A multiproxy (micro-XRF, pollen, chironomid and stable isotope) lake sediment record for the Lateglacial to Holocene transition from Thomastown Bog, Ireland

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Abstract

A multiproxy Lateglacial environmental record is presented for a c. 3.5 m lacustrine sequence retrieved from a small basin (c. 2 km^2) at Thomastown Bog in County Meath, Ireland. Sediment chemistry, pollen, chironomid and stable isotope data provide a detailed picture of catchment and lake system changes from the end of the last glacial (GS-2a) to the early Holocene that correspond closely to existing local and regional models of climate change. Concomitant adjustments in independent proxy records are matched to the NGRIP oxygen isotope curve giving 12 event-episodes ranging from major climatic shifts to lower amplitude, centennial to sub-centennial-scale adjustments, including a previously unreported regressive period of landscape instability during the northwest European 'Rammelbeek Phase' (RBP). The study emphasises the potential of palaeoenvironmental reconstruction from sediment chemistry where the sediment mixing system reflects autochthonous vs. allochthonous inputs. The investigation also indicates problems of interpreting isotope data derived from bulk marl due to possible lag effects controlling the delivery of soil and groundwater and multiple sources of HCO^{3-} (aq). These research findings have implications for core site selection and for studies attempting to use stable isotopes for correlation purposes.

KEYWORDS: Ireland, lake sediments, Lateglacial, multiproxy, palaeoclimate

1.0 Introduction

Research on lake sediment archives allied to the application of multiproxy environmental indicators has led to a significant increase in our understanding of terrestrial palaeoenvironmental change. The period spanning the end of the last glacial to the early Holocene has revealed important insights into the timing and magnitude of biogeomorphic system responses to climate forcing, with advancements in ^{14}C AMS dating establishing broadly synchronous or 'phase-locked' adjustments in northwest Europe across major climate boundaries (O'Hare *et al*., 2005; Walker *et al*., 2012). Palaeolimnological records have furthermore identified a number of centennial-scale cold episodes during periods of climate amelioration following the Weichselian glacial (Lowe *et al*., 1994; Björck *et al*., 1998; Walker, 2001; van Raden et al., 2013). These episodes, characterised by landscape instability, are believed to be related to climate deterioration following freshwater disruption of the North Atlantic thermohaline circulation (THC) (Clarke *et al*., 2001, 2002). These lower magnitude events are important because they reflect system adjustments that may be commensurate with contemporary climate shifts. They provide markers to test theory on landscape sensitivity to climate change at different temporal and spatial scales.

Palaeoenvironmental research on Irish lacustrine sediments has demonstrated local and regional biogeomorphic sensitivity to climate change (Swindles *et al*., 2013), based upon pollen, stable isotope and, in more recent studies, the use of chironomid palaeotemperature records (e.g. Holmes *et al*., 2010; Watson *et al*., 2010; van Asch *et al*., 2012). Major and centennial-scale shifts in climate have been reported across the Lateglacial, although there has been a lack of consistency in the timing of major and frequency of minor events (e.g. Walker *et al*., 2003). Modern studies on lake sediments have almost exclusively focused on the west and northwest of Ireland, where palaeoenvironmental records are expected to closely couple Atlantic Oceanic climate and open water bodies attest to the preservation of multimillennial-scale lake sediment sequences (e.g. Andrieu *et al*., 1993; Ahlberg *et al*., 1996; O'Connell *et al*., 1999; Diefendorf *et al*., 2006, 2008; Watson *et al*., 2010; van Asch *et al*., 2012). The east of Ireland, however, offers a wealth of palaeoenvironmental potential in the form of raised bogs and mires overlying lacustrine sediments. These sediment sequences provide an opportunity to explore temperospatial response to palaeoclimate events across Ireland, together with teleconnections to lake records in Britain and continental Europe. This paper presents an investigation of a palaeoenvironmental record for the Lateglacial to Holocene transition from a palaeolake sediment sequence at Thomastown Bog in the east of Ireland. The study employs a range of complementary palaeoenvironmental proxies, including for the first time in Ireland micro-XRF core scanning that enables geochemical sedimentary analysis at resolutions beyond conventional sub-sampling approaches (Croudace *et al*., 2006). The aim of the paper is to explore evidence of environmental change across the Lateglacial to Holocene transition in the context of existing national and regional palaeoclimate records. In so doing, the study considers the potential for multiproxy investigations in this setting and highlights some challenges for palaeoenvironmental reconstruction from non-laminated lake sediment sequences under these conditions.

2.0 Site description

Thomastown Bog (TTB) (53°39'26"N, 6°28'23"W) is located in a c. 2 km^2 basin, approximately 16 km due west of the Irish Sea coast (Fig. 1). The bog itself presently covers an area of c. 0.6 km^2 and is underlain by a lake marl sequence which is typical of raised bogs in Ireland (Mitchell and Ryan, 1997). The small size of the basin means that the lake has no major channel inlets and the surface hydrology is dominated by direct rainfall and sheetwash, with soil and groundwater flows contributing to lake recharge (Meehan *pers. comm.)*. The underlying geology comprises largely impermeable Namurian shales and sandstone to the northwest and Dinantian pure bedded limestone that forms part of regionally important aquifer to the southeast. The climate is predominantly oceanic, with some continental influences from the European landmass. Like most of lowland Ireland, the area was glaciated during the Weichselian glaciation (locally known as the Midlandian) and occurred between 18 and 17 ka BP, based on ice sheet deglaciation models (Clark *et al*., 2010). The origin of the basin is not documented, but is likely to relate to glacial scour (Meehan *pers. comm.*).

Soils in the basin are derived mainly from tills originating from the Namurian rocks to the north rather than Carboniferous limestone to the south with carbonates derived primarily from sub-surface drainage and groundwater.

3.0 Materials and methods

3.1 Fieldwork

Coring of Thomastown Bog (TTB) took place in October 2009 following preliminary assessment of lake sediment thickness and distribution at a number of test sites (Fig. 1). Inaccessibility prevented a complete bathymetry of the site being established, and borehole TTB1 was selected because it provided the thickest, and most intact and variable Lateglacial sequence. Test borehole sites towards the centre of the former lake contained less marl sediment and a higher proportion of organic-rich sediment less suitable for high resolution core scanning.

Cores were extracted using a Russian corer with a 50 mm diameter, which minimized contamination of the sequence. A total of 11 core sections with c. 10 cm overlaps were acquired to a depth of c. 5 m for core TTB1. Sections were individually sealed and stored at 4°C. Eight of these sections contained minerogenic lake sediments and were subject to detailed multiproxy analyses.

3.2 Lithological and geochemistry

Lithological composition was determined by loss-on-ignition (after Bengtsson and Enell, 1986; Heiri *et al*., 2001) on 1 cm^3 of sediment. Optical imaging, X-radiography and micro-XRF analysis was carried out using an Itrax™ Core Scanner, with a scan step-length of 200 μm and a count time of 30s. XRF core scanning data are recorded as peak area integrals and raw data were normalised using kilo counts per second (kcps) to account for variations in XRF intensities and reduce matrix effects (Jouve *et al*., 2013). Selected elements (Si, S, K, Ca, Ti, Fe, Mn, Sr) with an analytical precision of <10% are reported, together with the ratio of Compton (incoherent) to Raleigh (coherent) scatter that can be employed as a proxy for organic carbon (Guyard *et al*., 2007). The XRF data were used to composite and splice the overlapping core sections, using the UIC software Correlator (v. 1.65). The resulting integrated depth of core sections for the TTB sequence reported in cm represents a composite core depth.

3.3 Chronology

Radiocarbon dates were obtained from discrete 1 cm sub-samples along the TTB sequence. Poor preservation of macrofossils in the lower portion of the core meant that the two oldest dates were derived from bulk organic carbon. Ages were calibrated using Calib 7.0 software (Stuiver *et al*., 2013) and the INTCAL13 calibration curve (Reimer *et al*., 2013). Bchron (Haslett and Parnell, 2008) was used to construct an age-model. Due to limited radiocarbon dating potential, additional tests were conducted across 10 cm sections (10 cm^3) for the presence of crytotephra using heavy liquid separation (Turney, 1998). No evidence of tephra was found in the TTB1 sediments, but a more robust and wider assessment would be required to fully eliminate the potential for finding Lateglacial tephra shards at the TTB site.

3.4 Pollen

Pollen analysis was carried out on 37 sub-samples along the core length. Standard pollen extraction techniques were employed (Moore *et al*., 1991), with further acetolysis to remove the significant organic fraction. Pollen counts of up to 600 grains Total Land Pollen (TLP) per sample were identified and counted where absolute numbers and preservation permitted. Pollen diagrams based on these data were produced using Tilia and Tilia Graph (Grimm, 1991), with percentages calculated as follows: Sum = % total dry land pollen (tdlp); Marsh/aquatic herbs = % tdlp + sum of marsh/aquatics; Ferns = % tdlp + sum of fern spores; Misc. = % tdlp + sum of misc. taxa. Taxonomy follows that of Moore and Webb (1978) modified according to Stace (1992) and Bennett *et al*. (1994) for pollen types. Zonation of the diagram was undertaken by eye.

