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ORIGINAL PAPER

Geochemical responses to paleoclimatic changes in southern Sweden since the late glacial: the Hässeldala Port lake sediment record

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Abstract There is a relatively good understanding of the paleoenvironmental changes that have occurred in southern Sweden since the Late Glacial. A main exception, however, is the sedimentary response of lacustrine systems during this period of rapid climate shifts. To address this, high-resolution X-ray fluorescence core scanning, Total Organic Carbon (TOC), C/N and $\delta^{13}C$ analyses were made on a core from Hässeldala Port, a paleolake in the region. Site-specific geochemical analyses documented variations in silicate inputs (Zr/Ti, Si/Ti, K/Ti and K/Rb), productivity (TOC, Ca/Ti and Sr/Ti), as well as redox conditions in the sediment ($\delta^{13}C$, Mn/Ti and Fe/Ti), which were then linked to the regional climatic framework. During the Bølling/Older Dryas sediment accumulation was at its highest, particularly prior to colonization by terrestrial vegetation, and hydrological transport dominated. No clear signal of the Older Dryas was detected in the elemental chemistry. The Allerød was a period of relatively constant sediment accumulation, with the exception of during the Gerzensee oscillation when rates increased. There is evidence for increased within-lake and -catchment productivity and a change in silicate source during parts of the Allerød. As opposed to other records from the region, constant sediment accumulation rates were found during the Younger Dryas. Other proxies also suggest that this was a rather static period at Hässeldala Port. A gradual change in productivity and hydrological activity was observed from 12,000 cal year BP. The Preboreal section is rather short but the geochemical response was similar to that seen during other periods with milder climate conditions. The geochemical record archived in the sediments at Hässeldala Port was found to be the integrated result of physical erosion, landscape and soil development, vegetation changes, basin hydrology and moisture and temperature variations and it fills an important information gap in our understanding of the geochemical response of lake sediments to past climate change.

Keywords Lake sediment · Geochemistry · XRF core scanning · Late glacial · Sweden

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Introduction

The deglaciation of the province of Blekinge in southernmost Sweden started approximately ~14,800 cal year BP (Lundqvist and Wohlfarth 2001) and there is a good understanding of how the rapid, short-term climatic

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variations that occurred since the Weichselian Late Glacial have impacted the region. Based on fossil coleopteran assemblages, the maximum mean temperatures of the warmest month are estimated to be in the range of 13–15 °C during the Bølling (Greenland Interstadial, GI-1e), 11–13 °C during the Older Dryas (GI-1d), 9–11.5 °C during the Allerød (GI-1c to 1a) while temperatures fell to below 9 °C during the Younger Dryas (Greenland Stadial, GS-1). The final rise in maximum mean temperatures of the warmest month to above 19 °C occurred during the Preboreal (Holocene) pollen zone (Coope et al. 1998). Vegetation shifts reflect these temperature changes where pollen records show that arctic and sub-arctic species dominate up until the start of the Preboreal when woodland species then begin to colonize the area (Berglund et al. 1994; Björck and Möller 1987; Wohlfarth et al. 2006). In agreement with pollen records, coleoptera studies show largely exposed and unstable minerogenic soils during cold periods and acidic, humus-rich soils during the Allerød and the Preboreal (Lemdahl 1988).

Hässeldala Port is a small in-filled basin located in the province of Blekinge. Sediment accumulation is thought to have started during the early part of the Bølling (Björck and Möller 1987). Previous work on this lake sediment sequence has been focussed on tephrochronology where the Hässeldala Port (for the first time), Borrobol and the 10-ka Askja Tephras have been identified. Total Organic Carbon (TOC) analysis revealed significant variations ranging from 1 % up to 22 % (Davies et al. 2004; Wohlfarth et al. 2006). The pattern of these TOC shifts are characteristic of the lacustrine response to the climate changes occurring in southern Sweden since the last termination where the Allerød and Preboreal are indicated by more organic rich intervals.

How the geochemical signals in the lake sediments archived at Hässeldala Port have responded to the rapid climate shifts occurring since the Late Glacial is unknown. The spatial manifestation of these signals in the sediment record will vary and depends partly on the duration of the event *vis-à-vis* sedimentation rates. Some events appear clearly as stratigraphic changes in the sediment while others are recorded at sub-millimetre scales. If, for example, there is active fluvial transport of material from a rich sediment source to a lake acting over a long time scale, this will be recorded in the sediments over a wide span of sediment depth. Silicate weathering however, is affected by factors that are likely to have varied greatly since the ice margin retreat, including physical erosion rates, presence/depth of soil cover, temperature, mineralogy, runoff and the presence of acids (Anderson 2005; Klaminder et al. 2011; Mavris et al. 2010; Oliva et al. 2003; West et al. 2005; White and Blum 1995); these changes can be expressed on a variety of scales. On the shortest time/depth scale we can consider biogeochemical cycles in the water, which respond rapidly to environmental changes and thereby alter the inputs of elements to the sediment on sub-annual time scales.

The aim of this work is to assess the geochemical response to the climate changes that have occurred since the Late Glacial as recorded in the paleolake sediments at Hässeldala Port in southern Sweden. X-ray fluorescence (XRF) core scanning of the sediment produced an in situ elemental record at a sub-millimetre resolution (Croudace et al. 2006; Francus et al. 2009) allowing for the examination of both small-scale and large-scale elemental variations. High-resolution TOC, C/N and $\delta^{13}C$ analysis provide information on the vegetation/productivity in and around the site. The new organic and inorganic geochemical data is complemented by previously published dating and pollen data and is interpreted here in the context of the already established regional climatic framework. This work fills an important gap in our understanding of how rapid climate changes impact lake sediment geochemistry and links the lacustrine response with what is already known about changes in the landscape, vegetation, paleoproductivity, temperatures and insect populations in the region (Andersson 1997; Andresen et al. 2000; Berglund 1966; Berglund et al. 1994; Björck et al. 2002; Björck 1981; Björck and Möller 1987; Coope et al. 1998; Hammarlund et al. 1999; Ising 1990; Lemdahl 1988; Lundqvist and Wohlfarth 2001; Wohlfarth et al. 2006).

