



The Holocene isotopic record of aquatic cellulose from Lake Äntu Sinijärv, Estonia: Influence of changing climate and organic-matter sources

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ABSTRACT

The well characterized oxygen-isotopic fractionation during cellulose biosynthesis has been utilised by numerous studies of stable isotopes in fine-grained aquatic cellulose. We measured the $\delta^{13}\text{C}_{\text{cellulose}}$ and $\delta^{18}\text{O}_{\text{cellulose}}$ values of bulk cellulose and moss fragments from an ~11.4ka-long core obtained from a shallow, productive, spring-fed, hardwater lake, Äntu Sinijärv, Estonia (593.8'N; 2614.5'E; 94.6 m a.s.l.; maximum depth 7.3 m), in order to reconstruct regional Holocene climate and lake-basin evolution. Isotopically, the modern waterbody is a well-behaved, open, hydrological system with negligible evaporative effects. Cellulose-isotope records were compared with down-core measurements of loss-on-ignition (LOI), carbonate and mineral contents, total organic carbon (TOC), total nitrogen (TN), C/N ratio, $\delta^{13}\text{C}_{\text{TOC}}$, biomarker indices (P_{alg} and P_{aq}), published palaeoecological data and a $\delta^{18}\text{O}_{\text{carbonate}}$ record from the same palaeolake. Green microalgae, freshwater macroalgae (*Chara*) and aquatic bryophytes were important sources of sedimentary cellulose during different phases in the environmental history of the lake. Although a strong palaeoclimatic imprint can be detected in the $\delta^{18}\text{O}_{\text{cellulose}}$ record from Äntu Sinijärv, notably the Preboreal oscillation, the 8.2ka event and an unnamed cold oscillation ~3.25ka BP, the isotopic signal of these events may have been amplified by increases in ^{18}O -depleted spring snow-melt. In contrast, $\delta^{13}\text{C}_{\text{cellulose}}$ was tightly coupled to the Holocene evolution of terrestrial ecosystems and soils by significant inputs of biogenic carbon from the catchment and sublacustrine springs. During the early Holocene, ~11 – 9ka BP, the $\delta^{18}\text{O}_{\text{cellulose}}$ and $\delta^{18}\text{O}_{\text{carbonate}}$ records diverge markedly, which can be attributed to “no-analogue” seasonal, climatic, hydrological and isotopic conditions resulting from orbital forcing and residual ice-sheet impacts.

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1. Introduction and previous work

1.1. Introduction

Here, we present stable-isotope records from the organic fraction of lacustrine marls from Lake Äntu Sinijärv, Estonia, in order to investigate regional climatic and lake-basin evolution through the course of the Holocene. Use of both cellulose $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in lake-

sediment profiles is reviewed below. By employing a multi-proxy approach including geochemical analyses (C/N ratios and biomarker indices) and various published palaeoecological datasets, we are able to refine the interpretation of the cellulose record both in terms of climatic and local (autogenic and allogenic) influences on lake biogeochemistry. In addition to calculating the oxygen-isotope values of the lake waters through the Holocene, we present a preliminary palaeotemperature reconstruction based on the relationship between mean monthly temperatures and weighted-average $\delta^{18}\text{O}$ data for meteoric waters at the nearest Global Network of Isotopes in Precipitation (GNIP) station. This

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reconstruction relies on the uniformitarian assumptions that: 1) Äntu Sinijärvi was always a well-mixed, open, groundwater-fed lake with a short residence time and minimal evaporation; and 2) present-day isotopic relationships are applicable throughout the Holocene. Our $\delta^{18}\text{O}_{\text{water}}$ and palaeotemperature estimates are then used to simulate the expected $\delta^{18}\text{O}$ signal in endogenic carbonate from this lake, which is compared with measured $\delta^{18}\text{O}_{\text{carbonate}}$ data from a nearby core. The contrasting isotopic records from these two materials raise important questions about the stability of isotopic relationships on millennial to multi-millennial time scales.

1.2. Isotopic analyses of lacustrine cellulose

Lake-sediment cellulose has been used as a palaeoenvironmental indicator in a diverse range of lakes of varying size and climatic setting (Wolfe et al., 2007 and references therein). They include the Great Lakes of both North America (Duthie et al., 1996; Wolfe and Edwards, 1998; Wolfe et al., 2000a) and East Africa (Beuning et al., 1997; 2002). Smaller waterbodies in temperate North America, Europe, New Zealand and Patagonia have also been investigated (Edwards and McAndrews, 1989; Padden, 1996; Padden et al., 1996; Wolfe et al., 2000b, Wissel et al., 2008; Mayr et al., 2009, 2007; Lücke et al., 2009; Heikkilä et al., 2010; Rozanski et al., 2010; Buhay et al., 2012; Heyng et al., 2014), as well as lakes in the circumpolar arctic/subarctic of Canada (MacDonald et al., 1993; Edwards et al., 1996; Wolfe et al., 1996, 2012; Sauer et al., 2001), Russia (Wolfe and Edwards, 1997; Wolfe et al., 1999; 2000c) and Alaska (Anderson et al., 2001); high-altitude lakes in the subtropical Andes (Abbott et al., 2000; Wolfe et al., 2001a); and the sediments of Glacial Lake Agassiz (Buhay and Betcher, 1998). However, only a few studies so far have compared the sedimentary stable-isotope records of cellulose and freshwater carbonates from hardwater lakes, in which these materials are co-produced (Heikkilä et al., 2010; Rozanski et al., 2010; Buhay et al., 2012).

Palaeoclimatological and palaeohydrological applications of the $\delta^{18}\text{O}$ values of lake-sediment cellulose ($\delta^{18}\text{O}_{\text{cellulose}}$) developed to circumvent the problems inherent in attempting to obtain meaningful $\delta^{18}\text{O}$ time series from bulk organic matter (Meyers and Teranes, 2001). Interpretation of the latter is severely complicated by the contribution of oxygen from the oxygen-bearing compounds used to oxidise organic matter to CO_2 prior to isotopic analysis (Meyers and Teranes, 2001; Meyers and Lallier-Vergès, 1999). Oxygen- and carbon-isotopic analyses of cellulose have proven particularly useful in carbonate-free, soft-water lakes (Wolfe et al., 2001b).

Oxygen-isotope analyses of aquatic cellulose have been used to investigate past variations in the water balance of lakes and their relationship to past changes in climate by documenting shifts along the meteoric water line (MWL), which expresses the correlation between $\delta^{18}\text{O}$ and δD in precipitation (Craig, 1961; Dansgaard, 1964; Rozanski et al., 1993), or along a local evaporation line (LEL) in lakes where evaporation is important (Craig and Gordon, 1965; Gonfiantini, 1986). This displacement from the MWL in $\delta^{18}\text{O}/\delta\text{D}$ space occurs because evaporation affects the $^{18}\text{O}/^{16}\text{O}$ and D/H systems differently (Dansgaard, 1964; Gonfiantini, 1986). Stable carbon isotopes in lacustrine cellulose have also been used to elucidate the relationship between past hydrological changes and lake/catchment carbon cycling (Wolfe et al., 2001a,b).

Coupled analyses of the oxygen- and carbon-isotopic composition of lake-sediment cellulose were first undertaken by Edwards and McAndrews (1989), who studied the Holocene palaeohydrology of a Canadian Shield lake in southern Ontario. They argued that lake-sediment $\delta^{18}\text{O}_{\text{cellulose}}$ could be used as a tracer for lake-water $\delta^{18}\text{O}$, through the application of the constant (species- and temperature-independent) cellulose-water fractionation

factor, α , that had previously been demonstrated between terrestrial cellulose and water (e.g. Edwards et al., 1985). This fractionation factor has also been shown to apply to submerged aquatic plants irrespective of assumed metabolic pathway (DeNiro and Epstein, 1981; Sternberg et al., 1984). The Edwards and McAndrews (1989) study, combined with previous isotopic investigations in southern Ontario comparing terrestrial cellulose and lacustrine carbonates (Edwards et al., 1985; 1986; Edwards and Fritz, 1986; 1988) led to the conceptual recognition of analogous oxygen-isotope relationships between terrestrial cellulose, lacustrine endogenic carbonate, aquatic cellulose and their respective source waters (Wolfe et al., 2001a,b). The following equations summarise these relations for terrestrial-plant cellulose (Eq. (1)), endogenic carbonate (Eq. (2)) and aquatic cellulose (Eq. (3)):

$$\delta^{18}\text{O}_{\text{cellulose}} = \delta^{18}\text{O}_{\text{mw}} + \epsilon^{18}_{\text{evap}} + \epsilon^{18}_{\text{cellulose-leafwater}} \quad (1)$$

$$\delta^{18}\text{O}_{\text{carbonate}} = \delta^{18}\text{O}_{\text{mw}} + \epsilon^{18}_{\text{hydro}} + \epsilon^{18}_{\text{carbonate-lakewater}} \quad (2)$$

$$\delta^{18}\text{O}_{\text{cellulose}} = \delta^{18}\text{O}_{\text{mw}} + \epsilon^{18}_{\text{hydro}} + \epsilon^{18}_{\text{cellulose-lakewater}} \quad (3)$$

where $\delta^{18}\text{O}_{\text{mw}}$ is the isotopic composition of local meteoric water, $\epsilon^{18}_{\text{evap}}$ is the isotopic enrichment due to kinetic and equilibrium effects during transpiration in terrestrial plant leaves, $\epsilon^{18}_{\text{hydro}}$ is the isotopic enrichment in lakes due to hydrological factors (notably evaporative enrichment), $\epsilon^{18}_{\text{cellulose-leafwater}}$ and $\epsilon^{18}_{\text{cellulose-lakewater}}$ are the respective, temperature-independent biochemical enrichments that occur during cellulose synthesis, and $\epsilon^{18}_{\text{carbonate-lakewater}}$ is the temperature-dependent enrichment between lake water and endogenic carbonate (Wolfe et al., 2001a,b; 2007).

Edwards and McAndrews (1989) also argued that the fine-grained cellulose fraction of lake sediments was primarily of aquatic origin, based on: a) the coherent isotopic relations between surface-sediment cellulose and modern lake water; b) overlapping $\delta^{18}\text{O}$ time series from two widely separated sediment cores; and c) the lack of overlap between the $\delta^{13}\text{C}$ time series from the same cores, which is not surprising given the much broader range of $\delta^{13}\text{C}$ values encountered in aquatic plants and algae compared with terrestrial C_3 plants (Rau, 1978; Sharkey and Berry, 1985; Keeley and Sandquist, 1992); as well as d) a consideration of the expected $\delta^{18}\text{O}$ values for terrestrial and aquatic plants, based on measurements of modern terrestrial-plant cellulose from the study area. Their mass-balance calculations led to the conclusion that aquatic sources contributed ~90% of the fine-grained sediment cellulose under modern conditions.

In summary, two key conclusions were reached by the Edwards and McAndrews (1989) study: 1) that the biochemical fractionation between aquatic cellulose and source water was constant and well understood; and 2) that the fine-grained (<150 μm) cellulose fraction of lake sediments was predominantly derived from aquatic plants and/or algae. These conclusions have subsequently become fundamental assumptions in the routine estimation of $\delta^{18}\text{O}_{\text{lakewater}}$ from $\delta^{18}\text{O}_{\text{cellulose}}$. Many subsequent studies that utilised this method simply referred back to Edwards and McAndrews (1989) (MacDonald et al., 1993; Wolfe et al., 1996; Duthie et al., 1996; Wolfe and Edwards 1997; Buhay and Betcher, 1998). However, later work drew more heavily on C/N ratios and $\delta^{13}\text{C}$ values of cellulose and/or total organic carbon ($\delta^{13}\text{C}_{\text{TOC}}$) in order to demonstrate a largely aquatic source for the sedimentary-cellulose fraction (Wolfe et al., 1999; 2000c; 2001a,b; Abbott et al., 2000; Anderson et al., 2001). Comparisons between $\delta^{18}\text{O}_{\text{cellulose}}$ values of surface sediments, modern submerged aquatic-plant material and $\delta^{18}\text{O}$ values of modern lake water have also commonly been used as a “calibration” method in order to support (or constrain) both of these assumptions. However, the influence of seasonal hydrological

processes needs to be considered in surface-sediment calibrations in the case of studies that rely on a single measure of lake-water isotope composition (Wolfe and Edwards, 1997; Wolfe et al., 2001a).

1.3. Sources of cellulose in lake sediments

Given the diversity of potential aquatic- and terrestrial-cellulose sources, it is essential to consider the full range of possibilities in the light of the available indicators of sediment composition in any individual lake, such as C/N ratios, $\delta^{13}\text{C}$ values, biomarker indices and palaeoecological data.

1.3.1. Algae

Despite the assertions by Meyers and Ishiwatari (1993a; 1993b) and Meyers (1994; 1997) that algae do not contain cellulose, they often represent an important source of cellulose for lake sediments (Wolfe et al., 2001a,b). Emphasis is usually placed on the green microalgae (Chlorophyta), including the Zygnematales and Desmidiaceae, and the freshwater green macroalgae or stoneworts (Charophyta) (e.g. Wolfe et al., 2001a,b).

In the green algae, cellulose is usually the main structural polysaccharide (Lee, 1989). In some taxa, however, it may be replaced by xylan (Frei and Preston, 1964; Dodge, 1973), mannan (Frei and Preston, 1961; Mackie and Preston, 1968) or glycoprotein (Lee, 1989). A full review of the numerous taxa that contain cellulose is beyond the scope of this discussion. However, they include such common microalgal genera as *Pediastrum*, *Cladophora*, *Chlorococcoides*, *Botryococcus*, *Scenedesmus* and *Oocystis*, and the freshwater macroalgae *Chara* and *Nitella* (Prescott, 1969; Dodge, 1973; Tsekos, 1999).

Other algal taxa commonly or occasionally found in lakes that contain some cellulose-producing species include the Chrysophyceae (golden algae), which are important in soft waters, Xanthophyceae (yellow-green algae), Cryptophyta (cryptomonads), Haptophyta (haptophytes), Dinoflagellata (dinoflagellates), Rhodophyta (red algae) and Phaeophyceae (brown algae) (Brown et al., 1969; Brown et al., 1970; Dodge and Crawford, 1970; Chapman and Chapman, 1973; Dodge, 1973; Sheath et al. 1975; Trainor, 1978; Herth and Zugenmaier, 1979; Kumar and Singh, 1979; Lee, 1989; Zeeb and Smol, 2001).

1.3.2. Submerged and floating aquatic macrophytes

Among the macroscopic contributors to the sedimentary cellulose pool, submerged aquatic macrophytes often dominate in shallow lakes and littoral sediments. These include vascular plants such as *Myriophyllum*, *Ceratophyllum*, *Potamogeton*, *Callitriche* and *Littorella*, and aquatic mosses such as *Fontinalis*, *Drepanocladus* and *Scorpidium*. Macrophytes with floating leaves (notably the water-lilies *Nymphaea* and *Nuphar*) are often significant cellulose sources. Taxa with floating waxy leaves (e.g. *Nymphaea*) may be considered “honorary” submerged macrophytes with respect to their characteristic mid-chain-length lipid biomarkers (Ficken et al., 2000). Submerged and floating aquatic plants commonly contribute cellulose to profundal sediments through resuspension of littoral deposits during lake-level lowstands.

1.3.3. Emergent macrophytes and terrestrial vegetation

Emergent aquatic vegetation potentially contributes large amounts of cellulose to sediments in smaller lakes and/or marginal environments. Members of the Poaceae (reeds, e.g. *Phragmites*), Cyperaceae (sedges, e.g. *Carex*, *Cladium*) and Typhaceae (*Typha*) are usually the most important taxa. Allochthonous terrestrial plant material (seeds, leaves, bud scales, twigs etc.) derived from the lake’s watershed is another potentially large contributor of cellulose to lake sediments. This source may be particularly significant in

lakes surrounded by forest, or fed by large streams or rivers.

