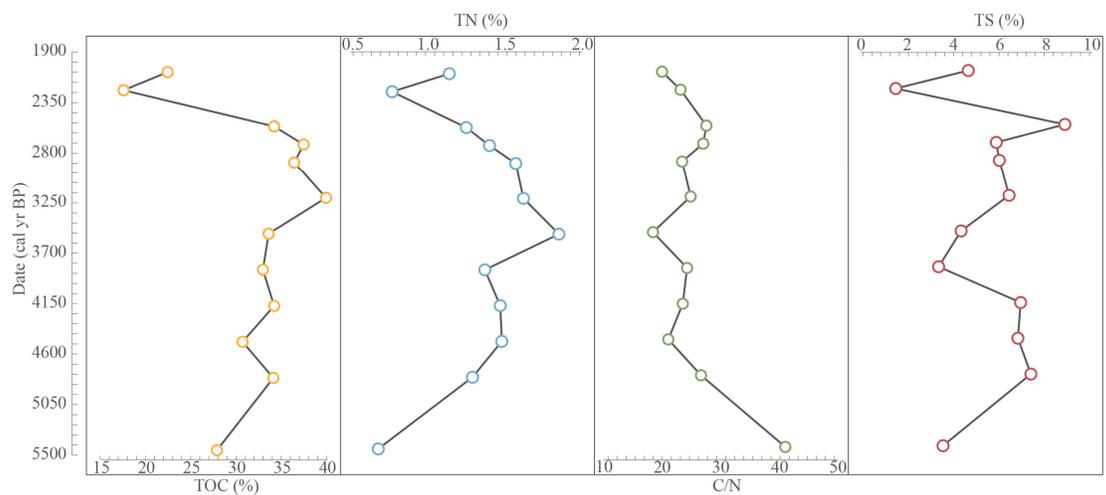
**Fig. 7.**  $C_{23}/C_{31}$  *n*-alkane ratio trend displaying shifts between relatively warm and dry conditions and relatively cold and wet conditions. Previously reported climatic events, the Subboreal-Subatlantic Transition (SB/SA) and 4.2 ka Event (4.2 ka), are marked with dashed lines.

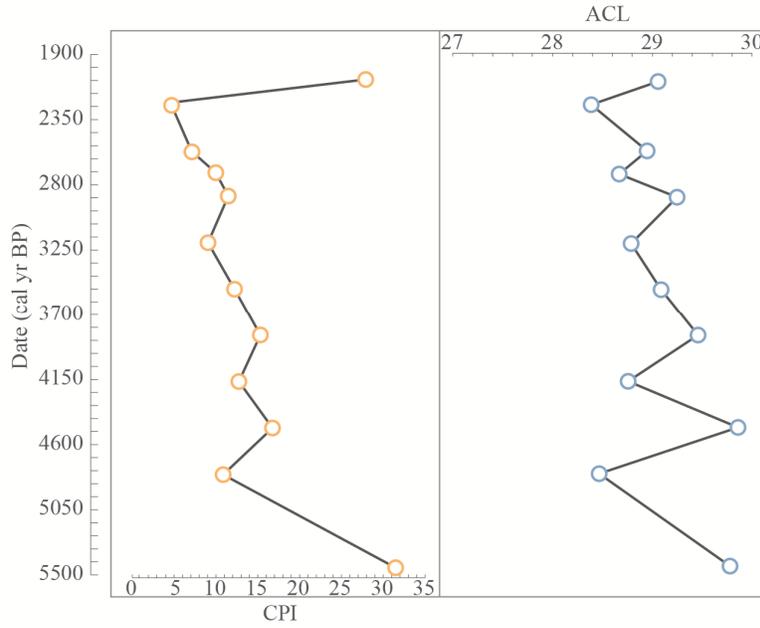
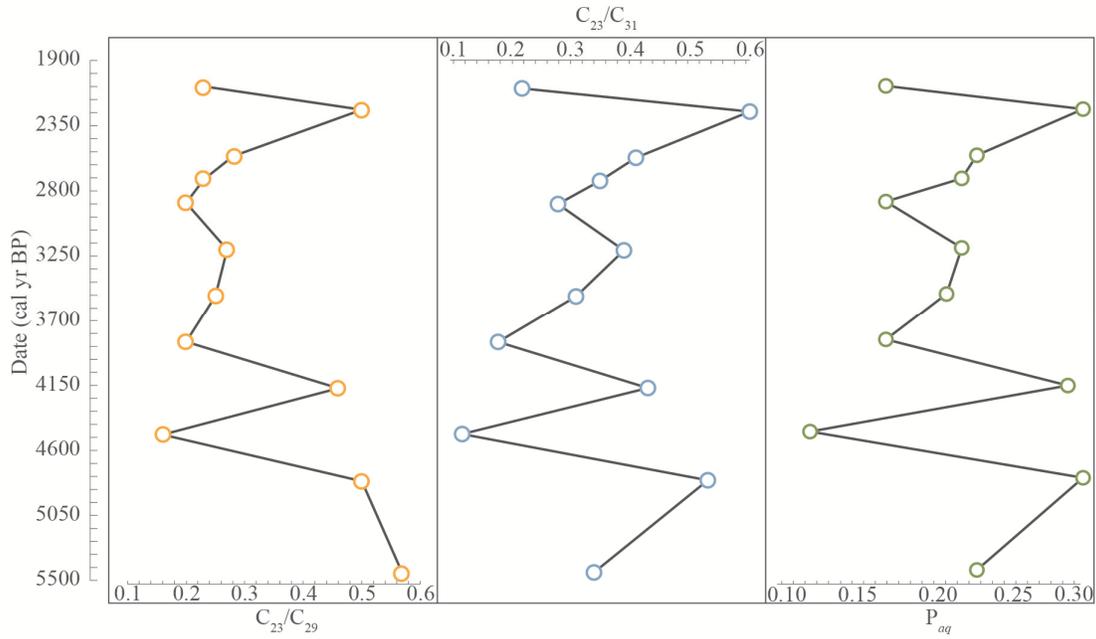


