A combined oxygen and silicon diatom isotope record of Late Quaternary change in Lake El'gygytgyn, North East Siberia.

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Abstract

Determining the response of sites within the Arctic Circle to long-term climatic change remains an essential pre-requisite for assessing the susceptibility of these regions to future global warming and Arctic amplification. To date, existing records from North East Russia have demonstrated significant spatial variability across the region during the late Quaternary. Here we present diatom $\delta^{18}O$ and $\delta^{30}Si$ data from Lake El'gygytgyn, Russia, and suggest environmental changes that would have impacted across West Beringia from the Last Glacial Maximum to the modern day. In combination with other records, the results raise the potential for climatic teleconnections to exist between the region and sites in the North Atlantic. The presence of a series of 2-3‰ decreases in $\delta^{18}O_{diatom}$ during both the last glacial and the Holocene indicates the sensitivity of the region to perturbations in the global climate system. Evidence of an unusually long Holocene thermal maximum from 11.4-7.6 ka BP is followed by a cooling trend through the remainder of the Holocene in response to changes in solar insolation. This is culminated over the last 900 years by a significant decrease in $\delta^{18}O_{diatom}$ of 2.3‰, which may be related to a strengthening and easterly shift of the Aleutian Low in addition to possible changes in precipitation seasonality.

Keywords: Arctic, Asia, Beringia, Holocene, MIS 2, palaeoclimate

1 Introduction

Understanding the long-term response and climatic variability of high latitude system becomes critical as the vulnerability of these regions to future climate change becomes increasing understood. Whilst considerable attention is now focused on marine environments such as the Southern Ocean (e.g., Ragueneau et al., 2002) as well as lacustrine sequences from Northern Europe and North America (e.g., Smol et al., 2005), there remains a scarcity of similar records from more remote regions within the Arctic Circle. Developing improved constraints as to the natural climatic and environmental stability of these regions remains essential, not only for improving our understanding of their long-term, decadal-centennial scale, palaeoclimatic history (e.g., Overpeck et al., 1997) but also for developing more accurate climate models that include Arctic amplification. In particular, existing attempts to understand the environmental and climatic history of west Beringia have been hindered by evidence of significant spatial climatic variability across the region over the last glacial and Holocene with conflicting evidence emerging with regards to the teleconnections that exist with other parts of the globe (e.g., Kokorowski et al., 2008 a,b).

Lake El'gygytgyn (altitude = 492 m asl) is a cold-monomictic and ultra-oligotrophic high-latitude crater lake situated on the Chukchi Peninsula, Russia, at 67.30ºN, 172.00ºE (Fig. 1). Formed following an impact event at 3.6 Ma (Layer, 2000), the lake covers an area of 110 km^2, extends to a maximum depth of 177 m, and is fed by 50 streams with a single outflow, the Enmyvaam River, located to the south east of the basin (Nolan and Brigham-Grette, 2007). An important feature of the lake is the prolonged annual ice-cover with open-water conditions today typically lasting from July to October (Nolan et al., 2003). The catchment, 293 km^2, is small relative to the lake surface area with vegetation characterised by discontinuous lichen and herbaceous taxa and permafrost extending down to depths of 100-300 m (Glushkova, 1993; Lozhkin et al., 2007). Importantly, there is strong evidence that neither Lake El'gygytgyn nor the catchment have been glaciated since the lake's formation, with the nearest evidence of glacial activity located c. 40 km to the west of the catchment (Glushkova, 2001; Glushkova and Smirnov, 2007). Accordingly, this remote lake is well positioned to document past environmental change in the region and further our understanding as to the long-term natural variability of high-latitude, Arctic, systems.

Existing sediment cores, dating back to 300 ka BP, were collected from Lake El'gygytgyn in 1998, 2000 and 2003. Geochemical and mineralogical measurements on these have provided an initial framework for understanding the palaeoenvironmental history of the site (Brigham-Grette et al., 2007; Nowaczyk et al., 2007; Juschus et al. 2007). In particular, marked changes in the lake biogeochemistry have been demonstrated over glacial-interglacial cycles in response to the duration of annual ice-cover over the lake (Melles et al., 2007). Interglacial conditions, for example, have been associated with a reduced ice-cover, increase nutrient mixing and input to the photic zone, and an associated increase in primary productivity and the oxygenation of bottom waters (Melles et al., 2007). Such conditions are believed to have peaked during the last interglacial, in agreement with pollen records from the lake which suggest that the Holocene Thermal Maximum and MIS 5e were the warmest periods over the core intervals studied to date (Lozhkin et al., 2007). In addition to geochemistry other proxy records, including those from inorganic chemistry and clay mineralogy, show clear changes over glacial-interglacial cycles, occurring both in response to changes in lake/catchment hydrology and atmospheric circulation (Asikainen et al.. 2007; Minyuk et al., 2007). These proxy records also show clear evidence of rapid short-term fluctuations, in agreement with magnetic susceptibility measurements which display high frequency changes tentatively linked to Heinrich/Dansgaard-Oeschger events in the Greenland/North Atlantic region during the last glacial (Nowaczyk et al., 2002, 2007). Most relevant to this study are the observation that these changes appear to have continued from MIS 2 through both the Younger Dryas and the Holocene. Indeed, whilst not widely discussed, records of nitrogen, organic carbon, opal concentrations as well as organic $\delta^{13}C$ measurements indicate marked changes of a similar magnitude during both the Holocene as well as the last glacial (Melles et al., 2007).

Whilst the number of palaeoenvironmental reconstructions covering the time interval from the Last Glacial Maximum (LGM) to the modern day will undoubtedly increase in response to further work on core material collected at Lake El'gygytgyn, records from the lake currently contrast with the wealth of data available from other sites in both East and West Beringia as well as other high latitude sites within the Arctic circle (e.g., Brigham-Grette et al., 2004; Kaufman et al., 2004; Kokorowski et al., 2008a and references within). Isotope records, in particular that of $\delta^{18}O$, provide a potentially powerful tool by which to extend existing research and to develop additional insights into both local and regional scale environmental and climatic changes (e.g., von Grafenstein et al., 1999). Due to the absence of lacustrine carbonates (authigenic or biogenic), thus far no $\delta^{18}O$ data has been obtained from the Lake El'gygytgyn sediment record. By generating an oxygen isotope record from diatom fossils ($\delta^{18}O_{diatom}$), which are both abundant and exceptionally well preserved in Lake El'gygytgyn, it becomes possible to complement existing and ongoing research on the lake as well as to extend palaeoclimate records from elsewhere in West Beringia that have largely relied upon palynological data (e.g., Anderson et al., 2002 Lozhkin et al., 2007). Such a record will ultimately permit comparisons with existing Holocene $\delta^{18}O_{diatom}$ records from Siberia/Alaska, allowing issues of continentality (e.g., Lake El'gygytgyn v Lake Baikal) and spatial variability in Beringian climatology to be addressed. A unique advantage of Lake El'gygytgyn, compared to other sites containing glacial aged sediments such as Lake Baikal, is the excellent preservation of diatom frustules beyond the last deglaciation with no evidence of increased dissolution or diagenesis (Fig. 2; Cremer et al., 2005; Cherapanova et al., 2007). Accordingly, the potential exist to extend records of $\delta^{18}O_{diatom}$ into the last glacial to develop a unique lacustrine insight into regional climatic changes during MIS 2, over the last deglaciation and into MIS 1.

A recent advance is the development of a method to analyse $\delta^{30}Si_{diatom}$ on the same samples as that for $\delta^{18}O_{diatom}$ (Leng and Sloane, 2008) to provide information on the biological community, nutrient input and export production of the lake. Whilst measurements of $\delta^{30}Si_{diatom}$ have yet to be fully utilised in palaeolimnology, the information from $\delta^{30}Si_{diatom}$ may provide additional context for interpreting records of $\delta^{18}O_{diatom}$ as well as itself generating important information with regards to catchment/lake environmental changes. Accordingly, records of $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ are presented here from Lake El'gygytgyn for the last 23,000 years (LGM through to the present day) to further investigate both the local and regional, West Beringian, scale changes that have occurred over this timeframe.

2 Methodology

2.1 Coring Site

A gravity (Lz1029-5) and piston (Lz1029-9) core were taken in July 2003 at core site Lz1029 (Latitude: 67º39.37'N, Longitude: 172º08.23'E) from the central eastern part of Lake El'gygytgyn at a water depth of 177 m (Fig. 1). The location of this site is the same as that for core PG1351, cored in 1998 which forms the basis of existing work published on Lake El'gygytgyn (see Brigham-Grette et al., 2007). Core chronology for Lz1029 is based upon five radiocarbon dates calibrated using CalPal (2007), incorporating a reservoir effect of 1.3 ka (unpublished data), using linear interpolation between age control points (Fig. 3). All samples were dated at the Leibniz Laboratory for Radiometric Dating and Isotope Research (Kiel, Germany). The ^{14}C reservoir effect for Lake El'gygytgyn is calculated from three radiocarbon measurements on surface sediment material from different cores collected from the lake. Whilst the estimated reservoir age of 1.3 ka is likely to be representative of the Holocene, Late Glacial and MIS 3, its accuracy may be less valid for MIS 2 when a perennial ice cover could have increased the lake reservoir age (Melles et al., 2007). Whilst this, combined with the absence of age constraints between 16.4 ka BP and 4.8 ka BP, limits the ability to chronologically relate events in Lake El'gygytgyn to other locations during MIS 2, the sediment record remains an important and valid tool for understand the nature of palaeoclimatic and palaeoenvironmental changes in the region during this interval.

2.2 Isotope measurements

Continuous 0.5 cm samples from cores Lz1029-5 and Lz1029-9 were prepared for diatom isotope analysis using previously published techniques in a series of steps designed to physically and chemically remove non-diatom material (Morley et al., 2004; Swann et al., 2006). Samples were initially treated with 30% H_2O_2 to disaggregate the material. Following centrifuge washing to removal remaining H_2O_2, samples were mixed with sodium polytungstate (SPT) at 2,500 rpm for 20 minutes using a series of specific gravities from 2.10-2.25 g/ml to separate diatoms from clays. Following further treatment in 30% H_2O_2 and 5% HCl to remove remaining organic matter and carbonates, samples were sieved using cellulose nitrate membrane filters and conventional stainless steel woven wire mesh sieves with the 5-75 µm fraction retained for analysis. All samples were visually checked for diatom purity and species biovolume composition using SEM and x1000 magnification light microscopy prior to isotope analysis. Sample purity was estimated following the semi-quantitative approach of Morley et al. (2004) in which the proportion of diatom to non-diatom material is calculated on 30 quadrants of a 100 µm by 100 µm grid graticule under light microscopy at x1000 magnification. Whilst the uppermost sections of cores from Lake El'gygytgyn above the redox boundary are likely characterised by incomplete oxygenation of organic matter (Melles et al., 2007), this does not influence the diatom isotope records as organic matter around the frustules are chemically removed prior to analysis. In addition visual analyses of the extracted diatoms confirms that the frustules have not been subject to dissolution or other processes that may alter their isotopic composition (Fig. 2).

Samples were analysed for $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ using a step-wise fluorination technique at NIGL (Leng and Sloane, 2008). All 74 purified samples were analysed for $\delta^{18}O_{diatom}$ with a subset of 28 samples also analysed for $\delta^{30}Si_{diatom}$. For each sample 6.5-7 mg of purified diatoms were loaded into nickel reaction vessels and outgassed for two hours at 250ºC to remove surficial water. Diatom -Si-OH layers, which contain exchangeable oxygen, were stripped using BrF_5 at 250ºC for six minutes. Oxygen and silicon from the -Si-O-Si layer were subsequently dissociated overnight using an excess of reagent at 550ºC with oxygen subsequently converted to CO_2 following the methodology of Clayton and Mayeda (1963) and silicon collected as SiF_4. Following extraction, gases were analysed for $\delta^{18}O$ and $\delta^{30}Si$ using a Finnegan MAT 253. Values were converted to the SMOW or NBS28 scale, for $\delta^{18}O$ and $\delta^{30}Si$ respectively, using the NIGL within-run laboratory diatom standard (BFC_{mod}) calibrated against NBS28. Replicate analyses indicate a mean analytical reproducibility (1σ) of 0.34‰ (range = 0.03 to 0.54‰, n = 17) and 0.06‰ (range = 0.01 to 0.13‰, n = 4) for $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ respectively in the sample material. Yield measurements for $\delta^{18}O_{diatom}$ varied from 62% to 74% whilst those for $\delta^{30}Si_{diatom}$ indicated 100% collection of all silicon.

