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Discussions**

Climate dependent diatom production is preserved in biogenic Si isotope signatures

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BGD

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Abstract

Climate change is likely to have the greatest impact on high-latitude ecosystems which are sensitive to climate fluctuations due to the relatively short growth season of diatoms. Biogenic silica (BSi) derived from diatoms provides a direct measure for tracking these processes although the knowledge gained from the amount of BSi preserved may be limited. In this study we report an application of a method based on Si isotope analyses of diatoms derived from a Gulf of Bothnia sediment core to reconstruct diatom production during the last two hundred years. During this time period large scale anthropogenic disturbances, such as the damming of rivers, can be observed. There is a relationship between measured Si isotope values of BSi, e.g. the silica incorporated into diatom frustules, in Bothnian Bay sediments and air temperature. This relationship suggests that the diatom Si isotope composition can be used to trace temperature variations over time. This method can be applied to other diatom dominated aquatic systems, i.e., a large part of the world's ocean and coastal seas, in order to improve our knowledge of impacts of temperature variations and thus also climate change and anthropogenic disturbance.

1 Introduction

Silicon 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 are an effective measure of environmental change due to their sensitivity to a variety of physical and ecological conditions. Due to the short growing season of diatoms this is especially emphasised in high-latitude ecosystems where even slight climate fluctuations may have major biological influence (Smol, 1988). After death and cell lysis, the siliceous cell walls of diatoms can be well preserved in sediments which allows for the reconstruction of diatom production by analysing the preservation of biogenic silica (BSi) through time (Conley and Schelske, 2002). BSi has been previously used to track

climate-related changes in aquatic production over millennial (Rosén et al., 2000) and hundred thousand years (Blass et al., 2007). Recently, 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., 2008).

The discovery of Si isotope fractionation of about 1.1‰ during formation of diatom cell walls (De La Rocha et al., 1997) has resulted in a variety of applications using Si isotope signatures to gain insights into diatom-related processes of, not only paleoclimatic and paleoceanographic studies (Beucher et al., 2007; Brzezinski et al., 2002; De La Rocha, 2006; De La Rocha et al., 1998; van den Boorn et al., 2010), but also ongoing environmental changes (Brzezinski et al., 2001; Cardinal et al., 2005; De La Rocha et al., 2000; Reynolds et al., 2006; Wille et al., 2010). This fractionation in a close system can be described by using a Rayleigh distillation equation (explained later). From the studies of three different diatom species it was found that the Si isotope fractionation was similar in the temperature range 12–22 °C between these species (De La Rocha et al., 1997). Therefore, shifts in the δ^{30}Si of diatoms in the close system are related to DSi utilization efficiency i.e. diatom production, in surface water. Study of the Si isotope signatures of sedimentary BSi has thus opened the possibility of being a tracer for the climate through diatom production in water columns.

In this study we report an application of Si isotope analyses of diatoms to reconstruct diatom production variations during the last two hundred years. Moreover, large scale anthropogenic impacts can be easily observed. Bothnian Bay is one of these areas that are suitable for studying diatom-related processes. Temperature variations are >15 °C and Si fluxes have been drastically reduced by river damming.

2 Study site

The 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

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ages. The last ice melted from the area about 9300 yr ago. The average and maximum depth of the Bay is 43 m and 147 m, respectively. The catchment 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
5 is 7% of the total water volume of the Baltic Sea. Furthermore, the total water discharge into the Bothnian Bay is 97 km^3 yr^{-1} (Humborg et al., 2008) and, 60% is derived from rivers regulated by dams (calculated from 23 major rivers running into the Bothnian Bay). Regional river regulation started at the beginning of 20th century and continued until ca. 1960 with most activities between 1940 and 1960, e.g. Kemijoki and Luleå
10 River (Humborg et al., 2006). As a consequence, this has caused a decrease in fluxes of weathering related elements like base cations and Si (Humborg et al., 2002, 2000) due to changes in water pathways through the catchments (i.e. hydrological changes, for example the river valleys have been inundated) and particle trapping of BSi behind dams (Humborg et al., 2006). This has ultimately led to a decreasing DSi load in the
15 northern Baltic Sea (Humborg et al., 2007).