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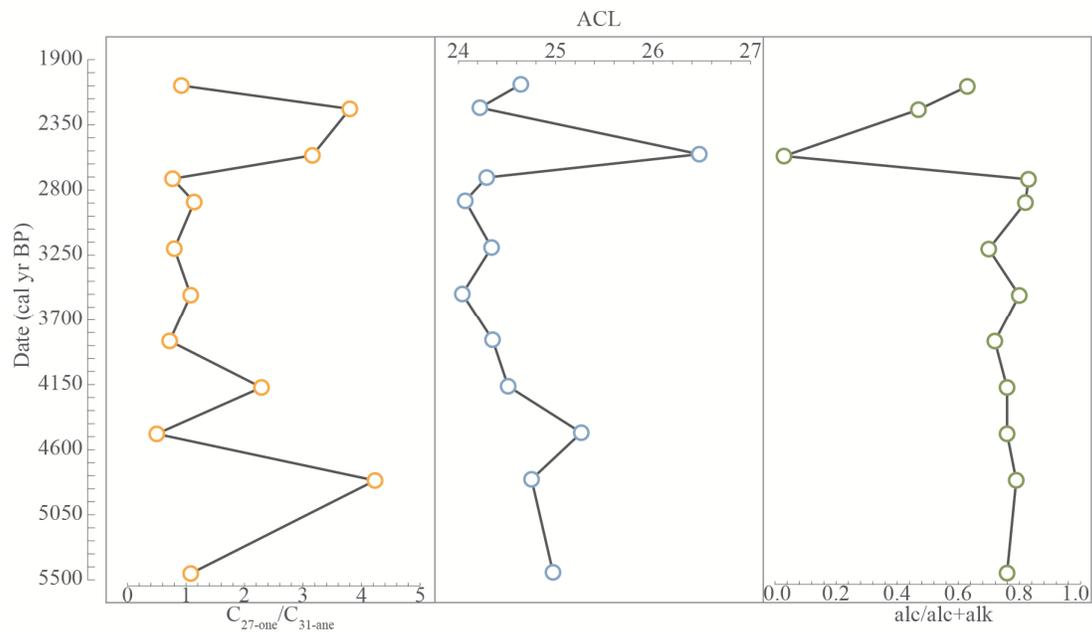




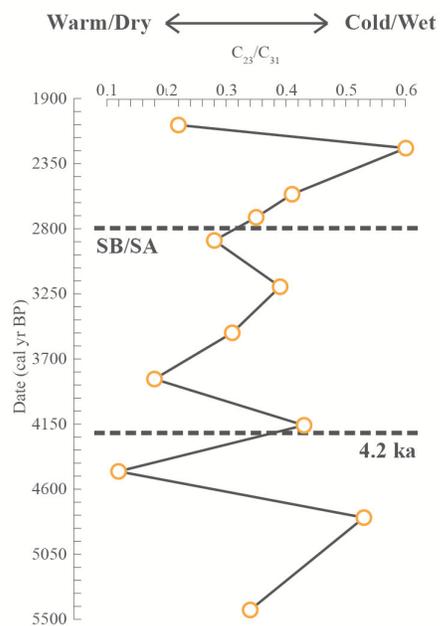




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### Highlights

•Elemental, GC-MS and GC-IRMS analysis of organic matter (OM) from a coastal peat bog. •Changes in climate over a ca. 3400 yr period during the mid-Holocene. •Evidence of the 4.2 ka event and Subboreal-Subatlantic transition in Ireland. •Implications for environmental conditions resulting in formation of a 'drowned' forest landscape.