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Palaeoenvironmental climate trend derived from $\delta^{18}O$ and palaeobotany data from freshwater tufa of Lake Äntu Sinijärv, Estonia

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Abstract

We investigated a 3.75-m-long lacustrine sediment record of Lake Äntu Sinijärv, northern Estonia, with modelled age ~13,590 cal yr BP. The applied multiproxy approach focuses on the stable oxygen isotope composition ($\delta^{18}O$) of freshwater tufa. New palaeoclimate information for the Eastern Baltic region based on high-resolution (219 samples) $\delta^{18}O$ is supported by palaeobotanical (pollen and plant macrofossil analysis) data. Radiocarbon datings were used to establish a chronology and estimate sedimentation rates.

Tufa precipitation at the site started at ca 11,800 cal yr BP, that is ca. 1000 years later than suggested previously. The time interval of about 2000 years between deglaciation of the area and beginning of tufa precipitation suggests that lacustrine carbonate sedimentation is not directly controlled by climate (temperature). A weakly detectable 9.3 ka cold climate event (9,310 cal yr BP, with $\delta^{18}O$ value –11.4‰) was recorded. The coldest climatic events occurred at ca. 5,800 and 900 cal yr BP and the warmest event at ca. 6,500 cal yr BP.

Introduction

Lacustrine carbonates are important archives of climatic and environmental changes for isotope and palaeoclimate research. Precipitation and deposition of freshwater tufa in hydrologically open mid- to high-latitude eutrophic hardwater lakes commonly takes place during the ice-free period: between early spring and late autumn, mostly during summer (Bartosh 1976; Goudie et al. 1993). This period coincides with increased evaporation and high photosynthetic activity (bloom) of aquatic plants.

For tufa precipitation groundwater rich in dissolved calcium carbonate is required (Bartosh 1976; Hyvärinen et al. 1990; Goudie et al. 1993; Leng and Marshall 2004). Generally, it is presumed that lake carbonates formed in isotope equilibrium conditions when local evaporation (non-equilibrium process) and direct precipitation have their strongest isotopic effects (Leng and Marshall 2004). Isotope studies of bulk lake carbonates have become very common, mostly because of relatively easy accessibility of this material and good preservation of deposits (authigenic and biogenic carbonate, etc.) (Leng and Marshall 2004). However, despite the popularity of lake sediment explorations, the interpretation of bulk carbonate records for palaeoenvironmental reconstructions is not simple. The oxygen isotopic composition of the precipitated endogenic calcite is dependent on the isotopic composition of the water body (e.g. lake water) and the water temperature during carbonate deposition. The hydrological balance of the lake also plays a considerable role. Hence, precipitated carbonate chemistry is influenced by biological activity in the lake, which affects the formation of isotope composition mechanisms. Water depth and the length of the warm period affect the oxygen isotope composition of the precipitated carbonate (Leng and Marshall 2004; Bernasconi and McKenzie 2007).

Only the authigenic particles of bulk carbonates, which formed in the surface waters, carry relevant isotopic information for palaeoclimatic reconstructions and interpretations (Bernasconi and McKenzie 2007). Cyclic changes in oxygen isotopes are principally controlled by temperature-dependent fractionation between calcite and water (Hori et al. 2009).

This article focuses on Holocene climatic and environmental changes recorded in freshwater tufa section in the Northern Baltic region, on the Pandivere Upland, approximately 50 km south of the Gulf of Finland (Fig. 1). Lake Äntu Sinijärv was chosen for study, because this is the only site in the region where freshwater tufa precipitation is still taking place. The lake has previously been studied by Saarse and Liiva (1995), Punning et al. (2000) and Sohar and Kalm (2008). The $\delta^{18}O$ composition of tufa deposits in the lake reflects also changes in the Atlantic Meridional Overturning Circulation (AMOC) (Bakke et al. 2008; Andersson 2010), which in turn gives insight into the deglaciation history of the area. The purposes of this paper are: to present and interpret the most detailed high-resolution isotopic ($\delta^{18}O$) data covering the entire Holocene Epoch, to discuss $\delta^{18}O$ and palaeobotanical (pollen and macrofossil) data in the context of the existing knowledge about local palaeoclimate, and to reconstruct Holocene climate trends.

Study area

Lake Äntu Sinijärv, one of the Äntu group of lakes, is located on the Pandivere Upland (59°03′ N; 26°14′ E), North Estonia (Fig. 1), on the bedrock of karstified Ordovician limestone. The average annual precipitation in Estonia is 530–730 mm and average annual temperature is around 5.3ºC (Treier et al. 2004). The evaporation in this region during ice-free periods varies from 575 to 600 mm/yr (Arold 2005). The area of Äntu Sinijärv was deglaciated from the Late Weichselian glaciation already around 13,800 cal yr BP (Saarse et al. 2009), This data is also supported by the results of Kalm (2006) and Rosentau et al. (2007), indicating dry land conditions in the Pandivere Upland area already before 13,300 cal yr BP. The average water level in the lake is approximately 94.6 m a.s.l., the surface area is 2.4 ha and maximum depth 7.3 m, shores are paludal and the bottom is covered with lacustrine lime (Saarse and Liiva 1995). Äntu Sinijärv is mainly a groundwater-fed hard-water lake (Olsson and Kaup 2001). The lake is considered to be a old-water lake (annual temperature varies between 6.4ºC and 18ºC), where the water is moderately alkaline (pH=7.4–8.0) and rich in mineral substances (HCO_3^- content 262–274 mg/l) (Mäemets 1977; Saarse and Liiva 1995). The mean water residence time in Äntu Sinijärv is 2–3 months (Saarse and Liiva 1995). The thickness of lake carbonate deposit varies between 1.5 and 5.1 m (average 3–4 m) (Saarse and Liiva 1995). Lake sediment contains subfossil molluscs and ostracods, fragments of mosses (*Scorpidium*) and water plants (Mäemets 1977). This alkalitrophic lake (Mäemets and Freiberg 2007) is surrounded by forest and the water is transparent and clear. It is the most transparent lake in Estonia ($z_{1\%}$=29.8 m) (Nõges 2000). It is assumed that carbonate sedimentation in Äntu Sinijärv took place at nearly chemical equilibrium conditions (Punning et al. 2000).

Materials and methods

Sampling and sediment composition

The sediment sequence was cored during the winter of 2008 from ice, using a Byelorussian-type corer with the diameter of 5 cm and tube length of 1 m. The water depth was 360 cm at the coring point. The sediment core covers the depth up to 375 cm. Sediment types and colours were described both on sight and in the laboratory. The Munsell colour system chart (1998) was used for colour determination.

The organic content of the sediment was estimated by loss on ignition (LOI) at a temperature of 500°C for 2 h from dry matter of 1 cm thick sediment samples after every 4 cm interval. Carbonate content was estimated from LOI between 500°C and 1,000°C during 1 h and the received values were multiplied by 2.27 (Gedda 2001). Mineral matter content was calculated from the dry matter by subtracting organic and carbonate content from it (Heiri et al. 2001).

Sediment dating

Accelerator mass spectrometry (AMS) radiocarbon dates from five aquatic moss samples (104–106 cm; 123–124 cm; 189–190 cm; 218–219 cm; 286–287 cm); two gyttja samples (306–308 cm; 335–336 cm) and one wood sample (360–363 cm) were determined in Poznań Radiocarbon Laboratory, Poland (Table **1**). Radiocarbon dates were calibrated using the IntCal09 calibration curve (Reimer et al. 2009) and the OxCal v.4.1 program

(Bronk Ramsey1995, 2001, 2009). The AMS dates were calibrated with 1σ uncertainty and are presented in Table **1** and Fig. 2.