3.5 Chironomids

Chironomid samples were analysed at low resolution (n=25) to provide an independent proxy for palaeotemperature changes at targeted positions along the TTB core. Sample preparation was carried out using standard techniques for carbonate-rich samples (Brooks et al., 2007). Chironomid head capsules were manually picked using fine forceps under a stereo microscope. Capsules were slide mounted using Hydromatrix™ and identified using Wiederholm (1983), Oliver and Roussel (1983), Schmid (1993), Rieradevall and Brooks (2001) and Brooks et al. (2007). At least 50 head capsules were found in all but three samples (422 cm, 47.5 head capsules; 457 cm, 27.5 head capsules) and 489 cm (11.5 head capsules), which is the minimum number it is sensible to use when producing quantitative reconstructions from Chironomid data (Heiri and Lotter, 2001; Larocque, 2001; Quinlan and Smol, 2001).

Chironomid count data were converted to percentages for the chironomid stratigraphic (percentage) diagram produced using Tilia 2.0 and TGView (Grimm, 2004). Zoning was carried out using CONISS (Grimm, 1987). Detrended correspondence analysis (DCA) was undertaken in CANOCO (ter Braak and Šmilauer, 2002) to establish the compositional gradient of the stratigraphic data. Mean July air temperatures were obtained from the fossil chironomid data by applying the Norwegian July air temperature transfer function (Brooks and Birks, 2000, 2001; Heiri *et al*., 2011; Self *et al*., 2011) to the chironomid percentage data using C2 version 1.4.3 (Juggins, 2006).

3.6 Stable isotopes and C/N

Analyses for $^{13}C/^{12}C$ on organic matter were performed on decarbonated 2 cm^3 sub-samples by combustion in a Costech Elemental Analyser (EA) on-line to a VG TripleTrap and Optima dual-inlet mass spectrometer, with isotope values ($\delta^{13}C$) calculated to the VPDB scale using a within-run laboratory standards calibrated against NBS18, NBS19 and NBS22. Replicate analysis of well-mixed samples indicated a precision of ±<0.1‰ (1σ). C/N ratios were calibrated against an Acetanilide standard. The C/N ratios were multiplied by 1.167 to yield atomic ratios (after Meyers and Teranes, 2001).

For $^{13}C/^{12}C$ and $^{18}O/^{16}O$ analysis of carbonates the same sampling intervals were used. Samples were disaggregated in 5% sodium hypochlorite solution to oxidise reactive organic material, washed in distilled water and sieved at 63 μm to remove any shelly material. The <63 μm fraction was dried at 40°C and ground. The isolated material was reacted with anhydrous phosphoric acid in vacuo overnight at a constant 25°C, and the CO_2 collected for analysis. Measurements were made on a VG Optima mass spectrometer. Overall analytical reproducibility for these samples was better than ±0.1‰ for $\delta^{13}C$ and $\delta^{18}O$ (2σ). Isotope values ($\delta^{13}C$, $\delta^{18}O$) are reported as per mil (‰) deviations of the isotopic ratios ($^{13}C/^{12}C$, $^{18}O/^{16}O$) calculated to the VPDB scale using a within-run laboratory standard calibrated against NBS standards.

4.0 Results and discussion

4.1 Lithology, geochemistry and chronology

The TTB sequence has been divided into seven sediment units based on lithology and chemostratigraphy (Fig. 2, Table 1). The full sequence shows the evolution of a lake sedimentary sequence from a system dominated by minerogenic sediments at the base (unit 1), through a phase of lake marl production, punctuated by periods of elevated minerogenic input (units 2-4), to a phase of lake shallowing (unit 5), and finally full terrestrialisation (units 6 and 7). The XRF profiles in Fig. 2A indicate a simple mixing system of autochthonous sediment, rich in carbonates, and allochthonous clastic silicates washed in from the surrounding lake basin. Principal components analysis (PCA) ordination performed on centred log ratios of the elements following methods developed for compositional data analysis (Aitchison, 2003; Tolosana-Delgado, 2012), supports this hypothesis with detrital indicator elements (e.g. Fe, Si, Ti and K) plotting opposite elements associated with autogenic biochemical precipitation (e.g. Ca, Sr) (Fig. 2B). Similar sediment mixing patterns have been widely reported in carbonate lakes (e.g. Mayle *et al*., 1997; Walker *et al*., 2003). The dominance of Component 1 in Fig. 2B suggests that detrital carbonate influences are less significant in explaining the elemental composition in the TTB lithological record, probably because of the predominance of non-calcareous tills and surface soils across much of the TTB basin. Additionally, the PCA plot shows that second order changes related to the relative proportions of Mn and inc/coh ratio exist. These secondary effects, which accounted for 16.2 % of the geochemical variance in the sequence, are possibly linked to variable redox conditions in the lake with the organic matter proxy (inc/coh) reflecting preservation of organic matter under reduced sediment oxygen conditions (Boyle, 2001).

The chronology of the TTB sequence is constrained by five ^{14}C dates spanning the Lateglacial to Holocene transition (Table 2). However, the relatively low number of ^{14}C dates and the absence of dateable material at the boundary between units 3 and 4 limits the construction of a robust age model (Fig. 3). The lower two ^{14}C dates acquired on bulk material may have been subject to hardwater effects that are difficult to model (Grimm *et al*., 2009). Diefendorf *et al*. (2006) reported hardwater effects of 1575 years for carbonate lake sediments in Lough Inchiquin, west Ireland. Among a number of studies in Ireland (e.g. Cwynar and Watts, 1989; Ahlberg *et al*., 1996; O'Connell *et al*., 1999; Diefendorf *et al*., 2006; Head *et al*., 2006; Waston *et al*., 2011, van Asch *et al*., 2012) and Britain (e.g. Walker *et al*., 2003) there have been differences in the ^{14}C dating of important event boundaries, including the end of the last glacial, and the start and termination of the Younger Dryas. Although this could be attributed to time transgressive climate forcing, this may result from imprecision in ^{14}C dating of this period (Telford *et al*., 2004; Walker *et al*., 2012). All factors considered the ^{14}C dates are presented here as range-finder dates rather than precise chronostratigraphic markers and the age model in Fig. 3 is not considered sufficiently robust for direct correlation to regional palaeoenvironmental change records.

4.2 Pollen

Pollen frequencies in the TTB sediment were relatively low for much of the sequence, and only in the top of the core was there sufficient pollen to establish c. 600 total sum counts. The pollen record nevertheless exhibits a vegetation succession, which can be divided into six local pollen assemblage zones (LPAZs) (Table 3, Fig. 4) on the basis of established models of regional vegetation development for the period (Watts, 1977, 1978; O'Connell *et al*., 1999).

From the base, LPAZ1 (495-c. 460 cm) is indicative of a cold, open environment, associated with heliophilous plants and plant communities. High values of *Pinus* (up to 60%) associated with pre-Quaternary spores and degraded *Tilia* pollen suggest reworking of sediment of earlier interglacial deposits and/or local bedrock (*c.f.* O'Connell *et al*., 1999), and reflects the very low pollen counts at the base of the TTB core. There was an absence of pollen from 465 cm to 445 cm reflecting a lack of preservation in the TTB sediments. Coupled with the low pollen counts (<200) and distortions that arise from the percentage data, this make definitive interpretation of the top of LPAZ1 problematic.

In general LPAZ II represents the local and regional vegetation in which a mixture of *Juniperus*, low shrub and herbaceous taxa are dominant. *Juniperus* which dominates TLP in LPAZ II appears in Irish pollen diagrams at around 12.4k ^{14}C cal a BP (Coxon and McCarron, 2009) and is linked to climate amelioration. Elevated *Pediastrum* values at the start of LPAZ II are indicative of the establishment of a lacustrine environment at the site, although the laminated sediments in unit 1 may be due to open water before this time. *Pediastrum* values increase to c. 60% and *Isoetes* (5-12%) and *Alisma* type (<2-6%) show that a lacustrine environment was well established by this time, and are indicative of climate amelioration and increasing biological productivity (Watts, 1997).

Zone LPAZ III is characterised by an abrupt decline in the domination of *Juniperus* and the expansion of rich and diverse open ground flora, in particular, Poaceae (70-80%), *Helianthemum* (3%) and *Thalictrum* (2-5%). A similar shift in vegetation assemblages is widely recorded in palaeobotanic records from Ireland. This is generally attributed to a cooling trend in climate (Walker *et al*., 1994; O'Connell *et al*., 1999; Coxon and McCarron, 2009), although a recent multiproxy investigation (chironomid, stable isotope and pollen) at Fiddaun in the west of Ireland reported no substantial decrease in summer temperature at this regionally-defined vegetational transition (van Asch *et al*., 2012; van Asch and Hoek, 2012).

The boundary between LPAZ III-IV is dated to 11,205+/-34 ^{14}C a BP (13015-13138 cal a BP) and appears to mark the onset of the Younger Dryas (YD) stadial. The pollen record shows plant communities associated with steppe tundra and low alpine scrub (e.g. *Artemisia*) typically associated with this period in Ireland (Walker *et al*., 1994). The position of the upper boundary of LPAZ IV is hampered by the gap in the pollen record where pollen counts were low <150. This could reflect a vegetation sparse landscape, but other palaeotemperature indicators in the TTB record indicate warming had begun by this time, so may be explained by higher sedimentation rates at the start of the Holocene combined with sparse vegetation following the end of the YD period.

