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Climate dependent diatom production is preserved in biogenic Si isotope signatures

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Abstract. The aim of this study was to reconstruct diatom production in the subarctic northern tip of the Baltic Sea, Bothnian Bay, based on down-core analysis of Si isotopes in biogenic silica (BSi). Dating of the sediment showed that the samples covered the period 1820 to 2000. The sediment core record can be divided into two periods, an unperturbed period from 1820 to 1950 and a second period affected by human activities (from 1950 to 2000). This has been observed elsewhere in the Baltic Sea. The shift in the sediment core record after 1950 is likely caused by large scale damming of rivers. Diatom production was inferred from the Si isotope composition which ranged between δ^{30} Si -0.18 ‰ and +0.58 ‰ in BSi, and assuming fractionation patterns due to the Raleigh distillation, the production was shown to be correlated with air and water temperature, which in turn were correlated with the mixed layer(ML) depth. The sedimentary record showed that the deeper ML depth observed in colder years resulted in less production of diatoms. Pelagic investigations in the 1990's have clearly shown that diatom production in the Baltic Sea is controlled by the ML depth. Especially after cold winters and deep water mixing, diatom production was limited and dissolved silicate (DSi) concentrations were not depleted in the water column after the spring bloom. Our method corroborates these findings and offers a new method to estimate diatom production over much longer periods of time in diatom dominated aquatic systems, i.e. a large part of the world's ocean and coastal seas.

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1 Introduction

Dissolved silicate (DSi) is an essential nutrient for diatoms, which play an important role in regulating the uptake and fate of C and N in the world oceans (Smetacek, 1998). Diatom dynamics is an effective measure of environmental change due to its sensitivity to a variety of physical and ecological conditions. In high-latitude ecosystems of the subarctic and arctic region, climate fluctuations on short growing seasons for diatoms may lead to major biological influences (Ding et al., 2011). After diatom death and cell lysis, the siliceous cell walls of diatoms can be well preserved in sediments. This allows for the reconstruction of diatom production by analysis of the preservation of biogenic silica (BSi) over time (Conley and Schelske, 2002). BSi has been used previously to track climate-related changes in aquatic production over millennial time scales (Blass et al., 2007; Rosén et al., 2000). Recently, the lacustrine BSi flux was used to reconstruct air temperature with decadal resolution back to 1580 CE in the Swiss Alps (Blass et al., 2007) and also to quantitatively infer summer temperature for the past 2 kyr in South-Central Alaska (McKay et al., 2002).

The discovery of Si isotopic fractionation of about -1.1 ‰ during formation of diatom cell walls (De La Rocha et al., 1997) has provided a proxy for investigation of diatom-related processes. Many other studies have shown that isotopic fractionation is independent of temperature, inter-species effect and the partial pressure of CO_2 (De La Rocha et al., 1997; Milligan et al., 2004; Varela et al., 2004). Hence, variations in the δ^{30}Si values of diatoms are therefore related to DSi utilization efficiency in water during diatom production and can provide information on the role of the biological pump (the transport of C into deep water body and the regulation of atmospheric concentrations of CO_2) in paleoclimatic and paleoceanographic studies (Brzezinski et al., 2002; De La Rocha et al., 1998; De la Rocha, 2006; Beucher et al., 2007; van den Boorn et al., 2010), but also ongoing environmental changes (Reynolds et al., 2006; Brzezinski et al., 2001; De La Rocha et al., 2000; Cardinal et al., 2005; Wille et al., 2010). For example, DSi utilization efficiency in the Baltic Sea is also controlled by environmental conditions such as the supply of macronutrients (N, P, Si) and light which are functions of the physical mixing regime of the upper water column (Wasmund et al., 1998). The physical mixing regime is a function of local wind and temperature conditions and overall climate. The Si isotope signature of sedimentary BSi could therefore be a potential tracer for climate variation.

In this study we report an application of Si isotope analyses of diatoms to reconstruct diatom production variability from 1820 to 2000 in the subarctic Bothnian Bay. The studied period can be divided into an unperturbed period from 1820 to 1950 and a perturbed period from 1950 to 2000.