An underestimated (terrestrial) source of cellulose is pollen (and possibly cryptogam spores). While the outer layer (exine) of the walls of pollen grains is composed of sporopollenin, the inner layer (intine) consists of cellulose (Shaw and Yeadon, 1964; Moore et al., 1991; Loader and Hemming, 2004). While intine may only be a minor component of the cellulose pool, its contribution should certainly be considered in lakes with low aquatic productivity, a slow sedimentation rate and/or a high pollen influx. Moreover, cellulose from this source may be preferentially preserved within the highly resistant exine in sediments where diagenesis impairs the preservation of aquatic cellulose. Similarly, bacterial sources of cellulose (e.g. *Acetobacter*) from soils or from within lakes do not appear to have been adequately explored.

1.4. Cellulose-water oxygen-isotope fractionation

Many laboratory and field studies have attempted to quantify the relationship between the $^{18}\text{O}/^{16}\text{O}$ ratios of aquatic cellulose and those of the water in which the organisms grew (Epstein et al., 1977; DeNiro and Epstein, 1981; Sternberg and DeNiro, 1983a; Sternberg et al., 1984; 1986; Yakir and DeNiro, 1990; Abbott et al., 2000). The majority suggest that fractionation between water and cellulose is constant and independent of temperature (DeNiro and Epstein, 1981), plant species, photosynthetic pathway (Epstein et al., 1977; Sternberg and DeNiro, 1983a; Sternberg et al., 1984; 1986), growth conditions (Yakir and DeNiro, 1990) and the $\delta^{18}\text{O}$ value of dissolved CO_2 (due to its equilibration with water in the cell prior to fixation) (DeNiro and Epstein, 1979).

A constant ^{18}O fractionation factor, α , has been observed between water and cellulose in a variety of aquatic organisms, including freshwater algae and vascular plants (e.g. Epstein et al., 1977; DeNiro and Epstein, 1981). A value of $\alpha = 1.028 \pm 0.003\text{‰}$ was observed in the majority of these studies. This results in a consistent ^{18}O enrichment in aquatic cellulose with respect to its source water, $\epsilon^{18}\text{ cellulose-lakewater} \approx 27\text{--}28\text{‰}$ (Yakir, 1992; Sternberg, 1989), which has been attributed to the isotopic signature of the water being “fixed” during the carbonyl hydration reaction (e.g. Sternberg and DeNiro, 1983b). The majority of these studies, however, have focused on temperate environments. Work in tropical East Africa has suggested a smaller fractionation factor, $\alpha = 1.025 \pm 0.003\text{‰}$ (Beuning et al., 1997; 2002). Their results imply a small temperature effect on the fractionation factor; more work is needed to clarify this possibility (Wolfe et al., 2001a,b, Waterhouse et al., 2013).

Comparisons between surface-sediment samples, overlying lake water and modern aquatic vegetation are often used in cellulose $\delta^{18}\text{O}$ studies in order to validate the technique (as well as the cellulose source). In open lakes with perennial outflows, single-episode surface-sediment calibration may produce coherent results (e.g. Abbott et al., 2000), but where strong seasonal variations in the isotopic composition of lake waters occur (e.g. where snowmelt is important) the contrasting temporal resolution of the sediment (a weighted average for the whole year) and water data (instantaneous) may result in a significant offset between results from the two data sources (Wolfe and Edwards, 1997; Wolfe et al., 2001a,b). Isotopic monitoring of the lake water/vegetation throughout the entire growing season is therefore desirable but was not feasible in this study.

1.5. Lipid biomarkers

Although C/N ratios are widely employed to distinguish between organic matter of terrestrial and aquatic origin (Meyers and Ishiwatari 1993a,b; Meyers and Lallier-Vergès, 1999), C/N on its

own is a blunt instrument due to the diversity of possible sources contributing to lake sediments and the impacts of early diagenesis (Tyson, 1995). In this paper, we also deploy two groups of lipid biomarkers to clarify the origin of the sedimentary cellulose. The organic fraction of lacustrine sediments comprises a mixture of autochthonous compounds synthesized by living organisms that lived within the lake, such as algae, bacteria and submerged/floating macrophytes, with allochthonous inputs derived from the catchment, notably from vascular land plants. *n*-Alkanes, which are least susceptible to degradation, are most commonly used in palaeoenvironmental reconstructions (Meyers, 1997; Meyers and Ishiwatari, 1993a,b). Suites of *n*-alkanes characteristic of certain plant groups can be used to investigate the relative importance of terrestrial versus aquatic sources. Odd-numbered, long-chain homologues (C_{27} – C_{35}) are generally characteristic of terrestrial higher-plant leaf waxes (Eglinton and Hamilton, 1967), whereas short-chain homologues (C_{17} – C_{21}) are characteristic of aquatic algae (Cranwell et al., 1987), but vulnerable to diagenesis. Ficken et al. (2000) demonstrated that odd-numbered, mid-chain-length (C_{23} , C_{25}) *n*-alkanes formed the dominant component of leaf waxes produced by submerged and floating aquatic plants (which include the macroalga *Chara* according to Nuñez et al. (2002) and Mead et al. (2005), although Ortiz et al. (2015) found that it maximized at C_{19}). Hence, Ficken et al. (2000) proposed the *n*-alkane P_{aq} proxy ($P_{aq} = (C_{23} + C_{25}) / (C_{23} + C_{25} + C_{29} + C_{31})$), with values that theoretically range from 0 to 1, to distinguish the relative contribution of leaf waxes derived from submerged/floating aquatic macrophytes from long-chain compounds produced by emergent aquatics/terrestrial plants. A P_{aq} value > 0.4 signifies that a significant proportion of the *n*-alkane fraction originated from submerged/floating plants (Ficken et al., 2000).

Zhang et al. (2004) formulated a similar proxy for algal inputs into lake sediments, based on the proportion of algal *n*-alkenes plus a hydrocarbon compound produced by *Botryococcus braunii* (cyclobotryococcatriene), relative to terrestrial-plant leaf waxes: $P_{alg} = (C_{23:1} + C_{25:1} + C_{27:1} + \text{cyclobotryococcatriene}) / (C_{23:1} + C_{25:1} + C_{27:1} + \text{cyclobotryococcatriene} + C_{29} + C_{31} + C_{33})$. The P_{alg} formula was revised by Cockerton et al. (2015) for

application to the sediments of Lakes Victoria and Edward, East Africa, which did not contain cyclobotryococcatriene: $P_{alg} = (C_{23:1} + C_{25:1} + C_{27:1}) / (C_{23:1} + C_{25:1} + C_{27:1} + C_{29} + C_{31} + C_{33})$. Here, we apply a version of the P_{alg} proxy applicable to the more abundant, even-numbered, *n*-alkanoic acids found in the Äntu Sinijärv sediment extracts: $P_{alg} = (C_{16} + C_{18}) / (C_{16} + C_{18} + C_{26} + C_{28})$ (cf. Meyers, 1997). Assuming good preservation of the easily degraded, short-chain homologues (Napolitano, 1999; Ortiz et al., 2015), higher values of this index would imply a predominantly algal source for the sedimentary organic matter, with the reservation that *Chara* may produce significant amounts of short-chain (C_{16} and $C_{16:1}$) fatty acids (Nuñez et al., 2002). However, it is possible to say with more confidence that low values of both P_{aq} and P_{alg} suggest a substantial contribution of leaf waxes derived from terrestrial plants and/or emergent macrophytes.

2. Site description, materials and methods

2.1. Site description

2.1.1. Late-glacial and Holocene history of the region

Lake Äntu Sinijärv (Äntu Blue Lake) (593.8°N; 2614.5°E: 94.6 m a.s.l., 2.4ha) is a shallow, calcareous lake (maximum depth 7.3 m), forming one of the Äntu group of lakes located on the southern slopes of the Pandivere Uplands in Eastern Estonia (Fig. 1). This area was ice-covered during the last glacial, but became largely ice-free during the Allerød interstadial, with the final disappearance of local ice and resulting meltwater by ~13.3ka at the latest (all dates quoted in this paper are in calendar years Before Present, unless otherwise stated) (Amon et al., 2016). However, the Fennoscandian Ice Sheet, which disappeared ~10.5ka (Cuzzone et al., 2016), may have continued to influence the climate of the Uplands even after glacial ice receded from Estonia. In addition, the Baltic Sea and its precursors had the potential to impact regional climate: these waterbodies varied in size and salinity as a result of ice-sheet melting, local and regional isostatic changes, and variations in global ocean volume (Berglund et al., 2005). Following deglaciation and prior to the start of Holocene warming, the Baltic Ice Lake



Fig. 1. Right. Map of Estonia and surroundings, showing the location of the Äntu group of lakes and other sites referred to in the text. Left. Lakes Äntu Sinijärv, Rohejärv and Valgejärv, showing the locations of the ANTU1+2 (black triangle) and ANTU3 (black square) core sites and the former extent of Palaeolake Äntu (heavy line) (Lehtmaa, 2006), with contours in metres.

occupied the basin. This was replaced by the Yoldia Sea, an initially brackish water body that persisted until ~10.7ka. The early, brackish phase of the Yoldia Sea corresponded to a brief cold reversal known as the Preboreal oscillation (PBO), which began ~11.3ka and lasted for 150–250yr (Björck et al., 1996; Fisher et al., 2002). Between 10.7 and 9.8ka, the cold, freshwater Ancylus Lake occupied the Baltic basin, to be replaced by the Littorina Sea, a variably brackish waterbody that has endured to the present day (Berglund et al., 2005).

The temperature of the Baltic region rose sharply after the PBO in response to orbital forcing and ice-sheet recession; winter and summer temperatures rose by $\leq 12^\circ\text{C}$ and $\leq 5^\circ\text{C}$, respectively, until ~8ka according to Veski et al. (2015), with a proposed Holocene Thermal Maximum (HTM) lasting from ~8 to ~4.5ka (Seppä and Poska, 2004), although some authors have argued for a somewhat earlier onset (Väliranta et al., 2015). Early to mid-Holocene warming was interrupted by a short-lived cooling, assumed to correspond to the 8.2ka event, during which temperatures in Eastern Estonia fell by $\leq 2^\circ\text{C}$ for ~200 years, in association with increased anticyclonic conditions and a weakening of zonal airflow (Veski et al., 2004; Heikkilä and Seppä, 2003). Progressive cooling characterized the interval after the HTM, from ~4.5ka onwards (Seppä and Poska, 2004).

Low lake levels at the start of the Holocene in the eastern Baltic region suggest dry conditions (Saarse and Harrison, 1992); in contrast, rising lake levels through the HTM point to wetter conditions, although Seppä and Poska (2004) have suggested, based on palynological evidence, that the HTM in Estonia was characterized by warmer, drier summers as a result of increased anticyclonic conditions accompanied by enhanced meridional airflow. Reconstructed water-level changes for Äntu Sinijärv (Sohar and Kalm, 2008) appear out of phase with those from the eastern Baltic during the early Holocene (Saarse and Harrison, 1992), possibly as a result of dating issues with earlier cores from the lake, although the reconstruction of a low-water phase during the HTM agrees with Seppä and Poska (2004).

Changes in temperature and effective moisture have led to marked shifts in vegetation on the Pandivere Uplands. Human impact became increasingly important from the mid- to late Holocene onwards. Treeless tundra vegetation during the cold, Younger Dryas stadial (YD) prior to ~11.5ka was replaced by dwarf *Betula* woodland during the earliest Holocene until ~10ka, when *Pinus* began to dominate, with other broadleaved taxa appearing by ~9.5ka (Punning et al., 2000; Amon et al., 2016). Deforestation, as a result of human impact, began in the mid-Holocene ~5.7ka (Saarse and Liiva, 1995) and occurred in several phases, although Äntu Sinijärv is still surrounded by mixed stands of Scots Pine (*Pinus sylvestris*) and Norway Spruce (*Picea abies*).

2.1.2. Modern limnology and climatology

Today, Lake Äntu Sinijärv is fed by direct precipitation and by groundwater from an Ordovician limestone aquifer that discharges into the lake through at least seven submerged spring vents, which are $\leq 2\text{ m}$ deep (Saarse and Liiva, 1995). It drains southwards through Lakes Rohejärvi (also known as Vahejärvi) and Valgejärvi, with which it was united before ~4ka (Nedelskaja, 2011) to form a single open lake, Palaeolake Äntu, which covered ~14.4ha. Palaeolake marls extend up to ~2 m above the present lake (Lehtmaa, 2006) (Fig. 1). Today, Äntu Sinijärv has an estimated water-residence time of ~2–3 months (Saarse and Liiva, 1995).

The climate of the region is characterized by warm/wet summers and cold/wet winters, with cool/drier conditions in spring and autumn. Annual-mean air temperature (MAT) for the period 1981–2010 at Väike-Maarja meteorological station, ~7 km north of the lake (Fig. 1) was 4.9°C , with minimum and maximum monthly

values, respectively, of -4.5°C in February and 17.4°C in July. Annual total precipitation was 693 mm over the same period, with maxima in August and October and a minimum in April. Relative humidity is high all year, peaking at 88% in November through to January (Estonian Weather Service: <http://www.ilmateenistus.ee/>).

The water temperature of Lake Äntu Sinijärv ranges from 6.4 to 18.0°C . A thermocline is typically found at a depth of 1–2 m (Mäemets, 1977). The lake has a pH of 7.4–8.0 and an HCO_3^- content of 262–274 mgL^{-1} (Laumets et al., 2014). It is surrounded by a narrow strip of peat on all but the eastern shore (Saarse and Liiva, 1995). It supports dense stands of submerged aquatic macrophytes, including the green macroalga *Chara*, the brown moss *Scorpidium*, and the vascular plants *Myriophyllum verticillatum* and *Ceratophyllum demersum* (Saarse and Liiva, 1995; Olsson and Kaup, 2001).

2.1.3. Sediment record

The lacustrine deposits, which vary from 5.1 m thick in the southern part of the basin to 3.3 m thick in the northern basin, consist of marl, calcareous mud and gyttja. Previous studies have investigated pollen (Saarse and Liiva, 1995; Punning et al., 2000; Nedelskaja, 2011; Laumets et al., 2014), plant macrofossils and non-pollen palynomorphs (Nedelskaja, 2011; Laumets et al., 2014), carbonate isotopes (Punning et al., 2000; Nedelskaja, 2011; Laumets et al., 2014) and ostracods (Sohar and Kalm, 2008), based on several cores recovered from the lake. No previous stable-isotope studies of the organic fraction have been conducted. Unfortunately, the age models for previous cores (apart from Nedelskaja, 2011) were based almost entirely on ^{14}C dates from aquatic material, which suffers from significant reservoir effects in hardwater lakes (Olsson and Kaup, 2001; Sensula et al., 2006). Our investigation aimed to provide new insights into local and regional environmental history using a more reliable chronology based exclusively on terrestrial-plant macrofossils (see Supplementary Data).

2.2. Methods

Here, we provide a short overview of the field and laboratory methods used: full details are provided in Supplementary Data. Investigations of oxygen and hydrogen isotopes in modern rainwater, groundwater and lake water were undertaken in order to aid the interpretation of isotope data from the lake sediments. Modern precipitation and groundwater samples were collected at Väike-Maarja and lake-water samples close to the lake centre (Fig. 1). The entire Holocene lake-sediment record (core ANTU1+2) was recovered beneath 4.1 m of water using a Russian corer and an age model developed using radiocarbon ages; only terrestrial macrofossils were used in order to avoid hardwater errors. The core sediments were sampled at typical intervals of 1–4 cm and analysed for bulk sediment composition; total organic carbon (TOC), total nitrogen (TN) and C/N ratio; and cellulose isotopes. In a novel step, P_{alg} and P_{aq} were analysed on the solvent extracts remaining after cellulose preparation. As a first approximation, Holocene variations in air temperature were estimated from $\delta^{18}\text{O}_{\text{lakewater}}$ values reconstructed from the $\delta^{18}\text{O}_{\text{cellulose}}$ measurements and the modern relationship between weighted-average $\delta^{18}\text{O}_{\text{mw}}$ and mean air temperature (MAT) (cf. Edwards et al., 1996; von Grafenstein et al., 1996) although we recognize that this relationship may be complicated by seasonal covariance between temperature and precipitation amount (Tyler et al., 2016). Since core ANTU1+2 contained refractory organic matter which made it hard to obtain a clean carbonate fraction for isotope analysis, its $\delta^{18}\text{O}_{\text{cellulose}}$ record is compared below with the $\delta^{18}\text{O}_{\text{carbonate}}$ curve for core ANTU3 (Nedelskaja, 2011; unpubl. data), the only other carbonate record from Palaeolake Äntu with a chronology based entirely on

terrestrial macrofossils. The location of ANTU3 is shown on Fig. 1.