3. Results

Diatoms represent the sole siliceous microfossil within the analysed material with the predominant contaminant comprising small, 5-10 µm, sized clay particles which are of a similar size to the diatom frustules. Levels of contamination are minimal throughout the core (mean sample purity as calculated under light microscopy is 95.9% [1σ = 1.9%]) with no relationship between changes in sample purity and $\delta^{18}O_{diatom}$ or $\delta^{30}Si_{diatom}$ (Fig. 2, 3). Extracted diatoms across all samples show excellent fossilised preservation with no evidence of dissolution or diagenesis (Fig. 2).

From 22.6 ka BP to 20.5 ka BP measurements reveal frequent, c. 1.5-3.0‰, changes in $\delta^{18}O_{diatom}$ with values reaching a maxima of +25.1‰ at 21.9 ka BP (Fig. 3). By comparison, changes from 19.0 ka BP to 16.9 ka

BP are more gradual, though the range of $\delta^{18}O_{diatom}$ values remains high. From 13.6 ka BP measurements of $\delta^{18}O_{diatom}$ increase by 2.1‰ through the deglaciation albeit for a reversal of 0.6‰ at 12.4 ka BP. Through the Holocene $\delta^{18}O_{diatom}$ display a long-term decrease of c. 4.0‰ punctuated by, often prolonged, decreases of 1.0-2.0‰ during the early- and mid-Holocene starting at 10.2 ka BP, 8.1 ka BP, 7.5 ka BP, 5.6 ka BP and 4.6 ka BP. After 1.9 ka BP fluctuations of c. 1.0‰ are apparent in the $\delta^{18}O_{diatom}$ record until 0.9 ka BP when a progressive decrease in $\delta^{18}O_{diatom}$ occurs from +25.5‰ to +23.2‰ in the surface sediments. Changes in $\delta^{30}Si_{diatom}$ vary by 0.46‰ through the analytical interval and can be split into five groups: 1) a progressive 0.3‰ increase between 22.6-21.9 ka BP and subsequent decrease to +1.2‰ at 17.1 ka BP during the last glacial; 2) a period of elevated, +1.2‰, values from 12.5-11.4 ka BP at the end of the last glacial; 3) an interval of reduced <+1.0‰ values from 9.3-7.8 ka BP during the early Holocene; 4) oscillations of c. 0.15‰ during the mid-Holocene from 7.5-4.3 ka BP; 5) further changes of c. 0.2‰ during the last 1.4 ka. The relative diatom species biovolume of the analysed material is dominated throughout by *Cyclotella ocellata* Pantocsek and *Pliocaenicus costatus* var. *sibiricus* (Skabitchevsky) Flower, Ozornina et Kuzmina (Fig. 3) with changes largely following those within the uncleaned sediment material (Cherapanova et al., 2007).

4. Discussion

<u>*4.1 Isotope controls*</u>

Sections 4.1.1 and 4.1.2 below discuss the current interpretation of $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ from lacustrine sequences. This is particularly important for $\delta^{30}Si_{diatom}$ with currently only one published down-core record in palaeolimnology.

<u>4.1.1 $\delta^{18}O_{diatom}$</u>

Recent work has increasingly focused on the role of isotope vital effects, diatom dissolution and silica maturation in altering $\delta^{18}O_{diatom}$. Whilst much remains unknown about these separate processes, evidence exists to suggest that none of the above are influential in altering the Lake El'gygytgyn $\delta^{18}O_{diatom}$ record. With regards to $\delta^{18}O_{diatom}$ vital effects, although evidence of such a process has been documented in marine diatoms (Swann et al., 2007, 2008), evidence from culture, sediment trap and fossilised taxa suggests that such effects are either non-existent or within analytical error for lacustrine taxa (Binz, 1987; Brandriss et al., 1998; Moschen et al., 2005; Schiff et al., 2009). The potential issue of vital effects in the Lake El'gygytgyn record is further eliminated by analysed samples being dominated by only two taxa (Fig. 3). Although there are significant correlations between *C. ocellata*/*P. costatus var. sibiricus* and $\delta^{18}O_{diatom}$ ($r = -0.77/0.76$), given the similarity between the purified and original, uncleaned, diatom sediment assemblages this likely indicates that a similar environmental process is controlling both the isotope and diatom assemblage record rather than being evidence of an isotope vital/species effect. With regards to dissolution, which may lead to isotope fractionation, experiments following the removal of the frustule organic coating using H_2O_2 have failed to indicate any isotopic alteration in either acidic or neutral pH waters (Schmidt et al., 2001; Moschen et al., 2006). With the pH in Lake El'gygytgyn c. 6.5-7 and the analysed diatoms well preserved and showing no signs of dissolution or diagenesis (Fig. 2), it appears safe to conclude that the $\delta^{18}O$ signature within the diatoms has not been altered by these processes.

A key assumption in using $\delta^{18}O_{diatom}$ for palaeoenvironmental reconstructions, is that no isotopic exchange occurs between the inner, –Si–O–Si, and outer hydroxyl layer, –Si–OH, during or after sedimentation. Observations, however, have indicated that silica maturation during sedimentation/early burial leads to ^{18}O from the –Si–OH layer forming isotopically enriched -Si-O-Si bonds (Schmidt et al., 1997, 2001; Brandriss et al., 1998; Moschen et al., 2006):

$$\text{Si–}^{18}\text{OH} + \text{Si–}^{16}\text{OH} \rightarrow \text{Si–}^{18}\text{O–Si} + \text{H}_2{}^{16}\text{O} \qquad \text{(Eq. 1)}$$

The extent to which these changes influences palaeoenvironmental reconstructions from $\delta^{18}O_{diatom}$ remains unknown. In conjunction with other evidence, a number of studies have documented strong correlations between records of $\delta^{18}O_{diatom}$ and other $\delta^{18}O$/proxy data that would not be expected were silica maturation significantly altering the fossilised $\delta^{18}O_{diatom}$ record (see summaries in Leng and Barker, 2006; Tyler et al., 2008; Swann and Leng, 2009). Consequently, whilst issues of silica maturation may instigate small scale variations in $\delta^{18}O_{diatom}$, evidence primarily points towards $\delta^{18}O_{diatom}$ being safe for use in palaeoenvironmental reconstructions (Swann and Leng, 2009). On this basis, a number of studies have successfully used lacustrine records of $\delta^{18}O_{diatom}$ to reconstruct palaeoenvironmental and palaeoclimatic changes from both high (e.g., Rosqvist et al., 1999, 2004; Jones et al., 2004) and low latitude localities (Hernández et al 2008; Barker et al., 2001, 2007). The former includes a number of studies over the deglaciation/Holocene from both Lake Baikal (Morley *et al*., 2005; Mackay et al., In Prep) and sites in Alaska (e.g., Hu and Shemesh, 2003; Schiff et al., 2009). In such studies, the interpretation of $\delta^{18}O_{diatom}$ is similar to that of biogenic carbonates (e.g., ostracods) with the controls dependent on the residence time of the lake and, consequently, whether the lake is open or closed (Leng and Marshall, 2004; Leng and Barker, 2006). Whilst uncertainty remains over the true relationship between $\delta^{18}O_{diatom}$ and temperature, increasing evidence exists to suggest that the coefficient is close to 0.2‰/°C (Brandriss et al., 1998; Moschen et al., 2005).

In order to accurately determine the palaeoenvironmental variables governing changes in $\delta^{18}O_{diatom}$ from Lake El'gygtgyn, a modern day calibration is ideally required between the $\delta^{18}O$ of precipitation (δp), lake ice, lake water ($\delta^{18}O_{lake}$) and $\delta^{18}O_{diatom}$. In the absence of such work, assumptions must be made as to the controls on $\delta^{18}O_{diatom}$. While $\delta^{18}O$ records from large lakes with long residence times are usually interpreted in terms of the balance between precipitation/evaporation, here this can be disregarded because there is evidence of only minimal evaporation and changes in the rate of precipitation both today and in the past (Brigham-Grette et al., 2004; Melles et al., 2007; Nolan and Brigham-Grette, 2007). Similarly the impact of other localised processes in controlling $\delta^{18}O_{diatom}$, such as changes in permafrost melting, direct changes in lake water temperature and changes in lake level, can also be eliminated. Firstly, whilst permafrost melting may lead to large influxes of water, values of c. −19‰ to −20‰ in the top 3.5 m of the permafrost are similar to lake water and so unlikely to significantly alter $\delta^{18}O_{diatom}$ (Schwamborn et al., 2006, 2008; pers. comm. Chapligin). Secondly, with modern lake water temperatures of less than 4ºC (Nolan and Brigham-Grette, 2007) any change in temperature is likely to be less than ±2ºC due to the high latitudinal position of Lake El'gygytgyn. Such a change would cause $\delta^{18}O_{diatom}$ to vary only marginally outside the limits of analytical reproducibility (0.34‰) when using a diatom temperature coefficient of −0.2‰/ºC (Brandriss et al., 1998; Moschen et al., 2005). Finally, whilst the lake level has undergone a c. 11 m decrease since the late Pleistocene in response to increased erosion (Glushkova and. Smirnov, 2007), such changes are not excessive given modern day lake depths of 170 m. As such, changes in lake level are unlikely to have significantly altered water residence time or $\delta^{18}O_{diatom}$.

Having discounted the above processes in controlling the $\delta^{18}O$ record in Lake El'gygytgyn, we suggest that the dominant controls on $\delta^{18}O_{diatom}$ are changes in δp. Understanding the isotope meteorology of the region around Lake El'gygytgyn is complicated by the presence of multiple possible source regions of precipitation and the recycling of precipitation over the continents (Numaguti, 1999; Ichiyanagi et al., 2003; Kurita et al., 2003, 2004, 2005; Schwamborn et al., 2006). With levels of precipitation low, it is unlikely that changes in the moisture source region or the $\delta^{18}O$ of the source have the capacity to cause the large changes observed in $\delta^{18}O_{diatom}$ given the volume and long residence time of water within the lake. Instead, the only process which has the capability of instigating these shifts in $\delta^{18}O_{diatom}$ are changes in atmospheric temperature at the point of condensation (dT). Air temperatures are highly variable in this region ranging in 2002 from −40ºC to +26ºC (Nolan and Brigham-Grette, 2007), although no suitable observational δp data exists to test whether this variability is transported to precipitation. If, however, we assume that a high latitude Dansgaard relationship ($\delta p/dT$) of +0.6‰/ºC (Dansgaard, 1964) applies for the region around Lake El'gygytgyn and use a daily average NCEP reanalysis record for the region which show temperatures ranging from c. −25ºC to c. +10ºC (Kalnay et al., 1996; Nolan and Brigham-Grette, 2007) then changes in dT can be estimated to result in δp variations through the year of 21‰. During glacial intervals it can be expected that intra-annual variations in δp will be significantly reduced in response to the colder values of dT during summer months. Whilst these calculations are subject to assumptions with regards to the Dansgaard relationship for the region and are certainly tempered by the multiple moisture sources that contribute to precipitation in Lake El'gygytgyn, such calculations indicate the potential for dT to impact lake water and so $\delta^{18}O_{diatom}$.

Further evidence to support the suggestion that changes in $\delta^{18}O_{lake}$ and so $\delta^{18}O_{diatom}$ are a function of d*T* can be found by considering the extent to which δp may have altered in response to changes in d*T* over the last deglaciation. By taking a modern day/interglacial mean annual air temperature of 10.3ºC (Nolan and Brigham-Grette, 2007) and estimating that mean annual air temperatures for glacials are close to the NCEP daily reanalysis minimum of −25ºC, long-term inter-decadal/centennial changes in δp due to changes in d*T* can be estimated to vary by c. 9‰ when applying a Dansgaard relationship of +0.6‰/ºC. If it is further assumed that these δp/d*T* changes are controlling similar long-term changes in lake water $\delta^{18}O$, values of $\delta^{18}O_{diatom}$ can be calculated to vary by c. 6‰ over glacial-interglacial cycles when using a lacustrine diatom-temperature coefficient of −0.2‰/ºC which results in a $\delta^{18}O_{diatom}$/d*T* relationship of +0.4‰ (Leng and Barker, 2006). This calculated $\delta^{18}O_{diatom}$ range of 6‰ over glacial-interglacial cycles is similar in magnitude to that observed in the Lake El'gygytgyn $\delta^{18}O_{diatom}$ record between the LGM and the early Holocene (Fig. 3), supporting our assumption that long-term changes in $\delta^{18}O_{diatom}$ are primarily controlled by d*T* over both short, intra-annual, and more importantly long, decadal-centennial, timescales. However, separating the extent to which a changes in $\delta^{18}O_{diatom}$ reflects a change in precipitation seasonality or a long-term inter-annual/decadal/centennial change, both of which will alter the mean annual d*T* of precipitation is problematic. For example, any inter-annual/decadal/centennial change in temperature will lead to a change in mean annual values of d*T* and δp and so alter $\delta^{18}O_{diatom}$ either with or without any associated changes in precipitation seasonality and vice-versa. Consequently both processes must be considered together when attempting to interpret the $\delta^{18}O_{diatom}$ record form Lake El'gygytgyn.