2 Study site

Bothnian Bay (235 499 km^2), located between the latitude 63.5° N and 66° N, is the northern portion of the Baltic Sea (Fig. 1). The area has been subjected to recurring ice ages. The last permanent ice melted from the area about 9300 yr ago. The average depth of the bay is 43 m and its maximum is 147 m. The catchment area is sparsely populated and consists mainly of forest, wetland, other natural areas and only a small amount (∼1 %) of agriculture land. The total water volume of the Bay is about 1500 km^3 which is 7 % of the total water volume of the Baltic Sea. Total water discharge into Bothnian Bay is 97 km^3 yr^{-1} (Humborg et al., 2008) and, 60 % of the water is derived from rivers regulated by dams. River regulation started at the beginning of the 20th century and continued until ca. 1960, with most of the dam construction between 1940 and 1960, e.g. on the Kemijoki and Luleå River (Humborg et al., 2006). A consequence of which is a decrease in fluxes of weathering related elements such as base cations and Si (Humborg et al., 2002, 2000) due to changes in water pathways through the catchments and particle trapping of BSi behind dams (Humborg et al., 2006). This has ultimately led to a decreased DSi load in the Northern Baltic Sea (Humborg et al., 2007).

Temperature variations in the water column are >15 °C annually. Formation of a winter ice cover in Bothnian Bay starts between the beginning of October and the end of November. The entire bay is generally covered by ice even during the mildest winters and the ice cover is often maintained for more than 120 days per year. During the years 1961–1990, the summer (ice-free period) average maximum surface temperature in the open sea is above 16 °C (Haapala and Alenius, 1994). A surface thermocline in Bothnian Bay develops about a month earlier than in the other sub-basins of the Baltic Sea and lasts for about three months. Mean DSi concentrations in Bothnian Bay observed between 1970–2001 are 31 µM in winters and decrease to an average concentration of 23 µM in summers (Danielsson et al., 2008). Residence time for DSi is approximate 3.3 yr (Papush et al., 2009).

3 Materials and methods

3.1 Sediment core

A short sediment core (∼38 cm) taken at a depth of 112 m in Bothnian Bay, Station 263870 (64°33.581 N and 21°54.769 E, Fig. 1) was sliced into 1 cm sections and freeze-dried. This core was dated and sediment accumulation rates were determined by analysing ^{210}Pb (46.51 keV), ^{214}Pb (351.99 keV) and ^{137}Cs (661.63 keV) on an EG&G ORTEC® co-axial low energy photo spectrometer (LEPS) with a high-purity germanium crystal. Each sediment section was measured for 2 to 3 days after having been left standing for 2 weeks to achieve radionuclide re-equilibrium of decay products. Thereafter, the externally calibrated standard (pitchblende, Stackebo, Sweden) was added to 5 of the already measured samples at different depths to determine the relatively efficiency of the gamma detector system. The sedimentation rate was calculated by Eq. (1):

$$^{210}\mathrm{Pb}_x = {}^{210}\mathrm{Pb}_0 \cdot e^{-\lambda t} \tag{1}$$

where $^{210}\mathrm{Pb}_x$ is the activity of ^{210}Pb per mass weight of sample at depth x, $^{210}\mathrm{Pb}_0$ is the activity of ^{210}Pb at the surface ($x = 0$), λ is the decay constant of ^{210}Pb (0.0311 yr^{-1}), and t is the age of the sediment sample. The BSi content in sediments was determined using the method described by Conley and Schelske (2002).

3.2 Diatom extraction

The method used for extraction of diatoms from the sediment was modified from Morley et al. (2004). Organic carbon was removed from each sediment slice by repeated mixing with 20 ml 15 % H_2O_2 followed by incubation for 12 h and then heating to 90 °C until no bubbles were evident after subsequent addition of H_2O_2. Addition of 10 ml 10 % HCl and allowing the reaction to proceed for several hours removed inorganic carbon. There was relatively little inorganic carbon, <0.1 %, in most of the samples. The samples were washed 3 times at each step using MilliQ-e water and centrifuged between each wash. Thereafter each sample was sieved through a 10 µm sieve cloth and an 80 µm steel mesh to recover the 10–80 µm fraction and to remove silt and clay. The 10–80 µm fraction contained most of the diatoms. Purity