Site description

Hässeldala Port (56°16′N; 15°03′E) is an in-filled lake basin, now covered with birch woodland, in the province of Blekinge, southern Sweden (Fig. 1). This site sits just above the highest shoreline of the Baltic Ice Lake that developed during the Late Glacial. The area is dominated by late Weichselian glaciofluvial deposits and till of varying thickness and morphology with an underlying bedrock of Karlshamn granite. The Karlshamn granite is composed of granites, quartz

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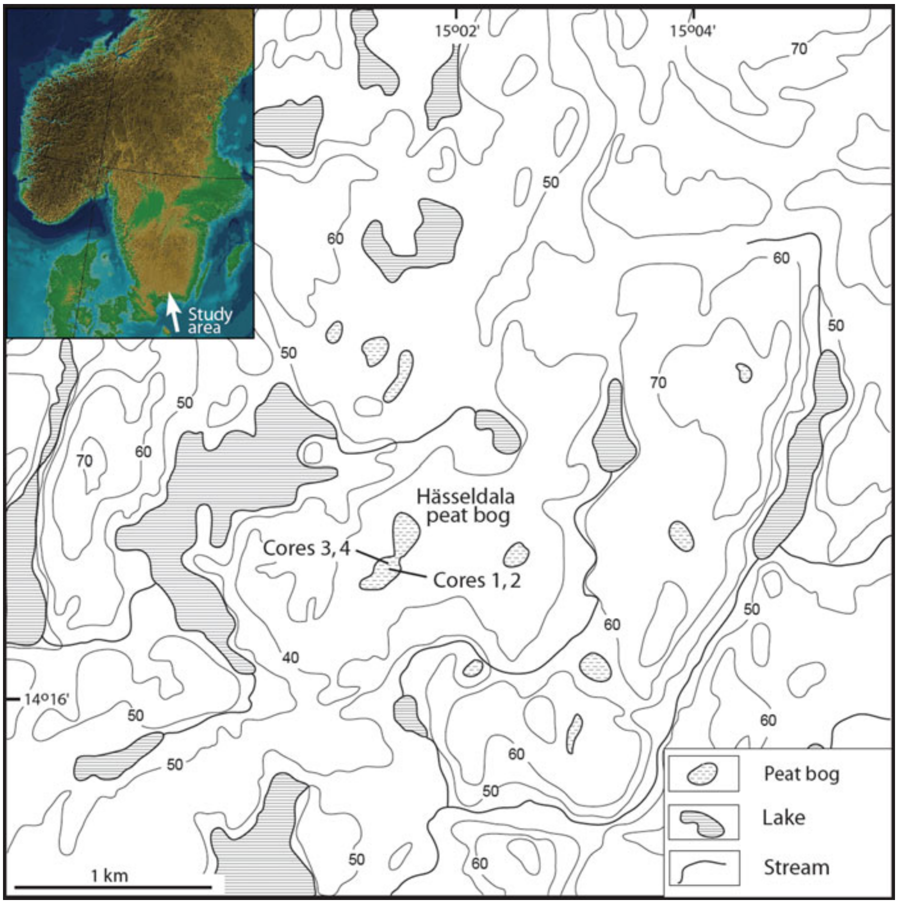

Fig. 1 The location of Hässeldala Port in southern Sweden

monzodiorites and quartz monzonites. This pluton has pockets, both within and surrounding the pluton, of coastal gneiss and granitiods while the area to the north is dominated by granites and granitoids (Čečys and Benn 2007). The province to the south-west of Blekinge, Skåne, is underlain by granites as well as sedimentary rock types, including limestone. Considering the dominance of granites in the region, and elsewhere in southern Sweden, it is assumed that the majority of the till and glaciofluvial material deposited by the Scandinavia ice sheet is granitic in nature.

Materials and methods

Sediment cores have been collected over several years at Hässeldala Port. Hässeldala Port Cores 1, 2 and 3 have mainly focussed on tephra, ^{14}C dating and pollen work, respectively (Wohlfarth et al. 2006). The new geochemical data presented here is from Hässeldala Port Core 4 which was recovered at the same time as Cores 2 and 3 in the autumn of 2002 and covers depths from 3.37 to 4.34 m. Cores were taken using a Russian corer (7.5 cm in diameter, 1 m in length), described and then wrapped in plastic and kept in cold storage until analysis.

Analyses

Prior to any sub-sampling, the sediment core was scanned at the Department of Geological Sciences at Stockholm University using an ITRAX XRF Core Scanner from Cox Analytical Systems (Gothenburg, Sweden). A radiographic image was acquired using a Mo tube set at 50 kV and 55 mA with a step size of 300 μm and a dwell time of 200 ms. XRF analyses was made using a Mo tube set at 30 kV and 20 mA with a step size of 300 μm and a dwell time of 25 s.

Sub-sampling for TOC, C/N and δ^{13}C analyses was made contiguously every centimetre. Analyses were made using a Carlo Erba NC2500 elemental analyzer

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coupled with a Finnigan MAT Delta + mass spectrometer. Samples were treated with 2 N HCl prior to analyses. The relative error for these measurements was <1 %. $\delta^{13}C$ is expressed as δ (‰) relative to the Vienna PeeDee Belemnite standard and measurement reproducibility is better than 0.15 ‰.

Chronology

The chronology of the Hässeldala Port Core 2 was modelled previously based on 28 ^{14}C dates and several tephra layers while pollen assemblages (HÄP 1 to HÄP 7) were established based on analyses from Core 3 (Wohlfarth et al. 2006; Fig. 2). The chronology of Core 4 was inferred by cross-correlation with Cores 2 and 3 based on the lithostratigraphy and TOC values. The calibrated ages for marker horizons were then transferred to Core 4 and the intervening ages were calculated between the tie points assuming constant accumulation.

Results

Five horizons are shown in Fig. 2 and were defined as follows: A (14,600 cal year BP) marks where TOC is at it's lowest; B (14,100 cal year BP) marks the clear upper boundary of Unit H3 which is far more