Oxygen isotope analyses

219 tufa samples were collected and analysed in 1 and 2 cm intervals along a 349 cm thick vertical sediment section. In order to remove organic matter (OM), the samples were pre-treated. Macroscopic organic pieces from tufa samples were washed out with distilled water and handpicked with tweezers, while microscopic OM particles were oxidized with Clorox (Cassidy and Mankin 1960). Although Grottoli et al. (2005) have detected slight changes in the isotopic compositions during pre-treatment with H_2O_2 and sodium hypochlorite, these changes (up to 0.15‰) are mainly within the analytical precision (0.10 ‰) and do not considerably affect the data interpretation. Organic-free samples were dried in an oven at a temperature of about 70°C and powdered afterwards. Stable oxygen isotope measurements were performed using an automated carbonate preparation device (GASBENCH II) attached to the Thermo Finnigan delta Plus XP continuous flow mass spectrometer at the Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences (Budapest, Hungary), following the technique described by Spötl and Vennemann (2003).

Standardization was conducted according to laboratory calcite standards calibrated against the NBS-18 and NBS-19 standards. All samples were measured at least in duplicates and the mean isotope values are given in the standard delta notation in parts per thousand (‰) relative to V-PDB ($\delta^{18}O$) according to $\delta\,[‰] = (R_{sample}/R_{standard} - 1) \times 1000$, where R_{sample} and $R_{standard}$ are the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios in samples and standards, respectively. Reproducibilities better than ±0.1‰ were obtained for $\delta^{18}O$ values.

Palaeobotanical analyses

Pollen sub-samples of known volume (0.5–2 cm^3) and thickness (1 cm) were taken from the core after every 5 to 10 cm from the depth interval 368–39cm. Pollen sample preparation followed a standard acetolysis method (Berglund and Ralska-Jasiewiczowa 1986). Samples rich in mineral matter were pre-treated with heavy liquid to remove inorganic particles (Berglund and Ralska-Jasiewiczowa 1986). *Lycopodium* spores were added to calculate pollen concentration (Stockmarr 1971). At least 500 terrestrial pollen grains were counted at each sampled level except for some lowermost samples, where only about 200 grains were counted due to low pollen concentration. Pollen data were expressed as percentages of the total terrestrial pollen sum (*Arboreal Pollen* (AP) + *Quercetum Mixtum* (QM) + *Non-Arboreal Pollen* (NAP)). Counts of spores, algae, charcoal and other microfossils were calculated as percentages of the total terrestrial pollen sum. The pollen diagrams were compiled using Tilia 1.0.1 software (Grimm 2007). Local Pollen Assemblage Zones (PAZ) were determined by the binary splitting by sum-of-squares method using the PSIMPOLL 4.10 program (Bennett 1996).

Sediments were also analysed for plant macrofossil content from a core depth of 375–100 cm. The sample size varied along the core: at a depth of 375–325 cm the sample volume was small (11–20 cm^3) due to shortage of sediment material. From 325 to 300 cm and from 230 to 100 cm the sample volume varied 40 to 80 cm^3, while the uniform sample size (100 cm^3) was used for sediment interval 300–230 cm. Sample preparation for plant macrofossil analysis followed conventional procedures (Birks 2001). The Material retained on sieves was examined under stereo- and light microscopes. Plant macrofossil and seed atlases (e.g. Cappers et al. 2006) were used for identification as well as seed reference collections. Plant macrofossil zonation is correlated with pollen subzones.

Based on pollen and plant macrofossil content, six subzones for pollen and five subzones for plant macrofossils were distinguished.

Results

Sediment composition

Based on lithology, sedimentation rate and colour determination, seven sedimentary units were determined in the section (Fig. 3): (1) the bottommost layer (375–336 cm; older than 13,590 cal yr BP) represented by light grey silt (5Y/5.1 grey according to Munsell colour chart); (2) interval of massive gyttja (336–307 cm; older than 13,590 until 11810 cal yr BP) (5Y/4.2, olive grey); (3) thick greyish (5Y/5.2 olive grey) layer of massive calcareous tufa rich in detritus/mosses (307–224 cm; layer age interval 11810–6720 cal yr BP). (4) grey (2.5Y/6.2, light brownish-grey) laminated freshwater tufa containing several fragments of subfossil shells (224–200 cm; 6720–5810 cal yr BP). (5) dark gyttja-rich tufa layer (200–122 cm; 5810–3220 cal yr BP) (2.5Y/5.3 light olive brown) with visible plant fragments also contain detritus in its bottommost part; (6) light (2.5Y/6.4 light yellowish brown) laminated organic rich tufa (122–60 cm; 3220–970 cal yr BP); (7) the topmost (60–0cm; 970–0 cal yr BP) peaty tufa layer (2.5Y/4.4 olive brown) containing a large amount of semi-decomposed plant remains (Fig. 3).

The LOI results of OM concentrations are between 3 and 65%, carbonate content varies between 4 and 77%. The mineral content of lake sediment fluctuates between 15 and 90% (Fig. 3)

Sediment dating, age-depth model and sedimentation rates

Eight AMS ^{14}C dates from different materials of Äntu Sinijärv are presented in the order of increasing depth (Table **1**). The age-depth model (Fig. 2) was constructed on the basis of these dates.

The compaction of older sediments or possible dissolution of tufa has not been taken into account. The topmost six ^{14}C dates are in stratigraphical order, but dates from the lower part are controversial. There may be some "apparent ages" among the dates of different materials– this could be the case of aquatic mosses and gyttja. Lake sediments (aquatic moss, gyttja) can contain carbon from various sources (carbon from atmosphere and water, dissolved bicarbonate from the carbonaceous bedrock) and because of the presence of "old radiocarbon'' in sediment, the obtained ages may be too old (in other words, have a "reservoir effect") (MacDonald et al. 1991; Hua 2009). The "reservoir effect" is not constant through time. Therefore and because of the lack of research about the “reservoir effect” on ages in Estonian lakes is hard to predict its value in different materials. However, the possible occurrence of the “reservoir effect” on the bottommost two gyttja samples still does not explain why the ages are in accordance with depth. This inconsistency might be explained by redeposition of lake bottom sediments or mixture of different sediments. The provenance of the wood sample is terrestrial (Table **1**). Hence it was carried into the lake and sank into lake deposits, thus the age of wood is in disagreement with the stratigraphical order and with the other dates. As we had no arguments for excluding some dates from the age-depth model, average linear between the four lowermost dates were drawn (Fig. 2). In the figure the calibrated median ages of the samples are presented.

The calculated linear sediment accumulation rate is 0.16 mm/yr in the lower part of sediment core from a depth of 375 cm up to 220 cm. Above that the sediment accumulation rates vary from 0.11 to 0.62 mm/yr; the average value is 0.31 mm/yr. Through the whole sediment core, on average 1 cm of the sample covers 42.5 years.