LPAZ V shows a typical pattern of seral vegetation changes indicative of rapid climate amelioration. The largely treeless landscape was initially colonised by the thermophilous taxon *Juniperus* and *Salix*, and subsequently *Betula*, which peaks at 80%. A drop in algal *Pediastrum* levels to <5% and a corresponding increase in *Potamogeton* type could indicate changes in lake productivity. However, drier conditions are evident from the growing presence of *Dryopteris* (monolete) type and a decline in *Cyperaceae* values from the previous zone. These vegetation changes correspond to evidence for lake shallowing in lithological unit 5. LPAZ VI marks the transition to a woodland landscape dominated by *Corylus* (up to 98% TDLP), which has been documented elsewhere in Ireland (e.g. Ghilardi and O'Connell, 2013). The continuing decline in Pediastrum and other aquatic indicators, together with the extirpation of *Salix* during this phase, indicates further contraction of the lake.

4.3 Chironomids

A total of 81 taxa were identified in the TTB samples. The chironomid stratigraphy shows a clear development of communities through the sequence that has been divided into five zones (Fig. 5, Table 4). The lowermost samples in zone TTB-C1 correspond to lithological unit 1. These have a low density of head capsules and are dominated by cold stenotherms including *Corynocera oliveri*. In Zone TTB-C2, *C. oliveri* remains present, while a warmer adapted community develops moving into lithological unit 2, with the appearance of *Ablabesmyia*, *Chironomus anthracinus*-type and *Dicrotendipes*. *Microtendipes*, commonly found in Lateglacial sediments from northern Europe, is known to be an indicator of intermediate temperatures and occurs at relatively high levels throughout this zone (Brooks and Birks, 2001). The assemblage in Zone TTB-C3 is dominated by *Corynocera ambigua*, noted for occurring in cold oligotrophic lakes in northern Europe (Brooks *et al*., 2007). However, Brodersen and Lindegaard (1999) found the taxon occurred in warm shallow eutrophic lakes in Denmark, and Brooks and Birks (2001) described it as an intermediate taxon in terms of temperature preference. *C. ambigua* often occurs abundantly in relatively short sections of a stratigraphic sequence (Brooks *et al*., 2007). In Zone TTB-C4 there is a change in chironomid assemblages suggesting a return to colder temperatures, which is correlated with the boundary between lithological units 2 and 3. There is a disappearance or decline in the presence of warm stenothermic taxa in this zone, accompanied by the appearance of, or increases in cold adapted taxa such as *C. Olivra, Micropsectra insignilobus*-type and *Sergentia*. The chironomid assemblages in zone TTB-C5 indicate a return of warm stenothermic chironomid taxa at the boundary between lithological units 3 and 4. A number of the taxa in this zone (e.g. *Ablabesmyia* and *Dicrotendipes* and *Endochironomus*) are known to be associated with macrophytes (Brooks *et al*., 2007) and support pollen and lithogenic evidence for lake shallowing at this time.

The chironomid-inferred mean July air temperature profile shows a reconstructed temperature range from 10.0 °C (282 cm) to 15.2 °C (196 cm). The mean sample specific prediction error is 1.25 °C, although this reduces to 1.17 °C without the two samples with the lowest head capsule count. The chironomid-inferred temperature reconstruction is similar in pattern to the DCA axis 1 scores (Fig. 5), suggesting that temperature parallels the main assemblage trends. The Younger Dryas cooling of approximately 4 °C is clearly indicated and corresponds to the lithological unit 2-3 boundary. The magnitude of temperature change is similar to that found using other proxy records from Britain and Ireland (e.g. Brooks and Birks, 2000; Bedford *et al*., 2004), while a cooling of c. 2 °C in the early Holocene is likely to represent the Preboreal Oscillation (Björck *et al*., 1997).

4.4 Stable isotopes and C/N

Total organic carbon (C_{org}), total nitrogen (N_{tot}) and the atomic C/N ratio are shown in Fig. 6A for the minerogenic portion of the TTB core (4.95-1.82 m), alongside $\delta^{13}C$ and $\delta^{18}O$ profiles. The C_{org} values range from <5% in the basal silty-clays of lithological unit 1, to c. 45% in the calcareous sediments of unit 5. Bulk C_{org} and N_{tot} values were strongly correlated throughout the core ($r^2 = 0.978$, intercept at origin), and the C/N ratio therefore provides an indicator of dominant source types for organic matter in the TTB lake sediments. The C/N values range from c. 10 at the base of the core to c. 16 at the top of unit 5 indicating a mixture of aquatic and terrestrial organic matter (Meyers and Lallier-Verges, 1999). C/N values generally show an upward increasing trend, punctuated by peaks that correspond to elevated detrital sediment inputs (see arrows in Fig. 6A), indicating inwash of terrestrial organic matter and/or reduction in lake productivity. The peak in C/N from 220 to 190 cm corresponds to the coarsening upwards sequence in unit 5 and is likely to reflect a terrestrial organic matter source from local plant material during lake shallowing (Meyers, 1997).

The $\delta^{13}C_{org}$ data ranges from –26‰ to –15‰, with major isotopic shifts (5‰ to 8‰) corresponding to the lithological unit boundaries. The most depleted values of –26‰ in units 1 and 3, correspond to low TOC and C/N suggesting lower productivity rather than a significant increase in terrestrial organics. The highest values (–15‰) are observed in unit 5, while a discrete peak of –16‰ at 395 cm in unit 3 is probably due to rapid burial of organic matter (Meyers, 1997). There is no clear trend through the profile, although unit 3 generally has increasingly negative values, punctuated by two broad peaks at c. 335 cm and c. 300 cm. In units 4 and 5 there are stepped increases to heavy isotopic values closely matching the C/N curve. While C/N values indicate a mixture of aquatic and terrestrial plants, the $\delta^{13}C_{org}$ values are higher than expected reaching values characteristic of C4 terrestrial plants in unit 5 (Fig. 6B). Given that C4 plants are more adapted to dryland conditions (Ehleringer *et al*., 1999), a probable explanation for this $\delta^{13}C_{org}$ enrichment is the use of HCO_3^- by submerged aquatics during photosynthesis (Talbot and Johannessen, 1992; Meyers and Lallier-Verges, 1999). The peak in unit 5 which parallels the C/N curve, however, is more problematic because C/N suggests a terrestrial plant influence that corresponds to the lithogenics. It is possible, however, that residues from aquatic plants have been incorporated into the carbonate-rich sediments of unit 5, with rapid burial contributing to the elevated $\delta^{13}C_{org}$ values (e.g. Veres *et al*., 2009 and references therein).

The $\delta^{13}C_{carb}$ record in TTB closely matches the $\delta^{13}C_{org}$ curve, with some minor variation in the position and relative magnitude of peaks. Differences between $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ have been attributed to the relative importance of lake productivity versus terrestrial plant inputs (Schelske and Hodell, 1991). Carbon isotope values in authigenic carbonates are related to the isotopic composition of inflowing water, CO_2 exchange to the atmosphere and lake primary productivity (Leng and Marshall, 2004). Aside from the very base of the core, where carbonate content is low, the values for the $\delta^{13}C_{carb}$ in TTB are high throughout the core ($\bar{x}$ = +5.0‰, σ = 1.2‰, range = +2.2 to +7.0‰). These values are higher than would be expected for a short residence time lake (Talbot, 1990), even accounting for the HCO_3^- dissolution of limestone (Leng and Marshall, 2004; Diefendorf *et al*., 2008). Elevated $\delta^{13}C_{carb}$ has been attributed to degassing or methonogenesis (Valero-Garces *et al*., 1999) in longer residence time lakes. However, the expected role of lake productivity driving the $\delta^{13}C_{org}$ curve would suggest that carbon isotopic composition of $HCO_3^-(aq)$ is affected by productivity of algae and submerged aquatics (Leng and Marshall, 2004). These effects can lead to the photosynthetic enrichment of $^{13}C(aq)$ (Siegenthaler and Eicher, 1986; Talbot and Johannessen, 1992) and appear to have happened rapidly once the warming occurred at end of the last glacial. Leng *et al*. (1999) observed similar patterns in the Konya Basin during the Lateglacial in Turkey. For the most part excursions to isotopically-lighter values correspond to inputs of detrital sediments, with the other proxies indicating that this corresponds to periods of lower lake productivity.