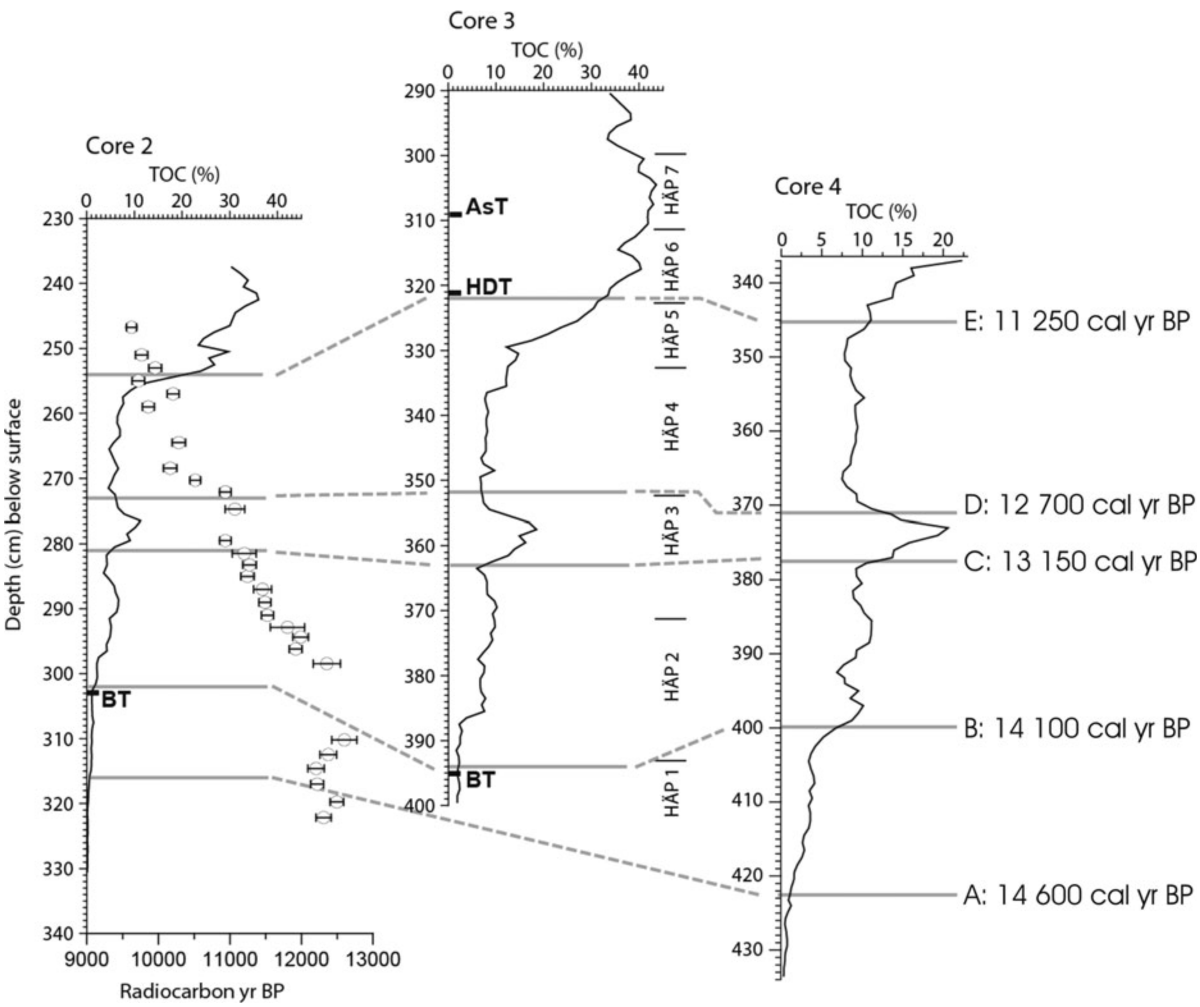

Fig. 2 Correlation of Hässeldala Port Cores 2, 3 and 4 using the TOC stratigraphic marker horizons. The pollen zones from Core 3 as well as the calibrated age dates transferred to Core 4 are shown. Tephra detected in these Cores 2 and 3 include the Borrobol (BT), the Hässeldala Port (HDT) and 10-ka Askja (AsT) Tephras. Core 4 has not been analysed for tephra

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minerogenic than the overlying Unit H4; C (13,150 cal year BP) and D (12,700 cal year BP) bracket the TOC increase in Unit H8 which was visibly more organic than the units above and below during core description; and E (11,250 cal year BP) marks the TOC increase at the top of the core.

The stratigraphy of the retrieved core is similar to that of previous Hässeldala Port cores and units therefore follow the established framework being numbered from H2 to H12 (Wohlfarth et al. 2006). As the penetration depth of the studied core was greater than that achieved at this site prior, two additional sand units are now included. These new sand units are however collectively referred to as Unit H2 rather than assigning a new unit number. The data are discussed using regional pollen zones and lithostratigraphic units of which four are highlighted as organic rich intervals (OI).

TOC, δ13C and C/N

The most significant changes in TOC are highlighted as OI-1 to OI-4 (Fig. 3). TOC values are <1 % in Unit H2 and <6 % in Unit H3. Unit H4 sees an increase in TOC to 10 % centred around 3.97 cm (OI-1). After a decrease in Unit H5 there is another moderate increase in TOC to 11 % in Unit H6 centred on 3.87 m (OI-2). The next major increase to values of 20 % occurs in Unit H8, peaking at 3.73 m (OI-3). Units H9 to H11 have TOC values ~9 % when at 3.48 m a gradual increase in TOC starts and continues until the top of the core reaching a value of 22 % (OI-4). Examination of the radiographic image shows that those intervals with low TOC are higher in density, i.e., more minerogenic (Fig. 3).

$\delta^{13}C$ shows a shift between 4.21 and 4.18 m from a basal mean value of approximately −21 ‰ in Unit H2 to approximately −14 ‰ in Unit H3 (Fig. 3). These values then decrease slightly in Units H4 to H7 to a minimum value of −18.8 ‰ and increase again to −17.0 ‰ in Unit H8. In the remaining units there is little variation in $\delta^{13}C$ values with the exception of a small increase at 3.55 m to −17.2 ‰ and a decrease at the surface of the core to −21.4 ‰. In general the recorded range in Units H7 to H12 is rather narrow falling between −21.4 ‰ and −17.0 ‰. The C/N values in Unit H2 increase from 7.8 at the base to an average value of 13.6 ± 1.3 (2σ, n = 22) in Unit H3.

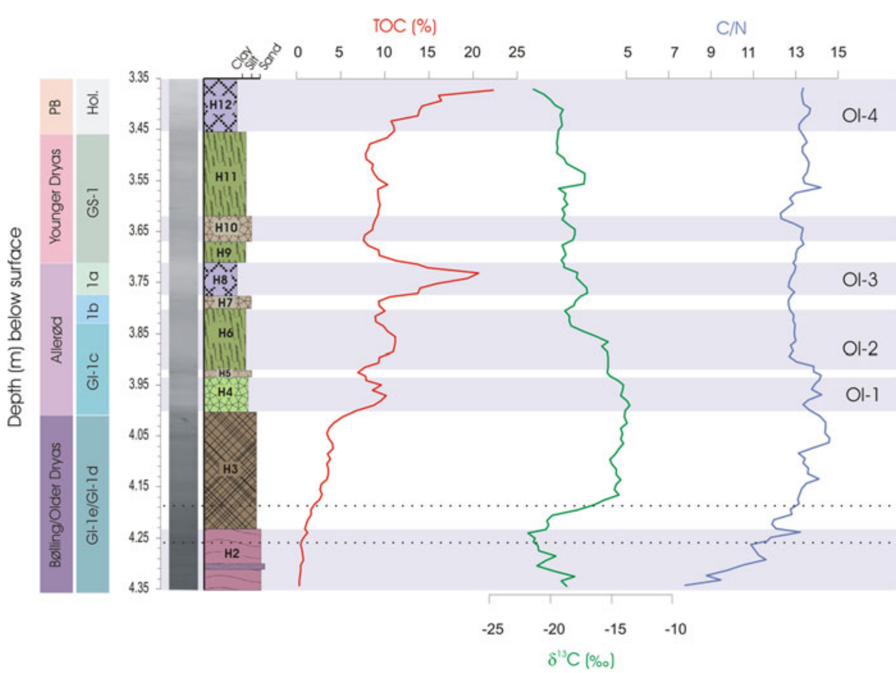

Fig. 3 Regional pollen zones, Greenland ice core event stratigraphy, radiographic image, lithostratigraphy, TOC, $\delta^{13}C$ and C/N variations versus depth for Hässeldala Port Core 4. The four organic rich intervals (O1-1 to OI-4) are indicated as are the two major shifts in Units H2 (at 4.26 m) and H3 (at 4.18 m) (*horizontal dashed lines*)

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C/N values in Units 4 to Unit H12 are stable with an average value of 13.2 ± 0.9 (2σ, n = 64) with only faintly elevated values in Units H4 and H5.