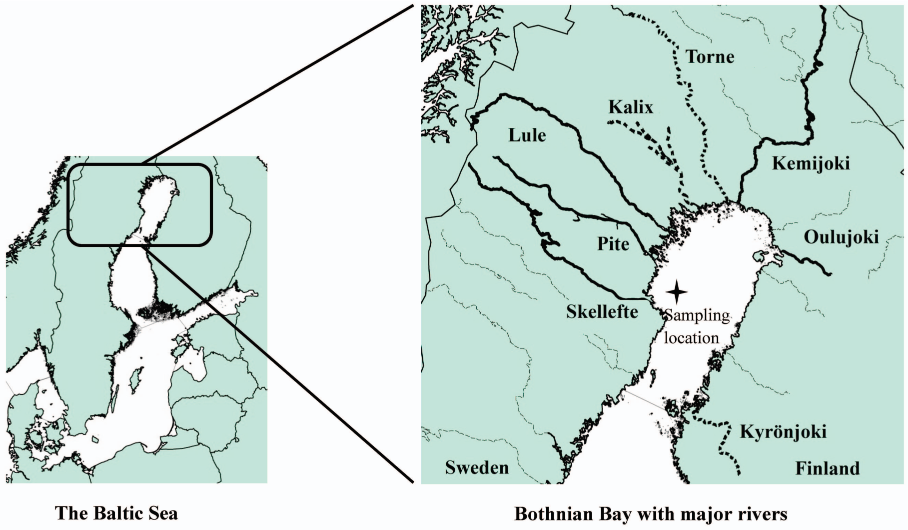

Fig. 1. Map of the study area. The regulated rivers are marked with solid lines. Unregulated rivers are indicated with dashed lines. The sampling site is marked with a star.

was evaluated with an optical microscope and diatoms were found to constitute about 95 % of the phytoplankton. The sieved samples were collected in centrifuge tubes containing sodium polytungstate (SPT, $3Na_2WO_49WO_3{\cdot}H_2O$). The density of the SPT was adjusted to be between 1.8 g cm^{-3} and 2.3 g cm^{-3} in order to separate diatoms from the remaining clay and mineral materials. Centrifugation was at 4200 rpm for 5 min and repeated until clean diatoms were retrieved. Subsequently, all diatom samples from each sediment slice were carefully rinsed with MilliQ-e water and sieved at 5 µm to remove all traces of SPT. Finally, the diatom samples were dried at 40 °C for 24 h.

3.3 Diatom fusion and chromatographic purification

About 5 mg of each extracted diatom sample were mixed with ca. 180 mg solid NaOH and fused in Ag crucibles at 730 °C for 10 min in a muffle furnace. This was followed by washing with MilliQ-e water into a 0.12 M HCl solution in order to neutralize the NaOH (Georg et al., 2006). The final stock solution was diluted to 200 ml to yield a Si concentration of ∼10 mg l^{-1} and stored in pre-cleaned HDPE bottles to minimize Si polymerization.

Interfering elements remaining after diatom dissolution were removed prior to Si isotope analyses by using cation exchange columns. A protonated 1 ml BioRad cation exchange resin AG 50W-X12 (100–200 mesh) was placed in 2 ml BioRad columns. The resin rinsing and diatom sample load processes are reported in Table 1, and the recovery shown in Fig. 2.

3.4 Si isotope analysis

The δ^{29}Si value of each sediment slice was measured using a single focus multiple-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) equipped with a hexapole gas-collision cell. Analytical precision for replicate samples was better than 0.2 ‰ (2σ) with a total Si consumption of less than 14 nmol (390 ng) and the internal reproducibility was tested by measuring IRMM-18 and Big Batch (Sun et al., 2010). The ^{30}Si could not be measured directly due to the instrumental limitation of using low mass resolution ($m/\Delta m^{-1}{\sim}450$) which does not fully resolve the isobars. However, the δ^{30}Si values were calculated from the mass ratio relationship $\delta^{30}\text{Si} = \delta^{29}\text{Si} \times 1.96$ which assumes mass-dependent fractionation (Reynolds et al., 2007). δ^xSi ‰ was expressed as relative to the standard material NBS 28 (Eq.2):

$$\delta^x\text{Si} = \left(\frac{\left(\frac{^x\text{Si}}{^{28}\text{Si}}\right)_{\text{sample}}}{\left(\frac{^x\text{Si}}{^{28}\text{Si}}\right)_{\text{NBS 28}}} - 1 \right) \cdot 1000 \qquad (2)$$

where $x = 29, 30$.

4 Results and discussion

4.1 Silicon recovery of cation-exchange columns

The quality of the chemical purification is of vital importance to obtain good precision and accuracy of the Si isotope analysis. Figure 2 shows the recovery of Si when using the cation-exchange column. Predominant Si species after NaOH fusion and HCl dissolution exhibit no affinity for the resin and thus pass directly through the resin. More than

Table 1. The purification process used in this study for dissolved diatom samples from Georg et al. (2006).

