Elsevier Editorial System(tm) for Quaternary Research
Manuscript Draft

Manuscript Number: YQRES-D-15-00014R2

Title: Climate changes, metal pollution and soil erosion in South Greenland over the past 700 years

Article Type: Research Paper

Keywords: Greenland; Norse; soil erosion; Little Ice Age; lead (Pb); metal pollution; FTIR; pollen; geochemistry

Corresponding Author: Ms. Noemí Silva-Sánchez, Msc

Corresponding Author's Institution: Universidad de Santiago de Compostela

First Author: Noemí Silva-Sánchez, Msc

Order of Authors: Noemí Silva-Sánchez, Msc; J. Edward Schofield, Dr.; Tim M. Mighall, Dr. ; Antonio Martínez Cortizas, Professor; Kevin J. Edwards, Professor; Ian Foster, Professor

Abstract: A peat core from southern Greenland provided a rare opportunity to investigate human-environment interactions, climate change and atmospheric pollution over the last ~700 cal years. X-ray fluorescence, gas chromatography-combustion, isotope ratio mass spectrometry, peat humification and fourier-transform infrared spectroscopy were applied and combined with palynological and archaeological evidence. Variations in peat mineral content seem to be related to soil erosion linked with human activity during the late Norse period (13th-14th centuries AD) and the modern era (20th century). Cooler conditions during the Little Ice Age (LIA) are reflected by both slow rates of peat growth and carbon accumulation, and by low bromine (Br) concentrations. Spörer and Maunder minima in solar activity may be indicated by further declines in Br and enrichment in easily-degradable compounds such as polysaccharides. Peat organic matter composition was also influenced by vegetation changes at the end of the LIA when the expansion of oceanic heath was associated with polysaccharide enrichment. Atmospheric lead pollution was recorded in the peat after AD 1845, and peak values occurred in the 1970s. There is indirect support for a predominantly North American lead source, but further Pb isotopic analysis would be needed to confirm this hypothesis.

Climate changes, lead pollution and soil erosion in South Greenland over the past 700 years

Noemí Silva-Sánchez*[a], J. Edward Schofield[b], Tim M. Mighall[b], Antonio Martínez Cortizas[a], Kevin J. Edwards[b,c], Ian Foster[d]

[a] Edafología y Química Agrícola, Fac. Biología, Campus Sur, Universidad de Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n. E-15782, Spain

[b] Department of Geography & Environment, School of Geosciences, University of Aberdeen, Elphinstone Road, Aberdeen AB24 3UF, UK

[c] Department of Archaeology, School of Geosciences, University of Aberdeen, Elphinstone Road, Aberdeen AB24 3UF, UK

[d] School of Science and Technology, University of Northampton, Newton Building, Northampton NN2 6JD, UK

*Corresponding author:
noemi.silva.sanchez@usc.es, n.o.e.s@hotmail.com
Tel. +34 881813315

Abstract

A peat core from southern Greenland provided a rare opportunity to investigate human-environment interactions, climate change and atmospheric pollution over the last ~700 cal years. X-ray fluorescence, gas chromatography-combustion, isotope ratio mass spectrometry, peat humification and fourier-transform infrared spectroscopy were applied and combined with palynological and archaeological evidence. Variations in peat mineral content seem to be related to soil erosion linked with human activity during the late Norse period (13^{th}-14^{th} centuries AD) and the modern era (20^{th} century). Cooler conditions during the Little Ice Age (LIA) are reflected by both slow rates of peat growth and carbon accumulation, and by low bromine (Br) concentrations. Spörer and Maunder minima in solar activity may be indicated by further declines in Br and enrichment in easily-degradable compounds such as polysaccharides. Peat organic matter composition was also influenced by vegetation changes at the end of the LIA when the expansion of oceanic heath was associated with polysaccharide enrichment. Atmospheric lead pollution was recorded in the peat after ~AD 1845, and peak values occurred in the 1970s. There is indirect support for a predominantly North American lead source, but further Pb isotopic analysis would be needed to confirm this hypothesis.

Keywords: Greenland, Norse, soil erosion, Little Ice Age, lead (Pb), metal pollution, FTIR, pollen, geochemistry

Introduction

Ombrotrophic peatlands, receiving their inputs (precipitation and dusts) solely from the atmosphere, are widely recognised as important environmental archives. The stratified records of chemical elements and biological proxies contained within raised mires and blanket bogs can be used, for example, to provide information about changes in climate or land use, and levels of atmospheric pollution, during prehistory through to post-industrial times (e.g. Chambers et al., 2012; Meharg et al., 2012; Martínez Cortizas et al., 2013; Pontevedra-Pombal et al., 2013). Peat geochemical studies are available for locations across the major continental land masses and peripheries of North America and Western Europe, yet relatively few Holocene records exist from mid to high latitude North Atlantic islands. Evidence from Greenland, Iceland and the Faroes would enhance spatial data coverage for sites influenced by related atmospheric systems. The North Atlantic islands have relatively short and frequently interrupted histories of human occupation, with continuous recent (European) settlement dating back only to Norse colonisation (*landnám*) during the period ~AD 800-1000 (Fitzhugh and Ward, 2000). Where environmental archives of sufficient continuity and antiquity present themselves, these potentially offer opportunities to establish a geochemical baseline for 'pristine' North Atlantic environments during periods when people were absent from the landscape (cf. Dugmore et al., 2005).

Few peat geochemical investigations have been conducted in Greenland (Fig. 1a). Apart from cost and logistics, this is because peatlands are not extensive and raised bogs are absent (Feilberg, 1984). Some data are available from minerotrophic, groundwater-fed fens which demonstrate that such wetlands may preserve a record of atmospheric deposition, even though the identification of regional atmospheric signals can be complicated by mineral inputs from local sources (e.g. slopewash). Shotyk et al. (2003) used a fen developed between two small lakes near Tasiusaq (Fig. 1b), southern Greenland, to reconstruct fluxes of selected elements, notably mercury (Hg), lead (Pb) and arsenic (As), and related these to atmospheric deposition of anthropogenic origins after ~AD 1950. Their profile extended back ~2500 cal yr BP, but at reduced temporal resolution through the older part of the sequence. Schofield et al. (2010) presented a geochemical record from the nearby site of Qinngua (Fig. 1b), concentrating on the behaviour of lithogenic elements and halogens, and linking this to patterns of soil erosion and storminess over the last *ca* 1000 cal yr, albeit noting a significant hiatus in the profile (~AD 1380-1950).

An investigation by Golding et al. (2011) at the Norse farmstead of Sandhavn (Fig. 1b), near the southern tip of Greenland, revealed a small peat-filled depression set within a rock platform (Figs 1c and 1d). The basin appears isolated from the groundwater table and radiometric dating indicates that peat growth has apparently been continuous since the mid-13th century AD. This provided a rare opportunity to characterise the geochemical signal contained within a predominantly rain-fed peat from a Greenlandic setting. The main objectives of the research reported here are: (i) to search for geochemical signatures that are representative of changes in climate and of possible impacts arising from past human activity at the site (e.g. soil erosion); (ii) to study the relationship between climate, vegetation and peat decomposition in a subarctic environment; (iii) to establish high resolution records for atmospheric metal pollution and to discuss likely sources for these. Although the peat profile from Sandhavn spans a relatively short timeframe (~AD 1250-2000) and cannot provide baseline environmental information for the period before the arrival of Norse settlers, the research is important because: (a) it provides data encompassing a significant climatic perturbation – the Little Ice Age (LIA; Grove, 1988); (b) the basin is adjacent to the homefields (i.e. the hay-producing areas) of a Norse farmstead (Fig. 1d) that was in use from ~AD 1000-1400, and the sampling location was anticipated to be particularly sensitive to the environmental impacts arising during the past human occupation and use of the site; (c) the results presented on peat decomposition may prove informative for studies with a focus on long-term carbon sequestration by peatlands.

Site background and context

Sandhavn (59º59'N, 44º46'W; Fig. 1) is located on the Ikigait peninsula on the outer coast of Greenland, approximately 50 km northwest of Cape Farewell (the most southerly point in Greenland). The prevailing climate is subarctic, with cold winters and cool summers and a notable feature of the climate regime is frequent strong winds. The seas here are regarded as the windiest in the world ocean with speeds exceeding 20 ms^{-1} (equivalent to a strong gale) around 20% of the time (Sampe and Shang-Ping, 2007). Wind direction is bimodal, with a strong probability of observing both westerly and easterly high speed wind events (Moore et al., 2008; Renfrew et al., 2008), which might have implications for the sourcing of atmospheric dusts deposited across the area.

The solid geology of south Greenland comprises granites and gneisses of the Ketilidian mobile belt, with basic and intermediate intrusions (Allaart, 1976). This creates a rugged alpine topography characterised by steep slopes and peaks sometimes exceeding 1000 m a.s.l. The soils can be broadly classified as cryosols, with many showing evidence for podsolization (Golding et al., 2011). *Empetrum nigrum* (crowberry) oceanic heath is the dominant vegetation in the coastal zone. This is replaced by more subcontinental plant communities – primarily *Betula-Salix* (birch-willow) dwarf heath – within the warmer and drier interior (Böcher et al., 1968; Feilberg, 1984). The basin featured in this investigation (Fig. 1c) supports nutrient-poor mire dominated by sedges (*Carex rariflora* and *C. bigelowii*), interspersed with small pools fringed by mare's-tail (*Hippuris vulgaris*). There are no inflowing streams entering the basin, which is set within a rock outcrop that is elevated slightly above the general level of the land around it (Fig. 1d). Consequently any minerogenic inputs reaching the basin via runoff from the surrounding area will have been restricted to an extremely localised radius (~10-20 m) defined by the rocky rim around the basin. Thus, whilst the setting cannot be defined as strictly ombrotrophic, the majority of inputs to the basin must come from the atmosphere. This supposition is further supported by high organic LOI values, high C contents and low concentrations of lithogenic elements in the peat (discussed below).

The ruins of a Viking/Norse farmstead and Thule Inuit dwellings can be found at Sandhavn. These, together with landscape, soils and pollen-based evidence from the site (Raahauge et al., 2003; Golding et al., 2011, 2014) attest to a local human presence between ~AD 1000-1400, i.e. throughout most of the period conventionally ascribed to the occupation of the Norse Eastern Settlement of Greenland (Krogh, 1967). The neighbouring farm and port of Herjolfsnes, ~3.5 km east-southeast of Sandhavn, was perhaps in use until slightly later (~AD 1450) before also being abandoned (Arneborg et al., 1999). The Royal Greenlandic Trading Company had a trading station here from AD 1834-1877. Sheep farming occurred briefly on the Ikigait peninsula from 1959-1972 (Arneborg, 2006), although pastoral agriculture has been in continuous operation more widely across southern Greenland since 1924 (Fredskild, 1988). The area immediately around Sandhavn has otherwise been uninhabited, with the possible exception of occasional Thule maritime hunters whose impact on the landscape would probably have been negligible.

Methods

Fieldwork

In August 2008, a short (40cm) peat monolith was recovered from a small (~30 m diameter) basin (59º59.875'N, 44º46.637'W) adjacent to the former homefields and Norse ruins at Sandhavn (Fig. 1c). Samples were collected by inserting a monolith tin into the open face of a pit dug into the mire. The field stratigraphy comprised a base of saturated coarse grey-brown sands overlain by ~36 cm of orange-brown *turfa* (rootlet) peat containing abundant bryophytes. The peat was visibly darker above 17 cm. The top of the profile (5-0 cm) contained the (living) root mat. The monolith was wrapped in polythene and returned to the University of Aberdeen, where it was kept refrigerated (4 ºC) prior to sub-sampling in the laboratory.

Radiocarbon dating and age-modelling

Four AMS (accelerator mass spectrometry) ^{14}C measurements were taken on bryophytes selected from the peat (Table 1). These were first reported in Golding et al. (2011) where they were used to produce an age-depth model based upon a polynomial fitted through the median probabilities of the calibrated radiocarbon dates. The addition of ^{210}Pb-dating to the profile (as outlined below) and developments in software now allow an improved age-depth model to be produced. The revised model uses 'classical' age-depth modelling (*Clam*; Blaauw, 2010) to apply a smoothed spline through the dates. The 'best estimates' from this model have been used to provide calendar dates for events in the geochemical and biological records through the organic (peat) section of the profile.

^{210}Pb-dating

The unsupported $^{210}Pb_{un}$ activity within samples towards the peat surface was ascertained by subtraction of the supported component (measured as ^{214}Pb at 295.22 and 351.93 keV) from the total ^{210}Pb activity measured at 46.54 keV (Wallbrink et al., 2002). ^{210}Pb and ^{214}Pb activities were measured using EG&G ORTEC hyper-pure Germanium detectors in a well configuration (11 mm diameter, 40 mm depth) housed at Coventry University. The method for calculating the age-depth relationship follows procedures described by Appleby and Oldfield (1978), Appleby (2001) and Walling et al. (2002). Accumulation rates varied down core and the CRS dating model was used to calculate ages (Appleby et al., 1988; Appleby, 2001).

Pollen analysis

Full details of the methods are described in Golding et al. (2011). Pollen samples were prepared using NaOH, HF and acetolysis techniques with samples embedded in silicone oil of 12,500 cSt viscosity (Moore et al., 1991). Palynomorphs were counted until a sum in excess of 500 TLP (total land pollen, excluding aquatics and spores) was achieved. Percentage data were calculated using TILIA (Grimm, 1992) and the pollen diagram of selected taxa constructed using TGView (Grimm, 2004). Coprophilous fungal spores (van Geel et al., 2003) were also counted and these are expressed as a percentage of the TLP sum. These spores are given the type numbers assigned by the Hugo de Vries-Laboratory, Amsterdam, and are prefixed *HdV-*.

Loss-on-ignition (LOI) and Dry Bulk Density

The organic content of samples was measured through LOI. This was calculated following the combustion of dried and milled samples in a muffle furnace for 3 hours at 550 ºC. Dry weights were also used to calculate dry bulk density of the peat which, in turn, allowed the determination of peat carbon accumulation rates (PCAR).

Elemental analysis and isotopic ratio mass spectroscopy

Laboratory sub-sampling for elemental analysis was done at 1 cm contiguous intervals. Prior to measurement, samples were dried and milled to a fine powder with an agate mill. Concentrations of major and minor elements (Si, Al, Fe, Ti, Ca, K, P and S), trace lithogenic elements (Rb, Sr, Zr, Nb, Y, Ga), trace metallic elements (Mn, Cr, Ni, Cu, Zn and Pb), halogens (Cl and Br) and selenium (Se) were determined by X-ray fluorescence (XRF) using an EMMA-XRF (Cheburkin and Shotyk, 1996) hosted at the XRD-XRF facility of RIAIDT (Red de Infraestructuras de Apoyo a la Investigación y al Desarrollo Tecnológico) at the University of Santiago de Compostela. Peat and mineral samples were calibrated using a calibration for organic and inorganic matrices respectively. Detection limits (DL) were as follows: Si (0.05%), Ti and Fe (0.002%), Al (0.002% for organic; 0.2% for inorganic matrices), Ca (0.002%; 0.01%), K (0.002%; 0.05%), P (0.009%; 0.03%), S (0.009%; 0.03%), Rb (0.5 $\mu g\ g^{-1}$; 5 $\mu g\ g^{-1}$), Sr (0.5 $\mu g\ g^{-1}$; 5 $\mu g\ g^{-1}$), Mn (5 $\mu g\ g^{-1}$; 30 $\mu g\ g^{-1}$), Pb (0.5 $\mu g\ g^{-1}$), Se (0.5$\mu g\ g^{-1}$; 2$\mu g g^{-1}$),Br (0.5 $\mu g g^{-1}$; 2 $\mu g g^{-1}$) and Cl (40 $\mu g\ g^{-1}$; 350 $\mu g\ g^{-1}$). Calibrations for Zr were not provided, thus we used normalized intensities with z-score transformation for comparison with other elements.

The elemental analyses of C and N, and the $\delta^{13}C$ and $\delta^{15}N$ isotopic ratio analyses, were carried out using a gas chromatography-combustion elemental analyser (GC/C; EA1108 CarboErba Instruments) coupled by a Conflowll interphase (ThermoFinnigan) with an isotope ratio mass spectrometer (IRMS; MAT253 ThermoFinnigan). Sample isotopic composition is expressed as units of $\delta^{13}C$ and $\delta^{15}N$ using Pee Dee Belemnite (PDB) and air atmosphere as the standards for C and N respectively.