3. Results and interpretation

3.1. Stable isotopes in precipitation, lake water and groundwater

Monthly precipitation $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{mw}}$) values for Väike-Maarja vary from -14.5‰ (December) to -9.8‰ (June), although data are lacking for January to April, inclusive (Fig. 2a). However, $\delta^{18}\text{O}_{\text{mw}}$ values from the most representative GNIP station at Tartu, ~ 100 km to the south (Fig. 1), provide a more complete record. Here, $\delta^{18}\text{O}_{\text{mw}}$ values range from -14‰ (January) to -7.9‰ (June); for the months for which data are available for both sites, there is reasonable agreement (albeit values are not for the same years) (Fig. 2a). For comparison, Figure 2a also shows the data for Vilsandi, a coastal GNIP station. At Tartu, there is a close relationship between monthly MAT and $\delta^{18}\text{O}_{\text{mw}}$ values ($T = 2.1 \times \delta^{18}\text{O} + 30.1$; $r^2 = 0.54$. See Supplementary Data). The precipitation data from Tartu fall on a local meteoric water line (LMWL) described by $\delta\text{D}_{\text{mw}} = 8.01 \times \delta^{18}\text{O}_{\text{mw}} + 8.57$, and have weighted mean-annual values of -10.51‰ for $\delta^{18}\text{O}_{\text{mw}}$ and -75.45‰ for $\delta\text{D}_{\text{mw}}$, respectively. Väike-Maarja rainfall values fall close to the LMWL for Tartu (Fig. 2c). Deuterium-excess (d_{mw}) values for Väike-Maarja precipitation vary between about $+7\text{‰}$ in June and about $+12\text{‰}$ in December and May; the more complete record for Tartu shows low values (around $+4\text{‰}$) in March, with higher values in August–December, peaking around $+11\text{‰}$, suggesting some autumnal recycling of surface water to the atmosphere (Fig. 2b).

Today, Äntu Sinijärv lake waters barely diverge from the LMWL for Tartu (Fig. 2c), implying limited isotopic evolution through evaporation, in contrast to many other modern Estonian lakes reported by Stansell et al. (2017), although this behaviour may not have applied throughout the Holocene. Äntu Sinijärv also exhibits damped seasonal variations in $\delta^{18}\text{O}$, with lake-water values ranging from -11.5 to -12.2‰ (Fig. 2d). However, two samples of snow and snowmelt collected from the surface of the lake ice in February 2005 yielded $\delta^{18}\text{O}$ values of -23.98 and -14.15‰ , respectively. Slight isotopic depth stratification probably reflects both minor surface evaporative enrichment during summer/autumn and groundwater inflow from the submerged springs (Fig. 2d). Groundwater $\delta^{18}\text{O}$ values also plot very close to the LMWL. They averaged $-12 \pm 0.16\text{‰}$.

3.2. Lake sediments

Overlapping cores ANTU1 and ANTU2 were aligned stratigraphically (see Supplementary Data) in order to provide a composite sequence (ANTU1+2), together with the short surface core SURF, for plotting and data description (Figs. 3,4). All plots presented here are based on corrected depths following stratigraphical alignment. The major sedimentary units and the corresponding environmental conditions reconstructed from published studies are described below.

Dark lacustrine silt (450 – 428 cm; 11.4 – 10.8ka BP). The basal unit is a minerogenic lake mud (residue $\leq 90\%$), with very low CaCO_3 (3–7%) and TOC contents (3–6%). Low C/N ratios (11–13), moderately high P_{alg} (0.35–0.77) and low P_{aq} values (0.28–0.41) suggest a mixture of lacustrine (mainly microalgal) and minor terrestrial cellulose sources. Low pollen concentrations (*Betula* incl. *nana*, *Pinus*, *Salix* and possibly reworked grains of *Picea* and temperate trees), with some charcoal (Laumets et al., 2014), suggest a cold, open landscape. $\delta^{13}\text{C}$ values for both TOC and cellulose (-30 to -25‰ and -23 to -20‰ , respectively) (Fig. 5a), are normal for lacustrine organic matter derived from atmospheric CO_2 . $\delta^{18}\text{O}_{\text{cellulose}}$ is low (6 – 13‰), corresponding to reconstructed $\delta^{18}\text{O}_{\text{lakewater}}$

values (-21 to -15‰) and cellulose-inferred palaeotemperatures (-14 to -1°C) much lower than the present day (Fig. 6).

Gyttja (427 – 413 cm; 10.8 – 10.4ka BP). This distinctive organic lake mud (cf. Saarse and Liiva, 1995, Sohar and Kalm, 2008, and Laumets et al., 2014), still has a low CaCO_3 content (3–6%) but a much higher TOC content (30–41%) (Figs.3,4). C/N ratios (12–13), P_{alg} (0.32–0.66) and P_{aq} (0.40–0.70) suggest dominantly aquatic organic-matter sources with minimal inputs from terrestrial ecosystems. This inference is confirmed by the presence of green, colonial, planktonic microalgae (*Botryococcus*), benthic macroalgae (Characeae) and pollen of vascular aquatic macrophytes (the waterlilies *Nuphar* and *Nymphaea*, and the emergent *Typha*: Nedelskaja, 2011; Laumets et al., 2014). Although *Botryococcus* has a wide tolerance (Tyson, 1995), it is common in European sediments of late-glacial to Preboreal age, where it reflects cold, clear, oligotrophic-dystrophic conditions (Jankovská and Komárek, 2000). $\delta^{13}\text{C}_{\text{TOC}}$ (-36 to -30‰) and $\delta^{13}\text{C}_{\text{cellulose}}$ values (-33 to -26‰) are transitional between those found in the basal mud and the overlying marls (Fig. 5c). $\delta^{18}\text{O}_{\text{cellulose}}$ (17 – 19‰) and $\delta^{18}\text{O}_{\text{lakewater}}$ (-11 to -9‰) both reach values higher than today, suggesting annual MATs (7 – 11°C) similar to, or higher than today's (Fig. 6). In apparent conflict, the surrounding vegetation reported by Laumets et al. (2014) was an open *Betula-Pinus* forest with a high proportion of non-arboreal pollen (notably *Artemisia* and Chenopodiaceae, with some Poaceae and Cyperaceae), together with pollen and macrofossils of subarctic shrubs and herbs (*Betula nana*, *Salix*, *Dryas octopetala*), and abundant microscopic charcoal (Laumets et al., 2014). A highly seasonal climate with cold winters and warm, dry summers can be inferred. This was associated with near-maximal orbital forcing and probably also increased winter ice cover over the freshwater Ancylus Lake to the north (Punning et al., 2000).

Pale marl (412 – 365 cm; 10.4 – 9.1ka BP). This unit marks the onset of Holocene marl deposition at the ANTU1+2 core site (Fig. 5d). The CaCO_3 content rises to 38–91%, with a variable organic content (TOC 37–42%). The origin of the organic matter was dominantly aquatic with a high algal contribution (C/N ratio 11–13, P_{alg} 0.64–0.89, P_{aq} 0.55–0.68), represented by the colonial green microalgae *Coelastrum reticulatum*, *Pediastrum boreanum* and *Botryococcus*, together with a modest presence of *Chara* oogonia and *Nuphar* pollen (Nedelskaja, 2011; Laumets et al., 2014). The association of *Coelastrum* and *Pediastrum*, with *Metacypris cordata* dominating the ostracod fauna, implies warmer but relatively shallow, mesotrophic-eutrophic conditions in the lake (Happay-Wood, 1988; Jankovská and Komárek, 2000; Sohar and Kalm, 2008), borne out by a rise in TN content to 2.9–3.7%. *Betula-Pinus* forest initially surrounded the site, with an increasing presence of temperate deciduous trees: *Ulmus*, *Corylus* and *Alnus* (Nedelskaja, 2011; Laumets et al., 2014). $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{13}\text{C}_{\text{cellulose}}$ decreased to unusually low values (-41 to -37‰ and -39 to -33‰ , respectively; see Discussion). High $\delta^{18}\text{O}_{\text{cellulose}}$ values (16 – 17.5‰) suggest $\delta^{18}\text{O}_{\text{lakewater}}$ (-12 to -10‰) and annual MATs (6 – 9°C) similar to the present or a little higher (Fig. 6).

Dark organic marl (364 – 328 cm; 9.1 – 7.6ka BP). This unit exhibits consistently high CaCO_3 (48–87%) and TOC contents (17–47%). Slightly increased C/N ratios (10–15), coupled with declines in both P_{alg} (0.43–0.77) and P_{aq} (0.39–0.72), imply a modest increase in the input of terrestrial detritus. Aquatic cellulose sources are represented by low counts of *Botryococcus*, accompanied by *Nuphar* pollen and abundant *Chara* oogonia (Nedelskaja, 2011; Laumets et al., 2014). At the base, the pollen assemblage is similar to the underlying unit, but with an increasing representation of *Alnus*, *Corylus* and thermophilous broad-leaved trees (*Ulmus*, *Tilia*, *Fraxinus*). A short-lived dip in *Alnus*, *Corylus* and *Ulmus* pollen, accompanied by a small peak in Upland Herbs (Nedelskaja, 2011),

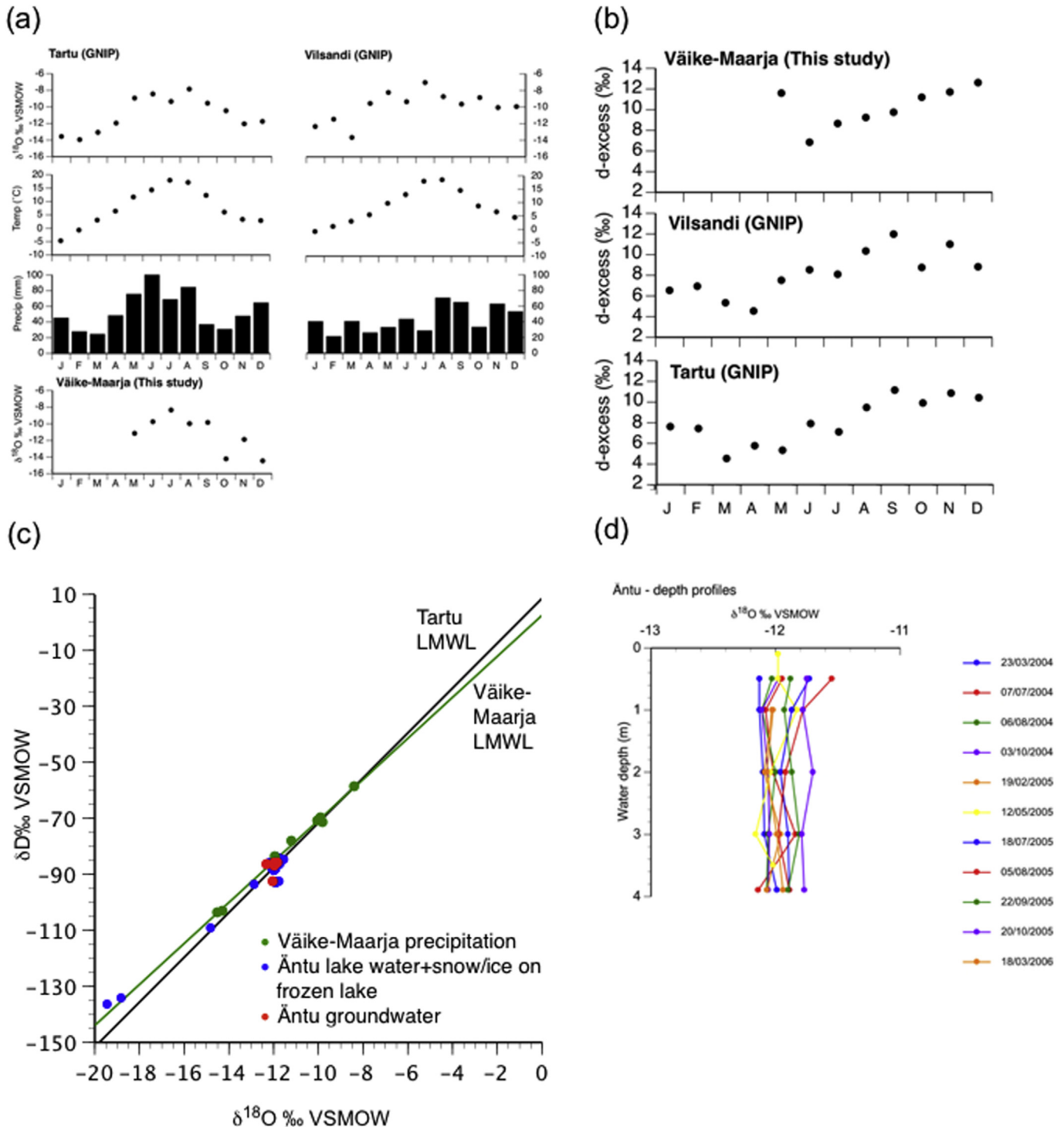


Fig. 2. Modern water-isotope data. (a) Climate and $\delta^{18}\text{O}_{\text{mW}}$ values from Global Network of Isotopes in Precipitation (GNIP) stations at Tartu and Vilsandi, and from Väike-Maarja (this study). (b) Deuterium-excess values (d_{mw}) in precipitation from the three precipitation isotope series. (c) $\delta^{18}\text{O}$ - δD biplot for lake water from Äntu Sinijärv, and for precipitation and groundwater from Väike-Maarja. Lake-water data with $\delta^{18}\text{O}$ values $< -14\text{‰}$ relate to snow and melted water on the frozen lake surface. Local meteoric water lines (LMWLs) for Väike-Maarja ($\delta\text{D} = 7.33 \times \delta^{18}\text{O} + 2.54$) and Tartu ($\delta\text{D} = 8.01 \times \delta^{18}\text{O} + 8.57$) are also shown. (d) Depth profiles of $\delta^{18}\text{O}_{\text{lake water}}$ for Äntu Sinijärv.

may mark the 8.2ka BP cold event. $\delta^{13}\text{C}$ values continued to be unusually low (-43 to -38‰ for both TOC and cellulose). In contrast, $\delta^{18}\text{O}_{\text{cellulose}}$ exhibited a marked perturbation in the middle of this unit which we attribute to the 8.2ka BP event (Figs. 3,4; see Discussion). Estimated MATs varied widely from -4 to $+12$ °C (Fig. 6).