Based on the age-depth model, carbonate precipitation began some 11,810 cal yr BP ago. However, the lowermost aquatic mosses from tufa yielded an age of 12,660 cal yr BP and gyttja under it an age of 13,310 cal yr BP, but the inconsistency of dates in the lower part of the core questions their reliability. According to this study, tufa precipitation started later than revealed by previous studies of Äntu Sinijärv (13,060 cal yr BP in Saarse and Liiva 1995; 12,850 cal yr BP in Sohar and Kalm 2008). In contrast, the age of wood (12,830 cal yr BP) from silt below gyttja is similar to the age of plant remains from the bottommost layer (12,100 cal yr BP) dated by Saarse and Liiva (1995).

Oxygen isotopic composition of lacustrine carbonates

The results of $\delta^{18}O$ analyses of freshwater tufa samples are presented in Fig. 3. To give a better overview of the isotopic fluctuations, the curve was smoothed with a step of 5 analyses on average. Stable isotope analysis of freshwater tufa revealed $\delta^{18}O$ values between –13.2 and –10.2‰ VPDB, with the average value of –11.2‰. Isotopic data cover the depth of 308–21.0 cm and the time interval from ~ 13,260 to 340 cal yr BP (Fig. 3). One exceptional sample from the carbonate fraction of the silt layer (at 13,300 cal yr BP with $\delta^{18}O$ value of –5.0‰) most probably indicates the isotopic composition of silt from the underlying Ordovician limestone (Kaljo et al. 2004) and has not been taken into account in palaeoclimate reconstructions.

In tufa, which precipitated between ca. 12,000 and 10,700 cal yr BP, isotope values increase upwards from –13.1 to –10.6‰. From 10,500 cal yr BP upwards, $\delta^{18}O$ values decrease to the age level of 9,200 cal yr BP (from –10.6 to –11.5‰). At 9,200–3500 cal yr BP isotope data remain relatively constant (from –10.7 to –11.5‰), interrupted only by a short negative excursion at ca. 5,800 cal yr BP with the $\delta^{18}O$ value of –11.9‰, and by a positive excursion (–10.4‰) at ca. 6,500 cal yr BP. From ca. 3,500 cal yr BP a cooling trend is recognizable until the ca. 900 cal yr BP age-level ($\delta^{18}O$ values decrease from –10.9 to –12.5‰). This trend of decreasing $\delta^{18}O$ values is interrupted by a positive shift at ca. 1,500 cal yr BP ($\delta^{18}O$ value –10.7‰). At ca. 900 cal yr BP $\delta^{18}O$ values start to increase again (with a maximum value of –11.4‰) with some minor fluctuations.

Pollen and plant macrofossil analysis

The pollen record of Lake Äntu Sinijärv was divided into six statistically significant subzones. The first five subzones correlate well with the five plant macrofossil zones (Fig. 4).

Äntu-1 (depth interval 375–360cm; age >13,310 cal yr BP). *Betula* (40%) and *Pinus* (20%) dominated. The *Pinus* stomata were present in the upper part of the zone. High relative abundance of thermophilous tree pollen types was recorded. The part of herbs was negligible Charcoal frequencies were high and the pollen concentration was very low (<2,000 grains/cm^2yr), except in the upper part of the zone where it reached 40,000 grains/cm^2yr.

The plant macrofossil assemblage contains two typical tundra species: *Betula nana* and more cold-tolerant *Dryas octopetala* leaves and seeds. The number of *Dryas* leaves is over seventy specimens per the lowermost sample.

Äntu-2 (360–300 cm; >13,310–11,380 cal yr BP). The AP/NAP ratio was 50/50. Among trees *Pinus* (20%) and *Betula* (30%) prevailed. Shrubs such as *Betula nana* and *Salix* expanded. The NAP was heavily dominated by *Artemisia* (up to 45%) and Chenopodiaceae (10%). *Dryas octopetala* and *Helianthemum nummularium* appeared. The amount of charcoal particles was high (40%) and pollen concentration was low (<10,000 grains/cm^{2}yr).

Dryas leaves are found in most samples albeit in small numbers. Few finds of *Pinus*, *Typha*, *Geum* and *Betula nana* are present the terrestrial/telmatic vegetation. Aquatic plants (*Ranunculus* sect. *Batrachium*) and organisms (*Characeae*, *Cristatella*) display a slightly rising number at the end of the subzone.

Äntu-3 (300–260 cm; 11,380–8,930 cal yr BP). AP was dominated by *Betula* (up to 80%) and *Pinus* (15%). Sporadic finds of *Pinus* stomata were recorded. *Ulmus*, *Corylus* and *Alnus* appeared. The amount of herbs and charcoal particles was low. Pollen concentration was increasing upwards from 100,000 to 200,000 grains/cm^{2}yr.

Betula dominates the macrofossil assemblage as in pollen spectra. Another deciduous tree remain appearing in the middle of the subzone is *Alnus* catkin scale. *Pinus* seeds and needles are sporadically present. Aquatic organisms, Characeae oospores and *Cristatella* statoblasts are found in most samples.

Äntu-4 (260–190 cm; 8,930–5,500 cal yr BP). QM formed up to 35%. *Tilia* (10%), *Ulmus* (20%), *Quercus* (10%), *Corylus* (15%) and *Picea* (20%) reached subsequent maxima. The amount of herbs and charcoal particles was low. The pollen concentration was high (>200,000 grains/cm^{2}yr).

The plant macrofossil assemblage contains both deciduous trees (*Betula* sect. *Albae*, *Alnus*) and conifers (*Pinus*, *Picea*). Other finds reflect mostly a telmatic environment (*Juncus*, *Cladium*). In an aquatic environment, *Cristatella* statoblasts are found in small numbers while *Nymphea* appears at the end of the subzone.

Äntu-5 (190–80 cm; 5,500–1,290 cal yr BP). AP was dominated by *Betula* (60%), *Pinus* (15%), *Alnus* (10%) and *Picea* (5%). The amount of QM and herbs was small. *Cerealia* appeared sporadically. Frequencies of charcoal particles were stable around 5%. Pollen concentration was high (>100,000 grains/cm^{2}yr).

Pinus and *Picea* macrofossils prevail in the zone, while *Betula* remains become scarce. Other deciduous trees (*Alnus* and *Populus*) are both represented by only a single macrofossil.

Äntu-6 (80–39 cm; 1,290–630 cal yr BP). AP was dominated by *Betula* (40%), *Alnus* (20%) and *Pinus* (15%). The part of QM was negligible. Clear increase in herbs and charcoal particles frequencies was observed. *Cerealia* had a maximum occurrence. Pollen concentration was low (<20,000 grains/cm^{2}yr).
Sediment of this interval was not analysed for plant macrofossil content.

Discussion

Sediment accumulation in the Lake Äntu Sinijärv basin started after ice retreat from the area in the course of the Late Weichselian deglaciation. Deposition of freshwater tufa began ca. 11,800 cal yr BP which is ~2,000 years after the area was deglaciated at 13,800 cal yr BP (Saarse et al. 2009) and 1,000 years later than indicated by Sohar and Kalm (2008). According to Männil (1967), freshwater tufa precipitation in the Pandivere area started at ca. 11,500 cal yr BP, which is 300 years later than our data indicate. Those data show that precipitation of tufa started at different times in different places in the lake. The beginning of tufa precipitation roughly correlates with the first Äntu low-water period (12,800–10,590 cal yr BP) determined by Sohar and Kalm (2008).