Fourier Transform Infrared Spectroscopy (FTIR)

Spectral characterization of peat samples was made in the IR-RAMAN unit of RIAIDT, and performed by FTIR spectroscopy using a Bruker IFS-66V FTIR spectrometer. The resolution was set to 4 cm^{-1} and 32 scans per sample were recorded. The operating range was 400-4000 cm^{-1}. One mg of homogenised (milled) sample was mixed thoroughly with 100 mg of KBr (FTIR grade) and a pellet was prepared using a press. To avoid differences in absorbance related to sample preparation and detection, various procedures were applied to transform the baseline corrected spectra (Solomon et al., 2007; Smidt et al., 2008). The main FTIR bands used in this study and their meaning are shown in Table SI1.

Degree of peat humification (DPH)

Peat humification was measured following the method of extracting humic acids from dried and milled peat samples using 8% NaOH and assessing the concentrations of solutions colorimetrically using a spectrophotometer (Blackford and Chambers, 1993). Results are expressed as percentage transmittance.

Statistics

The use of multivariate statistical approaches helps to summarize common patterns of variation within datasets and to gain insights into the underlying environmental factors that control these. For elemental composition data and LOI (collectively PCe), and organic matter properties – FTIR, C/N, $\delta^{13}C$, $\delta^{15}N$ and DPH – (collectively PCo), principal components analyses (PCA) were applied using SPSS 20 in correlation mode and by applying a varimax rotation. Prior to analysis, the dataset was standardized using z-scores (Eriksson et al., 1999).

Results and interpretation

Chronology

Radiocarbon dates are shown in Table 1 and an age-depth model for the profile is presented in Figure 2. This pertains to the organic part of the sequence; the basal sands, which are of unknown age, were not considered. The model shows that the peat accumulation rate has varied considerably over the last ~750 cal yr. The rate was initially very low, ~0.025-0.033 cm yr^{-1} from ~AD 1250-1400 (equivalent to a deposition time [DT] of ~30-40 yr cm^{-1}). The rate of peat growth reduced further during the period *ca* AD 1400-1800 (~0.020-0.025 cm yr^{-1}; DT ~40-50 $yrcm^{-1}$). The accumulation of organic matter accelerated rapidly during the last two centuries, especially during the second half of the 20th century when peat accumulation increased to ~0.2 cm yr^{-1} (DT ~5 yr cm^{-1}). This pattern translates into a low temporal resolution for the bottom half of the peat monolith, but a highly resolved archive above this.

Pollen analysis

Full details of the pollen analysis have already been presented in Golding et al. (2011). Selected taxa appropriate to the discussion of the new geochemical data are presented in Figure 3.

Elemental composition and LOI

The transition from basal sand to peat (36-35 cm) is the key stratigraphic change in the monolith. This is reflected by sharp differences in LOI and element concentrations across the sediment contact (Fig. SI.1). In order to optimise the visibility of changes through the peat section (Fig. 4), PCA was applied only to those samples above the transition (Fig. 5). Three principal components (PCe), which explain 77.1% of the total variance, were extracted (Table SI2).

The first principal component (PC1e) explains 38.9% of the variance. Most lithogenic elements and some trace metals (Ti, Si, Zr, Al and Rb), together with N, P and S, show high positive loadings for PC1e, whilst LOI displays a large negative loading. The record of factor scores can be divided into three main sections. From 35-32 cm the scores are positive but decreasing; from 32-16 cm the scores fluctuate between small negative and positive values; and the scores decrease steadily to large negative values from 16 cm to the surface. The large contribution of lithogenic elements and their opposition with LOI indicate that this component mainly reflects the mineral content of the peat.

The second principal component (PC2e) explains 20.2% of the variance. Iron, Br, Pb and Cl have high positive loadings for PC2e whilst S shows a moderate negative loading. Factor scores for PC2e (Fig. 5) are negative except for a broad peak from 22-9 cm. Iron accumulation in peat is largely controlled by redox conditions (Chesworth et al., 2006), with the concentration of Fe increasing under oxidisation (e.g. during water table drawdown). The halogens (Br and Cl) are likely to be of marine origin and are mostly preserved in peat as organohalogenated compounds formed by oxygen-dependent enzymatic processes. Thus, their concentrations in peat, although also dependent on atmospheric fluxes, are mainly controlled by biotic halogenation and dehalogenation (Myneni, 2002; Biester et al., 2004; Leri and Myneni, 2012). Lead may have both geogenic and pollution sources, but its increase here seems to be linked to atmospheric pollution as it does not have a strong association with the major and minor lithogenic elements.

The third principal component (PC3e) explains 18% of the variance and is most strongly related to K, Mn, Ca (high positive loadings), and to a lesser extent Sr (moderate positive loadings) and C (moderate negative loadings). PC3e scores show a similar record to PC1e scores below 16 cm, suggesting that in this peat section, K, Mn and Ca are mainly of geogenic origin. Contrary to PC1e, PC3e scores increase to the surface of the peat, most probably due to biocycling.

Characterization of peat organic matter: FTIR bands, C/N, $\delta^{13}C$, $\delta^{15}N$ and DPH

Trends in organic matter properties (C/N, $\delta^{13}C$, $\delta^{15}N$ and DPH) and selected FTIR bands are shown in Figure 6.Three principal components (PCo), which explain 86% of the total variance, were extracted from these data (Table SI3). The first principal component (PC1o) accounts for 48% of the total variance. Bands representative of recalcitrant compounds such as aliphatics (2852 cm^{-1} and 2922 cm^{-1}), lignins (1514 cm^{-1}), aromatics (3051 cm^{-1}), amides (1660 cm^{-1} and 1550 cm^{-1}), and $\delta^{15}N$ – the enrichment of which has been associated with peat decomposition (Létolle, 1980; Macko et al., 1993; Högber, 1997) – show high positive factor loadings. C/N ratio has a high negative loading, while $\delta^{13}C$ and DPH show moderate negative loadings. Decomposition via residual enrichment of N relative to C (Malmer and Holm, 1984; Kuhry and Vitt, 1996) is associated with a decrease in the C/N ratio. The large contribution of recalcitrant compounds, $\delta^{15}N$ and C/N ratios in this component indicates that the factor is heavily related to the decomposition of peat organic matter. Even variables with moderate loadings support this interpretation, as decreases in $\delta^{13}C$ in peatlands have been associated with enrichment of recalcitrant moieties (Alewell et al., 2011; Broder et al., 2012; Biester et al., 2013). Recalcitrant plant fractions appear to be more depleted in ^{13}C compared to the bulk plant material; for example, $\delta^{13}C$ in *Spartina* detritus gradually decreases during biogeochemical processing due to the preservation of substances like lignin which contain less ^{13}C (Benner et al., 1987). Similarly, studies performed on C4 grasses indicate that lignin-C is up to 4.7‰ lower in ^{13}C compared with the bulk plant material (Schweizer et al., 1999). As decomposition leads to an increase in solubilized humic acids, DPH has been widely used as a measure of the degree of peat decomposition (Blackford and Chambers, 1993, 1995; Borgmark, 2005; Borgmark and Schoning, 2006). From 35-15 cm, positive factor scores (Fig. 7) indicate a relatively high degree of decomposition compared to the rest of the core, although a generally decreasing pattern of values is detected, reflecting the depth-time dependent nature of decomposition. Lower scores from 29-25 cm and 20-16 cm coincide with smaller amounts of recalcitrant compounds. From 15cm to the surface, scores become negative, indicating a trend to less decomposed/fresh plant remains.

PC2o accounts for 23% of the total variance. Bands at 1271 cm^{-1}, 1419 cm^{-1}, 1450 $cm^{-1}$and 1720 cm^{-1}, show high positive loadings. These bands are indicative of lignin, with the exception of that at 1720 cm^{-1}, which represents carboxylic groups. $\delta^{13}C$ shows a moderate negative loading. The fractionation of commonalities (Table SI3) suggests that lignin and carboxylic acids are related, although with different magnitude, to both PC1o and PC2o. This implies that there are at least two factors affecting lignin and carboxylic groups in the peat. Decomposition (as outlined above) is one of the factors affecting the distribution of lignin, but a more complex behaviour (in addition to that of depth enrichment) is indicated by PC2o. Factor scores (Fig. 7) show an alternating distribution between positive and negative values, except for the section between 20-14 cm, where they are around zero. Factor scores are positive (i.e. the lignin content is higher) at 33-29 cm, 22-21 cm and 8-5 cm.

The third principal component (PC3o) accounts for 15% of the total variance. Bands of polysaccharides (1070 cm^{-1} and 1030 cm^{-1}) show high positive loadings (Table SI3) while the band at 3051 cm^{-1} (aromatics) shows moderate negative loadings. Peat decomposition leads to an enrichment in recalcitrant compounds (e.g. aliphatics and aromatics) of the organic matter as reflected by PC1o. PC3o seems to denote reduced decomposition of labile compounds (i.e. polysaccharides). Changes in vegetation type may also have affected the character of organic matter comprising the peat, and consequently the distribution of polysaccharides. PC3o factor scores indicate heavy enrichment in polysaccharides between 21 and18 cm (Fig. 7). Smaller increases are found at 35-32 cm, 30.5 cm, 27-25 cm and 12-5 cm.

Discussion

Mineral content of the peat: a link with induced soil erosion

Although it is possible that some of the lithogenic component might be sourced over long distances, our results suggest that local dusts dominate the signal of major and trace lithogenic elements. The geochemical composition of the peat, and the association of chemical elements in PC1e, is consistent with the character of the local geology (which is composed mostly of granites and gneises). Furthermore, the main chemical ratios (Ti/Zr, K/Rb; Fig. 8), which are commonly applied to determine changes in lithogenic sources, are near-constant through the profile, just increasing after the 1980's, indicating a quite constant composition of the mineral matter until last decades. Increased soil instability linked to human activity may be evidenced at Sandhavn by the enhanced mineral content of the peat and a suite of lithogenic elements (indicated by PC1e; Fig. 8). This would seem to reflect aeolian inputs which are highest (albeit steadily declining in concentration) through a period which is coincident with the end of the Norse settlement at the site. A caveat is required, however, as the peat geochemical record from Sandhavn commences during the settlement phase, which means there are no baseline environmental measurements available prior to the arrival of people. Moreover, this enrichment is registered immediately from above the contact with the mineral (sand) base, where sediment mixing might account for a part of the variation. Pollen and coprophilous fungi evidence intimate that land-use-induced erosion may have still played a role in the enrichment of mineral matter during the earliest stage of peat development.The decline in the mineral content of the peat (PC1e; Figs. 4 and 5) to lower values after ~AD 1400 coincides with reduced frequencies of fungal spores and Poaceae pollen (Figs. 3 and 8). This pattern reflects the Norse abandonment at Sandhavn (Golding et al., 2011), occurring at approximately the same time as many other farms across the Eastern Settlement were also falling into disuse (Edwards et al., 2011; Ledger et al., 2014). A number of other studies from the Eastern Settlement of Greenland have produced convincing evidence for an increase in soil erosion following Norse *landnám* on the basis of rising mineral content in peat or lake sediments (e.g. Sandgren and Fredskild, 1991; Fredskild, 1992; Edwards et al., 2008; Massa et al., 2012). At Sandhavn, the concentrations of lithogenic elements remain low throughout the LIA and show little variation until ~AD 1900.

Massa et al. (2012) noted that Ti remained elevated (14% above pre-*landnám* baseline concentrations) at Lake Igaliku for more than four centuries after the farmstead at *Garðar* (modern Igaliku) was abandoned. They suggest that Norse occupation may have altered the physicochemistry of the catchment soils, or that a change in climate at the onset of the LIA led to enhanced aeolian deposition (and hence Ti influx) to the lake because of increased wind speeds and storminess that were characteristic features of the climate after ~AD 1425 (cf. Dugmore et al., 2007). For the period available for examination, this pattern does not seem to be repeated at Sandhavn. The lack of a clear increase in lithogenics during the LIA at Sandhavn suggests that soil disturbance and exposure to wind erosion may have been spatially limited. Changes in vegetation took place immediately after the abandonment of the farm (zone SAN-3; Fig. 3). The increase in Cyperaceae pollen abundance reflects the likely spread of steppe-like vegetation communities (cf. Böcher et al., 1968) across disused home-field areas and the local extension of mire communities in response to cooler and possibly damper conditions. This change in vegetation cover, following the removal of direct human influence from the landscape, may have restricted the availability of erodible material.

The next simultaneous increase in most lithogenic elements (PC1e; Fig. 8) occurred in the early 20th century (~AD 1900-1940) and is broadly synchronous with the return of sheep farming to southern Greenland (Jacobsen, 1987; Fredskild, 1988).

A number of studies have shown the benefits of integrating chemical data with more traditional proxies such as pollen to reconstruct soil erosion and land use changes (e.g. Hölzer and Hölzer, 1998; Lomas-Clarke and Barber, 2004; Martínez Cortizas et al., 2005; Silva-Sánchez et al., 2014). Most of these studies were conducted in areas of relatively intense human activity and show that both proxies – the pollen and the geochemical record – responded to changing land use and were in good agreement with regional archaeological records. The current study also demonstrates the sensitivity of geochemical proxies to environmental change in a more remote landscape. In such circumstances, human activity was on a relatively reduced scale compared with the significant landscape transformations that have taken place in temperate environments (western Europe, for example). In spite of this, the data from Sandhavn not only clearly discriminated between periods of human activity and abandonment, but also recorded human impacts that appear to closely match the known historical record.

Peat growth, carbon accumulation, organic matter decomposition and bromine: links with climate change

Changes in the rate of peat accumulation at Sandhavn (Fig. 9) apparently reflect broad-scale patterns in the prevailing climate (Barlow, 1994; Dahl-Jensen et al., 1998; Box, 2002), with the cooler temperatures of the LIA coinciding with, and seemingly accounting for, the period of extremely slow peat growth witnessed from ~AD 1400-1800, and generally rising temperatures after this leading to the more rapid build-up of peat over the last ~100-150 cal yr. Autocompaction of the peat, whereby deeper layers become compressed relative to the surface, is likely to have acted to reinforce this pattern. Although controls over the rate of peat accumulation seem clear, the factors leading to paludification are less obvious.

Organic matter began to accumulate in the basin at Sandhavn from ~AD 1240, suggesting an environmental threshold (climatic or otherwise) had been exceeded. On the basis of the synthesis of various climate proxies, Ogilvie and Jónsson (2001) support the notion of it being slightly colder across the North Atlantic region from ~AD 1250-1900 in comparison to the 20th century. A chironomid record from a lake near Igaliku in southern Greenland also suggests a shift towards cooler conditions from ~AD 1280-1460 (Millet et al. 2014), a timeframe encapsulating the 14th century, the period of lowest temperature in central Greenland during the last 700 years (Barlow et al. 1997). Further evidence to suggest that the regional climate was beginning to deteriorate from the mid-13th century onwards can perhaps be seen in the archaeological record from the Eastern Settlement. There appears to have been a shift in Norse subsistence away from farming towards a marine-based diet (Arneborg et al., 1999; Dugmore et al., 2012), although the timing for this is not precise and there are many caveats (Arneborg et al., 2012). There are also indications of abandonment at some Norse farms (Ledger et al., 2014) but an intensification at others (Ledger et al., 2013). Yet all the above should be viewed against the baseline offered by Kaufman et al. (2009), in which a synthesis of terrestrial climate proxies (lakes sediments, glacier ice and tree rings) for latitudes above 60º N demonstrates a long-term cooling trend in the Arctic spanning the last two millennia, albeit punctuated by centennial-scale periods of greater relative warmth (e.g. AD 900-1060) and more severe cold (e.g. AD 1600-1860).

The very slow rate of peat growth observed at Sandhavn during the mid-second millennium is mirrored at some other sites across the region. For example, radiocarbon dates from the fen near Tasiusaq (Shotyk et al., 2003), approximately 100 km northwest of Sandhavn, demonstrate very rapid accumulation (~0.3 cm yr^{-1}) for the period after ~AD 1950 but extremely slow peat growth (~0.015 cm yr^{-1}) during the preceding ~950 cal yr. At the nearby site of Qinngua, a hiatus spanning ~AD 1400-1900 has been recorded in a peat profile (Schofield et al., 2010). This probably represents a period of zero peat growth, although a hiatus resulting from peat cutting should not be discounted. The cutting of peat may have played a part in creating gaps within late Holocene environmental archives drawn from mires across the region (cf. Schofield et al., 2008), although the importance of its role over any climatically-forced slowdown in peat accumulation due to lowered temperatures is difficult to ascertain. It does seem that high-resolution peat archives covering the mid-second millennium AD may be rare in this region, although some exceptions can be found (cf. Ledger et al., 2014).