Formation of winter ice cover in the 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 period of 1961–1990, the summer time (ice-free time) average
20 maximum surface temperature in the open sea varied between 16 and 16.5 °C (Haapala and Alenius, 1994). In the Bothnian Bay a surface thermocline is developed about a month earlier compared to other sub-basins of the Baltic Sea. This is due to haline stratification caused by freshwater from the melting of the ice cover and the river runoff (Haapala and Alenius, 1994). The thermal stratification lasts for about three months.
25 The Bothnian Bay can be considered to be a semi-closed system that is assumed to be close to steady state with respect to the physical input of nutrients and their biological removal. Mean dissolved Si (DSi) concentrations are >30 µM in winters and decrease to <25 µM in summers (Danielsson et al., 2008). Residence time for DSi is about 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 the 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. The sedimentation rate was calculated as follows:

$$^{210}Pb_x = {}^{210}Pb_0 \cdot e^{-\lambda t} \tag{1}$$

$^{210}Pb_x$ is the activity of ^{210}Pb per mass weight of sample at depth x, $^{210}Pb_0$ 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. BSi content in sediments was determined using the method described by Conley and Schelske (2002).

4 Diatom extraction

The method used for extraction of diatoms from the sediment is modified from (Morley et al., 2004). Organic carbon was removed from 2 grams of each sediment slice by repeatedly mixing with 20 ml 15% H_2O_2 followed by incubation for 12 h and thereafter heated 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 the 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 contains most of the diatoms. Purity 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, $3Na_2WO_4 9WO_3 \cdot H_2O$). The density of the SPT was continuously 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 matter. 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.

4.0.1 Diatom fusion and chromatographic purification

About 5 mg of each extracted diatom sample was 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 $\sim$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 1 ml BioRad cation exchange resin AG 50W-X12 (100–200 mesh) in H$^+$ form was filled in 2 ml BioRad columns. The resin rinsing and diatom sample load processes are reported in Table 1, and the recovery is shown in Fig. 2.

4.1 Si isotope analysis

The δ^{29} Si value of 1 cm depth intervals was measured on the 38 cm long sediment core from the Bothnian Bay (Fig. 1) 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) (Sun et al., 2010). The δ^{30} Si could not be measured directly due to the instrumental limitation of using low mass resolution (m/Δm~450, which does not fully resolve the isobars). However, the δ^{30} Si values were calculated from the relation δ^{30} Si = δ^{29} Si × 1.96, assuming mass-dependent fractionation (Reynolds et al., 2007). δ^{x} Si (‰) is expressed as relative to the standard material NBS 28 (Eq. 1):

$$\delta^{x}\mathrm{Si} = \left(\frac{\left(\frac{^{x}\mathrm{Si}}{^{28}\mathrm{Si}} \right)_{\mathrm{sample}}}{\left(\frac{^{x}\mathrm{Si}}{^{28}\mathrm{Si}} \right)_{\mathrm{NBS28}}} - 1 \right) \cdot 1000 \qquad (2)$$

5 Results and discussion

5.1 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 for our cation-exchange column. The predominant Si species after NaOH fusion and HCl dissolution exhibit no affinity for the column and pass directly through the resin. More than 60% of the loaded Si is recovered during the 2 ml sample load eluting through the resin and the remaining Si in the resin is eluted using 4 ml MilliQ-e water. No breakthrough of ambient cations was observed if only MilliQ-e water is added. The cations start to elute when adding 4 M Cl as shown in Fig. 2. Thus, Si is quantitatively recovered through this chromatographic purification with a recovery efficiency of 101.2% and the extra ~1.2% Si is most possibly from the large amount of NaOH used during the fusion process.

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5.2 ^{210}Pb dating

The sediment core was dated by ^{210}Pb as shown in Fig. 3. Figure 3a exhibits a gradually decreasing trend with increasing depth. Figure 3b shows the linear relation of ^{210}Pb decay with depth over the length of the core ($r^2 = 0.97$), indicating minimal bioturbation and an average sedimentation rate in Bothnian Bay of approximate 2.1 mm yr^{-1}, which is consistent with the previous measurements at this area (Mattila et al., 2006).

5.3 BSi vs. Si isotopes in BSi

The depth profiles of BSi content and δ^{30}Si is plotted in Fig. 4 with the corresponding time scale obtained from the ^{210}Pb dating. The BSi content of the sediment core (Fig. 4a) was approximately 3.5% below 10 cm depth, i.e. before the 1950s. The concentration increases to a maximum of 7.8% in the surface sediments. This is due to increased diatom production probably caused by anthropogenic nutrient enrichment in the Baltic Sea (Conley et al., 2008). Four periods with decreases in BSi concentration were observed around 1825, 1850, 1880 and 1912 (n.b. these dates are extrapolated from the sedimentation rate from the ^{210}Pb dating). The range in 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, showing a gradual increase to ∼0.5‰ toward the surface. Plotting the BSi against δ^{30}Si shows two groups, one with low BSi and low δ^{30}Si and one with high BSi and also high δ^{30}Si (Fig. 5). There is a general co-variation between the BSi and the δ^{30}Si, which can be described by a linear relationship ($R^2 = 0.69$) with a positive slope of 0.11. This indicates that there is a relationship between increased BSi production and higher δ^{30}Si values (Fig. 5).