Elemental data

Based on analytical performance (counting statistics), reliable data was acquired for Si, K, Ca, Ti, Mn, Fe, Rb, Sr and Zr. All data presented here are normalized to the (incoherent + coherent) scattering to remove various instrumental effects, and then smoothed using a 10-point running mean to capture the main shifts. In a paleoclimatic context, it is the relative changes in the elemental XRF core scanning profiles, rather than the absolute concentrations, that are of interest. Nonetheless, an approximation of the average elemental concentrations can be made using the built-in quantification feature in the Q-Spec software. The sum spectra, which is an average of all the spectra measured on the core, is the basis of this calibration since it has better counting statistics than the individually measured spectra. Two different calibration standards were tested (USGS SGR-1 Green River Shale and SCo-1 Cody Shale) with resulting average concentrations for each element (using either of the standards) of: Si: 2.6 %, K: 0.42 %, Ca: 0.14 %, Ti: 43 ppm, Mn: 3.3 ppm, Fe: 0.35 %, Rb: 17 ppm, Sr: 3.6 ppm while Zr: 18 ppm. These values are equal to the following average scattering normalized peak areas and indicated by the dashed vertical line (where applicable) in Fig. 4: Si: 0.0032, K: 0.024, Ca: 0.025, Ti: 0.020, Mn: 0.0062, Fe: 0.845, Rb: 0.017, Sr: 0.039 and Zr: 0.046.

The depth profiles of Ti, Si, K, Ca and Zr show the same broad pattern found for all the studied elements (Fig. 4). Specifically, elemental peak areas are highest at the base of the profile with several small peaks overlaying a long-term decreasing trend that continues up to the end of Unit H3 at 4.00 m. The profiles for Ca, Zr (Fig. 4), Sr, Mn and Fe (not shown), do however show a more distinct shift at 4.19 m. From 4.00 m up to 3.37 m, peak areas are rather constant, decreasing slightly during OI-1 to OI-4. This decrease is caused by organic matter dilution and the data must be handled with consideration to the changes in TOC.

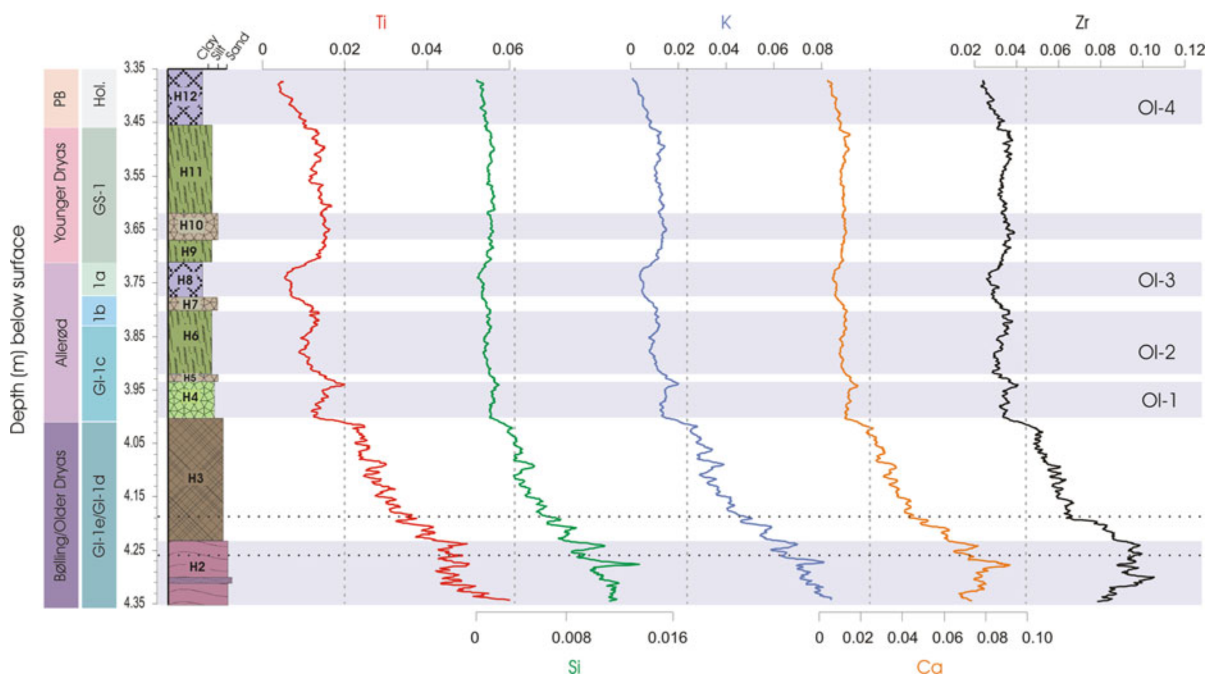

Fig. 4 Regional pollen zones, Greenland ice core event stratigraphy, lithostratigraphy and depth profiles for Ti, Si, K, Ca and Zr which are broadly representative of all the studied elements. The *dashed vertical line* represents the average scattering normalized peak areas. The four organic rich intervals (O1-1 to OI-4) are indicated as are the two major shifts in Units H2 (at 4.26 m) and H3 (at 4.18 m) (*horizontal dashed lines*)

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Elemental correlations and ratios

In a correlation matrix made using the scattering normalized elemental data, nearly every elemental pair had r values of 0.81 or greater. This agreement is an artefact of the significant TOC shift occurring between Units H2-H3 and Units H4-H12. Given the effect of organic matter on the elemental profiles, the data were normalized by a conservative, lithogenic element in order to reveal changes that would otherwise be masked by dilution (Löwemark et al. 2011). In this case Ti was selected because of its analytical quality, its conservative nature during transport and weathering and the fact that it is not biologically important. The depth profiles for Si/Ti, K/Ti, K/Rb and Zr/Ti are shown in Fig. 5. The Si/Ti profile is similar to the elemental profiles with a decreasing trend from the base to 4.00 m and then reduced variation between 4.00 and 3.45 m with an average value of 0.91 ± 0.03 (2σ, n = 544). At the very top of the profile there is a small increase to 0.18. Decreases in Si/Ti occur in Unit H2 at 4.26 and 4.18 m. K/Ti ratios show a long-term decreasing trend that begins at 4.26 m and continues up to 3.71 m. From 3.71 to 3.45 m the K/Ti ratio stays rather constant with an average value of 0.91 ± 0.09 (2σ, n = 165). In the remaining portion of the profile the same decreasing trend as in Units H3 to H8 is resumed. The K/Rb profile is similar to that of K/Ti with a long-term decreasing trend for most of the core that starts at 4.26 m and is interrupted between 3.71 and 3.45 m.