Associated with extremely slow peat growth at Sandhavn is an increase in *Hippuris vulgaris* pollen (Figs. 3 and 9), which is probably indicative of shallow open water (pools) at the bog surface, at least seasonally. Flooding during milder seasons due to increased ice/snow melt, combined with low spring-summer evaporation rates from lower temperatures between ~AD 1400 and1800, may have increased the habitat suitable for this taxon. Bromine concentrations in the Sandhavn record also seem to be strongly affected by climate as concentrations remain below 150 $\mu g g^{-1}$ until ~AD 1865, although values do begin to increase gradually after ~AD 1780 (Fig. 9). Research at Qinngua (Schofield et al., 2010) suggested a possible link between variation in the concentrations of halogens and storminess as rising amounts of Br and Cl in the peat appeared to be correlated with increased levels of Na+ (sea salt sodium) in the GISP2 ice core (a hiatus in the peat profile at Qinngua, spanning the period ∼AD 1380–1950, hindered attempts to directly compare the two records). No such link was found at Sandhavn. The incorporation of bromine into peat is a biological oxygen-dependent enzymatic processes (Myneni, 2002; Biester et al., 2004; Leri and Myneni, 2012) and it is possible that cooling would have slowed down the biological activity of micro-organisms involved in the process. Flooding of the mire during milder seasons, most favourable for biological activity, could have also limited the incorporation of Br to the peat, a process which in oceanic areas is mostly dependent on oxygen availability rather than atmospheric deposition (Martínez-Cortizas et al., 2007). Organo-bromine compounds can be dehalogenated under reducing conditions (Mohn and Tiedje, 1992; Monserrate and Häggblom, 1997; Bedard and Dort, 1998), but at Sandhavn anoxic environmental conditions were seemingly unsuitable for halogenation of organic compounds, and so this appears less likely to explain the patterns in Br as depicted in the data presented here.

Some of the variations in the proxies analyzed might have also been affected by solar forcing (Fig. 9), a factor that is considered to be a major influence on LIA cooling (Wigley and Kelly, 1990; Lean et al., 1995; Mann et al., 1998; van Geel et al., 1999; Bond et al., 2001). Increased PC3o values at ~AD 1480 and ~AD 1645-1740 broadly coincide with the Spörer and Maunder minima. It is necessary to be circumspect about this surmise given the dating and sample resolution constraints, but if correct, this could indicate that enrichment in polyssacharides (i.e. low degradation of labile organic compounds) might be associated with periods of decreased solar activity. The Br record, which shows systematic low concentrations during the whole LIA, has very low values at ~AD 1480 and ~AD 1645-1740, suggesting that cooler conditions during solar minima may also have strongly limited halogenation in the bog. These patterns indicate a possible link between sunspot minima and reduced microbial activity in the Sandhavn bog. Declines in PC1o also might have occured during solar minima (Fig. 9), indicating that cooling may have limited the decomposition of organic matter during such intervals. Clearly the data coupling proxy records with minima in solar activity during the last millennium at Sandhavn are only tentative, but such associations have been reported from other studies. Mauquoy et al. (2007) identified increases in *Sphagnum tenellum* and *S. cuspidatum* (indicative of cool, moist climatic conditions) in northwestern European bogs that appear linked to LIA solar minima. In their study of Lake Lehmilampi, Finland, Haltia-Hovi et al. (2007) noted a relationship between varve thickness and solar forcing, although the physical mechanism linking these is still to be established. Blackford and Chambers (1995b) also found an apparent correspondence between peat humification records and solar oscillations in Irish blanket peat.

Beginning ~AD 1870, a major change in vegetation occurred at Sandhavn with *Empetrum nigrum* oceanic heath replacing Cyperaceae-dominated steppe communities (Figs.3 and 9). This, plus a more rapid build-up of peat and PCAR over the last ~100-150 cal yr BP, provides evidence of generally rising temperatures following the end of the LIA. At the same time, PC3o variations indicate enrichment of the peat with polysaccharides; this is despite warmer climatic conditions being more conducive to the decay of organic matter (i.e. polysaccharide degradation). The process appears heavily influenced by peat composition, particularly the increased abundance of *Empetrum nigrum* remains which are more resistant to decomposition than the sedge-dominated vegetation that it replaced. The next simultaneous shift in the organic matter indicators (PC1o and Br), peat growth and PCAR, occurred during the last 50 years and seems to reflect the presence of less decomposed peat, typical of the superficial layers of an active mire.

Atmospheric deposition of lead: links with anthropogenic emissions and possible sources

Murozumi et al. (1969) first demonstrated that a record of lead pollution, dating back to the mid-18thcentury and coinciding with European Pb production, was recorded in Greenland ice (at Camp Century, Fig.1). Their findings attest to the long-range transport of pollutants to Greenland from sources in industrialized countries. Subsequent research has extended the onset of Pb pollution, as recorded in Greenland ice, to the early historic period. Studies by Hong et al. (1994) and Rosman et al. (1997) show that Greek and Roman lead and silver mining, and smelting, polluted the middle troposphere of the Northern Hemisphere around two millennia ago. In contrast to the investigations on ice cores, studies of lead contamination using minerotrophic peatlands in southern Greenland (Shotyk et al., 2003; Schofield et al., 2010) have up until this point failed to reveal any significant enrichment in Pb, although Shotyk et al. (2003) suggest that a decrease in the $^{206}Pb/^{207}Pb$ ratio noted in minerotrophic peat from Tasiusaq relates to lead pollution originating from the USA in the 20th century.

The lead record from Sandhavn covers a period of around 700 years, extending back from the present to ~AD 1300 (Fig. 10). Lead concentrations remain below 2.5 $\mu g g^{-1}$ throughout most of the sequence and then progressively increase after ~AD 1845. Maximum Pb levels (16.4-19.6 $\mu g g^{-1}$) were reached in the 1960s and 1970s, while later decades are characterized by a progressive decrease. Low loadings of Pb on PC1e indicate that Pb does not share a significant common variation with the lithogenic component along the sequence, intimating that in the majority of the record, Pb appears to be solely the result of atmospheric pollution. In order to normalise for any possible contribution of geogenic Pb to the bog at Sandhavn, we have calculated the Pb/Ti ratio (Fig. 10). Notwithstanding some minor differences, particularly between ~AD 1900 and AD 1940 where some of the Pb seems to be linked with increased soil erosion caused by the return of sheep farming to the region in the early 20th century, the pattern for Pb/Ti is almost the same as that of Pb concentrations: values above the baseline occur only after ~AD 1845, and from there they show a progressive increase which is more pronounced after ~AD 1940, peaking at the end of the AD 1970s, after which values steadily decrease. Recent research on atmospheric lead fluxes modelling in southern Greenland has estimated a maximum value for lead fluxes during the 1960s of 2400 ± 330 µg m^{-2} yr^{-1} (Massa et al., 2015).

The onset of lead pollution in the Sandhavn monolith occurs later than in records from the Greenland ice core (Murozumi et al., 1969) and lake sediments (Bindler et al., 2001b), where the highest levels of Pb pollution are recorded from ~AD 1750-1800 onwards. The pattern at Sandhavn is thus in closer agreement with the chronology of events from North America (i.e. the onset of the American industrial revolution) rather than that from Europe. Increased Pb deposition just after ~AD 1850 has been found in several North American records including the Great Lakes region (Graney et al., (1995), Maine (Big Heath and Sargent Mountain Pond), and Massachusetts (Plow Shop and Grove ponds), northeast USA (Norton et al., 1997, 2004), Hudson Bay (Imitavik and Far Lakes; Outridge et al., 2002), southern Quebec (Lake Tantaré; Gallon et al., (2005) and Point d'Escuminac, Eastern Canada (Kylander et al., 2009). High levels of Pb pollution at Sandhavn during the 20th century are also in good agreement with the Greenland ice core-based reconstructions made by Murozumi et al. (1969), who ascribed Pb pollution to lead smelting (for the period prior to ~AD 1940) and to the massive use of lead alkyls in gasoline (after ~AD 1940). Given that the dating uncertainty of sediment/peat records is often high for the 19th century, caution obviously needs to be exercised, and some comparable lead records also exist in Europe (e.g. Weiss et al, 1999).

A North American source for the lead is also indirectly supported by the presence of *Ambrosia*-type (ragweed) in the Sandhavn pollen record (Fig. 3). After ~AD 1885, *Ambrosia*-type pollen is consistently present at trace values (typically <1%). *Ambrosia* is a common weed of cultivated land and a prolific pollen producer. The plant is not native to Greenland (Böcher et al., 1968) and, although morphologically-similar pollen is produced by plants present throughout central Europe from the Iron Age forwards, the most likely source for this pollen type is North America. Studies from eastern-central North America (Bassett and Terasmae, 1962; Gordon, 1966; Brugam, 1978; McAndrews, 1988; McAndrews and Boyko-Diakonow, 1989; Baker et al., 1993; Ireland et al. 2014) have demonstrated a rise in *Ambrosia* pollen coinciding with the arrival and expansion of European settlers. It seems that the introduction of intensive agricultural practices linked with forest clearance promoted the increase in *Ambrosia*-type pollen. This pattern has been dated to the 19th century, with only one paper (Brugam, 1978) suggesting an earlier date. The timing of the '*Ambrosia* rise' in North America closely matches the presence of *Ambrosia*-type pollen in the Sandhavn monolith. Bassett and Terasmae (1962) showed that ragweed pollen can be transported through the atmosphere at least 600 km from any known source. Observations of long-distance pollen transport to southern Greenland similarly indicate that northeastern North American source areas are typical (Rousseau, 2003; Rousseau et al., 2006; Jessen et al. 2011). A source outside North America seems improbable; for example, *Ambrosia* is a recent introduction to Europe, first appearing after ~AD 1920 (Comtois, 1998) and spreading after the 1980s (Couturier, 1992; Dechamp and Dechamp, 1992; Thibaudon, 1992).

Cryptotephras have been recorded in peat profiles located adjacent to Norse sites in the Eastern Settlement and further demonstrate the potential for atmospheric particulates to reach southern Greenland from North America. Blockley et al. (2015) have identified tephra shards at three sites in the Eastern Settlement (Herjolfsnes, Hvalsey and Igaliku).These have geochemical signatures that are compatible with volcanic centres in the Aleutian Islands and Cascade Range, with the Augustine and Mount St Helen volcanoes being two of the likely sources.

Although a major North American source for the lead at Sandhavn seems most probable and is consistent with results from other studies, some qualifications remain. Rosman et al. (1993, 1994) analysed the Pb isotopic composition of Greenland snow collected at Summit to derive the relative lead contributions from the USA, Canada, and Eurasia between ~AD 1967 and 1989. They concluded that the United States was a significant source of lead during the 1970s (up to 67% of the measured total) before it declined considerably in relative importance (to 25% in the late 1980s), mirroring reductions in the use of leaded petrol, resulting in the Eurasian and Canadian contribution to the Pb signal becoming predominant. Seasonal investigations on the isotopic composition of Pb on snow collected at Dye 3 in southern Greenland also suggest that most of the Pb pollution signal was primarily sourced from leaded gasoline used in North America, but also that the same ice sheet surface received lead from elsewhere during certain parts of the year: Pb in autumn and winter snow originated in North America, while that in spring to mid-summer snow was from Eurasia (Rosman et al., 1998). In contrast, a recent isotopic analysis of west Greenland (near Kangerlussuaq) lake sediments (Bindler et al., 2001a, 2001b) suggests that the lead record at this location was derived from west European and Russian sources. The relative location/latitude of the sites (Fig. 1a) possibly accounts for the differences in lead sourcing. For example, studies have shown that high Arctic sites have largely Russian sources with pollutants transported over the North Pole, whereas lakes in southwest Greenland are considered to have a significant input from west European sources (Bindler et al., 2001b). The lead isotopic signature from aerosol and snowpack samples from Devon Island and from the Canadian High Arctic (Sturges and Barrie, 1989; Shotyk et al., 2005), and from a lake in Pearyland (Lake G07-10), north Greenland, favour a Eurasian source (Michelutti et al., 2009). The origin of lead deposited in Lake CF8 near Nunavut, Baffin Island, could not be determined unequivocally, but investigators suggested an American source to be unlikely (ibid.). In contrast, the evidence from Sandhavn supports atmospheric transfer from North America. Lead isotopic analysis is in progress to ascertain more precisely the sources for lead in the Sandhavn record, and clearly more research is required if a full understanding of the spatial and temporal variation in lead isotopic signatures across Greenland is to be achieved.

Conclusions

The Norse Age section of the Sandhavn peat profile may be compromised in its basal sand/peat interface segment, but variations in the mineral content of the overlying peat may be partly related to local human activity during the later stages of Norse occupation. A subsequent increase in the lithogenic content during the early 20thcentury may reflect soil erosion resulting from the return of (modern) sheep farming to southern Greenland.

Low concentrations of Br are recorded during the LIA – a climatic downturn which is also reflected in extremely low peat accumulation rates at Sandhavn from ~AD 1400-1800. Cold conditions, possibly combined with flooding of the mire surface during milder seasons, which would have created reducing conditions, appear to have caused a slowdown in halogenation that affected Br incorporation into the peat. Low Br concentrations and changes in levels of polysaccharides are possibly in phase with sunspot cycles (Spörer and Maunder minima), though confirmation of a direct link between these parameters and solar activity will require further testing. The local expansion of *Empetrum nigrum* oceanic heath at the end of the 19th century seems to have caused an attendant enrichment in polysaccharides within the peat, suggesting that vegetation type was a major influence over peat organic matter composition at this time.

The site at Sandhavn has proven more useful for reconstructing a record of lead pollution in southern Greenland than the minerotrophic fen peats that have previously been investigated for this purpose. At Sandhavn, atmospheric Pb pollution is recorded after ~AD 1845, with peak concentrations occurring during the AD 1970s. There is indirect evidence of a predominantly North American origin for this signal. Isotopic analyses will be required before the sources for the lead deposited around the southern tip of Greenland can be identified with greater certainty.

Acknowledgements

This research was made possible through funding provided by the Leverhulme Trust, the Spanish Ministry of Science and Innovation (Project CGL2010-20672) and Xunta de Galicia (grants R2014/001 and GPC2014/009). N Silva-Sánchez is currently supported by a FPU pre-doctoral grant (AP2010-3264) funded by the Spanish Government. Kirsty Golding, Andy McMullen, and Ian Simpson are thanked for their assistance with fieldwork. Alison Sandison produced the maps. Pete Langdon and two anonymous referees are thanked for comments that helped to improve the paper.

References

Alewell, C., Giesler, R., Klaminder, J., Leifeld, J., Rollog, M., 2011. Stable carbon isotopes as indicators for environmental change in palsa peats. Biogeosciences 8, 1769–1778.

Allaart, J.H., 1976. Ketilidian mobile belt in south Greenland, in: Escher, A., Stuart-Watt, W. (Eds.), Geology of Greenland. Geological Survey of Greenland, Copenhagen, pp. 120–151.

Appleby, P., 2001. Chronostratigraphic techniques in recent sediments, in: Last, W., Smol, J. (Eds.), Tracking Environmental Change Using Lake Sediments. Volume 1: Basin Analysis, Coring and Chronological Techniques. Kluwer, Dordrecht, pp. 171–204.

Appleby, P., Nolan, P., Oldfield, F., Richardson, N., Higgitt, S., 1988. 210Pb dating of lake sediments and ombrotrophic peats by gamma essay. Science of the Total Environment 69, 157–177.

Appleby, P., Oldfield, F., 1978. The calculation of Pb-210 dates assuming a constant rate of supply of unsupported Pb-210 to the sediment. Catena 5, 1–8.

Arneborg, J., 2006. Saga trails – Brattahlið, Garðar, Hvalsey Fjord’s Church and Herjolfsnes: four chieftain’s farmsteads in the Norse settlement of Greenland. A visitor’s guidebook. National Museum of Denmark, Nanortalik Museum, Narsaq Museum and Qaqortoq Museum.

Arneborg, J., Heinemeier, N., Lynnerup, N., Nielsen, H.L., Rud, N., Sveinbjornsdottir, A.E., 1999. Change of diet of the Greenland Vikings determined from stable carbon isotope analysis and C-14 dating of their bones. Radiocarbon 14, 157–168.

Arneborg, J., Lynnerup, N., Heinemeier, J. 2012. Human diet and subsistence patterns in Norse Greenland AD c. 980-AD c.1450: Archaeological interpretations. Journal of the North Atlantic, Special Volume 3, 119-133.

Baker, R.G., Schwert, D.P., Bettis, E.A., Chumbley, C.A., 1993. Impact of Euro-American settlement on a riparian landscape in northeast Iowa, midwestem USA: an integrated approach based on historical evidence, floodplain sediments, fossil pollen, plant macrofossils and insects. The Holocene 3, 314–323.

Barlow, L.K., 1994. Evaluation of seasonal to decadal scale deuterium and deuterium excess signals, GISP2 ice core, Summit, Greenland, A.D. 1270-1985. PhD thesis. University of Colorado.