4.1.2 $\delta^{30}Si_{diatom}$

Three stable isotopes of silicon exist, ^{28}Si, ^{29}Si and ^{30}Si. Whilst isotope measurement are commonly reported as $\delta^{30}Si$ ($^{30}Si/^{28}Si$), values are occasionally reported as $\delta^{29}Si$ ($^{29}Si/^{28}Si$) due to analytical limitations (e.g., Cardinal et al., 2003). The processes by which diatoms uptake Dissolved Silicic acid (DSi) during biomineralisation and deposit silicon within the cell wall are relatively well understood (Leng et al. In Press). Research has demonstrated that ^{28}Si is preferentially incorporated into the frustule over ^{29}Si and ^{30}Si with an enrichment factor in the open ocean of −0.6‰ to −1.9‰ (de la Rocha et al., 1997, 2000; Milligan et al., 2004; Varela et al., 2004; Cardinal et al., 2005; 2007; Reynolds et al., 2006; Beucher et al., 2008) independent of temperature, pCO_2 and other vital effects (de la Rocha et al., 1997; Milligan et al., 2004). With increased silicic acid usage resulting in a progressive increase in both the $\delta^{30}Si$ of DSi ($\delta^{30}Si_{DSi}$) and diatoms, $\delta^{30}Si_{diatom}$ can be used as a record of silicic acid utilisation, which in turn is controlled by diatom/siliceous productivity within the photic zone (e.g., de la Rocha et al., 1998). Under this rationale, $\delta^{30}Si_{diatom}$ has been used to investigate the role of the marine biological pump in regulating atmosphere pCO_2 (e.g., Brzezinski et al., 2002; Reynolds et al., 2008). In addition to productivity, however, consideration is also required over changes in the availability and delivery of silicic acid and other nutrient to the photic zone, all of which can trigger a change in the $\delta^{30}Si_{DSi}$ substrate and/or the biological demand for silicon without a corresponding change in productivity (Reynolds et al., 2006; Pichevin et al 2009).

In contrast to the oceans, measurements of $\delta^{30}Si_{diatom}$ have yet to been widely applied in palaeolimnology. To date there is a single published study of very low resolution recording changes in Si cycling of a Kenyan lake during the last glacial (Street-Perrott et al., 2008). In addition to the above ocean controls on $\delta^{30}Si_{diatom}$, additional consideration is required over to the extent to which lacustrine $\delta^{30}Si_{DSi}$ and DSi concentrations may vary as a function of catchment weathering, river/aeolian inputs, water residence time as well as changes in the stratification/overturning or other physical characteristics of an individual lake. Whilst the individual role of these processes in altering the $\delta^{30}Si_{DSi}$ and so $\delta^{30}Si_{diatom}$ will vary in each lake depending on the volume/surface area and other characteristics of both the lake and its catchment, $\delta^{30}Si$ research over the past decade has increasingly focused on understanding the terrestrial and continental component of the global $\delta^{30}Si$ cycle (e.g., De La Rocha et al., 2000; Ding et al., 2004; Basile-Doelsch et al 2005; Ziegler et al 2005a, b; Georg et al., 2006, 2007, 2009). Within the context of the ultra-oligotrophic status of Lake El'gygytgyn, changes in $\delta^{30}Si_{diatom}$ are likely to be driven by changes in the rate of nutrient supply to the photic zone with any increase/decrease initiating a decrease/increase in silicic acid utilisation and so $\delta^{30}Si_{diatom}$ due to the alleviation of nutrient limitation. Changes in nutrient input to the lake are likely to be primarily driven by catchment chemical weathering, which is predominantly formed of igneous rock including ignimbrites, basalts and tuffs. Accordingly, increases/decreases in temperature will result in a corresponding change in the availability of nutrients, including DSi (Struyf et al., In Press), that can be transported to the lake either as surface/riverine flow or through the active layer of the permafrost which extend to depths of c. 0.8 m (Schwamborn et al., 2006). Research has increasingly revealed the role of vegetation in both altering both rates of weathering (Drever, 1994) and acting as a major component of the terrestrial silicon cycle by taking up DSi from soils to form phytoliths, the silicon of which is rapidly recycled back into the soils as DSi during decomposition (Alexandre et al., 1997; Conley, 2002; Derry et al., 2005; Street-Perrott and Barker, 2008). Such changes would also alter the terrestrial $\delta^{30}Si$ cycle (e.g., Ding et al., 2008a,b; Hodson et al. 2008). Accordingly, over glacial-interglacial cycles it would typically be expected for changes in vegetation to have a marked impact on the flux of nutrients and $\delta^{30}Si_{DSi}$ to lakes. The long-term impact of vegetation around Lake El'gygytgyn on $\delta^{30}Si_{DSi}$, however, remain unclear with the catchment today marked by discontinuous lichen and herbaceous taxa (Lozhkin et al., 2007). Pollen records from Lake El'gygytgyn are distorted by the influx of exotic taxa, preventing an insight as to past vegetation patterns across the catchment (ibid). However with snow and ice covering both the lake/catchment in the modern day for all but c. 3 months of the year (Nolan et al., 2003), it is difficult to envisage that the tundra vegetation altered sufficiently over the Holocene to significantly alter the $\delta^{30}Si_{DSi}$ flux to the lake. Whilst it remains likely that an increase in lichen and herbaceous taxa may have accompanied the shift to warmer conditions following the last deglaciation, it is not possible at this time to estimate whether this altered catchment nutrient fluxes to the lake beyond the limits of $\delta^{30}Si_{diatom}$ analytical reproducibility.

Further changes in nutrient availability and so $\delta^{30}Si_{diatom}$ may have originated from lake mixing which has the potential to deliver nutrients from bottom waters to the photic zone (Melles et al., 2007). Under this scenario warmer intervals, marked by prolonged ice-free conditions, would have been characterised by extended lake mixing and increased nutrient supply to the photic zone, lowering the relative rate of biogenic silicic acid demand and so decreasing $\delta^{30}Si_{diatom}$. Conversely, reduced mixing combined with a lowering of catchment weathering during cooler intervals would decrease nutrient supply, increasing $\delta^{30}Si_{diatom}$ and the relative biological demand for silicon. Such a mechanisms, however, is only valid for the Holocene with evidence of minimal mixing during the last glacial (Melles et al., 2007). Whilst the presence of anoxic bottom waters, as inferred from total sulphur measurements, indicates a perennial ice-cover over the lake during the last glacial (Melles et al., 2007), nutrient supply to the photic zone must have occurred to maintain the relatively consistent levels of siliceous microfossil productivity inferred from diatom and biogenic silica measurements over glacial-interglacial cycles (Cherapanova et al., 2007; Melles et al., 2007; Vogel et al., 2008). With permafrost in the catchment extending to depths of 100-300 m (Glushkova, 1993), it is difficult to envisage groundwater being the main carrier of nutrients to the lake during the last glacial, particularly if the depth of the active layer was significantly reduced from the modern day value of 0.8 m in response to cooler conditions (Schwamborn et al., 2006). However, since the lake itself is underlain by bedrock, the role of groundwater fed nutrient can not be completely eliminated. Whilst it has been documented that small ice-free moats may have developed around the edge of the lake during summer months during the last glacial (Nolan and Brigham-Grette, 2007), these were restricted in number and limited to the near-shore localities. Accordingly, although nutrient inputs to the lake may have occurred via these moats, their limited size and spatial coverage is unlikely to have significant impacted the nutrient budget at open water sites such as Lz1029. Consequently we propose that nutrient and DSi supply to the photic zone, either from catchment weathering or aeolian deposition, must have primarily occurred via gravitational transportation and basal melting of the ice, permitting measurements of $\delta^{30}Si_{diatom}$ during MIS 2 to be interpreted in terms of nutrient utilisation similar to the Holocene. Whilst this would suggest a lag in MIS 2 between the deposition of nutrients on the ice and their delivery to the photic zone, this lag is likely to be on the order of a couple of years and should not distort our interpretations given that each analysed 0.5 cm sediment sample represent c. 100-200 years.

Two additional processes are capable of providing supplementary changes in $\delta^{30}Si_{diatom}$: 1) the direct impact of changes in snow cover on biological productivity; 2) diatom dissolution and the associated release of silicon into the water column. Today significant blooms of diatoms occur in Lake El'gygytgyn under the ice

(Cremer et al., 2005). It has been shown in other lakes that extensive and prolonged ice-cover, as well as the thickness of snow cover, can limit diatom productivity via light limitation (e.g., Granin et al., 2000). For example in Lake Baikal, Russia, between 4% and 11% of solar radiation can reach the surface waters through clear ice whilst at snow depths of 5 cm any light penetration is reduced by a factor of 50 (Kelley 1997). Measurements from Lake El'gygytgyn indicate that a snow cover of up to c. 50 cm can develop in the modern day during the winter months before rapidly melting at the beginning of June (Nolan et al., 2003). It is therefore reasonable to assume that any increase in the annual duration of thick snow cover over the lake during the Holocene, either in response to increased precipitation or decreases in air temperature, would also be capable of constraining diatom productivity and so biological silicic acid utilisation in Lake El'gygytgyn through light limitation, leading to a reduction in $\delta^{30}Si_{diatom}$. However, with only minimal levels of precipitation occurring over the lake during MIS 2 (Brigham-Grette et al., 2004; Melles et al., 2007; Nolan and Brigham-Grette, 2007), it is likely that levels of snow accumulation were only sufficient to cause light limitation and so alter $\delta^{30}Si_{diatom}$ during the Holocene. With regards to dissolution, it has been demonstrated that ^{28}Si is preferentially released during diatom dissolution, potentially altering measured values of $\delta^{30}Si_{diatom}$ when dissolution varies by >20% between individual samples (Demarest et al., 2009). Whilst no diatom dissolution index exists for Lake El'gygytgyn, the excellent preservation of diatoms and presence of ultra-oligotrophic conditions in both the isotope samples and sediment diatom assemblages (Fig. 2; Cremer et al., 2005; Cherapanova et al., 2007) suggests that inter-sample differences in dissolution are significantly less the 20% threshold over the analysed interval.

4.2 Palaeoenvironmental reconstructions

4.2.1 Last glacial

High, +1.2 to +1.4‰ values of $\delta^{30}Si_{diatom}$ from 22.6 ka BP to 17.1 ka BP indicate enhanced levels of nutrient utilisation during the last glacial in response to low rates of nutrient influx to the photic zone due an absence of water column mixing and minima in catchment weathering. Accordingly the increase in $\delta^{30}Si_{diatom}$ from 22.6-20.5 ka BP indicates a progressive deterioration in nutrient availability as conditions became gradually colder towards the LGM, increasing overall rates of silicic acid utilisation. Large, up to 3‰, variations in $\delta^{18}O_{diatom}$ through MIS 2 reflect the presence of significant climatic changes during the last glacial. Such fluctuations could either represent centennial scale changes in d*T* or alterations in precipitation seasonality. If the changes in Lake El'gygytgyn are predominantly a function of long-term changes in air temperature rather than precipitation seasonality, variations in $\delta^{18}O_{diatom}$ would suggest d*T* changes of c. 4-8°C (using 0.4‰/°C): typically half the temperature change experienced in Greenland over stadials-interstadials transitions (Severinghaus and Brook, 1999; Johnsen et al., 2001; Grachev and Severinghaus, 2003; Landais et al., 2004a,b). At this time insufficient diatom material exists to study the $\delta^{30}Si_{diatom}$ record over this interval and so assess the lake's ecosystem response to these events. Similarly, the absence of a high resolution $\delta^{18}O_{diatom}$

record for Lake El'gygytgyn limits investigations into the nature and regional/hemispheric significance of these oscillations. However, previous work in Lake El'gygytgyn has tentatively linked millennial scale fluctuations in magnetic susceptibility to equivalent events in the Greenland $\delta^{18}O_{ice}$ records (Nowaczyk et al., 2002, 2007) whilst teleconnections with the North Atlantic region have been documented for other regions of Arctic Russia during the last glacial (c.f. Voelker and Workshop Participants, 2002; Clement and Peterson, 2008). It therefore remains possible that climatic changes in the North Atlantic region could be manifested in the Lake El'gygytgyn $\delta^{18}O_{diatom}$ record through expansion/contraction of the polar front and its associated impact on d*T*. Confirmation as to the timing and frequency of the climatic fluctuations in the $\delta^{18}O_{diatom}$ record could verify this as well as provide further insight as to the sensitivity of disparate polar regions to global climatic processes.