In the sediment sequence the interval between the deglaciation and beginning of tufa precipitation is represented by late glacial lacustrine silt and gyttja. Pollen concentration in the corresponding sediment was very low. The composition of pollen flora with up to 20% of pollen, derived from nemoral thermophilous tree species, suggests that most of the organic material was redeposited from the sediments formed during the earlier interglacials and incorporated in the Late Weichselian till surrounding the lake. The in-wash event from the surroundings at the start of postglacial sedimentation in Äntu Sinijärv is confirmed by the content of the lowermost sample analysed for plant macrofossils: the small sediment sample (11 cm^3) contains an extremely high amount of *Dryas octopetala* leaves (72). Contrary to possible pollen redeposition from the previous interglacial period, *Dryas* leaves are clearly from the late glacial period but probably overrepresented due to allochthonous material in-wash. According to Rosentau et al. (2007), local ice-meltwater lakes disappeared from the area ca. 13,300 cal yr BP, which is 500 years later than suggested by Saarse et al. (2009). The gyttja layer ranges over a 1,500-year interval before it is replaced by pure freshwater tufa and includes abrupt mineral matter inflow (ca. 12,000 till 10,700 cal yr BP), which partly coincides with the Younger Dryas cold interval 12,850–11,650 cal yr BP (Isarin and Rennsen 1999, Björck 2007). The Younger Dryas cooling is clearly documented in Lake Äntu Sinijärv sediments by an abrupt change in pollen flora. The evidence from pollen analysis suggests the existence of an *Artemisia*- and Chenopodiaceae-dominated cold step tundra with shrub and herb communities, typical of open arctic environments incorporating shrubs such as *Betula nana* and *Salix*, and herbs such as *Dryas octopetala* and *Helianthemum nummularium*. The vegetation composition indicates both dry and cold conditions as well as open landscape, because light-demanding *Dryas octopetala* macrofossils are present in most samples. The aquatic plant remains reflect gradual amelioration of the water environment at the end of the Younger Dryas period. Characeae (12,100–11,500 cal yr BP; Fig. 4) are present in increasing amounts, although the number of oospores is relatively small. The presence of temperature-sensitive *Cristatella* (Økland and Økland 2000) suggests rather mild water environment conditions (11,500–10,900 cal yr BP; Fig. 4).

As Lake Äntu Sinijärv is fed by bottom springs (Mäemets 1977), water-level fluctuation reflects changes in groundwater level but also to some degree changes in the precipitation/evaporation ratio. Due to the low evaporation rate (575–600 mm/yr, Arold 2005) compared to the rate of precipitation (530–730 mm/yr, Treier et al. 2004) in Estonia, oxygen isotope ratios from Äntu Sinijärv are assumed to reflect mainly temperature signals (Leng and Marshall 2004). According to Punning et al. (1987), oxygen isotope values in Estonian Ordovician groundwater mostly fluctuate from –10.8‰ to –12.2 ‰. The monthly weighted mean value of $\delta^{18}O$ for precipitations is –

10.4‰ (during winter ca. –14‰ and during summer ca. –8.5‰; Punning et al. 1997, 2002). According to Martma (1988), average O-isotopic composition of northern Estonian lake waters is –10.5‰ and values which characterize inflow and river water composition are between –9.6‰ and – 12.7‰ (Punning et al. 1987). The lake water in general resembles (mean weighted) annual precipitation, but in lakes with groundwater input stable isotope composition reflects a mixture of groundwater and precipitation. Also catchment area inflow affects the isotope constitution of the lake (Leng and Marshall 2004).

Oxygen isotope data from lacustrine tufa of Äntu Sinijärv (Fig. 3) shows small-scale fluctuation (–12.6‰ to –10.2‰), which is characteristic of small lakes in high latitudes (Leng and Marshall 2004). According to Punning et al. (2000), freshwater tufa values from the same lake are between –12.2‰ and –10.1‰, which shows almost the same O-isotope values and fluctuation range of ca. 2‰. Other data from Estonian lake carbonates give average values for freshwater tufa between –12.5‰ and –7‰ (Punning et al. 2000, 2002, 2003). O-isotopic data from the neighbouring areas show $\delta^{18}O$ values of tufa between ca. –5‰ and ca. –14‰ (Hyvärinen et al. 1990; Makhnach et al. 2004; Jonsson et al 2010; Rozanski et al. 2010) and reflects regional environment fluctuations and location (e.g. latitude). The mean value of the Äntu tufa isotope curve is –11.1‰, which correlates well with the average groundwater $\delta^{18}O$ composition (–11.5‰; Punning et al. 1987) and suggests that Äntu Sinijärv is predominantly a groundwater-fed lake. Mean values are in a good correlation with the monthly weighted mean $\delta^{18}O$ value in contemporary precipitation (–10.4‰; differ by 0.6‰), but differ largely from summer precipitation (–8.4‰). It is suggested (Leng and Marshall 2004) that tufa is formed in the surface water layer of the lake during spring and summer, which is most affected by evaporation and photosynthesis. However, in case of groundwater-fed Äntu Sinijärv, the $\delta^{18}O$ composition is most affected by groundwater and less by surface waters.

Postglacial warming is detectable from isotope composition (rising values from – 12.4‰ up to –10.6‰, which is almost 2‰; 12,000–10,700 cal yr BP). This correlates quite well with low water level (Sohar and Kalm 2008), which reflects warmer climate conditions in the region. From 10,500 cal yr BP, there is a decrease in isotope composition till 9,200 cal yr BP (from –10.6‰ to –11.5‰), which most probably indicates the globally known (Yu et al. 2010) “9,300 yr” cold event. The vegetation response to Early Holocene climate amelioration was rapid forestation and loss of arctic and steppe components such as *Dryas octopetala*. Judging by extremely high pollen percentages, the birch tree was a major component of the land cover, which is well supported by numerous finds of variously preserved *Betula* seeds. From 9,200 till 3,500 cal yr BP isotope values remain quite constant (average value –11.1‰), interrupted only by a short negative excursion ca. 5,800 cal yr BP with the $\delta^{18}O$ value of –11.9‰ and positive shift ca. 6,500 cal yr BP (–10.4‰). This 5,700-year long and relatively stable period suggests a local Holocene Thermal Maximum (HTM). Based on ostracod data (Sohar and Kalm 2008), the low-water period also shows correlation between $\delta^{18}O$ values and climate: the higher values of $\delta^{18}O$ during 7,500–6,000 cal yr BP and 4,700–3,700 cal yr BP indicate warmer climate with higher temperatures and lower water level (due to more intensive evaporation and lower precipitation rate). This higher temperature trend is also marked by LOI which shows a stable and high carbonate content in the sediment representing this time period, as freshwater tufa precipitates during ice-free periods, with relatively high temperatures and humidity.

The HTM is palaeobotanically well documented by immigration and establishment of nemoral thermophilous taxa. The aquatic community took advantage of suitable climatic conditions as well – both Characeae and bryozoa and also relatively warm-demanding water lilies were present (minimum mean July temperature 12°C; Isarin and Bochnke 1999). Saw-sedge (*Cladium mariscus*) grew In wetland, which is often related to mild climatic conditions (minimum mean July temperature 13°C; Isarin and Bochnke 1999) and calcareous soils (Mauquoy and Van Geel 2007). After the Middle Holocene Thermal Maximum (8,000–6,000 cal yr BP), the birch and pine re-established their importance and, accompanied by the spruce and alder, became major forest-forming species in the area. The part of thermophilous broad-leaved species in forest composition diminished greatly.