It should be noted that the sedimentary BSi discussed here is not simply a measure of the entire Bothnian Bay primary production, but is a balance between diatom production, dissolution and detritus sedimentation. While the detritus sedimentation cannot be completely decoupled from the diatom flux in the water column, the nearly

linear sedimentation rate of Fig. 3 suggests that the relatively stable sedimentation does not drive the variability of the BSi content. i.e. changes in detritus sedimentation rate was minor in comparison to diatom flux. Therefore, diatom production and dissolution dominate the BSi sedimentation. During diatom production, there is a Si isotope fractionation of +1.1‰ (De La Rocha et al., 1997). However, the diatom dissolution also shows a Si isotope fractionation of −0.55‰ acting in the opposite direction in comparison to diatom production if dissolution varies by more than 20% of BSi (Demarest et al., 2009). This means that the δ^{30} Si values in the preserved BSi can potentially shift toward positive values, i.e. ^{28} Si is preferentially released during diatom dissolution. Although no diatom dissolution rate estimate exists for the Bothnian Bay, the excellent preservation of diatoms and presence of low nutrient concentrations combined with the shallow water depth of 112 m and rapid sedimentation rate imply that dissolution of BSi are likely less than 20% in this sediment core. This means the potential shift of Si isotope values in BSi caused by dissolution can be neglected in this study.

5.4 Quantitatively reconstructing temperature by Si isotopes

The extent and duration of ice cover governed by climate change have been demonstrated and documented for aquatic ecosystems at high-latitude lakes (Douglas and Smol, 2010; McKay et al., 2008; Smith, 2002; Smol et al., 2005). There is a sensitive relationship between BSi and summer temperature which is probably attributed to the influence of seasonal ice-cover on diatom production. In this study, we show that not only in lakes but also in high-latitude marine ecosystems diatom production is sensitive to climate. And this sensitivity can be observed through Si isotope values of the sedimentary BSi.

The remaining DSi in the water column is mainly controlled by diatom production which, in the Bothnian Bay, occurs between the middle of May and September. Due to the relatively long residence time of DSi compared to a short diatom growth season, the Bothnian Bay could be assumed to be a semi-closed system, where Rayleigh

distillation equations (Eq. 2) can be applied (Hoefs, 2009). The fraction of remaining DSi, here denoted f, is a factor between 0 and 1. A number close to 1 indicates that very little is taken up by BSi in the water body. DSi can then be calculated from δ^{30} Si values according to Eq. (2):

$$5 \quad \frac{1 - f^{\alpha}}{1 - f} = \frac{\delta^{30}\text{Si}_{\text{BSi}} + 1000}{\delta^{30}\text{Si}_{\text{river input}} + 1000} \hspace{3cm} (3)$$

α = 0.9989 and denotes the Si isotope fractionation factor during diatom production (De La Rocha et al., 1997); $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{30}\text{Si}_{\text{river input}}$ represent δ^{30}Si in BSi and the river input to Bothnian Bay respectively.

Calculated f values using Eq. (2) are shown in Fig. 6a, where each point represents the 5 yr average f value (each 1 cm section of sediments corresponds to approximately five years). The error of the calculated f values due to the uncertainty of the measured δ^{30} Si$_{\text{BSi}}$ was examined by Monto Carlo analysis. 10 000 random δ^{30} Si$_{\text{BSi}}$ values were generated assuming a normal distribution around the average value of measured δ^{30} Si$_{\text{BSi}}$ and the range of the standard deviation. The air temperature data displayed in Fig. 6b are the observed average temperatures between May–September of each year since 1896 with a 5-yr moving average corresponding to points in Fig. 6a. By plotting air temperature and the calculated fraction of the remaining DSi (f) from Si isotope measurements after 1896, we observe a pattern where cold periods give high f values, i.e. low BSi production, and warm periods show relatively low f values, i.e. high BSi production. These data imply that the variations of the BSi production and δ^{30} Si values are dependent upon temperature. It should be noted that the calculated f values are independent of the α-value, i.e. the absolute number of f values will change with the α-value but the variations will be unchanged. The temperatures plotted before 1896 are calculated, which will be explained below.