The ratio of Zr/Ti differs in pattern to the other ratios having a baseline value of ~2.5 with excursions occurring during the organic rich intervals. These changes in the Zr/Ti ratio increase in each successive organic interval up the profile. When performing in situ XRF analyses it is important to consider matrix effects on the elemental peak areas. Light elements like Ti are more affected by matrix effects than heavy elements like Zr. In most sediments the importance of matrix effects is assumed to be small and the peak area ratios can reasonably be assumed to be linearly related to concentration ratios. At Hässeldala Port however, TOC varies by some 20 %, which can cause variable attenuation of the Ti signal. As such, the Zr/Ti ratio in the organic-rich intervals can change without any

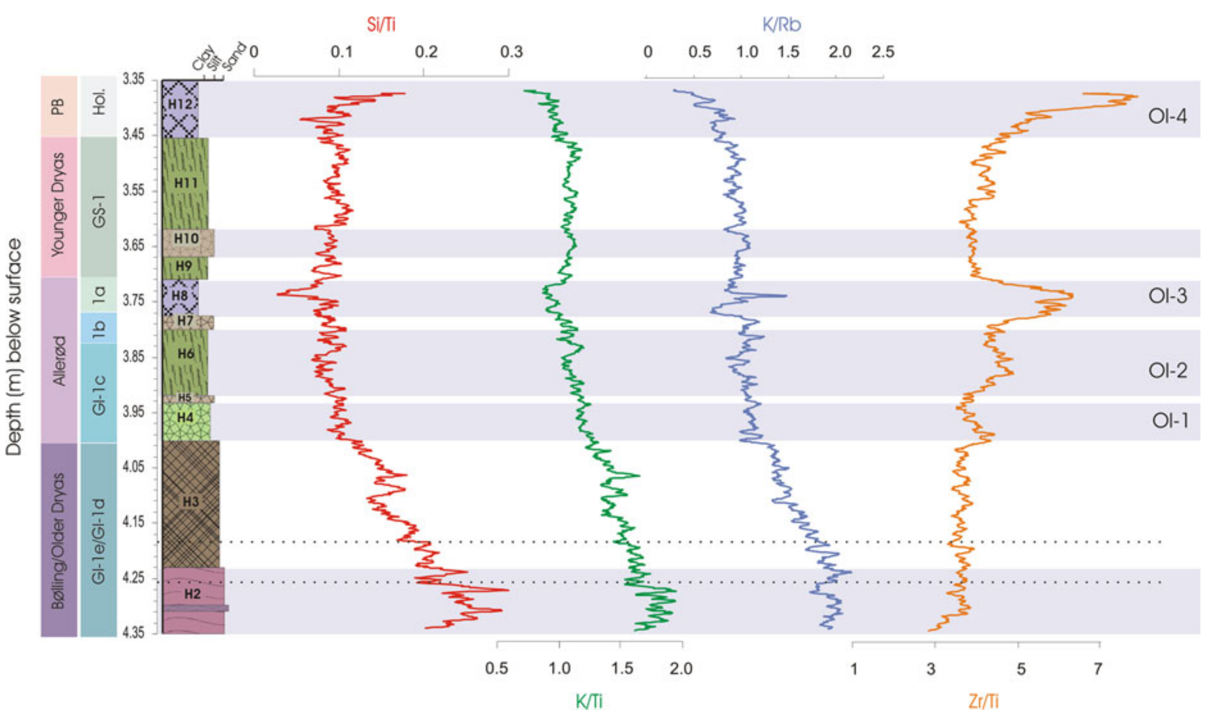

Fig. 5 Regional pollen zones, Greenland ice core event stratigraphy, lithostratigraphy and depth profiles for Si/Ti, K/Ti, K/Rb and Zr/Ti. The four organic rich intervals (O1-1 to OI-4) are indicated as are the two major shifts in Units H2 (at 4.26 m) and H3 (at 4.18 m) (*horizontal dashed lines)*

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change in the elemental concentration ratios. It is not possible with the present data to say how important or in which way TOC variation is affecting Zr/Ti ratios but in most cases the peak area ratio will change in parallel to the concentration ratio. Given the fact that we are well above instrumental detection limits and that we have large peak areas (>1,000) for both elements even in the most organic rich intervals, we assume that the direction of change in peak area ratio follows that of the elemental concentration ratio but that the magnitude of the change should be interpreted with care.

The Ca/Ti profile shows the familiar pattern of a decreasing trend from the base up to 3.90 m with two shifts at 4.26 and 4.18 m (Fig. 6). Two small increases occur in OI-2 and OI-3 followed by a decrease to the profile low of 0.75 at 3.68 m. This is followed by an increasing trend to the top of the core. In general, Sr/Ti ratios in Units H2 and H3 vary around a value of 2.2 with a shift occurring between 4.26 and 4.18 m. From 4.04 m Sr/Ti begins a long-term rise and fall that reaches similar values again at 3.45 m. Mn/Ti ratios show a first major shift at 4.18 m and in varies around a value of ~0.30. At 3.82 m where there is a decrease prior to a significant increase to 0.48 at 3.77 m which is followed by a decrease to 0.01 at 3.73 m. From 3.71 to 3.45 m there is a gradual increase, punctuated only by a decrease at 3.42 m, which continues to the surface of the core. The Fe/Ti ratios are an exact mirror to the Mn/Ti ratios, decreasing at every major Mn/Ti increase and vice versa.

Discussion

Processes controlling sediment geochemistry

Post depositional processes

The geochemistry of the analysed sediments is controlled by the chemistry of the initially deposited sediment as well as post-depositional processes. Post-depositional diffusion is unlikely to be an important driver of the sediment geochemistry at Hässeldala Port