The HTM is followed by a distinct cooling trend in $\delta^{18}O$ values, which decrease down to –12.7‰ by ca. 900 cal yr BP. The $\delta^{18}O$ values fluctuate by almost 2‰ (remain between –10.8‰ and –12.7‰). Loss on ignition results show increase in mineral matter content, with a peak around 900 cal yr BP. This trend of diminishing values is interrupted by a positive shift ca. 1,500 cal yr BP, with the $\delta^{18}O$ value up to –10.7‰. About 900 cal yr BP isotope values start to increase again (with some minor fluctuations), indicating warmer climate and possibly reflecting human impact (growth of population, increased consumption of food, intensive farming and cultivation, etc.). This observation is also supported by palaeobotany data – marked increase in the distribution of herb communities in late Holocene land cover. The growing input of crop pollen points at expanding agrarian activities in the area.

Many other smaller-scale (0.1–0.9‰) decreasing and increasing shifts of the $\delta^{18}O$ values were detected, reflecting short-term climate fluctuations.'

Conclusions

The sediment record of Lake Äntu Sinijärv provides the first high-resolution Holocene and late glacial oxygen isotope data from freshwater tufa in Estonia. In combination with other information, these data shed light on the regional environmental and climatic evolution during the Holocene.

Tufa precipitation in Äntu Sinijärv started approximately 11,800 cal yr BP ago, which is about 1,000–1,300 cal yr BP later than revealed by former works and ca. 2,000 cal yr BP after deglaciation of the area. The Younger Dryas cooling is clearly documented in the lake sediments by an abrupt change in pollen and macrofossil flora and isotope composition (lower than the average). Rise of O-isotope values by about 2‰ in correlation with low water level during that period shows postglacial temperature increase and reflects warmer climate conditions in the region. Relatively stable environmental conditions occurred between 9,200 and 3,500 cal yr BP and were followed by a cooling episode till 900 cal yr BP.

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List of figures and tables:

Table **1** AMS ^{14}C dates from Lake Äntu Sinijärv

Fig. 1 Location of the study area. ● Lake Äntu Sinijärv (59°03′ N, 26°14′ E)

Fig. 2 The age-depth model of the sediment section of Lake Äntu Sinijärv. Calibrated radiocarbon median ages are plotted against the depth from the sediment surface

Fig. 3 The Timescale, lithology, sediment description, loss-on-ignition and isotope curve (the bold curve indicates a smoothed line with a step of 5 analyses on average) of Lake Äntu Sinijärv. The $\delta^{18}O_{VSMOW}$ values of water were converted to $\delta^{18}O_{VPDB}$ values using the equation of Hut (1987): δ^{18}Owater (VPDB)= δ^{18}Owater (VSMOW)–0.27. Black bold line – weighted mean $\delta^{18}O$ value (–14.0‰) of winter precipitation in Estonia; dashed line – weighted mean $\delta^{18}O$ value (–8.7‰) of summer precipitation in Estonia (Punning et al. 1987), **1** – $\delta^{18}O$ values (–12.0‰ to –12.5‰) of the Ordovician groundwater in Estonia (Vaikmäe et al. 2001), **2** – monthly $\delta^{18}O$ variations (–11.1 to –13.1‰) in Ordovician groundwater in Estonia (Punning et al. 1987)

Fig. 4 Local Pollen Assemblage Zones (A) and zones of plant macrofossils (B) Identified in the studied sediment section. *Betula* section *Albae* sums up remains of tree-type *Betula*. Abbreviations: CS – catkin scale; CB – catkin bract; BS – budscale; s. – seed; o. – oospore; statob. – statoblasts; eph. – ephippia

Table **1**

Depth (cm) on sediment core	Lab.no.	Dated material	^{14}C AMS age BP	$\delta^{13}C$ ‰	cal. yr BP, 1σ	Median of cal. age
104-106	Poz-25535	aquatic mosses	1775 ± 35	-24,2	1610-1770	1700
123-124	Poz-25536	aquatic mosses	3125 ± 35	-32,4	3270-3390	3350
189-190	Poz-25537	aquatic mosses	4740 ± 40	-35,5	5330-5590	5490
218-219	Poz-25538	aquatic mosses	5610 ± 40	-29,6	6310-6440	6380
286-287	Poz-25539	aquatic mosses	10770 ± 70	-31,1	12590-12720	12660
306-308	Poz-25540	gyttja	11450 ± 70	-27,7	13240-13400	13310
335-336	Poz-25541	gyttja	10390 ± 60	-19,4	12140-12390	12260
360-363	Poz-25542	wood	10960 ± 70	-24,5	12700-12930	12830

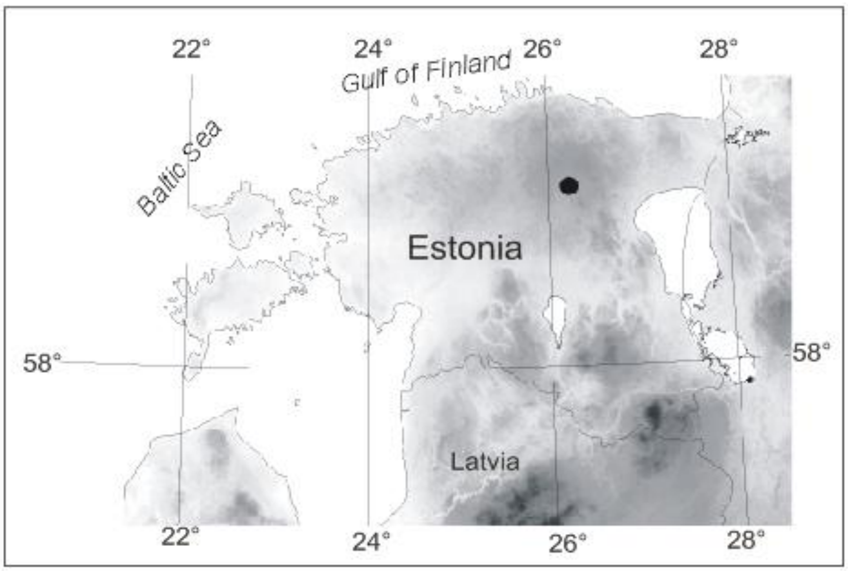
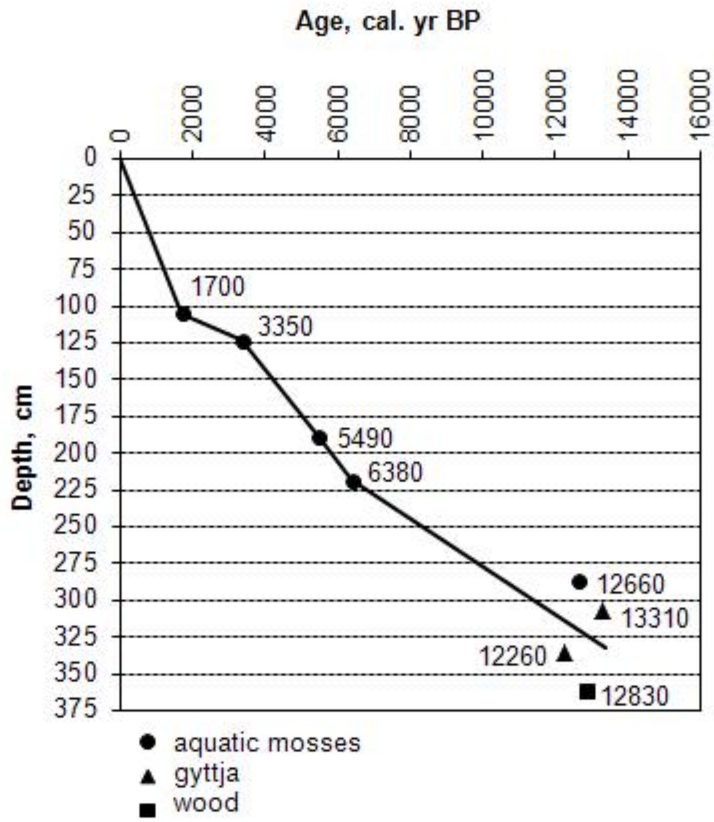
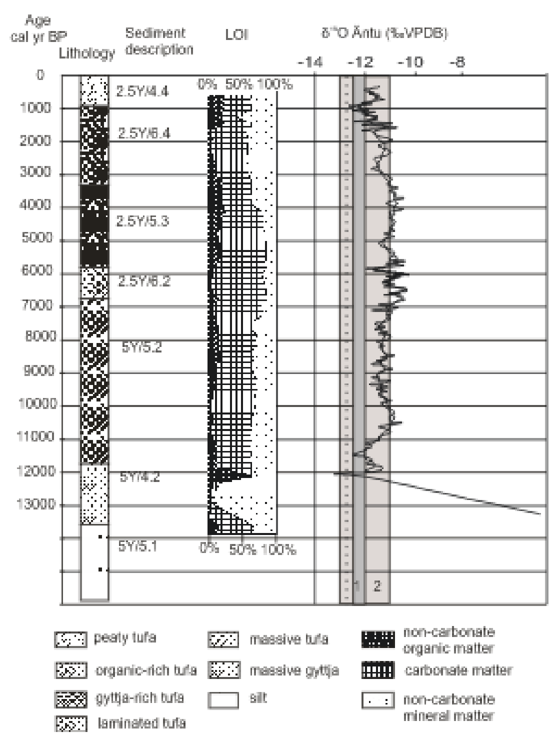