Grey marl (327 – 294 cm; 7.6 – 6.6ka BP). The grey marl displays similar bulk characteristics to the underlying dark organic marl, but with uniformly high CaCO_3 (87–92%) and TOC (37–42%) contents. Low C/N ratios (10–12), P_{alg} (0.38–0.73) and P_{aq} (0.26–0.52) suggest a mixture of aquatic (mainly algal) and minor terrestrial cellulose sources. *Botryococcus* and *Cosmarium* increased

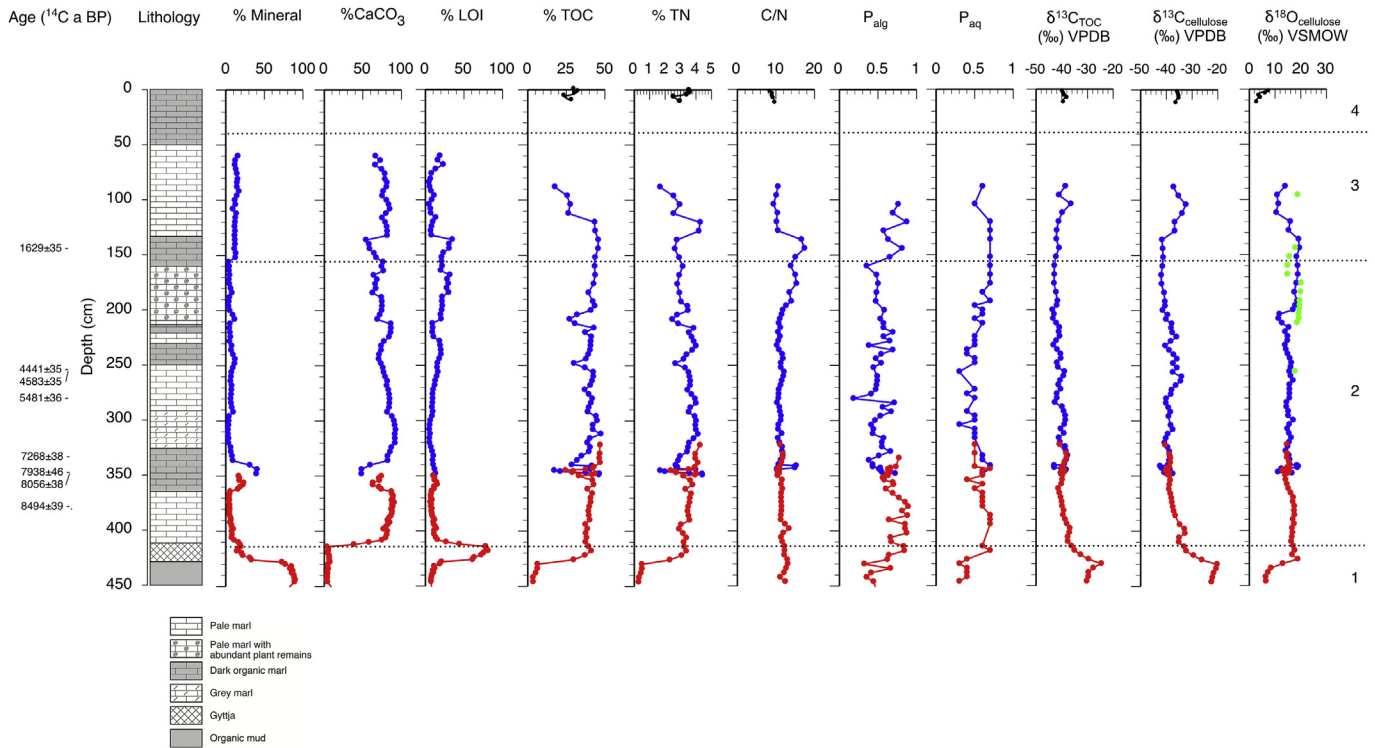


Fig. 3. Stratigraphy of the composite ANTU1+2 lake-sediment sequence plotted versus corrected depth, showing radiocarbon dates on terrestrial macrofossils (¹⁴C yr BP), bulk composition, TOC and TN contents, C/N ratios, biomarker indices P_{alg} and P_{aq}, $\delta^{13}\text{C}_{\text{TOC}}$, and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of cellulose. Black symbols denote measurements on the surface core SURF, blue symbols on core ANTU1 and red symbols on ANTU2. Green symbols on the $\delta^{18}\text{O}_{\text{cellulose}}$ plot denote analyses of aquatic-moss cellulose from ANTU1. Refer to [Supplementary Data](#) for details of depth correction. Biogeochimical phases 1–4 are indicated.

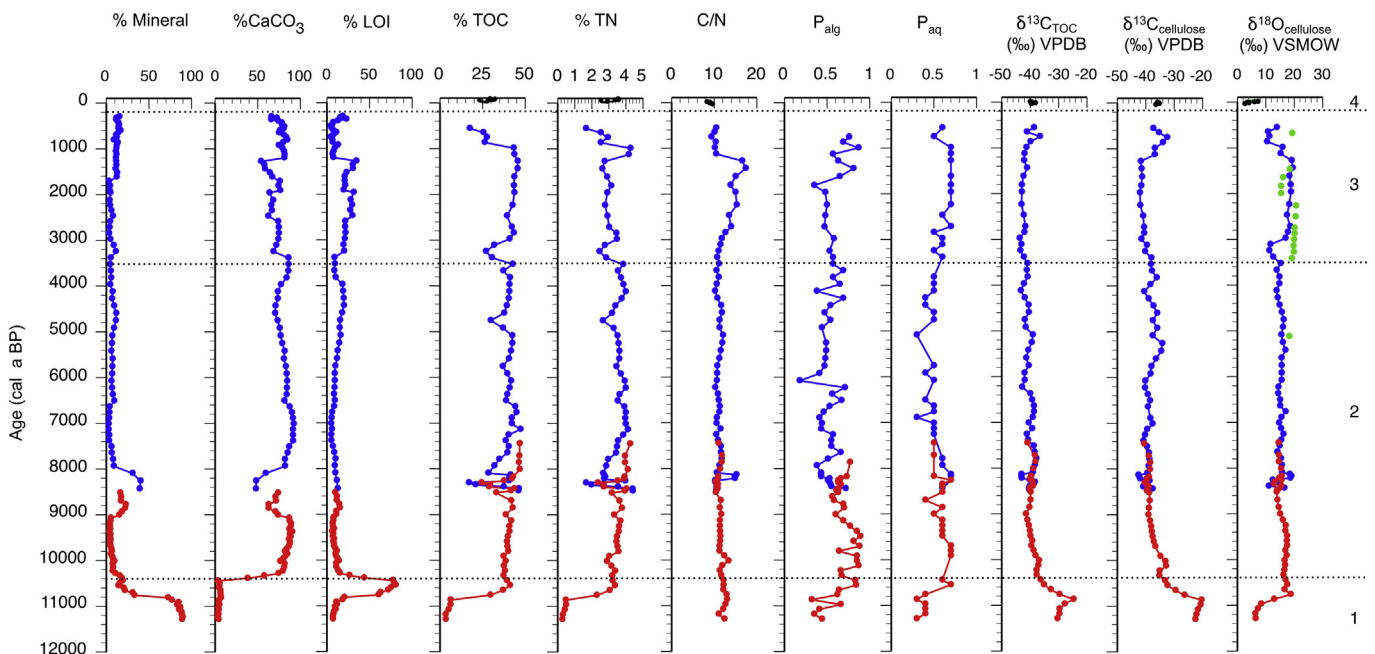


Fig. 4. Stratigraphy of the composite ANTU1+2 lake-sediment sequence plotted versus age in calendar years Before Present. Curves and symbols as for Fig. 3. Biogeochimical phases 1–4 are indicated. Refer to [Supplementary Data](#) for details of the age model used.

rapidly in this zone (Nedelskaja, 2011). *Cosmarium* is a large, single-celled, non-motile green microalga (desmid) that may occupy benthic niches, often in association with aquatic plants, and tends to be most common in summer to autumn (Happy-Wood, 1988).

Laumets et al. (2014) found large numbers of *Chara* oogonia in their core, together with pollen of the emergent macrophytes *Juncus* and *Cladium*. The surrounding vegetation was a moist, temperate forest dominated by *Betula*, *Alnus* and thermophilous broad-leaved trees.

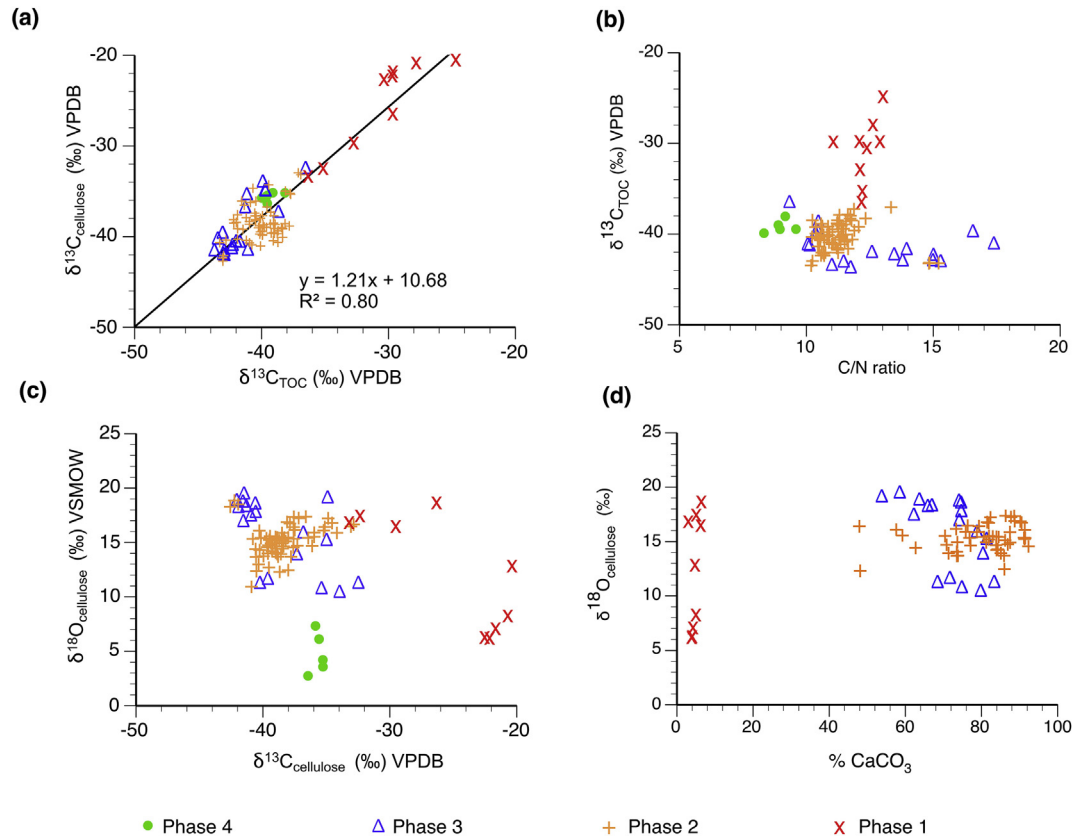


Fig. 5. Bivariate plots of selected geochemical and isotope variables for the composite ANTU1+2 lake-sediment sequence: (a) $\delta^{13}\text{C}_{\text{TOC}}$ versus $\delta^{13}\text{C}_{\text{cellulose}}$; (b) C/N ratio versus $\delta^{13}\text{C}_{\text{TOC}}$; (c) $\delta^{13}\text{C}_{\text{cellulose}}$ versus $\delta^{18}\text{O}_{\text{cellulose}}$; (d) $\delta^{18}\text{O}_{\text{cellulose}}$ versus % CaCO_3 . In all diagrams, Phase 1 is ~11.4–10.4 ka (450–413 cm); Phase 2 is ~10.4–3.5 ka (412–211 cm); Phase 3 is ~3.5 ka–0.23 ka (210–51 cm); and Phase 4 is ~0.23 ka–Present (50–0 cm). Figure (d) lacks points for phase 4 owing to the unavailability of % CaCO_3 data for this phase.

However, modest percentages of *Pinus* pollen and increasing numbers of Poaceae and Upland Herbs suggest the presence of conifers and open areas within the wider landscape (Nedelskaja, 2011). Anomalously low $\delta^{13}\text{C}$ values continued (TOC: –41 to –39‰; cellulose: –41 to –38‰). $\delta^{18}\text{O}_{\text{cellulose}}$ (15–17‰) and reconstructed $\delta^{18}\text{O}_{\text{lakewater}}$ values (–13 to –11‰) suggest MATs of 3–8 °C (Fig. 6), spanning modern observations.

Pale laminated marl, Organic marl, Pale marl, Dark laminated marl (293–215 cm; 6.6–3.5ka BP). This section is characterized by abundant to very abundant charophyte oogonia. CaCO_3 contents ranged from 70 to 86%, and TOC from 30 to 43%. C/N ratios remained very steady at 10–12, within the range observed in modern *Chara* (unpubl. ISOMAP-UK data; Aichner et al., 2010), while P_{alg} and P_{aq} were 0.18–0.69 and 0.33–0.53, respectively, suggesting some terrestrial input. During this interval, *Botryococcus* increased markedly, in association with *Cosmarium*; however, the latter declined after ~5ka BP. Stands of floating (*Nuphar*, *Nymphaea*) and submerged vascular macrophytes (*Potamogeton*) occupied the shallows (Nedelskaja, 2011). Significant changes also occurred in the wider landscape. *Picea*, *Pinus* and *Quercus* increased, while *Betula*, *Alnus* and thermophilous trees (*Ulmus* and *Tilia*) gradually declined (Nedelskaja, 2011). Signs of human impact also appeared after ~5ka BP, in the form of sporadic cereal grains, *Calluna*, *Pteridium*, weeds of cultivation and microscopic charcoal (Laumets et al., 2014). The appearance of *Sphagnum* and *Equisetum* spores, together with Cyperaceae and marshland herbs (Menyanthaceae), records the onset of paludification. Peat growth divided Äntu Sinijärvi from Vahejärvi after the level of Palaeolake Äntu fell around 4ka BP (Nedelskaja, 2011). Carbon-isotope values remained persistently low. $\delta^{18}\text{O}_{\text{cellulose}}$ (14–17‰) and reconstructed $\delta^{18}\text{O}_{\text{lakewater}}$ values

(–14 to –11‰) imply little change in MATs (1–8 °C), apart from a slight cooling after ~4.3ka (Fig. 6).

Pale marl, Marl with plant remains, Dark laminated marl, Pale laminated marl (214–51 cm; 3.5–0.23ka BP). The distinguishing feature of this part of the ANTU1+2 core is the presence of abundant aquatic moss fragments within the lake marls, particularly prior to ~1.2ka BP (Figs. 3,4). *Scorpidium scorpioides* is a calciphilous, brown, rich-fen moss that thrives in shallow water or on inundated peat bogs. It possesses special adaptations to prevent emergence and desiccation, favouring open, sunny habitats (Boryslawski, 1978; Proctor and Smirnov, 2000). The bulk characteristics of this core section are rather variable (CaCO_3 content: 54–86%; TOC content: 17–46%), reflecting increasing instability in the lake. C/N ratios (9–17) and biomarker indices (P_{alg} : 0.35–0.87; P_{aq} : 0.47–0.73) are compatible with varying proportions of algal and moss detritus, since *Scorpidium* has an average C/N ratio of ~35 and P_{aq} values ≥ 0.92 (Zibulski et al., 2017). Like other bryophytes, however, it does not produce a large amount of *n*-alkanes, although their distribution peaks at *n*-C₂₅ like *Chara* (Mead et al., 2005) and many submerged vascular plants (Ficken et al., 2000). Cyperaceae pollen, associated with sparse macrofossils of *Carex* and *Typha*, represents emergent aquatics. Coniferous forest (*Pinus*, *Picea*) dominated the regional landscape, together with *Alnus* and a declining percentage of *Betula*. Human impacts intensified after ~2ka BP (Laumets et al., 2014). Carbon-isotope values in this core segment edged up a little (TOC: –44 to –37‰; cellulose: –42 to –33‰), notably in the Pale laminated marl (134–51 cm; 1.2–0.23ka BP) (see Discussion). Bulk $\delta^{18}\text{O}_{\text{cellulose}}$ (11–19‰), moss $\delta^{18}\text{O}_{\text{cellulose}}$ (15–20‰), reconstructed $\delta^{18}\text{O}_{\text{lakewater}}$ (–17 to –8‰) and estimated MAT values (–6 to +13 °C), if taken at face value,