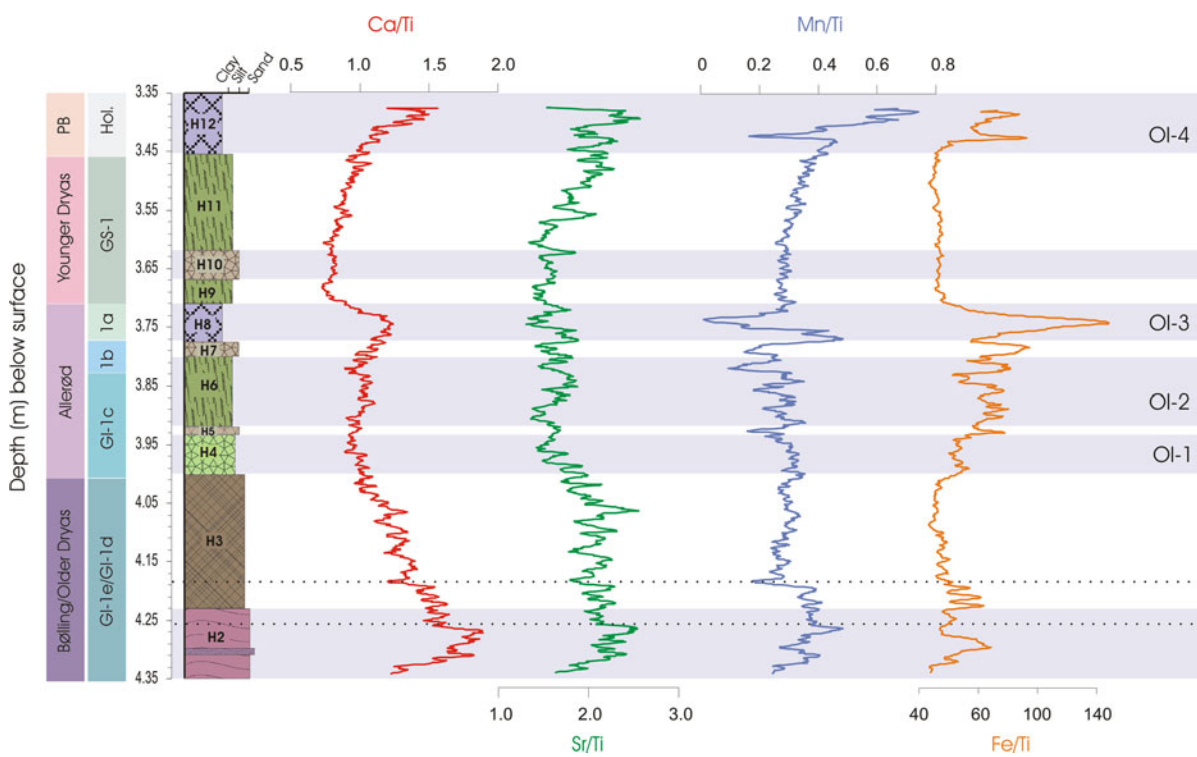

Fig. 6 Regional pollen zones, Greenland ice core event stratigraphy, lithostratigraphy and depth profiles for Ca/Ti, Sr/Ti, Mn/Ti and Fe/Ti. The four organic rich intervals (O1-1 to OI-4) are indicated as are the two major shifts in Units H2 (at 4. 26 m) and H3 (at 4.18 m) (*horizontal dashed lines*)

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considering that large peak area gradients (Fig. 4) and ratio gradients (Figs. 5, 6) have been preserved at a mm-scale in the sediment for >10,000 years. This interpretation is supported by a recent study showing that post-depositional diffusion of cations (^{137}Cs) ceased after a decade in varved sediment and that peak concentrations generated by accelerated inputs to the sediment remained visible decades after deposition (Klaminder et al. 2012). Therefore, the variation in sediment geochemistry in the studied record is mainly interpreted to be a result of variable sediment inputs from terrestrial and aquatic sources, biotic processes active in the catchment and variable particle sorting of the sediment. These processes themselves reflect, and are responding to, paleoenvironmental changes.

Silicate inputs

Zirconium and Ti do not play a role in biotic processes and are mainly found in weathering resistant silicate minerals such as zircon and rutile, respectively (Brady 1990). Changes in these elements are thus mainly a result of temporal variations in silicate mineral inputs to the lake basin, which can be caused by selective transport-depositional processes affecting the size and properties of the deposited minerals or by an altered balance between mineral sources in the catchment. Zirconium is normally enriched in medium to coarse silts while Ti is associated with finer fractions (Taboada et al. 2006) which means that increases in the Zr/Ti ratio may be indicative of less clay or more silt. Sorting of these particles is driven by a multitude of processes such as hill-slope transport, geomorphological developments of channels in the catchment and sediment focusing. We observe however, that the Zr/Ti ratio is fairly constant during the Bølling/Older Dryas and Younger Dryas, despite the differences in the sand, silt and clay contents (Fig. 5). As such we use this ratio as a proxy for alterations in silicate sources in the Hässeldala Port catchment.

Sand fractions are typically enriched in Ca, Sr, K and Si because of the dominance of feldspars and quartz, and thus have high Si/Ti, K/Ti and K/Rb ratios. Decreasing Si/Ti, K/Ti and K/Rb ratios towards the upper part of the core as the sediment becomes younger and more clay-rich (Fig. 5) is thus, most likely a result of sediment fining. In line with this interpretation, modelling efforts have illustrated that variable particle size of the settling sediment plays a more important role for the sediment geochemistry than decreasing weathering rates (Boyle 2007). This fining is also evidenced in Ca/Ti and Sr/Ti ratios in Units H2 and H3 but as the lake system develops these ratios begin to reflect other processes as described below.

Grain size, organic matter inputs and carbonate dynamics: Ca and Sr

In the Hässeldala Port record the Ca/Ti ratio responds to the environmental changes related to the transitions between climate zones (Fig. 6). Ca/Ti and, to some degree, Sr/Ti ratios decrease when moving from warmer to colder periods, namely from Unit H6 to H7 (roughly mid-Allerød to the Gerzensee oscillation) and Unit H8 to H9/H10/midway into H11 (roughly the late Allerød to the mid-Younger Dryas). Correspondingly, these ratios increase when moving from cold to warm periods as in Unit H7 to H8 (Gerzensee oscillation to the late Allerød) and in the upper portion of Unit H11 to H12 (mid-Younger Dryas to the Preboreal).

Calcium and Sr in lake sediments are related to silicate and carbonate weathering in the catchment, inputs of organic matter and in-water precipitation of $CaCO_3$ with co-precipitation of $SrCO_3$. The latter is driven biologically through algal fixation of CO_2 or abiotically when lake waters reach the point of carbonate saturation (Cohen 2003). Normalization by Ti eliminates the influence of silicate mineral input to the lake so variations in Ca/Ti and Sr/Ti ratios can be a signal of: (i) changed primary mineral inputs as a result of altered catchment sources or sizes of settling sediment particles; (ii) deposition of secondary formed minerals, i.e. authigenic formed carbonates; (iii) deposition of Ca-containing organic matter low in Ti; or (iv) some combination of these.

The data show that as the lake develops over time, the importance of these different mechanisms changes. As mentioned previously, in Units H2 and H3 the Ca/Ti and Sr/Ti ratios show a similar behaviour ($r = 0.66$) and are likely to be largely controlled by changes in grain size (Fig. 6). When TOC values start to increase however, the correlation between these two ratios falls ($r = 0.51$) suggesting that other processes not common to both elements become more important. Indeed, in Units H4-H12 the correlation between Ca/Ti and TOC is high ($r = 0.70$) while that between Sr/Ti and TOC is low ($r = 0.13$), suggesting that

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organic matter plays an important role in Ca changes in the sediment. In light of this relationship, the changes in Ca/Ti in Units H4-H12 must be largely driven by biological calcification and/or organic matter production and consequent deposition. The strong relationship between TOC and Ca/Ti speaks for the latter process dominating but it must be considered that Sr/Ti and Ca/Ti still show some similarities in behaviour; this could indicate some endogenic carbonate production. Thus at Hässeldala Port, the response of the Ca/Ti ratio is ultimately a gauge of the relationship between biological productivity and physical erosion in the catchment.