Results for $\delta^{18}O_{carb}$ range from -5.4 to 1.7‰ ($\bar{x}$ = –3.4‰, σ = 0.6‰). High values at the base of the core may be erroneous because of the very low carbonate content, and the elevated value at the very top of the sequence is likely to be evaporative (Leng and Marshall, 2004). For most of the sequence the ranges are relatively invariant especially in unit 2 ($\bar{x}$ = –

3.8‰, σ = 1.0‰, range = –5.4 to –2.7‰). In small open lake basins $\delta^{18}O_{carb}$ generally relates to temperature-precipitation, while evaporation-precipitation effects become more important where residence times are longer (Leng and Marshall, 2004). What is evident in the TTB sequence is the poor correspondence between the $\delta^{18}O_{carb}$ record and the $\delta^{13}C$ records that more closely match the lithogenic variations shown in Fig. 2A. This could be related to lag effects in lake and catchment system response to changing temperature, but would equate to c. 150 years across the 2000 year long Lateglacial Interstadial. A response-relaxation time of this magnitude is unlikely for chironomids that show strong evidence of warming coincident with the top of unit 2 (see Fig. 5). A more probable explanation is that the $\delta^{18}O_{carb}$ record in TTB reflects multiple influences in the authigenic signal (Ito, 2001). In unit 4, which is interpreted as Holocene in age, the low $\delta^{18}O_{carb}$ signal suggests a cool climate that is best explained by stored water discharges to the lake from formerly frozen soil and possibly groundwater stores dating to the preceding stadial conditions. Groundwater recharge to the lake could also explain off-sets to other proxies during the Lateglacial Interstadial. It is also possible that there is an overprinted evaporative signal in other parts of the core due to the small size and relatively shallow depth of the lake at Thomastown. The recovery and subsequent fall at 228 cm observed in the $\delta^{18}O_{carb}$ profile on the other hand is consistent with other proxies and appears to mark an event in the catchment during the early Holocene (c. 11.2 ka). These variable and inconsistent matches to the other environmental proxies means that the interpretation of the $\delta^{18}O_{carb}$ curve is problematic and therefore cannot be used as a reliable alignment (wiggle-matching) tool at this site.

4.5 Environmental synthesis and comparison to the NGRIP $\delta^{18}O$ record

In Fig. 7 the key environmental indicators are drawn together to examine the timing and magnitude of environmental changes in the TTB sequence and correlations to the NGRIP $\delta^{18}O$ record (Lowe *et al*., 2008). Due to the aforementioned uncertainties in the age model and $\delta^{18}O_{carb}$ curve, correlations are made to the Ca/Ti profile which shows the relative importance of autogenic and allogenic (detrital) lake sediment production, which relates to climate and lake productivity. Ti is used as a divisor being stable in the environment and not affected by diagenetic alteration (Young and Nesbett, 1998; Croudace *et al*., 2006; Parker *et al*., 2006). Although the lithogenic records may be subject to time-transgressive effects, the small size of the TTB catchment means that the relative responses of carbonate production and catchment sediment inputs would be expected to be broadly synchronous over the timescales reported.

In total 12 climate ‘event-episodes’ (labelled 'a' to 'l') have been highlighted on the basis of correlation across at least three independent proxies. Of these event-episodes, four major periods of environmental instability can be clearly demarcated. These show a sharp fall in the Ca/Ti profile reflecting marked changes in the relative balance between autocthonous and allochthonous sediment inputs. It is noted that the $\delta^{18}O_{carb}$ record does not agree for some of these event-episodes (e.g. 'c'), possibly because of lag effects and/or other factors related to the provenance of $\delta^{18}O_{carb}$. Despite the limitations of the $\delta^{18}O_{carb}$ record, these four periods can be confidently correlated to the NGRIP $\delta^{18}O$ record. Phase 'a' and 'j' represent the end of the last glacial (GS-2a) and Younger Dryas (GS-1) cold episodes, respectively. Temperature shifts of 6-8 °C degrees have been reported for Ireland (Mitchell and Ryan, 1997), resulting in major shifts in vegetation and increases in landscape instability. Similarly, there is a marked lowering in lake productivity, with no biochemically-driven carbonate precipitation during these cold periods. Sedimentation rates were lower during the Younger Dryas, which is not unexpected given the small size of the catchment and has been observed in other Irish lakes during this period (Diefendorf *et al*., 2006; van Asch *et al*., 2012). The shift to climate amelioration appears to have been rapid, shown by a sharp lithological boundary. Pollen data at this time appear to show a lag in the recovery of the catchment, although this could be related to higher sedimentation rates during the thawing phase.

Episodes 'c' and 'l' have less marked shifts in all proxies, but still suggest catchmentwide periods of instability that were most likely caused by climate. Episode 'c' in the Lateglacial Interstadial is likely to be the 'Older Dryas' (Aegelsee Oscillation), which marks a climatic downturn separating the Bølling and Allerød warm periods (Wohlfarth, 1996). This event is believed to relate to temporary slowing down of North Atlantic Ocean circulation and has been detected across much of northwest Europe including Ireland (Benson *et al*., 1997). Instability in phase 'k' corresponds to the Pre-Boreal Oscillation (PBO) (Björck *et al*., 1997), which is marked by the $\delta^{18}O_{carb}$ and C-IT records being in phase. The fall in the Ca/Ti curve is probably due to a drop in productivity rather than an increase in detrital inputs (see Fig. 6A), because the pollen records show that the TTB landscape was stabilising at this time. The detrital indicators (e.g. Si, Ti and K in Fig. 2) register only a small increase during this event, the corollary of a less sensitive landscape response to the climatic downturn.

On top of these major climate events there are a number of event-episodes of lower magnitude and/or duration, where not all proxies show the same synchronous and consistent response. Episodes 'b', 'd' and 'e' are highlighted on the basis of a fall in Ca/Ti showing detrital inwash that coincides with minor oscillations in the stable isotope curves in authigenic carbonates. A slight increase in C/N is also indicative of inwash of organic matter, but the pollen record does not show any clear changes and variations in the low resolution CIT record are inconclusive. These episodes appear to be minor, but nevertheless significant periods of catchment instability that led to accelerated catchment erosion and a minor lowering of lake productivity. The boundary between the glacial (GS-2a) to interstadial (GI1e), (episode ‘b’) conditions, in particular, is characterised by adjustments in the balance of detrital inputs and carbonate precipitation as the landscape transitioned into this warm phase.

In the second half of the Lateglacial Interstadial the proxy records show two episodes that may reflect climate instability (‘f’, ‘i’); each followed by a peak in the Ca/Ti curve indicative of amelioration in catchment conditions (indicated at ‘g’, ‘h’). The precise onset and maxima of these event-episodes is difficult to pinpoint because of the variable/staggered response of the multiple proxies. However, there is a concomitant shift in vegetation in episode 'f' to open grassland, coinciding with a phased increase in detrital inputs. In a recent publication, van Asch and Hoek (2012) question the importance of climate over environmental factors (e.g. grazing, fires) at this transition. At Thomastown Bog, the C-IT record reveals a minor (c. 1°C) fall in July temperatures immediately before the regression to grassland, but this is followed by an apparent recovery immediately post-dating this change. The $\delta^{18}O_{carb}$ record meanwhile shows no conclusive evidence for cooling around this time, but there is a marked drop in lake productivity and carbonate production. It is possible that the record at TTB reflects accelerated catchment erosion resulting in the decline in arboreal cover unconnected to climate, but the importance of regional cooling as a driver for landscape change cannot be discounted at this site. Although not reflected in the pollen record which has already changed, the later episodes 'h' and ‘f’ correspond to significant responses in all of the proxies bar the $\delta^{18}O_{carb}$ profile, suggesting system-wide adjustments across the TTB catchment and lake at this time. These event-episodes can be more confidently correlated with climate episode GI-1b (Gerzensee Oscillation) of the NGRIP event stratigraphy and subsequent recovery.

4.6 Comparison of the Thomastown Bog records to other sites in Ireland, Britain and continental Europe

Fig. 8 builds upon a recent comparative study by van Asch *et al*. (2012), integrating C-IT (Fig. 8A) and $\delta^{18}O_{carb}$ (Fig. 8B) profiles from the west of Ireland, including those from TTB, and selected sites in Britain. Data are plotted alongside the Ca/Ti curve and event-episodes at TTB. The multiproxy record at TTB provides a link between the lake records from the west and northwest coast of Ireland and those reported for lakes in Britain.

The lower resolution C-IT record strengthens the existing picture of palaeotemperature changes across the period collated by van Asch *et al*. (2012), with the amplitude of variations closer to the low altitude sites in northwest England than those located along the west coast of Ireland. As reported elsewhere, this may reflect differences in the calibration sets used in the temperature reconstructions, physiographic effects and/or micro-climatological factors at the site (see Lang *et al*., 2010; van Asch *et al*. 2012). The results for TTB are also consistent with recently published C-IT inferred isotherm maps for northwest Europe (Brooks and Landgon, 2014), although summer temperatures for the last glacial and Younger Dryas (GS-1) are c. 1 °C higher for the TTB dataset.

Across Ireland and Britain, the Aegelsee (GI-1d) and Gerzensee (GI-1b) oscillations in C-IT and $\delta^{18}O$ records have been identified in the majority of climate reconstructions in Ireland, and TTB is consistent with these findings. A number of the profiles including the TTB Ca/Ti data appear to show additional shorter or lower amplitude events during the Lateglacial Interstadial, especially Lough Inchiquin in Co. Kerry, Ireland and Hawes Water in Lancashire, England but these are not well constrained chronologically. Under these circumstances scientists have sought to use temperature-based transfer functions and, in particular, oxygen isotopes for correlation purposes, but the striking similarities between the Ca/Ti curve at TTB and the other records in Ireland shows that sediment chemostratigraphy may be applied for this purpose where authigenic calcite fluctuates with climate (Molloy and O'Connell, 2004; Schettler *et al*., 2006). At TTB there is compelling evidence for a regressive event in the Lateglacial Interstadial between the Aegelsee (GI-1d) and Gerzensee (GI-1b) oscillations (event-episode 'f'), which may be present in a number of extant records (see Fig. 8).