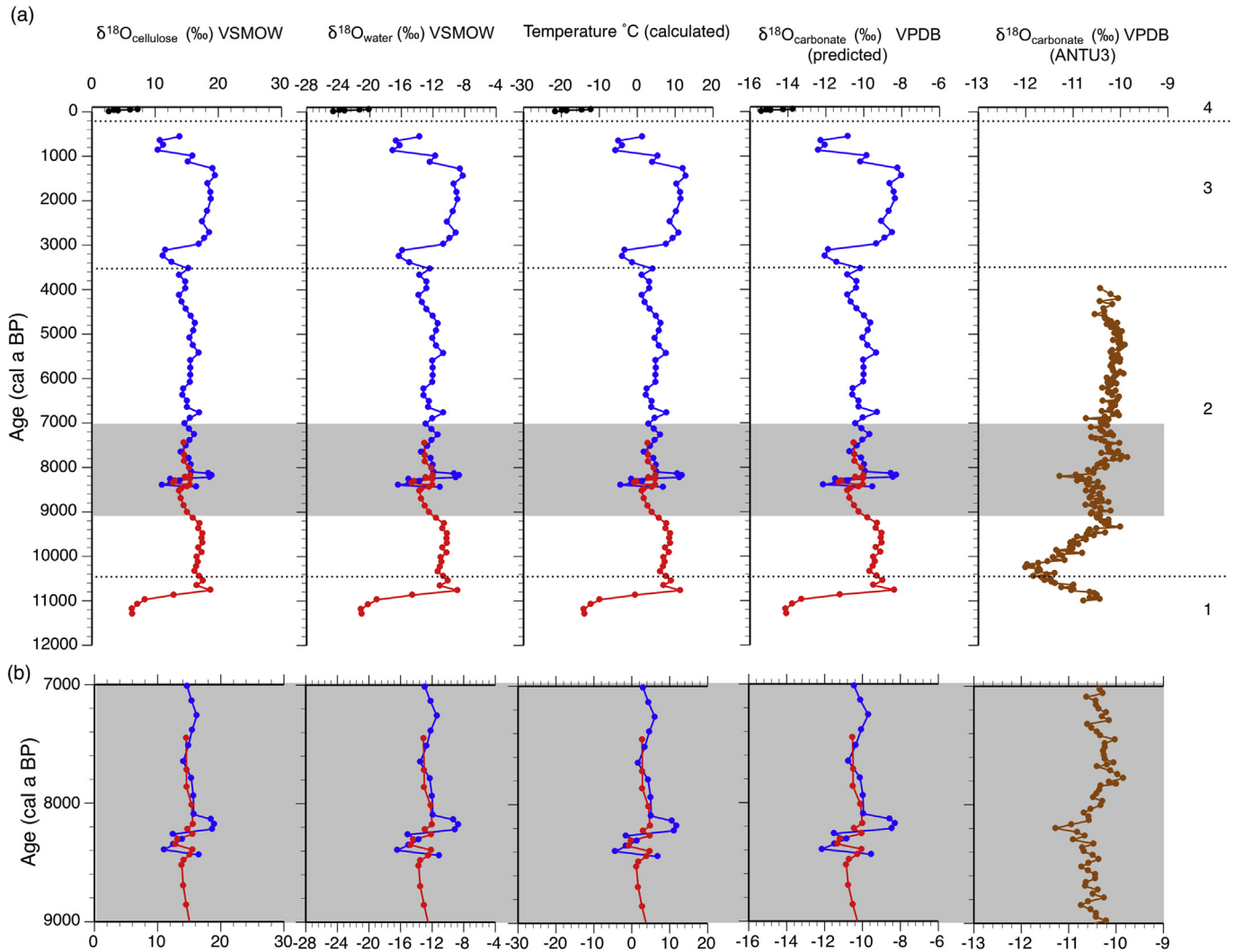


Fig. 6. Measured oxygen-isotope values of bulk cellulose ($\delta^{18}\text{O}_{\text{cellulose}}$), together with calculated lake-water $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}_{\text{lakewater}}$), reconstructed mean-annual palaeotemperatures and predicted $\delta^{18}\text{O}$ values of endogenic carbonate ($\delta^{18}\text{O}_{\text{carbonate}}$) for core ANTU1+2, compared with measured $\delta^{18}\text{O}_{\text{carbonate}}$ values in core ANTU3 (Nedelskaja, 2011; unpubl. data). Panel (a) shows the entire Holocene sediment record, with Phases 1–4 marked; and (b) the shaded region in (a), covering 9–7ka BP, on an expanded age scale. Calculations of $\delta^{18}\text{O}_{\text{lakewater}}$, palaeotemperature and predicted $\delta^{18}\text{O}_{\text{carbonate}}$ are described in Supplementary Data.

imply that the most pronounced warm period of the entire Holocene occurred between ~3.5 and 1.2ka BP (Fig. 6), which seems unlikely. We hypothesize that the marginal shallows and possible inundation of surrounding peatland recorded by *Scorpidium* resulted in warmer water temperatures and increased evaporation in summer, causing the isotopic composition of the lake to evolve along a local evaporative line (LEL), in contrast to the present day (Fig. 2c).

Marl (50 – 0 cm, 0.23ka BP - Present). Data for this interval are sparse, due to a shortage of material from surface core SURF and a lack of palaeoecological data. The five available samples only represent the uppermost 10 cm (the last few decades). Their TOC content ranged from 23 to 32% and their low C/N ratios (8–10) were typical of lacustrine plankton. $\delta^{18}\text{O}_{\text{cellulose}}$ (3–7‰) also deviated markedly from the rest of the core, implying implausibly low average lake-water temperatures (Fig. 6). These samples probably represent an algal floc deposited during the early spring bloom, when the isotopic composition of the water may be strongly influenced by snowmelt (section 3.1), especially as the lake has become enriched with N and other nutrients in recent years (Saarse and Liiva, 1995).

4. Discussion

4.1. Changing cellulose sources

The $\delta^{13}\text{C}$ values of cellulose and TOC were tightly coupled through the Holocene ($R^2 = 0.80$: Figs. 3, 4, 5 a), notably during the more variable periods. Hence, our measured C/N ratios ($\ll 20$) in bulk organic matter (Fig. 5b) and biomarker indices, supported by the available palaeoecological data, imply that aquatic-cellulose sources dominated the sediment record of Äntu Sinijärv. Nevertheless, several contrasting biogeochemical phases can be identified (Fig. 5). From the base of the sequence (~11.4ka BP) until ~10.4ka BP, when marl deposition was initiated, the lake was probably at least 3–5 m deeper than today (Saarse and Liiva, 1995); aquatic microalgal and minor terrestrial organic-matter sources prevailed (Phase 1). From ~10.4ka BP onwards, aquatic productivity increased. The organic fraction mainly comprised a diverse mixture of aquatic inputs from green micro- and macroalgae (charophytes) and floating/submerged vascular plants, with a minor contribution from emergent macrophytes (Phase 2). Increasing paludification after ~6.6ka BP heralded the separation of Palaeolake Äntu into the

three smaller modern lakes (Äntu Sinijärv, Rohejärv and Valgejärv) by declining water levels and peat growth (Lehtmaa, 2006; Nedelskaja, 2011). Phase 3 (~3.5 to at least 0.23ka BP) was characterized by the deposition of abundant brown-moss macrofossils within the lake marls, in response to continued infilling by sediment and expansion of marginal peatlands. Data for the last 200–300 years (Phase 4) are sparse. However, the uppermost sediments appear to be of planktonic origin.

In addition to hydrosere changes resulting from gradual infilling of the basin by lake sediments and marginal mires, the sediment record of Äntu Sinijärv carries the imprint of major shifts in the biogeochemistry of surrounding terrestrial ecosystems. Phase 1 records the transition from the open landscape of the Preboreal to a birch-conifer forest. During Phase 2, the arrival of first, temperate and later, thermophilous deciduous tree species was accompanied by the development of a more diverse and nutrient-demanding lacustrine ecosystem including flourishing stands of benthic macroalgae (charophytes). After ~6.6ka BP, re-invasion by conifer (spruce-pine) forest, followed by human impact and paludification, began to reverse this trend, culminating in the creation of shallow and/or marginal habitats in which calciphilous brown mosses could thrive (Phase 3). Phase 4 appears to reflect recent cultural eutrophication (Saarse and Liiva, 1995).

4.2. Carbon- and oxygen-isotope records from Äntu Sinijärv

4.2.1. Carbon isotopes

A remarkable feature of the $\delta^{13}\text{C}$ records from Äntu Sinijärv is the large decrease in the average $\delta^{13}\text{C}$ values of both TOC and cellulose (by 10‰ and 14‰, respectively) between Phase 1 and Phase 2 (Fig. 5a,c). More than half this change took place around 10.4ka BP in core ANTU1+2, coinciding with the onset of biogenic decalcification of the lake water, resulting in marl deposition (Fig. 5d). It represents a major shift in the entire lake-catchment carbon cycle. Similar (3–10‰) decreases in the $\delta^{13}\text{C}$ values of bulk organic matter and carbonates during the early Holocene in Sweden and Estonia were attributed by Hammarlund (1993), Hammarlund et al. (1997), Punning et al. (2000) and Stansell et al. (2017) to soil development associated with the transition from pioneer herb communities to subarctic birch and then boreal pine forests, resulting in an increased flux of ^{13}C -depleted terrestrial biogenic carbon into the lakes from their catchments.

The ^{13}C content of the dissolved organic carbon (DIC) pool in lakes may be far from equilibrium with the atmosphere. It is mainly controlled by: i) the $\delta^{13}\text{C}$ value of the DIC in inflowing waters; ii) isotopic exchange with atmospheric CO_2 ; iii) the photosynthetic and respiratory processes of aquatic macrophytes and algae; and iv) the decay of organic matter (Oana and Deevey, 1960; Street-Perrott et al., 1993). Extremely ^{13}C -depleted carbon-isotope values (–22 to –10‰ in DIC and –47 to –40‰ in plankton) were reported by Rau (1978) from a small, deep, oligotrophic lake surrounded by dense conifer forest on the Cascade Range, USA. Typical $\delta^{13}\text{C}$ values for the forest biomass were –29 to –25‰. He attributed the extraordinarily low $\delta^{13}\text{C}$ values measured on plankton mainly to uptake of ^{13}C -deficient respiratory CO_2 released from catchment soils and in-washed terrestrial detritus. However, more fertile hardwater lakes like Äntu Sinijärv, which receive substantial inputs of groundwater with DIC chemically and isotopically controlled by both respiration and reactions with aquifer carbonates, may also exhibit marked ^{13}C disequilibrium with the atmosphere, as exemplified by Land and Epstein (1970), Street-Perrott et al. (1993) and Holmes et al. (1995), who reported ^{13}C -depleted values between –13 and –5‰ for DIC in Jamaican river- and groundwaters. Chemical weathering of limestone associated with high concentrations of soil CO_2 transmits this depleted carbon-isotope

signature of biogenic carbon from the catchments into surface waterbodies via the karst drainage system, resulting in lacustrine carbonates with isotope values as low as –12‰.

Isotopic re-equilibration of the waters of small lakes with the atmosphere may be surprisingly inefficient (Street-Perrott et al., 1993; Holmes et al., 1995). However, had Äntu Sinijärv ever become hydrologically closed during the Holocene, productivity-driven ^{13}C -enrichment of the DIC, and the resulting organic and carbonate fractions, would probably have occurred (Talbot, 1990). Alternatively, Hammarlund et al. (2005) have suggested that oxidation of ^{13}C -depleted CH_4 generated in anoxic sediments lowered the ^{13}C content of the DIC during the 8.2ka event in a Swedish marl lake. A requirement of the CH_4 hypothesis as an explanation for very low $\delta^{13}\text{C}$ values in lacustrine organic matter from Äntu Sinijärv, however, is that the ^{13}C -enriched co-genetic CO_2 produced by methanogenesis (Herczeg, 1988) be effectively dissipated.

In the case of Äntu Sinijärv, temporal changes in the carbon metabolism of the lake were closely coupled to the biogeochemistry of terrestrial ecosystems throughout the Holocene. At different stages, it was populated by a range of aquatic organisms with adaptations to different carbon sources and concentrations. During Phase 1, cold, subarctic conditions with pioneer vegetation and weakly developed soils (Punning et al., 2000) were associated with low counts of the slow-growing, green colonial alga *Botryococcus*. This has evolved several highly specialized strategies for coping with oligotrophic, C- or N-limited waters (Belcher, 1968; Ohmori et al., 1984; Cepák and Lukavský, 1994). It is able to assimilate HCO_3^- , the dominant DIC species in moderately alkaline lakes, as a C source. It also produces abundant oil droplets (isoprenoid alkenes), which keep the algal colonies afloat at the water surface where light intensity and atmospheric CO_2 influx are maximized.

The greatest limnic biodiversity occurred during Phase 2, registered by abundant fossils of charophytes, green microalgae and floating/submerged aquatics, implying a sustained influx of DIC and nutrients from the catchment, corresponding to the development of brown forest soils (Punning et al., 2000) under thermophilous deciduous forest. During this phase, very low $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{13}\text{C}_{\text{cellulose}}$ values below –40‰ were persistently registered. A high proportion of the aquatic organisms recorded (apart from macrophytes with floating leaves, e.g. *Nuphar*, *Nymphaea*) are able to utilize bicarbonate as a C substrate (Maberly and Spence, 1983). The abundance of oogonia suggests that *Chara* stands were a particularly important cellulose source. This macroalga possesses sophisticated ion pumps that enable it to assimilate dissolved HCO_3^- (McConnaughey and Falk, 1991). For every two HCO_3^- ions taken up from the water, one is precipitated in the form of carbonate encrustations on the plant surfaces and one is used for photosynthesis. This process results in substantial carbon-isotope fractionation between organic- and carbonate-C, measured by Pentecost et al. (2006) as ~19‰. Since the organic fraction of *Chara* decomposes rapidly (cf. Nuñez et al., 2002), it provides an additional ^{13}C -deficient CO_2 source during periods of marl formation (Hammarlund et al., 1997).

From ~6.6ka BP onwards, the supply of biogenic DIC and dissolved organic carbon (DOC) may have been maintained by the development of boreal conifer forest and peatland around the lake, augmented after ~5ka BP by human-induced land-use changes (deforestation and agriculture), which have been shown to increase the flux of DIC into lakes via the hydrological system (Maberly et al., 2013). Measurements by Bain and Proctor (1980) suggest that *Scorpidium scorpioides*, like other aquatic bryophytes of hardwater lakes, is an obligate dissolved- CO_2 user, thereby helping to perpetuate the low ^{13}C values of TOC and cellulose observed in the

lake muds. No carbon-isotope analyses are available for the cellulose fraction of the surface sediments in core SURF, due to shortage of material.

4.2.2. Oxygen isotopes in cellulose and carbonate

The $\delta^{18}\text{O}_{\text{cellulose}}$ record from the ANTU1+2 core (Figs. 3–4) exhibits both step changes attributable to local hydrological and ecological perturbations, and centennial-scale palaeoclimatic events that are discussed below in section 4.3. The pronounced isotopic shift in $\delta^{13}\text{C}/\delta^{18}\text{O}$ space across the Phase 1–2 transition, ~10.4ka BP (Fig. 5c) is accompanied by such a marked discontinuity in sediment properties (Fig. 5b,d) that a local hydrological change superimposed on more gradual processes like forest development and soil formation can be suspected. For example, a strong increase in groundwater discharge could have suddenly unblocked a veneer of glacial deposits that previously plugged the large spring vents (Saarse and Liiva, 1995), which now discharge HCO_3^- -rich limestone groundwaters through the lake bed. Another event that may reflect local hydrological and hydroseral changes is the sharp rise in $\delta^{18}\text{O}_{\text{cellulose}}$ values starting during the late Holocene (~3.1ka BP), early in Phase 3 (Figs. 3–4), which was attributed above to inundation of expanding marginal peatlands.

Several recent papers have made quantitative comparisons between $\delta^{18}\text{O}_{\text{cellulose}}$ and $\delta^{18}\text{O}_{\text{carbonate}}$ in order to reconstruct lake-water temperatures by means of the so-called “calcite-cellulose geothermometer” (Rozanski et al., 2010; Heikkilä et al., 2010; Buhay et al., 2012). This involves using measured $\delta^{18}\text{O}_{\text{cellulose}}$ values to calculate $\delta^{18}\text{O}_{\text{lakewater}}$ and then applying an empirical calcite-water equilibrium equation (usually Kim and O’Neil, 1997) to paired $\delta^{18}\text{O}_{\text{lakewater}}$ and $\delta^{18}\text{O}_{\text{carbonate}}$ values in order to calculate past changes in epilimnion temperature. This approach works well if the cellulose and calcite $\delta^{18}\text{O}$ curves are broadly parallel. In Fig. 6, we compare the $\delta^{18}\text{O}_{\text{cellulose}}$ record from core ANTU1+2 with the $\delta^{18}\text{O}_{\text{carbonate}}$ data from core ANTU3 (Nedelskaja, 2011, supplemented by additional, unpublished analyses). Unfortunately, although these two curves vary largely in concert from ~9ka onwards, they diverge substantially between ~11ka and ~9ka. This discrepancy is most evident from a comparison between our predicted $\delta^{18}\text{O}_{\text{carbonate}}$ curve for core ANTU1+2 and the $\delta^{18}\text{O}_{\text{carbonate}}$ measurements from core ANTU3 (Fig. 6). The maximum difference (Predicted-Actual) is ~2.5%. Buhay et al. (2012) also reported decoupling of carbonate $\delta^{18}\text{O}$ and cellulose-inferred lake-water $\delta^{18}\text{O}$ values in Deep Lake, Minnesota, between 11 and 9ka BP, in a not-dissimilar palaeogeographical situation on the southern side of the remnant Laurentide icesheet and the large, meltwater-fed proglacial Lake Agassiz.