<u>4.2.2 Deglaciation</u>

Increases in $\delta^{18}O_{diatom}$ from 13.7 ka BP, particularly from 12.0 ka BP, reflect a progressive warming of the climate which again corresponds with similar changes in the Greenland ice core records (NGRIP Project Members, 2004) (Fig 3). However, the continuing presence of relatively high $\delta^{30}Si_{diatom}$ until 10.7 ka BP indicates that while primary productivity may have increased, overall rates of nutrient influx to the lake must have remained limited by the cold conditions, inhibiting both lake mixing and rates of weathering/nutrient input. Whether the 0.9‰ decrease in $\delta^{18}O_{diatom}$ from 12.7-12.4 ka BP ($\delta^{18}O_{diatom}$ = +26.6 to +25.7‰) represents a climate reversal similar to the Younger Dryas/Greenland Stadial 1 (GS-1) and/or a short lived increase in the relative amount of winter precipitation remains to be seen given the brevity of this interval compared to the longer, 1.2 ka, duration of the GS-1 event in the Greenland ice cores (Rasmussen et al., 2006). However, the presence of a possible GS-1 signal in $\delta^{18}O_{diatom}$ would be in agreement with similar trends observed in magnetic susceptibility, clay mineralogy and grain size measurements from Lake El'gygytgyn (Nowaczyk et al., 2002; Asikainen et al., 2007), re-emphasising the possible existence of strong climatic teleconnection between the region and the North Atlantic during the last glacial. Since measurements of $\delta^{18}O_{diatom}$ in Lake El'gygytgyn do not return to glacial equivalent values, however, it can be assumed that any change in climatic deterioration associated with this event was similar in magnitude to the reversal experienced in East Beringia/Alaska (Hu and Shemesh, 2003) as well as elsewhere in North East Siberia (Müller et al 2009) rather than the return to near-glacial conditions that occurred in Europe (c.f. von Grafenstein et al., 1999). Evidence of a GS-1 event in Lake El'gygytgyn would, however, contrast with a number of other records from North East Siberia arguing for a warmer climate during this interval (Kokorowski et al., 2008a and references within), making it clear that the region may be marked by significant spatial variability over Termination I.

<u>4.2.3 Holocene thermal maximum</u>

The direction and magnitude of change in $\delta^{18}O_{diatom}$ during the Holocene is significantly different in Lake El'gygytgyn to the mass-balanced corrected $\delta^{18}O_{diatom}$ record for Lake Baikal, Russia, situated in the continental interior of Central Siberia (Morley et al., 2005; Mackay et al., In Prep), highlighting the different climatic controls between these two regions. A period of high, +26‰ to +27‰, $\delta^{18}O_{diatom}$ in Lake El'gygytgyn from the end of the deglaciation until 7.6 ka BP suggests a prolonged interval of warmer climatic conditions similar to the early Holocene thermal maximums seen elsewhere across the globe including Central Siberia and North East Siberia (e.g., Koshkarova and Koshkarov, 2004; Müller et al 2009), the western Arctic (Kaufman et al., 2004) and the Lake El'gygytgyn catchment (Schwamborn et al., 2006; Lozhkin et al., 2007). Although we believe that evaporation did not play a significant role in controlling long-term changes in $\delta^{18}O_{diatom}$ (Section 4.1.1), it is possible that increased evaporation during this warmer interval may have assisted in driving the upward trend in $\delta^{18}O_{diatom}$ by increasing $\delta^{18}O_{lake}$.

A transition to warmer climatic conditions through this period is also reflected by the shift in $\delta^{30}Si_{diatom}$ to values of <1.0‰. Whilst a relative increase in summer precipitation alone would have increased catchment weathering and rates of nutrient delivery to the lake, $\delta^{30}Si_{diatom}$ values of <1.0‰ indicate a marked reduction in photic zone nutrient limitation. Given the ultra-oligotrophic status of Lake El'gygytgyn, it is proposed that such an alleviation could only arise by maximising nutrient supply to the photic zone. This may have been achieved by a marked shift to warmer climatic conditions which, in addition to increasing catchment nutrient inputs, would increase water column mixing and so the recycling of bottom water nutrients to the photic zone as well as prolonging the annual ice-free conditions which would increase the duration over which allochthonous nutrients could have been delivered to the lake. Although palaeoclimatic conditions around the lake likely remained favourable following this thermal optima, a progressive long-term decrease in $\delta^{18}O_{diatom}$ begins from 7.5 ka BP through to the modern day. In particular, increases in $\delta^{30}Si_{diatom}$ from 7.5-4.3 ka BP suggest the emergence of an increasingly unstable climate marked by reductions in nutrient input to the photic zone and a return to increasingly silicon limited surface waters.

As with GS-1, evidence of a thermal maximum signal in both the $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ records from Lake El'gygytgyn (11.4-7.6 ka BP) contrasts with pollen data from other regional sites arguing against a maximum in West Beringia (Lozhkin et al., 1995, 1998; Shilo et al., 2001). In addition, compared to other Arctic sites displaying evidence of a thermal maximum (Kaufman et al., 2004), the duration and impact of this warm interval at Lake El'gygytgyn appears to have prevailed significantly longer than elsewhere with $\delta^{30}Si_{diatom}$ implying relatively warm conditions and high levels of nutrient input until c. 7.6 ka BP. On the one hand the long duration of the Holocene Thermal Maximum in Lake El'gygytgyn may reflect that the region immediately around the lake is unusually sensitive to any environmental perturbation, making the sediment record particularly apt for reconstructing changes across the region. Alternatively, these differences may reflect the separate environmental controls on individual proxy records. Whereas changes in $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ are largely a direct function of d*T* and rates of nutrient utilisation, the pollen and plant macrofossils records which form the majority of existing data from the Arctic may be additionally controlled by a series of non-climatic processes including dispersal, competition and other local-scale processes. Whilst neither set of techniques can be regarded as superior to the other, it is conceivable in this instance that pollen/macrofossil records from the region are biased towards reflecting the impact and timing of local-scale catchment changes whilst the isotope records better reflect regional changes and their impact on the lake ecosystem. Deriving an improved understanding of the different environmental controls on individual techniques is therefore an essential step that is needed before attempts can be made to fully understand the divergent palaeoenvironmental signals being observed across the Arctic.

4.2.4 Mid-Late Holocene climatic variability

The gradual 1-2‰ decrease in $\delta^{18}O_{diatom}$ from 7.6 ka to c. 1.5 ka BP reflects a progressive cooling signal seen across Holocene sediment records from the Northern Hemisphere caused by changes in orbital insolation (Berger and Loutre, 1991). Throughout this interval several reversals are apparent in the $\delta^{18}O_{diatom}$ record from 7.5-6.8 ka BP, 5.6-5.1 ka BP and at 4.6 ka BP which are marked by similar decreases in $\delta^{30}Si_{diatom}$ (Fig. 3). Whilst values of $\delta^{30}Si_{diatom}$ initially increase at the beginning of the 7.5 ka BP event, this may simply reflect the recovery of the lake ecosystem from the lower rates of silicic acid utilisation that prevailed during the preceding thermal maximum. The late Holocene interval is further marked by a series of 0.5-1.0‰ $\delta^{18}O_{diatom}$ oscillations from 1.7-0.9 ka BP for which no $\delta^{30}Si_{diatom}$ data exists but which may be related to associated changes over Northern Europe (Seppä et al., 2009). Whilst changes on the order of this magnitude from 1.7-0.9 ka BP are not unusual in the context of the rest of the $\delta^{18}O_{diatom}$ record and are close to the analytical reproducibility of $\delta^{18}O_{diatom}$ (0.34‰), their frequency, as with the earlier Holocene reversals in the diatom isotope records, suggests the operation of some forcing mechanism.

These decreases in $\delta^{18}O_{diatom}$ may reflect a short-term change in local/regional atmospheric circulation patterns which led to a marked cooling in the region. Interpreting the changes in $\delta^{18}O_{diatom}$ purely in terms of climatic cooling is in disagreement with low values of $\delta^{30}Si_{diatom}$ during these intervals, which suggest high rates of nutrient delivery to the photic zone that would be unexpected in a shift to cooler conditions. Since the decrease in $\delta^{30}Si_{diatom}$ can only indicate lower rates of silicic acid utilisation caused by an increase of both nutrient inputs and water column mixing we suggest that these changes actually reflect a shift to warmer, not cooler, climatic conditions. Under this scenario, decreases in $\delta^{18}O_{diatom}$ are proposed to primarily reflect a relative increase in winter/early spring precipitation. This would not only lower the net annual value of δp entering Lake El'gygytgyn, due to reduced d*T*, but also potentially increase the transportation of catchment derived nutrients into the lake leading to the observed decrease in $\delta^{30}Si_{diatom}$.

A number of studies have documented abrupt climatic changes during the Holocene (Mayewski et al., 2004 and references within), related to changes in both solar variability (Bond et al., 2001; Hu et al 2003; Dergachev et al., 2007), volcanic aerosols in the atmosphere (Robock, 2000; Shindell et al., 2003) and ocean circulation (Bond et al., 1997, 2001; Denton and Broecker, 2008). However, significant debate exists as to the exact timing and spatial variability of these events and the extent to which these intervals are controlled by the aforementioned processes (see Bard and Frank (2006), Wanner et al., (2008) and references within both manuscripts). In the absence of a higher-resolution record, additional ^{14}C dates and improved constraints on the ^{14}C reservoir effect in Lake El'gygytgyn, the nature of these fluctuations with regards to their regularity, duration and timing can not be conclusively established or related to similar events in other terrestrial/marine sequences. However, the observed transitions in the $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ records could, for example, be associated with variations in atmospheric circulation patterns such as short-term migrations of the polar front. Regardless of the mechanism, this section illustrates the benefits gained by interpreting $\delta^{30}Si_{diatom}$ in conjunction with $\delta^{18}O_{diatom}$ in lacustrine systems.

4.2.5 Last 1,000 years

The overall decrease in $\delta^{18}O_{diatom}$ from 0.9 ka BP through to the modern day is in marked contrast to the rest of the Holocene interval implying, at face value, a return to glacial equivalent conditions. Whilst a small, up to c. 1°C, decrease in temperature has occurred across the Northern Hemisphere from c. 0.9-0.4 ka BP and from 2.0 ka BP in the Arctic (Jones and Mann, 2004; Moberg et al., 2005; Kaufman et al., 2009), such change are not consistent with the 2.3‰ decrease here which is equivalent to a reduction of c. 6°C when assuming the isotope variation is purely a dT dependent function. In particular, the potential "cooling" trend indicated by changes in $\delta^{18}O_{diatom}$ over this interval contrast markedly with the warming trend observed elsewhere at other sites in the Northern Hemisphere during the last c. 200 years (e.g., Mann, 2007; Kaufman et al., 2009). Large and variable changes in $\delta^{30}Si_{diatom}$ from 1.4 ka BP onwards suggests the decoupling of the $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ environmental signals and the emergence of a dynamic ecosystem marked by pronounced changes in ice cover/duration and nutrient delivery to the photic zone. As such, interpretation of the $\delta^{18}O_{diatom}$ decrease can not be aided by the $\delta^{30}Si_{diatom}$ data. Increased permafrost melting is unlikely to significantly alter lake water $\delta^{18}O_{diatom}$ given that upper permafrost isotope values are similar to that of lake water (Schwamborn et al., 2006, 2008). However, it is conceivable that melting of deeper (>3 m) permafrost, which has a slightly lower $\delta^{18}O$ values of −21‰ to −20‰, may be making minor contributions to the decreases in $\delta^{18}O_{diatom}$. In conjunction with cooling trends observed at other sites in North East Russia (Popp et al., 2006) and the Arctic Circle (Bjune et al., 2009), we propose that the region around Lake El'gygytgyn has undergone a significant cooling over the past millennia, for example in response to a strengthening and easterly shift of the Aleutian Low (Mock et al, 1998). Understanding why this apparent cooling trend continues through to the modern day, $\delta^{18}O_{diatom}$ decreases by 0.5‰ during the last 200 years, is problematic. Although a similar shift in the Aleutian Low, bringing cooler conditions to West Beringia, has been invoked to explain 20th Century changes in $\delta^{18}O_{diatom}$ from a lake from Southern Alaska (Schiff et al., 2009), both satellite observations and NCEP reanalysis data suggests a marked increase in mean annual temperature around Lake El'gygytgyn in recent decades (Comiso, 2003; Nolan and Brigham-Grette, 2007). Whilst NCEP reanalysis suggests that this trend is caused by warmer winters over the last 15 years, this is disputed by satellite observations that reveal a cooling signal in winter months from 1981-2001 with warmer trends only prevailing from spring-autumn (ibid). Accordingly the continuing decrease in $\delta^{18}O_{diatom}$ in the uppermost samples from Lake El'gygytgyn may be associated with a relative change in precipitation seasonality toward the winter months. Such a mechanism may have altered $\delta^{18}O_{lake}$ and so $\delta^{18}O_{diatom}$ sufficiently to counteract any mean annual increase in temperatures over the last 200 years. Deriving a better understand of these and other "irregularities" in the Arctic palaeoclimate record is likely essential for furthering our understanding as to the future response of these regions to a globally warming climate.