In continental Europe, new isotopic research at Gerzensee lake, Switzerland indicates a number of centennial to decadal oscillations indicative of climate change during the Lateglacial (van Raden et al., 2013), and recent investigations on authigenic carbonates in SW Denmark have revealed lithostratigraphic evidence for a previously unreported phase of landscape instability during the 'Rammelbeek Phase' (RBP), post-dating the Preboreal Oscillation (Larsen and Noe-Nygaard, 2014). The timing of this latter event closely corresponds to the relative position of event-episode 'l' at TTB (Fig. 8A), which has not previously been reported in Ireland.

Although caution is urged in the independent interpretation of chemostratigraphic records for correlation purposes, lithological analysis employing high-resolution core scanning has the potential to glean new information from sedimentary deposits, meaning the preservation potential and sensitivity of allochthonous vs. autochthonous signals takes on a wider significance. The traditional approach of coring at the deepest part of a lake may therefore be less desirable in this context, because of the impacts of lake dynamics on both authigenic calcite precipitation (i.e. the presence and/or thickness of marl deposits) and the sedimentation of detrital clastics (c.f. Fig. 2, van Asch et al., 2012). Results from the TTB study moreover raise concerns about the suitability of isotopic records as an alignment tool where radiocarbon dating precision is poor (e.g. Hoek and Bohncke, 2001). In the former lake basin at TTB factors governing oxygen isotope composition are complex and appear to be controlled by a combination of non-linear provenance patterns of water bearing bicarbonate to the lake (e.g. Ito, 2001), evaporation effects, and possibly variations in rainfall regime (c.f. Candy et al., 2013). These effects cannot be solely attributed to the former size of the lake, with comparative systems elsewhere in Ireland (e.g. Fiddaun) showing much higher amplitude variations in $\delta^{18}O_{carb}$. However, the resultant steady-state variations observed in much of the $\delta^{18}O_{carb}$ temperature-precipitation signal through the Lateglacial Interstadial does make this arguably the least reliable proxy for palaeoenvironmental reconstruction at the TTB site.

5.0 Conclusion

Investigations of former lake sediments at Thomastown Bog (TTB), using sediment geochemistry, pollen, stable isotopes and chironomids, provides the first modern multiproxy palaeolimnological record spanning the Lateglacial to Holocene Transition from the east of Ireland. Climate amelioration marking the end of the last glacial are clearly identified across all proxies, plus clear evidence for at least two distinct cold events during the Lateglacial Interstadial. Correlation across proxies also suggests the preservation of shorter centennial to sub-centennial scale events that have been tentatively linked to climate-controlled changes in the $\delta^{18}O$ NGRIP record and existing palaeoenvironmental records in Ireland although, with the exception of the Pre-Boreal Oscillation, these have not been formerly assigned to an event stratigraphy for the time period. In total 12 event-episodes are identified.

Dating of the TTB sequence was limited to range finder radiocarbon dates because of an absence of dateable material, and attempts to use $\delta^{18}O$ as an alignment tool (*sensu* Hoek and Bohncke, 2001) were constrained due to the complex $\delta^{18}O_{carb}$ record. This is believed to reflect multiple sources of HCO_3^- (aq) to the lake at TTB, together with possible lag effects controlling the delivery of soil and groundwater recharge, particularly at climostratigraphic boundaries. An alternative approach to cross-correlation in this study employs chemostratigraphy linked to sediment lithological variations recorded using micro-XRF core scanning. In multiproxy palaeoenvironmental reconstruction relatively little emphasis is given to lithology, but the small size of the lake and catchment at TTB means that the lake sedimentary record exhibits high sensitivity to environmental change reflecting the relative importance of carbonate precipitation vs. detrital inwash. These modes of sediment delivery appear to have been primarily controlled by climate variations linked to vegetation response and phases of landscape instability, coupled with fluctuations in lake productivity. The TTB lithological record is shown to correspond closely to the regional climate change record recovered in the $\delta^{18}O$ of Greenland ice cores throughout the Lateglacial Interstadial. As the TTB sequence moves into the early Holocene, increasing land cover means that landscape sensitivity to climate change is buffered, although not altogether masked in the lake sediment record, and at least two regressive phases are indicated in the authogenic carbonate sequence during the Preboreal, one of which during the northwest European Ramelbeek Phase, postdates the Preboreal Oscillation and has yet to be documented in Ireland.

Acknowledgements

The authors would like to thank Gary Mulrooney, Welsey van Breda and Thomas Cummins for field support and the landowner who kindly provided access to the Thomastown Bog site. Chris Kendrick and Hilary Sloane at the British Geological Survey undertook the isotope analysis. John Lowe and Pete Coxon are thanked for their constructive feedback during the review process, as too are Alun Jones, Colman Gallagher and Steve Brooks for helpful comments on an earlier version of the manuscript. This study was funded by the Heritage Council under the INSTAR Grant Programme (#16711).

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Table 1. Lithostratigraphic description of the lacustrine sediment sequence at Thomastown Bog. The description includes the Munsell colour code.

Unit	Depth (cm)	Description	Micro-XRF
7	182-160	Sharp transition to dark brown to black (7.5YR 3/2) fibrous peat	Lower in all reported elements and high inc/coh values
6	191-182	Sharp transition to massive, dark grey (10YR 2/2/) organic mud (gyttja)	Increase in Fe
5	222-191	Gradual transition to sub-horizontally banded very dark grey (10YR 3/1) organic detritus and pale yellow (2.5YR 8/3) carbonate (40%) fine sands	High Ca and Sr, slight increase in Ti, K and Fe at lower unit boundary
4	257-222	Sharp transition to laminated, pale yellow (5Y 7/3), carbonate (c. 40%) mud	High Ca and Sr, high Mn at lower unit boundary, low and falling Si, K, Ti, and Fe
3	291-257	Sharp transition to finely laminated (not varved), very dark grey (10YR 2/2), noncalcareous, clay silts	High Si, K, Ti, Fe. Low Ca and Sr, generally low Mn

2	454-291	Graded transition to series of olive grey (5Y 4/2) calcareous (c. 30%) muds with high Ca and Sr content, intercalated with beds (>1cm) and laminations (<1cm) of dark grey (10YR 2/2) clay silts containing elevated Ti, K, Fe and Si	High and variable Ca and Sr, occasional moderate Si, K, Ti, Fe and Mn
1	495-454	Horizontally bedded, very dark grey (10YR 3/1) silty clay, with some evidence of subvertical fracturing towards the unit top	High and variable Si, K, Ti, Fe and Mn. Low Ca and Sr

Table 2. Thomastown Bog ^{14}C dates

Depth (cm)	**Lab. code**	**^{14}C a BP**	±	**AMS δ^{13}C**	**Cal a BP ±σ**	**Material (g)**
160	Beta-265370	8,500	50	-25.2	9,445-9,545	Peat (>1)
188	UBA-11839	9,553	37	-20.6	10,719-11,089	Moss (1.6)
217	UBA-11840	9,740	33	-14.4	11,128-11,234	Moss (0.2)
295	UBA-11841	11,205	34	-13.9	13,015-13,138	Bulk (0.2)
446	UBA-11842	12,912	41	-11.5	15,234-15,630	Bulk (0.2)

Table 3. Thomastown Bog pollen and local pollen assemblage zones (LPAZs)

LPAZ	**Depth (cm)**	**Description and interpretation**
6	198-160	*Corylus*
5	c. 250-198	*Betula-Juniperus-Salix-Potamogeton*-Dryopteris type
4	291-c. 250	*Salix-Thalictrum-Filipendula-Rumex-Artemisia*
3	368-291	Poaceae-*Helianthemum*
2	c. 460-368	*Betula (B. nana)-Juniperus-Empetrum-Rumex –Isoetes*-Pediastrum
1	495-c. 460	*Pinus-Rumex -Artemisia*-Poaceae.