Bassett, I.J., Terasmae, J., 1962. Radweeds, Ambrosia species, in Canada and their history in postglacial time. Canadian Journal of Botany 40, 141–150.

Bedard, D.L., Dort, H.M. Van, 1998. Complete reductive dehalogenation of brominated biphenyls by anaerobic microorganisms in sediment. Applied and Environmental Microbiology 64, 940–947.

Benner, R., Fogel, M.L., Sprague, E.K., Hodson, R.E., 1987. Depletion of 13C in lignin and its implications for stable carbon isotope studies. Nature 329, 708–710.

Biester, H., Keppler, F., Putschew, A., Martinez-Cortizas, A., Petri, M., 2004. Halogen retention, organohalogens, and the role of organic matter decomposition on halogen enrichment in two Chilean peat bogs. Environmental Science & Technology 38, 1984–1991.

Biester, H., Knorr, K.-H., Schellekens, J., Basler, A., Hermanns, Y.-M., 2013. Comparison of different methods to determine the degree of peat decomposition in peat bogs. Biogeosciences Discussions 10, 17351–17395.

Bindler, R., Anderson, N.J., Renberg, I., Malmquist, C., 2001a. Palaeolimnological investigation of atmospheric pollution in the Søndre Strømfjord region , southern West Greenland: accumulation rates and spatial patterns. Geology of Greenland Survey Bulletin 53, 48–53.

Bindler, R., Renberg, I., John Anderson, N., Appleby, P.G., Emteryd, O., Boyle, J., 2001b. Pb isotope ratios of lake sediments in West Greenland: inferences on pollution sources. Atmospheric Environment 35, 4675–4685.

Blaauw, M., 2010. Methods and code for “classical” age-modelling of radiocarbon sequences. Quaternary Geochronology 5, 512–518.

Blackford, J., Chambers, F., 1993. Determining the degree of peat decomposition for peat-based palaeoclimatic studies. International Peat Journal 5, 7–24.

Blackford, J.J., Chambers, F.M., 1995. Proxy climate record for the last 1000 years from Irish blanket peat and a possible link to solar variability. Earth and Planetary Science Letters 133, 145–150.

Blockley, S.P.E., Edwards, K.J., Schofield, J.E., Pyne-O’Donnell, S.D.F., Matthews, I.P., Jensen, B.J.L., Cook, G.T., 2015. First evidence of cryptotephra in palaeoenvironmental records associated with Norse occupation sites in Greenland. Quaternary Geochronology 27, 145-157.

Böcher, T.W., Holmer, K., Jakobsen, K., 1968. The flora of Greenland. Haase & Son, Copenhagen.

Bond, G., Kromer, B., Beer, J., Muscheler, R., Evans, M.N., Showers, W., Hoffmann, S., Lotti-Bond, R., Hajdas, I., Bonani, G., 2001. Persistent solar influence on North Atlantic climate during the Holocene. Science 294, 2130–6.

Borgmark, A., 2005. Holocene climate variability and periodicities in south-central Sweden, as interpreted from peat humification analysis. The Holocene 15, 387–395.

Borgmark, A., Schoning, K., 2006. A comparative study of peat proxies from two eastern central Swedish bogs and their relation to meteorological data. Journal of Quaternary Science 21, 109–114.

Box, J., 2002. Study of Greenland instrument temperature records: 1873-2001. International Journal of Climatology 22, 1829–1847.

Broder, T., Blodau, C., Biester, H., Knorr, K.H., 2012. Peat decomposition records in three pristine ombrotrophic bogs in southern Patagonia. Biogeosciences 9, 1479–1491.

Brugam, R.B., 1978. Pollen indicators of land-use change in southern Connecticut. Quaternary Research 9, 349–362.

Chambers, F.M., Booth, R.K., De Vleeschouwer, F. Lamentowicz, M., Le Roux, G., Mauquoy, D., Nichols, J.E., van Geel, B., 2012. Development and refinement of proxy-climate indicators from peats. Quaternary International 268, 21–33.

Cheburkin, A.K., Shotyk, W., 1996. An energy dispersive miniprobe multielement analyzer (EMMA) for direct analysis of Pb and other trace elements in peat. Journal of Analytical Chemistry 354, 688–691.

Chesworth, W., Martínez Cortizas, A., García-Rodeja, E., 2006. The redox-pH approach to the geochemistry of the Earth´s land surface, with application to peatlands, in: Martini, I.P., Martínez Cortizas, A., Chesworth, W. (Eds.), Peatlands: Evolution and Records of Environmental and Climate Changes. Amsterdam, pp. 175–196.

Cocozza, C., D’Orazio, V., Miano, T.M., Shotyk, W., 2003. Characterization of solid and aqueous phases of a peat bog profile using molecular fluorescence spectroscopy, ESR and FT-IR, and comparison with physical properties. Organic Geochemistry 34, 49–60.

Comtois, P., 1998. Ragweed (Ambrosia sp.): the phoenix of allergophytes, in: Spieksma, F.T.M. (Ed.), Ragweed in Europe. 6th Int. Congr. Aerobiol. Satellite Symp. Proc. Horsholm DK, Perugia, pp. 3–5.

Couturier, P., 1992. Dispersion of ragweed in the Drome-Ardeche region. Allergie et immunologie 24, 27–31.

Dahl-Jensen, D., Mosegaard, K., Gundestrup, N., Clow, G.G.D., Johnsen, S.S.J., Hansen, A.A.W., Balling, N., Clow, D.G., 1998. Past temperatures directly from the Greenland ice sheet. Science 282, 268–271.

Dechamp, C., Dechamp, J., 1992. Ragweed pollen counts (P. Cour collection apparatus) from Lyon-Bron from 1982 to 1989: results, informing the public. Allergie et immunologie 24, 17 – 21.

Dugmore, A.J., Borthwick, D.M., Church, M.J., Dawson, A., Edwards, K.J., Keller, C., Mayewski, P., McGovern, T.H., Mairs, K-A. Sveinbjarnardóttir, G., 2007. The role of climate in settlement and landscape change in the North Atlantic islands: an assessment of cumulative deviations in high-resolution proxy records. Human Ecology 35, 169–178.

Dugmore, A.J., Church, M.J., Buckland, P.C., Edwards, K.J., Lawson, I., McGovern, T.H., Panagiotakopulu, E., Simpson, I. a., Skidmore, P., Sveinbjarnardóttir, G., 2005. The Norse landnám on the North Atlantic islands: an environmental impact assessment. Polar Record 41, 21–37.

Dugmore, A.J., McGovern, T.H., Vésteinsson, O., Arneborg, J., Streeter, R., Keller, C. 2012. Cultural adaptation, compounding vulnerabilities and conjunctures in Norse Greenland. Proceedings of the National Academy of Sciences 109, 3658-3663.

Edwards, K.J., Schofield, J.E., Kirby, J.R., Cook, G.T., 2011. Problematic but promising ponds? Palaeoenviromental evidence from the Norse Eastern Settlement of Greenland. Journal of Quaternary Science 26, 854-865.

Edwards, K.J., Schofield, J.E., Mauquoy, D., 2008. High resolution paleoenvironmental and chronological investigations of Norse landnám at Tasiusaq, Eastern Settlement, Greenland. Quaternary Research 69, 1–15.

Eriksson, L., Johansson, E., Kettaneh-Wold, N., Wold, S., 1999. Introduction to multi- and megavariate data analysis using projection methods (PCA & PLS). Umetrics AB, Umea.

Feilberg, J., 1984. A phytogeographical study of south Greenland. Bioscience 15, 1–70.

Fitzhugh, W.W., Ward, E.I., 2000. Vikings: the North Atlantic saga. Smithsonian Institution Press, Washington.

Fredskild, B., 1988. Agriculture in a Marginal area- South Greenland from the Norse Landnam (985 A.D.) to the present (1985 A.D.), in: Birks, H.H., Birks, H.J.B., Kaland, P.E., Moe, D. (Eds.), The Cultural Landscape—Past, Present and Future. Cambridge University Press, Cambridge, pp. 381–393.

Fredskild, B., 1992. Erosion and vegetational changes in South Greenland caused by agriculture. Geografisk Tidsskrift 92, 14–21.

Gallon, C., Tessier, A., Gobeil, C., Beaudin, L., 2005. Sources and chronology of atmospheric lead deposition to a Canadian Shield lake: inferences from Pb isotopes and PAH profiles. Geochmica et Cosmochimica Acta 69, 3199–3210.

Golding, K.A., Simpson, I.A., Schofield, J.E., Edwards, K.J., 2011. Norse-Inuit interaction and landscape change in southern Greenland? A geochronological, Pedological, and Palynological investigation. Geoarchaeology: an international journal 26, 315–345.

Golding, K.A., Simpson, I.A., Wilson, C.A., Lowe, E.C., Schofield, J.E., Edwards, K.J., 2014. Europeanization of sub-Arctic environments: perspectives from Norse Greenland's outer fjords. Human Ecology.

González, J.A., González-Vila, F.J., Almendros, G., Zancada, M.C.C., Polvillo, O., Martín, F., 2003. Preferential accumulation of selectively preserved biomacromolecules in the humus fractions from a peat deposit as seen by analytical pyrolysis and spectroscopic techniques. Journal of Analytical and Applied Pyrolysis 68-69, 287–298.

Gordon, J.G., 1966. Forest History of Ohio . I , Radiocarbon Dates and Pollen Stratigraphy of Silver Lake , Logan County , Ohio. The Ohio Journal of Science 66, 387–400.

Graney, J., Halliday, A., Keeler, G., Nriagu, J., Robbins, J., Norton, S., 1995. Isotopic record of lead pollution in lake sediments from the northeastern United States. Geochimica et Cosmochimica Acta 59, 1715–1728.

Grimm, E.C., 1992. Tilia. Version 2.0.

Grimm, E.C., 2004. TGView.

Grove, J., 1988. The Little Ice Age. Methuen, London.

Grube, M., Lin, J.G., Lee, P.H., Kokorevicha, S., 2006. Evaluation of sewage sludge-based compost by FT-IR spectroscopy. Geoderma 130, 324–333.

Guo, Y., Bustin, R.M., 1998. FTIR spectroscopy and reflectance of modern charcoals and fungal decayed woods: implications for studies of inertinite in coals. International Journal of Coal Geology 37, 29–53.

Haberhauer, G., Rafferty, B., Strebl, F., Gerzabek, M.H., 1998. Comparison of the composition of forest soil litter derived from three different sites at various decompositional stages using FTIR spectroscopy. Geoderma 83, 331–342.

Haltia-Hovi, E., Saarinen, T., Kukkonen, M., 2007. A 2000-year record of solar forcing on varved lake sediment in eastern Finland. Quaternary Science Reviews 26, 678–689.

Högber, P., 1997. 15N natural abundance in soil-plant systems. New Phytologist 137, 179–203.

Hölzer, A., 1998. Silicon and titanium in peat profiles as indicators of human impact. The Holocene 8, 685–696.

Hong, S., Candelone, J.J.-P., Patterson, C.C., Boutron, C.F., Civilizations, R., 1994. Greenland Ice Evidence of Hemispheric Lead Pollution Two Millennia Ago by Greek and Roman Civilizations. Science 265, 1841–1843.

Ibarra, J. V, Muñoz, E., Moliner, R., 1996. FTIR study of the evolution of coal structure during the coalification process. Organic Geochemistry 24, 725–735.

Ireland, A.W., Clifford, M.J., Booth, R.K., 2014. Widespread dust deposition on North American peatlands coincident with European land-clearance. Vegetation History & Archaeobotany 23, 693-700.

Jacobsen, N.K., 1987. Studies on soils and potential for soil erosion in the sheep farming area of South Greenland. Arctic and Alpine Research 19, 498–507.

Jessen, C.A., Solignac, S., Nørgaard-Pedersen, N., Mikkelson, N., Kuijpers, A., Siedenkrantz, M-S., 2011. Exotic pollen as an indicator of variable atmospheric circulation over the Labrador Sea region during the mid to late Holocene. Journal of Quaternary Science 26, 286-296.

Kaufman, D.S., Schneider, D.P., McKay, N.P., Ammann, C.M., Bradley, R.S., Briffa, K.R., Miller, G.H., Otto-Bliesner, B.L., Overpeck, J.T., Vinther, B.M., Arctic Lakes 2k project members, 2009. Recent warming reverses long-term Arctic cooling. Science 325, 1236–1239. doi:10.1126/science.1173983

Krogh, K.J., 1967. Viking Greenland. National Museum, Copenhagen.

Kuhry, P., Vitt, D.H., 1996. Fossil carbon/nitrogen ratios as a measure of peat decomposition. Ecology 77, 271–275.

Kylander, M.E., Weiss, D.J., Kober, B., 2009. Two high resolution terrestrial records of atmospheric Pb deposition from New Brunswick, Canada, and Loch Laxford, Scotland. The Science of the Total Environment 407, 1644–57.

Lean, J., Beer, J., Bradley, R., 1995. Reconstruction of solar irradiance since 1610: Implications for climate change. Geophysical Research Letters 22, 3195–3198.

Ledger, P.M., Edwards, K.J., Schofield, J.E., 2013. Shieling activity in the Norse Eastern Settlement: palaeoenvironment of the 'Mountain Farm', Vatnahverfi, Greenland. The Holocene 23, 810-822.

Ledger, P.M., Edwards, K.J., Schofield, J.E., 2014. Vatnahverfi: a green and pleasant land? Palaeoecological reconstructions of environmental and land-use change. Journal of the North Atlantic, Special Volume 6, 29-46.

Leri, A.C., Myneni, S.C.B., 2012. Natural organobromine in terrestrial ecosystems. Geochimica et Cosmochimica Acta 77, 1–10.

Létolle, R., 1980. Nitrogen-15 in the natural environment, in: Fritz, P., Fontes, J.C. (Eds.), Handbook of Environmental Isotope Geochemistry, Vol. 1. Elsevier, Amsterdam, pp. 407– 429.

Lomas-Clarke, S.H.S.H., Barber, K.E.K.E., 2004. Palaeoecology of human impact during the historic period: palynology and geochemistry of a peat deposit at Abbeyknockmoy, Co. Galway, Ireland. The Holocene 14, 721–731.

Macko, S., Entzeroth, L., Parker, P., 1993. Early diagenesis of organic matter in sediments. Assessment of mechanisms and preservation by the use of isotopic molecular approaches, in: Engel, J. (Ed.), Organic Geochemistry: Principles and Applications. Plenum, New York, pp. 211–224.

Malmer, N., Holm, E., 1984. Variation in the C/N-quotient of peat in relation to decomposition rate and age determination with 210 pb. Oikos 43, 171–182.

Mann, M.E., Bradley, R.S., Hughes, M.K., 1998. Global-scale temperature patterns and climate forcing over the past six centuries. Nature 392, 779–787.

Martínez Cortizas, A., López-Merino, L., Bindler, R., Mighall, T., Kylander, M., 2013. Atmospheric Pb pollution in N Iberia during the late Iron Age/Roman times reconstructed using the high-resolution record of La Molina mire (Asturias, Spain). Journal of Paleolimnology 50, 71–86.

Martínez Cortizas, A., Mighall, T., Pontevedra Pombal, X., Nóvoa Muñoz, J.C.C., Peiteado Varela, E., Piñeiro Rebolo, R., 2005. Linking changes in atmospheric dust deposition, vegetation change and human activities in northwest Spain during the last 5300 years. The Holocene 15, 698–706.

Martínez-Cortizas, A., Biester, H., Mighall, T., Bindler, R., Mart, A., 2007. Climate-driven enrichment of pollutants in peatlands. Biogeosciences 4, 905–911.

Massa, C., Bichet, V., Gauthier, É., Perren, B.B., Mathieu, O., Petit, C., Monna, F., Giraudeau, J., Losno, R., Richard, H., 2012. A 2500 year record of natural and anthropogenic soil erosion in South Greenland. Quaternary Science Reviews 32, 119–130.

Massa, C., Monna, F., Bichet, V., Gauthier, E., Losno, R., Richard, H. 2015. Inverse modeling of past lead atmospheric deposition in South Greenland. Atmospheric Environment 105, 121-129.

Matthews, J.A., Briffa, K.R., 2005. The “Little Ice Age”: re-evaluation of an evolving concept. GeografiskaAnnaler 87, 17–36.

Mauquoy, D., Geel, B. Van, Blaauw, M., Plicht, J. Van Der, 2007. Evidence from northwest European bogs shows “ Little Ice Age ” climatic changes driven by variations in solar activity. The Holocene 1, 1–6.