Provided that the discrepancy between the Äntu Sinijärv $\delta^{18}\text{O}_{\text{cellulose}}$ and $\delta^{18}\text{O}_{\text{carbonate}}$ records does not merely reflect unresolved stratigraphical or dating issues, or divergent limnological settings within different sub-basins of Palaeolake Äntu, it can be attributed to several types of “no-analogue” behaviour compared with the present day. First, it may not be valid to extrapolate the modern relationship between $\delta^{18}\text{O}_{\text{mw}}$ and air temperature, derived from the very short GNIP record, to reconstruct palaeotemperatures from the cellulose-based $\delta^{18}\text{O}_{\text{lakewater}}$ estimates (Fig. 6), especially beyond ~9ka BP (cf. Guan et al., 2016; Tyler et al., 2016). Furthermore, the expanded Palaeolake Äntu may have evolved along a LEL during the dry early Holocene, without ever becoming hydrologically closed (cf. modern Estonian lakes sampled by Stansell et al., 2017).

Secondly, past reconstructed variations in cellulose sources (section 4.1) suggest that the $\delta^{18}\text{O}_{\text{cellulose}}$ signal may represent different seasons and environments of cellulose synthesis at different times. Algal blooms may have captured the low isotope values of spring snowmelt to a greater degree during Phase 1 and

the early part of Phase 2 than during the mid-Holocene (cf. Wolfe and Edwards, 1997). In contrast, after ~9ka, co-production of cellulose and calcite within dense *Chara* beds may have occurred predominantly during warmer conditions in summer and early autumn. Significant kinetic effects may also have occurred during rapid calcite precipitation (Coplen, 2007; Rozanski et al., 2010).

Thirdly, the regional climate and palaeogeography of Scandinavia and the Baltic Basin were markedly different from today during the interval ~11 – 9ka BP. Orbital forcing and seasonal insolation anomalies were close to their maximum post-glacial values. The rapidly shrinking Fennoscandian and Laurentide Ice Sheets, major oceanographic changes in the North Atlantic and the impact of $\delta^{18}\text{O}$ -depleted glacial meltwater on the greatly expanded predecessors of the modern Baltic Sea (section 2.1.1) would also have significantly affected seasonal airflow patterns (Mitchell et al., 1988; Renssen and Isarin, 2001; Tindall and Valdes, 2011) as well as the proximity, availability and isotope values of regional moisture sources (Heikkilä et al., 2010). Estimates of summer temperatures in Estonia based on rapidly responding proxies such as aquatic macrofossils (Väliranta et al., 2015) and chironomids (Heiri et al., 2014) suggest conditions $\leq 2^\circ\text{C}$ warmer than today during the early Holocene. However, pollen-based reconstructions of Estonian summer and winter temperatures are bedevilled by very low pollen counts and by the delayed arrival of forest trees from their glacial refugia (Väliranta et al., 2015; Veski et al., 2015). The development of fully self-consistent, climatic, hydrological and isotopic scenarios for the early Holocene needs to draw on the power of isotope-enabled GCMs to simulate regional anomalies throughout the entire annual cycle in response to past changes in orbital forcing and climatic-boundary conditions (cf. LeGrande and Schmidt 2008; Daley et al., 2011; Tindall and Valdes, 2011; Liu et al., 2014; Holmes et al., 2016).

4.3. Centennial-scale palaeoclimatic events

Three $\delta^{18}\text{O}$ minima of wide palaeoclimatic significance are recorded in the Äntu Sinijärv cellulose sequence: the PBO, the 8.2ka event and an unnamed event centred on ~3.25ka BP (Fig. 6). The first two have been linked to oceanic impacts of meltwater discharges from the decaying Laurentide and Fennoscandian Ice Sheets (Björck et al., 1996; Fisher et al., 2002; von Grafenstein et al., 1998, 1999; Hammarlund et al., 2005; Daley et al., 2011; Tindall and Valdes, 2011), whereas the third has an uncertain cause. It is one of a series of mid-Holocene climatic oscillations recorded in European bogs and lakes (Barber et al., 2004), but is particularly pronounced in Äntu Sinijärv.

The PBO is recorded by the deep $\delta^{18}\text{O}$ minimum (reconstructed $\delta^{18}\text{O}_{\text{lakewater}}$ –21.06 to –20.97‰) at the base of the Äntu Sinijärv sequence, dated ~11.3–11.2ka (Fig. 6a). Although these values are similar to present-day February snowfall, both they and the mean-annual palaeotemperatures derived from them (–14.1 to –13.9 °C) seem implausibly low, given that the TOC content of the sediment is minimal, the dominant carbon source was microalgae, which may have adopted the isotopic signature of spring snowmelt, and the available GNIP record used to calibrate the lakewater $\delta^{18}\text{O}$ values is uncomfortably short; hence, the slope of the MAT/ $\delta^{18}\text{O}$ regression line is not well constrained.

The ANTU1 core confirms that $\delta^{18}\text{O}_{\text{cellulose}}$ has the potential in principle to provide a detailed record of the 8.2ka cold event (Fig. 6a,b). It displays double isotope minima at ~8.39 and ~8.26ka BP, with reconstructed $\delta^{18}\text{O}_{\text{lakewater}}$ values of –16.4 and –15.1‰, corresponding to estimated annual MATs of –4.4 and –1.6 °C, respectively, followed by a warm “overshoot” to +11.8 °C at ~8.17ka (which has been identified by Andersen et al. (2017) in several other $\delta^{18}\text{O}$ records ranging from Greenland to Austria). Although

many high-resolution records of the 8.2ka event from around the North Atlantic also exhibit double isotope minima, there is as yet little consensus about the timing of the two events, in part due to dating issues (Daley et al., 2011). Unfortunately, however, not only does the amplitude of isotopic variation in core ANTU1 seem rather large in comparison with both more proximal and more distal sites (von Grafenstein et al., 1998; Daley et al., 2011; Baker et al., 2017), but the ANTU2 core displays a much more muted signal than ANTU1 in the region of overlap (Fig. 6b), making it difficult to draw firm palaeoclimatic conclusions from this part of the $\delta^{18}\text{O}_{\text{cellulose}}$ record.

The 3.25ka $\delta^{18}\text{O}$ minimum lasted for ~300 years, from ~3.4 to ~3.1ka BP (Fig. 6a). $\delta^{18}\text{O}_{\text{cellulose}}$ reached a low of +11.3‰, implying a $\delta^{18}\text{O}_{\text{lakewater}}$ value of -16.3‰ and an annual MAT around -4.0 °C, similar to the modern January mean in Tartu (Fig. 2a). A search for other palaeoclimatic records from eastern Europe that include this cold event would help to determine its wider significance.

4.4. Cellulose isotopes as palaeoenvironmental indicators in a shallow, hardwater lake

Hardwater lakes offer significant advantages for cellulose-isotope studies. They are often more productive and biodiverse than softwater lakes, leading to sediments rich in cellulose, which provides a standard chemical material for isotope analysis, unlike TOC. $\delta^{13}\text{C}_{\text{cellulose}}$ and $\delta^{18}\text{O}_{\text{cellulose}}$ analyses can be coupled with isotope measurements on endogenic and biogenic carbonates or biogenic silica from the same core levels, thereby offering detailed insights into past changes in hydrology and carbon cycling, not just on a whole-lake basis but also with a prospect of resolving different trophic levels, habitats and seasons. Given ideal conditions, cellulose-calcite and cellulose-silica geothermometry can be attempted (Rozanski et al., 2010; Heikkilä et al., 2010; Buhay et al., 2012). In Äntu Sinijärv, shifts in $\delta^{13}\text{C}_{\text{cellulose}}$ values were related to major events affecting the carbon cycle in the coupled lake-catchment ecosystem. This study has also demonstrated that with a soundly based chronology, major abrupt palaeoclimatic events can be identified within a century or so of their accepted dates of occurrence, although their isotopic magnitude and estimated palaeotemperature implications may be exaggerated in this sequence due to past departures from observed seasonal, hydrological and isotopic behaviour resulting from orbital forcing and changing climatic-boundary conditions (section 4.2.2). The signature of local and regional hydrological events such as lake-level variations and hydroseral succession has also been detected in the $\delta^{18}\text{O}_{\text{cellulose}}$ record.

However, the diverse range of aquatic cellulose sources prevalent in a hardwater lake (microalgae, macroalgae, calciphilous bryophytes and vascular plants), not to mention potential “terrestrial” sources (emergent macrophytes and land vegetation that use atmospheric CO_2) could be viewed as a disadvantage. With some success, but also with significant effort, this study has identified past changes in major cellulose sources with the aid of C/N ratios and biomarker indices calculated from GC-MS analyses of the solvent extracts remaining after cellulose preparation, together with several types of palaeoecological data (pollen, plant macrofossils and other microfossils) that are available for earlier cores from the same lake. The rich plant-physiological literature on aquatic plants and algae provides a valuable resource for understanding the carbon metabolism of the major cellulose producers identified in this way, although more detailed work on non-pollen palynomorphs could well lead to surprises.

The temperature-independent oxygen-isotope fractionation between source water and cellulose is an important advantage of cellulose-isotope analysis, as noted in the Introduction. However,

the greater the degree of water-column stratification, variability of dominant water sources (rainfall, groundwater, snowmelt), diversity of microhabitats or seasonality of cellulose production by different organisms, the greater the need for isotope analyses of modern plants and waters in order to resolve the resulting complexity. Fortunately, the present-day Äntu Sinijärv is an open lake with a short water-residence time that only displays very weak oxygen-isotope stratification. This study has attempted to estimate Holocene palaeotemperatures using monthly weighted-average $\delta^{18}\text{O}_{\text{mw}}$ and temperature data from the nearest GNIP station; however, the results should be treated with caution, as noted in section 4.2.2. It is also important to recognize that submerged vascular plants and *Chara* living on the bed of the lake are probably bathed in ^{14}C - and ^{13}C -depleted spring waters throughout their respective growing seasons (cf. Sensula et al., 2006). Unfortunately, only one relevant plant analysis from Äntu Sinijärv (*Ceratophyllum demersum*: $\Delta^{14}\text{C}$ on carbonate encrustations $-147 \pm 6.7\%$ in 1970; $\delta^{13}\text{C}_{\text{TOC}} -35\%$: Olsson and Kaup, 2001) and no $\delta^{13}\text{C}$ analyses of the DIC are available to gauge the magnitude of groundwater impacts.

The limited $\Delta^{14}\text{C}$ data for Äntu Sinijärv nevertheless confirm another well-recognized issue with the sediments of hardwater lakes, amply illustrated by Ralska-Jasiewiczowa et al. (1998), Olsson and Kaup (2001) and Sensula et al. (2006): namely, the need to base radiocarbon chronologies exclusively on recognizable terrestrial macrofossils such as seeds, twigs, conifer needles or bud scales (Nedelskaja, 2011), rigorously avoiding TOC, carbonates, aquatic macrofossils and amorphous terrestrial materials such as peat, all of which may display significant radiocarbon reservoir effects. However, the palaeoclimatic comparisons made in section 4.3 suggest that the Äntu Sinijärv chronology used in this study, which was based exclusively on terrestrial macrofossils (Supplementary Data) stands up very well in this respect.

5. Conclusions

1. Shallow hardwater lakes have significant advantages for cellulose-isotope analysis, including biodiverse ecosystems that produce abundant cellulose, which can be analysed in parallel with lacustrine carbonates in order to achieve a more multi-dimensional perspective on past limnological changes.
2. Particular attention must be paid to the need for modern isotope data, supporting geochemical analyses and detailed palaeoecological records in order to resolve past shifts in dominant cellulose sources.
3. In this study, C/N ratios and biomarker indices were successfully employed in conjunction with data on pollen, plant macrofossils and *Chara* oogonia to reconstruct Holocene changes in the origin of the cellulose fraction.
4. ^{14}C chronologies based exclusively on terrestrial macrofossils are essential in order to avoid serious reservoir effects common to hardwater lakes.
5. The Äntu Sinijärv record described here begins in the Preboreal, ~11.4ka BP. The dominant sources of organic matter were aquatic throughout. The sequence can be divided into four main biogeochemical phases distinguished by significant cellulose inputs from microalgae (~11.4–10.4ka), charophytes (~10.4–3.5ka), bryophytes (~3.5 to at least 0.23ka) and microalgae (the last few decades), respectively.
6. The $\delta^{13}\text{C}_{\text{cellulose}}$ record from Äntu Sinijärv exhibits major variations that agree well in timing with published $\delta^{13}\text{C}_{\text{carbonate}}$ curves but are significantly larger in amplitude. Throughout the Holocene, temporal changes in the carbon metabolism of the lake were closely coupled to the biogeochemistry of terrestrial ecosystems.

7. The $\delta^{18}\text{O}_{\text{cellulose}}$ record displays both step changes of probable local hydrological origin, and major centennial-scale cold events of wide palaeoclimatic significance (the Preboreal Oscillation, the 8.2ka event and an unnamed event at ~3.25ka), the ages of which correspond closely in timing with published syntheses.
8. The $\delta^{18}\text{O}_{\text{cellulose}}$ and $\delta^{18}\text{O}_{\text{carbonate}}$ curves for Palaeolake Äntu are in good agreement though the period of overlap after ~9ka BP. However, during the “no-analogue” interval between ~11ka and ~9ka they diverge markedly. At that time, the orbitally forced increase in Northern-Hemisphere seasonality, combined with rapidly changing North Atlantic palaeoceanography and substantially altered regional palaeogeography, probably resulted in isotopic relationships and seasonal patterns of cellulose and carbonate synthesis that deviated markedly from modern observations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.quascirev.2018.05.010>.