BioRad cation-exchange resin AG 50W-X12 (100–200 mesh) in H$^+$ form, 1 ml resin bed		
Step	Solution	Volume (ml)
Pre-cleaning	4 M HCl	3
Pre-cleaning	8 M HCl	3
Pre-cleaning	4 M HCl	3
Conditioning	MQ-e water	6
Sample load	Acidified diatom samples	2
Elution	MQ-e water	4

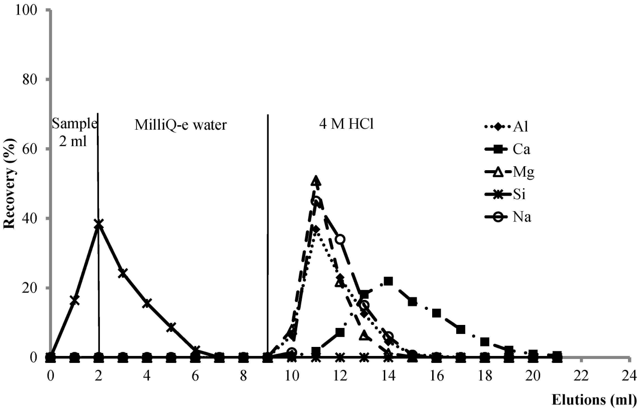

Fig. 2. Recovery of Si using a cation-exchange resin (AG 50W-X12, 100–200 mesh) in a 1 ml resin bed.

60 % of the loaded Si is recovered from the initial elution of the 2 ml sample aliquot through the resin. The remaining Si in the resin is eluted using 4 ml MilliQ-e water. No breakthrough of ambient cations is observed if only MilliQ-e water is added. The cations start to elute when adding 4 M HCl (Fig. 2). Si is quantitatively recovered using this chromatographic purification with recovery efficiencies greater than 99 %.

4.2 ^{210}Pb dating

The sediment core is dated using ^{210}Pb as shown in Fig. 3. Figure 3a exhibits a gradually decreasing trend with increasing depth. Fig. 3b shows the linear ^{210}Pb decay relation with depths in the sediment core ($r^2 = 0.97$). The linearity suggests minimal bioturbation and the slope indicates an average sedimentation rate in this Bothnian Bay core of approximate 2.1 mm yr^{-1} which is consistent with previous measurements from this area (Grasshoff et al., 1983).

4.3 BSi vs. Si isotopes in BSi

The depth profiles of BSi contents and δ^{30}Si values are plotted in Fig. 4 with the corresponding time scale obtained from the ^{210}Pb dating. The BSi content of the sediment core (Fig. 4a) is approximately 3.5 % below 10 cm depth which is material deposited before the 1950s. It increases to a maximum of 7.8 % in the surface sediments. This is due to increased diatom production, probably caused by anthropogenic nutrient emissions, especially N and P, to the Baltic Sea (Conley et al., 2008). Four periods of decreases in BSi contents were observed around 1825, 1850, 1880 and 1912. These dates are extrapolated from the sedimentation rate from the ^{210}Pb dating. The range of δ^{30}Si values are displayed in Fig. 4b and vary between −0.18 ‰ and 0.58 ‰. Before the 1950s the average δ^{30}Si is about 0.16 ‰ with a small negative peak of −0.18 ‰ at 17 cm, i.e. 1910s, followed by a gradual increase to ∼0.5 ‰ toward the surface. In general, increased BSi contents result in higher δ^{30}Si values.

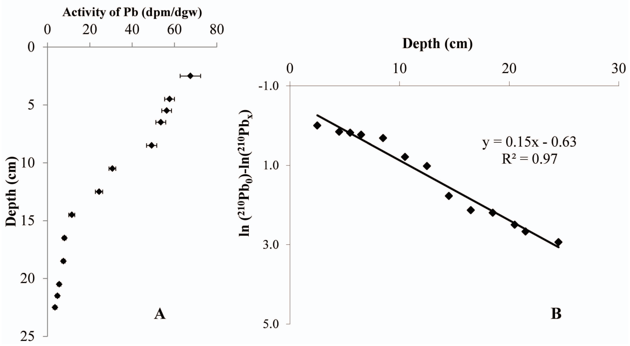

Fig. 3. Downcore variations in ^{210}Pb. **(A)** The depth profile of total ^{210}Pb activity in the sediment core. The error bars represent one standard deviation. **(B)** Correlation between depth and ln (^{210}Pb$_0$−^{210}Pb$_x$), i.e. sample ^{210}Pb activity normalized to the surface value.