McAndrews, J.H., 1988. Human disturbance of North American forests and grasslands: the fossil pollen record, in: Huntley, B., Webb, T. (Eds.), Vegetation History Volume of Handbook of Vegetation Science Series. Kluwer Academic Publishers, Utrech, pp. 673–697.

McAndrews, J.H., Boyko-Diakonow, M., 1989. Pollen analysis of varved sediment at crawford lake, Ontario: evidence of indian and european farming, in: Fulton, R.D. (Ed.), Quaternary Geology of Canada and Greenland. Geological Survey of Canada, Ottawa, pp. 528–530.

Meharg, A.A.A., Edwards, K.J.J., Schofield, J.E.E., Raab, A., Feldmann, J., Moran, A.C., Bryant, C.L.L., Thornton, B., Dawson, J.. J.C., 2012. First comprehensive peat depositional records for tin, lead and copper associated with the antiquity of Europe’s largest cassiterite deposit. Journal of Archaeological Science 39, 717–727.

Michelutti, N., Simonetti, A., Briner, J.P., Funder, S., Creaser, R. a, Wolfe, A.P., 2009. Temporal trends of pollution Pb and other metals in east-central Baffin Island inferred from lake sediment geochemistry. The Science of the Total Environment 407, 5653–5662.

Millet, L., Massa, C., Bichet, V., Frossard, V., Belle, S., Gauthier, E., 2014. Anthropogenic versus climatic control in a high-resolution 1500-year chironomid stratigraphy from a southwestern Greenland lake. Quaternary Research 81, 193-202.

Mohn, W., Tiedje, J., 1992. Microbial reductive dehalogenation. Microbiological and Molecular Biology Reviews 56, 482–507.

Monserrate, E., Häggblom, M., 1997. Dehalogenation and biodegradation of brominated phenols and benzoic acids under iron-reducing, sulfidogenic, and methanogenic conditions. Applied and Environmental Microbiology 63, 3911–3915.

Moore, G.W.K., Pickart, R.S., Renfrew, I.A., 2008. Buoy observations from the windiest location in the world ocean, Cape Farewell, Greenland. Geophysical Research Letters 35.

Moore, P.D., Webb, J.A., Collinson, M.E., 1991. Pollen Analysis. 2nd Edition, 2nd editio. ed. Blackwell Scientific Publications, London.

Murozumi, M., Chow, T.J., Patterson, C., 1969. Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. Geochimica et Cosmochimica Acta 33, 1247–1294.

Myneni, S.C.B., 2002. Formation of stable chlorinated hydrocarbons in weathering plant material. Science (New York, N.Y.) 295, 1039–41.

Niemeyer, J., Chen, Y., Bollag, J.-M., 1992. Characterization of humic acids, composts, and peat by diffuse reflectance fourier- transform infrared-spectroscopy. Soil Science Society of America Journal 56, 135–140.

Norton, S.., Evans, G.C., Kahl, J.S., 1997. Comparison of Hg and Pb fluxes to hummocks and hollows of ombrotrophic Big Heath and to nearby Sargent Mt. Pond, Maine. Water, Air, and Soil Pollution 100, 271–286.

Norton, S.A., Perry, E.R., Haines, Terry, A., Dieffenbacher-Krallc, A.C., 2004. Paleolimnological assessment of Grove and Plow Shop Ponds, Ayer, Massachusetts, USA – A superfund site. Journal of Environmental Monitoring 6, 457–465.

Ogilvie, A.E.J., Jónsson, T., 2001. "Little Ice Age" research: a perspective from Iceland. Climatic Change 48, 9-52.

Outridge, P.M., Hermanson, M.H., Lockhart, W.L., Utridge, P.M.O., Ermanson, M.H.H., Ockhart, W.L.L., 2002. Regional variations in atmospheric deposition and sources of anthropogenic lead in lake sediments across the Canadian Arctic. Geochimica et Cosmochimica Acta 66, 3521–3531.

Parker, F.S., 1971. Applications of Infrared Spectroscopy in biochemistry, biology and medicine. Adam Hilger, London.

Pontevedra-Pombal, X., Mighall, T.M., Nóvoa-Muñoz, J.C., Peiteado-Varela, E., Rodríguez-Racedo, J., García-Rodeja, E., Martínez-Cortizas, A., 2013. Five thousand years of atmospheric Ni, Zn, As, and Cd deposition recorded in bogs from NW Iberia: prehistoric and historic anthropogenic contributions. Journal of Archaeological Science 40, 764–777.

Renfrew, I.A., Petersen, G.N., Outten, S., Sproson, D., Moore, G.W.K., Hay, C., Ohigashi, T., Zhang, S., Kristjánsson, J.E., Føre, I., Ólafsson, H., Gray, S.L., Irvine, E. a., Bovis, K., Brown, P.R. a., Swinbank, R., Haine, T., Lawrence, A., Pickart, R.S., Shapiro, M., Woolley, A., 2008. The Greenland Flow Distortion Experiment. Bulletin of the American Meteorological Society 89, 1307–1324.

Raahauge, K., Hoegh-Knudsen, P., Gulløv, H.C., Mohl, J., Krause, C., Møller, N.A., 2003. Tidlig ThulekulturI Sydgrønland. Rapport om undersøgelserne I Nanortalik Kommune, sommeren 2002, Feltrapport 9. SILA, Nationalmuseets Center for Grønlandsforskning, Copenhagen.

Rosman, K.J.., Chisholm, W., Hong, S., Candelone, J.-P., Boutron, C.F., 1997. Lead from Carthaginian and Roman Spanish Mines Isotopically Identified in Greenland Ice Dated from 600 B.C. to 300 A.D. Environmental Science & Technology 31, 3413–3416.

Rosman, K.J.R., Chisholm, W., Boutron, C.F., Candelone, J.P., Görlach, U., 1993. Isotopic evidence for the source of lead in Greenland snows since the late 1960s. Nature 362, 333–335.

Rosman, K.J.R., Chisholm, W., Boutron, C.F., Candelone, J.-P., Jaffrezo, J.-L., Davidson, C.I., 1998. Seasonal variations in the origin of lead in snow at Dye 3, Greenland. Earth and Planetary Science Letters 160, 383–389.

Rousseau, D., Schevin, P., Duzer, D., Cambon, G., Ferrier, J., Jolly, D., Poulsen, U., 2006. New evidence of long distance pollen transport to southern Greenland in late spring. Review of Palaeobotany and Palynology 141, 277–286.

Rousseau, D.-D., 2003. Long distance transport of pollen to Greenland. Geophysical Research Letters 30, 1765.

Sampe, T., Shang-Ping, X., 2007. Mapping high sea winds from space: a global climatology. Bulletin of the American Meteorological Society 88, 1965–1978.

Sandgren, P., Fredskild, B., 1991. Magnetic measurements recording Late Holocene man-induced erosion in S. Greenland. Boreas 20, 315–331.

Schofield, J.E., Edwards, K.J., 2011. Grazing impacts and woodland management in Eriksfjord: Betula, coprophilous fungi and the Norse settlement of Greenland. Vegetation History and Archaeobotany 20, 181–197.

Schofield, J.E., Edwards, K.J., Christensen, C., 2008. Environmental impacts around the time of Norse landnám in the Qorlortoq valley, Eastern Settlement, Greenland. Journal of Archaeological Science 35, 1643–1657.

Schofield, J.E., Edwards, K.J., Mighall, T.M., Martínez-Cortizas, A., Rodríguez-Racedo, J., Cook, G., Martínez Cortizas, A., 2010. An integrated geochemical and palynological study of human impacts, soil erosion and storminess from southern Greenland since c. AD 1000. Palaeogeography, Palaeoclimatology, Palaeoecology 295, 19–30.

Schweizer, M., Fear, J., Cadisch, G., 1999. Isotopic (13C) fractionation during plant residue decomposition and its implications for soil organic matter studies. Rapid communications in mass spectrometry 13, 1284–1290.

Shotyk, W., Goodsite, M.E.E., Roos-Barraclough, F., Frei, R., Heinemeier, J., Asmund, G., Lohse, C., Hansen, T.S.S., 2003. Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the 14C “bomb pulse curve”. Geochimica et Cosmochimica Acta 67, 3991–4011.

Shotyk, W., Zheng, J., Krachler, M., Zdanowicz, C., Koerner, R., Fisher, D., 2005. Predominance of industrial Pb in recent snow (1994–2004) and ice (1842–1996) from Devon Island, Arctic Canada. Geophysical Research Letters 32, L21814.

Silva-Sánchez, N., Martínez Cortizas, A., López-Merino, L., 2014. Linking forest cover, soil erosion and mire hydrology to late-Holocene human activity and climate in NW Spain. The Holocene 24, 714–725.

Smidt, E., Meissl, K., Schwanninger, M., Lechner, P., 2008. Classification of waste materials using Fourier transform infrared spectroscopy and soft independent modeling of class analogy. Waste management 28, 1699–1710.

Solomon, D., Lehnmann, J., Thies, J., Schafer, T., Liang, B., Kinyangi, J., Neves, E., Petersen, J., Luizao, F., Skjemstad, J., 2007. Molecular signature and sources of biochemical recalcitrnace of organic C in Amazonian Dark Earths. Geochimica Cosmochimica Acta 71, 2285–2298.

Sturges, W.T., Barrie, L.A., 1989. Stable lead isotope ratios in Arctic aerosols: Evidence for the origin of Arctic air pollution. Atmospheric Environment 23, 2513 – 2520.

Thibaudon, M., 1992. Ragweed in France; some air pollen data for the years 1987 – 1990. Allergie et immunologie 24, 9– 16.

Van Geel, B., Buurman, J., Brinkkemper, O., Schelvis, J., Aptroot, A., van Reenen, G., Hakbijl, T., 2003. Environmental reconstruction of a Roman Period settlement site in Uitgeest (The Netherlands), with special reference to coprophilous fungi. Journal of Archaeological Science 30, 873–883.

Van Geel, B., Raspopov, O.M., Renssen, H., van der Plicht, J., Dergachev, V. a., Meijer, H. a. J., 1999. The role of solar forcing upon climate change. Quaternary Science Reviews 18, 331–338.

Wallbrink, P.J., Walling, D.E., He, Q., 2002. Radionuclide measurement using Hpge Gamma Spectrometry, in: Zapata, F. (Ed.), Handbook for the Assessment of Soil Erosion and Sedimentation Using Environmental Radionuclides. Kluwer, Dorderecht, pp. 67–96.

Walling, D.E., He, Q., P.G., A., 2002. Conversion models for soil-erosion, soil-redistribution and sedimentation investigations, in: Zapata, F. (Ed.), Handbook for the Assessment of Soil Erosion and Sedimentation Using Environmental Radionuclides. Kluwer, Dordrecht, pp. 111–164.

Wigley, T., Kelly, P., 1990. Holocene climatic change, 14C wiggles and variations in solar irradiance. Philosophical Transactions of the Royal Society 330, 547–560.

WRB, I.W.G., 2014. World Reference Base for Soil Resources 2014.International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome.

Zaccheo, P., Cabassi, G., Ricca, G., Crippa, L., 2002. Decomposition of organic residues in soil: experimental technique and spectroscopic approach. Organic Geochemistry 33, 327–345.

List of figures

Figure 1: (a) Map of Greenland and northeast North America showing the locations of sites and places mentioned in the text. Key to numbering: (1) Plow Shop and Grove Ponds; (2) Big Heath and Sargent Mountain Pond; (3) Lake Tantaré; (4) Point d'Escuminac; (5) Imitavik Lake; (6) Far Lake; (7) Lake CF8; (8) Devon Island; (9) Camp Century; (10) Lake G07-01; (11) Summit; (12) Kangerlussuaq; (13) Sandhavn and Cape Farewell; (b) the area around Sandhavn, southern Greenland, showing sites and places mentioned in the text; (c) the sampling location at Sandhavn. The white star marks the position from which the peat monolith was taken; (d) the landscape around the sampling location at Sandhavn showing the position of the Norse ruins and former homefields. (Photographs by J.E.Schofield, August 2008).

Figure 2. Age-depth model for Sandhavn (after Golding et al. [2011] with minor changes). Shaded (greyscale) boxes represent the 2σ calibrated ranges of radiocarbon dates used in the model; clear boxes are the ^{210}Pb dates (with associated errors). One ^{14}C date – depicted here in black – was considered to be an outlier and has been removed from the model. The solid black line connecting the ^{14}C and ^{210}Pb dates represents the 'best estimate' based on the model, with the grey envelope around this demonstrating the maximum and minimum (95%) confidence limits.

Figure 3. Percentage pollen diagram for Sandhavn displaying selected taxa (after Golding et al. [2011] with minor changes). The SAN-2/3 pollen zone boundary represents the replacement of hayfields and pastures (Poaceae-dominated assemblages) with tundra or steppe vegetation (Cyperaceae-dominated assemblages), and with it the Norse abandonment

of the site. This vegetation was to persist until around AD 1850 and the development of *Empetrum nigrum* oceanic heath. *Ambrosia* pollen is recorded in SAN-5. This genus is not native to southern Greenland (Böcher et al., 1968) and must be part of the long-distance component arriving at the site. Curves for *Hippuris vulgaris*, *Sporormiella*-type (coprophilous fungi) and C:P (ratio of charcoal to pollen concentration) act as proxies for the presence of standing water, grazing by animals, and fires/burning respectively.

Figure 4: LOI and elemental composition through the peat section of the Sandhavn monolith. Note that x-axes scales and units vary between graphs.

Figure 5: Factor scores for the first three principal components (PC1e, PC2e, and PC3e) extracted from the PCA performed on LOI and elemental composition data from the peat section of the Sandhavn monolith. Boxes with dashed outlines indicate sections with higher PC1e scores (i.e. higher mineral content).

Figure 6. Variations in organic matter indicators through the peat section of the Sandhavn monolith: (A) C/N ratio, degree of peat humification (DPH), and variations in $\delta^{13}C$ and $\delta^{15}N$; (B) Selected FTIR bands (expressed as z-scores).

Figure 7: Factor scores for the first three principal components (PC1o, PC2o, and PC3o) extracted from the PCA performed on selected FTIR bands, C/N, $\delta^{13}C$, $\delta^{15}N$ and DPH through the peat section of the Sandhavn monolith.

Figure 8: PC1e factor scores (reflecting the mineral content of the peat), Ti/Zr and K/Rb plotted against selected pollen types and spores from the Sandhavn monolith.

Figure 9: Selected variables through the Sandhavn monolith. From top to bottom: peat growth rate and peat carbon accumulation rate (PCAR: grey line) with y-axis truncated such that very high values recorded after AD 1950 (shown on the embedded graph) are not depicted; percentage of *Hippuris vulgaris* pollen; Br concentration; levels of recalcitrant compounds in the peat (reflected by PC1o factor scores); levels of polysaccharides in the peat (reflected by PC3o factor scores); percentage of *Empetrum nigrum* pollen; variations in Rδ^{14}C (Reimer et al., 2004). Light grey shading indicates the approximate timeframe of Little Ice Age climate and dark grey bands indicate the Spörer and Maunder minima in solar activity.

Figure 10: Pb concentration and Pb/Ti ratio (expressed as z-scores) through the peat unit of the Sandhavn monolith.

Figure SI.1. LOI and elemental composition through the full depth of the monolith (40-0 cm) from Sandhavn. Note the major changes between the sand layer at the base and the peat above this.

List of tables

Table 1. Radiocarbon dates from Sandhavn. All measurements are AMS on bryophytes (*Dicranium*, *Drepanocladus*, *Hypnum*, *Hylocomium* and *Racomitrium* spp.). Calendar ranges are those used by the (*Clam*) age-depth model (Fig. 2) following calibration against the Intcal13 calibration curve (Reimer et al., 2013). See Golding et al. (2011) for a further discussion of the radiocarbon dates.

Table SI1. Assignment and characterization of FTIR bands included in the principal components analysis of the peat organic matter properties from Sandhavn (vertical variation of bands plotted in Fig. 6).

Table SI2. Factor loadings from the three first principal components extracted from the PCA of the elemental composition (PCe) of Sandhavn (factor scores plotted in Fig. 5).

Table SI3. Factor loadings from the PCA of the peat organic matter indicators (PCo)from Sandhavn (factor scores plotted in Fig. 7). The prefix ‘b’ relates to FTIR band widths.