References

- Abbott, M.B., Wolfe, B.B., Aravena, R., Wolfe, A.P., Seltzer, G.O., 2000. Holocene hydrological reconstructions from stable isotopes and paleolimnology, Cordillera Real, Bolivia. *Quat. Sci. Rev.* 19, 1801–1820.
- Aichner, B., Hertzschuh, U., Wilkes, H., 2010. Influence of aquatic macrophytes on the stable carbon isotopic signatures of sedimentary organic matter in lakes on the Tibetan Plateau. *Org. Geochem.* 41, 706–718.
- Amon, L., Saarse, L., Vassiljev, J., Heinsalu, A., Veski, 2016. Timing of the deglaciation and the late-glacial vegetation development on the Pandivere Upland, North Estonia. *Bull. Geol. Soc. Finland* 88, 69–83.
- Andersen, N., Lauterbach, S., Erlenkeuser, H., Danielopol, D.L., Namiotko, N., Hüls, M., Belmecheri, Dulski, P., Nantke, C., Meyer, H., Chaplignin, B., von Grafenstein, U., Brauer, A., 2017. Evidence for higher-than-average air temperatures after the 8.2 ka event provided by a Central European $\delta^{18}\text{O}$ record. *Quat. Sci. Rev.* 172, 96–108.
- Anderson, L., Abbott, M.B., Finney, B.P., 2001. Holocene climate inferred from oxygen isotope ratios in lake sediments, Central Brooks Range, Alaska. *Quat. Res.* 55, 313–321.
- Bain, J.T., Proctor, M.C.F., 1980. The requirement of aquatic bryophytes for free CO_2 as an inorganic carbon source: some experimental evidence. *New Phytol.* 86, 393–400.
- Baker, J.L., Lachniet, M.S., Chervyatsova, O., Asmerom, Y., Polyak, V., 2017. Holocene warming in western continental Eurasia driven by glacial retreat and greenhouse forcing. *Nature Geosci.* 10, 430–436.
- Barber, K., Zolitschka, B., Tarasov, P., Lotter, A.F., 2004. Atlantic to Urals – the Holocene climate record of mid-latitude Europe. In: Battarbee, R.W., Gasse, F., Stickley, C.E. (Eds.), *Past Climatic Variability through Europe and Africa*, Kluwer, Dordrecht, pp. 417–442.
- Belcher, J.H., 1968. Notes on the physiology of *Botryococcus braunii* Kützing. *Arch. Mikrobiol.* 61, 335–346.
- Berglund, B.E., Sandgren, P., Barnekow, L., Hannon, G., Jiang, H., Skog, G., Yu, S.Y., 2005. Early Holocene history of the Baltic Sea, as reflected in coastal sediments in Blekinge, southeastern Sweden. *Quat. Int.* 130, 111–139.
- Beuning, K.R.M., Kelts, K., Ito, E., Johnson, T.C., 1997. Paleohydrology of lake Victoria, East Africa, inferred from $^{18}\text{O}/^{16}\text{O}$ ratios in sediment cellulose. *Geology* 25, 1083–1086.
- Beuning, K.R.M., Kelts, K., Russell, J., Wolfe, B.B., 2002. Reassessment of Lake Victoria—upper Nile River paleohydrology from oxygen isotope records of lake-sediment cellulose. *Geology* 30, 559–562.
- Björck, S., Kromer, B., Johnsen, S., Bennike, O., Hammarlund, D., Lemdahl, G., Possnert, G., Rasmussen, T.L., Wohlfarth, B., Hammer, C.U., Spurk, M., 1996. Synchronized terrestrial atmospheric deglacial records around the North Atlantic. *Science* 274, 1155–1160.
- Boryslawski, Z.R., 1978. Notes on the ecology and biology of *Scorpidium scorpioides* (Hedw.) Limpr. *Acta Soc. Bot. Pol.* 47, 15–23.
- Brown, R., Franke, W., Kleineg, H., Falk, H., Sitte, P., 1969. Cellulosic wall component produced by the Golgi apparatus of *Pleurochrysis scherffellii*. *Science* 166, 894–896.
- Brown Jr., R.M., Franke, W.W., Kleineg, H., Falk, H., Sitte, P., 1970. Scale formation in Chrysophycean algae. I. Cellulosic and noncellulosic wall components made by the Golgi apparatus. *J. Cell Biol.* 45, 246–271.
- Buhay, W.M., Betcher, R.N., 1998. Paleohydrologic implications of ^{18}O enriched Lake Agassiz water. *J. Paleolimnol.* 19, 285–296.
- Buhay, W.M., Wolfe, B.B., Schwab, A., 2012. Lakewater paleothermometry from Deep Lake, Minnesota during the deglacial-Holocene transition from combined $\delta^{18}\text{O}$ analyses of authigenic carbonate and aquatic cellulose. *Quat. Int.* 260, 76–82.
- Cepák, V., Lukavský, J., 1994. The effect of high irradiances on growth, biosynthetic activities and the ultrastructure of the green alga *Botryococcus braunii* strain Droop 1950/801-1. *Algol. Stud.* 72, 115–131.
- Chapman, V.J., Chapman, D.J., 1973. *The Algae*, second ed. London, Macmillan and Co. Ltd.
- Cockerton, H.E., Street-Perrott, F.A., Barker, P.A., Leng, M.J., Sloane, H.J., Ficken, K.J., 2015. Orbital forcing of glacial/interglacial variations in chemical weathering and silicon cycling within the upper White Nile Basin, East Africa: stable-isotope and biomarker evidence from Lakes Victoria and Edward. *Quat. Sci. Rev.* 130, 57–71.
- Coplen, T.B., 2007. Calibration of the calcite-water oxygen-isotope geothermometer at Devil’s Hole, Nevada, a natural laboratory. *Geochem. Cosmochim. Acta* 71, 3948–3957.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133, 1702–1703.
- Craig, H., Gordon, L.I., 1965. Deuterium and oxygen-18 variations in the ocean and marine atmosphere. In: Tongiorgi, E. (Ed.), *Stable Isotopes in Oceanographic Studies and Palaeotemperatures*. Cons. Naz. Rich. Lab. Geol. Nucl., Pisa, pp. 9–130.
- Cranwell, P.A., Eglinton, G., Robinson, N., 1987. Lipids of aquatic organisms as potential contributors to lacustrine sediments—II. *Org. Geochem.* 11, 513–527.
- Cuzzone, J.K., Clark, P.U., Carlson, A.E., Ullman, D.J., Rinterknecht, V.R., Milne, G.A., Lunkka, J.P., Wohlfarth, B., Marcott, S.A., Caffee, M., 2016. Final deglaciation of the Scandinavian Ice Sheet and implications for the Holocene global sea-level budget. *Earth Planet. Sci. Lett.* 448, 34–41.
- Daley, T.J., Thomas, E.R., Holmes, J.A., Street-Perrott, F.A., Chapman, M.R., Tindall, J.C., Valdes, P.J., Loader, N.J., Marshall, J.D., Wolff, E.W., Hopley, P.J., Atkinson, T., Barber, K.E., Fisher, E.H., Robertson, I., Hughes, P.D.M., 2011. The 8200 yr BP cold event in stable isotope records from the North Atlantic region. *Global Planet. Ch* 79, 288–302.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 436–468.
- DeNiro, M.J., Epstein, S., 1979. Relationship between the oxygen isotope ratios of terrestrial plant cellulose, carbon dioxide, and water. *Science* 204, 51–53.
- DeNiro, M.J., Epstein, S., 1981. Isotopic composition of cellulose from aquatic organisms. *Geochim. Cosmochim. Acta* 45, 1885–1894.
- Dodge, J.D., 1973. *The Fine Structure of Algal Cells*. Academic Press, London.
- Dodge, J.D., Crawford, R.M., 1970. A survey of the fine structure in the Dinophyceae. *Bot. J. Linn. Soc.* 63, 53–67.
- Duthie, H.C., Yang, J.-R., Edwards, T.W.D., Wolfe, B.B., Warner, B.G., 1996. Hamilton Harbour, Ontario: 8300 years of limnological and environmental change inferred from microfossil and isotopic analyses. *J. Paleolimnol.* 15, 79–97.
- Edwards, T.W.D., Fritz, P., 1986. Assessing meteoric water composition and relative humidity from ^{18}O and ^2H in wood cellulose: paleoclimatic implications for southern Ontario, Canada. *Appl. Geochem.* 1, 715–723.
- Edwards, T.W.D., Fritz, P., 1988. Stable-isotope paleoclimate records for southern Ontario, Canada: comparison of results from marl and wood. *Can. J. Earth Sci.* 25, 1397–1406.
- Edwards, T.W.D., McAndrews, J.H., 1989. Paleohydrology of a Canadian Shield lake inferred from ^{18}O in sediment cellulose. *Can. J. Earth Sci.* 26, 1850–1859.
- Edwards, T.W.D., Aravena, R.O., Fritz, P., 1986. Comparison of Postglacial Paleoclimatic Records in Southern Ontario from Stable Isotope Studies of Terrestrial Plant Cellulose and Lacustrine Carbonate. AMQUA Abstract.
- Edwards, T.W.D., Wolfe, B.B., MacDonald, G.M., 1996. Influence of changing atmospheric circulation on precipitation $\delta^{18}\text{O}$ -temperature relations in Canada during the Holocene. *Quat. Res.* 46, 211–218.
- Edwards, T.W.D., Aravena, R.O., Fritz, P., Morgan, A.V., 1985. Interpreting paleoclimate from ^{18}O and ^2H in plant cellulose: comparison with evidence from fossil insects and relict permafrost in southwestern Ontario. *Can. J. Earth Sci.* 22, 1720–1726.
- Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. *Science* 156, 1322–1335.
- Epstein, S., Thompson, P., Yapp, C.J., 1977. Oxygen and hydrogen isotopic ratios in plant cellulose. *Science* 198, 1209–1215.
- Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An *n*-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. *Org. Geochem.* 31, 745–749.
- Fisher, T.G., Smith, J.T., Andrews, J.T., 2002. Preboreal oscillation caused by a glacial Lake Agassiz flood. *Quat. Sci. Rev.* 21, 873–878. [https://doi.org/10.1016/S0277-3791\(01\)00148-2](https://doi.org/10.1016/S0277-3791(01)00148-2).
- Frei, E., Preston, R.D., 1961. Variants in the structural polysaccharides of algal cell walls. *Nature* 192, 939–943.
- Frei, E., Preston, R.D., 1964. Non-cellulosic structural polysaccharides in algal cell walls. I. Xylan in siphonous green algae. *Proc. Roy. Soc. London B160*, 293–313.
- Gonfiantini, R., 1986. Environmental isotopes in lake studies. In: Fritz, P., Fontes, J.C. (Eds.), *Handbook of Environmental Isotope Geochemistry*, 2. The Terrestrial Environment. Elsevier.
- Guan, J., Liu, Z.Y., Wen, X.Y., Brady, E., Noone, D., Zhu, J., Han, J., 2016. Understanding

- the temporal slope of the temperature–water isotope relation during the deglaciation using isocAM3: the slope equation. *J. Geophys. Res.-Atm* 121, 10342–10354.
- Hammarlund, D., 1993. A distinct $\delta^{13}\text{C}$ decline in organic lake sediments at the Pleistocene–Holocene transition in southern Sweden. *Boreas* 22, 236–243.
- Hammarlund, D., Björck, S., Buchardt, B., Thomsen, C.T., 2005. Limnic responses to increased effective humidity during the 8200 cal. yr BP cooling event in southern Sweden. *J. Paleolimnol.* 34, 471–480.
- Hammarlund, D., Aravena, R., Barnekow, L., Buchardt, B., Possnert, G., 1997. Multi-component carbon isotope evidence of early Holocene environmental change and carbon-flow pathways from a hard-water lake in northern Sweden. *J. Paleolimnol.* 18, 219–233.
- Happay-Wood, C.M., 1988. Ecology of freshwater planktonic green algae. In: Sandgren, C.D. (Ed.), *Growth and Reproductive Strategies of Freshwater Phytoplankton*. Cambridge University Press, Cambridge, pp. 175–226.
- Heikkilä, M., Seppä, H., 2003. A 11,000 yr palaeotemperature reconstruction from the southern boreal zone in Finland. *Quat. Sci. Rev.* 22, 541–554.
- Heikkilä, M., Edwards, T.W.D., Seppä, H., Sonninen, E., 2010. Sediment isotope tracers from Lake Saarikko, Finland, and implications for Holocene hydroclimatology. *Quat. Sci. Rev.* 29, 2146–2160.
- Heiri, O., Brooks, S.J., Renssen, H., Bedford, A., Hazekamp, M., Ilyashuk, B., Jeffers, E.S., Lang, B., Kirilova, E., Kuiper, S., Millet, L., Samartin, S., Toth, M., Verbruggen, F., Watson, J.E., van Asch, N., Lammertsma, E., Amon, L., Birks, H.H., Birks, H.J.B., Mortensen, M.F., Hoek, W.Z., Magyar, E., Muñoz Sobrino, C., Seppä, H., Tinner, W., Tonkov, S., Veski, S., Lotter, A.F., 2014. Validation of climate model-inferred regional temperature change for late-glacial Europe. *Nature Commun.* 5, 4914. <https://doi.org/10.1038/ncomms5914>.
- Herczeg, A.L., 1988. Early diagenesis of organic matter in lake sediments: a stable carbon isotope study of pore waters. *Chem. Geol. (Isotope Geosci.)* 72, 199–209.
- Herth, W., Zugenmaier, P., 1979. The lorica of *Dinobryon*. *J. Ultrastruct. Res.* 69, 262–272.
- Heyng, A.M., Mayr, C., Lücke, A., Wissel, H., Striewski, B., 2014. Late Holocene hydrologic changes in northern New Zealand inferred from stable isotope values of aquatic cellulose in sediments from Lake Pupuke. *J. Paleolimnol.* 51, 485–497.
- Holmes, J.A., Street-Perrott, F.A., Darbyshire, D.P., Davies, N.C., Hales, P.E., 1995. Chemical and isotopic composition of karstic lakes in Jamaica, West Indies. *Hydrobiologia* 312, 121–138.
- Holmes, J.A., Tindall, J., Roberts, N., Marshall, W., Marshall, J.D., Bingham, A., Feeser, I., O'Connell, M., Atkinson, T., Jourdan, A.-L., March, A., Fisher, E.H., 2016. Lake isotope records of the 8200-year cooling event in western Ireland: comparison with model simulations. *Quat. Sci. Rev.* 131, 341–349.
- Jankovská, V., Komárek, J., 2000. Indicative value of *Pediastrum* and other coccal green algae in palaeoecology. *Folia Geobotan.* 35, 59–82.
- Kim, S.T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta* 61, 3461–3475.
- Keeley, J.E., Sandquist, D.R., 1992. Carbon: freshwater plants. *Plant, Cell Env.* 15, 1021–1035.
- Kumar, H.D., Singh, H.N., 1979. *A Textbook on Algae*. The Macmillan Press, London.
- Land, L.S., Epstein, S., 1970. Late Pleistocene diagenesis and dolomitization, north Jamaica. *Sedimentology* 14, 187–200.
- Laumets, L., Kalm, V., Poska, A., Kele, S., Lasberg, K., Amon, L., 2014. Palaeoclimate inferred from $\delta^{18}\text{O}$ and palaeobotanical indicators in freshwater tufa of Lake Äntu Sinijärvi, Estonia. *J. Paleolimnol.* 51, 99–111.
- Liu, Z., Wen, X., Brady, E.C., Otto-Bliessen, B., Yu, G., Lu, H., Cheng, H., Wang, Y., Zheng, W., Ding, Y., Edwards, R.L., Cheng, J., Liu, W., Yang, H., 2014. Chinese cave records and the East Asian Summer Monsoon. *Quat. Sci. Rev.* 83, 115–128.
- Lee, R.E., 1989. *Phycology*, second ed. Cambridge University Press, Cambridge.
- LeGrande, A.N., Schmidt, G.A., 2008. Ensemble, water-isotope enabled, coupled general circulation modeling insights into the 8.2-kyr event. *Paleoceanography* 23, PA3207. <https://doi.org/10.1029/2008PA001610>.
- Lehtmaa, K., 2006. Äntu järvede arengust holotseenis. MSc Thesis. Euroülikool, Estonia.
- Loader, N.J., Hemming, D.L., 2004. The stable isotope analysis of pollen as an indicator of terrestrial palaeoenvironmental change: a review of progress and recent developments. *Quat. Sci. Rev.* 23, 893–900.
- Lücke, A., Roosen, C., Wissel, H., Mayr, C., Schäbitz, F., Ohlendorf, C., Zolitschka, B., Salsa Team members, 2009. Carbon and oxygen isotopes of sedimentary cellulose from Laguna Azul reflect hydrological variations in the Patagonian steppe of southern Argentina since AD 600. In: EGU General Assembly Conference Abstracts, 11, p. 8815.
- Maberly, S.C., Spence, D.H.N., 1983. Photosynthetic inorganic carbon use by freshwater plants. *Ecology* 71, 705–724.
- Maberly, S.C., Barker, P.A., Stott, A.W., De Ville, M.M., 2013. Catchment productivity controls CO₂ emissions from lakes. *Nature Clim. Change* 3, 391.
- MacDonald, G.M., Edwards, T.W.D., Moser, K.A., Pienitz, R., Smol, J.P., 1993. Rapid response of treeline vegetation and lakes to past climate warming. *Nature* 361, 243–246.
- Mackie, W., Preston, R.D., 1968. The occurrence of mannan microfibrils in the green algae *Codium fragile* and *Acetabularia crenulata*. *Planta* 79, 249–253.
- Mäemets, A., 1977. Eesti NSV järved ja nende kaitses. Valgus, Tallinn, p. 263.
- Mayr, C., Lücke, A., Maidana, N.I., 2007. Precipitation origin and evaporation of lakes in semi-arid Patagonia (Argentina) inferred from stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$). *J. Hydrol.* 334, 53–63.
- Mayr, C., Lücke, A., Maidana, N.I., Wille, M., Haberzettl, T., Corbella, H., Ohlendorf, C., Schäbitz, F., Fey, M., Jansen, S., Zolitschka, B., 2009. Isotopic and geochemical fingerprints of lacustrine organic matter sources reflect environmental changes during the last 16,000 years in semi-arid Patagonia. *J. Paleolimnol.* 42, 81–102.
- McConnaughey, T.A., Falk, R.H., 1991. Calcium-proton exchange during algal calcification. *Biol. Bull.* 180, 185–195.
- Mead, R., Xu, Y., Chong, J., Jaffe, R., 2005. Sediment and soil organic matter source assessment as revealed by the molecular distribution and carbon isotopic composition of *n*-alkanes. *Org. Geochem.* 36, 363–370.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* 114, 289–302.
- Meyers, P.A., 1997. Organic geochemical proxies for paleoceanographic, paleolimnologic and paleoclimatic processes. *Org. Geochem.* 27, 213–250.
- Meyers, P.A., Ishiwatari, R., 1993a. Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. *Org. Geochem.* 20, 867–900.
- Meyers, P.A., Ishiwatari, R., 1993b. The early diagenesis of organic matter in lacustrine sediments. In: Engel, M.H., Macko, S.A. (Eds.), *Organic Geochemistry: Principles and Applications*. Plenum Press, New York, pp. 185–209.
- Meyers, P.A., Lallier-Vergès, E., 1999. Lacustrine sedimentary organic matter records of late Quaternary paleoclimates. *J. Paleolimnol.* 21, 345–372.
- Meyers, P.A., Teranes, J.L., 2001. Sediment organic matter. In: Last, W.M., Smol, J.P. (Eds.), *Tracking Environmental Change Using Lake Sediments, 2. Physical and Chemical Techniques*. Developments in Paleoenvironmental Research 2. Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 239–269.
- Mitchell, J.F.B., Grahame, N.S., Needham, K.J., 1988. Climate simulations for 9000 Years before present - seasonal variations and effect of the Laurentide ice sheet. *J. Geophys. Res.-Atm* 93, 8283–8303.
- Moore, P.D., Webb, J.A., Collinson, M.E., 1991. *Pollen Analysis*, second ed. Blackwell, Oxford.
- Napolitano, G.E., 1999. Fatty acids as trophic and chemical markers in freshwater ecosystems. In: Arts, M.T., Wainman, B.C. (Eds.), *Lipids in Freshwater Ecosystems*. Springer, New York, pp. 21–44.
- Nedelskaja, A., 2011. *Öietolmu spektrite ning hapniku ja süsiniku isotoop-andmete analüüs mõnede Eesti väikejärvede setetes*. MSc Thesis. Tallinn University, Estonia.
- Núñez, R., Spiro, B., Pentecost, A., Kim, A., Coletta, P., 2002. Organo-geochemical and stable isotope indicators of environmental change in a marl lake, Malham Tarn, North Yorkshire, U.K. *J. Paleolimnol.* 28, 403–417.
- Oana, S., Deevey, E.S., 1960. Carbon 13 in lake waters and its possible bearing on paleolimnology. *Am. J. Sci.* 258, 253–272.
- Ohmori, M., Wolf, F.R., Bassham, J.A., 1984. *Botryococcus braunii* carbon/nitrogen metabolism as affected by ammonia addition. *Arch. Microbiol.* 140, 101–106.
- Olsson, I., Kaup, E., 2001. The varying radiocarbon activity of some recent submerged Estonian plants grown in the early 1990s. *Radiocarbon* 43, 809–820.
- Ortiz, J.E., Sánchez-Palencia, Y., Torres, T., Domingo, L., Pilar Mata, M., Vegas, J., Gościąg, Central Poland, a Monographic Study. Part I. W. Szafer Institute of Botany, Polish Academy of Science, Kraków.
- Rau, G., 1978. Carbon-13 depletion in a subalpine lake: carbon flow implications. *Science* 201, 901–902.
- Renssen, H., Isarin, R.F.B., 2001. The two major warming phases of the last deglaciation at similar to 14.7 and similar to 11.5 ka cal BP in Europe: climate reconstructions and AGCM experiments. *Global Planet. Ch* 30, 117–153.
- Rozanski, K., Araguás-Araguás, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), *Climate Change in Continental Isotopic Records*. Geophysical Monograph, 78. American Geophysical Union, Washington, pp. 1–36.
- Rozanski, K., Klisch, M.A., Wachniew, P., Gorczyca, Z., Goslar, T., Edwards, T.W.D., Shemesh, A., 2010. Oxygen-isotope geothermometers in lacustrine sediments: new insights through combined $\delta^{18}\text{O}$ analyses of aquatic cellulose, authigenic calcite and biogenic silica in Lake Gościąg, central Poland. *Geochim. Cosmochim. Acta* 74, 2957–2969.
- Saarse, L., Harrison, S.P., 1992. Holocene lake-level changes in the eastern Baltic