Fig 1.



Age, cal. yr BP
0
2000
4000
6000
8000
10000
12000
14000
16000
Depth, cm
0
25
50
75
100
125
150
175
200
225
250
275
300
325
350
375
1700
3350
5490
6380
12660
13310
12260
12830
aquatic mosses
gyttja
wood

Fig 2.



Age cal yr BP
Lithology
Sediment description
LOI
-14
-12
-10
-8
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
2.5Y/4.4
2.5Y/6.4
2.5Y/5.3
2.5Y/6.2
5Y/5.2
5Y/4.2
5Y/5.1
0% 50% 100%
0% 50% 100%
1
2
peaty tufa
organic-rich tufa
gyttja-rich tufa
laminated tufa
massive tufa
massive gyttja
silt
non-carbonate organic matter
carbonate matter
non-carbonate mineral matter

Fig 3.

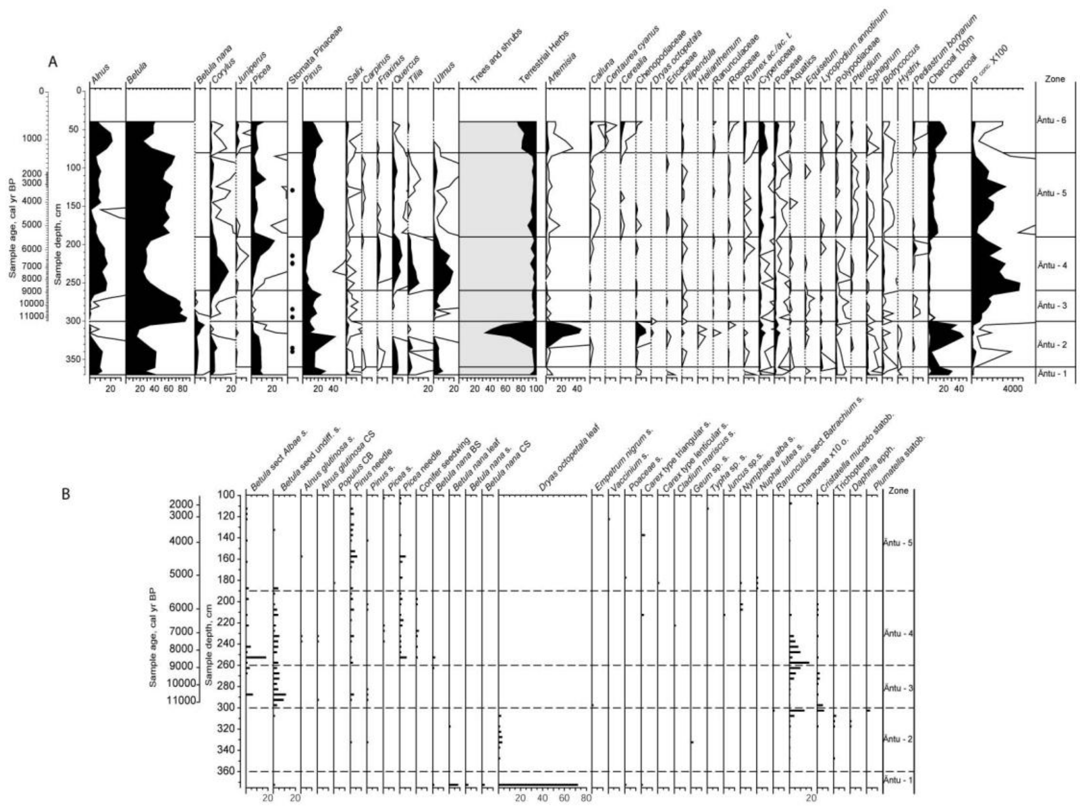
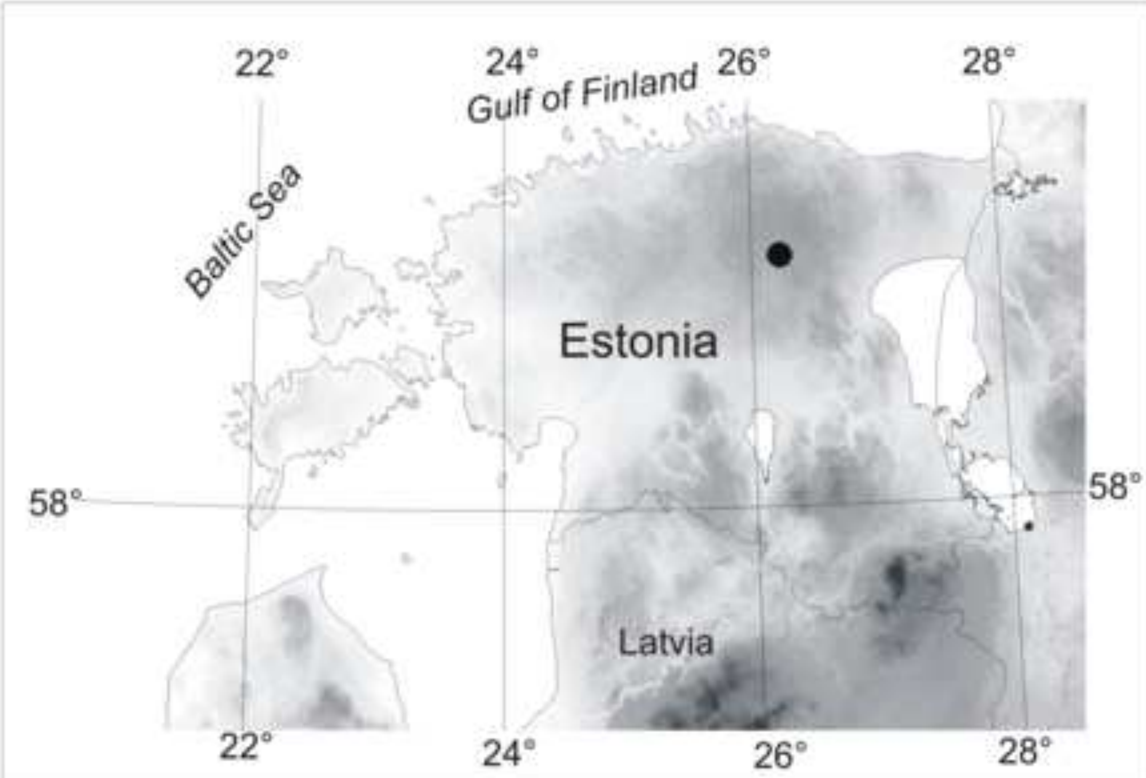