It should be noted that the sedimentary BSi is not simply a measure of the entire Bothnian Bay primary production, but is a balance between diatom production and dissolution. The nearly linear sedimentation rate (Fig. 3) suggests that the variation in the sedimentation rate does not drive the variability of the BSi contents. During diatom production, there is Si isotopic fractionation of −1.1 ‰ (De La Rocha et al., 1997). However, dissolution of diatoms also exhibits Si isotopic fractionation of −0.55 ‰ if the dissolution is more than 20 % of the total amount of BSi (Demarest et al., 2009). This means that the δ^{30}Si values of the preserved BSi can potentially increase, i.e. ^{28}Si is preferentially released during diatom dissolution. Although no diatom dissolution rate estimates exist for Bothnian Bay, the excellent preservation of diatoms and the low mineralization rate in the bottom water combined with a shallow water depth of 112 m and rapid sedimentation rates imply that dissolution of BSi is probably low. This means that the potential shift of Si isotope values in BSi caused by dissolution may be ignored in this study.

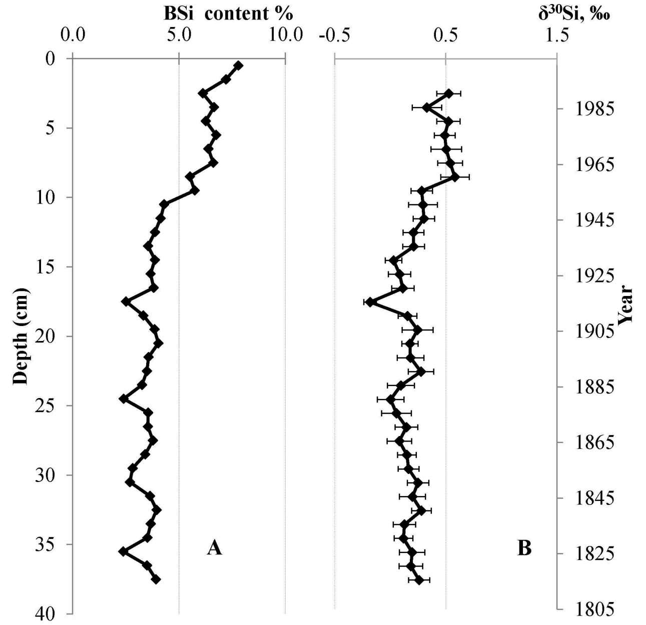

Fig. 4. Sediment profiles. **(A)** BSi content (%); **(B)** δ^{30}Si values in BSi. The bars in 4 B represent the 95 % confidence interval.

4.4 Quantitatively reconstructing diatom production

The amount of DSi remaining in the water column is controlled by diatom production which occurs between the middle of May and September in Bothnian Bay. Due to the relatively long residence time of DSi compared to a short diatom growing season, Bothnian Bay can be assumed to be a closed system, i.e. a steady state with respect to the physical input of nutrients and its biological removal, to which Rayleigh distillation equations (Eq. 3) can be applied (Hoefs, 2009). The fraction of remaining DSi (f), is a factor between 0 and 1. A number close to 1 indicates that very little DSi is taken up by BSi in the water. The f-values can be calculated using δ^{30}Si values according to Eq. (3):

$$\frac{1-f^{\alpha}}{1-f}=\frac{\delta^{30}\mathrm{Si}_{\mathrm{BSi}}+1000}{\delta^{30}\mathrm{Si}_{\mathrm{river\,input}}+1000} \tag{3}$$

where $\alpha = 0.9989$ and denotes the Si isotope fractionation factor during diatom production (De La Rocha et al., 1997); $\delta^{30}\mathrm{Si}_{\mathrm{BSi}}$ and $\delta^{30}\mathrm{Si}_{\mathrm{river\ input}}$ represent δ^{30}Si of BSi and of the river input to Bothnian Bay, respectively. $\delta^{30}\mathrm{Si}_{\mathrm{BSi}}$ is the values shown in Fig. 4 and the $\delta^{30}\mathrm{Si}_{\mathrm{river\ input}}$ value is taken to be +1.1 ‰ which is derived from measurements of an unregulated boreal river, the Kalix River (Opfergelt et al., 2011). This represents unperturbed river inflow.

Each point in Fig. 5 represents the calculated 5 yr average f value using Eq. (3) (each 1 cm section of sediments corresponds to approximately five years). The error of the calculation due to the uncertainty of the measured $\delta^{30}\mathrm{Si}_{\mathrm{BSi}}$ values was examined by Monte Carlo analysis. 10 000 random $\delta^{30}\mathrm{Si}_{\mathrm{BSi}}$ values were generated assuming a normal distribution around a mean value and the standard deviation of that mean. Here the average of measured $\delta^{30}\mathrm{Si}_{\mathrm{BSi}}$ values and its standard deviation is used to produce 10 000 f-values. The first quartile and third quartile for each f value were calculated and are shown in Fig. 5 as error bars, which means that 50 % of the f-values fall in this range. It should also be noted that the calculated variations in f-values are independent of the α-value, i.e. the absolute values of f will change with the α-value, but the variation will be unchanged.