Redox conditions: Mn, Fe and $\delta^{13}C$

The organic $\delta^{13}C$ bulk sediment record at Hässeldala Port is unusual in its heavy isotopic signal. In lake systems algae tend to have $\delta^{13}C$ signatures around −20 ‰ while terrestrial carbon has $\delta^{13}C$ ratios around −28 ‰ (Meyers and Ishiwatari 1995). At the base of the profile in Unit H2 signatures are roughly −21 ‰ but then show a 7 ‰ increase to around −14 ‰ (Fig. 3). This shift is opposite to that expected when considering the vegetation succession at Hässeldala Port; $\delta^{13}C$ should decrease as more C3 plants colonize the area. The C/N data indicate that in Unit H2 aquatic species dominate, but in Unit H3 this shifts to some mix between aquatic and terrestrial vegetation and remains so throughout the rest of the record.

Given the clear trend in the profile, the possibility that this is analytical noise can be excluded. If this were the case, the signal would be more random in nature. These results were double-checked in another Hässeldala Port core and both acid treated and untreated samples gave similarly heavy $\delta^{13}C$ results. One of the only ways to generate such heavy $\delta^{13}C$ signatures is through anaerobic decomposition of sedimentary organic matter (methanogenesis) where isotopically depleted CH_4 is produced and released via diffusion and ebullition processes, leaving behind the isotopically enriched CO_2 in the sediment (Gu et al. 2004).

When reconstructing paleoclimate Mn and Fe variations are often of secondary interest because post-depositional mobilization can overprint the climatic signal. At this site however these elements can however help to establish if the sediments were indeed anoxic. The fact that the Mn/Ti ratio is the reverse of the Fe/Ti ratio throughout the core (Fig. 6) is a strong indication that reduced iron species (Fe^{2+}) have served as an important electron donor in the reduction of Mn during lake sediment diagenesis, as often occurring in marine sediments and laboratory environments (Haese 2006; Van Der Zee et al. 2005). This reaction produces Mn^{2+} ions that are highly mobile in sediments simultaneously converting mobile Fe^{2+} iron species into Fe^{3+} ions that form more immobile complexes in the sediment. Consequently, the reduction of Mn and oxidation of Fe species stimulates the release of the former from the sediment at the same time as it maintains Fe in the sediment. Favourable conditions for this process are anaerobic, and the sediment underlying the largest variations in Fe/Ti and Mn/Ti peaks (Ol-3 and Ol-4) have, as previously argued, $\delta^{13}C$ signatures indicating active methanogenesis and thus favourable conditions for dissimilarity reduction of Fe and Mn species.

Paleoclimatic context

The Bølling/Older Dryas pollen zone (GI-1e/GI-1d)

After the retreat of the ice sheet margin the landscape was a patchwork of stagnant ice, water, unstable cryoturbated mineral soils, scattered vegetation and unconsolidated glacial sediments (Björck and Möller 1987; Lemdahl 1988). Sediments at the bottom of the core from 4.35 to 4.00 m accumulated during this time and are composed of two main units, Units H2 and H3, where fine sands dominate. A rough estimate of accumulation made using the available age model sees the highest accumulation rates occurring in Units H2 and H3 (0.51 and 0.46 mm $year^{-1}$, respectively). The long-term decreasing trend in peak areas (Fig. 4) as well as the greater accumulation rates in Unit H2 and H3 suggests an initially high influx of material to the basin, which declines as sediment supply decreases and the landscape stabilizes. This decreasing sedimentation co-occurs with a progressive fining of the material as indicated by the decreasing Ca/Ti, Sr/Ti, Si/Ti, K/Ti and K/Rb ratios (Figs. 5, 6), which is an expected outcome as the landscape stabilizes. Given the low variability of the Zr/Ti ratio, it appears that the balance between silicate sources in the catchment remained unchanged during the Bølling/Older Dryas.

Two significant shifts are more noticeable in Units H2 and H3 expressed in both the elemental peak area and ratio profiles. One of these shifts occurs at 4.26 m

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(ca 14,660 cal year BP) and is recorded in Ca, Si/Ti, K/Ti, Ca/Ti, and Sr/Ti (Figs. 4, 5, 6). These ratios are all linked to sands and larger grain sizes and the drop in the elemental peak areas and ratios of these cations in the lake sediment record is abrupt. This suggests that a given sediment source was rapidly exhausted and/or that a change in hydrology occurred such as the final melting of stagnant ice in the catchment during the relatively mild Bølling (Coope et al. 1998).

The second major feature of Units H2 and H3 is the change in sediment geochemistry occurring at 4.18 m (ca 14,500 cal year BP). There is a decrease in the Mn/Ti ratios (Fig. 6) and an increase in the $\delta^{13}C$ ratio (Fig. 3). These changes suggest that the sediment in this section has been exposed during anoxic conditions favouring mobility of Mn and methanogenesis in contrast to that of the early stage of the H2 unit. Ice cover and organic matter content are important drivers of methanogenesis in lakes (Wetzel 2001) and increased inputs of terrestrial carbon in combination with long ice-covered winters was likely important for forming anoxic conditions at this time.

Leading up to the start of the Allerød pollen zone there is no clear evidence in the elemental geochemistry, TOC, C/N or $\delta^{13}C$ data of the Older Dryas. This is similar to a recent record from southern Jutland, Denmark where they found that the vegetative response to the Older Dryas was slight (Mortensen et al. 2011). The pollen record from Hässeldala Port Core 3 shows that just prior to the Allerød *Salix* and *Rumex* are important species (Wohlfarth et al. 2006) which can be an indication of relatively moist soils (Björck and Möller 1987). Evidence of ice wedge formation during the Older Dryas (Berglund et al. 1994; Björck and Möller 1987; Rapp et al. 1986) and hence, permafrost, exists in southern Sweden. At Hässeldala Port the presence of the Baltic Ice Lake may however have precluded the possibility of permafrost by modulating winter temperature extremes. Nonetheless cool summers and shorter growing seasons are likely during this time (Björck and Möller 1987). In the presence of waterlogged and/or frozen soils a decrease in sedimentation and thus reduced peak areas like those observed at the end of the Bølling/Older Dryas zone would be expected. Therefore, in contrast to the record from southern Jutland in Denmark where locally dry conditions were established (Mortensen et al. 2011), the Hässeldala Port record suggests that conditions were not overly arid on the Blekinge coast.