Figure 6a shows that the fraction of the remaining DSi (f) can be divided into two periods, before and after 1950. During the period before 1950, the δ^{30} Si$_{\text{river input}}$ value used for calculations in Eq. (2) was +1.1‰ derived from measurements of an

unregulated boreal river, the Kalix River (Engström et al., 2010), because data from other rivers are not available. Although we cannot state that the Kalix River value can be extended to be representative of all the unperturbed rivers draining into the Bothnian Bay during the studied period it is unlikely that there is a significant difference of δ^{30} Si between different rivers. This is due to the fact that the catchments have similar soil covers derived from the last glacial retreat. Soils in the area are mainly tills of local origin and reflect the local bedrock. The mineral composition of the bedrock in the entire region is dominated by granite and gneiss and is rather homogenous. The soils show small disturbance by human activities and surprisingly homogenous Si isotopic compositions observed in eight of the most common species of vegetation in the boreal forest (Engström et al., 2008).

Variable uptake of Si by diatoms might be more an effect of ice cover than temperature. However, ice cover which influences light availability in the water column is still a proxy for temperature. The f value varies from 0.6 to 0.98 prior to 1950 and show a relation with temperature (Fig. 6). The largest amount of remaining DSi, $f = 0.98$, is observed around 1910 which corresponds to a period with very cold summers. The average temperatures were less than 9 °C. The cold temperatures likely limited diatom production by preventing the formation of a stratified water column. Another period with high f values is observed in sediments deposited in around 1983 which also was a period with cold summers. Although measured air temperature data are not available for the earliest investigated time period, i.e. before 1896, features of the temperature history shown by the isotopically derived f values stand out. 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 was possibly caused by the Dalton Minimum, a period with low solar activity (Büntgen et al., 2006). The co-variation between the Si isotopes and temperature over the last 110 yr due to temperature and ice-cover (Fig. 7) is compelling evidence that the diatom production in the Bothnian Bay is climate dependent.

A positive, exponential relationship (Eq. 3, $r^2 = 0.81$) can be calculated by the comparison of the fraction of remaining DSi (f) with the 5-yr moving average of air temperature (T) based on HELCOM (Helsinki Commission) data from 1896 to 1955 (Fig. 6b).

$$f = 1.95e^{-0.092T} \tag{4}$$

Equation (3) implies that, under conditions of no nutrient limitation, there will be very high diatom production with air temperatures above 30°C and almost no diatom production when air temperatures decrease below 5°C. Based on field observations of the remaining fraction of DSi remaining in the water (f), DSi concentrations are calculated for the summers between 1980 and 2000 and compare with f values calculated from Eq. (3) using the observed air temperatures. A paired t-test shows that there is no significant difference between the observed and calculated f values ($p \leq 0.003$). This indicates the reliability of Eq. (3), which is independent of Si isotope values of river input used for the calculated f values. We therefore suggest that Eq. (3) can be used to predict air temperature variations based on the utilization of DSi derived from Si isotope measurements of BSi. The predicted air temperatures for the 19th century are plotted in Fig. 6b.

5.5 Anthropogenic disturbance in the Bothnian Bay

After ca. 1950 the f values show a large drop and, if the δ^{30}Si$_{\text{river input}}$ continues to be +1.1‰, the calculations would indicate an unsustainable drop of the fraction of the remaining DSi (f) utilised for diatom production (Fig. 6a). This is not a plausible scenario and is not consistent with the f values calculated using field observations from 1980 onwards in the Bothnian Bay. The only possible explanation is that there is a shift in the system that changes the δ^{30}Si$_{\text{river input}}$ superimposed on the temperature variations. The δ^{30}Si$_{\text{river input}}$ value used for calculations in Eq. (2) has to be shifted to +1.4‰ in order to fit field observations. This shift coincides with the period of large scale hydro-electric and flood control projects installed in major rivers draining into Bothnian Bay

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(Humborg et al., 2002, 2006) leaving only a few rivers unregulated today. This isotope shift is also consistent with what is expected to occur if there is increased diatom production in the reservoirs behind the dams. This would lead to the enrichment of the heavier Si isotopes in the river water, i.e., increasing δ^{30} Si$_{\text{river input}}$.