A
Alnus
Betula
Betula nana
Corylus
Juniperus
Picea
Stomata Pinaceae
Pinus
Salix
Carpinus
Fraxinus
Quercus
Tilia
Ulmus
Trees and shrubs
Terrestrial Herbs
Artemisia
Calluna
Centaurea cyanus
Cerealia
Chenopodiaceae
Dryas octopetala
Ericaceae
Filipendula
Helianthemum
Ranunculaceae
Rosaceae
Cyperaceae
Poaceae
Aquatics
Equisetum
Lycopodium annotinum
Polypodiaceae
Pteridium
Sphagnum
Botryococcus
Hystrix
Pediastrum boryanum
Charcoal 100m
Charcoal
Zone
Sample age, cal yr BP
Sample depth, cm
Äntu - 6
Äntu - 5
Äntu - 4
Äntu - 3
Äntu - 2
Äntu - 1
B
Betula sect Albae s.
Betula seed undiff. s.
Alnus glutinosa s.
Alnus glutinosa CS
Populus CB
Pinus needle
Pinus s.
Picea s.
Picea needle
Conifer seedwing
Betula nana BS
Betula nana leaf
Betula nana s.
Betula nana CS
Dryas octopetala leaf
Empetrum nigrum s.
Vaccinium s.
Poaceae s.
Carex type triangular s.
Carex type lenticular s.
Cladium mariscus s.
Geum sp. s.
Typha sp. s.
Juncus sp. s.
Nymphaea alba s.
Nuphar lutea s.
Ranunculus sect Batrachium s.
Characeae x10 o.
Cristatella mucedo statob.
Trichoptera
Daphnia epph.
Plumatella statob.
Zone
Sample age, cal yr BP
Sample depth, cm

Fig 4.

Figure
Click here to download high resolution image



Figure
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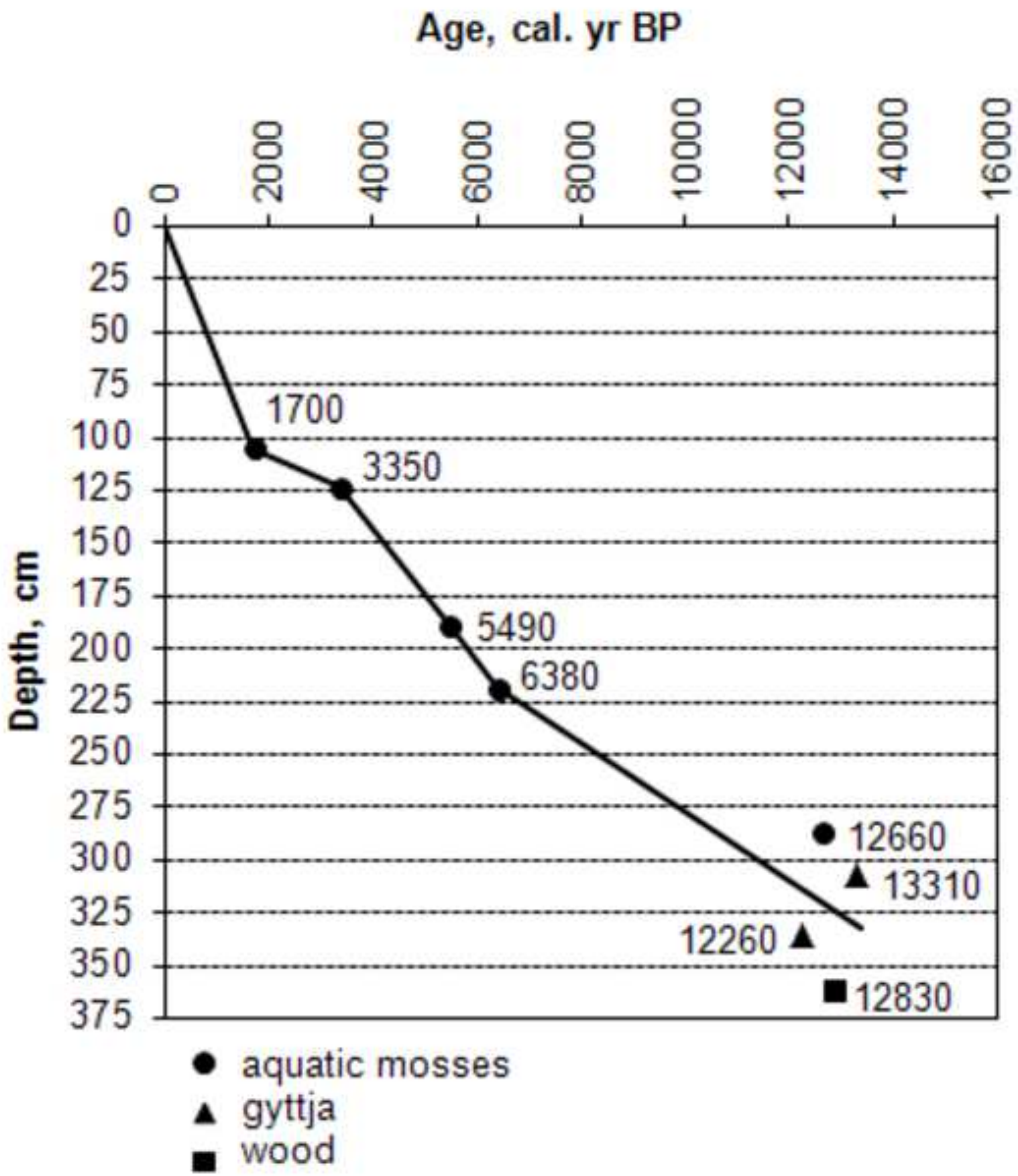