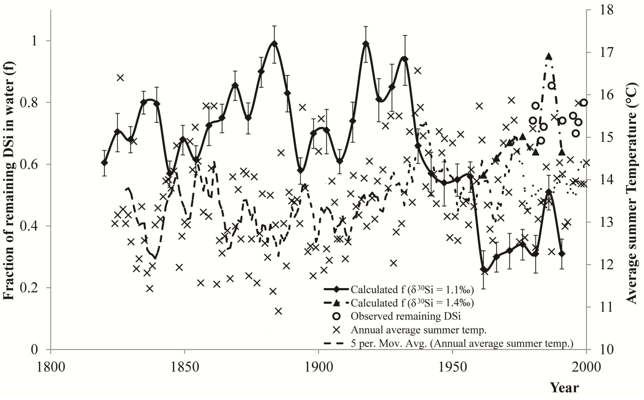

Fig. 5. Fraction of the remaining DSi (f) in the water column of Bothnian Bay using Eq.(3) and f-values calculated from observations during the summers 1980 to 2000, plotted together with average summer air temperature through years. The inferior and superior error bars on f-values are the first quartile and third quartile for each f-value derived from Monte Carlo simulations, respectively.

The air temperature data displayed in Fig. 5 are the observed average temperatures between May and September of each year from 1824 to 2000 with a 5 yr moving average. By plotting air temperature and the calculated fraction of the remaining DSi (f) from Si isotope measurements a clear pattern emerges where cold periods are associated with high f-values, i.e. low diatom production, and warm periods show relatively lower f-values, i.e. high diatom production.

The temperature history and correlation with the isotopically derived f-values stand out particularly for several peaks. For example, the last period of cooling associated with the Little Ice Age corresponds to the late 19th century (Bradley and Jonest, 1993). Another cold period in the early 19th century is possibly caused by the Dalton Minimum, a period with low solar activity (Büntgen et al., 2006). The largest amount of remaining DSi, $f = 0.98$, is observed around 1910 which corresponds to a period with very cold summers. More recently, another period with high f-values is observed around 1983, which also was a period with cold summers.

Wasmund et al. (1998) showed that diatom blooms in the southern Baltic Sea were triggered by the reduction in depth of the mixed layer (ML) improving light conditions

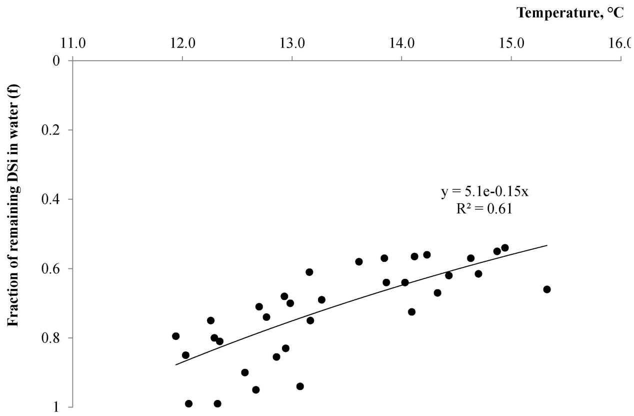

Fig. 6. Exponential regression fit of the fraction of remaining DSi (f) vs. the 5 yr moving average of air temperature for each depth interval.

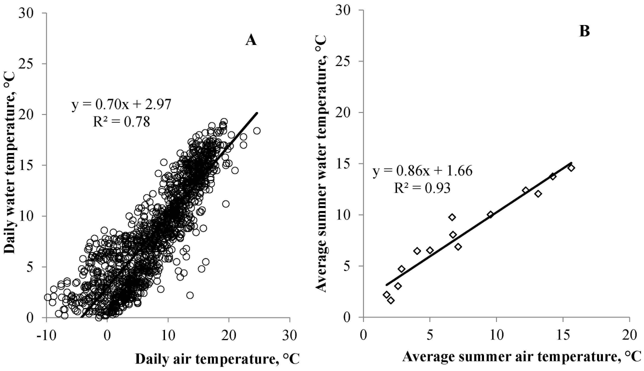

Fig. 7. Comparison of air temperature and water temperature between 1948 and 1963. **(A)** Plot of daily air temperature vs. daily water temperature. **(B)** Plot of average summer air temperature vs. average summer water temperature.