- region. In: Kaare, T., Mardiste, H., Merikalju, L., Punning, J.M. (Eds.), *Estonia. Man and Nature*. The Academy of Sciences of Estonia. Estonian Geographical Society, Tallinn, pp. 6–20.
- Saarse, L., Liiva, A., 1995. Geology of the Äntu group of lakes. *Proceedings of Estonian Academy of Science, Geology* 44, 119–132.
- Sauer, P.E., Miller, G.H., Overpeck, J.T., 2001. Oxygen isotope ratios of organic matter in arctic lakes as a paleoclimate proxy: field and laboratory investigations. *J. Paleolimnol.* 25, 43–64.
- Sensula, B., Böttger, T., Pazdur, A., Piotrowska, N., Wagner, R., 2006. Carbon and oxygen isotope composition of organic matter and carbonates in recent lacustrine sediments. *Geochronometria* 25, 77–94.
- Seppä, H., Poska, A., 2004. Holocene annual mean temperature changes in Estonia and their relationship to solar insolation and atmospheric circulation patterns. *Quat. Res.* 61, 22–31.
- Sharkey, T.D., Berry, J.A., 1985. Carbon isotope fractionation of algae as influenced by an inducible CO₂ concentrating mechanism. In: Lucas, W.J., Berry, J.A. (Eds.), *Inorganic Carbon Uptake by Aquatic Photosynthetic Organisms*. American Society of Plant Physiologists, pp. 389–401.
- Shaw, G., Yeadon, A., 1964. Chemical studies on the constitution of some pollen and spore membranes. *Grana Palyn.* 5, 247–252.
- Sheath, R.G., Hellebust, J.A., Sawa, T., 1975. The statospore of *Dinobryon divergens* Imhoff: formation and germination in a subarctic lake. *J. Phycol.* 11, 131–138.
- Sohar, K., Kalm, V., 2008. A 12.8-ka-long palaeoenvironmental record revealed by subfossil ostracod data from lacustrine freshwater tufa in Lake Sinijärv, northern Estonia. *J. Paleolimnol.* 40, 809–821.
- Stansell, N.D., Klein, E.S., Finkenbinder, M.S., Fortney, C.S., Dodd, J.P., Terasmaa, J., Nelson, D.B., 2017. A stable isotope record of Holocene precipitation dynamics in the Baltic region from Lake Nuudsaku, Estonia. *Quat. Sci. Rev.* 175, 73–84.
- Sternberg, L., 1989. Oxygen and hydrogen isotope ratios in plant cellulose: mechanisms and applications. In: Rundel, P.W., Ehleringer, J.R., Nagy, K.A. (Eds.), *Stable Isotopes in Ecological Research*. Ecological Studies, 68. Springer-Verlag, New York, pp. 124–141.
- Sternberg, L., DeNiro, M.J., 1983a. Isotope composition of cellulose from C3, C4, and CAM plants growing near one another. *Science* 220, 947–949.
- Sternberg, L.O., DeNiro, M.J., 1983b. Biogeochemical implications of the isotope equilibrium fractionation factor between the oxygen atoms of acetone and water. *Geochim. Cosmochim. Acta* 47, 2271–2274.
- Sternberg, L., DeNiro, M.J., Keeley, J.E., 1984. Hydrogen, oxygen, and carbon isotope ratios of cellulose from submerged aquatic crassulacean acid metabolism and non-crassulacean acid metabolism plants. *Plant Physiol.* 76, 68–70.
- Sternberg, L., DeNiro, M.J., Sloan, M.E., Black, C.C., 1986. Compensation point and isotopic characteristics of C3/C4 intermediates and hybrids in *Panicum*. *Plant Physiol.* 80, 242–245.
- Street-Perrott, F.A., Hales, P.E., Perrott, R.A., Fontes, J.C., Switsur, V.R., Pearson, A., 1993. Late Quaternary palaeolimnology of a tropical marl lake: Wallywash Great Pond, Jamaica. *J. Paleolimnol.* 9, 3–22.
- Talbot, M.R., 1990. A review of the palaeohydrological interpretation of carbon and oxygen isotope ratios in primary lacustrine carbonates. *Chem. Geol. (Isot. Geosci. Sect.)* 80, 261–279.
- Tindall, J.C., Valdes, P.J., 2011. Modeling the 8.2 ka event using a coupled atmosphere-ocean GCM. *Global Planet. Ch* 79, 312–321.
- Trainor, F.D., 1978. *Introductory Phycology*. John Wiley & Sons, New York.
- Tsekos, I., 1999. The sites of cellulose synthesis in algae; diversity and evolution of cellulose-synthesizing enzyme complexes. *J. Phycol.* 35, 935–955.
- Tyler, J.J., Jones, M., Arrowsmith, C., Allott, T., Leng, M.J., 2016. Spatial patterns in the oxygen isotope composition of daily rainfall in the British Isles. *Clim. Dyn.* 47, 1971–1987.
- Tyson, R.V., 1995. *Sedimentary Organic Matter. Organic Facies and Palynofacies*. Chapman & Hall, London.
- Väliranta, M., Salonen, J.S., Heikkilä, M., Amon, L., Helmens, K., Klimaschewski, A., Kuhry, P., Kultti, S., Poska, A., Shala, S., Veski, S., Birks, H.H., 2015. Plant macrofossil evidence for an early onset of the Holocene summer thermal maximum in northernmost Europe. *Nature Comm.* 6, 6809. <https://doi.org/10.1038/ncomms7809>.
- Veski, S., Seppä, H., Ojala, A.E.K., 2004. Cold event at 8200 yr BP recorded in annually laminated lake sediments in eastern Europe. *Geology* 32, 681–684.
- Veski, S., Seppä, H., Stančikaitė, M., Zernitskaya, V., Reitalu, T., Gryguc, G., Heinsalu, A., Stivrins, N., Amon, L., Vassiljev, J., Heiri, O., 2015. Quantitative summer and winter temperature reconstructions from pollen and chironomid data between 15 and 8 ka BP in the Baltic-Belarus area. *Quat. Int.* 388, 4–11.
- von Grafenstein, U., Erlenkeuser, H., Müller, J., Trimborn, P., Alefs, J., 1996. A 200 year mid-European air temperature record preserved in lake sediments: an extension of the $\delta^{18}\text{O}_p$ -air temperature relation into the past. *Geochim. Cosmochim. Acta* 60, 4025–4036.
- von Grafenstein, U., Erlenkeuser, H., Müller, J., Jouzel, J., Johnsen, S., 1998. The cold event 8200 years ago documented in oxygen isotope records of precipitation in Europe and Greenland. *Clim. Dyn.* 14, 73–81.
- von Grafenstein, U., Erlenkeuser, H., Brauer, A., Jouzel, J., Johnsen, S.J., 1999. A mid-European decadal isotope-climate record from 15,500 to 5000 years B.P. *Science* 284, 1654–1657.
- Waterhouse, J.S., Cheng, S.Y., Juchelka, D., Loader, N.J., McCarroll, D., Switsur, V.R., Gautam, L., 2013. Position-specific measurement of oxygen isotope ratios in cellulose: isotopic exchange during heterotrophic cellulose synthesis. *Geochim. Cosmochim. Acta* 112, 178–191.
- Wissel, H., Mayr, C., Lücke, A., 2008. A new approach for the isolation of cellulose from aquatic plant tissue and freshwater sediments for stable isotope analysis. *Org. Geochem.* 39, 1545–1561.
- Wolfe, B.B., Edwards, T.W.D., 1997. Hydrologic control on the oxygen-isotope relation between sediment cellulose and lake water, western Taimyr Peninsula, Russia: implications for the use of surface sediment calibrations in paleolimnology. *J. Paleolimnol.* 18, 283–291.
- Wolfe, B.B., Edwards, T.W.D., 1998. Comment on “Stable carbon and oxygen isotope records from Lake Erie sediment cores: mollusc aragonite 4600 BP–200 BP” (JGLR 23: 307–316). *J. Great Lakes Res.* 24, 736–738.
- Wolfe, B.B., Edwards, T.W.D., Aravena, R., 1999. Changes in carbon and nitrogen cycling during tree-line retreat recorded in the isotopic content of lacustrine organic matter, western Taimyr Peninsula, Russia. *The Holocene* 9, 215–222.
- Wolfe, B.B., Edwards, T.W.D., Aravena, R., MacDonald, G.M., 1996. Rapid Holocene hydrologic change along boreal tree-line revealed by $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in organic lake sediments, Northwest Territories, Canada. *J. Paleolimnol.* 15, 171–181.
- Wolfe, B.B., Edwards, T.W.D., Duthie, H.C., 2000a. A 6000-year record of interaction between Hamilton Harbour and Lake Ontario: quantitative assessment of recent hydrologic disturbance using ^{13}C in lake sediment cellulose. *Aquat. Ecosyst. Health Manag.* 3, 47–54.
- Wolfe, B.B., Buhay, W.M., Schwalb, A., 2000b. A varved lake sediment carbonate and organic isotope record of late Glacial–early Holocene paleohydrology and paleotemperature in the Northern Great Plains, USA. In: *International Paleolimnology Symposium*. Queens University, Kingston, Canada.
- Wolfe, B.B., Edwards, T.W.D., Aravena, R., Forman, S.L., Warner, B.G., Velichko, A.A., MacDonald, G.M., 2000c. Holocene paleohydrology and paleoclimate at tree-line, North-Central Russia, inferred from oxygen isotope records in lake sediment cellulose. *Quat. Res.* 53, 319–329.
- Wolfe, B.B., Aravena, R., Abbott, M.B., Seltzer, G.O., Gibson, J.J., 2001a. Reconstruction of paleohydrology and paleohumidity from oxygen isotope records in the Bolivian Andes. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 176, 177–192.
- Wolfe, B.B., Edwards, T.W.D., Beuning, K.R.M., Elgood, R.J., 2001b. Carbon and oxygen isotope analysis of lake sediment cellulose: methods and applications. In: Last, W.M., Smol, J.P. (Eds.), *Tracking Environmental Change Using Lake Sediments: Physical and Chemical Techniques, Developments in Paleoenvironmental Research*. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 373–400.
- Wolfe, B.B., Falcone, M.D., Clogg-Wright, K.P., Mongeon, C.L., Yi, Y., Brock, B.E., St. Amour, N.A., Mark, W.A., Edwards, T.W.D., 2007. Progress in isotope paleohydrology using lake sediment cellulose. *J. Paleolimnol.* 37, 221–231.
- Wolfe, B.B., Hall, R.L., Edwards, T.W.D., Johnston, J.W., 2012. Developing temporal hydroecological perspectives to inform stewardship of a northern floodplain landscape subject to multiple stressors: Paleolimnological investigations of the Peace-Athabasca Delta. *Environ. Rev.* 20, 191–210.
- Yakir, D., 1992. Variations in the natural abundance of oxygen-18 and deuterium in plant carbohydrates. *Plant Cell Env.* 15, 1005–1020.
- Yakir, D., DeNiro, M.J., 1990. Oxygen and hydrogen isotope fractionation during cellulose metabolism in *Lemna gibba* L. *Plant Physiol.* 93, 325–332.
- Zeeb, B.A., Smol, J.P., 2001. Chrysophyte scales and cysts. In: Smol, J.P., Birks, H.J.B., Last, W.M. (Eds.), *Tracking Environmental Change Using Lake Sediments. Vol. 3: Terrestrial, Algal and Siliceous Indicators, Developments in Paleoenvironmental Research*, 3. Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 203–223.
- Zhang, Z., Zhao, M., Yang, X., Wang, S., Jiang, X., Oldfield, F., Eglinton, G., 2004. A hydrocarbon biomarker record for the last 40 kyr of plant input to Lake Heqing, southwestern China. *Org. Geochem.* 35, 595–613.
- Zibulski, R., Wesener, F., Wilkes, H., Plessen, B., Pestryakova, L.A., Herzschuh, U., 2017. C/N ratio, stable isotope ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$), and n-alkane patterns of brown mosses along hydrological gradients of low-centred polygons of the Siberian Arctic. *Biogeosciences* 14, 1617–1630.