The Allerød pollen zone (GI-1c to GI-1a)

After the Older Dryas, the climate amelioration drove the replacement of herbs and grasses by *Juniperus* and trees which included birch and pine (Wohlfarth et al. 2006). The arrival of *Empetrum* at Hässeldala Port later in the Allerød (Fig. 2, HÄP 3, Hässeldala Port Core 3) during the cold Gerzensee oscillation (GI-1b) event in southern Scandinavia signals that tundra soils were forming and were stable (Berglund 1966) which has also been suggested by coleopteran work (Lemdahl 1988). The colonization by *Empetrum* may be an effect of the opening of the birch forest during the Gerzensee oscillation allowing for this light-demanding shrub (Andresen et al. 2000). There is some evidence of permafrost during the Gerzensee oscillation in southern Sweden (Berglund et al. 1994) although the identification of pine and birch pollen at Hässeldala Port speaks against this. While the presence of the Baltic Ice Lake may have precluded the possibility of permafrost as mentioned previously (Björck and Möller 1987), a maximum mean temperature of the warmest month based on fossil coleopteran assemblages is in the range of 9–11.5 °C during the Allerød (Coope et al. 1998). These temperatures would see cryogenic processes playing some role in sedimentation regardless of whether permafrost was present or not.

The units that comprise the Allerød pollen zone (GI-1c to GI-1a) vary in composition from gyttja silt to silt gyttja to gyttja (Units H4-H8). This is reflected in the TOC profile where there is an increase in Unit H4 (OI-1, ca 14,100–13,800 cal year BP), H6 (OI-2, ca 13,670–13,370 cal year BP) and H8 (OI-3, ca 13,150–12,700 cal year BP) while intervening layers are darker on the radiographic image, i.e., more minerogenic (Fig. 3).

Accumulation rates during the Allerød are rather stable (0.23 mm year^{-1} in Unit H4 and H5, 0.22 mm year^{-1} in Unit H6) until the Gerzensee oscillation where they increase to 0.35 mm year^{-1} (Unit H7) and then decrease to 0.16 mm year^{-1} at the end of the Allerød (Unit H8). During this period the fining of the sediment seems to cease as indicated by the fairly stable Si/Ti, K/Ti and K/Rb ratios. The most remarkable feature of the Allerød portion of the record is the three step-wise increasing TOC peaks (OI-1 to OI-3; Fig. 3). While the increased Zr/Ti ratios are interpreted with caution during these OI intervals, the

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detected variations in this ratio suggest that a change in silicate source is likely (Fig. 5). Enhanced or changed hydrological transport from the catchment soil during these periods can account for the inferred changes in silicate sources. This would also explain the increased TOC in the sediment (Fig. 3) as well as the increased Ca/Ti ratios during these OI intervals (Fig. 6), both generated through increased in-wash of terrestrial plant material. The increased TOC and Ca/Ti ratios could also partly explained by increased with-in lake productivity and biologically induced carbonate precipitation. Interestingly, the decreasing $\delta^{13}C$ ratio trend towards less methanogenic values have its onset in the middle of the Allerød, suggesting that altered hydrological conditions and within lake production could to some extent be generated by longer ice–free conditions.

The Younger Dryas (GS-1)

At Hässeldala Port the Younger Dryas sees a shift towards more herbs and shrubs, an increase in birch and a decrease in *Empetrum* and pine (HÄP 4; Wohlfarth et al. 2006). The decrease in *Empetrum* has been associated with soil disturbance linked to this climate deterioration. There is again evidence of ice wedge formation and thus, permafrost, in southern Sweden but in Blekinge this is not observed; this is again likely an effect of the Baltic Ice Lake that prevented low winter temperature extremes. The Baltic Ice Lake also kept summer temperatures cool with a short growing season (Björck and Möller 1987; Hammarlund et al. 1999). Maximum mean temperature of the warmest month based on fossil coleopteran assemblages are below 9 °C (Coope et al. 1998). Soil development, which is affected by similar integrated factors as chemical weathering, was reportedly hampered during the Younger Dryas in southern Jutland, Denmark (Mortensen et al. 2011). Younger Dryas records from the region suggest that this is a period with increased erosion (Andresen et al. 2000; Hammarlund et al. 1999) but this is not readily obvious at Hässeldala Port; minerogenic additions are rather constant ($\sim$0.23 mm year^{-1}).

At Hässeldala Port the Younger Dryas (GS-1) is marked by a drop in TOC values to $\sim$9 % and units of silt gyttja (Units H9 and H11) and gyttja silt (Unit H10; Fig. 3). On the whole the proxies for particle size and silicate sources are relatively static (Fig. 5). However, there is a slight steady increase in Zr/Ti, Ca/Sr, Sr/Ti and Mn/Ti from midway (3.57 m, ca 12,000 cal year BP) into the Younger Dryas to the beginning of the Preboreal (Figs. 5, 6). This implies a progressive change from the mid-younger Dryas in conditions in terms of source and/or hydrology and productivity as compared the conditions at the start of the Younger Dryas. The start of this gradual change is also marked in TOC, C/N and $\delta^{13}C$ data by a short excursion. This mid-Younger Dryas change has also been recorded elsewhere in southern Sweden in the form of increased terrestrial pollen influx (Björck and Möller 1987; Ising 1990) and increases aquatic productivity as inferred by $\delta^{13}C$ records (Hammarlund et al. 1999).

The Preboreal (Holocene)

During the Preboreal at Hässeldala Port *Empetrum*, *Juniperus* and pine return (HÄP 5; Wohlfarth 1996) suggesting more stable soils. The Hässeldala Port Core 4 contains a very short section from the Preboreal with an estimated age of 11,200 cal year BP at the top of the core. Similar to the other organic intervals Ca/Ti, Sr/Ti, Ca/Sr, Mn/Ti and Fe/Ti all increase. Indeed, there is a strong similarity in the signals captured from the Gerzensee/Late Allerød (GI-1b/GI-1c) and the Younger Dryas/Preboreal (GS-1/Holocene) transitions. There is no significant signal that could be associated with the Preboreal Oscillation as it would be expected that the above ratios would decrease.

Conclusions

High-resolution in situ elemental analyses from the Hässeldala Port record explores for the first time the response of the sediment geochemistry in a lake system during the rapid climate shifts that have occurred in southern Sweden since the Late Glacial. Several site-specific geochemical proxies were examined in order to determine silicate inputs (Zr/Ti, Si/Ti, K/Ti and K/Rb), productivity (TOC, Ca/Ti and Sr/Ti), as well as redox conditions during the past ($\delta^{13}C$, Mn/Ti and Fe/Ti). These proxies show that the sediment was subject to variable silicate inputs (source and grain size), conditions for methanogenesis and catchment productivity. These changes were linked to the established climatic framework of the region and

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allow insight into the geochemical response of lakes to climate change.

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