Table 4. Thomastown Bog chironomid assemblage zones

Zone	**Depth (cm)**	**Assemblage**
TTB-C5	257-180	*Ablabesmyia, Dicrotendipes, Tanytarsus glabrescens*
TTB-C4	289-257	*Corynocera oliveri, Micropsectra insignilobus, Paratanytarsus austriacus, Sergentia, Tanytarsus chinyensis*
TTB-C3	398-289	*Chironomus anthracinus, Corynocera ambigua, Dicrotendipes*
TTB-C2	450-398	*Ablabesmyia, Chironomus anthracinus, Microtendipes pallens, Psectrocladius sordidellus*
TTB-C1	489-450	*Corynocera oliveri, Stictochironomus, Tanytarsus chinyensis*

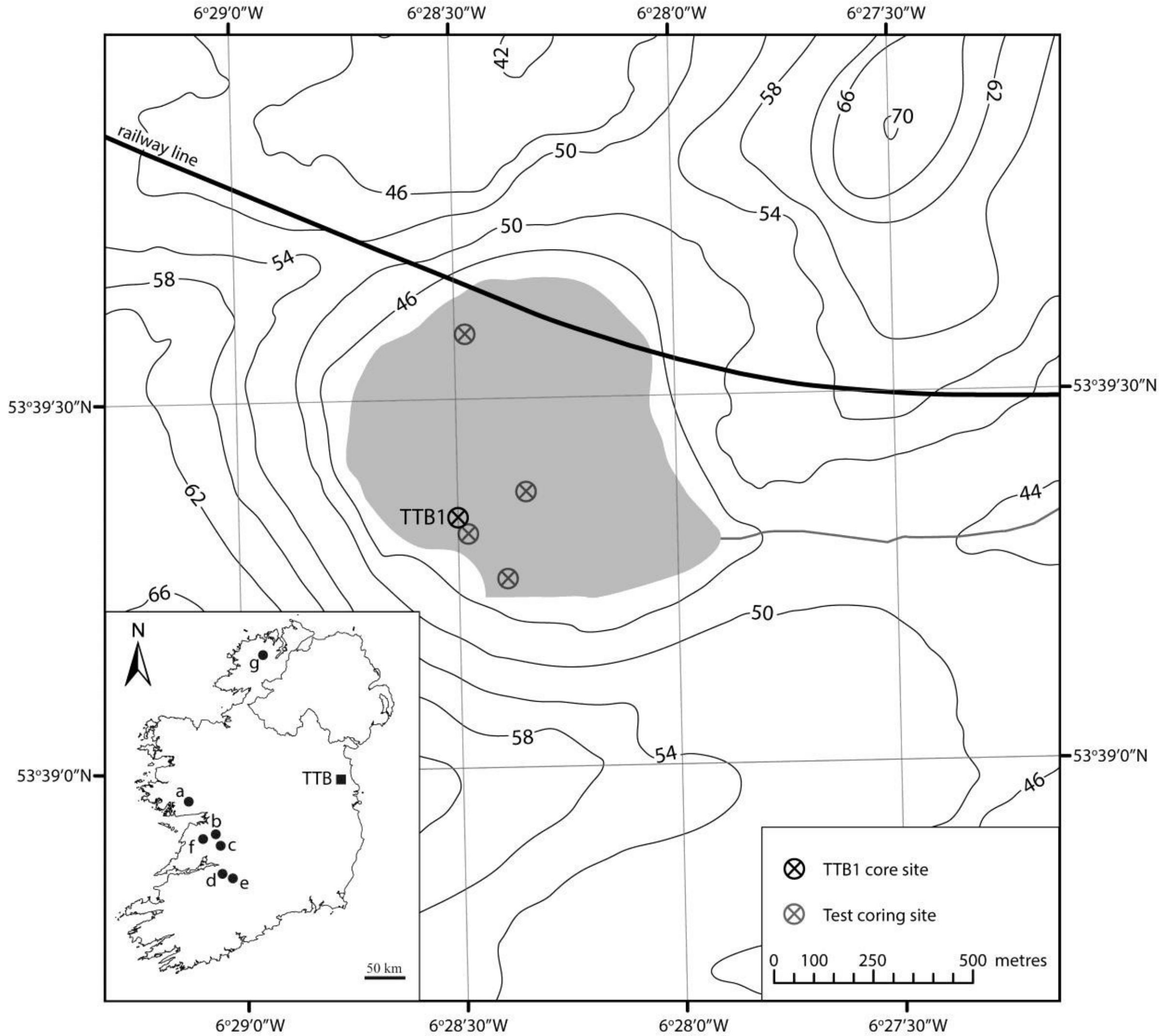

Fig. 1. Place map showing the location of Thomastown Bog and other lake sites in Ireland referred to in the text: (a) Lough Namacknabeg; (b) Lurga and Fiddaun; (c) Illaunacronan; (d) Tory Hill (Andrieu *et al*., 1993 and O'Connell *et al*., 1999); (e) Lough Gur & Red Bog (Ahlberg *et al*., 1996); (f) Lough Inchiquin (Diefendorf *et al*., 2006, 2008) (g) Lough Nadourcan (Watson *et al*., 2010); (h) Fiddaun (Van Asch *et al*., 2012). TTB = Thomastown Bog.

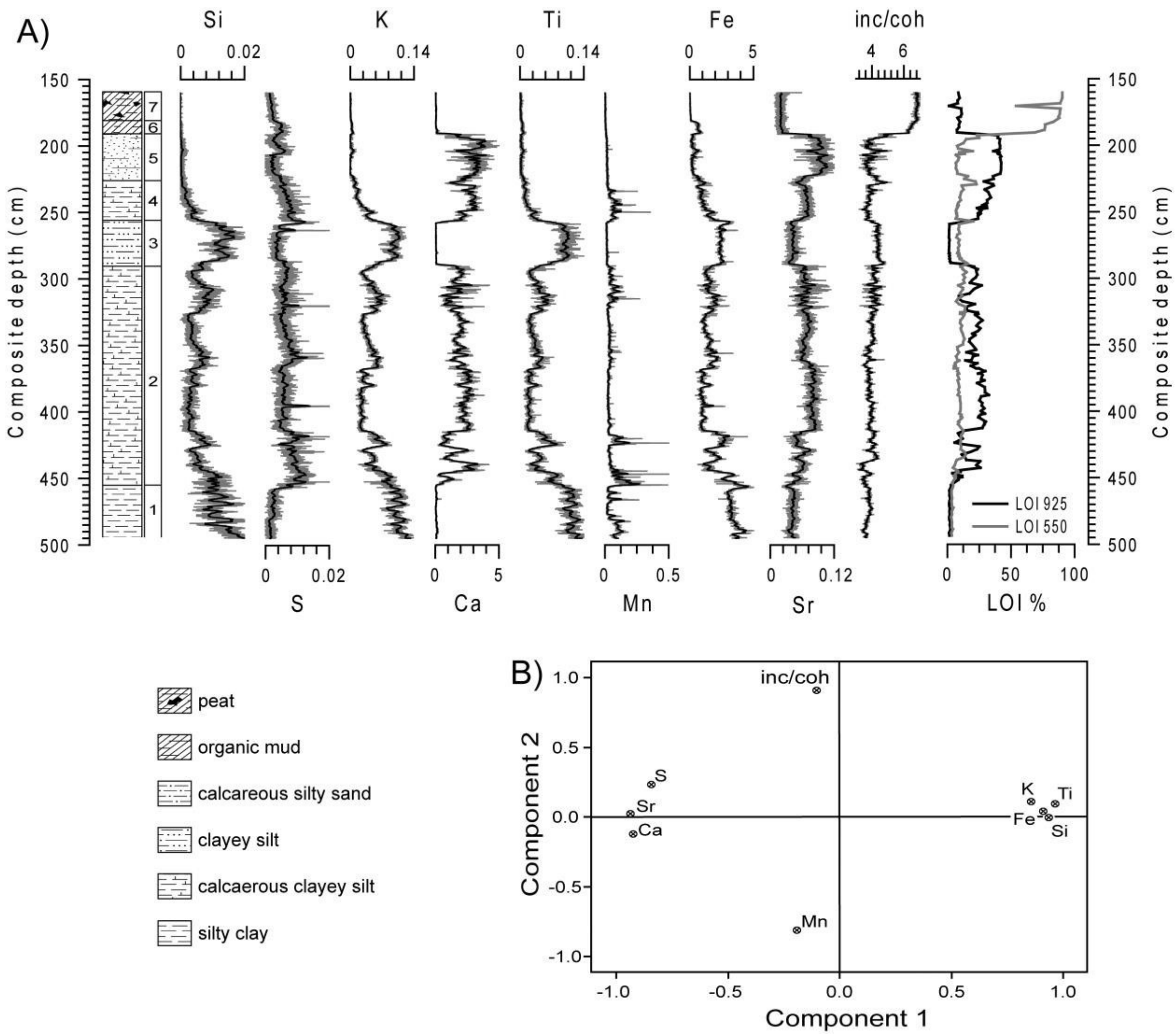

Fig. 2. (A) Lithology and XRF-based chemostratigraphy from the Thomastown Bog core. The grey shaded profile shows raw count data at 200 µm step lengths that have been normalised using total kilo counts per second (signal intensity) at each corresponding interval and the black line shows a 10 point running average for these data (B) PCA Ordination plots for the selected elements and inc/coh ratio performed using centred-log ratios (TolosanaDelgado, 2012).

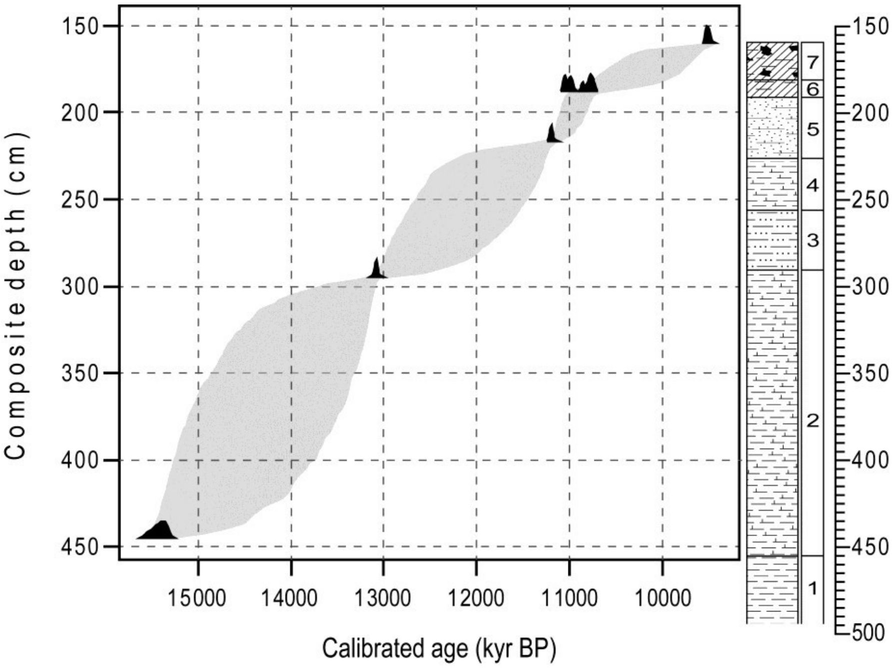

Fig. 3. Thomastown Bog chronology and age model plotted alongside lithology.