Fig SI1

Click here to download high resolution image

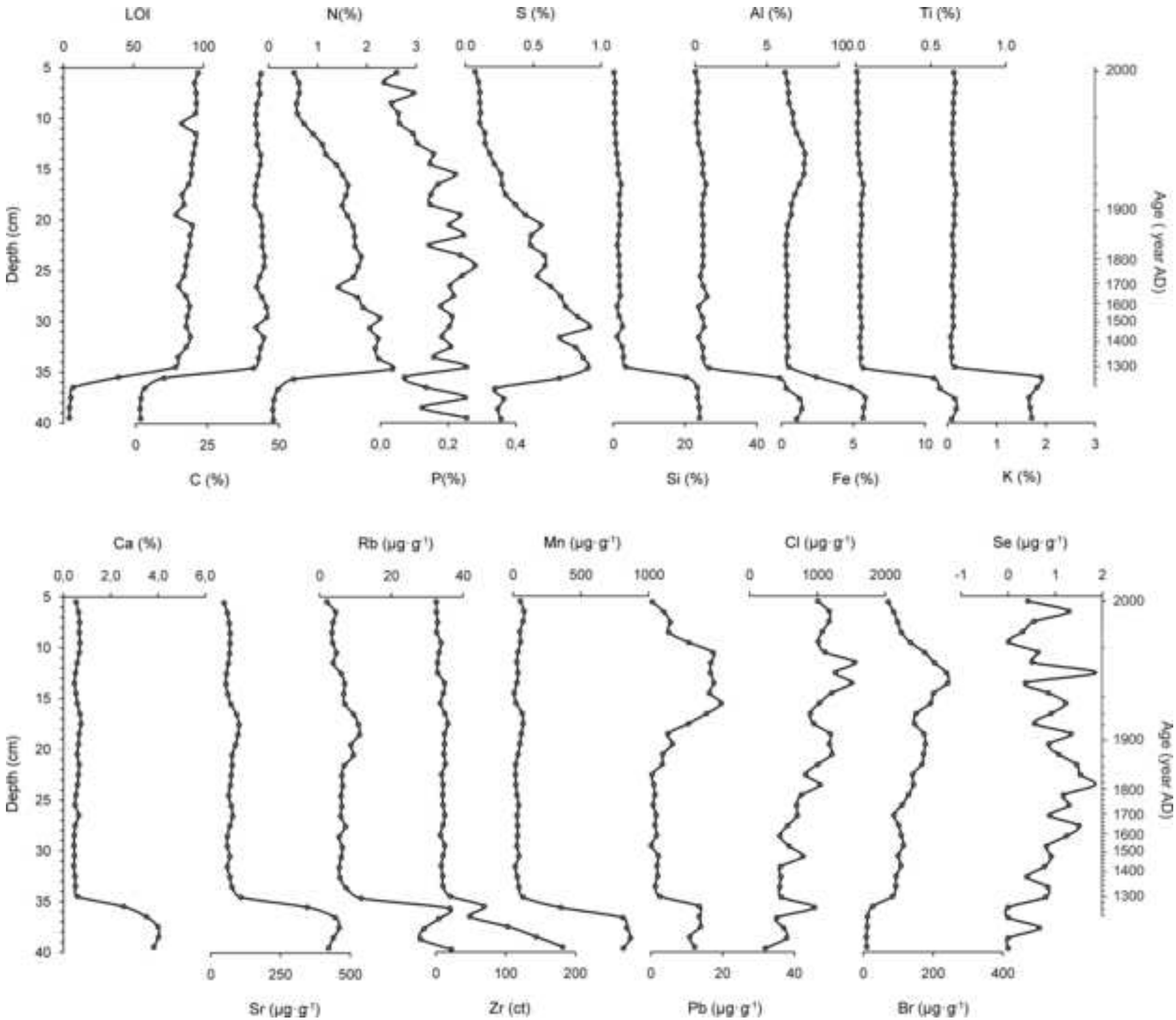

Table SI1

Table SI1. Assignment and characterization of FTIR bands included in the principal components analysis of the peat organic matter properties from Sandhavn (plotted in Fig. 6).

Wavenumber (cm^{-1})	Assignment and Characterisation	References
3050-3030 (3051)	Aromatic CH stretching	(Guo and Bustin, 1998)
2922	Antisymmetric CH2. Fats, wax, lipids	(Niemeyer et al., 1992; Cocozza et al., 2003)
2852	Symmetric CH2; Fats, wax, lipids	(Niemeyer et al., 1992; Cocozza et al., 2003)
1720	C=O stretch of COOH or COOR; Carboxylic acids, aromatic esters	(Niemeyer et al., 1992; Haberhauer et al., 1998)
1660	amides coming from preserved proteinaceous materials	(González et al., 2003)
1550	N-H in plane (amide II); Proteinaceous origin	(Ibarra et al., 1996; Zaccheo et al., 2002; González et al., 2003)
1514	Aromatic C=C stretching; Lignin/Phenolic backbone	(Cocozza et al., 2003)
1450-1371 (1450)	C-H deformations; Phenolic (lignin) and aliphatic structures	(Parker, 1971)
1420-1430 (1419)	Aromatic C=C ring streching; lignin	(Guo and Bustin, 1998; González et al., 2003)
1250-1270 (1271)	Aromatic CO- and phenolic -OH stretching; lignin	(Guo and Bustin, 1998; González et al., 2003)
1080-1030 (1070, 1030)	Combination of C-O stretching and O-H deformation; Polysaccharides	(González et al., 2003; Grube et al., 2006)

Table SI2

Table SI2: Factor loadings from the PCA of the elemental composition from Sandhavn (plotted in Fig. 5).

	PC1e	PC2e	PC3e
Ti	**0.94**	-0.09	0.10
Si	**0.93**	-0.22	-0.05
Zr	**0.92**	0.02	0.08
Al	**0.91**	0.02	0.04
Rb	**0.86**	0.20	0.33
N	**0.83**	-0.30	-0.39
P	**0.78**	-0.11	-0.32
Sr	**0.74**	0.02	0.59
S	**0.69**	-0.55	-0.41
LOI	**-0.78**	0.21	-0.07
Fe	0.01	**0.94**	-0.01
Br	-0.01	**0.94**	-0.09
Pb	-0.14	**0.92**	0.06
Cl	-0.45	**0.71**	0.32
K	0.11	0.04	**0.87**
Mn	-0.01	-0.21	**0.84**
Ca	-0.07	0.18	**0.81**
Se	0.21	0.00	-0.04
C	-0.15	-0.32	***-0.54***

Table SI3

Table SI3. Factor loadings from the PCA of the peat organic matter indicators from Sandhavn (plotted in Fig. 7). The prefix 'b' relates to FTIR band widths.

	PC1o	PC2o	PC3o
b2852	**0.97**	0.18	0.04
b2922	**0.94**	0.24	0.11
b1514	**0.89**	0.43	-0.06
b1660	**0.88**	0.35	-0.21
b1550	**0.87**	0.30	-0.21
$\delta^{15}N$	**0.84**	-0.07	-0.10
b3051	**0.76**	-0.02	***-0.53***
C/N	**-0.96**	-0.05	0.03
$\delta^{13}C$	***-0.65***	***-0.56***	0.24
DPH	***-0.53***	0.07	0.16
b1450	0.18	**0.97**	0.01
b1271	0.27	**0.89**	0.22
b1419	-0.39	**0.81**	0.16
b1720	0.47	**0.72**	0.12
b1030	-0.12	0.11	**0.97**
b1070	-0.10	0.14	**0.95**