5. Conclusions

Results here provide further insights into the variability of palaeoclimatic events across Beringia indicating that the region around Lake El'gygytgyn has undergone significant climatic and environmental changes both during the last glacial and the Holocene. By combining measurements of $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ it has proven possible to extract a more detailed perspective into both regional climatic events as well as the internal response of the lake and its ecosystem to these changes. Such records, as demonstrated when interpreting the reversals that characterise the mid-late Holocene provide a further means of separating the different signals that can alter records of $\delta^{18}O$. Without this, changes in $\delta^{18}O_{diatom}$ through this section may have been misinterpreted in terms of dT rather than changes in precipitation seasonality. Whilst there are currently no other laboratories analysing $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ on the same sample, the development of new $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ techniques capable of analysing small, c. 0.5-1.5 mg, samples (e.g., Lücke et al., 2005; Reynolds et al., 2008) raise the potential for future diatom isotope lacustrine studies to routinely obtain both $\delta^{18}O$ and $\delta^{30}Si$ records.

Observations of large changes in $\delta^{18}O_{diatom}$ of up to 2-3‰ through both MIS 2 and the Holocene, combined with evidence of a marked cooling trend over the last 900 years, highlights the sensitivity of the sediment record to environmental change and suggest evidence of possible teleconnections between the North Atlantic region and West Beringia. Without a higher resolution diatom isotope record and improved chronological constraints, it is not possible to fully link these changes with existing hemispheric or global records. However, with evidence of potential spatial variability between Lake El'gygytgyn and other sites across West Beringia and the Arctic, there is a need for further research in the region in order for these findings to be integrated into climate predictions and models. Recent drilling of Lake El'gygytgyn has resulted in the collection of cores to depths of 312 m below the lake floor, enabling future investigations to study the long-term, glacial-interglacial, environmental changes back to the date of the lake's formation at c. 3.6 Ma. By combining diatom isotope measurements with other proxy records, it is expected that further insights will be achieved with regards to understanding the palaeoclimatic and palaeoenvironmental history of this region.

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References

Alexandre, A., Meunier, J-D., Colin, F., Koud, J-M., 1997, Plant impact on the biogeochemical cycle of silicon and related weathering processes. Geochimica et Cosmochimica Acta, 61, 677-682.

Anderson, P.M., Lozhkin, A.V., Brubaker, L.B., 2002. Implications of a 24,000-Yr palynological record for a Younger Dryas cooling and for boreal Forest Development in northeastern Siberia . Quaternary Research, 57, 325-333.

Asikainen, CA, Francus, P., Brigham-Grette J., 2007. Sedimentology, clay mineralogy and grain-size as indicators of 65 ka of climate change from El’gygytgyn Crater Lake, Northeastern Siberia. Journal of Paleolimnology, 37, 105-122

Bard, E., Frank, M., 2006. Climate change and solar variability: what's new under the sun? Earth and Planetary Science Letters, 248, 480-493.

Barker, P.A., Street-Perrott, F.A., Leng, M.J., Greenwood, P.B., Swain, D.L., Perrott, R.A., Telford, R.J., Ficken, K.J., 2001. A 14,000-year oxygen Isotope record from diatom silica in two alpine lakes on Mt. Kenya . Science, 2307-2310.

Barker, P.A., Leng, M.J., Gasse, F., Huang, Y., 2007. Century-to-millennial scale climatic variability in Lake Malawi revealed by isotope records . Earth and Planetary Science Letters, 261, 93-103.

Basile-Doelsch, I., Meunier, J.D., Parron, C., 2005. Another continental pool in the terrestrial silicon cycle. Nature, 433, 399-402.

Berger, A., Loutre, M.-F., 1991. Insolation values for the climate of the last 10 million years. Quaternary Science Reviews, 10. 297-317.

Beucher, C.P., Brzezinski, M.A., Jones, J.L., 2008, Sources and biological fractionation of Silicon isotopes in the Eastern Equatorial Pacific . Geochimica et Cosmochimica Acta, 72, 3063-3073.

Binz P., 1987. Oxygen-isotope analysis on recent and fossil diatoms from Lake Walen and Lake Zurich (Switzerland) and its application on paleoclimatic studies, PhD Thesis, Swiss Federal Institute of Technology, Zurich, pp. 165.

Bjune, A.E., Seppä, H., Birks, H.J.B., 2009. Quantitative summer-temperature reconstructions for the last 2000 years based on pollen-stratigraphical data from northern Fennoscandia. Journal of Paleolimnology, 41, 43-56.

Bond, G., Showers, W., Cheseby, M., Lotti, R., Almasi, P., deMenocal, P., Priore, P., Cullen, H., Hajdas, I., Bonani, G., 1997. A pervasive millennial-scale cycle in North Atlantic Holocene and glacial climates. Science, 278, 1257–65.

Bond, G., Kromer, B., Beer, J, Muscheler, R., Evans, M.N., Showers, W., Hoffmann, Lotti-Bond, R., Hajdas, I., Bonani, G., 2001. Persistent solar influence on North Atlantic climate during the Holocene. Science, 294, 2130-2136.

Brandriss, M.E., O'Neil, J. R., Edlund, M.B., Stoermer, E.F., 1998. Oxygen isotope fractionation between diatomaceous silica and water. Geochimica et Cosmochimica Acta, 62, 1119-1125.

Brzezinski, M.A., Pride, C.J., Franck, V.M., Sigman, D.M., Sarmiento, J.L., Matsumoto, K., Gruber, N., Rau, G.H. Coale, K.H., 2002. A switch from $Si(OH)_4$ to NO_3^- depletion in the glacial Southern Ocean. Geophysical Research Letters, 29: 1564. doi: 10.1029/2001GL014349.

Brigham-Grette, J., Lozhkin, A., Andersen, P., Glushkova, O., 2004. Paleoenvironmental conditions in western Beringia before and during the last glacial maximum. In: Madsen DB (eds) Entering America: Northeast Asia and Beringia before and during the last glacial maximum. Univ of Utah Press, pp 29–61.

Brigham-Grette, J, Melles, M, Minyuk, P, Scientific Party 2007. Overview and significance of a 250 ka paleoclimate record from El'gygytgyn Crater Lake, NE Russia. Journal of Paleolimnology, 37, 1-16.

Cardinal, D., Allegan, L.Y., de Jong, J., Ziegler, K., André, L., 2003. Isotopic composition of silicon measured by multicollector plasma source mass spectrometry in dry plasma mode. Journal of Analytical Atomic Spectrometry, 18, 213-218.

Cardinal, D., Alleman, L.Y., Dehairs, F., Savoye, N., Trull, T.W., André, L., 2005. Relevance of silicon isotopes to Si-nutrient utilization and Si-source assessment in Antarctic waters. Global Biogeochemical Cycles. 18, GB2007, doi: 10.1029/2004GB002364.

Cardinal, D., Savoye, N., Trull, T.W., Dehairs, F., Kopczynska, E.E., Fripiat, F., Tison, J-L., André, L. 2007. Silicon isotopes in spring Southern Ocean diatoms: Large zonal changes despite homogeneity among size fractions. Marine Chemistry, 106, 46-62.

Cherapanova, MV, Snyder, JA, Brigham-Grette, J., 2007. Diatom stratigraphy of the last 250 ka at Lake El'gygytgyn, northeast Siberia . Journal of Paleolimnology, 37, 155-162.

Clayton, R.N., Mayeda T.K., 1963. The use of bromine pentafluoride in the extraction of oxygen from oxide and silicates for isotope analysis. Geochimica et Cosmochimica Acta, 27, 43–52.

Clement, A.C., Peterson, L.C., 2008. Mechanisms of abrupt climate change of the last glacial period. Reviews of Geophysics, RG4002, doi:10.1029/2006RG000204.

Comiso, J.C., 2003. Warming trends in the Arctic from clear sky satellite observations. Journal of Climate, 16, 3498-3510.

Conley, D.J., 2002. Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochemical Cycles, 16, 1121-1129.

Cremer, H., Wagner, B., Juschus, O., Melles, M., 2005. A microscopical study of diatom phytoplankton in deep crater Lake

El'gygytgyn, Northeast Siberia. Algological Studies, 116, 147-169.

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus, 16, 436-468.

De La Rocha C.L., Brzezinski M.A., and DeNiro, M.J., 1997. Fractionation of silicon isotopes by marine diatoms during biogenic silica formation. Geochimica et Cosmochimica Acta, 61, 5051–5056.

De La Rocha, C.L., Brzezinski, M.A., DeNiro, M.J., Shemesh, A., 1998. Silicon-isotope composition of diatoms as an indicator of past oceanic change. Nature, 395, 680–683.

De La Rocha, C.L., Brzezinski, M.A., DeNiro M.J., 2000. A first look at the distribution of the stable isotopes of silicon in natural waters. Geochimica et Cosmochimica Acta, 64, 2467-2477.

Demarest, M.S., Brzezinski, M.A., Beucher, C.P., 2009. Fractionation of silicon isotopes during biogenic silica dissolution. Geochimica et Cosmochimica Acta, 73, 5572-5583.

Denton, G.H., Broecker, W.S., 2008. Wobbly ocean conveyor circulation during the Holocene? Quaternary Science Reviews, 27, 1939-1950.

Dergachev, VA., Raspopov, OM., Damblon, F., Jungner., H, Zaitseva, G.I., 2007. Natural climate variability during the Holocene. Radiocarbon, 49, 837-854.

Derry, L.A., Kurtz, A.C., Ziegler, K.,, Chadwick, O.A., 2005. Biological control of terrestrial silica cycling and export fluxes to watersheds. Nature, 433, 728-731.

Ding, T., Wan, D., Wang, C., Zhang, F., 2004. Silicon isotope compositions of dissolved silicon and suspended matter in the Yangtze River, China . Geochimica et Cosmochimica Acta, 68, 205-216.

Ding, T.P., Zhou, J.X., Wan, D.F., Chen, Z.Y., Wang, C.Y., Zhang, F., 2008a, Silicon isotope fractionation in bamboo and its significance to the biogeochemical cycle of silicon . Geochimica et Cosmochimica Acta, 72, 1381-1395.

Ding, T.P., Tian, S.H., Sun, L., Wu, L.H., Zhou, J.X., Chen, Z.Y., 2008b, Silicon isotope fractionation between rice plants and nutrient solution and its significance to the study of the silicon cycle . Geochimica et Cosmochimica Acta, 72, 5600–5615.

Drever, J.I., 1994, The effects of land plants on weathering rates of silicate minerals. Geochimica et Cosmochimica Acta, 58, 2325-2332.

Georg, R.B., Reynolds, B.C., Frank, M., Halliday, A.N., 2006. Mechanisms controlling the silicon isotopic compositions of river waters. Earth and Planetary Science Letters, 249, 290-306.

Georg, R.B., Reynolds, B.C., Burton, K.W., Halliday, A.N., 2007. Silicon isotope variations accompanying basalt weathering on Iceland. Earth and Planetary Science Letters. 261, 476-490.

Georg, R.B., Zhu, C., Reynolds., B.C., Halliday, A.N., 2009. Stable silicon isotopes of groundwater, feldspars, and clay coatings in the Navajo Sandstone aquifer, Black Mesa, Arizona, USA . Geochimica et Cosmochimica Acta, 73, 2229–2241.

Glushkova, O.Yu., 2001. Geomorphology and history of relief development of El'gygytgyn Lake Region. In: Bely V.F, Chershnev IA (eds) The nature of the El'gygytgyn Lake Hollow. Russian Academy of Science, Magadan, pp 26–48.

Glushkova, O.Yu., 2001. Geomorphological correlation of Late Pleistocene glacial complexes of Western and Eastern Beringia.

Quaternary Science Reviews, 20, 405–417.

Glushkova, O.Yu., Smirnov, VN., 2007. Pliocene to Holocene geomorphic evolution and palaeogeography of the El'gygytgyn Lake region, NE Russia. Journal of Paleolimnology, 37, 37-47.

Grachev, A.M., Severinghaus, J.P., 2003. Determining the thermal diffusion factor for ^{40}Ar/^{36}Ar in air to aid paleoreconstruction of abrupt climate change. Journal of Physical Chemistry A, 107, 4636-4642.