6 Conclusions

The findings of this study can be summarised as: (1) temperature dependent diatom production can be detected and air temperatures can be predicted using the Si isotopic signature of BSi preserved in the sediments of marine ecosystems, and (2) large-scale anthropogenic activities such as changing the hydrological regimes in rivers by damming can also be revealed in marine sediments by analysing the Si isotopes in the BSi fraction.

By using a Rayleigh distillation model this method can be applied to other diatom dominated aquatic systems, including lakes and marine systems. The correlation between the measured Si isotopic compositions of BSi and air temperature suggests that Si isotopic composition in diatoms is a useful indicator for tracking temperature variations. The method may also be of use as a historical record in aquatic ecosystems where DSi concentrations have varied either by diatom production or large scale disturbance such as anthropogenic influence. Analyses of Si isotopes in BSi in sediment cores extending across the last glacial and interglacial periods of the Holocene also offers a new tool to unravel climate change and the effect of anthropogenic disturbance.

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Smol, J. P., Wolfe, A. P., Birks, H. J. B., Douglas, M. S. V., Jones, V. J., Korhola, A., Pienitz, R., Rühland, K., Sorvari, S., Antoniades, D., Brooks, S. J., Fallu, M.-A., Hughes, M., Keatley, B. E., Laing, T. E., Michelutti, N., Nazarova, L., Nyman, M., Paterson, A. M., Perren, B., Quinlan, R., Rautio, M., Saulnier-Talbot, É., Siitonen, S., Solovieva, N., and Weckström, J.: Climate-driven regime shifts in the biological communities of arctic lakes, P. Natl. Acad. Sci. USA, 102, 4397–4402, 2005.

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

BioRad cation-exchange resin AG 50W-X12 (100–200 mesh) in H^+ form, 1 ml resin bed		
Steps	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

The Baltic Sea

Bothnian Bay with major rivers
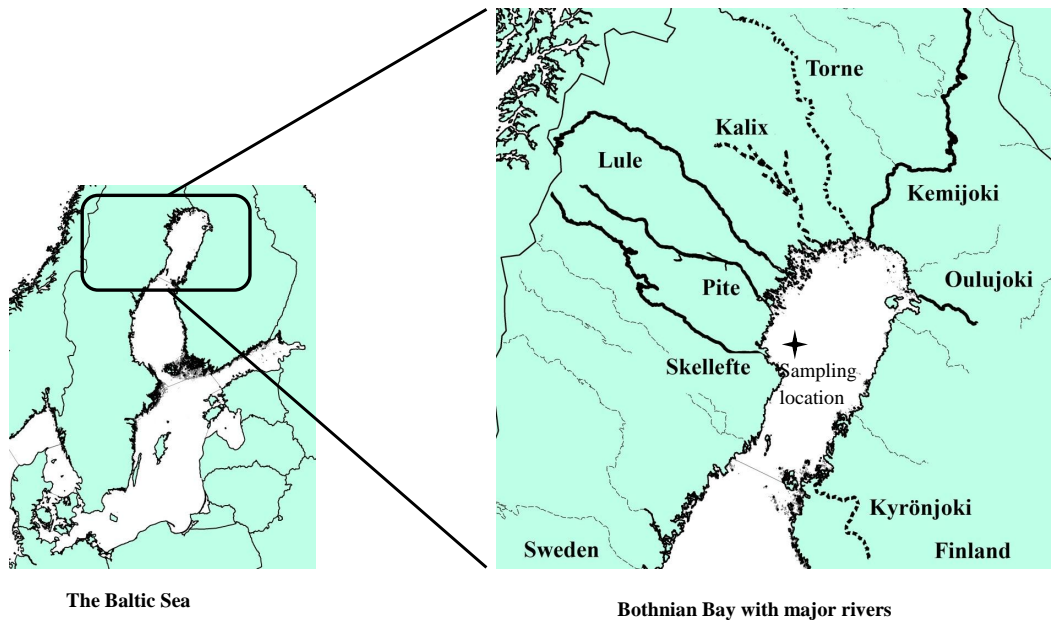
Fig. 1. Map of the study area, the Bothnian Bay, in the Baltic Sea, Northern Europe. The regulated rivers are marked with solid lines. Unregulated rivers are marked by dashed line. The sampling site is marked with a star.
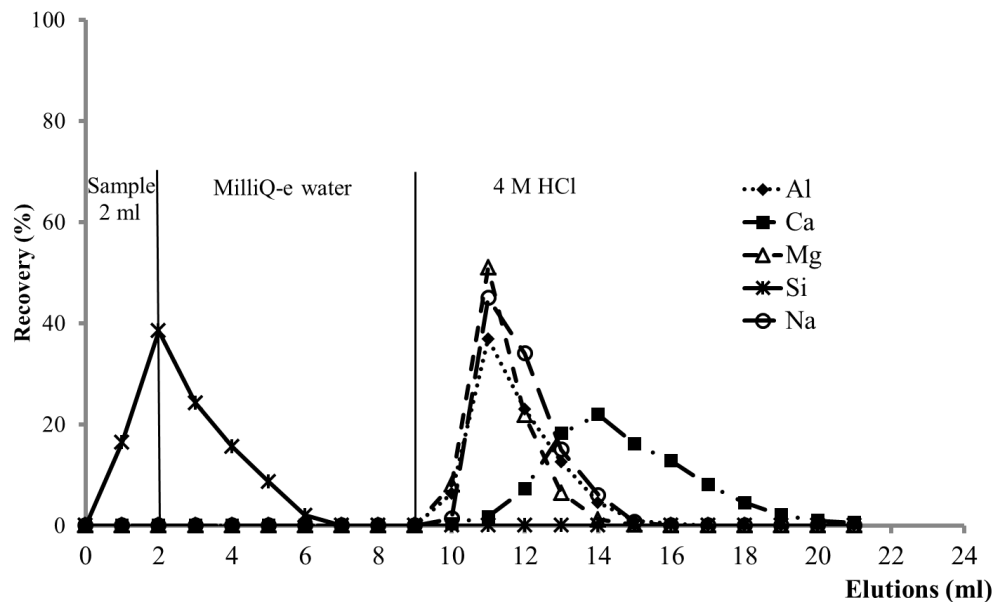
Fig. 2. The recovery of Si using a cation-exchange resin (AG 50W-X12, 100–200 mesh) in a 1 ml resin bed.