Figure 1
Click here to download high resolution image

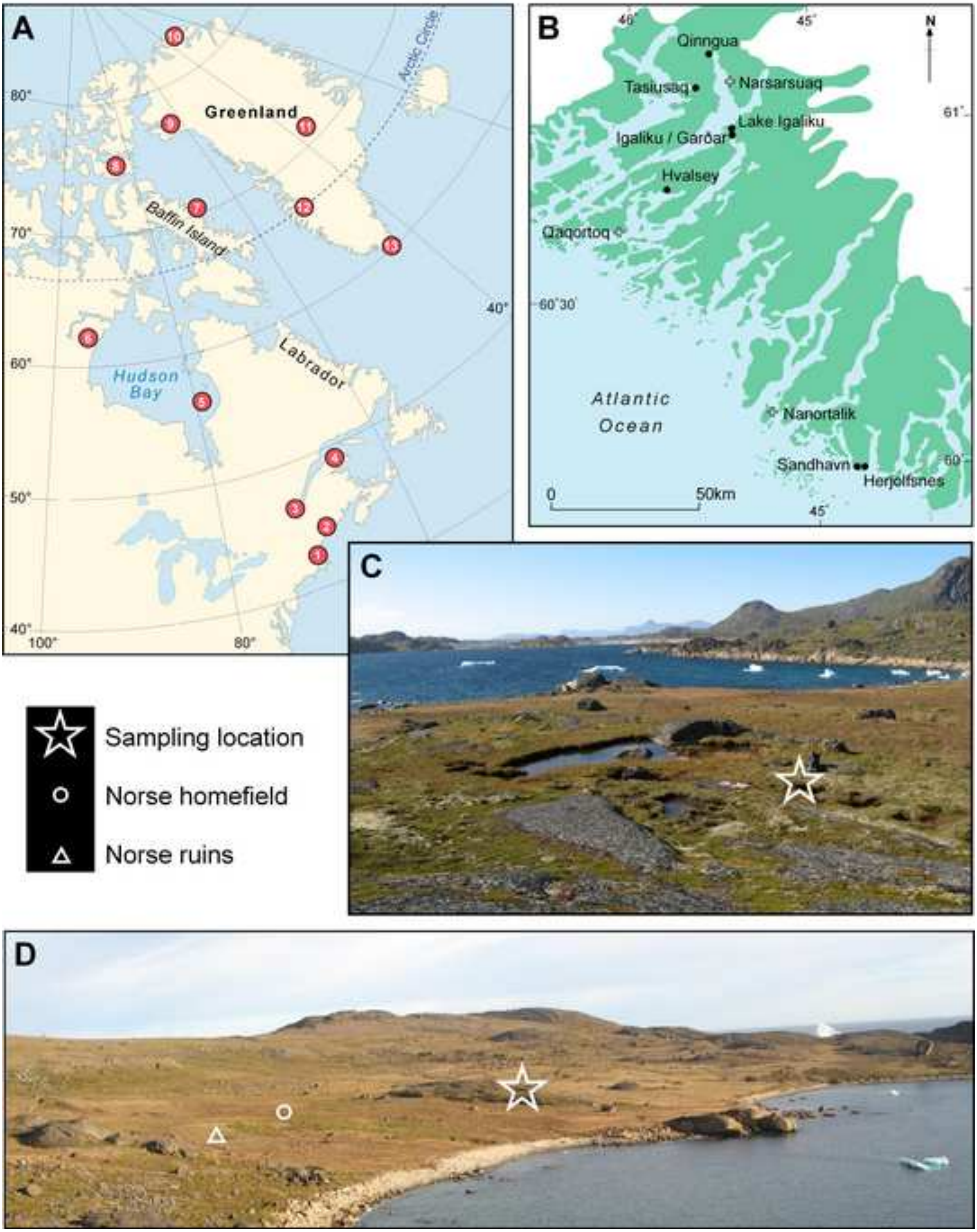

Figure 2

Click here to download high resolution image

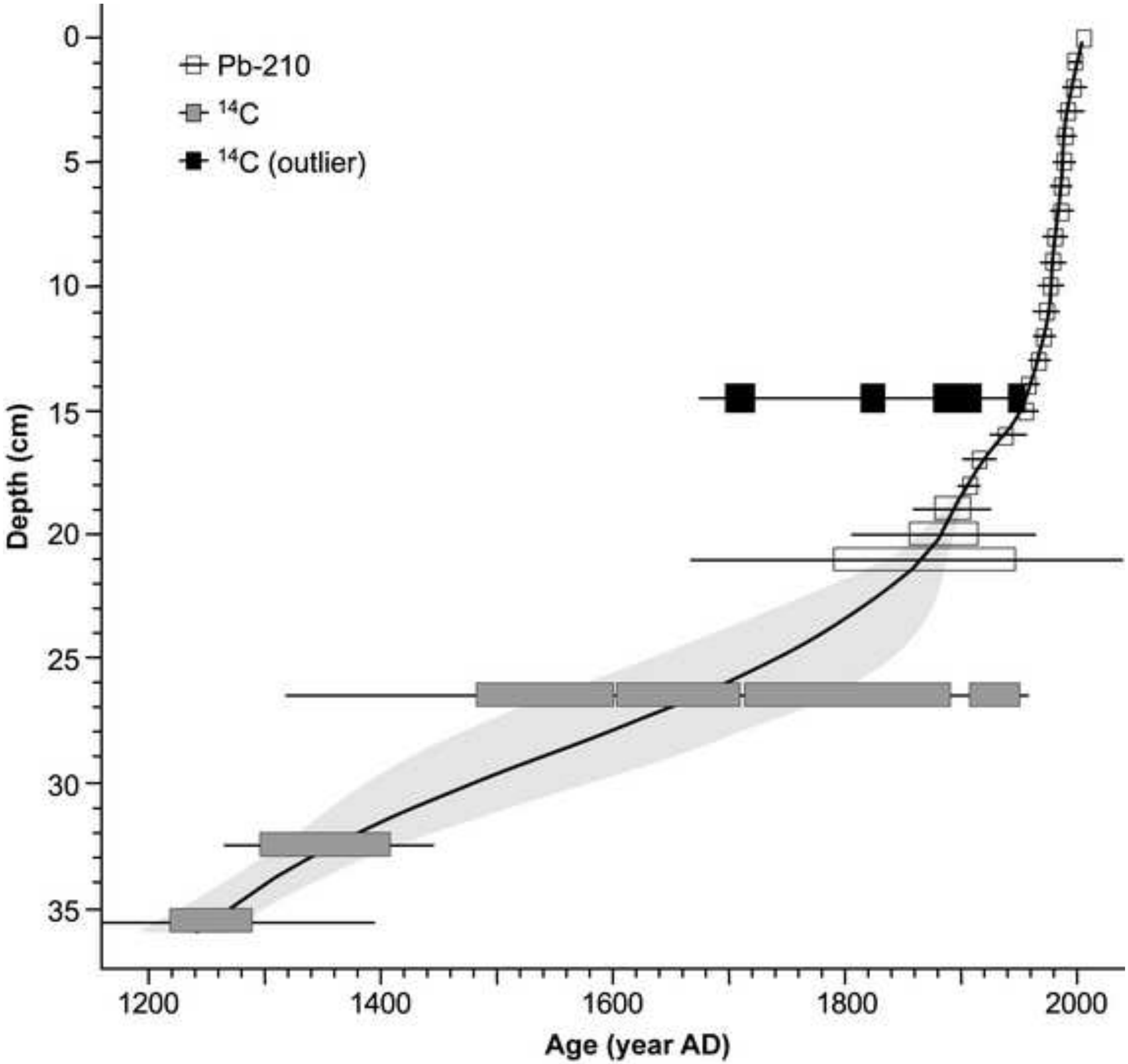

Figure 3 B&W
Click here to download high resolution image

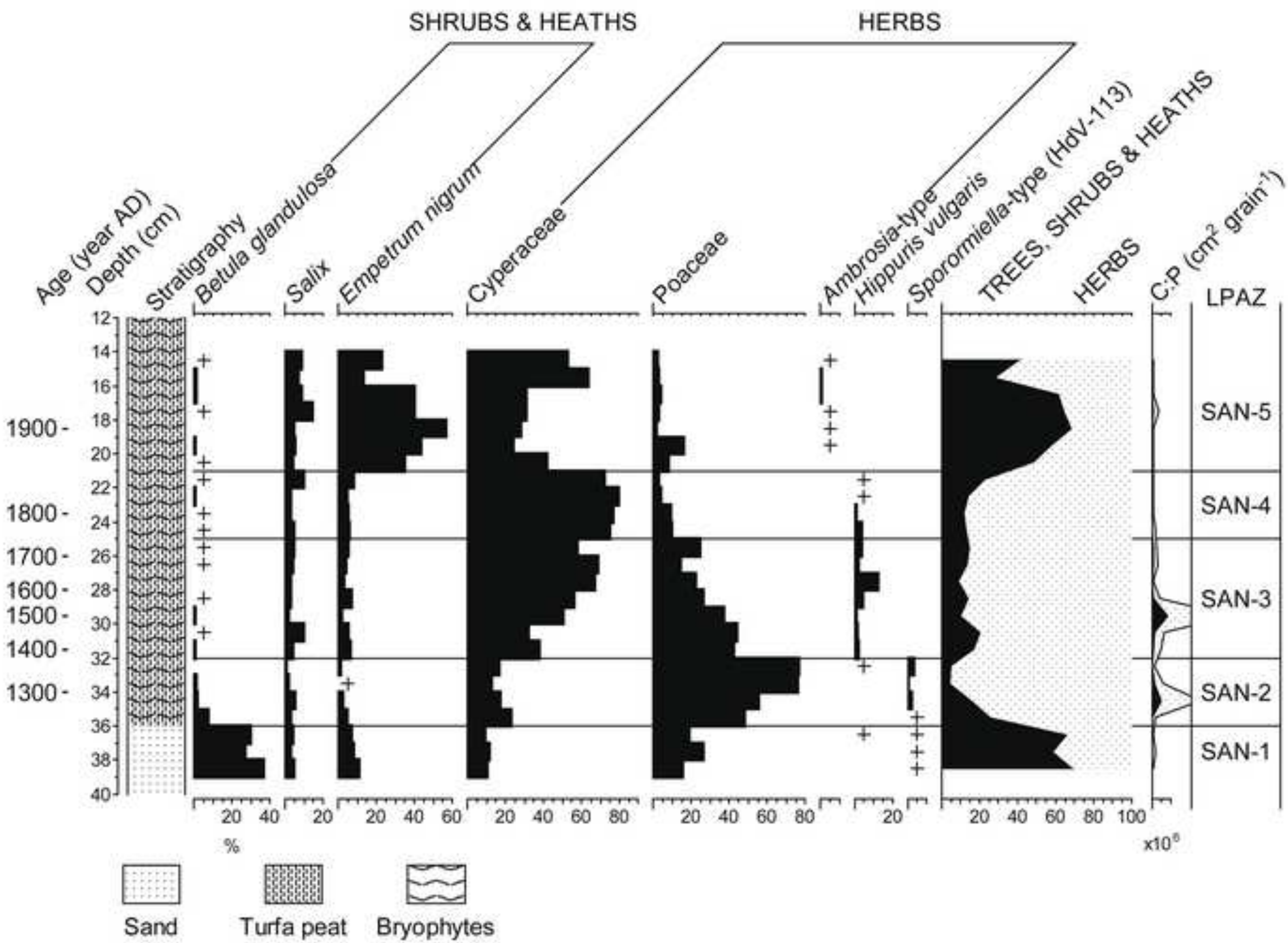

Figure 3 col
Click here to download high resolution image

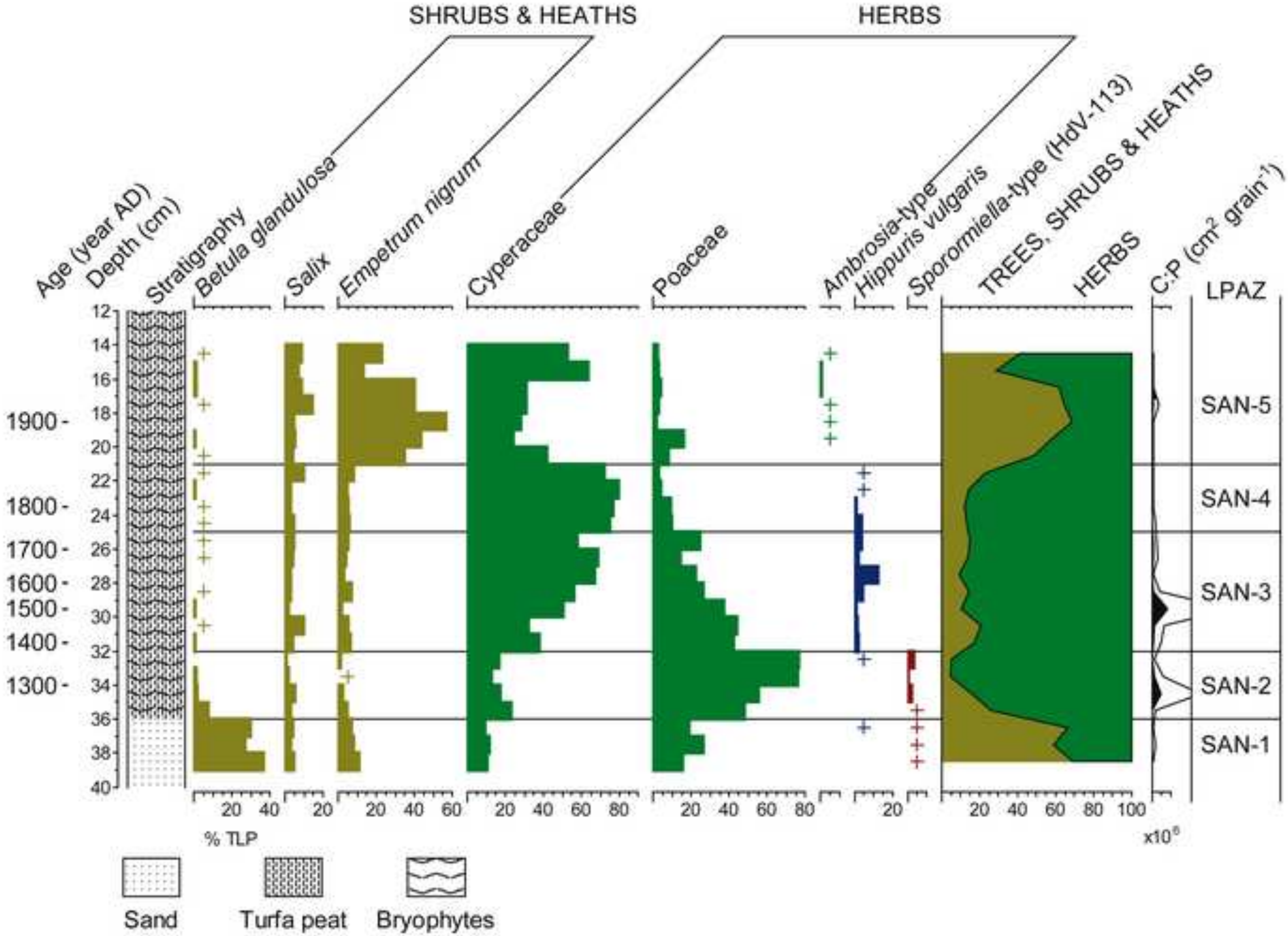

Figure 4

Click here to download high resolution image

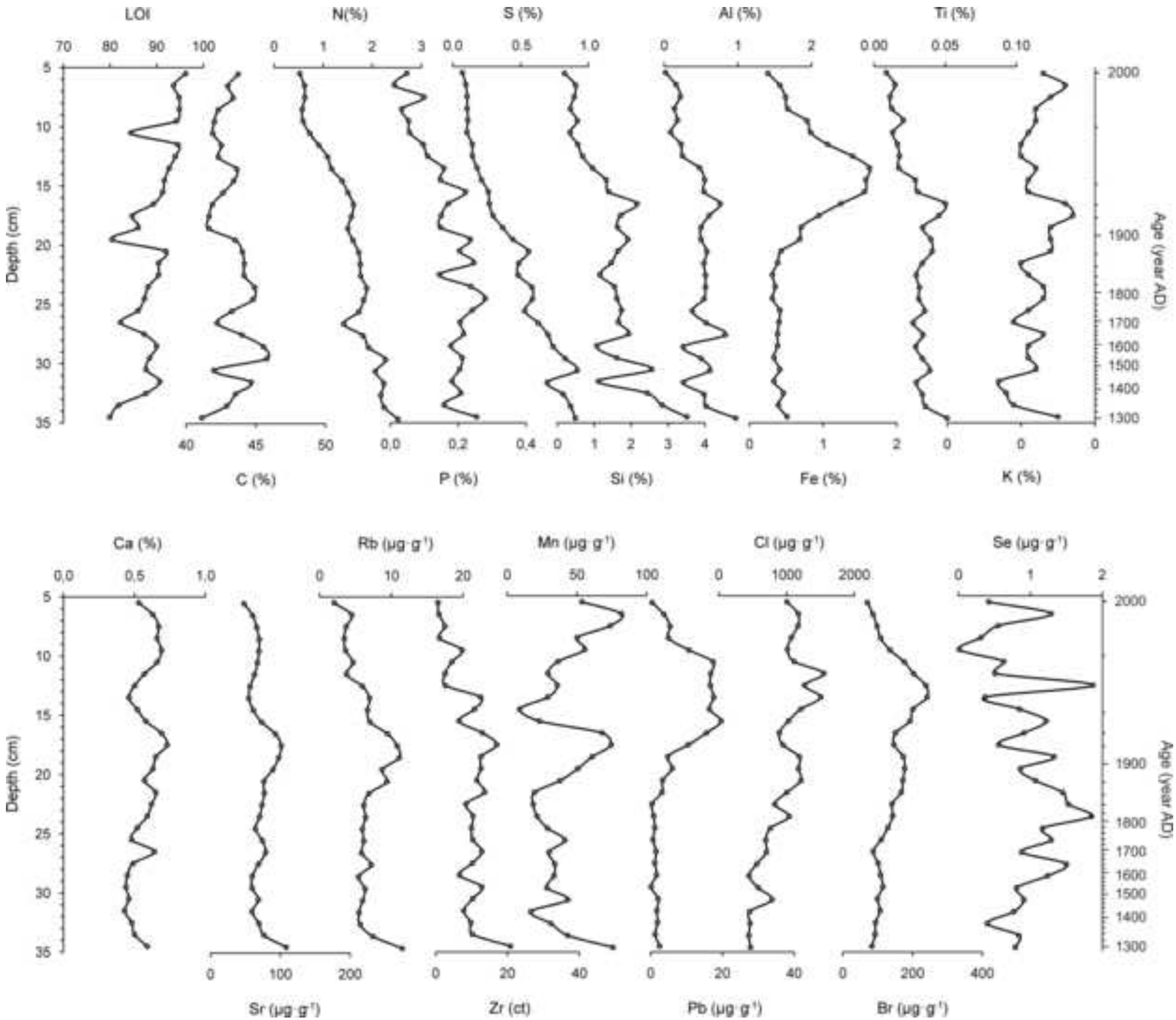

Figure 5

Click here to download high resolution image

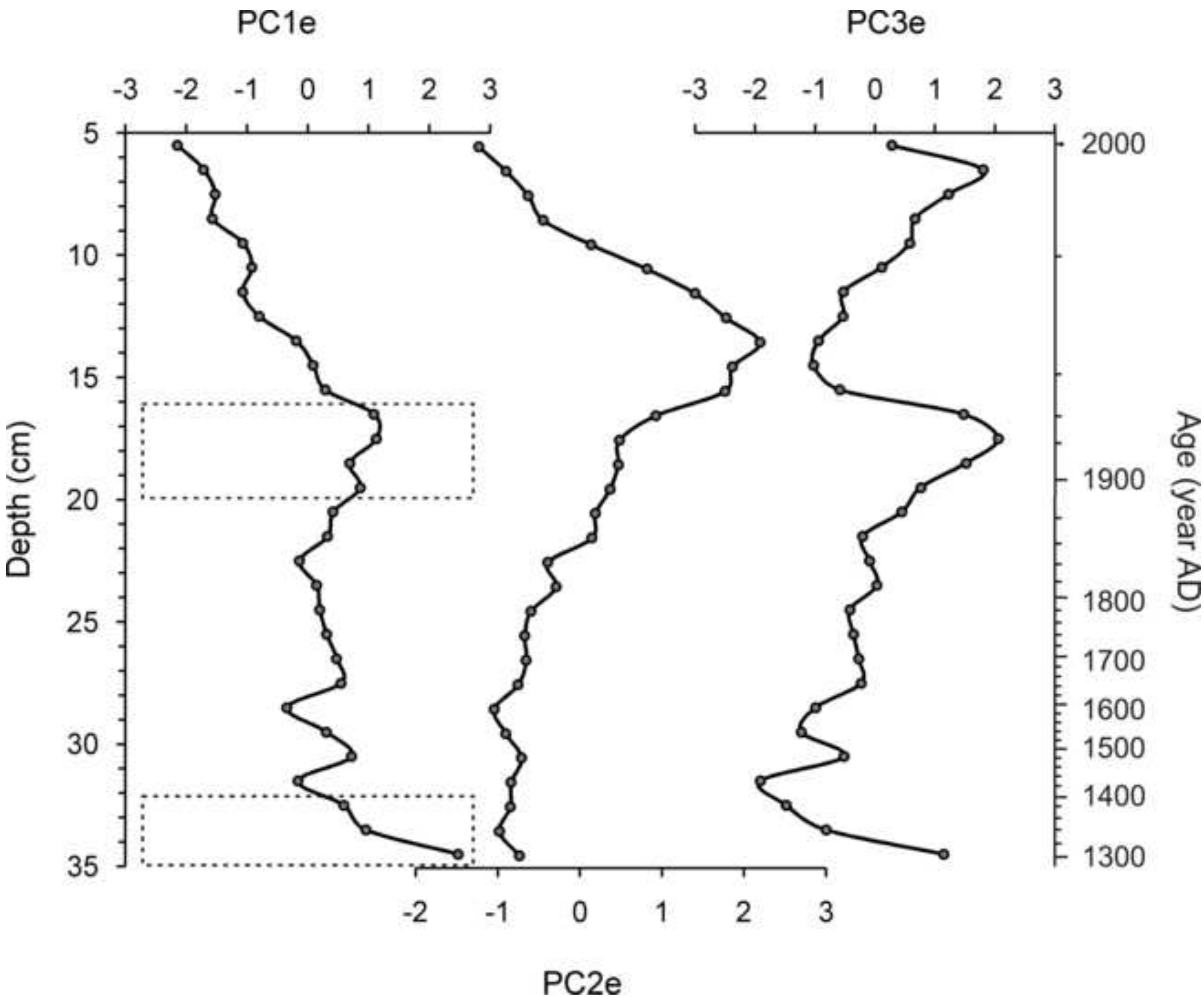

Figure 6

Click here to download high resolution image

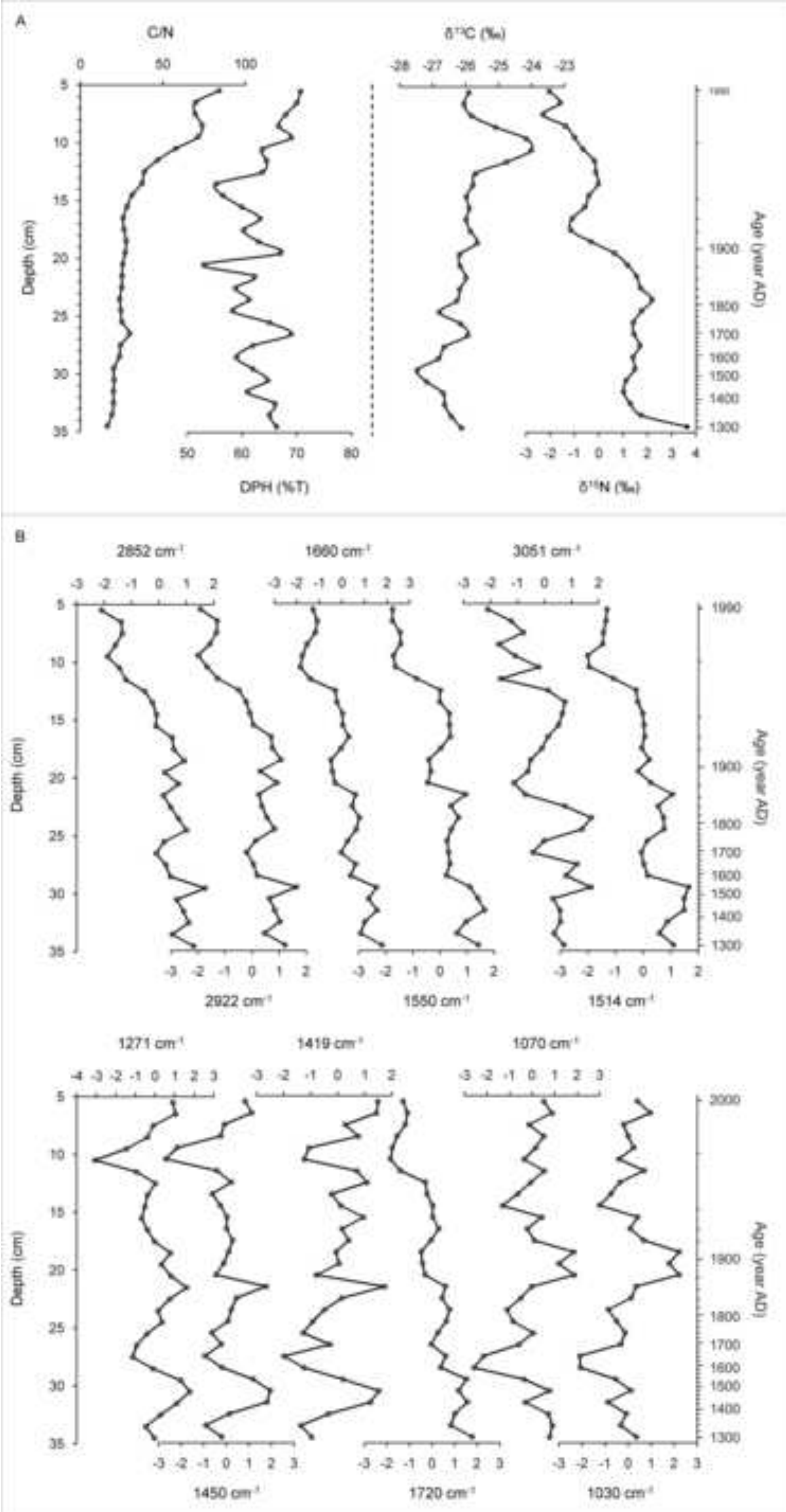

Figure 7

Click here to download high resolution image

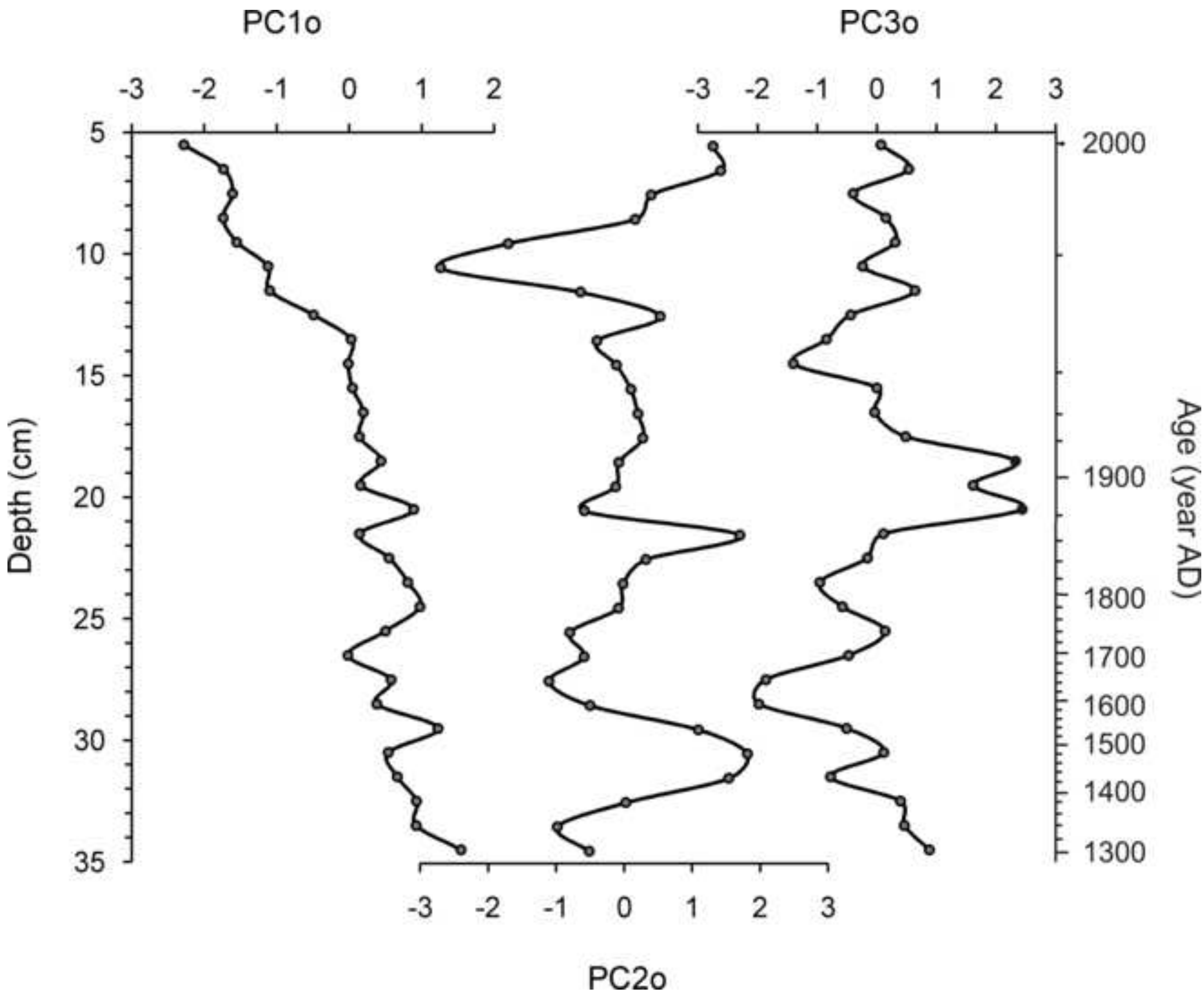

Figure 8
Click here to download high resolution image