Granin, N.G., Jewson, D.H., Gnatovsky, R.Yu., Levin, L.A., Zhdanov, A.A., Gorbunova, L.A., Tsekhanovsky, V.V., Doroschenko, L.M., Mogilev, N.Yu., 2000. Turbulent mixing under ice and the growth of diatoms in Lake Baikal. Verh. Internat. Verein. Limnol. 27, 2812-2814.

Hernández, A., Bao, R., Giralt, S., Leng, M.J., Barker, P.A., Sáez, A., Pueyo, J.J., Moreno, A., Valero-Garcés, B.L., Sloane, H.J., 2008. The palaeohydrological evolution of Lago Chungará (Andean Altiplano, northern Chile) during the Lateglacial and early Holocene using oxygen isotopes in diatom silica . Journal of Quaternary Science. 23, 351-363.

Hodson, M.J., Parker, A.G., Leng, M.J., Sloane, H.J., 2008. Silicon, oxygen and carbon isotope composition of wheat (*Triticum aestivum* L.) phytoliths- implications for palaeoecology and archaeology. Journal of Quaternary Science, 23, 331-339.

Hu, F.S., Shemesh, A., 2003. A biogenic silica δ^{18}O record of climatic change during the last glacial-interglacial transition in southwestern Alaska. Quaternary Research, 59, 379-385.

Hu, F.S., Kaufman, D., Yoneji, S., Nelson, D., Shemesh, A., Huang, Y., Tian, J., Bond, G., Clegg, B., Brown T., 2003. Cyclic variations and solar forcing of Holocene climate in the Alaskan Subarctic. Science, 301, 1890-1893.

Ichiyanagi, K., Sugimoto, A., Numaguti, A., Kurita, N., Ishii, Y., Ohata, T., 2003. Seasonal variation in stable isotopic composition of alas lake water near Yakutsk, Eastern Siberia. Geochemical Journal, 37, 519-530.

Johnsen, S.J., Dahl-Jensen, D., Gundestrup, N., Steffensen, J.P., Clausen, H.B., Miller, H., Masson-Delmotte, V., Sveinbjörnsdottir, A.E., White, J. .2001. Oxygen isotope and palaeotemperature records from six Greenland ice-core stations: Camp Century, Dye-3, GRIP, GISP2, Renland and NorthGRIP. Journal of Quaternary Science, 16, 299-307.

Jones, P.D., Mann, M.E., 2004. Climate over past millennia. Reviews of Geophysics, 42, RG2002, doi:10.1029/2003RG000143.

Jones, V.J., Leng, M.J., Solovieva, N., Sloane, H.J., Tarasov, P., 2004. Holocene climate of the Kola Peninsula; evidence from the oxygen isotope record of diatom silica . Quaternary Science Reviews, 23, 833-839.

Juschus, O., Preusser, F., Melles, M., Radtke, U., 2007. Applying SAR-IRSL methodology for dating fine-grained sediments from Lake El'gygytgyn, north-eastern Siberia. Quaternary Geochronology, 2, 187-194.

Kalnay, E.M., Kanamitsu, M., Kistler, R., Collin, W., Deaven, D., Gandin, L., Iredell, M., Saha, S., White, G., Woollen, J., Zhu, Y., Chelliah, M., Ebisuzaki, W., Higgins, W., Janowlak, J., Mo, K.C., Ropelewski, C., Wang, J., Leetmaa, A., Reynolds, R., Jenne. R., Joseph, D., 1996. The NCEP/NCAR 40 year reanalysis project. Bull Am Meteorol. Soc., 77, 437–471.

Kaufman, D.S., Ager, T.A., Anderson, N.J., Anderson, P.M., Andrews, J.T., Bartlein, P.J., Brubaker, L.B., Coats, L.L., Cwynar, L.C., Duvall, M.L., Dyke, A.S., Edwards, M.E. Eisner, W.R., Gajewski, K., Geirsdottir, A., Hu, F.S., Jennings, A.E., Kaplan, M.R., Kerwin, M.W., Lozhkin, A.V., MacDonald, G.M, Miller, G.H., Mock, C.J., Oswald, W.W., Otto-Bliesner, B.L., Porinchu, D.F., Ruhland, K., Smol, J.P., Steig, E.J., Wolfe, B.B., 2004. Holocene thermal maximum in the western Arctic (0-180°W). Quaternary Science Reviews, 23, 529-560.

Kaufman, D.S., Schneider, D.P., McKay, N.P., Ammann, C., Bradley, R.S., Briffa, K.R., Miller, G.H., Otto-Bliesner, B.L., Overpeck, J.T., Vinther, B.M., Arctic Lakes 2k Project Members., 2009. Recent warming reverses long-term Arctic cooling. Science, 325, 1236-1239.

Kelley, D.E., 1997. Convection in ice-covered lakes: effects on algal suspension. Journal of Plankton Research, 19, 1859-1880.

Kokorowski, H.D., Anderson, P.M., Mock, C.J., Lozhkin, A.V., 2008a. A re-evaluation and spatial analysis of evidence for a Younger Dryas climatic reversal in Beringia. Quaternary Science Reviews, 27, 1710-1722.

Kokorowski, H.D., Anderson, P.M., Sletten, R.S., Lozhkin, A.V., Brown, T.A., 2008b. Late Glacial and Early Holocene Climatic Changes Based on a Multiproxy Lacustrine Sediment Record from Northeast Siberia. Arctic, Antarctic, and Alpine Research, 40, 497–505

Koshkarova, V.L,, Koshkarov, A.D., 2004. Regional signatures of changing landscape and climate of northern Central Siberia in the Holocene; Geologiya Geofizika, 45, 717-729.

Kurita, N., Numaguti, A., Sugimoto, A., Ichiyanagi K., Yoshida N., 2003. Relationship between the variation of isotopic ratios and the source of summer precipitation in eastern Siberia . Journal of Geophysical Reseach, 108, 4339, doi:10.1029/2001JD001359.

Kurita, N., Yoshida N., Inoue, G, Chayanova, E.A., 2004. Modern isotope climatology of Russia: A first assessment. Journal of Geophysical Reseach. 109, doi:10.1029/2003JD003404.

Kurita, N., Sugimoto, A., Fujii, Y., Fukazawa, T., Makarov, V.N., Watanabe, O., Ichiyanagi K., Numaguti, A., Yoshida, N., 2005. Isotopic composition and origin of snow over Siberia. Journal of Geophysical Research, 110, doi:10.1029/2004JD005053.

Landais, A., Caillon, N., Goujon, C., Grachev, A.M., Barnola, J.M., Chappellaz, J., Jouzel, J., Masson-Delmotte, V., Leuenberger, M., 2004a. Quantification of rapid temperature change during DO event 12 and phasing with methane inferred from air isotopic measurements . Earth and Planetary Science Letters, 225, 221-232.

Landais, A., Barnola, J.M., Masson-Delmotte, V., Jouzel, J., Chappellaz, J., Caillon, N., Huber, C. Leuenberger, M., Johnsen, S.J., 2004b. A continuous record of temperature evolution over a sequence of Dansgaard-Oeschger events during Marine Isotopic Stage 4 (76 to 62 kyr BP). Geophysical Research Letters, 31, L22211, doi:10.1029/2004GL021193.

Layer P.W., 2000. Argon-40/argon-39 age of the El’gygytgyn impact event, Chukotka, Russia. Meteorit Planet Sci., 35, 591–599.

Leng, M.J., Marshall, J.D., 2004. Palaeoclimate interpretation of stable isotope data from lake sediment archives . Quaternary Science Reviews, 23, 811-831.

Leng, M.J., Barker, P.A., 2006. A review of the oxygen isotope composition of lacustrine diatom silica for palaeoclimate reconstruction. Earth Science Reviews, 75, 5-27.

Leng, M.J., Sloane, H.J., 2008. Combined oxygen and silicon isotope analysis of biogenic silica. Journal of Quaternary Science, 23: 313-319.

Leng, M.J., Swann, G.E.A., Hodson, M.J., Tyler, J.J., Patwardhan, S.V., Sloane, H.J., In Press). The potential use of silicon isotope composition of biogenic silica as a proxy for environmental change . Silicon.

Lozhkin, A.V., Anderson, P.M., Brubaker, L.B., Prokhorova, T.P., 1995. The first results of palynological analyses of lacustrine sediments from Chukotka. Doklady Akademii Nauk., 342, 540–542.

Lozhkin, A.V., Anderson, P.M., Brubaker, L.B., Kotov, A.N., Kotova, L.N., Prokhorova, T.P., 1998. The herb pollen zone from sediments of glacial lakes. In: Simakov, K.V. (Ed.), Environmental Changes in Beringia During the Quaternary. North East Interdisciplinary Research Institute, Far East Branch, Russian Academy of Sciences, Magadan, pp. 96–111.

Lozhkin, A.V. Anderson P.M., Matrosova, T.V., Minyuk, P.S., 2007. The pollen record from El'gygytgyn Lake: implications for vegetation and climate histories of northern Chukotka since the late middle Pleistocene. Journal of Paleolimnology, 37, 135-153.

Lücke, A., Moschen, R., Schleser, G.H., 2005. High temperature carbon reduction of silica: A novel approach for oxygen isotope analysis of biogenic opal. Geochimica et Cosmochimica Acta. 69, 1423-1433.

Mackay, A.W., Swann, G.E.A., Brewer, T. S., Leng, M.J., Morley, D.W., Rioual, P., White, D., In Prep. A late glacial – Holocene record of hydrological variability in Lake Baikal.

Mann, M.E., 2007. Climate over the past two millennia. Annual Review of Earth and Planetary Sciences. 35, 111-136.

Mayewski, P.A., Rohling, E.E., Stager, C.J., Karlen, W., Maasch, K.A., Meeker, L.D., Meyerson, E.A., Gasse, F., van Kreveld, S., Holmgren, K., Lee-Thorp, J., Rosqvist, G., Rack, F., Staubwasser, M., Schneider, R.R., Steig, E.J., 2004. Holocene climate variability. Quaternary Research, 62, 243–255.

Melles M., Brigham-Grette J, Glushkova O.Yu, Minyuk PS., Nowaczyk NR., Hubberten H-W., 2007. Sedimentary geochemistry of core PG1351 from Lake El'gygytgyn—a sensitive record of climate variability in the East Siberian Arctic during the past three glacial–interglacial cycles. Journal of Paleolimnology, 37, 89-104.

Milligan, A.J., Varela, D.E., Brzezinski, M.A., Morel, F.M.M., 2004. Dynamics of silicon metabolism and silicon isotopic discrimination in a marine diatom as a function of pCO_2. Limnology and Oceanography, 49, 322-329.

Minyuk, P.S., Brigham-Grette, J., Melles, M., Borkhodoev, V.Y., Glushkova, O.Y., 2007, Inorganic geochemistry of El'gygytgyn Lake sediments (northeastern Russia) as an indicator of paleoclimatic change for the last 250 kyr . Journal of Paleolimnology, 37, 123-133.

Moberg, A., Sonechkin, D.M., Holmgren, K., Datsenko, N.M., Karlén W., 2005. Highly variable Northern Hemisphere temperatures reconstructed from low- and high-resolution proxy data. Nature, 433, 613-617.

Mock CJ., Bartlein PJ, Anderson PM., 1998. Atmospheric circulation patterns and spatial climate variations in Beringia. International Journal of Climatology, 10, 1085-1104.

Morley, D.W., Leng, M.J., Mackay, A.W., Sloane, H.J., Rioual, P., Battarbee, R.W., 2004. Cleaning of lake sediment samples for diatom oxygen isotope analysis. Journal of Paleolimnology, 31, 391–401.

Morley, D.W., Leng, M.J., Mackay, A.W., Sloane, H.J., 2005. Late Glacial and Holocene environmental change in the Lake Baikal region documented by oxygen isotopes from diatom silica. Global and Planetary Change, 46, 221-233.

Moschen, R., Lücke, A., Schleser, G., 2005. Sensitivity of biogenic silica oxygen isotopes to changes in surface water temperature and palaeoclimatology. Geophysical Research Letters, 32, L07708, doi:10.1029/2004GL022167.

Moschen, R., Lücke, A. , Parplies, J., Radtke, U., Schleser, G.H., 2006. Transfer and early diagenesis of biogenic silica oxygen isotope signals during settling and sedimentation of diatoms in a temperate freshwater lake (Lake Holzmaar, Germany). Geochimica et Cosmochimica Acta, 70: 4367–4379.