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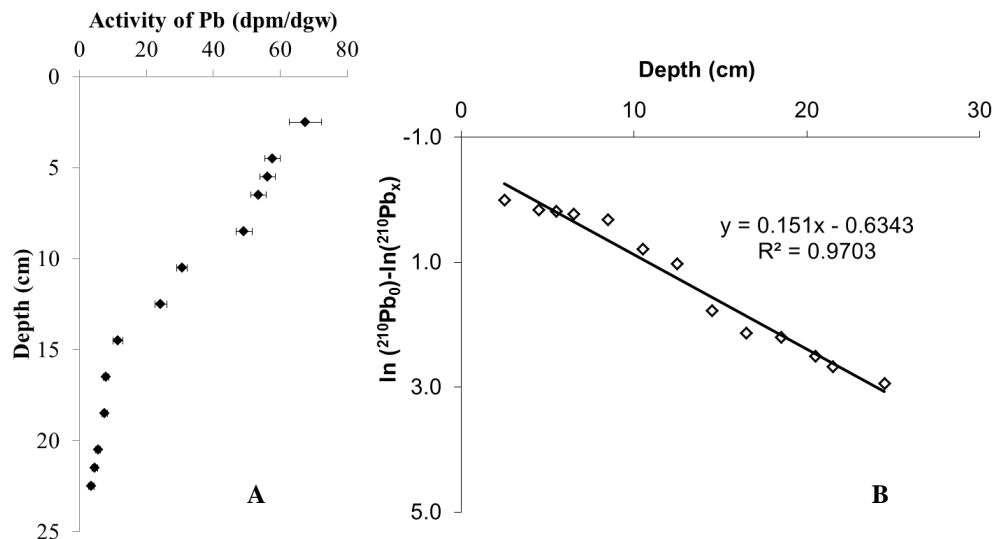
Fig. 3. (A) The depth profile of total ^{210}Pb activity in the sediment core from the Bothnian Bay. The error bars represents one standard deviation; **(B)** correlation between depth and ln $(^{210}$Pb$_0 - ^{210}$Pb$_x)$, i.e. the surface Pb activity corrected data. Each sediment section, i.e. each point, was measured for 2 to 3 days after 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.