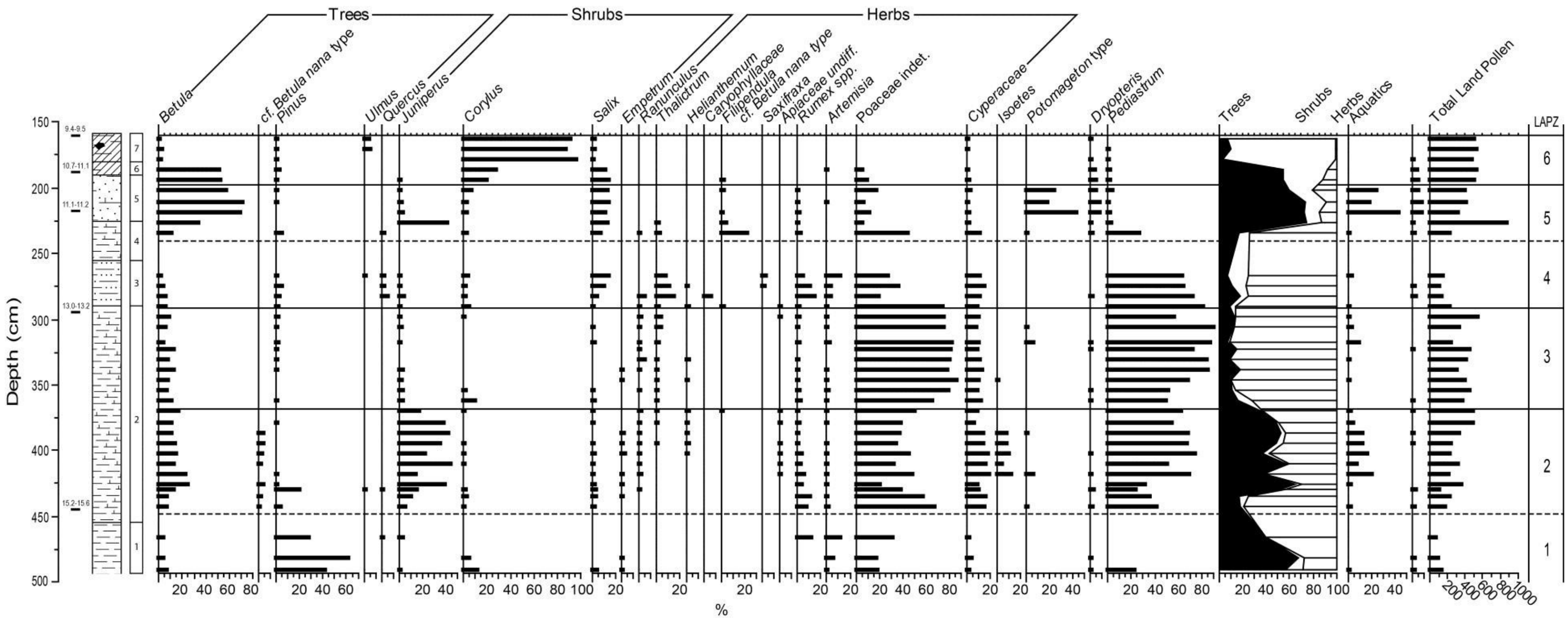

Fig. 4. Thomastown Bog percentage pollen diagram plotted alongside lithology and sedimentary units.

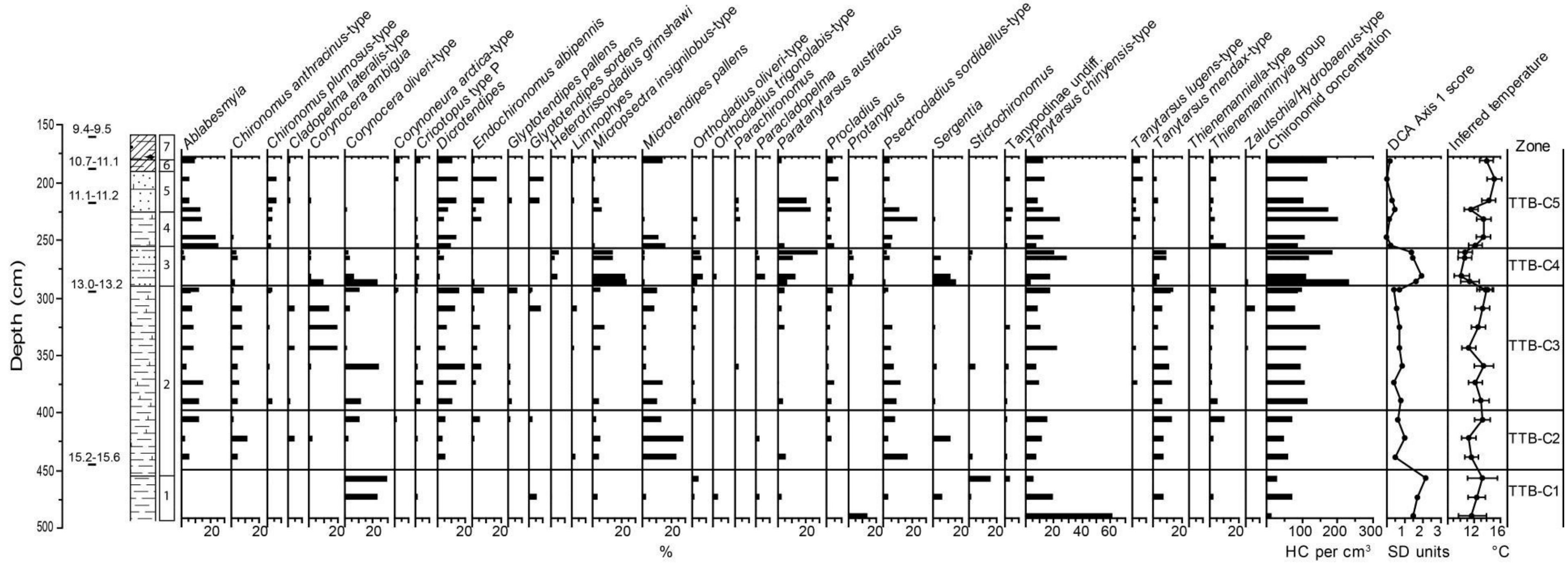

Fig. 5. Thomastown chironomid percentage diagram (selected taxa only). DCA scores and chironomid-inferred mean July air temperature reconstruction, with error bars, are shown on the right.

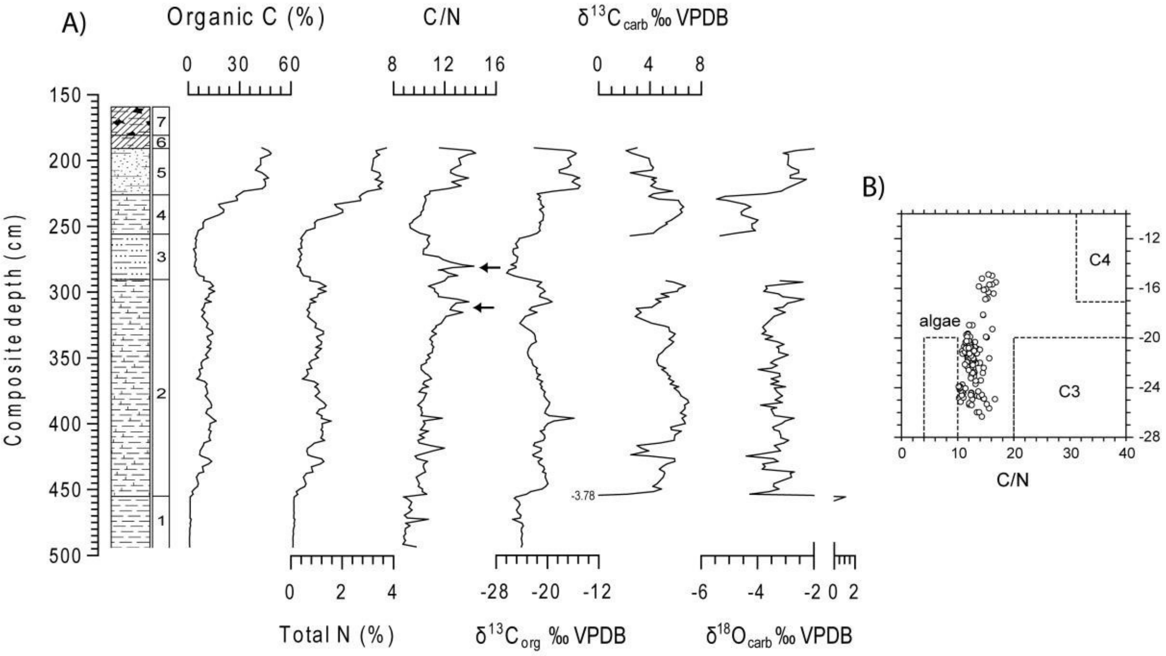

Fig. 6. (A) Organic C, total N and stable isotope profiles from the Thomastown Bog core. The arrows in the C/N profile are referred to in the text (B) Crossplot of C/N and $\delta^{13}C_{org}$.