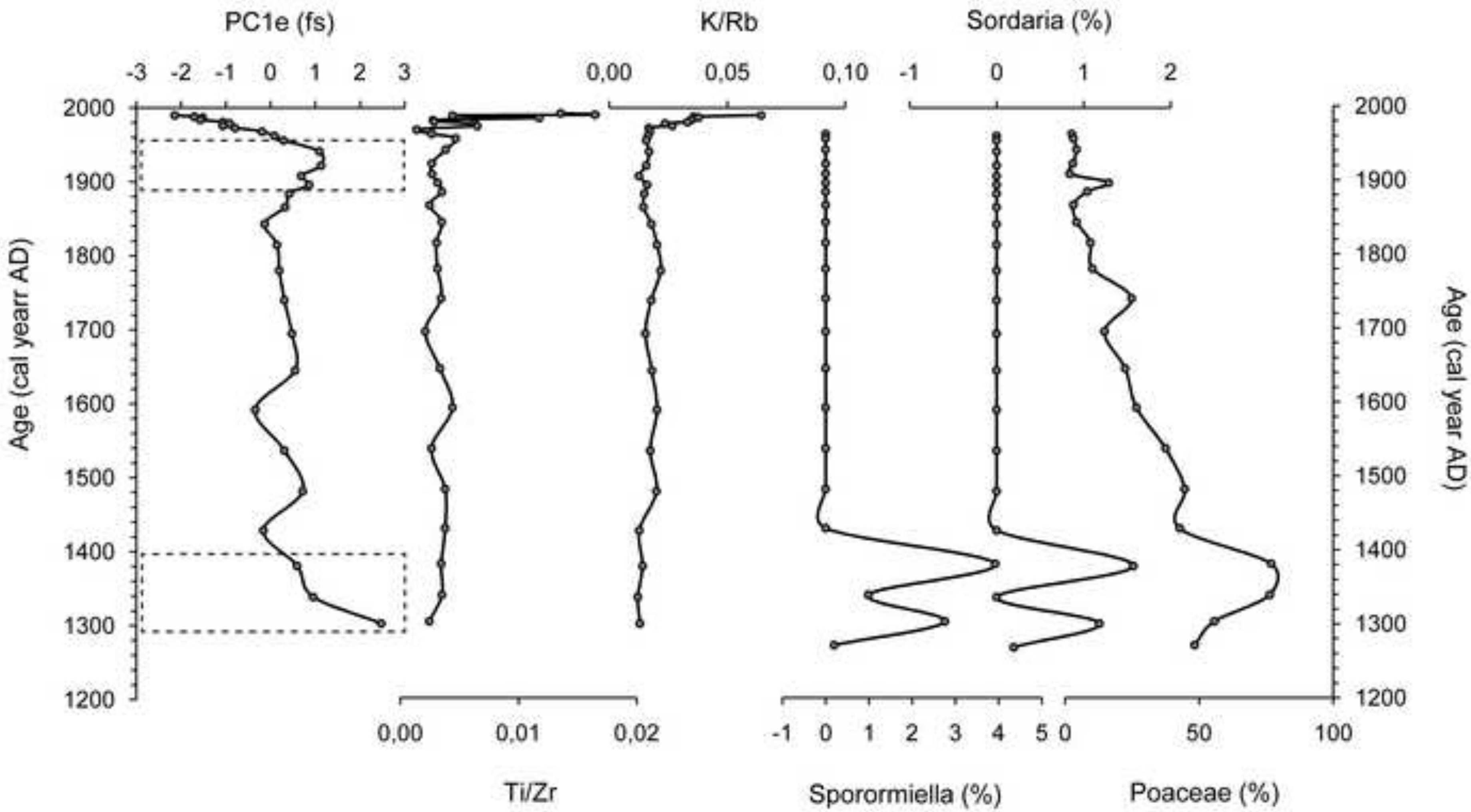

Figure 9

Click here to download high resolution image

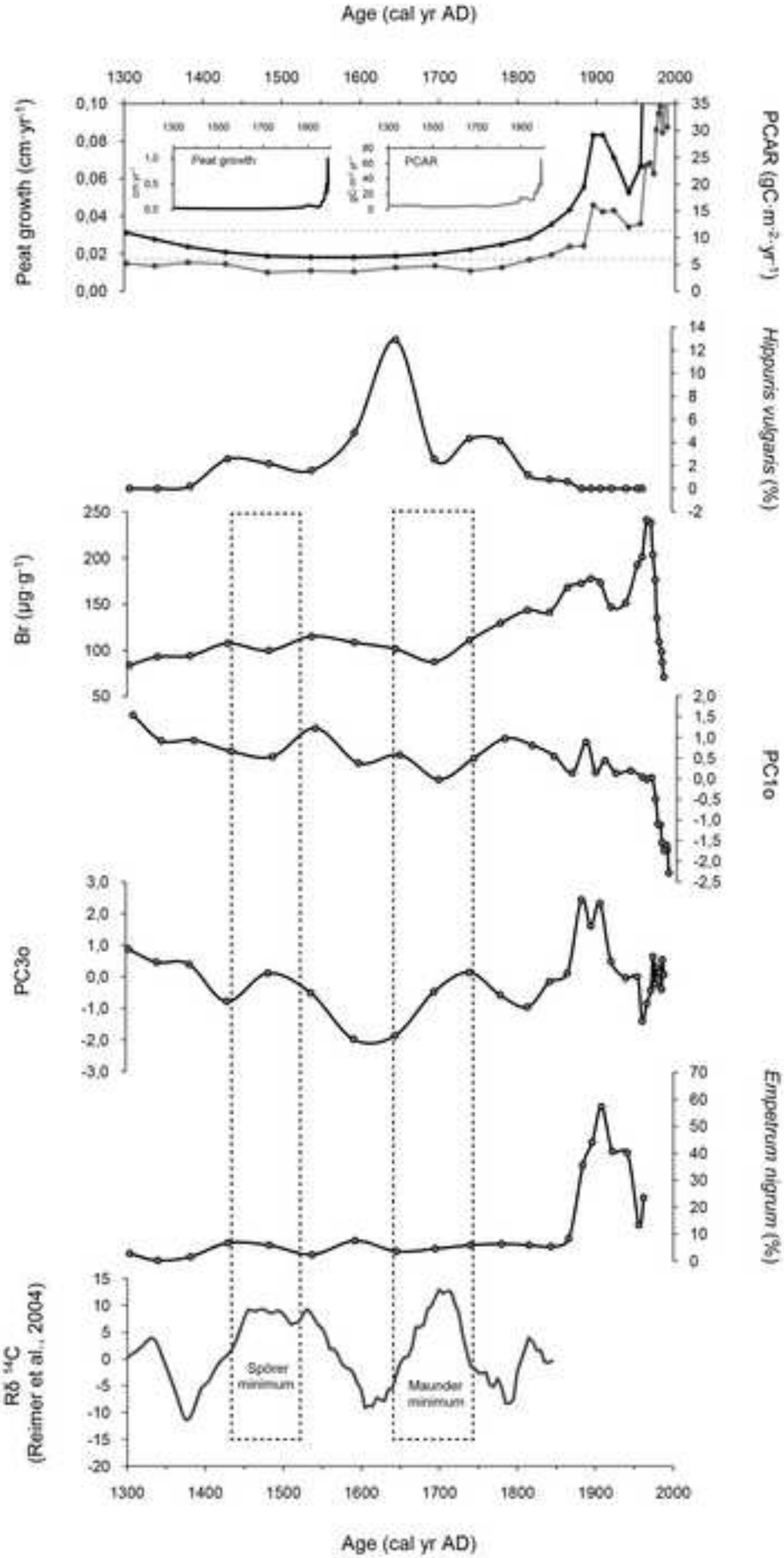

Figure 10
Click here to download high resolution image

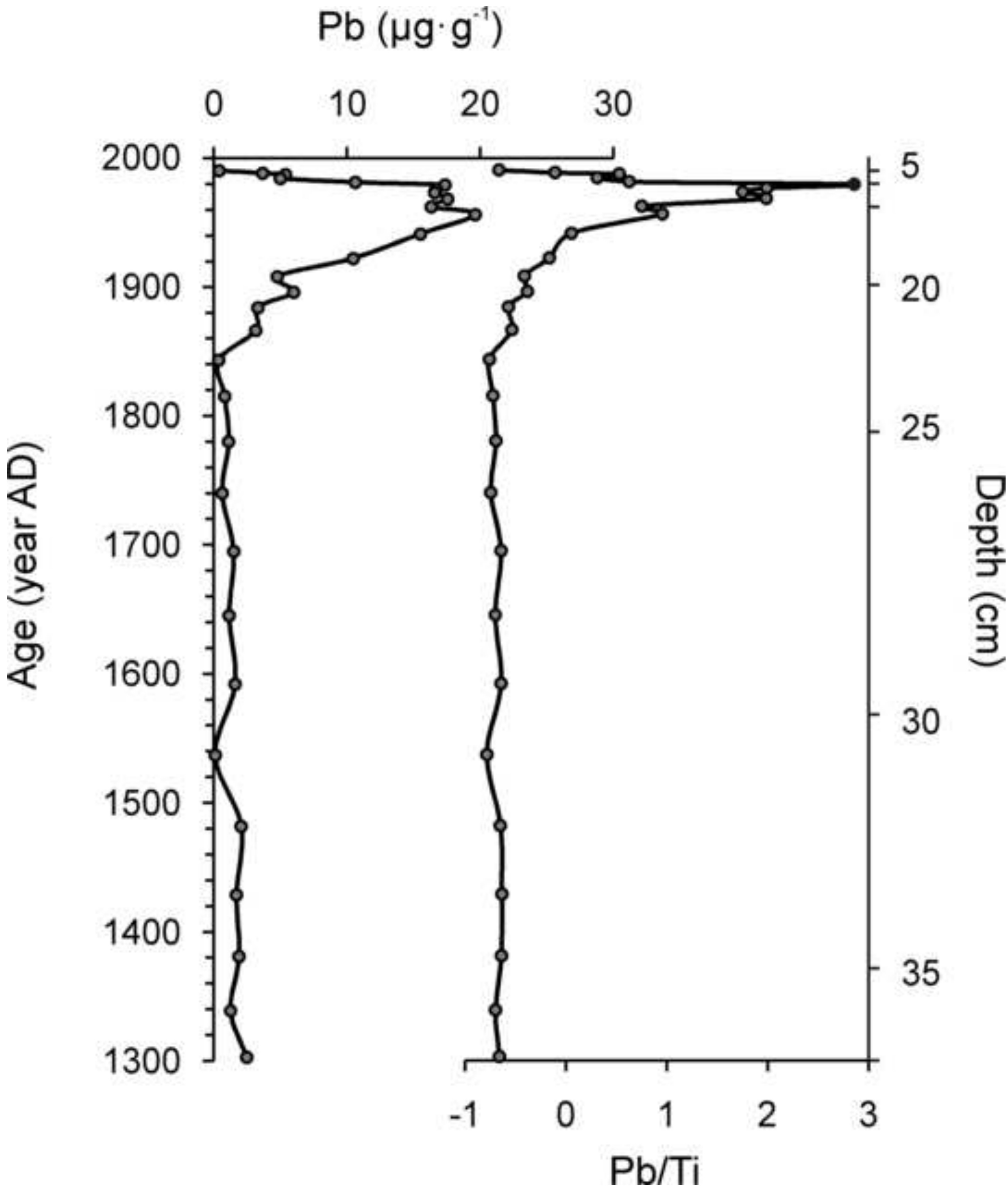

Table 1

Table 1: Radiocarbon dates from Sandhavn. All measurements are AMS on bryophytes (*Dicranium*, *Drepanocladus*, *Hypnum*, *Hylocomium* and *Racomitrium* spp.). Calendar ranges are those used by the (*Clam*) age-depth model (Fig. 2) following calibration against the Intcal13 calibration curve (Reimer et al., 2013). See Golding et al. (2011) for a further discussion of the radiocarbon dates.

Depth (cm)	Lab code (SUERC-)	^{14}C age (BP)	AD range (2σ)	$\delta^{13}C$ (‰)
15-14	24657	0 ± 35	1698-1955	-23.6
27-26	24866	230 ± 90	1484-1953	-25.0
33-32	24658	600 ± 35	1297-1408	-25.6
36-35	24659	750 ± 35	1219-1290	-24.8