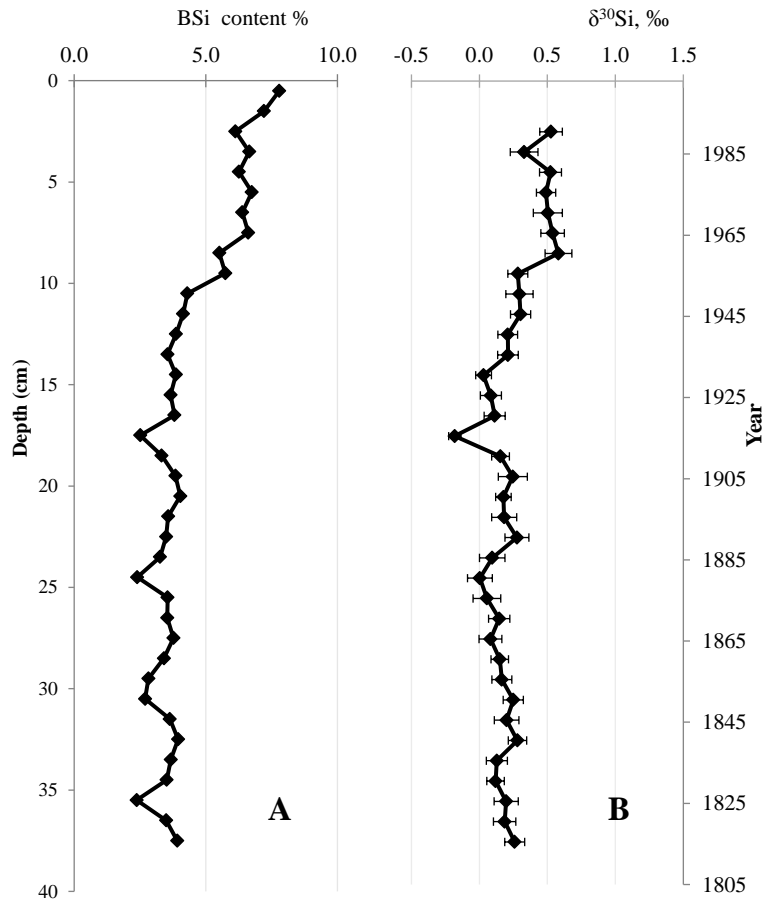Full Screen / Esc

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Fig. 4. Sediment profiles of Bothnian Bay sediments, **(A)** BSi content (%); **(B)** δ^{30}Si in BSi. The error bars in **(A)** represent 95% confidence interval since each sample had seven brackets, i.e. seven times (Sun et al. 2010).
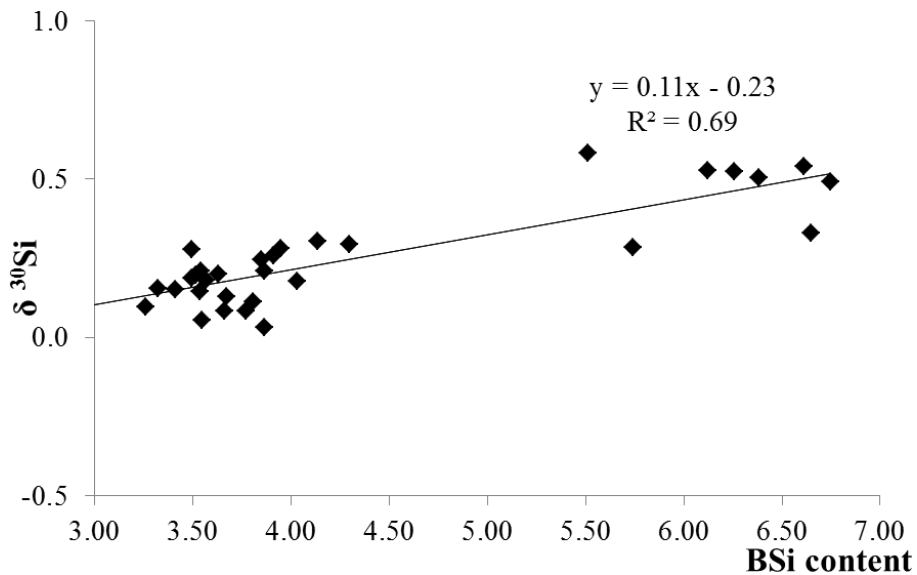
Fig. 5. Plot of BSi against δ^{30}Si values with the linear regression displayed.