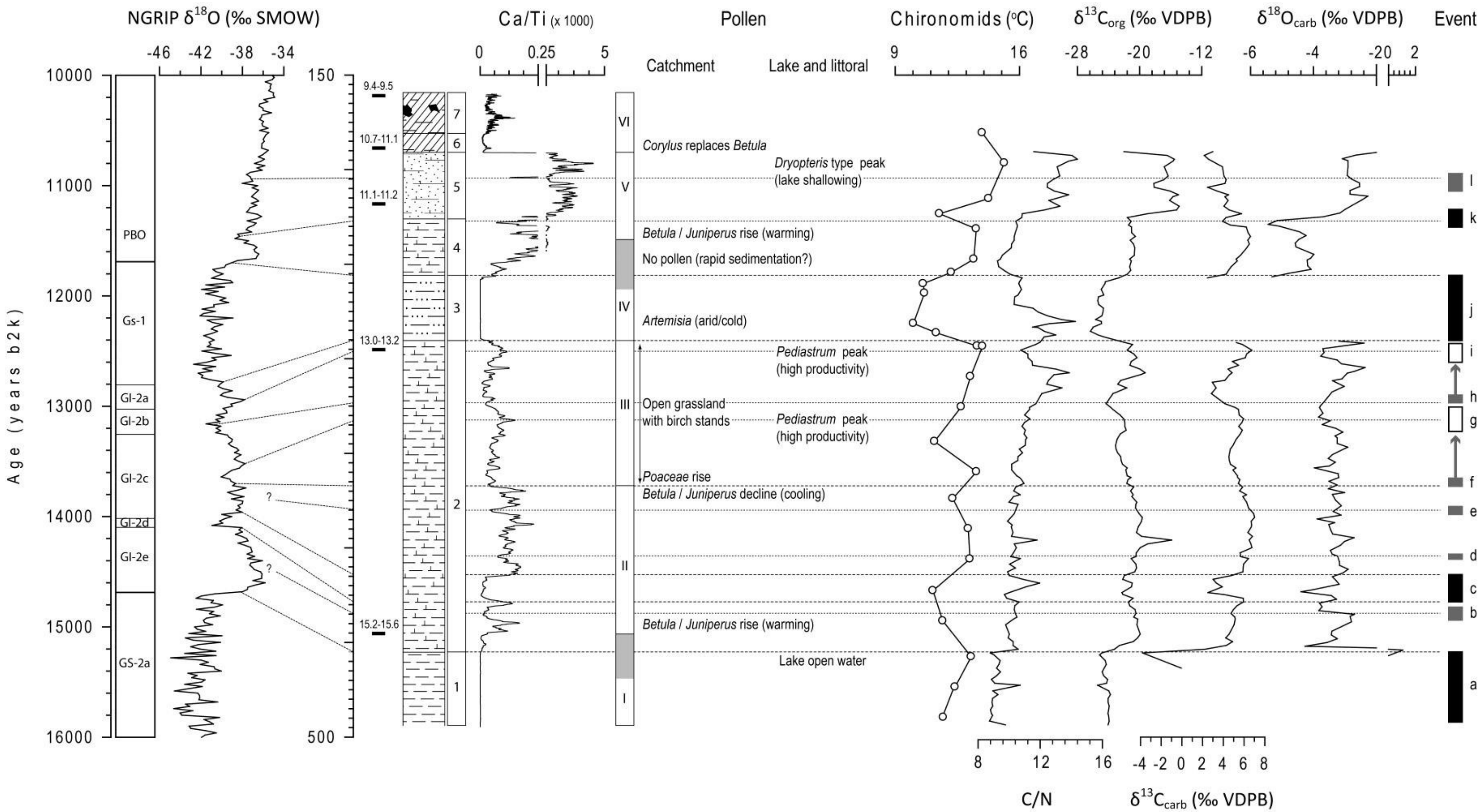

Fig. 7. Synthesis of palaeoenvironmental proxies for Thomastown Bog core mapped to the NGRIP δ^{18}O curve (http://www.ncdc.noaa.gov/paleo/pubs/ngrip2004/ngrip2004.html), showing 12 event-episodes corresponding to concomitant changes across independent proxies. Major climate events are shaded black, minor 'event-episodes' indicating possible climate deterioration and amelioration are shown in grey and white, respectively (see text for description).

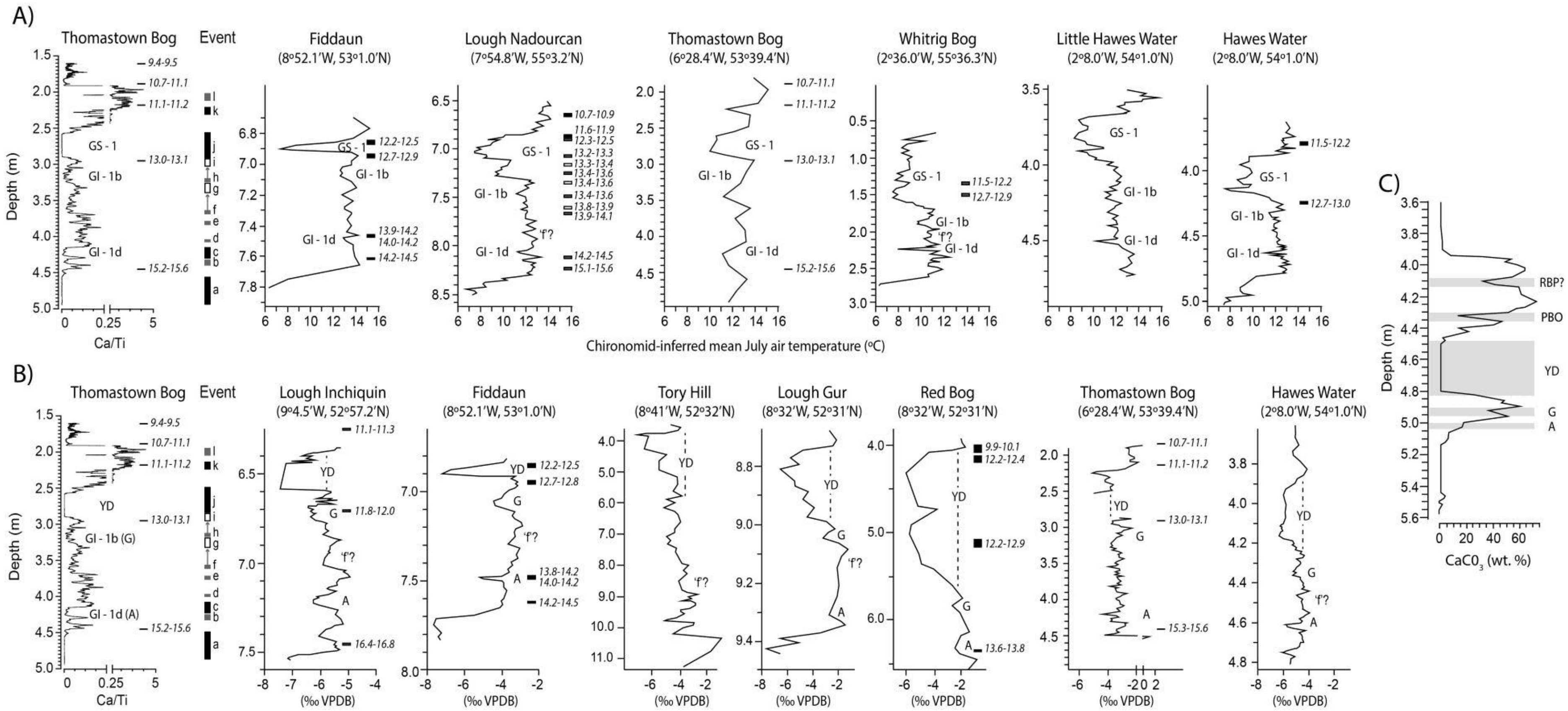

Fig. 8. Comparison of (A) chironomid-inferred palaeotemperature and (B) $\delta^{18}O$ profiles for sites for sites in Ireland and Britain. Profiles are drawn alongside the Ca/Ti curve at Thomastown Bog and are presented from west to east (modified from van Asch *et al*., 2012, Figs. 7 and 8) (C) Bulk carbonate log for Store Sloteseng basin, Denmark redrawn from Larsen and Noe-Nygaard (2013, Fig. 2). A = Aegelsee Oscillation (GI1d); G = Gerzensee Oscillation (GI-1b), YD = Younger Dryas (GS-1); PBO = Preboreal Oscillation; RPB = Rammelbeek Phase. Possible position of event episode ‘f’ is shown on selected records.