for phytoplankton growth. A possible explanation for the Si isotope-based diatom-temperature relationship observed in Bothnian Bay is therefore that temperature-induced variations of the ML depth control diatom production. This would imply that air temperature regulates the water temperature which is correlated with the ML depth. In fact, Fig. 7a shows daily air temperature plotted vs. daily water temperature between 1948 and 1963 giving a correlation coefficient of $R^2 = 0.78$. The correlation is improved if average summer temperatures are used, $R^2 = 0.93$ (Fig. 7b). To further support our hypothesis that diatom growth and air temperature are linked via the depth of the ML, an estimate of the correlation is calculated between stratification strength and surface water temperature for each month from May to August (Appendix A, Fig. 8). Generally, the depth of the ML represented by the pycnocline depth is negatively correlated with summer surface temperature. The steepest slope appears in June and July (Fig. 8b and 8c), indicating a strong correlation between the pycnocline depth and the surface temperature. Figure 8a shows a gentle slope possibly due to the ice cover in May causing low diatom production. In August, the slope is less steep than those in June and July. This indicates that summer stratification isolates the growing diatoms from the deep nutrient reservoir, leading to phosphorus-limited diatom production (Humborg et al., 2003). Therefore, diatom production in June and July represents classical spring growth conditions and contributes most to the diatoms found preserved in sediments. In summary, diatom production in Bothnian Bay is controlled by depth of the ML, which is negatively correlated with the air temperature.

Figure 5 shows that the fraction of the remaining DSi (f-values) can be divided into two periods, before and after 1950. Before 1950, Bothnian Bay is likely to have been less disturbed due to anthropogenic eutrophication and river regulations (Humborg et al., 2006) and may be used here to infer the general relationship between diatom production and air temperature in Bothnian Bay. Earlier than 1950, the $\delta^{30}\mathrm{Si}_{\text{river input}}$ value used for the calculations of the f-value is +1.1 ‰ derived from measurements in the unperturbed Kalix River (Engström et al., 2010). Although we cannot state with absolute certainty that the Kalix River value can be extended to represent all the unperturbed rivers draining into Bothnian Bay during the studied period it is unlikely that there is a significant difference in δ^{30}Si values among Nordic unperturbed rivers. This assumption can be made because the catchments have similar soil covers derived from the last glacial retreat. Soils in the area are mainly tills of local origin reflecting the Fennoscandian bedrock. The mineral composition of the bedrock in the entire region is dominated by granite and gneiss and is homogenous. The soils show little disturbance due to human activities. Homogenous Si isotopic compositions have been observed in eight of the most common species of vegetation in the boreal forest (Engström et al., 2008).

However, if we assume that the data before the 1950s represent a relatively undisturbed situation both on land and in the sea, a positive exponential relationship (Eq. (3), $r^2 = 0.61$) can be derived by the comparison of the fraction of remaining DSi (f) with the 5 yr moving average of air temperature (T) from 1824 to 1955 (Fig. 6).

$$f = 5.1e^{-0.15T} \tag{4}$$

Equation (4) is valid as long as temperature controls the ML depth and no nutrient limitation occurs. We also have to keep in mind that our calculated f-values are dependent on the isotopic fractionation factor (α in Eq. 3), which might vary between different areas. Although the exact α-value for Bothnian Bay is lacking, the validation using the data between 1980 and 2000 indicates that an α-value of 0.9989 is representative of the Si isotopic fractionation factor. For other areas, calculations with Eq. (4) might change. In addition, this method is only valid as long as Rayleigh distillation can be applied, i.e. the assumption of a closed system, in our

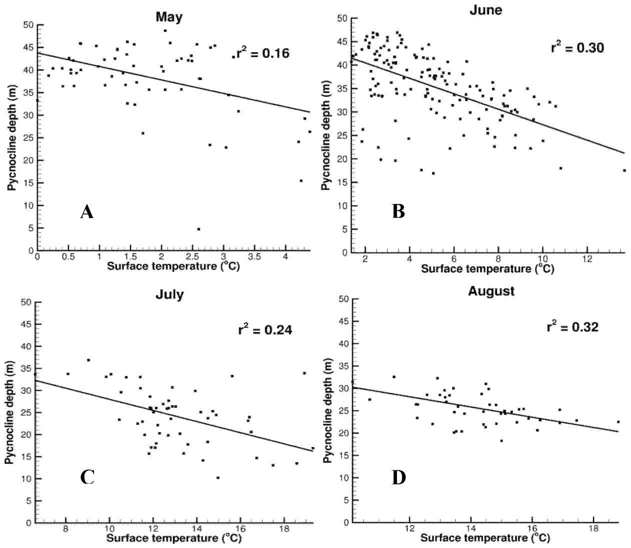

Fig. 8. Plot of the estimated pycnocline depth vs. water surface temperature for May **(A)**, June **(B)**, July **(C)**, August **(D)**. The correlation squared is also indicated in each panel.

case, much longer DSi residence time than diatom growth periods in Bothnian Bay.