Figure
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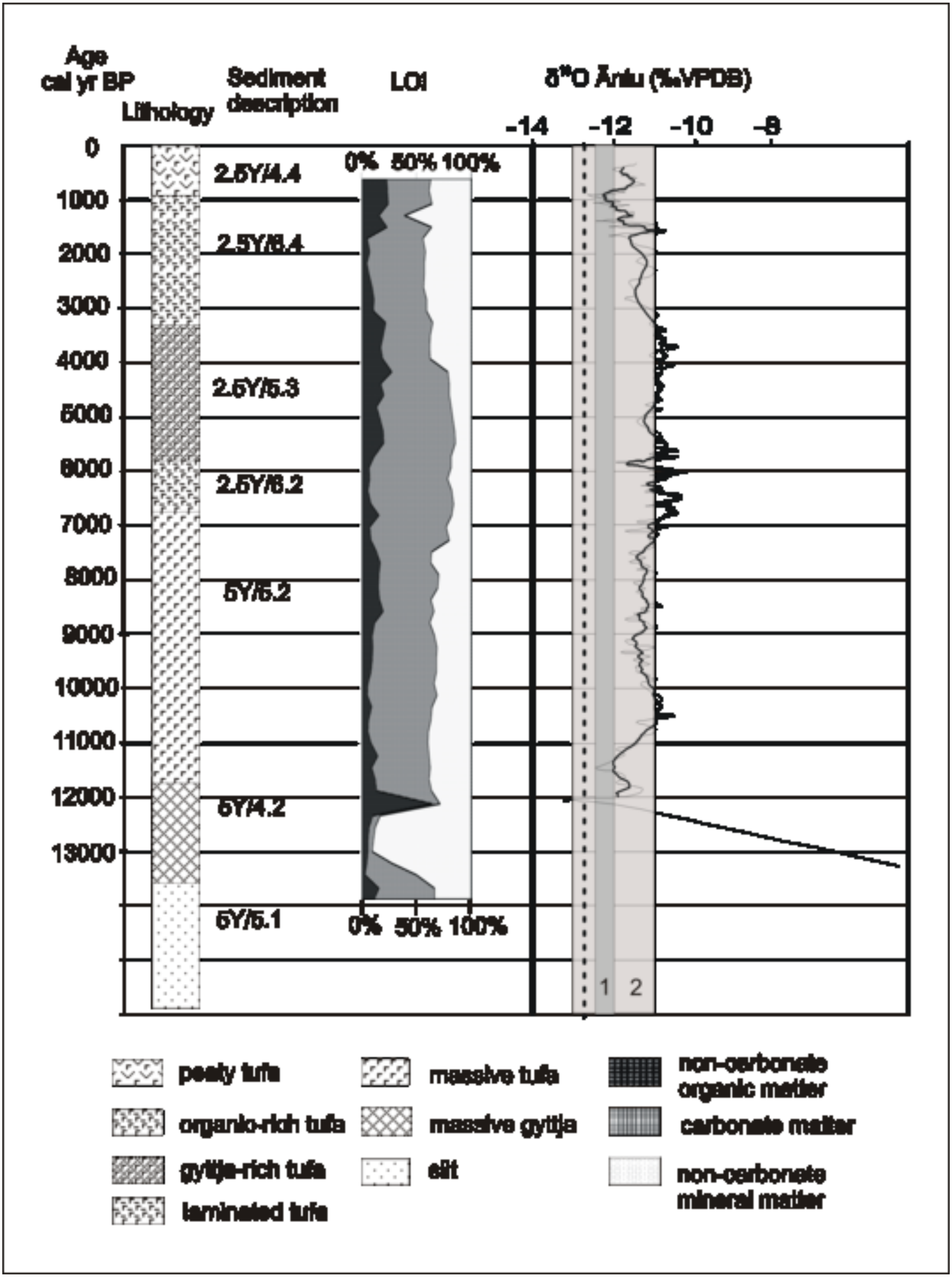

Figure

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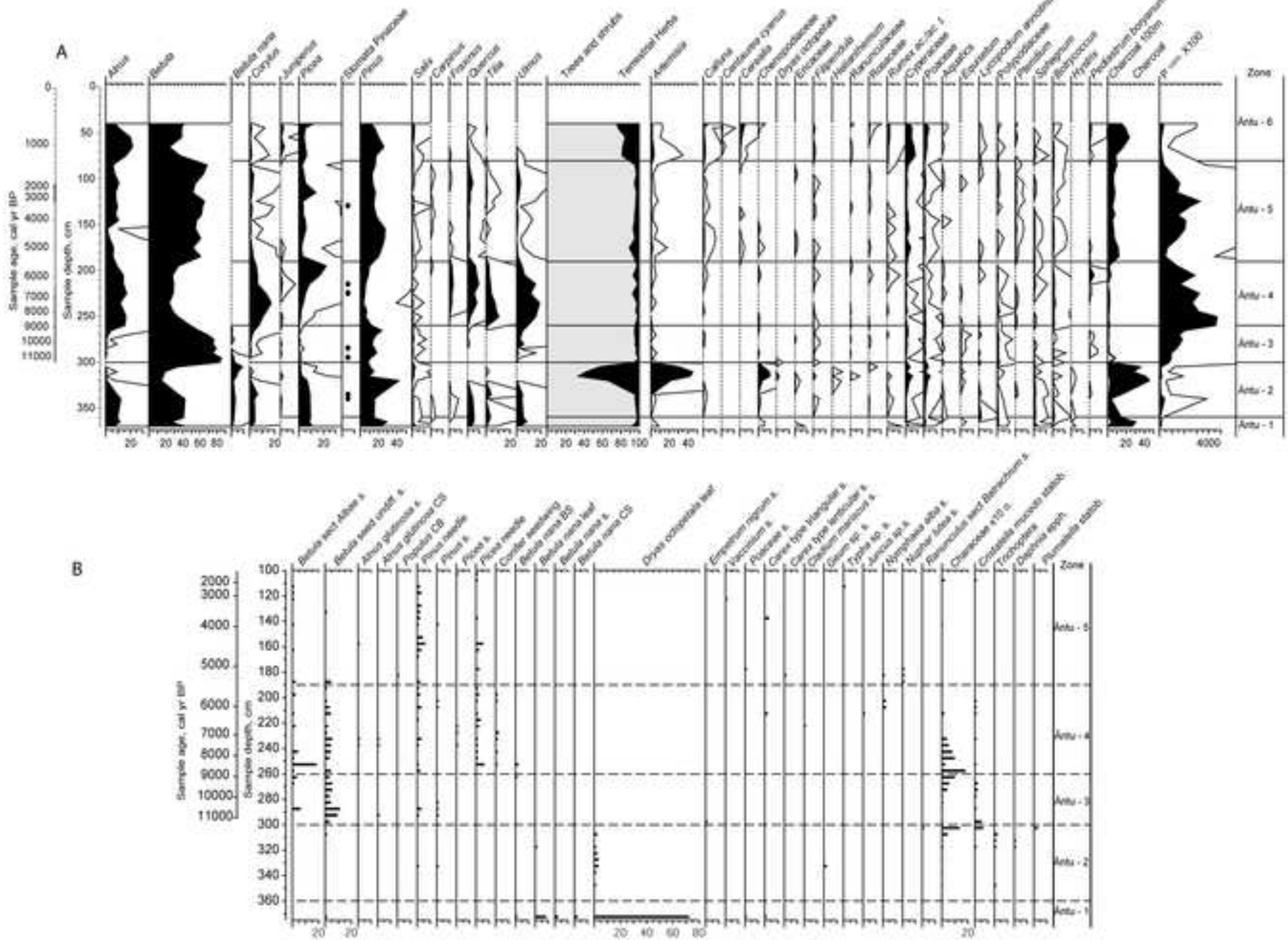

table
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