Müller, S., Tarasov, P.E., Andreev, A.A, Diekmann, B., 2009. Late Glacial to Holocene environments in the present-day coldest region of the Northern Hemisphere inferred from a pollen record of Lake Billyakh, Verkhoyansk Mts, NE Siberia. Climates of the Past, 5: 73-84.

NGRIP Project Members 2004. High-resolution record of Northern Hemisphere climate extending into the last interglacial period. Nature, 431, 147-151.

Nolan, M., Brigham-Grette, J., 2007. Basic hydrology, limnology, and meteorology of modern Lake El'gygytgyn, Siberia. Journal of Paleolimnology, 37, 17-35.

Nolan, M., Liston, G., Prokein, P., Brigham-Grette, J., Sharpton, V., Huntzinger, R., 2003, Analysis of lake ice dynamics and morphology on Lake El'gygytgyn, NE Siberia, using synthetic aperture radar (SAR) and Landsat. Journal of Geophysical Research, 108, D2, 8162, doi:10.1029/2001JD000934.

Nowaczyk, N.R., Minyuk, P., Melles, M., Brigham-Grette, J., Glushkova, O., Nolan, M., Lozhkin, A.V., Stetsenko, T.V., Andersen, P.M., Forman, S.L., 2002. Magnetostratigraphic results from impact crater Lake El'gygytgyn, northeastern Siberia: a 300 kyr long high-resolution terrestrial palaeoclimatic record from the Arctic. Geophys. J. Int., 150, 109-126.

Nowaczyk, N.R., Melles, M., Minyuk, P., 2007. A revised age model for core PG1351 from Lake El'gygytgyn, Chukotka, based on magnetic susceptibility variations tuned to northern hemisphere insolation variations. Journal of Paleolimnology, 37, 65-76.

Numaguti, A., 1999. Origin and recycling processes of precipitating water over the Eurasian continent: experiments using an atmospheric general circulation model. Journal of Geophysical Research, 104, 1957-1972.

Overpeck, J., Hughen, K., Hardy, D., Bradley, R., Case, R., Douglas, M., Finney, B., Gajewski, K., Jacoby, G., Jennings, A., Lamoureux, S., Lasca, A., MacDonald, G., Moore, J., Retelle, M., Smith, S., Wolfe, A., Zielinski, G., 1997. Arctic environmental change of the last four centuries. Science, 278, 1251-1256.

Pichevin, L.E., Reynolds, B.C., Ganeshram, R.S., Cacho, I., Pena, L., Keefe, F., Ellam, R.M., 2009. Enhanced carbon pump inferred from relaxation of nutrient limitation in the glacial ocean . Nature, 459, 1114-1118.

Popp, S., Diekmann, B., Meyer, H., Siegert, C., Syromyatnikov, I., Hubberten, H-W., 2006. Palaeoclimate signals as inferred from stable-isotope composition of ground ice in the Verkhoyansk Foreland, Central Yakutia . Peramfrost and Periglacial Processes, 17, 119-132.

Ragueneau, O., Dittert N., Pondaven P., Tréguer, P., Corrin., 2002. Si/C decoupling in the world ocean: is the Southern Ocean different? Deep-Sea Research II, 49, 3127-3154.

Rasmussen, S.O., Andersen, K.K., Svensson, A.M., Steffensen, J.P.,Vinther, B.M., Clausen, H.B., Siggaard-Andersen, M.-L., Johnsen, S.J., Larsen, L.B., Dahl-Jensen, D., Bigler, M., Röthlisberger, R., Fischer, H., Goto-Azuma, K., Hansson, M.E., Ruth, U., 2006. A new Greenland ice core chronology for the last glacial termination. Journal of Geophysical Research, 111, D06102. doi:10.1029/2005JD006079.

Reynolds, B.C., Frank, M., Halliday, A.N., 2006. Silicon isotope fractionation during nutrient utilization in the North Pacific. Earth and Planetary Science Letters, 244, 431-443.

Reynolds, B.C., Frank, M., Halliday, A.N., 2008. Evidence for a major change in silicon cycling in the subarctic North Pacific at 2.73 Ma . Paleoceanography, 23, PA4219, doi:10.1029/2007PA001563.

Robock, A., 2000. Volcanic eruptions and climate. Reviews of Geophysics, 38, 191-219.

Rosqvist, G., Rietti-Shati., M., Shemesh, A., 1999. Late glacial to middle Holocene climatic record of lacustrine biogenic silica oxygen isotopes from a Southern Ocean island . Geology, 967-970.

Rosqvist, G., Jonsson, C., Yam, R., Karlén, W., Shemesh, A., 2004. Diatom oxygen isotopes in pro-glacial lake sediments from northern Sweden: a 5000 year record of atmospheric circulation. Quaternary Science Reviews, 23, 851-859.

Schiff, C., Kaufman, D.S., Wolfe, A.P., Dodd, J., Sharp, Z., 2009. Late Holocene storm-trajectory changes inferred from the oxygen isotope composition of lake diatoms, south Alaska. Journal of Paleolimnology, 41, 189-208.

Schmidt, M., Botz, R., Stoffers, P., Anders, T., Bohrmann, G., 1997. Oxygen isotopes in marine diatoms: A comparative study of analytical techniques and new results on the isotopic composition of recent marine diatoms. Geochimica et Cosmochimica Acta, 61: 2275-2280.

Schmidt, M., Botz, R., Rickert, D., Bohrmann, G., Hall, S.R., Mann, S., 2001. Oxygen isotope of marine diatoms and relations to opal-A maturation. Geochimica et Cosmochimica Acta, 65: 201-211.

Schwamborn, G., Meyer, H., Fedorov, G., Schirrmeister, L., Hubberten, H-W., 2006. Ground ice and slope sediments archiving late Quaternary paleoenvironment and paleoclimate signals at the margins of El'gygytgyn Impact Crater, NE Siberia. Quaternary Research, 66, 259-272.

Schwamborn, G., Fedorov, G., Schirrmeister, L., Meyer, H., Hubberten, H-W., 2008. Periglacial sediment variations controlled by late Quaternary climate and lake level change at Elgygytgyn Crater, Arctic Siberia. Boreas 37, 55-65.

Severinghaus, J.P., Brook, E.J. 1999. Abrupt climate change at the end of the last glacial period inferred from trapped air in polar ice. Science, 286, 930-934.

Shilo, N.A., Lozhkin, A.V., Anderson, P.M., Belaya, B.V., Stetsenko, T.V., Glushkova, O.Yu., Brigham-Grette, J., Mellis, M., Minyuk, P.S., Novachek, N., Forman, S., 2001. First continuous pollen record of climate and vegetation changes in the Bering Sea region for the past 300 ka. Doklady Akademii Nauk., 376, 231-234.

Shindell, D.T., Schmidt, G.A., Miller, R.L., Mann, M.E., 2003. Volcanic and solar forcing of climate change during the Preindustrial era. Journal of Climate, 16, 4094-4107.

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, E., Siitonen, S., Solovieva, N., Weckström, J., 2005. Climate-driven regime shifts in the biological communities of Arctic lakes. Proceedings of the National Academy of Sciences, 102, 4397–4402.

Street-Perrott, F.A., Barker, P.A., 2008. Biogenic silica: a neglected component of the coupled global continental biogeochemical cycles of carbon and silicon . Earth Surface Processes and Landforms, 33, 1436-1457.

Street-Perrott, F.A., Barker, P.A., Leng, M.J., Sloane, H.J., Wooller, M.J., Ficken, K.J.. Swain, D.L., 2008. Towards an understanding of late Quaternary variations in the continental biogeochemical cycle of silicon: multi-isotope and sediment-flux data for Lake Rutundu, Mt Kenya, East Africa, since 38 ka BP . Journal of Quaternary Science, 23, 375-387.

Struyf, E., Smis, A., van Damme, S., Meire, P., Conley, D.J., In Press. The global biogeochemical silicon cycle. Silicon.

Swann, G.E.A., Maslin, M.A., Leng, M.J., Sloane, H.J., Haug, G.H., 2006. Diatom $\delta^{18}O$ evidence for the development of the modern halocline system in the subarctic northwest Pacific at the onset of major Northern Hemisphere glaciation. Paleoceanography, 21, PA1009, doi: 10.1029/2005PA001147.

Swann, G.E.A., Leng, M.J., Sloane, H.J., Maslin, M.A., Onodera, J., 2007. Diatom oxygen isotopes: evidence of a species effect in the sediment record. Geochemistry, Geophysics, Geosystems, 8, Q06012, doi:10.1029/2006GC001535.

Swann, G.E.A., Leng, M.J., Sloane, H.J., Maslin, M.A., 2008. Isotope offsets in marine diatom δ^{18}O over the last 200 ka. Journal of Quaternary Science, 23, 389-400.

Swann, G.E.A., Leng, M.J., 2009. A review of diatom δ^{18}O in palaeoceanography. Quaternary Science Reviews, 28, 384-398.

Tyler, J.J., Leng, M.J., Sloane, H.J., Sachse, D., Gleixner G., 2008. Oxygen isotope ratios of sedimentary biogenic silica reflect the European transcontinental climate gradient. Journal of Quaternary Science, 23: 341-350.

Varela, D.E., Pride, C.J., Brzezinski, M.A., 2004. Biological fractionation of silicon isotopes in Southern Ocean surface waters. Global Biogeochemical Cycles, GB1047, doi:10.1029/2003GB002140.

Voelker, A.H.L & workshop participants., 2002. Global distribution of centennial-scale records for Marine Isotope Stage (MIS) 3: a database. Quaternary Science Reviews. 21, 1185-1212.

Vogel, H, Rosén, P, Wagner, B, Melles, M, Persson, P., 2008. Fourier transform infrared spectroscopy, a new cost- effective tool for quantitative analysis of biogeochemical properties in long sediment records. Journal of Paleolimnology, 40: 689-702.

von Grafenstein, U., Erlenkeuser, H., Brauer, A., Jouzel, J., Johnsen, S.J. 1999. A mid-European decadal isotope-climate record from 15,500 to 5000 years B.P. Science, 284, 1654-1657.

Wanner, H., Beer, J., Bütikofer, J., Crowley, T.J., Cubasch, U., Flückiger, J., Goosse, H., Grosjean, M., Joos, F., Kaplan, J.O., Küttel, M., Müller, S.A., Prentice, I.C., Solomina, O., Stocker, T.F., Tarasov, P., Wagner, M., Widmann, M., 2008. Mid- to Late Holocene climate change: an overview. Quaternary Science Reviews, 27, 1791-1828.

Ziegler, K., Chadwick, O.A., Brzezinski, M.A., Kelly, E.F., 2005. Natural variations of δ^{30}Si ratios during progressive basalt weathering, Hawaiian Islands. Geochim Cosmochim Acta, 69, 4597-4610.

Ziegler, K, Chadwick, O.A., White, A.F., Brzezinski, M.A., 2005. δ^{30}Si systematics in a granitic saprolite, Puerto Rico. Geology, 33, 817-820.

Figures

Figure 1: Location of Lake El'gygytgyn, Russia, and coring site Lz1209.

Figure 2: Light microscopy (2.9 ka BP) (A) and SEM (17.0 ka BP) (B) images of cleaned diatom material from Lake El'gygytgyn showing the excellent preservation of the diatoms and the absence of any significant contamination.

Figure 3: Changes in $\delta^{30}Si_{diatom}$ and $\delta^{18}O_{diatom}$ in Lake El'gygytgyn with Greenland, NGRIP, $\delta^{18}O_{ice}$ (NGRIP Project Members 2004), diatom species biovolumes, diatom sample purity in the analysed material and ^{14}C age model for site Lz1029. Grey line for $\delta^{18}O_{ice}$ indicates the original NGRIP data (http://www.glaciology.gfy.ku.dk/data/GICC05_NGRIP_GRIP_20y_27nov2006.txt), black line is a Local

Polynomial Regression (Loess) used to predict comparable values of $\delta^{18}O_{ice}$ for the $\delta^{18}O_{diatom}$ data using a smoothing window to reflect the mean temporal resolution of the Lake El'gygytgyn samples. Age model uses a linear interpolation between calibrated ^{14}C dates (plotted) that incorporate a 1.3 ka reservoir effect correction. HTM on zonation indicates duration of Holocene Thermal Maximum in Lake El'gygytgyn. GS-1 indicates the short period of climatic cooling in Lake El'gygytgyn that occurs during the GS-1 event in the Greenland ice core record.

Tables

Table 1: Radiocarbon ages for site Lz1029. Errors are 1σ.