After ca. 1950, the f-values exhibit a decrease (Fig. 5). This is not consistent with calculated f-values using field observations from 1980 and onwards. To get a good fit between observed and calculated data the $\delta^{30}\mathrm{Si}_{\text{river input}}$ value used for calculations in Eq.(3) has to be shifted to +1.4 ‰. The shift coincides in time with a period of large scale hydroelectric and flood control projects in the major rivers draining into Bothnian Bay (Humborg et al., 2002, 2006), leaving only a few rivers unregulated today. There is no change in bedrock and vegetation in the catchment which suggests that the isotope composition of source Si is constant. The shift in the fractionation factor is thus most likely to occur during the transport of DSi into the Bothnian Bay. Damming of rivers increases diatom production in the reservoirs behind the dams (Humborg et al., 2006) and enriches the remaining DSi in the river water with the heavier isotopes, ultimately leading to increased $\delta^{30}\mathrm{Si}_{\text{river input}}$ values. To test this hypothesis, additional analysis of samples from major rivers draining into Bothnian Bay and behind dams as well as diatoms should be made. However, assuming that the $\delta^{30}\mathrm{Si}_{\text{river input}}$ value of +1.4 ‰ is correct, the remaining fraction of DSi (f) can be calculated for the summers between 1980 and 2000 and can be compared with f-values calculated with Eq.(4) using the observed air temperatures for the same period. A paired t-test shows that there is no significant difference between the observed and calculated f-values ($p \leq 0.003$).

5 Conclusions

Three conclusions can be drawn from this study in the subarctic area of the Baltic Sea, Bothnian Bay as follows:

1. stable Si isotope signature in sedimentary BSi can be used to study variations in time of diatom production;
2. air and water temperatures can be used as a proxy for the mixed layer depth (which controls diatom production) and as shown also correlates well with diatom production;
3. large scale anthropogenic activities such as changing the hydrological regimes in rivers by damming are likely to be imprinted on the sedimentary Si isotopic record.

Appendix A

Estimations of the relation between stratification strength and surface temperature

A1 Estimation of stratification strength from observations

A convenient way of analysing continuous stratification is to use the integrated properties profile potential energy and integrated buoyancy, i.e. steric height. This is analogous to the applications in various systems of the world (e.g. Gustafsson, 1999; Björk et al., 2001; Andersson and Stigebrandt, 2005). The profile potential energy is defined as:

$$P = \frac{g}{\rho_0}\int_D^0 (\rho_0 - \rho) z dz \tag{A1}$$

$$B = \frac{g}{\rho_0}\int_D^0 (\rho_0 - \rho) dz \tag{A2}$$

where g is the acceleration of gravity, $\rho 0$ is the density at depth D and ρ is the density profile.

The two layer equivalents for these are

$$P = \frac{g(\rho_0 - \rho_1)}{2\rho_0} h^2 \tag{A3}$$

$$B = \frac{g(\rho_0 - \rho_1)}{\rho_0} h \tag{A4}$$

where $\rho 1$ is a surface layer density and h the depth of the surface layer. From Eqs. (A3–A4) we can derive:

$$h = \frac{2P}{B} \tag{A5}$$

$$\frac{g(\rho_0 - \rho_1)}{\rho_0} = \frac{B^2}{2P} \tag{A6}$$

Thus, by integrating Eqs. (A1–2) from measured profiles, we can estimate an equivalent homogeneous surface layer using Eqs (A5–6). In the present application, the equivalent depth h gives us a rough estimate on the depth of the surface layer.

A2 Application to Bothnian Bay

606 profiles were extracted from the BED data base. A criterion for selection was that the vertical resolution was at least 5 m in the upper 20 m and at least 10 m down to the reference depth D, which was chosen to 50 m. Each profile was interpolated to 1 m resolution using a cubic spline, with normal conditions at the surface and at a maximal depth of the analysis. h was calculated for each profile using eq.s (A1–2 and 5).

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