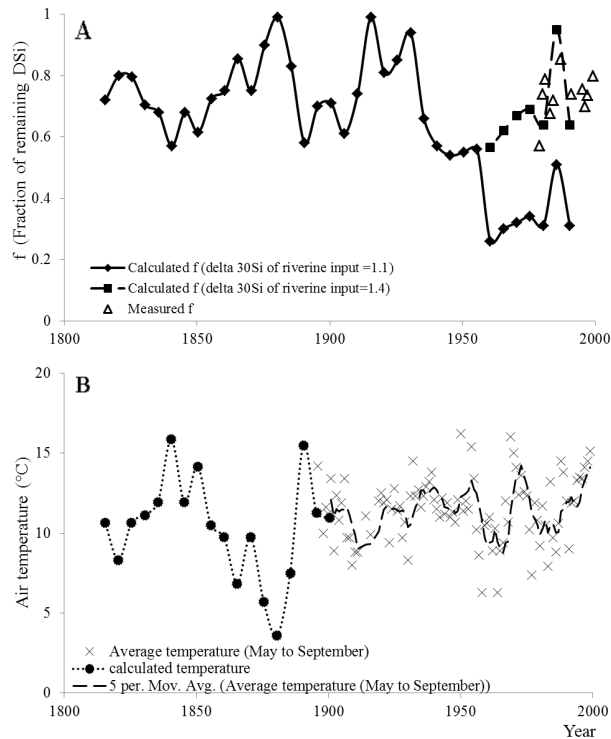**Climate dependent diatom production**

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Fig. 6. (A) Fraction of the remaining DSi (*f*) in the water of Bothnian Bay calculated using a Rayleigh distillation equation (Eq. 2) and *f* values derived from DSi observations during the summers between 1980 and 2000. The δ^{30} Si river input value is 1.1‰ from the pristine boreal Kalix River (Engström et al., 2010) before 1950. For the time period after 1950 the data are adjusted to +1.4‰ in order to fit the observations. It should be noted that each point is measured and calculated from 1 cm sediment slices, which correspond to ca. 5 yr of deposition; **(B)** air temperature data with 5-yr moving average in the comparison to the data in **(A)**. The predicted temperatures are based on the pattern of *f* values in **(A)** and the exponential equation in Fig. 3.
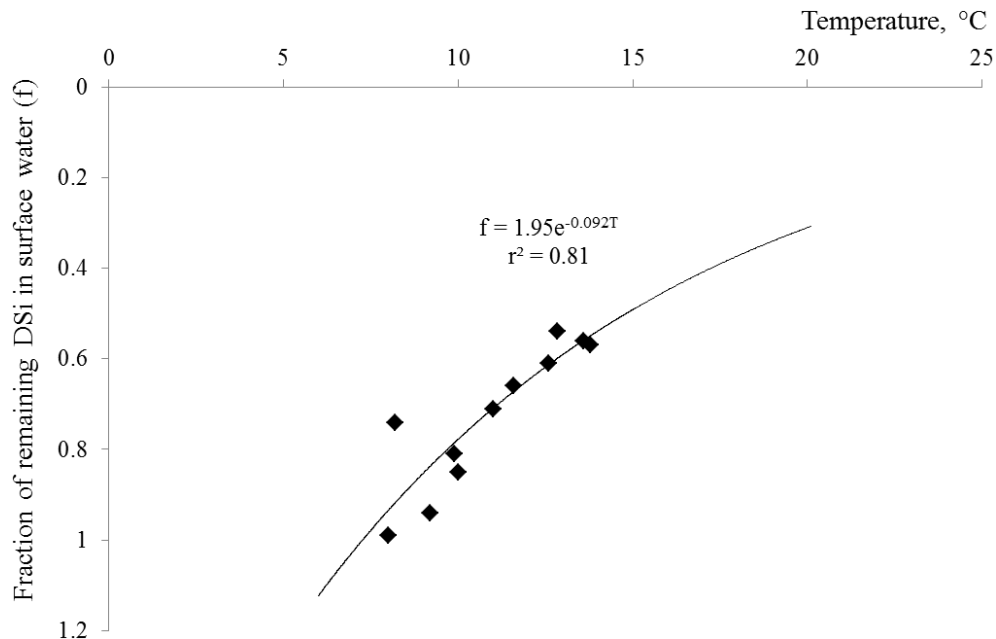
Fig. 7. The fraction of remaining DSi (f) vs. 5-yr moving average of air temperature fit with the exponential regression.

The plot shows Temperature, °C on the top axis (0 to 25) and Fraction of remaining DSi in surface water (f) on the vertical axis (0 to 1.2), with the fit:

$$f = 1.95e^{-0.092T}$$
$$r^2 = 0.81$$