Depth (cm)	Uncalibrated ^{14}C date (yr BP)	Calibrated ^{14}C date with 1.3 ka reservoir effect (yr BP)	Kiel Laboratory sample no.
5.75	3235 ± 40	1888 ± 43	KIA24666
17.25	5521 ± 45	4753 ± 83	KIA24667
51.75	14800 ± 110	16435 ± 428	KIA24668
59.75	15140 ± 100	17060 ± 205	KIA24669
83.25	22670 ± 170	25512 ± 366	KIA24670

Supplementary Data

Supplementary table 1: $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ from Lake El'gygytgyn core Lz1029 (attached file: “lz1029_diatom_isotopes.xls”).

Figure 1

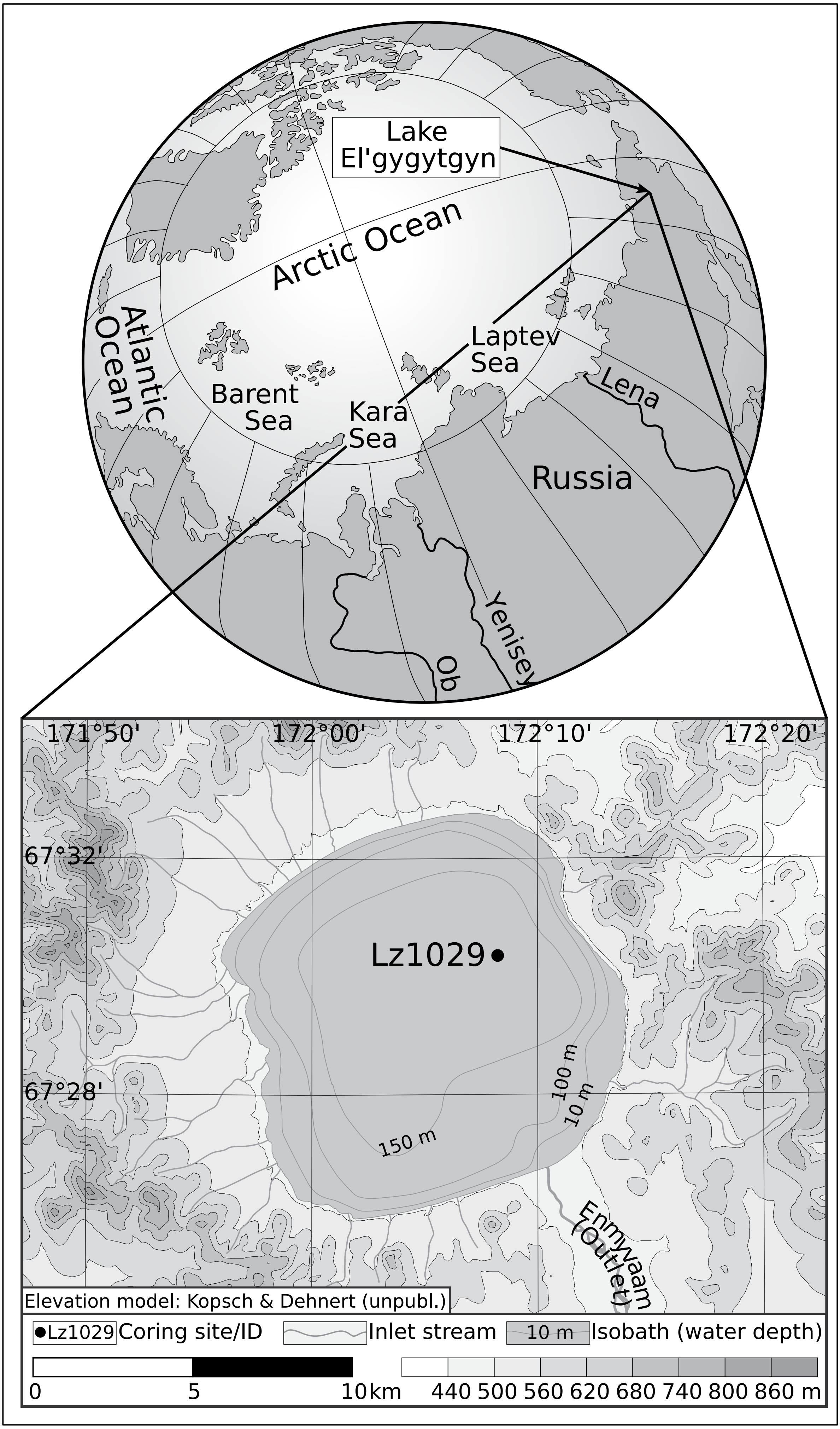

Lake
El'gygytgyn
Arctic Ocean
Atlantic
Ocean
Laptev
Sea
Barent
Sea
Kara
Sea
Lena
Russia
Yenisey
Ob
171°50'
172°00'
172°10'
172°20'
67°32'
67°28'
Lz1029
100 m
10 m
150 m
Enmyvaam
(Outlet)
Elevation model: Kopsch & Dehnert (unpubl.)
Lz1029 Coring site/ID
Inlet stream
10 m Isobath (water depth)
0
5
10km
440 500 560 620 680 740 800 860 m

Figure 2

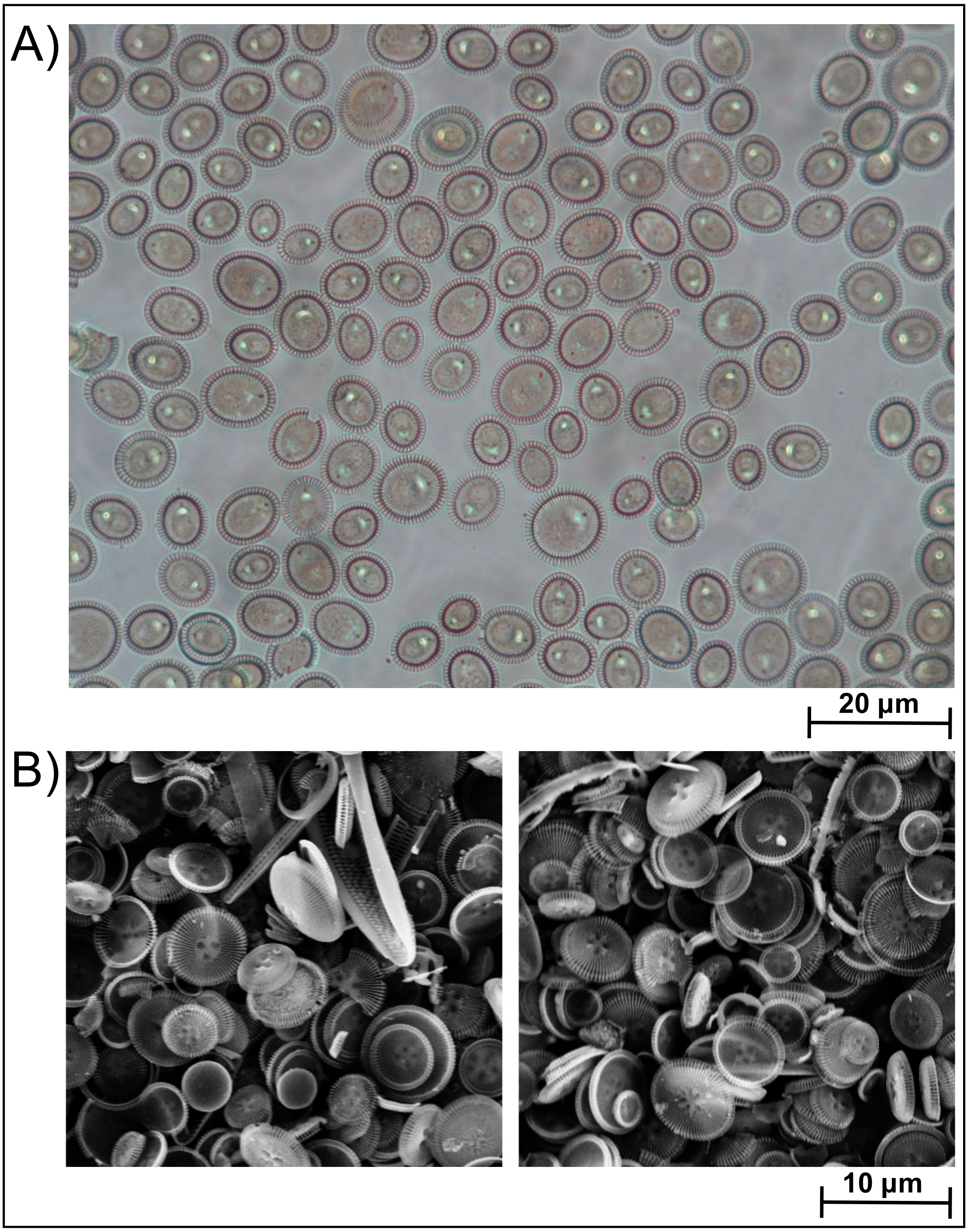
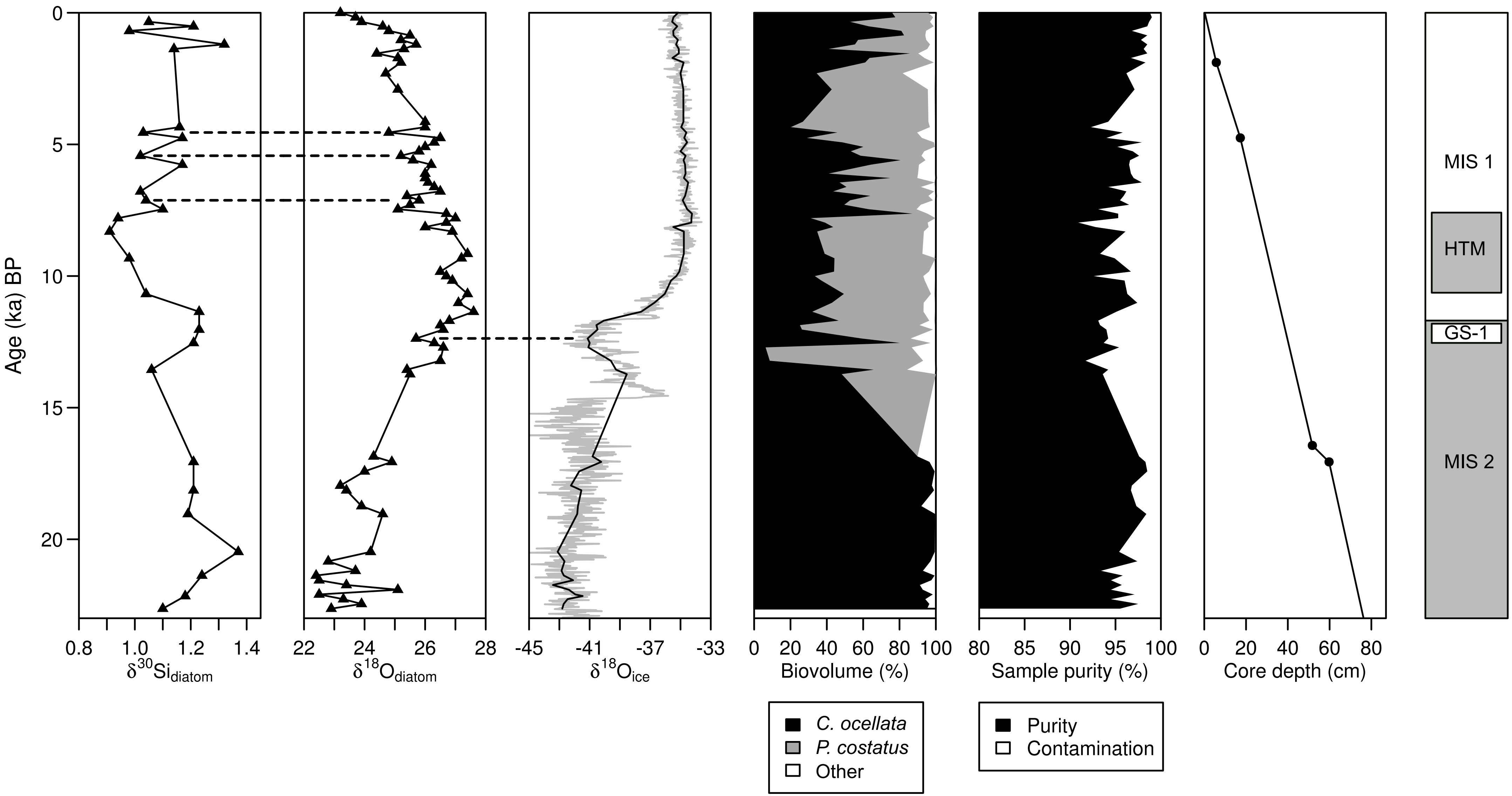


Figure 3



Age (ka) BP
δ30Si diatom
δ18O diatom
δ18O ice
Biovolume (%)
Sample purity (%)
Core depth (cm)
C. ocellata
P. costatus
Other
Purity
Contamination
MIS 1
HTM
GS-1
MIS 2